

Progress in the application of silicon-based materials in lithium-ion batteries anodes

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Abstract. From the battery that powers the remote control to the battery that powers electric cars, lithium-ion batteries (LIBs) are a crucial component of contemporary energy storage. The large theoretical capacity of silicon anodes provides significant benefits inside LIBs. However, the main issue with the conventional silicon bulk anode is its considerable volume expansion, which forms an unstable Solid Electrolyte Interface (SEI) layer during the charge and discharge process and severely reduces battery performance and lifespan. Therefore, to solve these issues, researchers have explored multiple improved silicon anodes, three of which are mentioned in this essay. Firstly, the researchers delve into the usage of nanotechnology. When manipulating silicon particles at the nano-scale, the nano-silicon can mitigate the volume expansion, improving the reaction kinetics. Then, a composite of carbon and silicon is proposed, combining silicon's high capacitance and carbon's high conductivity. After that is the silicon-metal composite, which utilizes metals' mechanical strength and conductivity to stabilize Si anodes further and improve thermal stability. Overall, the significance of this study lies in the exploration of the application of silicon anodes in LIBs, highlighting the potential of these composite materials and advanced technology, which may help guide the future exploration of better silicon anodes.

Keywords: Lithium-ion batteries; silicon-based materials; negative.

1. Introduction

With the rapid development of electronic equipment and electric vehicles and the urgent need for high-performance power supply, LIBs stand out for their outstanding energy density, long battery life, etc., and have become the primarily used battery in the public market. In LIBs, a cathode and anode are used on either side of the battery, storing and releasing the lithium ions. Between them are an electrolyte and a separator, facilitating the movement of the ions and preventing short circuits, respectively. The anode, in LIBs especially, is a crucial component as its performance determines the battery's overall performance, including the lifespan, charging speed, capacity, and safety. The anode used is graphite anode, but its limited lithium-ion capacitance can no longer satisfy the increasing needs of high-capacity LIBs. Therefore, a better performance LIBs anode material is in demand [1].

Among all the anode materials, silicon is considered one of the most promising materials, as its theoretical capacity can be up to 4200mAh/g, about ten times graphite's capacity. Silicon is also the second most abundant element in the earth's crust, with ample reserves and an enormous potential for raw material supply. Moreover, silicon-based materials are non-toxic, aligned with environmental requirements, and conducive to sustainable development. In addition, more importantly, silicon-based materials have relatively low de/embedded lithium potentials (e.g., 0.37 V or 0.5 V), which makes it difficult to form "lithium dendrites" during the charging process, thus improving the safety performance of the battery [2, 3].

Despite these advantages, several disadvantages limit their commercial application. Silicon negative electrodes expand during charging and discharging, reforming the SEI layer and destroying the negative electrode structure, inexorably consuming the electrolyte and shortening its service life. Therefore, this paper will summarize methods to improve the performance of LIBs by employing silicon nano-anodes, silicon carbon composites, and silicon metal composites.

2. Working principles and Challenges of Si-based LIBs

2.1. Working Principles

The battery goes through delithiation and lithiation during the charge and discharge phases. Lithium ions (Li^+) intercalate when the battery is charged into a silicon anode after moving from the cathode via the electrolyte. When lithium ions are absorbed by the silicon anode, lithium silicides (Li_xSi) are created. This technique may considerably enhance the anode capacity up to roughly 4200mAh/g, which is more than most of the anode material utilized, thanks to silicon's fantastic capacity to hold lithium ions. Lithium ions will depart from the silicon anode and return to the cathode when the battery empties. Electrical energy is produced by this process and used to power electronics [1]. The formation of a solid electrolyte interphase layer (SEI) is also notable during the charge and discharge process. SEI is a product formed during the initial cycles of the battery. When the lithium ions intercalate into the silicon anode, the electrolyte decomposes at the anode surface, which is a thin layer composed of various lithium compounds like lithium carbonate (LiCO_3), lithium fluoride (LiF), depending on the cathode material [2].

2.2. Challenges for Si-based Materials

The development of LIBs is hampered by the volume expansion and SEI film instability that typically accompany Si-based materials, such as the negative electrode of LIBs. Si and Li undergo an electrochemical reaction that results in a sizeable volumetric expansion. After complete lithiation, silicon can expand by up to 300%, which can put a lot of mechanical stress on the particles' surface and cause them to shatter and pulverize. Additionally, if the electrode expands repeatedly, it may swell and lose electrical contact with the Si particle and the current collector, reducing conductivity and battery performance [1]. The solid electrolyte interphase layer, which protects the anode, will be cracked and reformed as the volume expands. As the layer gets thicker, many serious problems arise. This process will lead to irreversible consumption of active lithium and electrolytes and affect the electronic contact because of the insulation of SEI film [2]. The continuous formation and cracking of the SEI layer will increase the resistance of the battery, limiting the development of total capacity and cycle life [3]. In addition, silicon is a semiconductor material with a low intrinsic and poor electrical conductivity. This increases battery polarization during charging and discharging, reducing the battery's power density and multiplier performance. The cycle life of silicon-based anode is relatively short. The cycle life of silicon-carbon anode materials is usually around 300-500 cycles, much lower than the cycle life of graphite anodes.

3. Nano Silicon

Using nano-sized silicon anodes can offer solutions to multiple challenges that traditional silicon anodes face and other advantages. One of the perhaps most significant advantages is the mitigation of the volume expansion. Nano-silicon particles have a smaller physical size than the silicon bulk used in traditional silicon anodes, resulting in less volume expansion during the lithiation and delithiation cycle. Also, the nanoparticles can better distribute the stress and strain due to expansion, reducing the risks of cracking and pulverization [3]. Another vital advantage is the better battery anode performance. Because they are smaller, the nanosilicon offers more available area for reaction, allowing more lithium ions to react simultaneously. Therefore, less time will be required during the charge and discharge process [4]. Apart from that, nanosilicon is also attributed to a more stable SEI layer. As smaller sizes lead to a higher surface area to volume ratio, the interaction between the electrolytes will be more stable, so the SEI formation will be more uniform, helping to create protection over the electrode surface and reducing the possible positions where degradation could occur. Notably, smaller dimensions can lead to shorter diffusion paths for lithium ions to travel during the charge and discharge process, increasing the kinetic for ion transportation. The nanocrystallization of silicon anode experiences the development from 0D to 2D. Zhu et al. reported a method using

high-energy mechanical milling to produce nano-silicon materials, as shown in Figure 1 [5]. The two kinds of produced nano-particles are around 100nm in size. After carbon coating, its reversible capacity stabilizes above 1200 mAh/g, reducing less than 3% after 100 cycles.

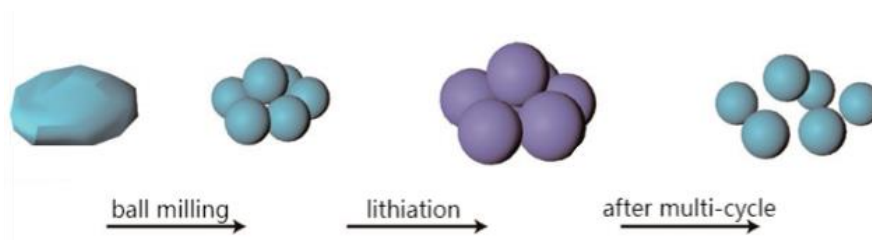


Fig 1. Preparation process of nano-silicon [5].

Salt may now be melted without a catalyst or template, according to Wang et al. Silicon nanotubes are created by regulating the electrode-oxidation of SiO_2 in melted salt. The particulate SiO_2 first changes into layered CaSiO_3 in the melt during electrode-oxidation; as the process proceeds, it delaminates into SiO_x . It eventually bends to form silicon nanotubes, and at a current density of 0.2 S/g, the first capacities of 3099 and 2485 mAh/g were attained for both charge and discharge. 82% was the first coulombic efficiency. This nanotube structure preserves the electrode's integrity by efficiently reducing the stress from volume expansion [6]. Ren et al. employed magnesiothermic reduction to prepare nanosilicon using zinc as an additive [7]. The addition of zinc can help facilitate the formation of nanosilicon inside the internal pores and protect nanosilicon from melting at low temperatures. This method can prepare nano silicon with more developed and regular pores without introducing too many impurities. The silicon material gained can better mitigate the volume expansion, having a high reversible capacity and maintaining good cycling stability. It still has a specific 855 mAh/g capacity after 1000 cycles.

4. Si/C composites

The significant advantage of silicon-carbon composite is its ability to mitigate volume expansion. The carbon matrix, a framework made of carbon materials, can evenly distribute the mechanical stress from the expansion, acting as a buffer to suit the volume change. Additionally, traditional silicon bulk anode has a relatively poor conductivity, affecting the battery's overall performance. But carbon, like graphene, has an outstanding conductive capability; therefore, in the silicon-carbon composite, by incorporating carbon materials, the battery improves its overall conductivity significantly, which allows faster charging and discharging, enhancing the charging rate. The formation of a stable layer is also a benefit of silicon-carbon composite. The carbon coating embedded in the silicon particles prevents direct contact between the electrolyte and the silicon, significantly reducing the formation of an unstable SEI layer. Accompanied by less volume expansion, reducing the continuous break and reform, the SEI layer formed in the silicon-carbon composite is more stable and uniform, less likely to consume electrolytes, and improves overall battery life. In recent years, the structural design of silicon-carbon composite has aroused broad interest.

Huang et al. treated nano-silicon with octadecyl dimethyl hydroxyethyl ammonium nitrate, then added phenolic resin and graphene oxide to prepare a precursor gel. After freeze-drying and high-temperature carbonization to obtain a precursor, chemical vapor deposition in an Ar environment produced the final product SGC. The initial discharge capacity reached 2455 mAh/g. The reversible specific capacities at 0.1 C, 0.25 C, and 0.5 C were 1679, 1510, and 1285 mAh/g, respectively [8]. Liu et al. used hydrogen to facilitate the decomposition of chloromethyl silane on the surface of graphite, depositing silicon nanowires, as shown in Figure 2 [9]. Chloromethylsilane is less sensitive than silane in terms of oxygen sensitivity, making it less likely to explode and much safer. After further coating with carbon through acetylene decomposition, a silicon-carbon material composed of C/silicon nanowires/graphite microspheres is formed, a silicon-carbon composite.

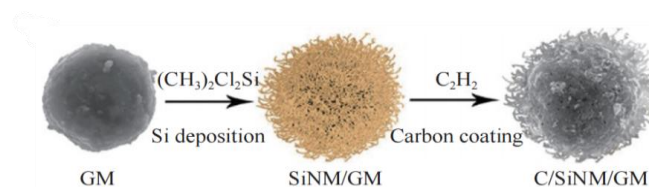


Fig 2. Preparation process of silicon-carbon composites [9].

5. Silicon-metal Composites

Other than carbon, combining silicon with metal can also be very beneficial. Due to the metal's unique properties, the silicon-metal composite contributes to a more durable, efficient, and safer lithium-ion battery. Just like the other two silicon anodes, the application of silicon-metal composite can better manage the volume expansion of silicon. When silicon is alloyed with other metals, like aluminum, forming inter-metallic compounds, the alloys can produce a matrix that can buffer the volume expansion, similarly to the carbon matrix. Therefore, the stress on the anodes can be spread out more evenly and safely. Integrating highly conductive metals like copper or nickel enhances the electrical battery conductivity, providing adequate pathways for electrons to transport. It can also be achieved by applying a conductive metal coating, like a thin copper layer, on the silicon particles to improve electron transportation across the composite material. The application of metal coating can also help to stabilize the SEI layer. The coating can prevent direct contact with the electrolyte, helping minimize the unstable formation. Metal often tends to have higher mechanical strength. Silicon-metal composite also makes full use of this property, strengthening the mechanical strength of the electrode material and preventing potential structural damage from volume expansion. Some of the metals have good thermal conductivity and high-temperature resistance. The composite material can, therefore, enhance the thermal stability of the battery, minimizing the risks when overheated.

Li et al. produced $\text{SiO}_x@\text{TiO}_2$ composite materials with a watermelon-like structure obtained through ball milling [10]. The highly dispersed conductive TiO_2 nanoparticles within the material and the outer carbon shell result in the rapid transportation of electrons and Li^+ , enhancing the electrode reaction kinetics. This structure also helps to homogenize volume changes and reduce structural stress, maintaining the integrity of the active particles. As a result, the material retains a reversible specific capacity of 804 mAh/g after 100 cycles at a current density of 100 mA/g. Xiao et al. used SiO_2 and GeO_2 as raw materials to synthesize a SiGe alloy with a structure similar to carbon nanotubes through electroreduction in molten chlorides, as shown in Figure 3 [11]. The SiGe alloy shows excellent rate performance, achieving reversible specific capacities of 916 mAh/g at 200 mA/g, 779 mAh/g at 500 mA/g, and 666 mAh/g at 1000 mA/g. He et al. prepared a Si-Cu thin film material on Ti using the non-lithium active metal Cu. The electrode material's cycling performance and rate capability improved as the annealing temperature increased. Compared to pure silicon thin films, the silicon-copper alloy thin films exhibited better cycling stability and rate performance [12].

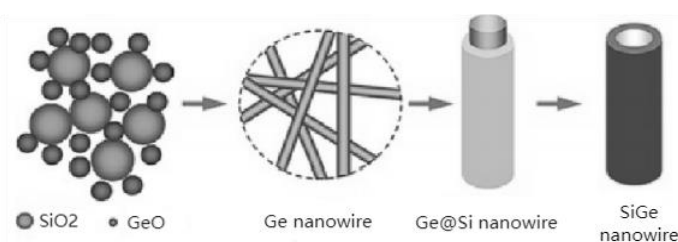


Fig 3. Preparation of Si-Ge nanowire [11].

6. Conclusion

This essay mainly discusses the challenges and possible solutions for silicon anodes in LIBs. Silicon, with an outstanding theoretical capacity of 4200 mAh/g, can be a new anode material for

LIBs to better accommodate the increasing needs of the market. However, certain existing drawbacks limit its more comprehensive application, like volume expansion during the charge and discharge process and the formation of an unstable SEI layer, limiting the overall performance of LIBs. To solve these issues, three ways were examined: nano-silicon, silicon-carbon composite, and silicon-metal composite. All three silicon-based anodes can mitigate the volume expansion in their ways and reduce the formation of an unstable SEI layer. Each composite also has its benefits as well. Silicon-metal offers advantages such as increased mechanical strength and better conductivity, while silicon-carbon composite has better structural integrity and conductivity.

Despite these advancements, some challenges remain. For instance, producing nano-silicon can be pretty tricky as manufacturing items on the nanoscale can be costly and complex, not to mention for mass production. Also, even though combining metals and carbon with silicon can mitigate the expansion, it does not mean solving the problem thoroughly. As time goes on, the expansion will still hurt the lifespan. Moreover, all the experiments mentioned above are under experimental conditions. The actual performance of these composites under real-world conditions requires further investigation.

In the future, other types of silicon-based anodes, such as silicon-polymer composite and silicon-metal oxide composite, will be researched. By leveraging the unique properties and advantages of each material and fully utilizing the high capacity of silicon, better performance LIBs may be possible. Or, finding ways to overcome current challenges can be feasible, like cutting down the cost to produce nano-silicon anode. Combining all these efforts, creating a new generation of LIBs with longer lifespans, higher energy density, and better overall performance is possible.

References

- [1] Zhang C., Wang F., Han J., et al. Challenges and recent progress on Silicon-Based anode materials for Next-Generation Lithium-Ion batteries. *Small Structures*, 2021, 2(6).
- [2] Wang Q., Liu B., Shen Y., et al. confronting the challenges in lithium anodes for lithium metal batteries. *Advanced Science*, 2021, 8(17).
- [3] Berhaut C.L., Dominguez D.Z., Tomasi D., et al. Prelithiation of silicon/graphite composite anodes: Benefits and mechanisms for long-lasting Li-ion batteries. *Energy Storage Materials*, 2020, 29: 190-197.
- [4] Sun L. Nanotechnology in the field of electric vehicles. *Science Engineering and Technology*, 2023, 43: 327-332.
- [5] Zhu B., Jin Y., Tan Y., et al. Scalable production of Si nanoparticles directly from low grade sources for Lithium-Ion battery anode. *Nano Lett*, 2015, 15(9): 5750-5754.
- [6] Wang F., Ma Y., Li P., et al. Electrochemical conversion of silica nanoparticles to silicon nanotubes in molten salts: Implications for high-performance lithium-ion battery anode. *Nano Materials*, 2021, 4(7): 7028-7036.
- [7] Ren Y., Zhou X., Zhou H., et al. Zn-assisted magnesiothermic reduction is used to prepare ultra-fine silicon nanocrystals for lithium ion batteries. *Chemical Engineering Journal*, 2017, 328: 691-696.
- [8] Huang Y., Luo J., Peng J., et al. Porous silicon-graphene-carbon composite is a high-performance anode material for lithium ion batteries. *Journal of Energy Storage*, 2020, 27: 1075-1079.
- [9] Liu B., Huang P., Xie Z., et al. Large-scale silicon nanowire/graphite composites anode production via the CVD method for high-performance lithium-ion batteries. *Energy & Fuels*, 2021, 35(3): 2758-2765.
- [10] Li Z., Zhao H., LV P., et al. Watermelon-like structured SiO_x-TiO₂@C nanocomposite as a high-performance lithium-ion battery anode. *Advanced Functional Materials*, 2018, 28(31): 1616-1627.
- [11] Xiao W., Zhou J., Yu L., et al. Electrolytic formation of crystalline silicon/germanium alloy nanotubes and hollow particles with enhanced lithium-storage properties. *Angewandte Chemie*, 2016, 55(26): 7427-7431.
- [12] He Y., Wang Y., Yu X., et al. Si-Cu thin film electrode with Kirkendall voids structure for lithium-ion batteries. *Electrochemical Society*, 2012, 159(12): A2076.