Enhancing Lithium-Ion Battery Performance: Silicon-Carbon Composite Anodes

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Abstract: With the growth of global energy concerns, lithium-ion batteries (LIBs) are at the forefront of research for efficient energy storage solutions. The objective of this study is to explore the potential of silicon anodes, which can theoretically hold up to 4200 mAh/g, far exceeding the 372 mAh/g of traditional graphite anodes. Significant volume expansion and instability during lithiation prevent the practical application of silicon anodes. To address these issues, various carbon materials, including graphite, carbon nanotubes (CNTs), and graphene, are integrated with silicon to enhance capacity, stability, and cyclability. In addition, research on graphite, carbon nanotube, and graphene composite anodes suggests that hybrid approaches can capitalize on the strengths of each material, potentially surpassing the performance of single-material anodes. As graphene production technology improves and becomes more cost-effective, graphene-silicon anodes may eventually become the optimal solution for high-performance lithium-ion batteries. This paper provides a systematic review of the mainstream silicon-carbon composite anode materials at the present stage, and makes an outlook on the future development trend of silicon-carbon composites.

1 INTRODUCTION

In recent years, nations around the world have become increasingly concerned about energy issues. Solutions to energy depletion and the energy crisis are in the spotlight. A mass of policies are proposed in order to save energy and encourage renewable energy exploitation. These policies all point to the same core, which is electricity. Research on batteries, especially LIBs, has been carried out extensively to be able to better utilize and store electricity. The development of LIBs is mainly focused on several aspects like capacity, stability, and charging and discharging efficiency. Among these, capacity is of the most vital significance, and countless works have been carried out to increase the capacity of LIBs. LIBs transform chemical energy into electrical energy via an electrochemical redox reaction. In every cell, the area that experiences oxidation is referred to as the anode, and the area that experiences reduction is referred to as the cathode. Lithium atoms and lithium ions are stored and received at the anode and cathode.

The silicon anode instead of the traditional graphite anode is thought to be promising because the theoretical maximum capacity is 4200 mAh/g. The silicon anode has a specific capacity that is over ten times larger than that of graphite's theoretical maximum capacity of 372 mAh/g (Min et al, 2024). In fact, in the last five years, research on silicon anodes has kept growing. However, when the lithium ions enter the silicon anode, the silicon-lithium alloy will be formed, and the volume will expand dramatically. It not only leads to instability of the lithium-ion battery itself but also makes silicon anodes unsuitable for solid-state lithium-ion batteries because the two solid-phase interfaces collide and crush each other, leading to damage. This property seriously affects the actual capacity and service life of silicon anode LIBs and raises the risk of using silicon anode lithium-ion batteries as well.

Many studies are being carried out to solve this problem, such as using nanoprecipitation, redesigning the structure, and doping silicon with other atoms. Carbon doping now turns out to be effective and low-cost. But carbon doping will inevitably decrease the capacity. Thus, researchers are trying to find a way to get a composite of silicon and carbon with optimal capacity and volume extension. This study will review different types of carbon-silicon anodes, compare the performance of various composite materials, and provide guidance for further research.

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2 CLASSIFICATION AND COMPARISON OF CARBON-SILICON COMPOSITES

2.1 Graphite-Silicon Anode

The advantages of using graphite are obvious. The cost of graphite is low, the specific surface area is low, the tap density is high, and graphite itself is eco-friendly. Another thing of interest is that graphite-silicon anodes are made in a very diverse and sophisticated process. Based on these properties, graphite is promising to be processed into a graphite-silicon anode. However, the performance of the graphite-silicon anode is not satisfying for many reasons, such as specific capacity and aging. The performance of graphite-silicon anodes through different preparation methods can vary a lot.

There’re quite a lot of preparation methods to get graphite-silicon anodes. Peng Li et al. concluded that several methods, like mechanical ball milling, the spraying method, chemical vapor deposition, and the and the wet processing method, were the most commonly used preparation methods. Among these, ball milling and CVD are the most widely used and easy to adjust for the final product (Peng et al, 2021). Zhao et al. (2022) synthesized a high-performance Si-G-C-15 anode material using a cost-effective routine. The resulting composite showed a specific capacity of 965 mAh/g as well as retained over 70% capacity after 100 cycles. The small particle size and uniform distribution of components in the composite play a crucial role in promoting the rapid diffusion of lithium ions within the electrode. This uniform distribution contributes to the overall performance and stability of the battery. Hu et al. (2023) prepared a graphite-silicon composite using chemical vapor deposition (CVD). They grew nano-sized silicon on HCl-purified graphite in a CVD chamber with SiCl4 in an argon atmosphere and hydrogen. The CVD anode showed better capacity retention and specific capacity at high current density compared to one prepared by ball milling. In the composite, the graphite matrix acts as a semi-enveloping structure around the silicon particles, providing confinement that buffers the volume growth of silicon during electrochemical cycles, which is shown in Figure 1. This confinement helps to protect the silicon particles from breaking away from the conductive network, thereby enhancing the life span of the anode.

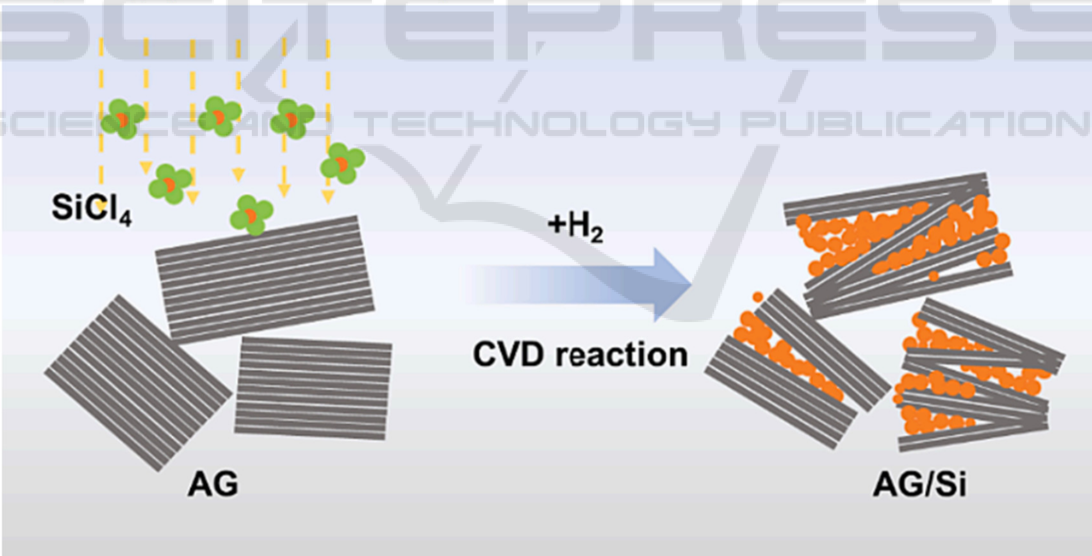

Figure 1: The composite was prepared using CVD (Hu et al., 2023)

The content of silicon in graphite-silicon composites is relatively low (around 10% to 20%) to prevent anode damage. In order to reduce the side-effects of volume expansion in anodes, lots of space should be spared for silicon particles to grow up. Since the volume expansion is constant as long as the silicon content is constant, what can be improved is the unoccupied space. So, it’s definitely accessible to better disperse silicon atoms in the graphite or make the micro-silicon smaller. However, the performance of the graphite anode is not satisfying. The ball milling method, which is the most applied preparation process, turned out to be inefficient. The lifespan and specific capacity of the composite prepared through ball milling are greatly inferior to the ones made through CVD (Hu et al., 2023). Though the specific capacity of graphite-silicon anodes has reached a high level. Its lifespan is still worrying, as the retention has fallen to 70% only after 100 cycles.

2.2 Carbon Nanotube-Silicon Anode

Carbon nanotubes (CNTs) is famous for its outstanding mechanical properties and its stability. It ’s as strong as a diamond, while its ductility is also great. Its tensile strength is up to 60 GPa and the tensile strain is up to 15% (Daoyang et al., 2018). Carbon nanotubes are categorized into single-walled (SWCNTs) and multi-walled (MWCNTs) varieties. Both exhibit excellent electrical and thermal conductivity. So, they can also work equally well as electrodes and conductors. The working mechanism of Si/CNTs composite electrodes is shown in Figure.2. Carbon nanotubes possess a large specific surface area, providing ample space for hosting nanoparticles and enhancing the performance of energy storage devices (Ha et al., 2024). In the case of cost, CNTs are relatively low-priced because they have been able to be mass manufactured. But some difficulties need to be overcome for the carbon nanotube-silicon anode. The specific surface area of a carbon nanotube is quite high since it is actually the rolling of several carbon atom layers. The high specific surface area contributes to the van der Waals force, so the carbon nanotubes tend to form clusters. Thus, the preparation of a carbon nanotube-silicon anode is trickier than that of a that of a graphite-silicon anode. How to design a high-performance anode obtained through one-step synthesis or simple methods is the main problem. Several one-step syntheses have now been developed. The products turned out to have a higher specific capacity and a longer service life.

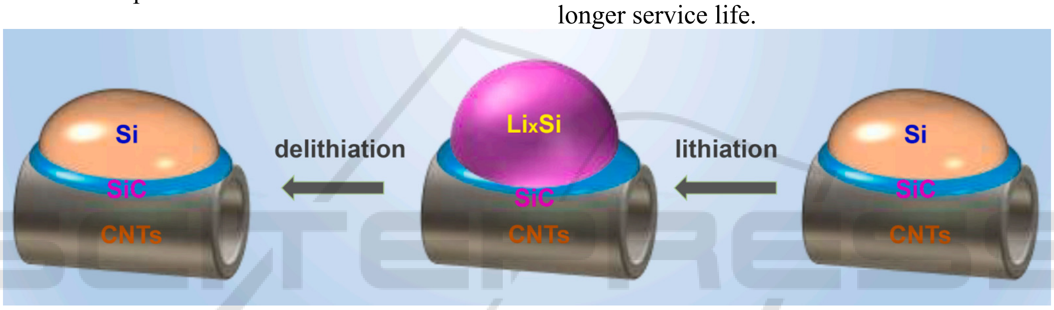

Figure 2: The working mechanism of Si/CNTs composite electrodes (Guo et al., 2024)

Guo et al. (2024) developed a practical method to prepare Si/CNTs composites. SiO_2, Mg powder, and CNTs were mixed in argon, enclosed in carbon paper, and heated for hours. The samples were treated with HCl and HF solutions to remove impurities, resulting in purified Si/CNTs composites. The SiO_2 to CNT weight ratio is critical in shaping the interface between silicon nanoparticles and carbon nanotubes. When the ratio is high, silicon nanoparticles react with CNTs, forming Si-C bonds that enhance interaction and improve electrochemical performance. Thus, adjusting the SiO_2 weight ratio controls Si-C bond formation can alter the performance of the carbon nanotube-silicon anode. The composite they synthesized has outstanding performance. Si/CNTs-2 with enhanced interfacial bonding through Si-C chemical interactions has high specific capacity and duration. At 0.2 A/g, it has an initial reversible capacity of 1100.2 mAh/g and maintains a capacity retention rate of 83.33% after 200 cycles. Gonzalez et al. (2022) created silicon-doped carbon nanotubes (Si-CNTs) using metal-catalyzed chemical vapor deposition (M-CVD) at 800 ℃and 900 ℃ separately, producing two different Si-CNT anodes, Si-CNT8 and Si-CNT9. The Si-CNT anodes were treated with nitric acid before characterization and electrochemical assessment. Si-CNT8 demonstrated a consistent capacity of approximately 400 mAh/g throughout 120 cycles. In contrast, Si-CNT9 delivered 360 mAh/g over 120 cycles. It indicates that the Si/CNT composite should better be synthesized in at 800 ℃. The synthesis temperature influenced the resistance to oxidation of the Si-CNT samples, with Si-CNT9 showing higher resistance compared to Si-CNT8. At a higher temperature, the Si-C bond formation was observed, suggesting that higher temperatures favor make it easier to insert silicon in the CNTs network.

According to these researches, it is rational to get the conclusion that the specific capacity of carbon nanotube-silicon anodes is much higher than traditional graphite anodes and the graphite-silicon anodes mentioned above. Though the carbon nanotube-silicon anodes created by Isaías Zeferino Gonzalez et al. is not impressive enough, it proves that CVD can be applied in both graphite anodes and carbon-nanotube anodes. Based on these cases, the upper limit of carbon nanotube-silicon anode is very high, with extremely superior specific capacity and life time, but also due to its own difficult-to-process characteristics, the performance gap will be very large in different processing, and perhaps even under slightly different processing conditions, which requires a very mature preparation process for carbon nanotube-silicon anode.

2.3 Graphene-Silicon Anode

Graphene possesses high electrical conductivity, excellent stability, outstanding mechanical properties. Besides these advantages, graphene is more beneficial to the anode duration than CNT (Poonam et al., 2021). This is because graphene layers can alleviate the stress caused by volume expansion, buffering the damage to the anode as long as graphene can uniformly cover the carbon-silicon particles. It's also essential to address the problem of its large specific surface area. Li et al. (2024) developed a method to create high-performance silicon/graphene carbon composites. They dispersed graphene oxide (GO) with silicon nanoparticles in a solvent, added coal tar pitch, evaporated the solvent, and carbonized the composite at a certain temperature under nitrogen. This formed multi-interface structures, enhancing the composite's performance as an anode material for LIBs. The composite is beneficial for the formation of a homogeneous solid electrolyte interphase (SEI) film and lithium-ion transport, reducing resistance and improving electrochemical properties. The graphene-silicon anode exhibits outstanding service life and high specific capacity, with a specific capacity of 820.8 mAh/g at 50 mA/g and 93.6% capacity retention after 1000 cycles at 2 A/g. These results demonstrate its excellent performance and stability, surpassing all previously mentioned anode materials. Graphene's specific capacity and longevity make it the best material for carbon-silicon anodes, highlighting its potential in lithium-ion batteries.

But unlike the CNTs which can be mass-produced, the graphene mass production has not been established. Even if high performance graphene can be produced in some certain ways like mechanical peeling, reduced graphene oxide (rGO) methods and so on, few graphene-silicon anode are produced and applied into practice, let alone the usage in business. To address this problem, Zhang et al. (2024) introduced a novel method to mass-produce oriented Si/rGO films. They utilized a layer assembly technique with GO as a binding agent. Nano-Si particles were dispersed, sonicated, and combined with GO to form a nano-Si/GO composite. In Figure 3, the high-order layer and dense structure formed by the nano-Si embedded into the gap between layers of graphene is clearly visible. In this case, the Si/rGO composite exhibits an initial specific capacity of 1222.5 mAh/g at 200mA/g. Notably, this capacity remains consistent over 1000 mAh/g after 200 cycles, highlighting the electrode's exceptional cycling stability.

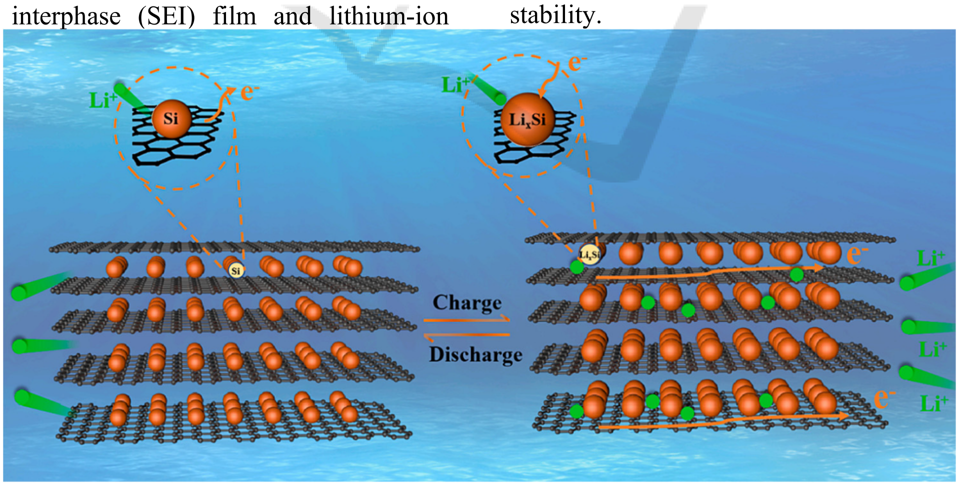

Figure 3: The layer-to-layer structure and its working mechanism (Zhang et al., 2024)

It's a fact that there are numerous high-performing graphene-silicon anodes that can hold more than 2300mAh/g at 210 mA/g after 50 cycles (Fei et al., 2014). However, most of the preparation methods are time-consuming and not eco-friendly. Though the performance of Zhang's product needs to be improved, its preparation method inspires others to invent more methods to obtain graphene-silicon anodes with mass production. Though the cost is not affordable now, with more and more researches realizing the promising performance of graphene and graphene-silicon anode, the price will definitely decrease in near future.

3 PROSPECTS FOR SILICON-CARBON ANODES

In recent years, the integration of carbon materials with silicon has offered a viable solution to mitigate the challenge. Carbon, such as graphite, carbon nanotubes, and graphene, brings a suite of desirable properties to the composite, including high electrical conductivity, mechanical robustness, and the ability to accommodate volume changes during lithiation. By synergistically combining silicon with carbon, researchers aim to develop composite anode materials that offer enhanced capacity, stability, and cyclability compared to traditional graphite-based anodes.

One thing that has been mentioned many times in so many studies and is considered crucial is homogeneity. How the silicon particles are arranged between the individual carbon layers can greatly affect the properties of the composite. when the silicon particles can be uniformly distributed, the carbon layers can best buffer the damage caused by the increase in volume and maximize the contact area, which is beneficial to improving the specific capacity. Therefore, this paper argues that CVD is a highly desirable material for preparing carbon-silicon anodes because CVD allows for precise control of film thickness, composition, and properties by adjusting process parameters such as temperature, pressure, precursor concentration, and gas flow rate. This level of control allows for customization of the film to meet the specific requirements of various applications. Defects are minimized and the overall performance and reliability of the deposited material is improved.

Another important case is about the carbon content. With the content of carbon increases, the specific capacity of carbon-silicon anode will inevitably decrease because the specific capacity of silicon is much higher than carbon. It's not rational to criticize a specific processing of carbon-silicon anode for a single reason that in one's research, the capacity of anode is lower than another research without taking carbon content into account. So, if we can get the ideal performance of carbon-silicon composite at any particular carbon doping level, then the difference between the ideal performance and actual performance can be computed. We can also try to get an optimal proportion of carbon and silicon to get a relatively high specific capacity ensuring the service life as well. Wu. et al. (Min et al, 2024) has showed the ideal volume expansion and capacity in different doping concentration using first-principles study. They compute the anode volume expansion and specific capacity at different Li embedding ratio and different carbon concentration. Their work can be an indication, but quite a lot factors will be omitted as it's a first-principles study, so the calculated data is not able to be realized.

By comparing the performance of graphite, carbon nanotubes and graphene, it is clear that carbon nanotubes stand out at the moment with better performance, moderate cost and no longer cumbersome fabrication process. But this does not mean that the future development can only be centered around carbon nanotubes, now there are also researchers began to explore the graphite / carbon nanotubes / graphene composite carbon silicon anode preparation and performance, through the nature of each material, the cost of complementary to achieve a better state. And in the future, once graphene can be mass-produced, better performance of graphene can replace the current status of carbon nanotubes. Therefore, the future development of carbon silicon anode should be centered on graphene and carbon nanotubes or graphite composite carbon doping to carry out research.

4 CONCLUSIONS

In conclusion, combining carbon materials with silicon anodes is a viable approach to improving the performance of lithium-ion batteries. The study provides a comprehensive comparison of different types of carbon-silicon anodes, including graphite-silicon, carbon nanotube-silicon, and graphene-silicon composites. Each type offers unique advantages and challenges. Graphite-silicon anodes, while cost-effective and environmentally friendly, have issues with capacity and stability. On the other hand, carbon nanotube-silicon anodes show excellent specific capacity and mechanical properties but require precise and often complex preparation methods to overcome their tendency to agglomerate. Graphene-silicon anodes exhibit excellent electrical conductivity and mechanical stability with outstanding specific capacity and lifetime, but large-scale production remains a major obstacle.

It has been shown that a uniform distribution of silicon particles in the carbon matrix is essential to maximizing anode performance. Methods such as chemical vapor deposition allow precise control of the fabrication process to produce high-quality carbon-silicon composites with optimal properties. Furthermore, the ratio of carbon to silicon can have a significant impact on the capacity and stability of the anode, suggesting that an optimal balance must be achieved to ensure high performance and long life. Current research advances indicate that carbon nanotube-silicon anodes are leading the way in terms of performance and utility. However, continued research on graphite, carbon nanotube, and graphene composite anodes suggests that hybrid approaches can capitalize on the strengths of each material, potentially surpassing the performance of single-material anodes. As graphene production technology improves and becomes more cost-effective, graphene-silicon anodes may eventually become the optimal solution for high-performance lithium-ion batteries.

In the search for a sustainable energy future, carbon-silicon anodes are a beacon of hope for the transformative potential of advanced materials and engineering solutions. By harnessing the power of carbon and silicon, we can open up new possibilities for energy storage, transportation, and electrification, thereby creating a brighter and cleaner tomorrow for future generations.

REFERENCES

Daoyang H, Hui M, Shanshan X, Konstantinos G D, Laifei C 2018 *J.Eur.Ceram.Soc.* **38** Pages 3695-3708

Fangfang Z, Min Z, Yanru D, Lei M, Yu Z, Sulin N and Liangming W 2022 *Powder Technol.* **404** 117455

Fei L, Hongwei Y, Zhibo Y, Xiuwan L, Yanli Q and Deyan H 2014 *Mater. Lett.* **128** Pages 132-135

Ha E K, Jaehwan K, Sung G S, Young S Y 2024 *Carbon* **219** 118800

Isaías Z G, Hsien-Chieh C, Raynald G, George P. D, Ysmael V 2022 *Mater. Today Commun.* **30** 103158

Mengfei H, Houzheng W and Guo-Jun Z 2023 *Chemical Physics Letters* **833** 140917

Min W, Guangkai C, Zhe L, Lan Y and Cen W 2024 *Vacuum* **225** 113222

Peng L, Hun K, Seung-Taek M and Yang-Kook S 2021 *Energy Storage Mater.* **35** Pages 550-576

Poonam S, Abgeena S, Abid, Julien C M and Islam S S 2021 *J. Power Sources* **501** 229709

Xiaobei G, Zhongtang Y, Wei W, Yi Z, Nengfei Y, Chunhua L 2024 *Surf. Interfaces* **48** 104223

Xin L, Kun L, Man Y, Jiapeng Z, Haiyan L, Ang L, Xiaohong C and Huaihe S 2024 *J. Colloid Interface Sci* **667** Pages 470-477

Yanlin Zhang, Dafang He, Junhong Lu, Jie Huang, Haoyang Jiang, Junfeng Rong, Guolin Hou and Haiqun Chen 2024 *Chem. Eng. J* **487** 150564