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The Effect of Silicon Anode Morphology on the Energy Storage Performance of Lithium-Ion Batteries

Yulong Zhang[1, *]

[1]American Overseas School of Rome, Rome, Italy
*Corresponding author: yulongzhang20080330@gmail.com

Abstract:
With the transition of traditional energies to more environmentally friendly options, due to environmental protection and the energy crisis, this has further pushed the need for environmentally friendly but also high performing energy sources. For electrical batteries, lithium-ion batteries (LiBs), are being used a lot due to their long lifespan and high energy density. However, the conventional graphite anode used in these batteries seems to have halted development for LiBs, restricting further improvement. With this issue, Silicon has emerged as a frontrunner as an alternative anode material due to its high theoretical capacity, it is also relatively cheap, while being heavily abundant. This study will investigate the influence of silicon anode morphology on the energy storage performance of Lithium-ion batteries through a literature and analytical lens, putting emphasis on the structural evolution, mechanism, and the advantages and disadvantages of Lithium, while diving deeper on four key morphologies, them being nanoparticles, nanotubes/nanowires, bulk silicon, and thin films. Recent research shows that nanoscale structures and core–shell composites can help relieve mechanical stress from volume expansion, while interface engineering and advanced binders improve SEI stability and performance cycles. Results show that combining interface design with stable synthesis, is crucial to bringing out silicon's full potential. This study will therefore contribute to the development of durable and high-capacity anodes for next-generation energy Lithium-ion batteries and storage technology as a whole.

Keywords: Lithium-ion battery; silicon negative electrode; silicon morphology.

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1. Introduction

In the current world, one of the most large-scale energy landscape transformations in modern history is occurring right now. Driven by the urgent need to reduce and omit the utilization of green-house gas emissions, alleviate the dependence on fossil fuels, and look to utilize more renewable energy sources. Among various methods, electrification, especially in the field of transportation, has recently emerged as a staple in sustainable energy. Electric vehicles (EVs), portable electronic devices, and other large-scale systems are all heavily relying on Lithium-ion batteries (LIBs). Lithium-ion batteries are highly popular and acknowledged due to their low discharge rate, high energy density, and a long-life cycle. However, as demand rises, specific performance related limitations in Lithium-Ion batteries have started to emerge and become more and more apparent. This is especially seen in the batteries which implement a graphite, which are really common in LIBs. Graphite as an anode, even though it is utilized heavily and commercially dominant, Graphite offers a relatively low theoretical capacity of 372 mAh g^{-1}, a low theoretical capacity further restricts the improvements that could be made in battery energy density. Due to this issue, Silicon has been identified as a promising alternative anode material to Graphite.

Silicon, with a theoretical capacity around 3579 mAh g^{-1} [1], which is nearly 10 times that of graphite, silicon has been identified by researchers to dramatically enhance the performance of batteries, this coupled with Silicon's natural abundance and environmentally friendly capability further pushes and strengthens its position for large-scale applications. Although there are a lot of advantages that sway in favor of Silicon anodes, the transition of silicon's intrinsic advantages into real-world applications is still difficult. This is because Silicon has its own issues, such as severe volume expansion, specifically in which when silicon absorbs lithium, it expands and swells up to 300% of its original size [2]. This in return causes mechanical stress (particle cracking, pulverization, etc.), structural pulverization, an unstable solid-electrolyte interphase (SEI) formation [3], and rapid capacity fading. Recent research has therefore shown us that the composition of silicon anode materials plays a crucial role in helping nullify the performance issues. This is because the different composition structures (i.e. nanoparticles, nanotubes, thin films, and bulk silicon), exhibit different behaviors that affect their ability to accommodate for certain changes. For instance, Nanoscale Structures can help alleviate stress of the material and maintain its structure, while more hollow tubes provide space to help buffer the expansion. On the other hand, bulkier silicones offer poor cycle stability due to its inability to withstand repeated morphing and mechanical stresses. So, understanding the different morphological structures and how they benefit batteries is key to understanding and designing an efficient yet powerful silicon-based anode. Looking at this in the case of EVs and large-scale energy storage, optimizing the silicon anode structure could really help boost the energy density without sacrificing crucial aspects such as its life cycle and safety.

Therefore, this paper aims to examine and analyze how the morphology of Silicon-anodes can help improve the performance in Lithium-ion batteries [4]. By reviewing recent papers and research that show the advancement in technology and development in silicon morphologies, analyzing their pros and cons, assessing whether they would have any impact on key performance indicators such as, capacity retention, rate capability, and structural stability [5], this paper seeks to find a practical understanding of the design principles for silicon-based anodes. Thus, this research seeks to identify and contribute to the broader goal of enabling high performance, long-lasting, and cost-effective lithium-ion batteries that are environmentally friendly and cost effective.

2. Nano-Silicon Anode with Different Morphologies

2.1 Silicon Nanoparticles

Silicon nanoparticles (SiPNs), are typically found with particle sizes of 150nm. This small size is an advantage, as it provides a high surface-to-volume ratio which therefore allows a better accommodation for strain during lithiation/DE lithiation. There are different types of preparation methods for Silicon nanoparticles, such as chemical vapor deposition (CVD), which is when a chemical reaction in the vapor phase places a silicon solid onto a surface. Then a silicon-containing gas precursor (i.e. Silane, SiH_4) is introduced into a reaction chamber with high temperature. This is because the heat decomposes the gas particles, and Silicon atoms are then deposited layer-by-layer onto a substrate, which ultimately forms nanoparticles. Thinking about this in a more realistic way, imagine when you come out of a hot shower, and the steam of that hot shower flowing out and making contact with your cold mirror, condensing into wet water droplets. But in CVD, a reactive gas "condenses" into a solid silicon [6]. Some of the key advantages are the fact that this method produces very high-quality silicon, with this comes also excellent control over particle size, shape, and film thickness, this is done by adjusting gas flow, pressure and temperature. This method is also able to create highly crystalline nanoparticles that are of great quality. The disadvantages though is that due to the precision and quality of the nanoparticles produced, this method also comes with a high cost, as the equipment is really expensive, and with the high cost, it is harder to scale into mass production compared to other methods, which is a big problem.

2.1.1 Laser pyrolysis

Another method that exists to prepare silicon nanoparticles is laser pyrolysis; this is when you use a high-power infrared laser that is used to rapidly form a flowing stream of silicon precursor gas. Then, because the heat is so intense and so strong, this localized layer of heat from the laser "pyrolyzes" (or decomposes) the gas molecules. This then causes nucleation and the growth of silicon nanoparticles in the gas stream. Using a realistic everyday example, it is like when you use a magnifying glass to shine the sun and to focus that ray of sunshine onto a tiny, but super-hot point on the leaf in order to burn it. In the case of Laser Pyrolysis, the laser is a magnifying glass, and the gas would be the leaf. Some of the key advantages are the fact that this method is excellent for producing small sized and uniform nanoparticles often smaller than 10nm, it is also really quick and occurs in a confined zone, and the gas flow allows for this process to be continuous, so that the production never stops in batches and batches. Some disadvantages are the fact that, this is again very expensive and hard to mass produce, another reason to this is because of the fact that the amount of powder produced is really low considering the amount of time it takes, and with that, it is also a complex and tedious method to set up as it requires careful planning and precision.

2.1.2 High energy balling

Another method that exists to prepare Silicon Nanoparticles is High energy balling of bulk silicon, this is a top-down approach where silicones that come in chunks or powder are placed in the same container with hard balls, usually made of steel or zirconia. With this, the container is then violently shaken multiple times, and the energy produced from the collisions between the balls and the silicon pieces fractures them into smaller and smaller particles, eventually to the point where they become nano sized. It is like when you use a mortar and pestle to grind grains into flour, but this is on a much more powerful and larger scale. Some of the key advantages to this method is the fact that this is really inexpensive and simple to do, as the materials used are cheap and they are simple, with this, it is also possible to scale this into industrial levels for mass production, this method is also versatile, as this method can be used to make nanoparticles from many different materials that are brittle. Some disadvantages are the fact that due to this being very easy and cheap to make, this method produces particles with a wide range of sizes and irregular shape, which is really inconvenient for manufacturers to use. Contamination is also a problem, as due to the heavy shaking and the force produced, some of the material from the steel balls can wear off, which contaminates the silicon powder. This violent process can also create many defects and damages within the crystalline structure of the silicon, which is not good for manufacturers who are looking for perfect crystalline structures to use in anodes.

2.1.3 Coatings and doping

However, more recent works often employ methods such as using coatings and doping in order to enhance the electrochemical stability of the nanoparticles. For instance, in a 2024 study, the synthesizing of hollow nitrogen-doped carbon layer-coated nano-Si (Si@HNC) via in-situ polymerization and carbonization, which forms a core–shell structure with internal void space. Some of the advantages are the fact that there is a High specific capacity, as Si@HNC composites achieved ~2655 mAh g^{-1} at 0.5 A g^{-1} and maintained 921 mAh g^{-1} after 300 cycles [7]. Another advantage is that the carbon shell inside buffers the expansion and improves the conductivity, while utilizing N-doping would help with the transport of Li^+ and SEI stability. Other designs such as boron-doped silicon nano-flakes managed to achieve ~800 mAh g^{-1} at 2 A g^{-1} with stable cycling [8]. Some disadvantages would be that a large surface area can cause unwanted chemical reactions, which drains the battery power. Also, agglomeration and low tap density means that you cannot fit as much energy into a small battery, and complex fabrications increase costs [9]. Some application scenarios are that they are applied in battery materials in order to achieve a higher energy output while trying to prevent the material from breaking. Which makes them a good candidate for EVs when used with other special supporting metals.

2.2 Bulk/Micro Structured Silicones

Scientists nowadays are testing out Bulk silicon, which are micron-sized (>1 μm) particles or continuous structures. Embedding them into a strong and conductive Carbon network, scientists are looking to find a combination that is both high-performance and cost-effective to produce. A recent 2024 study shows a strategy that mixes large silicon chunks with webs of tiny nanotubes or fibers [10]. This web then holds everything together, which prevents cracking and also helps carry electricity. Some advantages are the fact that the material is very dense, and due to how dense it is, it can fit a lot of energy into a small amount

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of space, which is great for making compact batteries but also wanting high performance. Silicon is also cheap and easy to make, so costs will be low. Disadvantages are also apparent, as Silicon swells up a lot when it charges, like when a sponge soaks up water, this makes the silicon crack and break, which ruins the electrical connections within the battery. There is also an unstable SEI formation, essentially a wasteful coating continuously forming on the surface, which permanently uses up the battery's chemicals. Causing energy storage to drop quickly after a few recharges. Another disadvantage is that it requires supportive material such as carbon to hold everything together, so it needs support. Some fields of applications it is used in are used as micron-Si/C composites for high areal capacity anodes; this combo is used as a high-power material on the negative side of the battery. It is also mixed with graphite [11]. This mixture offers it a good compromise, as there is more power than lone graphite, but longer life than just pure silicon.

2.3 Thin-Film Silicones

One last type of Silicon anode material is thin-film silicones. Thin-film silicones (SiTF), is a continuous layer of silicon that typically only has thicknesses ranging from tens to hundreds. It is a smooth, thin layer of silicon that is sprayed onto a surface in a special machine. The key advantages of this material are the fact due to its thinness, it would not swell or shrink very much to the point where it would negatively affect the battery when charging or discharging, this therefore means it is a lot less likely to crack or break. Due to the fact that it is so stable, Scientists also use it as a test tool to see how silicon batteries would operate. Researchers managed to make a new version of this very thin material that works really well. It holds lots of power, charges quickly, and after 300 charges, maintains 99.77% of its capacity [12]. Some of the big downsides of this material is that due to the fact it is so thin, it is hard to store lots of energy in it. Coupled with the fact that these materials are expensive and would be difficult to mass produce. Manufacturing this material in Electric Vehicles could be really difficult.

3. Future Outlook on Silicon Anodes

Overall, the future outlook for silicon anodes depends on the different strategies of controlling their problems of expansion and instability. One main method is to change the structure of the anode. This can be done by creating smaller hollow silicon nanoparticles in order to give them room to expand without cracking. Another way is by adding more elements, making the material stronger and more conductive, while wrapping up bigger silicon pieces in a carbon shell to improve performance. But at the same time, managing the surface and the binders is crucial, adding protective artificial coating may reduce the harm from chemical reactions. Scientists are also finding ways to improve special electrolyte additives, by creating new, more powerful glues to hold the silicon particles tightly together. Other new ideas include designing more textured surfaces to support super thin silicon films. Replacing liquid state electrolytes with solid state ones could be a great solution, as although they can limit swelling, managing pressures would be hard. Thus, the goal is to combine all these brilliant ideas such as new structures, surface controls, and practical manufacturing, to create good silicon anodes that offer high capacity, high energy density, and a long lifespan all at once. It is a difficult task, but a very vital and crucial one for the future in lots of industries to aid everyday life. The future is really bright for Silicon Anodes, as the development and research for Silicon anodes are well underway, alongside the fact that Silicon anodes have such high potential, coupled with the fact that society is moving into a more environmentally friendly way for energy consumption. The future for Silicon Anodes is bright, as scientists are developing new ways in order to nullify the disadvantages and bad parts alongside improving and maintaining its high energy output, even though this task is not going to be easy at all, it will be crucial to everybody's day-today lives in the very near future and would benefit society in a very positive way.

4. Conclusion

Throughout this research, the silicon is an anode material in Lithium-ion batteries that has the most promise due to its high theoretical capacity, it is also relatively cheap, while being heavily abundant. However, the practical application of this material is still limited due to volume expansion, mechanical fracture and cracking, and unstable interfacial chemistry during cycles. By analyzing four key morphologies, them being nanoparticles, nanotubes/nanowires, bulk tubes and thin films. This paper concludes that nanoscale design, core–shell architectures, and multiscale composites, are key methods to nullifying expansion, while advanced binders alongside artificial SEI layers provide important stability. While thin-film and nanotube structures show how methods of structural engineering can sustain cycling stability while improving rate capability, challenges of cost and scalability still remain.

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