

# Review-Recent development on silicon-based anodes for high-performance Lithium-Ion Batteries

Chengwei Zhang <sup>1,a</sup>

<sup>1</sup>Material Science and Engineering, McMaster University, 1280 Main St W, Hamilton, ON, L8S 4L8, CA

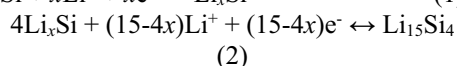
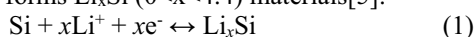
**Abstract.** Silicon has been recognized as one of the most promising anode materials for lithium-ion batteries (LIBs) due to its high theoretical specific capacity and similar working voltage as the lithium anode. However, there are some unavoidable drawbacks including volume expansion effects, low conductivity, the constant formation of SEI during lithiation and delithiation contributes to its fewer possibilities for commercialization. Therefore, modification of silicon for better performance is required for future applications. This review demonstrates recent progress and development of modification for the silicon-based anode including silicon-carbon composite with yolk-shell structure, nanostructured silicon, and alloying method. Finally, the existing problems and future improvements are also discussed based on current development.

## 1 Introduction

As the most widely used energy storage equipment, lithium-ion batteries (LIB) have many advantages, such as high working voltage, remarkable specific energy (100-250 Wh/kg[1]), long life cycle, low environmental pollution and less battery memory effect. Among the practical anode materials, carbon materials or graphite with low theoretical specific capacity of graphite (372 mAh/g)[2] could not satisfy the demand of large equipment such as electric vehicles. Lithium is difficult to be applied in practical batteries at present due to the safety problem resulting from lithium dendrites[3]. Compared to graphite and lithium, silicon has incredibly high specific capacity (4200 mAh/g)[4], much higher than the theoretical capacity of graphite, and no lithium dendrites generated during use. Moreover, silicon has other commercial advantages such as fairly low cost, environment friendly and large reserves in the earth. But several potential existing problems need to be solved before commercialization. In this work, several typical applications of silicon-based composites are introduced and discussed with their improvement and drawbacks to summarize the current development of LIBs and predict potential solutions for future optimization.

## 2 Problem Statement

The mechanism of lithium storage in silicon is alloying, which forms  $\text{Li}_x\text{Si}$  ( $0 < x < 4.4$ ) materials[5]:



The most essential problem impacting the cycling performance of Si anode is the volume expansion effect.

During the charging and recharging stage, the inorganic bond between silicon becomes the ionic bond of lithium and silicon, which results in the larger space between two silicon atoms to barely reform the inorganic bond, leading to the expansion of volume[6]. Since silicon is a brittle material, when the volume is expanded, it is hard to recover to its original state. The crushing effect causes the fresh silicon inside to be exposed, and then reacts with the electrolyte to produce a new SEI film. The repeated rupture and regrowth of SEI film leads to the continuous consumption of electrolyte and the increase of interface impedance, which increases the diffusion distance of lithium-ion and hinders the transfer of lithium-ion[7]. Finally, the volume expansion effect causes the capacity loss of the silicon anode and the shortening of its cycle life.

### 2.1 Silicon-carbon composite

A commonly used method to improve the performance of silicon is designing silicon-based composite[8]. Such method can revise various disadvantages of silicon material by introducing carbon into silicon-based anode. In contrast to silicon, carbon has good conductivity and low expansion. Different microstructures of silicon-carbon composite have different purposes and advantages for anode[9]. Several typical applications of introducing carbon in silicon have been listed below for analyzing essential improvement on performance of silicon-carbon composite.

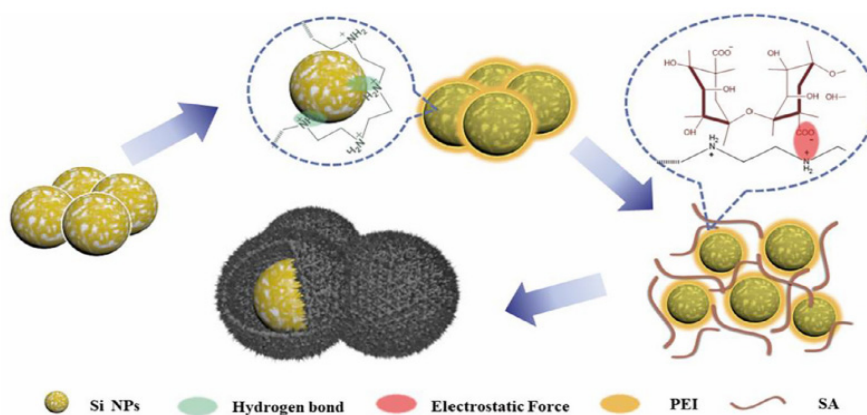
One modification is to apply carbon coating around silicon to prevent larger volumetric expansion[10]. The carbon coating layers work as an outer shell to increase the conductivity, and restrain volume expansion of silicon, which prevents silicon particles from being overexposed in the electrolyte to constantly form SEI. Thus, the more stable SEI can prevent capacity loss and maintain fluent

<sup>a</sup>zchengwei2016@gmail.com

flow of lithium ion, which dramatically increases the life cycle of the LIBs. Moreover, since the carbon is only used for coating and protection, the percentage of silicon in the anode composite is still high compared with silicon-core anode, which means the reversible capacity and energy density are still similar to the raw silicon anode. J. Yang et al's group[11] developed a yolk-shell structured silicon-mesoporous carbon anode by using a nanocasting route. The phenolic resin was used as the carbon source and Si@SiO<sub>2</sub> was used as the core nanoparticles. The mesoporous carbon coating provides an excellent contact between the active materials and the electrolyte for faster diffusion of lithium ions and better rate capability. Moreover, such shells are beneficial for the generation of a homogeneous and compact SEI layer, which maintains the internal void space to resist larger volumetric expansion and maintain its high capacity. Such design dramatically increased the cycle life (around 1000 mAh/g, 78.6% capacity remained, after 400 cycles) and good rate-capability (62.3% capacity remained at a high current of 8.4 A/g).

Volume expansion effect can also cause problems such as mechanical stress on the shells and pulverization of electrode materials. Thus, higher dimensional carbon-

silicon composite is required to provide more void space for the relief of volume expansion and better electronic conductivity. According to H. Mi et al group's research[12], an one-step self-sacrifice template strategy is proposed for crafting yolk-shell silicon@void@C composite by preparing porous carbon consisting of a carbon precursor and a labile polymer, where the polyethyleneimine (PEI) works as the labile polymer for coating to provide void space without using acid or base etching between the carbon shell and silicon yolk. The labile PEI coating can provide enough void space between the carbon shell and silicon yolk to prevent large volumetric expansion when decomposing into gas as well as capture the particles to prevent them from aggregation. The carbon precursor was created by introducing sodium alginate (SA) on the PEI surface, where the SA gradually forms a carbon nanosheets framework to reduce the diffusion distance for both lithium ions and electrons, resulting in better conductivity. As a result, such method provides an increase in the 854.1 mAh/g at the current density of 0.2 A/g after 200 cycles compared to 372 mAh/g of commercialized graphite LIBs and a capacity of 510 mAh/g at 1 A/g after 100 cycles.



**Figure 1.** Demonstration of fabrication process of Silicon@void@C composite

Overall, compared to lower dimensional composite, even though higher dimensional materials[13] can provide better initial Coulombic efficiency and better conductivity as well as alleviating volume expansion effect, the complex synthesis process, including technology limitations and high cost result in more practical problems when commercialization. Therefore, in order to effectively address such problems, a mixture of multi-dimensional products might provide more solutions while maintaining the excellent properties the silicon possesses[14].

## 2.2 Nanostructure Silicon

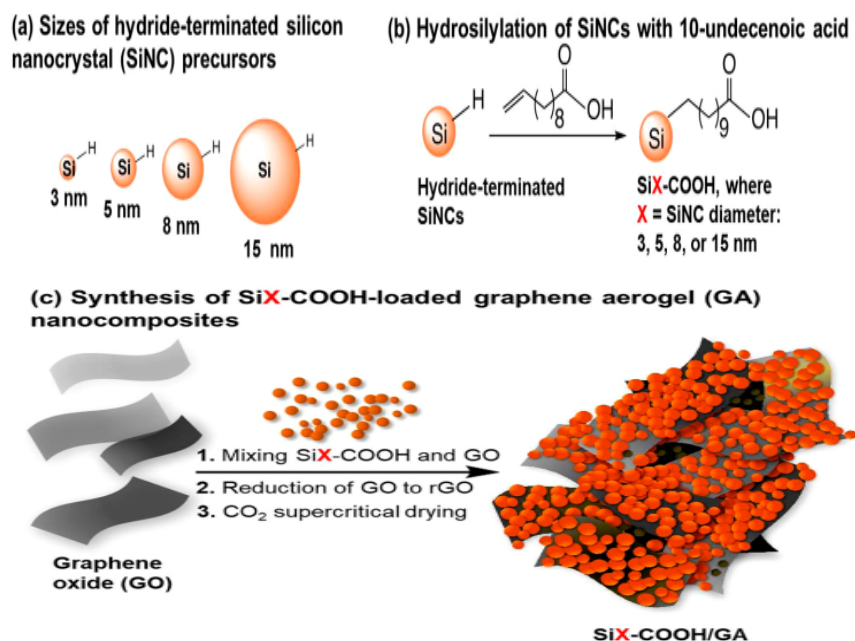
Bulk silicon as a pure anode material is not stable and still suffers from problems such as low first Coulombic efficiency or constant formation of SEI. As a fast-growing and eye-catching technology, nano-sized treatment on materials exhibits many positive influences on their

performances including interfacial effect, small size effect or quantum size effect[15]. When such treatment is applied to silicon, the properties and behavior of silicon change dramatically. Several applicable treatments of obtaining nanostructured silicon from recent research progress for anode materials of LIBs are compared and discussed below.

For the lowest dimensional product, the silicon nanoparticles (SiNP) show dramatic changes in electrochemical performances due to smaller particle radius and relatively larger particle distances for the resistance to volume expansion effect. According to Maryam Aghajamali and her group's work[16], they tested different size silicon nanocrystal combined mesoporous graphene aerogels (GAs) by synthesizing undecanoic acid-functionalized silicon nanocrystals in different sizes with graphene aerogels. The graphene aerogels functions as a better medium making up for the poor conductivity of silicons. From the result, the electrochemical performance exhibits high dependency on particle size of silicon

nanocrystals, where the initial capacity is higher for larger silicon nanoparticle size due to its larger capability of contacting area but showed fast decay of capacity maintained after 100 cycles while the smaller particles showed exactly the opposite. Moreover, due to the special processing, thermal treatment used in the synthesis, they also studied the effect of thermal processing in electrochemical performance, where the smallest silicon nanocrystals, Si<sub>3</sub>/GAs demonstrated a very stable capacity around 1100 mAh/g and a retaining capacity more than 90%

after 500 cycles under 400 mA/g current density. This research shows promising results that changes of silicon nanoparticles size does generate better performances in both electrochemical and capacity retention for the use of anode of LIBs. Wang et al. also prepared larger SiNP (50nm compared to 15 nm in Buriak's research) for comparison, where the result also shows the dependency of electrochemical performances on particle size, showing that 3nm SiNP has better performances.



**Figure 2.** (a) Different Sizes of sample Hydride-Terminated SiNPs. (b) Hydrosilylation of SiNPs with acids. (c) Fabrication of nanosized Si<sub>x</sub>-COOH/GA composites

Nanowire structured silicon shows great strain relaxation and volume accommodation property and dramatically increased improved electrochemical performances. The overall volume change rate is smaller than that of the SiNP due to the vertical direction limiting the growth of volume expansion. According to Xu Chen's group[17] on fabricating 1D porous SiNW with the assistance of an one-step metal chemical etching with a size around 7 nm. The porous structure provides sufficient void space to not only accommodate the volume expansion effect but also increase the chance of lithium migration and thus increase the diffusion rate while maintaining a steady and stable charge-discharge rate and capacity. The result from the research shows that the under 1.5 A/g current density, the 1D porous SiNW demonstrated a reversible specific capacity of 2061.1 mAh/g after 1000 cycles. Moreover, under rapid charge-discharge current rate of 16.0 A/g, the anode can still hold a capacity of 586.7 mAh/g after 5000 cycles. Such results prove that under specific design, 1D SiNWs exhibit excellent electrochemical performances with the help of creating uniform porous structure while maintaining a stable life cycle time.

In short for both 0D and 1D Si nano-sized materials, they show promising changes with the design of nanonization to overcome part of its volume expansion effect while maintaining reasonable life cycle time and

capacity for future application. However, during the volume expansion effect in 1D Si, holes tend to form on the surface due to the removal of lithium ions during the discharge stage. Such holes are left with unchanged shape but larger size in each cycle of lithiation/delithiation, causing the memory effects which should not happen in lithium ion batteries[18]. Such effect will trigger the decay of capacity and thus affect the electrochemical performances.

### 2.3 Alloying Silicon

In addition to the above methods, the alloying of silicon is also a measure to improve its performance. Unlike carbon, metals or metal oxide usually possess decent mechanical properties, especially its mechanical strength, to sufficiently buffer the volume change as well as provide the silicon with good conductivity to improve the transmission efficiency. Several silicon-metal mixtures are discussed below to compare the actual result of performance for the practical application in commercialization.

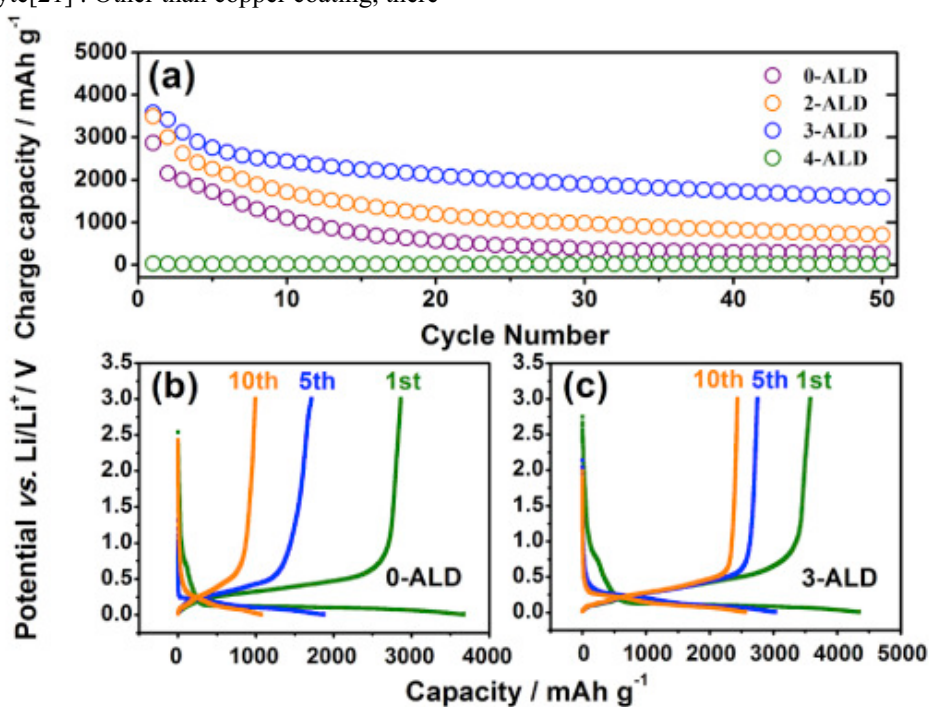
One common way to apply metal or metal oxide with Si is to coat silicon particles as a shell, protecting the silicon from side reactions with electrolytes, which further reduces the consumption of silicon and prevents constant

formation of SEI. Among commonly used metals, copper is known for its low cost with decent conductivity and good mechanical properties[19]. An example experiment carried out by Yen's group[20] shows a surprising improvement of performances by sputtering 12nm copper thin film on nano-Si/graphite composite anode. The sputtered copper acts as a shell to prevent severe volume expansion and its mechanical properties provide a more densely-packed microstructure of the anode. Such changes ensure the preservation of most of the superior performances of silicon-based anode by maintaining the silicon from contacting the electrolyte to minimize the irreversible capacity loss. The experimental result shows that, with sputtered copper thin film, the capacity of the anode is 434.16 mAh/g and first Coulombic efficiency is around 90.5%. And the charge rate retention of sputtered copper anode maintained very stable, 96.46%, compared with general silicon/graphite anode used for comparison, which is reduced from 98.5% to 89.5%.

Most of the applications of copper serve similar purposes at current development as a shell for better conductivity and reduce the chance of silicon interacting with the electrolyte[21]. Other than copper coating, there

are also metals serving same or similar purpose to improve efficiency of applying silicon anode such as Ag[22], Ni-Si alloy[23], Fe[24], Mn[25], Ti[26], Zn[27] etc[28]. Those metals can either be used to alloy with silicon to increase capacity retention, specific capacity or act as shell structure like the copper mentioned above.

Except for metals, metal oxide such as TiO<sub>2</sub> can also provide similar enhancement for silicon anode. Ying Bai's group[29] proposed TiO<sub>2</sub> for coating on the Si nanoparticles anode via atomic layer deposition (ALD) with controlled thickness (2, 3, 4, 5nm) to reduce the volume expansion effect. Titanium oxide coating effectively restrains the expansion of silicon particles and thus dramatically suppresses the pulverization and aggregation of silicon nanoparticles. Moreover, they found out that the coating layer with 3nm thickness is the most beneficial thickness to make up for the relatively low conductivity of silicons and provides the anode with good mechanical property. The result shows that with the 3nm coating layer, the Coulombic efficiency and charge capacity reaches 97.97% and 1580.3 mAh/g respectively after 50 cycles.



**Figure 3.** The electrochemical performances of Si nanospheres before and after TiO<sub>2</sub> coating: (a) The charge capacity of different electrodes (from top to bottom: 3-, 2-, 0- and 4-ALD), (b) galvanostatic cycling profiles of 0-ALD and (c) 3-ALD.

Application of metals and metal oxides as layers on the Si anodes acting as the protective shell provides many benefits such as suppressing volume expansion, improving conductivity, good mechanical properties etc. Moreover, it is fairly cheap to obtain the required materials and structures and achieve a practical application. But even though metals can bring improvement to the silicon anode, specific treatment is also required to further optimize the potential of silicon.

### 3 Conclusion

Overall, in the area of high-energy-storage lithium-ion batteries, silicon and silicon-based materials have the advantages of high specific energy, long life cycle, various silicon sources, and proper working voltage. However, the large volume expansion effects become the main challenge and make it difficult to reach the theoretical specific capacity in real application and its



semiconducting property restrain its efficiency in transmitting the ions. The yolk-shell structure provides the anodes with high conductivity and the ability to restrain the constant contact with the electrolyte, decreasing the consumption of silicon particles to increase the life cycle time. But the difficult producing process and high cost raise the practical problem when commercialization. Nanostructured silicon and composites further reduce the volume expansion effects and provide enough void space for the expansion while maintaining good life cycle time and capacity. But new problems such as the memory effect, which is not supposed to happen in LIBs, heavily affects the performance, especially its life cycle time and decay of the capacity. The alloyed silicon also suppresses the volume change well and provides high conductivity due to the good mechanical properties and good conductivity provided by the metal. It is fairly cost less to both obtain the raw materials and modified structure. However, more improvement in modification and production methods is required to optimize the electrochemical performances of silicon anodes, which could satisfy the practical usage and commercialization. Moreover, it happens to all the modification methods that the cost and difficulties in mass production still occupy a large percentage for stopping the commercialization of LIBs.

## Reference

1. Quinn, J.B., et al., *Energy Density of Cylindrical Li-Ion Cells: A Comparison of Commercial 18650 to the 21700 Cells*. Journal of The Electrochemical Society, 2018. **165**(14): p. A3284-A3291.
2. Zafar Abbas Manj, R., et al., *Toward understanding the interaction within Silicon-based anodes for stable lithium storage*. Chemical Engineering Journal, 2020. **385**: p. 123821.
3. Xu, W., et al., *Lithium metal anodes for rechargeable batteries*. Energy & Environmental Science, 2013. **7**: p. 513.
4. Boukamp, B.A., G.C. Lesh, and R.A. Huggins, *All-Solid Lithium Electrodes with Mixed-Conductor Matrix*. Journal of The Electrochemical Society, 1981. **128**(4): p. 725-729.
5. Zhu, C., et al., *Achieving High-Performance Silicon Anodes of Lithium-Ion Batteries via Atomic and Molecular Layer Deposited Surface Coatings: an Overview*. Electrochimica Acta, 2017. **251**: p. 710-728.
6. Shi, F., et al., *Failure mechanisms of single-crystal silicon electrodes in lithium-ion batteries*. Nature communications, 2016. **7**: p. 11886-11886.
7. Li, T., et al., *Failure mechanism of bulk silicon anode electrodes for lithium-ion batteries*. Rare Metals, 2013. **32**: p. 299-304.
8. Zhao, X., et al., *In-Plane Vacancy-Enabled High-Power Si-Graphene Composite Electrode for Lithium-Ion Batteries*. Advanced Energy Materials, 2011. **1**(6): p. 1079-1084.
9. Chae, S., et al., *Integration of Graphite and Silicon Anodes for the Commercialization of High-Energy Lithium-Ion Batteries*. Angew Chem Int Ed Engl, 2020. **59**(1): p. 110-135.
10. Dou, F., et al., *Silicon/Carbon Composite Anode Materials for Lithium-Ion Batteries*. Electrochemical Energy Reviews, 2019. **2**(1): p. 149-198.
11. Yang, J., et al., *Yolk-shell silicon-mesoporous carbon anode with compact solid electrolyte interphase film for superior lithium-ion batteries*. Nano Energy, 2015. **18**: p. 133-142.
12. Mi, H., et al., *A self-sacrifice template strategy to fabricate yolk-shell structured silicon@void@carbon composites for high-performance lithium-ion batteries*. Chemical Engineering Journal, 2018. **351**: p. 103-109.
13. Kim, H., et al., *Three-dimensional porous silicon particles for use in high-performance lithium secondary batteries*. Angew Chem Int Ed Engl, 2008. **47**(52): p. 10151-4.
14. Bang, B.M., et al., *Scalable approach to multi-dimensional bulk Si anodes via metal-assisted chemical etching*. Energy & Environmental Science, 2011. **4**(12).
15. Sun, L., J. Xie, and Z. Jin, *Different Dimensional Nanostructured Silicon Materials: From Synthesis Methodology to Application in High-Energy Lithium-Ion Batteries*. Energy Technology, 2019. **7**(11).
16. Aghajamali, M., et al., *Size and Surface Effects of Silicon Nanocrystals in Graphene Aerogel Composite Anodes for Lithium Ion Batteries*. Chemistry of Materials, 2018. **30**(21): p. 7782-7792.
17. Chen, X., et al., *One-Dimensional Porous Silicon Nanowires with Large Surface Area for Fast Charge-Discharge Lithium-Ion Batteries*. Nanomaterials (Basel, Switzerland), 2018. **8**(5): p. 285.
18. Ulldemolins, M., F. Le Cras, and B. Pecquenard, *Memory effect highlighting in silicon anodes for high energy density lithium-ion batteries*. Electrochemistry Communications, 2013. **27**: p. 22-25.
19. Murugesan, S., et al., *Copper-Coated Amorphous Silicon Particles as an Anode Material for Lithium-Ion Batteries*. Chemistry of Materials, 2012. **24**(7): p. 1306-1315.
20. Yen, J.-P., et al., *Sputtered copper coating on silicon/graphite composite anode for lithium ion batteries*. Journal of Alloys and Compounds, 2014. **598**: p. 184-190.
21. Lin, L., et al., *Copper-Nanoparticle-Induced Porous Si/Cu Composite Films as an Anode for Lithium Ion Batteries*. ACS Nano, 2017. **11**(7): p. 6893-6903.
22. Yoo, S., et al., *Highly dispersive and electrically conductive silver-coated Si anodes synthesized via a simple chemical reduction process*. Nano Energy, 2013. **2**(6): p. 1271-1278.

23. Du, Z., et al., *NixSi1-xAlloys Prepared by Mechanical Milling as Negative Electrode Materials for Lithium Ion Batteries*. Journal of The Electrochemical Society, 2015. **163**(2): p. A13-A18.
24. Adpakpang, K., et al., *A magnesiothermic route to multicomponent nanocomposites of FeSi2@Si@graphene and FeSi2@Si with promising anode performance*. Electrochimica Acta, 2014. **136**: p. 483-492.
25. Deng, L., et al., *High-performance Si Mn/C composite anodes with integrating inactive Mn4Si7 alloy for lithium-ion batteries*. Electrochimica Acta, 2018. **260**: p. 830-837.
26. Shin, M.-S., et al., *Post-annealing effects on the electrochemical performance of a Si/TiSi2 heteronanostructured anode material prepared by mechanical alloying*. Journal of Power Sources, 2017. **344**: p. 152-159.
27. Kim, D., et al., *Conversion Reaction of Nanoporous ZnO for Stable Electrochemical Cycling of Binderless Si Microparticle Composite Anode*. ACS Nano, 2018. **12**(11): p. 10903-10913.
28. Martinez-Garcia, A., et al., *High rate and durable, binder free anode based on silicon loaded MoO3 nanoplatelets*. Sci Rep, 2015. **5**: p. 10530.
29. Bai, Y., et al., *Core-shell Si@TiO2 nanosphere anode by atomic layer deposition for Li-ion batteries*. Journal of Power Sources, 2016. **308**: p. 75-82.