Progress in Multidimensional Modification of Lithium-Ion Batteries Based on Silicon-Based Anode Materials: From Structural Design to Interface and Binder Optimization

Zefeng Dang*

School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing,100083, China

Abstract. Lithium-ion batteries are considered an important energy storage technology due to its high energy density against the background of the global carbon neutrality strategy. This paper provides a systematic review of four mainstream modification strategies and the related advancements in research relating to these issues. First, nanocrystallization engineering is effective in reducing the mechanical strain by reducing particles sizes, thereby reducing the risks of fracture, but at the cost of high specific surface area, which reduces initial Coulombic efficiency. Second, carbon Silicon composite designs allow confinement designs that include yolk shell structures to allow silicon to expand and increase the stability in the cycling respectably but there is a trade-off between the volumetric capacity and production costs. Third, surface and interface engineering creates artificial protective layers through such methods as molecular layer deposition (MLD), which truly isolates unfavorable electrolytic responses and greatly enhances interfacial kinetics under heavy loading provisions. Finally, functional binders employ self-healing in the dynamically self-healing to maintain the mechanics of electrodes in the microscale. The results show that the personal modification strategies cannot be used to simultaneously cover all the performance measures.

1 Introduction

Along with the further global transformation of the energy industry and the overall use of carbon-neutrality policies, more rigorous requirements are being imposed on the overall efficiency of lithium-ion batteries. The current graphite anode materials, which offer cost benefits and are industrially ready, are coming to the theoretical limit of specific capacity and it is difficult to sustain the development demands of future high-energy-density battery technology. Besides, the graphite anodes under high rate charge discharge are likely to lead to uncontrolled growth of lithium dendrites posing serious safety risks.

In order to reduce these bottlenecks, studies on alternative anode material systems have mainly developed in two major directions. The silicon based anodes form the first and has a

* Corresponding author: 2310340117@student.cumtb.edu.cn

significantly greater theoretical specific capacity than graphite and is regarded as one of the key material systems to realising high-energy density anodes. The interfacial instability of silicon is an issue that is being targeted by researchers in the last few years. Indicatively, Hansen et al. have invented an innovative method of deposition of molecular layers to form a very stable artificial SEI film [1]. Meanwhile, a long cycle life with high loading was realized in China by building hierarchically porous silicon nanoparticles on carbon supports [2]. Nevertheless, the significant volumetric growth throughout the cycling and the interfacial decay still needs organized remedies by designing nanostructures, assembly of composite matrices and surface/interface system engineering. The second trend is associated with lithium metal anodes that can be considered as the ultimate solution in leapfrog energy density breakthrough because of the very high theoretical capacity. In overcoming safety complications, Chen et al. came up with a approach that embraces space confinements to cause homogeneous lithium nucleation to effectively inhibit the growth of dendrites at high current densities [3]. It has been demonstrated by Zhang Qiang and his colleagues that the rich dynamic evolution mechanism of the lithium metal interface under the electrochemical environment was systematically summarized, which provides valuable clues to anode construction in the all-solid-state batteries [4]. Presumably, however, there exist some critical issues, including growing of the dendrites, non-uniformity of the solid electrolyte interphase, and active lithium loss on the course of cycling. Also, lithium titanate and some transition metal compounds are as anode materials showing potential to be used in special applications under high-energy and long-life and decentral temperature environments due to their structural stability and high ion diffusion kinetics.

Overall, research activities in this direction are focused on the systematic value addition of the energy density, rate performance and long term cycling stability of lithium-ion batteries by innovating the material system and optimization of their structure design. The initiatives are central to developing the electric vehicle market and contribute to the building of huge energy storage units.

The paper will focus on an organized discussion of the modification mechanisms of silicon based anodes in lithium-ion batteries and the four fundamental strategies that will be discussed, which are: nanostructural design, carbon composite engineering, interfacial modification and high-performance binders. The paper starts with the failure modes of silicon during lithiation and then gives a discussion on how nanostructuring reduces structural stress, carbon composites increase conductivity and slow down volume expansion and interfacial engineering and functional binders stabilize the interphase of solid electrolytes (SEI). The aim is to explain the synergetic relationship between these modification strategies and analyse its real effect on the enhancement of the stability and early Coulombic efficiency of bicycle cycling. This review, finally, aims at providing theoretical guidance to the structural optimization of high-energy-density silicon-based anodes and give future recommendations towards their scalability utilization in high-energy lithium-ion batteries in the next generation.

2 Overview of silicon-based anode materials

2.1 Mechanism and electrochemical reactions of lithium storage

Silicon (Si) in its elemental state is mainly two allotropes, crystalline silicon, which is a well-organized structure with three dimensions or crystal, and amorphous silicon, which is long-range atomic disordered. The metal crystalline silicon has a metallic silvery gray luster and is rather hard with a Mohs value usually gray-black when in powdered form, amorphous silicon on the other hand is a black powder. The two types have a definite melting and boiling point, and are typical of a semiconductor.

2.2 Positioning

The behavior of silicon in storing the lithium is fundamentally different to that of intercalation in the manner of the familiar graphite anodes, and occurs in accordance to standard alloying reactions. In the process of the first lithiation, when lithium ions are moving from the surface to the center of silicon particles, crystalline silicon is subjected to a step-by-step structural change pace. Lithium-silicon amorphous (Li_xSi) is formed first. As the further polarization of the potential is reached to about 60 mV (vs. Li/Li^+), this amorphous phase itself spontaneously rearranges to form a highly lithiated metastable crystalline form -$Li_{15}Si_4$ [4]. This change of phase is the basis of the ultrahigh theoretic specific capacity of silicon anodes, in which every silicon atom is able to form a stable intermetallic compound with a rough of 4.4 lithium atoms. Later delithiation cycles Lithium ions progressively release in the Li15Si4 phase which returns to intermediate Li_xSi and eventually runs back to amorphous silicon at the end of discharge. This oxidation or irreversible structural change of crystalline into amorphous does not only determine the electrochemical properties of silicon anode in the initial charge-discharge cycle but also has far-reaching implication on the kinetic characteristics and structural integrity in the future cycling.

2.3 Advantages and challenges

2.3.1 Core advantages

Silicon as a new generation anode material of the lithium-ion batteries possesses considerable inherent merits in improving the energy density and providing safety performances. To begin with, its theorical opportunity potential is 4200 mAh g^{-1} (equivalent to the $Li_{4.4}Si$ alloy phase), which was almost ten times higher than the conventional commercial graphite anodes, thus providing a promising way to break the energy density bottleneck of the battery presently experienced [5]. Secondly, silicon exhibits an average current of about 0.4 V (vs Li/Li^+) both in the lithiation and delithiation reaction. This value is less than that of most alloy-type anodes to give high full-cell energy output, but with slightly better operating potential than graphite, its ability to discourage lithium dendrite growth under high current chargedischarge conditions overcomes the situation. This system significantly lowers the chances of lithium plating thus improving safety and functioning life of cycling [2]. Also, the silicon is available naturally in the crust of the earth and has low cost. Its great accessibility of the resources makes it a possible competitor to large-scale industrial applications and a cornerstone material in achieving leapfrog improvements in the high-energy-density lithium batteries [3].

2.3.2 Challenges

Although very high on theoretical capacity, the practical application of silicon-based anodes has been impeded by highly complicated failure modes and interfacial bottlenecks. The biggest problem is the high volume effect of the lithiation and delithiation process, where volume expansion up to 300% and much higher than the 12 percent in the conventional graphite anodes is realized. This type of uncondensed volatility changes causes large-scale mechanical stress on the active material that leads to excessive pulverization and abrasion of particles. These mechanical failures of the electrode architecture and loss of electrical contact are precipitated by these structural degradations [6].

Furthermore, these strong changes of volume cause additional destabilization of the interface. When cycling the solid electrolyte interphase (SEI) is formed on the surface of the active particles, it cracks and regenerates many times. Not only does it cause permanent consumption of active lithium ions on the cathode and consumption of electrolytes, but also

uncontrolled thickening of the SEI layer and higher inner resistance. These mirror themselves as reduced initial Coulombic efficiency and faster capacity capture with more extensive cycling [7]. Moreover, silicon has low conductivity of electricity in it by nature, which limits a quick movement of charge of the electrode. These dynamic constraints hinder the entire exploitation of its high specific capacity when charging and discharging at high-rate conditions, which significantly limits the power output and rapid charging system of the battery [1,3].

3 Strategies for silicon-based anode modification

3.1 Nanostructured design

On the nanostructured design, scholars successfully model mechanical stress caused by lithium intercalation through scaling of silicon to less than the critical fracture size (around 150 nm), and the geometric size prevents fracture of particles due to the expansion volume. An example is the further development of the nanocrystallization theory by Hansen, Cui and others who have acquired control on the thickness of the surface oxide layer, by a fine control of nano-silicon morphology [1]. The novelty of the research is identified in the exposure of the feedback mechanism between the surface chemical conditions and the stress distribution at the nanoscale indicating that not just physical pulverization is suppressed, but also that ultra-small silicon nanoparticles have a synergistic effect on the cycling stability by the chemical coating of silicon nanoparticles. It has been experimentally shown that the optimized nanostructure does not suffer any substantial loss in structural integrity over time during cycling. The case is well founded in justifying the inherent benefits of nanostructured design in solving the volume expansion problem. Studies also prove that nanoscale sizes have a substantial effect in reducing mechanical strain during lithiation to keep the physical integrity of the electrode structure intact. But there are significant inherent limitations of this strategy as well. To begin with, the high specific surface area of nanomaterials will cause the electrolyte decomposition to be faster making inevitable low initial Coulombic efficiency. Secondly, the low tap density of nanomaterials, which is often very low, limits badly the volumetric energy density of batteries. Finally, these physical constraints greatly add to the engineering problems of large-scale commercial encapsulation.

3.2 Construction of silicon-carbon composites

Besides pure physical structural optimization, siliconcarbon composites can provide a more economically feasible route to achieving all of these simultaneously through a high-performance carbon skeleton stabilizing interfaces by enhancing the electrical conductivity of the material. Recently interesting is the hierarchically porous carbon-confined silicon composite selected by Hou et al. whose main contribution was made in assembling a high-mechanical modulus carbon framework. This design employs space confinement effect to provide very small regulated breathing space to the silicon volume expansion [8]. The results of this approach are impressive: despite a high specific capacity, the composite has much better capacity retention following 1, 000 cycles than non-confined counterparts. The case goes a long way to support the synergistic benefits of the composite strategies in terms of overcoming the volume expansion as well as creating an effective electron conduction network. Research has shown that it has the potential of boosting the mechanical strength of active materials and provide better conductive modes. However, there are certain limitations that are also noted in the strategy. To begin with, complicated fabrication techniques, including high temperature pyrolysis or chemical vapor deposition are a major cost to the

production. Secondly, to the extent that incorporation of carbon leads to an increase in structural stability, it also decreases the overall gravimetric specific capacity of the material, to some level.

3.3 Surface and interface engineering

Based on the stability of macrostructural framework of the electrodes, surface and interface engineering instead works on the creation of protective layers within the molecular level. These layers are mechanically flexible and lithium-ion permeable, and thus, efficiently segregate the electrode centuries of undes pricey side reactions to the electrolyte. Kozen et al. used molecular layer deposition (MLD) to create in vivo an adaptive coating of inorganic and organic layers on silicon surfaces in their study. Innovation within The concept of artificial skin that introduces the ability of the interfacial layer to actively adjust to the volumetric changes in expansion and contraction of silicon particles is an innovation, thus eliminating the uncontrolled thickening of solid electrolyte interphase (SEI) film [9]. This method also goes a long way in stabilizing the electrodes with high loading, where the stated conditions of fast-charging are required. The findings are convincing to highlight the usefulness of the accurate modification of chemical characteristics of interfaces. By means of these approaches, scientists can manage to balance out the physical constraints of active materials. Nevertheless, the limitations of interfacial engineering are also noteworthy in this case. First, due to the atomic-level accuracy needed by the process, there is an extremely low manufacturing throughput. Second, the inappropriate design of the interfacial layer can also add further interfacial impedance and eventually reduce the rate capability of the battery.

3.4 Optimization of binders

Since the chemical bonding agent that guarantees mechanical integrity in the electrode system, optimization of binder in tribal-scale guarantees thorough protection of silicon-based anodes, whether in microscopic or macroscopic scapelessness, via devolution of dynamic feedback processes. He and colleagues have designed a self-healing polymer binder using dynamic covalent bonding, the key innovation through which they have utilized the reversible character of chemical bonds to allow mechanical cracks arising in cycling to be self-healing dynamically, hence actively maintaining the bonding of active materials and current collectors [10]. Remarkable electrochemical stability of micron-sized silicon particles is demonstrated to this strategy even without complicated nanocrystallization. The results of these studies highlight that functionalized binders are high cost-effective to cover mechanical degradation. Research suggests that these binders contribute greatly to the electrical continuity of the active material in the course of cycling thus being macroscopically able to maintain the structural integrity of the electrode. Nevertheless, there are also some shortcomings in this method as applied in practice. To begin with, the kinetic mobility of chain molecules of a polymer is extremely important to the self-healing process. Second, at either very high charge-discharge rates or very low temperature conditions, the chemical repair rate can frequently lag at all behind the physical degradation rate. Lastly, the long-term chemical durability of such materials during long-term service needs new experimental confirmation.

4 Conclusion

In brief, silicon based anodes have become an essential technological route to remove the particular energy bottleneck of conventional lithium ion batteries, due to their better lithium

storage capability and mediocre operating potential. This article analyzed four mainstream alteration strategies known as nanostructured design, carbon silicon composite fabrication, surface and interface and optimization of binder systematically. The results indicate that governance of specificity and physical architecture in addition to customization of interfaces at the molecular level are critical in curbing the silicon volume expansion and stabilizing the interphase between the solid electrolyte (SEI). Even though nanostructured design reduces mechanical stress geometrically, there simultaneously is an initial Coulombic efficiency trade-off due to the related rise in specific surface area. The carbon-silicon composite method balances the conductivity and buffering material through the effect of spatial confinement, but involves tradeoffs on tap density and manufacturing cost. Instead, surface engineering and functional binders offer chemical protection of long-term electrode stability by molecular-level protection and repair. These contributions do not only enrich the scientific knowledge of the underlying mechanisms of failure in silicon-based systems, but also form a strong theoretical and technical ground on how to construct the high-performance and safe power batteries.

In the future, the massive commercialization of silicon-based anodes would require the concerted work on several dimensions. Research on the subject in the future must go beyond the cycle of refinement in single techniques of modification, and concentrate on the multiplier effect of combining multi techniques to use. Since it is possible to build multi-scale hybrid designs (core-shell, porous, coating, etc.) without compromising volumetric energy density, it is possible to realize breakthroughs in overall electrochemical performance. Also, the emergence of both cost-effective and scaleable future technologies of prelithiation, as well as compatible highly resilient electrolyte systems, will be an important step by silicon-based anodes within laboratory scope to high-energy-density battery systems.

References

1. S. Hansen, Z. Liu, Y. Cui, et al., Molecular layer deposition for highly stable interfacial engineering of silicon anodes. Nature Energy **6**, 1102–1110 (2021).
2. M. Wang, Y. Sun, W. Zhang, Interfacial Engineering and Performance Optimization of Silicon-Based Anode Materials for Lithium-Ion Batteries. Progress in Chemistry **34**, 2015–2028 (2022).
3. D. Ma, Z. Cao, A. Hu, Si-based anode materials for Li-ion batteries: A mini review. Nano-Micro Lett. **6**, 347-358 (2014). https://doi.org/10.1007/s40820-014-0008-2
4. X. Yan, Y. Chen, et al., Research progress of silicon suboxide-based anodes for lithium-ion batteries. Frontiers in Materials **8**, 628233 (2021).
5. H. Wu, Y. Cui, Designing nanostructured Si anodes for high energy lithium ion batteries. Nano Today **7**, 414-429 (2012). https://doi.org/10.1016/j.nantod.2012.08.004.
6. Y. Chai, Y. Chen, et al., Research Progress in Relieving Volume Expansion of Si Anode for Lithium-Ion Batteries. ACS Appl. Energy Mater. **8**, 16416–16437 (2025).
7. A. Casimir, H. Zhang, O. Ogoke, et al., Silicon-based anodes for lithium-ion batteries: Effectiveness of materials synthesis and electrode preparation. Nano Energy **27**, 359–376 (2016).
8. L. Hou, H. Zheng, R. Cui, et al., Silicon carbon nanohybrids with expandable space: A high-performance lithium battery anodes. Microporous Mesoporous Mat. **275**, 42-49 (2019).https://doi.org/10.1016/j.micromeso.2018.08.014
9. A.C. Kozen, C.F. Lin, A.J. Pearse, et al., Artificial solid electrolyte interphase to address the electrochemical degradation of silicon electrodes. ACS Applied Materials & Interfaces **6**, 5404–5409 (2014).

10. J. He, W. Ding, L. Xiao, et al., A dynamic boronic ester/hydrogen bonding enriched binder with self-healing chemistry for silicon anodes in lithium-ion batteries. Chem. Eng. J. **518**, 164454 (2025).https://doi.org/10.1016/j.cej.2025.164454