

Low-Dimensional Nanostructures for Silicon-Based Anode Materials in Lithium-Ion Batteries

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Abstract. Electricity is becoming more important as an alternative energy replacing fossil fuels, as it can be obtained from solar, tide, and wind while being mostly harmless to the environment. The lithium-ion battery (LIB) has high potential in this regard. The silicon-based anode of LIB is a strong performer among different designs of LIBs and entered into service due to high specific energy and low operation potential. However, volume expansion during charging is a pressing problem. Low dimensional nanomaterials possess high specific surface area and special micro-mechanical properties, which can mitigate this problem effectively. This article focuses on cutting-edge nanoscale research from three-dimensionality angles, including 0D, 1D and 2D. For 0D, the core-shell structure is discussed, and modified structures based on the core-shell structure are introduced with a brief discussion on the preparation and structural features. For 2D anodes, silicon-based thin-film materials offer better stability and higher specific capacity. The preparation method of magnetron sputtering is discussed, and p-type doped SiO_x/Si/SiO_x sandwich LIB anodes are also introduced.

Keywords: Silicon anode, Lithium-Ion battery, Structure design, Mechanical analysis.

1. Introduction

Energy is closely linked to the increase in scientific productivity. However, as a series of global ecological problems such as environmental pollution and forest destruction are worsening and fossil fuels are gradually becoming scarce, it is urgent to electrify energy consumption, which can be sourced from green energy sources. As a result, a great demand for energy storage solutions formed, including lithium-ion batteries (LIBs). LIBs have good operating voltage, energy density, low self-discharge and low relative environmental footprint [1]. They now have an irreplaceable role in electric vehicles, portable electronic devices, and the aerospace industry [2]. Notably, silicon has striking potential as the anode of LIBs because of its high theoretical specific energy reaching about 4200 mA h g⁻¹, which is ten times graphite's [3, 4]. However, the lithiation process comes with volume expansion which restricts the cycle lifetime of silicon anodes of lithium-ion batteries [4, 5]. Low dimensional nanomaterials possess high specific surface area, giving them excellent cycle retention and effectively declining the haul distance of electrons and lithium ions [6]. This article will classify silicon-based nanomaterials through their dimensions and choose some typical and cutting-edge structures to introduce. The first part discusses the core-shell structure and its successors, including structures such as core-shell, yolk-shell, Si-C-(ZIF-67-800N) and Si-C-Al₂O₃ nanopetals. Their different improvements compared to the initial model are sorted, and new ideas to improve the capacity are analyzed. Carbon-coating, alloying (with copper) and hybridization via multi-walled Nanowires and nanotube complexes are discussed in the second part, which naturally arises as a solution to the micro-mechanical weaknesses of silicon as it naturally gives silicon contact area with the electrolyte and room for expansion while maintaining structural integrity. However, the unstable nature of the SEI layer due to mechanical strain on the surface causes performance and capacity decay over many cycles and compensating measures such as carbon coating, and metallic mesh scaffolding was discussed. The recent maturation of carbon nanomesh, which allows hollow, multi-walled

nanotubes to be made, also provides new avenues to tackling these challenges. The third part focuses on the performance, preparation of silicon thin films as anodes for LIBs; the physical, micromorphological and electrochemical properties corresponding to different sputtering frequencies when prepared by the magnetron sputtering method, and the best sputtering power at 120 W, which gives the best performance of Si thin films, is concluded. Potential solutions are also given for p-type doped $\text{SiO}_x/\text{Si}/\text{SiO}_x$ intercalation anodes on how to improve the performance of Si thin film anodes, and the design of Zn/Si/ZnO thin film anodes was also discussed.

2. Zero-Dimension nanomaterials

0D silicon nanomaterials have excellent performance, including bare silicon nanoparticles, porous silicon nanoparticles, hollow silicon, etc. [7, 8]. The excellent performance is due to the stress release, which prevents silicon cracking during the Li^+ insertion [9, 10]. The core-shell structure and its derivative structures possess better cycle retention and conductivity [11].

2.1. Core-shell Structure

Core-shell silicon/carbon structure is an excellent structure with capacities of tight electrical connection, excellent surface isolation with electrolytes and strength shell to resist volume expansion [12]. In 2007 the core-shell silicon/carbon structure was proposed by Jung et al. They surface-treated silicon nanoparticles with a silylating reagent to attach the hydrophobic character and then obtained the silicon@resorcinol-formaldehyde resin sol core-shell structure RF microemulsion polymerization. After carbonization, final samples were prepared, and the carbon shell encapsulated in the silicon nanoparticle was uniform. Because of the intimate connection between the carbon shell and silicon nanoparticles, the improvement of anodic performance is noteworthy. Its ability of cycle retention is better than that of bare silicon. The decline of specific charge capacity is only about 35% compared to 50% with bare silicon after twenty cycles [11].

2.2. Yolk-Shell Structure

The cycle retention of core-shell structures is shored for attention among researchers. However, volume expansion is also a serious problem. With more and more researchers pitched into this field, many novel structures have been proposed. Among these, the yolk-shell structure is a potential one.

2.2.1 Initial Yolk-Shell Structure

Liu's group first proposed the yolk-shell structure. The shell is constituted of amorphous carbon, and the "yolk" is a silicon nanoparticle. The silicon nanoparticle sticks on one side of the carbon shell, and a void appears on another side like an "egg". Liu's approach is a room temperature preparation. They coated the silicon nanoparticle with a silicon dioxide layer and a polydopamine layer. After that, carbonized the surface to obtain the nitrogen-doped layer. Finally, hydrofluoric acid (HF) was employed to selectively remove the silicon dioxide sacrificial layer, and the yolk-shell structure was obtained. Compared with the core-shell structure, the void provides more buffer space to resist silicon nanoparticles' volume expansion, leading to better cycle retention abilities. The capacity wastage is only about 26% after 1000 cycles, which is better than the core-shell structure [13].

2.2.2 Si-C-(ZIF-67-800N)

Conventional preparation of yolk shell is the sacrificial templates method. This method usually uses selective etching, resulting in toxic elements, while the cost of production makes mass production unrealistic. Thus, the method still requires improvements to satisfy the commercial process [13, 14]. However, developing an in-situ template can be used in yolk-shell carbon/silicon structures. Besides, the specific surface area of metal-organic frameworks (MOFs) is high, and the pore structure can be selected [15]. Liu et al. combined the MOFs in-situ template and silicon nanoparticles with phenolic resin coated. Specifically, the nanoparticles were inlaid in the MOFs and then carbonized together. (Figure 1) This composite possesses a porous structure and double

carbon shells with cobalt and nitrogen, which bring the great ability of electrons to transfer and buffer the volume expansion. The sample demonstrated ultra-large lithium storage capacity with a reversible capacity of 1107 mA h g^{-1} at a current density of 0.5 A g^{-1} after 100 cycles and a cycling stability capacity of 852 mA h g^{-1} at a current density of 1 A g^{-1} over 300 cycles [16].

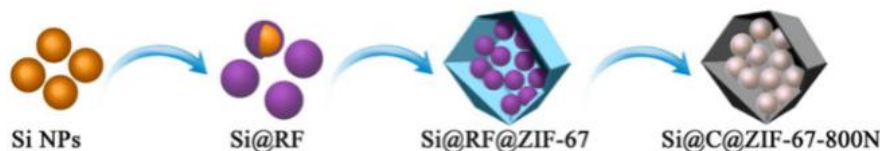


Figure 1 Preparation process of Si-C-ZIF-67-800N structure [16].

2.3. Si-C-Al₂O₃ Nanopetal Structure

Another strategy for resisting the volume is establishing a high-intensity multi-dimensional structure. Si-C-Al₂O₃ nanopetals structure is a pinecone-like carbon spherical shell with Si particles inserted (Figure 2). In past Research, alumina layers were used to improve the C/Si composites due to their special physical properties. [17, 18] Fu's group chose Al₂O₃ as the integument via the vertical growth from the nanoparticles. The final product is coated with independent but tight silicon nanosheets, which look like petals. The petal structure also brings some unique properties. Because of relatively loose nano-petals and abundant mesopores, the electrolyte and ions can deliver more quickly. Besides, the Al₂O₃ petals can neutralize HF derived from the decomposition of electrolyzing, which causes a stable Solid Electrolyte Interface (SEI) layer. The final product's reversible capacity reached 1405 mA h g^{-1} at 5 A g^{-1} after 1000 cycles when the environment temperature in 80°C . This also brings a potential solution of utilizing Li-ion batteries in hot environments [19].

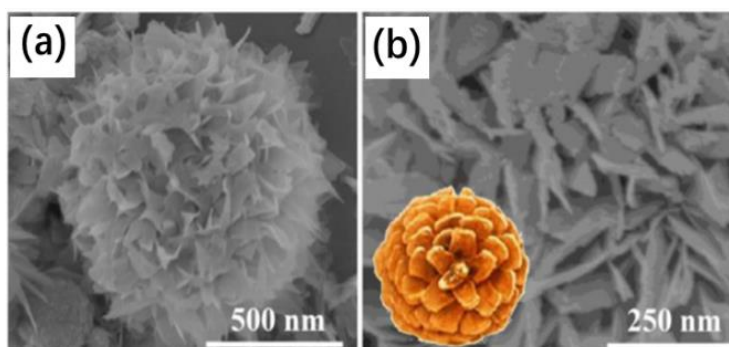


Figure 2 Si-C-Al₂O₃ sample (A pinecone in B part) [19].

3. One-Dimension nanomaterials

3.1. Basic Model of SiNW Structure

The basic silicon nanowire (SiNW) structure, as a logical development to combat the pulverization of silicon material caused by expansion during lithiation, was first explored by Chan et al. [4]. They discovered the potential of SiNW as a high energy density anode material for LIBs. SiNWs of 50-250 nm thick were grown on a steel substrate which acts as the conducting baseplate, and the space between each wire can accommodate the expansion during the lithiation process, giving this design a very high energy density. By having a large interacting surface with the electrolyte, SiNW also has high utilization coefficient, reflective of the higher ion transmission rate.

The two more mature processes of manufacturing SiNW involve two different approaches: the bottom-up Vapor-Liquid-Solid (VLS) method and the top-down Metal-Assisted Chemical Etching (MACE) method. VLS methods entail passing silane gas (SiH₄) onto the surface under temperature and pressure, growing silicon crystals under catalyst metal atoms [20]. (Silicon becomes amorphous after the first lithiation-de-lithiation cycle.) Metal-assisted chemical etching uses metal catalysts to

prioritize oxidation of silicon in contact with it under erosion, thus carving out larger diameter SiNWs from a stock silicon wafer [21]. These 2 processes can produce a range of diameters of SiNWs, from 10nm to 1 μ m. Chemical Vapor Deposition is the preferred method of applying silicon of various densities and thicknesses when a base structure is provided [22].

Despite the various advantages of SiNW, the conductivity of amorphous silicon crystals in nanowire form is low, leading to poor conductivity and thus higher resistance during charging (for longer nanowire lengths) [4, 12]. Another problem involves the solid-electrolyte interface (SEI), which forms a potential electrical mediator in ion transfer in a typical organic electrolyte. While not pulverizing the silicon, the repeated expansion and contraction constantly breaks up SEI layers, eventually building up a thick deposit layer around the wires, lowering cycle life.



Figure 3 Solid SiNW expands upon lithiation. SEI is a solid deposit that forms a layer around silicon. However, it does not undergo volume change during cycling, resulting in the deposited layer being torn off and a fresh one forming on the now exposed silicon. After many cycles, a thick SEI agglomeration is formed. [5]

These two obstacles have been the focus of development in the last decade, with some significant breakthroughs produced from different approaches.

3.2. Recent Development on SINW Concept

Recently Amprius has developed a high-performance anode structure consisting of layered silicon deposited on nanowires already attached to the substrate. [23] This mechanical support greatly enhances the durability of the anode, while a structurally controlled deposition process allows for a more uniform and restrained lithiation process, extending the lifetime of this anode greatly. However, this design only uses silicon of various porosities as the electrochemically active agents, so other studies with other materials and approaches are discussed.

3.2.1 Alumina and Other Metal Oxide Coating

Aluminum oxide can be coated on SiNWs to stabilize the SEI layer and help it overcome depository buildup. The alumina will alloy with lithium on the electrolyte side while also changing its composition on the silicon side, becoming a much better li-ion transporter [24]. Combined with its mechanical strength, a thin aluminum oxide coating can act as an artificial solid-electrolyte interface while limiting the volume change of SiNW. This allows for good capacity retention over 100 cycles, although the inflexible coating breaks as mechanical strain pulverizes it, losing its effects.

3.2.2 Metal Infusion/Composition

The coulomb efficiency and cycle life can be improved by alloying copper into the nanowire trunks and growing branching thinner SiNWs [25]. Cu₃-Si alloy structure gives good conductivity and mechanical strength to the anode structure, although the method of participation and the role of such a compound during lithiation is still unclear. Copper at the interface layer changes the interaction with the SEI layer by participating in the chemical process during charging [26]. Cu₃-Si's participation stabilizes the lithiation process as shown by the stable and long-lasting performance (500 mA h/g for over 1000 cycles) of the copper-silicon mesh anode at over 12 A/g charging rate, which the authors credit to the thick trunk portion of the structure.

3.2.3 Carbon Coating

Note that carbon is inflexible and hinders efficient ion transport; hence initial attempts to use carbon as an exterior structural element provided relatively mediocre capacities. [27] However, when the thickness of the carbon layer is reduced to ~2 nm, the effects become less pronounced, as

demonstrated by Wang et al. [28]. In their study, they have also made room for the expansion during lithiation by using porous nanowires, further reducing the strain on the carbon sheath and achieving a reversible capacity of 1275 mA h/g under a fast charge/discharge rate of 7C, retaining 90% of its performance after 500 cycles.

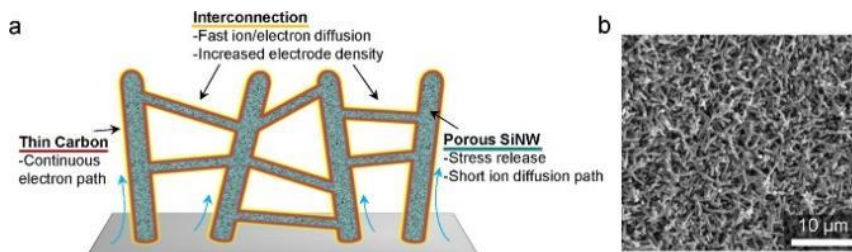


Figure 4 Structure of networked porous silicon in carbon with schematics in a) and an SEM image in b). [28]

3.2.4 Silicon Nanotubes (SiNT)

In early 2012, Wu et al. published their work on double-walled Silicon Nanotubes (DWSiNT). [5] By creating a hollow tube of silicon with a layer of mechanically resistant SiO_2 on the exterior side, the structure was able to both allow silicon to expand during lithiation by filling the interior of the tube with a stable SEI layer on the hard SiO_2 exterior, which is also a Li^+ transporter. This greatly lengthened this anode's cycle life to 6000 cycles without a major performance drop. From the scan images (Figure 4), double-wall nanotube (DWSiNT) is an extremely stable structure under repeated cycles, while homogenous silicon suffers from clotting of SEI deposits and SiNW completely losing its integrity at comparable levels of cycles. However, this cumbersome structure comes at the cost of lower base capacity at only ~ 600 mA h/g.

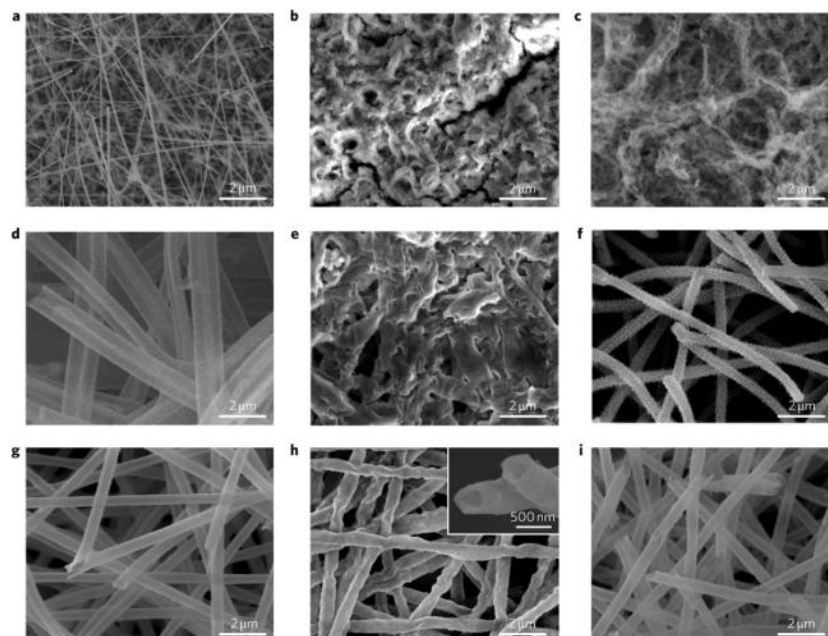


Figure 5 SEM images of different nanostructures in stages of cycling life. The three rows show SiNW, SiNT and DWSiNT in their initial form, after 200 cycles, and after removing SEI layers chemically. ((i) shows DWSiNT after 2000 cycles after SEI removal.) Thick SEI layers can be seen for homogenous silicon(b)(e), while a stable SEI has developed for DWSiNT(h) [5].

Further to the 2012 study, the potential of a multi-walled tube is explored further by sandwiching silicon in layers of carbon (C-Si-C) and rolling the membrane up into a multi-walled tube. [29] This structure achieves 1000 mAh/g capacity at 0.5 A/g after 300 cycles. However, adjacent layers are not bound, resulting in slow degradation.

4. Two-Dimension nanomaterials

4.1. Properties of Silicon Thin Films

The anode film material has the same chemical composition as the bulk powder electrode material but is made into a film by different physical or chemical methods. Compared with bulk powder electrode materials, thin-film materials do not need a binder and conductive agent and have the advantages of uniform thickness, composition, low internal resistance, good adhesion to the collector fluid and good charging and discharging performance.

4.2. Magnetic Sputtering and the Effect of Different Sputtering Power on Si Film

Si has an excellent theoretical mass-specific capacity, a low de-lithium plateau and excellent safety properties. The volume expansion of silicon material causes structural collapse of the material and electrode material flaking from the collector during battery cycling, giving rod materials poor cycling performance retention [30]. Nanofiltration of silicon materials is a way of suppressing silicon materials' volume changes. The advantages of magnetron sputtering, such as controlled thickness, uniform composition, low internal resistance, good collector adhesion and charge/discharge properties, have led to its widespread use.

4.2.1 Physical Phase Analysis

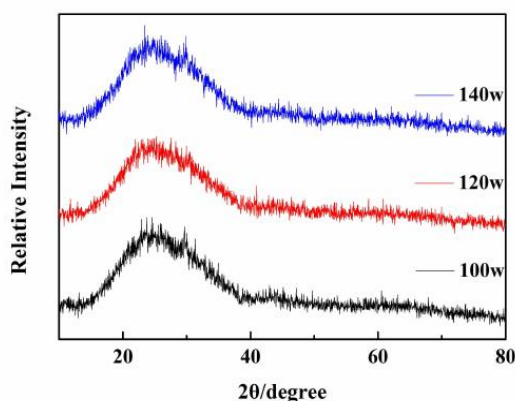


Figure 6 XRD spectra of Si thin film materials at different sputtering powers [31].

Figure 5 shows that the Si thin film anode obtained with three different sputtering powers of 100, 120 W and 140 W all show an obvious bulging phenomenon at about 28° . However, none show any characteristic peaks of crystalline Si diffraction, indicating that the Si thin film anode materials deposited at all RF sputtering powers are amorphous.

4.2.2 Micromorphological Analysis

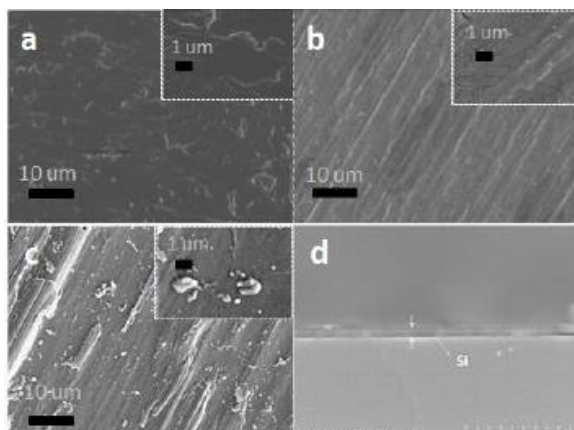


Figure 7 SEM images of Si thin film materials at different sputtering powers (a) Si-100W; (b) Si-120W; (c) Si-140W; (d) Si-120W [30].

It is observed that the sputtering power has a significant effect on the surface morphology of silicon thin film. At a sputtering power of 120 W, no aggregation of particles was found on the surface of the silicon anode. The Si atoms are closely arranged, and the film is very dense and of uniform thickness with no pores. Figure 2 (d) shows the cross-sectional view at 120 W. The Si thin film is approximately 80 nm thick, the layer is relatively uniform and dense, and it is tightly bonded to the substrate, which will help improve the adhesion of the silicon anode and the collector fluid.

4.2.3 Analysis of Electrochemical Properties

The sputtering power strongly influences the Si film material's capacity, cycling, and multiplier performance. The optimum sputtering power of the silicon target is 120 W when the Si film anode material has excellent density, uniformity, and good cycle life. At the first cycle, the flow rate dedicated to charging at a current density of 0.2C was 3595 mAh g⁻¹; after 150 cycles, the value was still high, at 2768 mAh g⁻¹, retaining 76% of the original capacity.

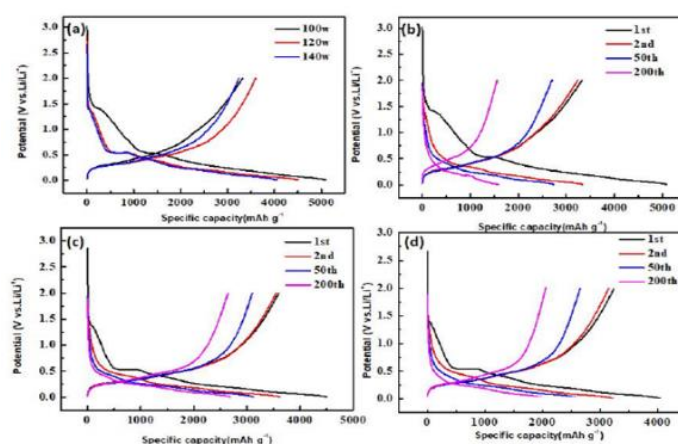


Figure 8 (a) First week charge/discharge curve for Si with different power co-sputtering; (b) Charge/discharge curve for Si-100 W with different cycle cycles. (c) Si-120 W with different cycle cycles; (d) Si-140 W with different cycle cycles [31].

The sputtering power is strongly related to the thin film material's first cycle charge/discharge capacity, which initially increases as the power increases, but decreases as the sputtering power increases.

This is because, under the same sputtering time conditions, the power level not only changes the thickness of the film but also affects the density of the film, which in turn determines the anodic properties of the material, and too much sputtering power is detrimental to the embedding and detachment of Li-ions.

4.2.4 Multiplicative Properties

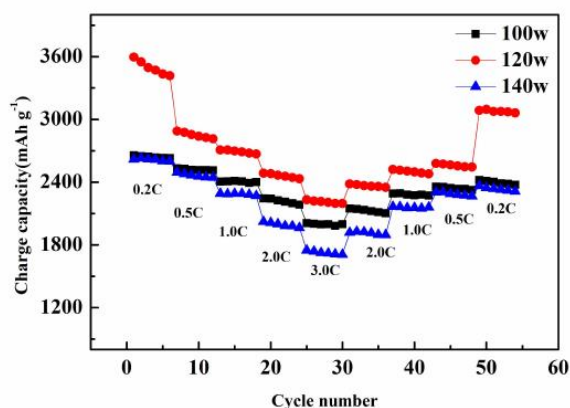


Figure 9 Multiplicative performance curves of Si thin film materials at different sputtering powers [31].

As the current density slowly adds between 0.2 C and 3.0 C, the effective capacity drops significantly. This is because the polarization of the Si film material intensifies at higher currents, leading to more severe irreversible cycling and ultimately causing the capacity of the battery to decay rapidly. However, at the same charge/discharge current density, the Si film anode material with a sputtering power of 120 W has the highest specific capacity for charging. As the current density decreases, the specific charge capacity of the Si film anode material gradually increases, indicating that the material has a good multiplier performance. It also shows that the sputtering power significantly influences the multiplicative performance of the Si thin film materials.

4.3. Enhancing the Performance of Silicon Thin Film

4.3.1 P-Doped SiO_x/Si/SiO_x Sandwich Anode

A new sandwich silicon anode (SiO_x/Si/SiO_x) using a layered structure consisting of P-doped and SiO_x without pre-lithiation is used to overcome this challenge.

The new anode has excellent specific capacity and conductivity. In addition, the sandwich structure allows the Si to survive volume changes during charge and discharge cycles. The sandwich structure consists of central Si and SiO_x films on both sides. SiO_x is active with a specific capacity of $\approx 2680 \text{ mAh g}^{-1}$ [32]. Due to its greater mechanical stability, SiO_x is more robust and can be used to buffer the Si layer from the forces.

SiO_x adheres more firmly to the collector than Si and can prevent violent pulverization [33]. The length constituted by the diffusion path of ions is small when the film is used as an anode, and SiO_x impacts the performance of Si. Furthermore, SiO_x leads to different compositions of the SEI. These compositions ultimately help the silicon anode to adapt to volume expansion.

4.3.2 Zn/Si/ZnO Porous Composite Film

The electrochemical performance of silicon anodes can be improved by surface modification. In addition, the construction of multilayer structures can effectively moderate the volume changes that occur when silicon film is used as an anode [34]. Zn metal has good ductility and can help moderate silicon's volume change, build a 3D conducting framework and improve the stability of the electrode. In the lithiated Zn phase metal, the Li⁺ moves rapidly, which is beneficial for improving the multiplicative performance. Therefore, Zn is suitable for the intercalation treatment of Si films.

After 100 cycles, the four-layer (4L) Zn/Si/ZnO film peaks in capacity at 1826 mAh g^{-1} , 86% capacity retention, and the best multiplicative performance as a result of its porous and multilayer structure. It can be observed that the cycling stability and specific capacity also differ between the different layers. The maximum value is achieved at 4L. Therefore, the fabrication of 4L Zn/Si/ZnO shows promise in enhancing silicon's electrochemical performance.

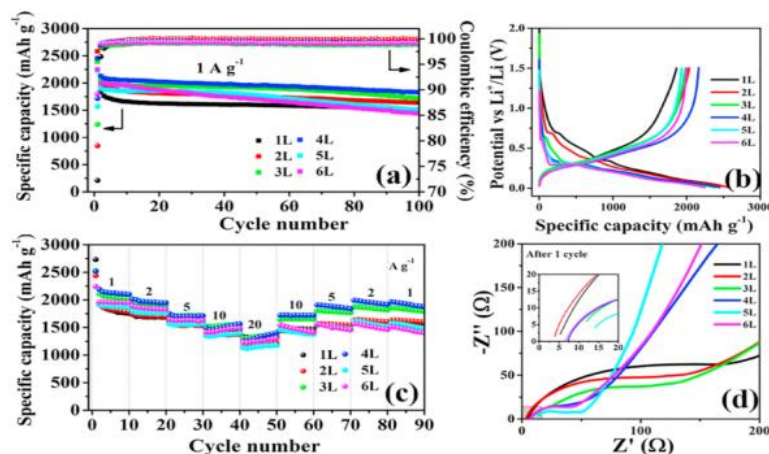


Figure 10 Capacity and columbic efficiency over cycles (a), charge-discharge profiles during the first cycle (b), performance at different current densities (c), and EIS spectra after the first cycle (d) [35].

5. Conclusion

Silicon nanomaterials have huge protentional due to their high theoretical capacity, but volume expansion and other problems are still considerable. Although cost is a major issue, the yolk-shell model gives a competitive performance among contemporaries and warrants further development. Based on this, the Si-C-(ZIF-67-800N) structure was proposed for a lower cost. The copper-silicon hybrid nanomesh by Song et al. and the carbon-constricted porous nanowire network by Wang et al. show promise as the basis of future development into more stable anode materials as both show advantages of different structural designs. Similarly, the placement of silicon, or other lithium intercalation-active agents within carbon casings, be it nanotubes or surface-coated carbon greatly boosts the endurance of the entire structure while providing an electron conduit. The experiment with layered nanotubes may lead to longer-lasting anode architecture. For Si thin films, pure Si thin film anode materials with high specific capacity should be ideally prepared by RF magnetron sputtering. The optimal sputtering power for Si film gives excellent dense homogeneity, good cycling stability, and high reversible specific capacity. A new sandwich silicon anode ($\text{SiO}_x/\text{Si}/\text{SiO}_x$) improved the reaction kinetics during charge and discharge.

With these developments in mind, a few common trends can be observed in improving the performance of silicon material and should be taken into consideration for future developments:

1. The structure attempts to compensate or make room for the expansion of silicon during lithiation. Both providing expansion room can achieve this through allocating space or with a porous structure and mechanical constriction, either by a strong material acting as support or binding/casing, or a ductile surface coating to prevent pulverization.

2. Surface treatment of amorphous silicon. Exposed silicon suffers from unstable SEI formation. The solution is to have a layer of material friendly to Li^+ diffusion be the primary interface between the main silicon body and the electrolyte. Certain metals appear suitable for this purpose, including copper and zinc, on top of silicon oxides. Aluminum oxide, while unable to resist the expansive forces, should also be explored more as an additive to certain structures to help the lithium-ion diffusion process.

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