Application of silicon nanotechnology in lithium-ion battery anodes

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Abstract. The lithium-ion batteries (LIBs) are considered one of the significant parts of an electric vehicle and have become a hot research topic regarding how to improve the lifespan and energy capacity of lithium-ion batteries. Silicon, which has excellent electric conductivity and high specific capacity, could vastly improve performance and electric conductivity compared with graphite-based lithium-ion batteries. However, the issue of silicon volume expansion and the formation of solid electrolytes hinder the use of pure silicon as anodes. With the prevalence of nanotechnology, using silicon as a marvelous substitute for graphite anodes is possible again as silicon nanotechnology could dramatically alleviate the volume expansion issue and improve the performance on a large scale. As a result, the application of silicon nanotechnology in lithium-ion batteries seems promising in the next several years. In this paper, the working principle of LIBs is first summarized. Then, the shortcomings of current silicon-based materials as negative electrodes are presented. Finally, the application of nanotechnology in the negative electrode of silicon-based LIBs is discussed, highlighting the role of different dimensions of silicon nanomaterials in LIBs.

Keywords: Lithium-ion batteries, nanotechnology, silicon anodes, electric vehicles.

1. Introduction

LIBs have the advantages of long lifespan, excellent electric conductivity, high energy capacity, and being environmentally friendly. As the main portable power supply in electric vehicles and mobile handsets, lithium-ion batteries always tend to possess better energy capacity, longer lifespan, and greater electric capacity. The most conspicuous form of lithium-ion batteries is the graphite-based lithium-ion batteries. Graphite-based lithium-ion batteries face several insufficient issues: first, the graphite-based lithium batteries might form crystalline structures called dendrites due to the uneven distribution of lithium moving ions on anodes, increasing the potential safety risks and shortening the lifespan of lithium-ion batteries dramatically; second, the rapid battery discharge process under extreme freezing circumstances and the short energy capacity, and graphite, as a commercial anode material, offers only 372 mAh/g [1]. However, silicon, the second most abundant element on Earth, has unapparelled semiconductor properties, providing nearly ten times the energy capacity compared with graphite-based batteries [2,3]. As a result, silicon-based lithium batteries have recently been researched to promote performance. To promote lithium batteries, nanotechnology in silicon anodes proved to become a promising material, preventing volume expansion issues encountered in pure silicon anodes and improving performance. This paper delves into essential information about the lithium-ion battery principle and the necessity of four primary types of silicon nanotechnology.

2. Principles of LIBs

2.1. Working Principles

A lithium battery consists of several parts: an anode, a cathode, a separator, an electrolyte, and two current collectors, including a positive and a negative one. Most commercialized and widely used lithium batteries have the following working process and principles: when the lithium batteries are being charged, Li^+ is released from the lithium cobalt oxide positive electrode and is embedded in graphite through the electrolyte and the separator. Electrons reach the negative electrode from the

positive electrode through the external circuit, and the lithium-ion concentration in the positive electrode material decreases. In contrast, the lithium-ion concentration in the harmful electrode material increases as Co^{3+} in the positive electrode material is oxidized. On the other hand, the discharge process is just the opposite. Li^{+} spontaneously releases from the negative electrode, passes through the electrolyte and the separator, and is embedded in the positive electrode material [4]. Electrons reach the positive electrode from the external circuit and trigger the reduction of highly charged cobalt. As mentioned above, graphite is used as the primary material to make the negative anode in a lithium-ion battery due to its inherent hexagonal honeycomb structure in a two-dimensional plane, extending the reaction area to a large scale and as a result, engenders its excellent electric conductivity and performances. However, the anodes using graphite may also encounter some ineluctable shortages.

2.2. Disadvantages of Graphite Materials

Though graphite has marvelous electric conductivity, some obstacles still need to be tackled to boost the performance of lithium batteries. To start up, graphite might raise potential safety risks: One big problem with today's graphite anodes and the lithium metal anodes that preceded them is that the lithium ions returning to the anode when the battery is being charged do not coat the surface evenly. Instead, they grow like tree limbs in tiny crystalline structures called dendrites, indicating that if anodes made of graphite are used for excessive times, the tiny crystalline structures called dendrites might puncture the diaphragm, resulting in direct contact between the positive and negative electrodes, resulting in thermal runaway and other safety accidents. Furthermore, the lifespan of batteries using graphite as anodes might be shortened significantly because of this phenomenon, lessening the available energy capacity in lithium batteries. Simultaneously, lithium dendrites will increase the battery's internal resistance and reduce the charge and discharge efficiency. As a result, energy might be wasted, which could trigger low efficiency. In addition, a substantial capacity would be lost at room temperature, reaching approximately over 50% of capacity in batteries with graphite anodes, from which we can infer that the outer influential factors such as temperature may result in the capacity of batteries fluctuate, giving rise to the shortened driving range of electric vehicles under cold circumstances while using graphite as anodes [5]. In conclusion, using graphite as the anode in lithium batteries might result in a series of problems, including safety risks and the issues of degrading performances, lower efficiency, shortened range, and minor lifespan after excessive utilization. However, through investigations done by some researchers, silicon might be one of the most promising materials that can be used to produce the anodes of lithium batteries.

3. Challenges for Silicon Anode Materials

The abundance of silicon helps decrease the cost of producing a lithium battery compared with lithium batteries with graphite anodes, which take a lot to extract the graphite and turn it into electric anodes. Silicon makes up 27.7 percent of Earth's crust, and it is the second most abundant element in the crust, being surpassed only by oxygen, making the price lower using silicon as the anode of lithium batteries compared with using carbon as the ingredient.

In LIBs, graphite as a commercial anode material exhibits a good cycle performance. Still, its use as an active substance alone offers a theoretical specific capacity of 372 mAh/g. To obtain higher capacity LIBs, new generation anode materials with high capacity were investigated. Silicon has a high theoretical capacity of 3576 mAh/g, 10 times higher than graphite. Furthermore, the existing materials using silicon to make anodes in lithium batteries have already proved that silicon-anode batteries have better performances than graphite-anode batteries. Although graphite has been used as the anode of commercial lithium-ion batteries, its theoretical capacity (LiC_6: 372 mAh/g) still cannot meet the requirements of lithium-ion batteries anodes with high-energy density. Therefore, Silicon is considered to be a desirable candidate due to its abundance and high theoretical capacity ($Li_{4.4}Si$, up to 4200 mAh/g), indicating that for the same weight, the silicon negative electrode can store more

lithium ions, which significantly increases the energy density of the battery, and reveals that during the same period, the batteries using silicon as anodes may have a more extended range as well as larger energy capacity and better performances [6].

In conclusion, using silicon as the anode of lithium batteries brings commercial advantages, outstanding capacity, and a more extensive range.

Unfortunately, colossal volume expansion at approximately 300% of silicon is accompanied by the lithiation inside the batteries, leading to consequences. For instance, this expansion could generate significant mechanical stress on the surface of Si particles, leading to electrode swelling and pulverization of Si particles. According to experiments, the expansion volume of silicon anodes might deter the standard working mechanism inside lithium batteries, which means that using silicon anodes inside lithium batteries might lead to an even shorter lifespan in contrast with graphite anode batteries.

Another major challenge for applying Si anodes is stabilizing the SEI film with the electrolyte. The repetitive volume change exposes the fresh surface of Si, continuously creating the new SEI. Finally, the thicker SEI film causes fatal problems—first, the irreversible Li consumption and excessive Li-ion consumption in electrolytes. Secondly, there is poor electronic contact between Si particles and conductive additives due to the electrically insulating SEI film. Lastly, the increased lithium diffusion distance and electrode impedance or polarization are due to the passivation effects. The form of solid electrolyte interphase is also a significant factor in the degrading performance of silicon-based anode batteries. It shortens the capacity of lithium batteries, hampering ions moving from cathodes and anodes. Additionally, the form of solid electrolyte might also raise safety risks as the instability of the SEI surface would produce gases inside the batteries, thus increasing the pressure of the cells and potentially causing safety issues such as swelling or even cell rupture [6].

Therefore, using solely silicon as anode is unreliable due to potential safety risks and its shorter lifespan despite its better performance and efficiency than graphite-based anode batteries. How do we solve the demerits and take advantage of both sides? The nanotechnology of silicon might be an unprecedented and necessary answer to improving the performance and lifespan of lithium batteries.

4. Nanotechnology in Silicon Anodes

Si hollow nanospheres, nanotubes, and 3D porous structures with ample void space can easily accommodate the volume change and relieve the diffusion-induced stress during charge-discharge cycles, indicating that the use of nanotechnology in making silicon anodes might facilitate the expansion of silicon inside the anodes, lengthening the lifespan of lithium batteries, and might ultimately decrease the maintenance price of electric cars with lithium batteries made by the technique of Si nanotechnology.

Using nanotechnology in silicon anodes might also improve the energy capacity of lithium batteries: Nanostructures derived from the pyrolysis of silane, such as silicon nanospheres, nanotubes, and nanowires, have all demonstrated excellent storage behavior. This means that using nanotechnology in silicon anodes could improve their energy capability, and batteries could be more supportive of long car journeys.

In conclusion, using nanotechnology in Si solves significant problems in producing solely silicon and graphite-based anodes. Although nanotechnology improves capability and lifespan in batteries, diverse types of Si nanotechnology, including nanoparticles, nanowires, nanofilms, and porous nanotechnology, can have different characteristics and serve various functions.

4.1. Zero-dimensional Silicon Nanostructures

One-dimensional silicon nanostructures majorly refer to silicon nanoparticles. Silicon nanoparticles have low self-stress and high mechanical strength. Combined with a matrix that can act as a buffer, they can effectively alleviate volume expansion and release internal stress, thereby significantly improving their electrochemical performance. Additionally, due to the small size of

silicon nanoparticles, composite materials such as graphite are allowed to be added to enhance the performance and electric conductivity and avoid the volume expansion of silicon.

Combining silicon nanoparticles with graphite can dramatically improve the stability and prevent the volume expansion of silicon. Liu et al. synthesized a nanoparticle silicon and carbon composite electrode material with a yolk-eggshell structure. This structure comprises a thin, stable, self-supporting carbon shell protecting the internal silicon particles. The hollow structure can well buffer the volume expansion effect, showing good cycle stability: the first capacity is 2833 mAh/g at 400 mA/g, and the capacity retention rate after 1000 cycles is 74%. The materials show high coulombic efficiency, reaching approximately 99.84% [7].

Xu et al. designed and synthesized a "watermelon-shaped" nano-Si/C composite material with a high tap density that can sufficiently alleviate the mechanical stress caused by volume expansion, showing significantly improved Electrochemical properties. At a current density of 2.45 mA/cm^2, the reversible capacity after 500 cycles is 620 mAh/g, and the average coulombic efficiency is 99.8% [8].

In conclusion, one-dimensional silicon nanostructures like silicon nanoparticles can combine with composite materials, improving electrochemical properties. Therefore, silicon nanoparticles lead to better performance and longer lifespan; however, due to the reason that the process of producing silicon particles and composites, it is hard to produce silicon nanoparticles on a large scale, deterring applying one-dimensional silicon nanostructures into standard lithium batteries for electric vehicles.

4.2. One-dimensional Silicon Nanostructures

The one-dimensional silicon nanostructures mainly contain two methods: silicon nanowires and silicon nanotubes. Compared with zero-dimensional silicon nanostructures, one-dimensional silicon nanostructures can expand contact area, significantly improving the cycle performance of lithium batteries. Additionally, electron transfer no longer requires overcoming the interface caused by particle contact. The application of one-dimensional silicon nanostructures majorly solves the volume expansion problem, expanding the lifespan of lithium batteries and vastly improving electric conductivity, which boosts the performance of lithium batteries.

Currently, the primary methods for preparing these materials include template, chemical vapor deposition, chemical etching, and gas-liquid-solid methods.

Hwang et al. successfully prepared silicon and carbon composite core-shell nanowires by double-nozzle electrospinning, which still had a reversible capacity of 721 mAh/g after 300 cycles at a current density of 2750 mA/g, with a capacity retention rate of 99%. Its good cycle stability is mainly because this one-dimensional core-shell structure can release the mechanical stress caused by volume expansion, strengthen the connection between C and Si, and stabilize the SEI film. This indicates that nanowires could vastly expand the lifespan as nanowires stabilize SEI film and avoid volume expansion. These are the two major problems encountered using solely silicon as anodes in lithium batteries. Therefore, silicon nanowires bring the superiority of silicon anodes into the whole place and simultaneously avoid the demerits of silicon anodes [9].

Wu et al. proposed a failure model for the capacity attenuation of Si nanotubes during the cycle process. They designed a layer of silicon oxide coated on the outside of the Si nanotube structure as a fixed layer of the Si nanotube. This structure blocks the direct contact between the Si nanotube and the electrolyte, but lithium ions can still contact the Si nanotube through the fixed layer. This design helps to prevent the volume expansion of the Si nanotube during the charge and discharge process, which leads to the repeated formation of the SEI film and can improve the cycle stability of the harmful electrode material. The cycle test results show that the capacity retention rate of the Si nanotube protected by the fixed layer reaches 88% after 4000 charge and discharge cycles at a rate of 10 C, and the capacity retention rate reaches 93% after 6000 cycles. Nanotubes combined with composite materials majorly solve the issue of short lifespan, stabilizing the SEI firm and avoiding the expansion volume of silicon [10].

In conclusion, one-dimensional silicon nanostructures have similar advantages as zero-dimensional silicon structures and better expand the lifespan of lithium batteries than zero-dimensional silicon structures.

4.3. Two-dimensional Silicon Nanostructures

Due to their unique nanostructures, two-dimensional silicon nanofilms can effectively mitigate this volume expansion and improve the cycle life and stability of the battery. For example, introducing mesopores in 2D silicon nanofilms through molecular stencils can significantly enhance their ability to cope with volume changes. The 2D Si nanofilm has a sizeable planar structure that can shorten the lithium-ion transport path, which is conducive to stable lithium adsorption and rapid diffusion. This property enables the battery to perform better under high-rate charging and discharging conditions. Two-dimensional silicon nanofilms have a large active specific surface area, which can expose enough adsorption sites to enhance storage capacity and energy density significantly. This advantage allows the battery to store more electrical energy in the same volume or weight. The structural design of the 2D Si nanomembrane helps to reduce polarization, allowing the battery to maintain a more stable performance at different charging and discharging rates. This property is essential for improving the fast-charging and fast-discharging capability of batteries. In addition, unlike powder materials, 2D Si nanofilms can be used directly as electrodes without the involvement of binders and conductive agents. This not only simplifies the preparation process of electrodes but also reduces the impact on electrode performance [10].

4.4. Three-dimensional Silicon Nanostructures

The three-dimensional silicon nanostructures refer to the porous silicon nanostructure. Because porous silicon has a large specific surface area, fragile pore walls, and sufficiently large pore spaces, it can effectively suppress electrode short circuits and shorten the transmission path of lithium ions, thereby increasing the battery's power density and extending the battery life. The porous silicon nanostructure contains nearly all the advantages of silicon nanotechnology.

Three-dimensional silicon nanostructures typically have more complex geometries and pores, providing a higher specific surface area. Compared to two- and one-dimensional structures, three-dimensional structures can fully contact the electrolyte, thus creating more active sites and facilitating electrochemical reactions. The voids and pores in the 3D silicon nanostructures provide more accommodating space for the volume expansion of silicon that occurs during the lithiation process. Compared with the two-dimensional and one-dimensional structures, the three-dimensional structure is more effective in alleviating the problems of stress concentration and electrode structure damage caused by volume expansion. The interconnected porous network in the 3D silicon nanostructures facilitates the penetration and filling of the electrolyte and provides more migration paths for lithium ions. This design shortens the diffusion distance of lithium ions and reduces the ion transfer impedance, enabling the battery to maintain excellent performance even under high-rate charging and discharging conditions. Due to the high specific surface area and excellent volume expansion buffering capability of the 3D silicon nanostructures, the battery can hold more active material without sacrificing cycling stability. This helps increase the battery's energy density and meet the demand for high-energy-density batteries [11].

Various preparation methods, such as the template, chemical vapor deposition, and radio frequency magnetron sputtering technology, can obtain three-dimensional silicon nanostructures. Each preparation method has advantages and disadvantages and can be selected according to specific application requirements and cost considerations. Compared with two-dimensional and one-dimensional structures, three-dimensional structures may be more complicated to prepare. Still, with the continuous optimization and advancement of the preparation process, the cost is expected to decrease gradually.

5. Conclusion

This paper briefly summarized the application of silicon nanotechnology in lithium-ion batteries. Different silicon nanotechnology has a diverse focus on the improvement of lithium-ion batteries. Low-dimensional silicon nanotechnology might focus on combining with other composite materials, hence facilitating the expansion volume problem, stabilizing the SEI firm, and prolonging the lifespan of lithium batteries. Two-dimensional and three-dimensional silicon technologies mainly focus on improving performance, expanding the energy capacity, and helping stabilize the SEI firm, and they are the most promising silicon nanotechnology.

The silicon nanotechnology still has demerits. For instance, the high cost of producing lithium-ion batteries with silicon nanotechnology, the high failure rate in nanosilicon materials, and the complicated manufacturing process deter the widespread commercialized application in average electric vehicles. Additionally, though silicon nanotechnology has already alleviated the volume expansion issues, the problem still exists and might still have potential safety risks. Furthermore, due to the large contact area in porous silicon nanostructures, the SEI firm would still be formed, suppressing the performance of lithium-ion batteries.

Silicon nanotechnology still faces the issues of volume expansion and the formation of SEI. These are the future trends of improving and applying silicon nanotechnology. The future tendency of lithium-ion batteries might be to expand their lifespan and enhance their energy capacity without forming a greater area for SEI firms.

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