Enhancement Strategies for Si/C Electrodes in Lithium-Ion Batteries

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Abstract. The escalating dependence on energy within contemporary society while facing the limitations of traditional fossil fuels has spurred the advancement of energy storage technologies, with particular emphasis on lithium-ion batteries (LIBs). Si/C composite anodes have emerged as a viable alternative to graphite anodes, primarily owing to their superior specific capacity and improved cycling performance. However, Si anodes face the challenge of volume expansion during charge/discharge cycling, which leads to capacity degradation and limits their practical application in LIBs. Recent research has focused on addressing these issues through various strategies aimed at optimizing the structural stability and enhancing the electrochemical performance of Si/C composites. The explored key methodologies include the implementation of double carbon shells, the optimization of porosity, and innovative microelectronic printing techniques. These approaches have demonstrated significant improvements in the cycle life and energy retention of the batteries, positioning Si/C composites as a promising solution for next-generation high-performance energy storage systems.

Keywords: Si/C composite anodes; Lithium-ion batteries; Electrochemical performance; Capacity and structural stability.

1. Introduction

The increasing global energy demand, driven by societal progress and conventional fossil fuels depletion alongside their associated environmental pollution, has catalyzed the development of new energy resources. Energy technologies such as wind, solar, and nuclear energy have appeared as feasible substitutes. Renewable resources exhibit intermittent availability, so it is necessary to build up the large-scale, efficient energy storage systems for effective electricity management. Lithium-ion batteries (LIBs) have risen as one of the most important energy storage approaches, which characterized by prolonged cycle life, minimal maintenance expenditures, the high energy density and high operating voltage [1]. They can be used in portable electronics, photovoltaic energy storage systems and electric vehicles. In the process of manufacturing, people are demanding higher energy density, stronger rate capability and longer cycle life, making them indispensable to future sustainable energy strategies.

In 1991, SONY first commercialized LIB, utilizing $LiCoO_2$ for cathode and hard carbon for anode. At present, there are various of cathode, such as $LiCoO_2$, $LiFePO_4$, $LiMn_2O_4$ and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. Nowadays, commercial LIBs typically have energy densities between 150 and 180 $Wh \cdot kg^{-1}$ [2]. However, the potential for future promotion is limited by the low specific capacities of current electrode materials, such as layered oxides, $LiFePO_4$, and graphite. Graphite is the most commonly used anode material. It has a theoretical capacity of 372 $mAh \cdot g^{-1}$, corresponding to its composition with lithium as LiC_6 [3]. However, its development has nearly reached the bottleneck, restricting its application in large-scale energy storage systems and electric vehicles. Therefore, research has transformed into discovering new anode materials with higher capacities, suitable charge/discharge voltages, and better safety features, trying to surpass these constraints and enhance holistic LIBs performance.

For performance improvement of LIBs, choosing high-capacity anode materials is significant. Si and various lithium-alloying metals, including Al, Sn, and Sb, have been examined as possible candidates. Among them, Si has garnered significant attention as one of the most viable anodes

replacements for commercially used graphite, owing to its distinct advantages. Si is a notably promising alternative to commercial graphite anodes due to its remarkable specific capacity of approximately 4200 $mAh \cdot g^{-1}$ [4], almost ten times as much as graphite. Its abundance, environmental friendliness, and appropriate working potential are noteworthy [5]. Despite its advantages, the application of Si anodes in practice encounters significant challenges, primarily due to the substantial volume expansion (up to 400%) in lithiation-delithiation process [6]. This expansion leads to mechanical stress, particle fracture, and the formation of unstable solid electrolyte interphase (SEI) [7], causing rapid capacity decay and poor initial Coulombic efficiency. In addition, issues such as low ionic conductivity and the complexity and costliness of preparation methods further impede the industrial application of silicon-based anodes. Overcoming these difficulties is essential for harness the full potential of Si as a replacement for traditional graphite anodes in LIBs.

The recurrent volume fluctuations associated with silicon-based anodes during electrochemical cycling induce instability within the SEI, accelerating the depletion of lithium ions and electrolytes, consequently reducing specific capacity and coulombic efficiency. Nevertheless, extensive projects have been investigated, with particular emphasis placed on Si/C composites due to their efficacy in coping with volume expansion and enhancing electrical conductivity [8]. The Si particles are tiny with a restricted size distribution to reduce volume variation of Si/C composites. Uniform dispersion of Si particles within the carbon structure is essential for achieving regular lithiation-delithiation [9]. Carbonaceous materials act as stress-buffering matrices that not only accommodate the mechanical strain induced by the volumetric variations of Si but also contribute to the stabilization of the SEI layer. This synergistic integration of silicon and carbon leverages the high lithium storage capacity inherent in Si while exploiting the mechanical resilience and conductive properties of carbon [10], resulting in enhanced cycling stability and improved overall anode performance. Si/C composite materials have illustrated significant potential in addressing the inherent limitations of Si anodes, rendering them a reliable candidate for boosting the efficiency and lifespan of LIBs.

This research aims to summarize the contemporary advancements in Si/C anode materials. Particular emphasis lies on five strategies aimed at enhancing the stability of capacity and structure in these Si/C composite systems.

2. Different enhancement strategies for Si/C electrodes

2.1. Synthesis methods

Through the synthesis of Si/C microspheres utilizing nonsynchronous nucleation (SCM-1), hydrothermal coupling (SCM-2), and magnesium thermal reduction methodologies (SCM-3), meticulous regulation of the Si/C shell thickness, layer quantity, and structural configuration was accomplished [11]. The synthesized materials used in anodes demonstrated noteworthy electrochemical properties for LIBs.

Among the prepared samples, SCM-2 demonstrated exceptional performance metrics. Its double carbon shell architecture effectively alleviated the volume-expansion of Si during lithiation-delithiation phases, thereby averting pulverization and maintaining intact structure. Thanks to the increased specific surface area (201.7 $cm^2 \cdot g^{-1}$) and pore volume (0.92 $cm^3 \cdot g^{-1}$) of the material, which facilitated electrolyte infiltration and promoted lithium-ion diffusion. Furthermore, the carbon shells established a stable conductive framework, thus fostering the progress of a resilient SEI layer.

The electrochemical performance of SCM-2 was corroborated through galvanostatic charge/discharge evaluations. At a current rate of 0.1 C, it attained an initial specific capacity of 2455 $mAh \cdot g^{-1}$, ranking among the highest verified for Si/C composites. Following 200 cycles, it sustained the capacity of 2178 $mAh \cdot g^{-1}$, indicative of remarkable cycling stability. Even under a heightened rate of 2 C, SCM-2 preserved 98% of its initial capacity after 500 cycles, which emphasizes its formidable rate capability.

SCM-1 and SCM-3 also manifested steady electrochemical performance, although they are somewhat inferior to SCM-2. SCM-1, characterized by a singular carbon shell, gave a specific

capacity of 1797 mAh·g^{-1} (0.1 C) at the initial stage, retaining 1489 mAh·g^{-1} post-200 cycles. SCM-3, possessing a triple-layered configuration, demonstrated an initial capacity of 2065 mAh·g^{-1} at 0.1 C and maintained 1606 mAh·g^{-1} after 200 cycles.

The disparities in performance outcomes among SCM-1, SCM-2, and SCM-3 can be ascribed to the differential carbon shell thickness and layer count. The increased thickness and number of carbon layers in SCM-2 conferred enhanced structural stability and buffering capabilities, culminating in improved cycling stability and rate performance. The augmented surface area and pore volume also facilitated the expedited penetration of electrolytes and lithium-ion diffusion, which in turn led to an enhanced capacity.

The EIS further substantiated the superior performance of SCM-2, revealing diminished charge transfer resistance (RCT) and Warburg diffusion resistance in comparison to SCM-1 and SCM-3, and indicating enhanced electron and ion conductivity. The TEM and SEM imagery confirmed that SCM-2 retained its spherical morphology even after 100 cycles, whereas SCM-1 and SCM-3 exhibited substantial structural deterioration.

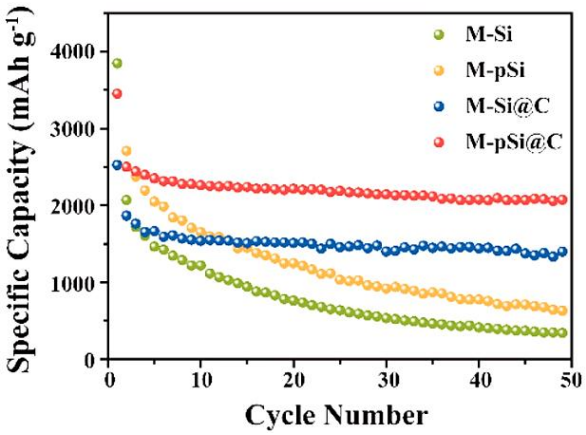

Fig. 1 Cycle performance of M-Si, M-pSi, M-Si@C and M-pSi@C electrodes [12].

2.2. Porosity and carbon coating

After the process of characterization, the SEM images show that the p-SiO_2 particles are spherical in shape, with a particle size range of 1-5 μm. Since p-SiO_2 is composed of many small grains of SiO_2, resulting in a rough and uneven-looking surface. Comparing the acid-etched material (M-pSi) with the non-acid-etched material (M-Si), it is clear that the HF etching technology significantly improves the microspheric porosity of SiO_2 and retains the sphere well. However, its porosity should not be too high, otherwise it cannot withstand high temperature and high pressure. A thin amorphous carbon shell is CVD deposited on M-pSi, facilitating electrical conductivity and reducing volume expansion [12].

To test the electrical properties, the four materials (M-Si, M-pSi, M-Si@C and M-pSi@C) were assembled into a half-cell. This experiment shows the Nyquist plots and the carbon coated electrodes were found to have lower resistance. The four curves shown in the figure of cycle performance illustrate that they all have high capacity, but the capacity of M-Si, M-pSi slump with increasing cycles.

The next step was to compare M-Si@C and M-pSi@C by measuring the fabrication rate capacity at a range of current densities from 0.1 to 2 A·g^{-1}, and it was clear that M-pSi@C had a definite advantage. M-pSi@C was further explored by measuring CV which using long term cycling at different current densities, and the results exhibits superior capacity and cycle stability of M-pSi@C (Fig. 1). This is due to two aspects, the high porosity inside the material and the outermost carbon as a protective layer inducing the formation of a stable SEI. Moreover, M-pSi@C provides thinner and higher density SEI layer, which ensure the status of exceptional stable performance.

2.3. Particles size

The experiment was carried out with three grinding programs (5 min, 20 min, 180 min), which resulted in different particle sizes [13]. The initial experiments with ball milled Si particles found that while particle size reduction was achieved, there was no significant benefit to coulombic efficiency or long-term capacity. The discharge capacity of the samples degraded rapidly, with only 40% of the initial capacity remaining after 10 cycles. Interestingly, the charge/discharge capacity of Si after 180 minutes of milling is lower rather than superior because of its higher surface area, the formation of more SiO2 results in a reduction of the capacity in theory. This underscores the challenges faced with Si anodes and emphasizes the need for continued optimization.

To solve these problems, the buffer solution can be employed. The robustness of covalent bonds was enhanced by maintaining the pH level beneath the isoelectric point of silicon particles (3.5) and the pKa of CMC (3.5), which served to neutralize the SiO- and COO- functional groups into SiOH and COOH. The long-term cycling performance of the Si anode and Si/C composite electrode was significantly improved using this method. The cycling life of the raw materials test doubled with the use of the buffer solution, which did not show a sudden drop after 10 cycles. Its effectiveness in promoting adhesive grafting and improving electrode stability was substantiated.

The role of binders in maintaining electrode structure and cycle stability was also explored. While PVDF, a commonly used binder in graphite anodes, failed to accommodate the volume changes of Si, CMC showed better performance. In addition, stability can be improved over CMC alone by combining CMC with the elastomeric styrene butadiene rubber (SBR). The Si-C-CMC cell exhibited a capacity of 161 cycles before degradation occurred, whereas the Si-C-CMC/SBR cell displayed a considerably longer operational lifespan, with a capacity of 190 cycles at the set capacity. The water-soluble and thickening properties of CMC are complemented by the high flexibility and adhesive properties of SBR, resulted in a promising Si anode binder composition.

Electrolyte additives in modulating the formation of the SEI layer and enhancing the cyclability of silicon-based anodes. Incorporating 10 wt% FEC into the electrolyte matrix, coupled with a restricted capacity cycling program, has demonstrated the ability to sustain a specific capacity of 1000 mAh·g-1 for the Si anode over 1200 cycles. The decomposition of FEC during the first cycle yields a malleable and resilient SEI layer, which confers improved stability to the composite electrode system. The resultant flexible polycarbonate-based SEI layer is found to be more accommodating to the significant volume changes associated with the Si phase during lithiation-delithiation processes.

2.4. Component ratio and the addition of $CaCO_3$

Si/C composites are undoubtedly an optimal choice due to the incorporation of an elastic carbon matrix, which effectively mitigates the volume change of the active material. Nevertheless, the cycle efficiency was still low after the incorporation of fine Si particles within the matrix of pyrolyzed pitch during the initial test cycle, with a value of only 59%. By dispersing fine graphite powder into 250 mesh composite particles, this was changed. Optimizing the ratio of Si fractions, graphite, and pitch resulted in a higher efficiency of approximately 81%. The data from electrical tests conducted with various ratios of materials indicate that a moderate amount of graphite is advantageous for enhancing the Coulombic efficiency of the composite, while the addition of a suitable quantity of pitch is beneficial for stabilizing the bonding of the graphite and silicon particles [14].

The voltage associated with lithium insertion into the Si/C composite electrode demonstrated a significant improvement subsequent to the initial cycle and subsequently stabilized. In comparison to CMS, the discharge voltage of Si/C is observed to be positively shifted by 0.12 V, which prevent the formation of lithium dendrite. The capacity of Si/C far exceeds that of CMS.

Despite the enhanced cycling performance exhibited by Si/C composites relative to pure Si, the capacity decay remains rapid during the first cycling phase. To perform well, the Si particles must be enclosed by carbon. Pitch pyrolysis produces a significant number of micropores in the composite, which results in the facile separation of Si from carbon. To enhance the cycling stability of the composite, a modest quantity of nanosized $CaCO_3$ is incorporated as an additive [14]. $CaCO_3$

decomposes at elevated temperatures to generate a silica-calcium alloy layer, which fortifies the interfacial bonding between carbon and silicon, impedes the fracturing of Si particles, and facilitates the formation of an amorphous structure. The aforementioned factors led to a significant improvement in the cycling performance of the composites, with a stabilized capacity of 500 $mAh \cdot g^{-1}$.

2.5. Microelectronic printing techniques

The research introduces an innovative method for the synthesis of a flexible Si/C composite anode intended for LIBs, employing advanced microelectronic printing techniques [15]. The unique combination of a layered slit structure and an amorphous carbon coating effectively addresses the challenges associated with Si anodes, demonstrating significant improvements in electrochemical performance and structural stability.

The layered slit structure within the anode reduces the volume expansion of Si throughout the lithiation and delithiation process due to its essential buffer zone. This design prevents the formation of cracks and maintains the electrode's integrity throughout the cycling process. The TEM images clearly demonstrate the reversible expansion and contraction of the layered slits, accommodating the Si expansion without causing pulverization. This dynamic behavior ensures that the anode maintains its structural integrity and retains its electrochemical activity over extended cycling.

The PVP-derived amorphous carbon coating plays a multifaceted role in improving the performance of the anode. It acts as a protective barrier, preventing direct contact between Si and the electrolyte. This effectively reduces the formation of the SEI layer, resulting in a thinner and more stable interface. The EIS analysis confirms this, as evidenced by the diminished semicircular diameter in the high-frequency spectrum for double-layer electrodes with amorphous carbon coating compared to single-layer electrodes. It exhibits minimal resistivity and incorporates layer of amorphous carbon to improve anode electronic conductivity.

The microelectronic printed anode has impressive electrochemical performance. The double-layer electrode exhibits a reversible capacity of 941.1 $mAh \cdot g^{-1}$ at a current density of 0.1 $A \cdot g^{-1}$, accompanied by an initial Coulombic efficiency of 79%. Following 100 cycles, the capacity retention rate persists at 81.82%, highlighting the distinguished stability in cycling. The efficacy with respect to charge retention is remarkable, demonstrating a capacity retention rate of 98.67% following 50 cycles at a current density of 1.0 $A \cdot g^{-1}$. Such findings suggest the microelectronic printed anode possesses the ability to provide elevated capacity and consistent performance, even when subjected to conditions of rapid charge and discharge.

The research examines the structural integrality of the anode by analyzing the surface morphology subsequent to cycling. The single-layer electrode devoid of the amorphous carbon coating demonstrates significant degradation and disintegration, primarily attributed to the recurrent expansion of Si. In contrast, the double-layer electrode with the amorphous carbon coating maintains its structure with only slight layering and peeling. This demonstrates the effectiveness of the amorphous carbon layer in mitigating the volume expansion and maintaining the electrode's shape.

3. Conclusion

Si/C composite anodes signify a breakthrough in the progression of high-performance LIBs, which is attributed to their exceptional specific capacity and promising electrochemical characteristics. Despite their potential, significant challenges remain, such as volumetric expansion during cycling and the formation of unstable SEI. This research highlights the various strategies employed to mitigate these challenges. Among the advancements, the use of double carbon shells and the optimization of porosity through HF etching and carbon coating have shown to effectively buffer the mechanical stress induced by silicon's expansion. Innovations such as microelectronic printing techniques have demonstrated the potential to further stabilize the structural integrity of Si/C composites, ensuring better cycling performance and longevity. By introducing additives like $CaCO_3$ and using innovative binder formulations, the cycling efficiency and capacity retention have

significantly improved. Further research is essential to enhance composites for commercial viability, emphasizing structural stability, energy density, and cost-effectiveness. Investigating material synthesis and incorporating innovative additives and manufacturing methods will be vital for realizing the potential of Si/C anodes in future LIBs.

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