Advances in Silicon Anode Morphology for Enhanced Lithium-Ion Battery Performance: Current Status and Future Perspectives

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Abstract: Lithium-ion batteries with high energy density are regarded as highly promising electrochemical energy storage systems. However, traditional liquid electrolytes present significant safety risks due to their propensity for leakage and flammability. In contrast, solid-state electrolytes have garnered extensive attention for their enhanced safety performance, high energy density, and superior stability with lithium anodes. Consequently, research on solid-state electrolytes has become increasingly prominent. Despite this, the development of solid-state electrolytes remains in an exploratory phase, primarily hindered by issues such as high solid-state impedance and side reactions with electrodes. Moreover, the challenge lies in integrating the performance advantages of various solid-state electrolytes. The primary obstacle is the poor compatibility between solid-state electrolytes and electrodes. Current strategies to address these issues include electrode modification, electrolyte recombination, and the introduction of interface layers. Nevertheless, solid-state electrolytes have not yet achieved the level of development necessary to fully replace liquid electrolytes. This article provides a comprehensive review of the status of organic polymer and inorganic solid-state electrolytes and discusses the future development trends of these materials.

1 INTRODUCTION

Today, the problems of energy supply and the environment are becoming increasingly prominent and have become the focus of global attention. With the development of industrialisation and urbanisation and the gradual depletion of traditional energy resources, the energy crisis has become an urgent problem. In order to meet this challenge, people have turned to electrification technology and are constantly exploring innovations in the field of new energy sources. As an important energy storage and release device, lithium-ion batteries are gradually becoming the mainstream choice for electric vehicles, renewable energy systems and other fields. In the research field of automotive batteries, lithium-ion batteries are favoured for their high energy density, long cycle life and low self-discharge rate. However, conventional carbon anode materials are restricted in terms of capacity and energy density, making it difficult to meet the growing market demand for electric vehicles. Therefore, the search for new anode materials has become one of the hotspots of current research (Deng et al., 2020 & Manzetti and Mariasiu, 2015).

Silicon, as a potential high-capacity anode material with advantages such as abundant resources, high theoretical specific capacity, and good electrical conductivity, is widely regarded as an ideal alternative to traditional carbon anode materials. Silicon materials are characterised by their ability to hold more lithium ions and therefore have a higher specific capacity, which is expected to significantly increase the energy density and range of batteries. However, there are some challenges associated with silicon anode materials. Firstly, silicon materials undergo volume expansion and contraction during charging and discharging, leading to problems such as electrode particle fatigue and electrode structure damage, affecting the cycle life and stability of the battery. Second, the low conductivity and high surface area of silicon materials also increase electrode polarisation and charge transport resistance, reducing the charge and discharge rate and power performance of the battery (Speirs et al., 2014).

Recently, silicon electrodes have garnered significant research interest. Strategies like nanostructure engineering, composite development, electrolyte additives, and novel polymer binders have been extensively developed, leading to notable improvements in the electrochemical performance of

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silicon materials. Nanostructure engineering, in particular, has demonstrated significant potential for enhancing cycling stability and rate capability. Various silicon nanostructures, including nanoparticles, nanowires, thin films, and porous structures, have been extensively studied. These nanostructures significantly improve the electrochemical performance of silicon materials by efficiently accommodating volume expansion, increasing active surface area, shortening lithium-ion diffusion paths, and reducing electron and ion transport distances. These advances provide new ideas to address the practical applications of silicon anode materials (Li et al., 2022).

This paper reviews and analyses the research progress on the morphology of silicon anode materials for lithium-ion batteries, and summarizes the current research progress of silicon anode morphology regulation in the field of lithium batteries based on the existing research background and status quo, pointing out its potential application prospects in improving the energy storage performance of the batteries, prolonging the battery life and improving the safety. In view of the problems and shortcomings of the current research, the possible future research directions and development trends are proposed, and the future research prospects of silicon anode materials are envisioned.

2 RESEARCH PROGRESS OF SILICON ANODE FOR LITHIUM-ION ELECTRODE

2.1 Block Silicon

Lumpy silicon refers to large-size silicon particles or lumpy silicon negative electrode materials, as shown in Figure 1. Under the consideration of the influence of morphology on energy storage performance, lumpy silicon is used as a common silicon negative electrode material morphology, which has its unique superior high specific capacity and can achieve higher energy density. The volume expansion is relatively small, which is conducive to maintaining the stability of the electrode structure. The preparation method is relatively simple and can be mass-produced.

The high specific capacity of bulk silicon is mainly due to its large volume and relatively small surface area. This allows bulk silicon to store more lithium ions, thereby increasing the energy density of the battery. However, the volume expansion of bulk silicon during charging and discharging may lead to the destruction of the electrode structure. This is because the silicon undergoes volume expansion as lithium ions react with the silicon during charging and discharging. Although the volume expansion of bulk silicon is relatively small, it may still lead to structural damage and performance degradation during long-term cycling. Therefore, improving the cycling stability and suppressing the volume expansion of bulk silicon is the focus of current research.

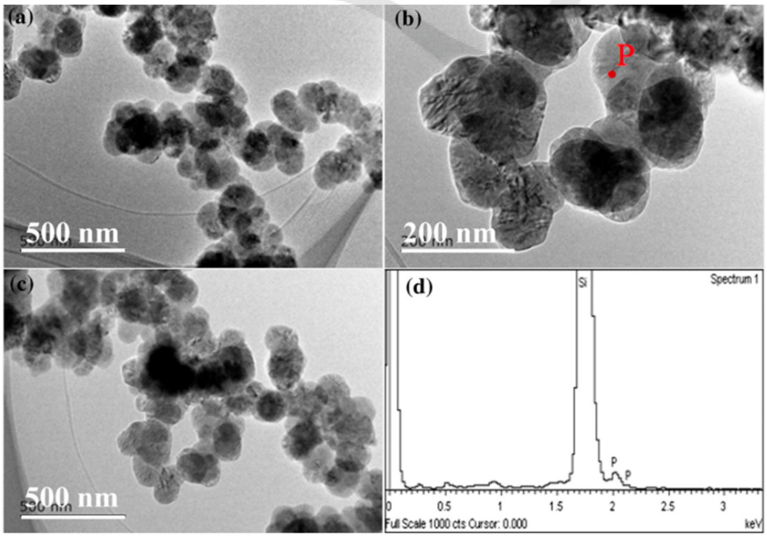

Figure 1: TEM images of P-Si (Rajaeifar et al., 2022)

2.2 Silicon Nanoparticles

In nanostructure engineering, nanoparticles are one of the most common silicon nanostructure. Nanoparticles have the advantages of high specific surface area and short ion diffusion paths, which are beneficial to improve the cycling stability and rate performance of batteries. In addition, nanoparticles can be modified with suitable surface modifications to improve the interfacial properties between them and the electrolyte, thereby inhibiting SEI formation and improving the cycle life of the battery.

Particle-forming silicon materials, with sizes spanning the micron to nanometer scale, are of great interest in commercial mass production and are considered as one of the most promising candidates for next-generation lithium-ion battery (LIB) anode materials. The particle size of silicon materials has a substantial influence on the battery's lifespan and stability of the electrodes. In particular, when the particle size is reduced to the nanoscale, mechanical stresses can be released quickly, thus exhibiting greater resistance to structural fracture compared to larger particle sizes. The results of Kim et al. showed that the particles do not continue to grow when the particle diameter is below 10 nm, which also applies to lithium metal. Similar results were found in tin-based electrodes, where further fracture of the particles does not occur when the particle diameter is below a certain critical size.

The technology for engineering silicon nanoparticles is fairly well established, with the main methods including chemical vapour deposition (CVD), ball milling, molten salt electrolysis and ferrothermal (carbothermal) reduction. Silicon nanoparticles synthesised by CVD usually have a uniform size distribution, however, the method suffers from the high cost of precursors and complexes, harmful silane gases, and low yields, which limit its application in large-scale production. In contrast, the ball milling method has the advantages of high production capacity, low cost, and easy doping with other elements, so it is widely used in the preparation of silica nanoparticles. Wang et al. The morphology of silica nanoparticles as a raw material is shown in Figure 2. From this figure, it can be seen that there is an aggregate of spherical particles with diameters between 20 and 70 nm, and its average particle size is about 30 nm. In addition, the FESEM images of the three graphites used in this study are shown in Figure 2b-d.

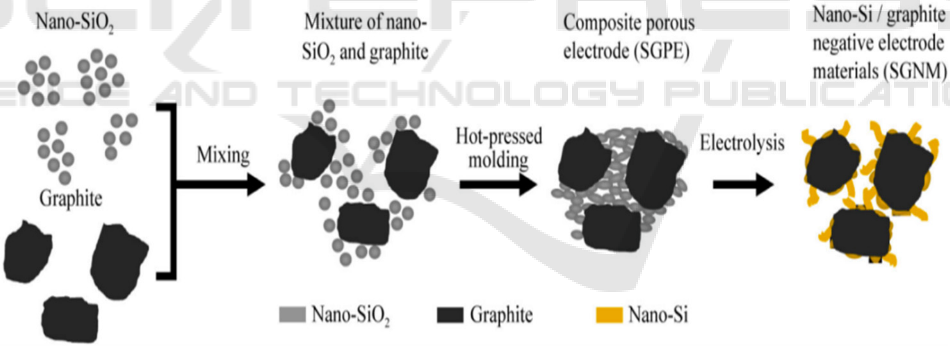

Figure 2: The SGNM preparation process (Wang et al., 2022)

Recently, Zhu et al. proposed a simple and scalable method to prepare silicon nanomaterials by high-energy mechanical milling. This method produces silicon nanoparticles of about 100 nm size, which exhibit an exceptionally stable and reversible capacity when coated with carbon, with a capacity drop of less than 3% after 100 cycles. Although this method is commercially available, there are still many challenges in the process, such as large amounts of impurities, surface oxidation, and size variation (Tang et al., 2022).

In addition to ball milling and CVD, molten salt electrolysis and ferrothermal (carbothermal) reduction are also commonly used methods to obtain silicon nanoparticles. Although these methods are carried out at high temperatures, recently Lin et al. proposed a strategy for the synthesis of silicon nanocrystals at lower temperatures, which was achieved in aluminium chloride molten salt. However, silicon nanoparticles are seldom chosen as anode materials because they tend to fragment during repeated charge/discharge cycles, resulting in a loss of electrical contact with the collector and a rapid decay in capacity. To address these issues, various additives such as carbonaceous materials, graphene, conductive polymers, and metallic materials have been incorporated into silicon nanoparticles. (Palomares et al., 2022).

2.3 Silicon Nanoparticles

Silicon nanotubes have a larger surface area and smaller volume due to their hollow tubular structure, so they can effectively slow down the volume expansion of silicon when it alloys with lithium, thus improving the stability and cycle life of the electrode. As shown in Figure 3, the walls of the silicon nanotubes can provide more electron transport channels and reduce the transport distance of electrons inside the material, and thus have higher electron conductivity, which helps to improve the conductivity and power performance of the electrodes (Moyassari et al., 2022). The hollow structure and nanoscale size of the silicon nanotubes facilitates the rapid diffusion of lithium ions inside the tubes, and therefore improves the lithium-ion diffusion rate of the electrodes, which in turn improves the charging and discharging rate and cycling performance of the batteries. Silicon nanotubes have better deformability due to their flexible tubular structure, which can better adapt to the volume change during the alloying reaction between silicon and lithium and reduce the structural damage of the electrode material (Roland et al., 2022; Sanad and Shenouda, 2023 & Li et al., 2023). Overall, silicon nanoparticles and silicon nanotubes, as an important form of silicon anode materials, have unique advantages in enhancing the efficiency and reliability of batteries, and controlling the parameters of silicon nanotubes, such as tube diameter and wall thickness, can further regulate their electrochemical properties. However, the preparation of silicon nanotubes usually requires more complex processes, and thus there may be some challenges in terms of cost and process control (Patel et al., 2023 & Ishii et al., 2024).

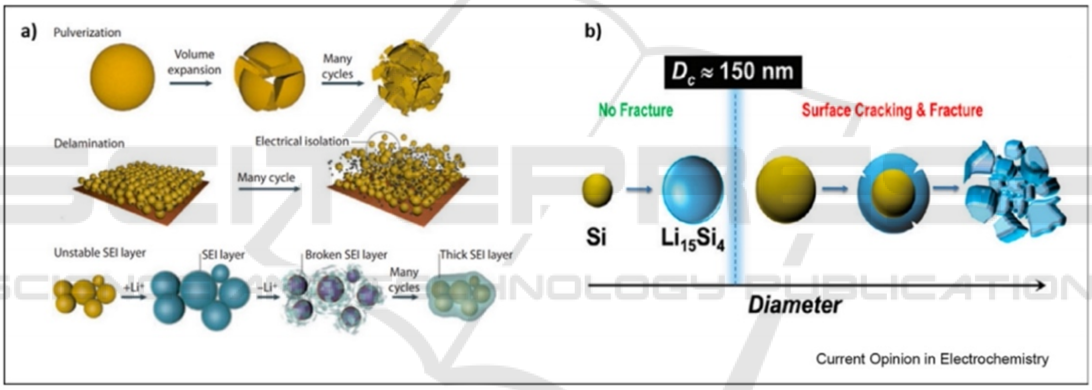

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Figure 3: The mechanisms of Si electrodes (Patel et al.., 2023)

2.4 Thin Film Silicon

The main feature of thin-film silicon as a battery anode material is to form a thinner silicon layer by precisely controlling the thickness of silicon to cope with the problems caused by the volume expansion of the traditional bulk silicon material during the charging and discharging process. As shown in Figure 4, thin-film silicon can mitigate the volume expansion problem more effectively than bulk silicon. Due to its smaller thickness, the volume expansion will be more uniform, resulting in less damage to the electrode structure (Ishii et al., 2024). Thin-film silicon usually has a large surface area, which is conducive to increasing the contact area between the electrodes and the electrolyte, thus improving the charge transfer rate and electrochemical capability of the cell. By controlling the preparation process of thin films, precise modulation of their microstructure can be achieved to further optimise their electrochemical performance (Bonkile et al., 2024). Thin-film silicon also has some relative technical limitations. Compared to bulk silicon, the preparation of thin-film silicon is typically more complex and requires more sophisticated processes and equipment, which can increase costs and reduce production efficiency. Although thin-film silicon can mitigate volume expansion, it may still face poor cycling stability during long-term cycling, which requires further improvement and optimisation (Li et al., 2023 & Yao, 2023).

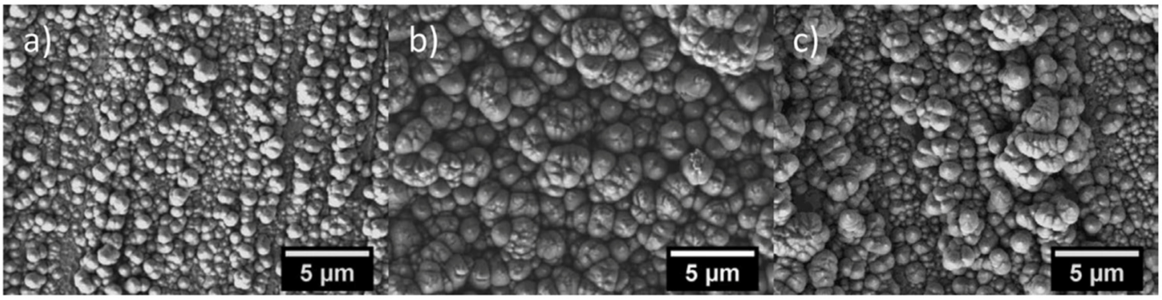

Figure 4: SEM images of Si electrode (Lukin et al., 2023)

The mechanism of slowing down the volume expansion of thin-film silicon mainly stems from its smaller thickness, which makes the volume change more uniform and thus reduces the stress concentration in the electrode structure and prolongs the life of the cell. The large surface area, on the other hand, helps to improve the contact between the electrode and the electrolyte, which facilitates the rapid transport of electrons and ions, and thus improves the performance of the cell (ElKhamisy et al., 2024). However, the complexity of the preparation process and the challenge of cycling stability still need to be addressed through process optimisation and material design to drive further application and development of thin-film silicon in batteries. These advantages and challenges make thin-film silicon a promising area in the study of battery materials and provide important directions and challenges for future research (Ette et al., 2020).

3 OUTLOOK OF SILICON ANODE

Currently, for the technological innovation aspect of silicon negative electrode, researchers should further explore the properties of silicon negative electrode materials with different morphologies and optimise their electrochemical properties, especially the rod-shaped nano-silicon materials which have great potential to increase the capacity and energy density, improve the cycling performance, and increase the charge transfer rate. At the same time, the challenges of complex and costly preparation processes need to be focused on, and efforts should be made to develop low-cost and large-scale preparation technologies for silicon anode materials, and to use renewable materials or waste resources to reduce the preparation cost (Haneke et al., 2023).

In terms of the development trend, the mechanism of the effect of morphology modulation on the energy storage performance needs to be explored in depth through experimental and theoretical analyses to reveal the mechanism of its action at both the macro- and microscopic levels. The experimental results and discussion should focus on the performance differences of different morphology silicon anode materials in lithium batteries, and explore the influence of morphology modulation on energy storage performance and the possible direction of improvement. Meanwhile, in terms of application prospects, this paper predicts the application prospects of silicon anode materials in electric vehicles and energy storage systems, and explores the research and application of multifunctional silicon anode materials, such as silicon nanowire anode materials with self-repairing ability or porous structure.

4 CONCLUSION

In this paper, the impact of silicon anode morphology on the energy storage performance of Li-ion batteries is reviewed, and several ideas are put forward in terms of technological innovation, cost reduction and development trends. In addition, comprehensive analyses have been conducted to consider how to overcome the volume expansion and contraction of Si anode materials during charge/discharge cycles, how to improve the cycling stability and capacity retention of Si anode materials, how to increase the conductivity of Si anode materials to enhance the charge/discharge performance of batteries, and how to reduce the interfacial problems between the Si material and the electrolyte to enhance the battery's durability and safety.

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