



Review article

From electrochemical performance to mechanical Issues: A review on silicon anode architectures for advanced lithium-ion batteries

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HIGHLIGHTS

- Silicon anodes offer high specific capacity for next-generation lithium-ion batteries.
- Volume expansion issues in silicon anodes severely limit battery cycling stability.
- Nanostructures, buffers, and additives combat conductivity and volume expansion problems.
- Continued research on Si anodes holds the key for robust future LIBs.

GRAPHICAL ABSTRACT



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ABSTRACT

The increasing demand for high-energy-density lithium-ion batteries in electronics and electric vehicles has spurred significant research into silicon anodes. This article reviews key structural variants—nanostructured, micron-scale, and three-dimensional (3D) silicon anodes—highlighting their advantages, challenges, and solutions. While nanostructured silicon offers high specific capacity and stability, it suffers from low conductivity, significant volume expansion, and poor cycling life. To address these, strategies such as nanostructural Si designs, introducing conductive/buffering agents (e.g., graphene, MXene), and polymeric binders are discussed. Micron-scale silicon partially alleviates expansion due to its larger size, but still faces challenges in conductivity and cycling stability; morphological optimization strategies are explored. Conversely, 3D structured silicon demonstrates excellent electrochemical performance from its unique architecture, though conductivity and volume expansion remain issues. The review covers state-of-the-art methods, including the above approaches and functional additives, to achieve stable cycling. Finally, future development pathways such as novel structural designs, material innovation, and application prospects are considered, indicating silicon's potential as a robust anode material for future lithium-ion batteries.

Abbreviation list

Si	Silicon	CV	Cyclic voltammetry
LIBs	Lithium-Ion Batteries	DEM	Discrete Element Method
3D	Three-dimensional	CP	Co particles
CE	Coulombic efficiency	HA	humic acid
ICE	Initial coulombic efficiency	Si@TiO ₂	Silicon @ titanium dioxide
SEI	Solid electrolyte interface	APTES	3-aminopropyltriethoxysilane
Si NSs	Silicon nanosheets	PECVD	Plasma enhanced chemical vapor deposition
Cu	Copper	GO	Graphene oxide
RGO	Redox graphene oxide	SWCNTs	Single-walled carbon nanotubes
SiNWs	Si nanowires	SiA	Si alloy
SINPs	Si nonoparticles	AAO	Anodic aluminum oxide
2D	Two-dimensional	MACE	Metal Assisted Chemical Etching
HC	Hard carbon	PVA	Polyvinyl alcohol
CNT	Carbon nanotube	PAA	Polyacrylic acid
VACNTs	Vertically aligned carbon nanotubes	FEC	Fluoroethylene carbonate
CVD	Chemical vapor deposition	SS-SiNPs	Secondary submicron silicon nanoparticles
MLC	Multi-layered carbon	PAN	Polyacrylonitrile
GSs	Graphene shells	NC	Nitrogen-doped carbon
EC	Ethylene carbonate	PAA-c-ECH	Polyacrylic acid-epichlorohydrin
PC	Propylene carbonate	PANI	Polyaniline
CMC	Carboxymethyl cellulose	PPy	Polypyrrole
Si@C	Silicon@carbon	PEDOT: PSS	Poly (3,4-ethylenedioxythiophene): polystyrene sulfonate
Si@G	Silicon@graphene	PDA-c-PAM	Polydopamine grafted crosslinked polyacrylamide
TNO	TiNbO ₄	HEA	High entropy alloy
DFT	density functional theory	EGDE	Ethylene glycol dibutyl ether
XRD	X-ray diffraction	LIGGGHTS	LAMMPS improved for General Granular and Granular Heat Transfer Simulations
SEM	Scanning electron microscopy	(PAA-P (HEA co DMA))	Poly(acrylic acid)-poly(2-hydroxyethyl acrylate-co-dopamine methacrylate)
TEM	Transmission electron microscopy		
XPS	X-ray photoelectron spectroscopy		

1. Introduction

With the continuous growth of global energy demand and improved environmental protection awareness, lithium-ion batteries (LIBs), being efficient and reliable energy storage devices, have become an essential component of electric vehicles, portable electronic devices, and large-scale energy storage systems [1–3]. However, due to relatively low energy density and limited theoretical capacity, traditional graphite anode materials can no longer meet the needs of future high-performance batteries. Therefore, developing new anode materials with high discharge capacity, long cycle life, and excellent electrochemical performance has become a research hotspot [4,5].

To overcome the limitations of existing LIBs, alternative negative electrode materials are being explored, focusing on higher capacity, longer lifespan, and safety [2,6–8]. Silicon (Si), as a potential high-capacity negative electrode material with a theoretical capacity of up to 3579 mAh g⁻¹, is more than ten times that of traditional graphite negative electrode materials, and is expected to significantly improve the energy density of LIBs [9–11]. However, silicon materials experience severe volume expansion during the charging and discharging process, up to 300 %, far exceeding the limit of 10 % observed for graphite [12]. This expansion damages the Si-based electrode structural integrity, reduces conductivity, reduces cycling stability, and may cause safety issues [13,14]. Volume expansion affects the cycling life and safety performance of the battery and leads to pulverization of electrode structures [15]. Silicon can also form solid electrolyte interface (SEI)

films during charge-discharge cycles and damage electrode structures due to mechanical stress, resulting in capacity degradation and shortened cycle life. In addition, the low conductivity of silicon materials themselves limits the diffusion of lithium ions in electrode materials, reducing the charging and discharging efficiency and rate performance of batteries [16]. Therefore, solving the problems of volume expansion, low conductivity, and poor cycling stability of silicon materials is a key challenge in developing high-performance silicon-based negative electrode materials [17–19].

In recent years, significant progress in the research on silicon anodes has been made. Silicon anodes' initial coulombic efficiency (CE), surface capacity, and cycling stability have been significantly improved by introducing strategies such as composite materials, engineered nanostructures, artificial SEI layers, prelithiation technology, and efficient adhesives [20]. For example, recent works have shown that their performance can be significantly improved by understanding and addressing the mechanism of low initial Coulombic efficiency (ICE) of SiO_x anodes in LIBs [21]. In addition, some studies have proposed various innovative design schemes, such as core-shell heterostructures, single-layer layered silicon, and nano-fabric network structures, further improving the performance of silicon anodes. In all-solid-state batteries, the chemical mechanical failure mechanism of silicon-based negative electrodes has also been extensively studied, providing important references for the development of more stable batteries [22]. Moreover, the strain mismatch problem in the thin film bonding technology of silicon-based all-solid-state batteries has also been revealed, and corresponding solutions have been proposed. The transition study of silicon nanoparticles as negative electrode materials also shows the potential of LIBs for sodium-ion batteries. By modeling the degradation process of silicon graphite composite electrodes, researchers can better evaluate the value of silicon materials in practical applications. Furthermore, the influence of SiO_2 stress on the electrochemical performance of silicon anodes also provides new insights, which can help optimize the design of silicon-based electrodes [23,24]. Through these efforts and innovations, the future application prospects of silicon-based negative electrode materials have become even broader. However, further research and optimization are still needed to address existing technological challenges and promote sustained progress in LIB technology.

The anode materials critically impact battery capacity, and cathode materials fundamentally determine the achievable energy density of lithium-ion batteries (LIBs). Recent studies on high-voltage LiCoO_2 (LCO) cathodes exemplify this relationship. By increasing the charging cut-off voltage to 4.6 V, the volumetric energy density of LCO cathodes can be significantly enhanced [25]. However, such high-voltage operation accelerates electrolyte decomposition and LiPF_6 degradation, generating HF that corrodes the cathode interface and increases impedance [26]. These interfacial instabilities limit the practical realization of high energy density. Innovative strategies—such as MXene modification to suppress interfacial catalytic activity (reducing decomposition product thickness from 10 nm to 5 nm) and electronegativity-regulated coatings to weaken electrolyte adsorption—demonstrate that stabilizing cathode interfaces is equally essential for advancing LIB energy density [25,26].

While the existing reviews have explored general challenges and strategies for silicon anodes [27], only a few comprehensively classify advances through the critical lens of structural hierarchy (nano-/micro-/3D) and their distinct mechanistic advantages in mitigating volume expansion, enhancing conductivity, and prolonging cycle life. Recent breakthroughs in nanostructured porous silicon [28], binder-engineered microcomposites [29], and 3D scaffold designs [30] necessitate a timely synthesis correlating structure with performance across scales. This review uniquely bridges this gap by: (1) Systematically categorizing innovations by structural dimensionality, (2) Quantitatively comparing preparation methods and electrochemical outcomes within each category, and (3) Integrating the role of binders as structural stabilizers into this framework—a perspective overlooked in

prior syntheses. Publications on Si anodes and LIBs have shown distinct trends (Fig. 1a–b): Si anode research output remained relatively stable between 2016 and 2023 (maintaining 800–1200 publications annually), while LIB publications exhibited more pronounced fluctuations, peaking at approximately 10,000 in 2024. This work consolidates fragmented knowledge to guide targeted material development.

This review paper classifies different structural types of silicon anodes in lithium-ion batteries to properly address the challenges of volume expansion, improved conductivity, and enhanced cycling stability through their respective advantages and strategies. Among them, nanostructures exhibit improved conductivity through a high specific surface area but need to be optimized to enhance stability. The micrometer-scale structures alleviate expansion problems but require improving conductivity, while three-dimensional structures effectively adapt to volume changes and maintain good cycling stability through porous or buffering design. Further, this article summarizes a series of innovative advances made by researchers in the design of silicon anode structures, including nanostructures, microstructures, and three-dimensional (3D) structures of silicon anodes. These different structures of silicon anodes have their advantages and characteristics and are considered to solve the challenges of silicon materials. This review paper will focus on the latest research progress on silicon anode structures, including the advantages of different structures, preparation methods, electrochemical performance, and application status. In addition, a detailed analysis of the role of different structured silicon anodes in improving the performance of LIBs is provided, and the challenges they face are proposed. The binder significantly improves the conductivity, cycling stability, and overall performance of the battery by enhancing the integrity of the electrode structure, adapting to volume expansion, alleviating interface degradation, improving conductivity and ion transport, and enhancing thermal safety and electrode homogeneity. In order to further promote the application of silicon anodes in the field of batteries, this review will delve into the advantages, preparation methods, electrochemical performance, current application status, and future development directions of silicon anode structures.

2. Classification of Si anode structures

Different types of silicon anode structures (nanostructures, micrometer scale, and three-dimensional structures) have different physical and chemical properties, which directly influence the performance of the cell. Through segregation of nanostructures, we can better understand the advantages and limitations of each type, thereby guiding performance optimization. Each Si anode structural type has its specific challenges, such as conductivity, volume expansion, and cycling stability issues. Thus, classification of various anodes helps to focus on addressing critical issues related to particular types rather than making ineffective attempts at a macro level. After understanding the characteristics of different silicon anode structures, customized solutions can be provided for each type. Classification research has promoted the exploration of new materials and modification methods. Understanding the requirements of different structures can drive the development of new silicon materials, which may have better conductivity, lower volume expansion, or higher cycling stability.

The classification of silicon anodes into three structural types—nanostructures, micrometer-scale structures, and three-dimensional (3D) structures—provides a systematic framework for addressing the key challenges of silicon anodes. Each structural type exhibits distinct advantages and limitations in tackling issues such as volume expansion, conductivity, and cycling stability. For instance, **Nanostructures** effectively mitigate volume expansion due to their high surface area and small particle size, but they suffer from low tap density and poor conductivity. **Micrometer-scale structures** offer higher tap density and better mechanical stability but are more prone to cracking during cycling. **3D structures** combine the benefits of high structural stability and efficient electron/ion transport, making them suitable for high-

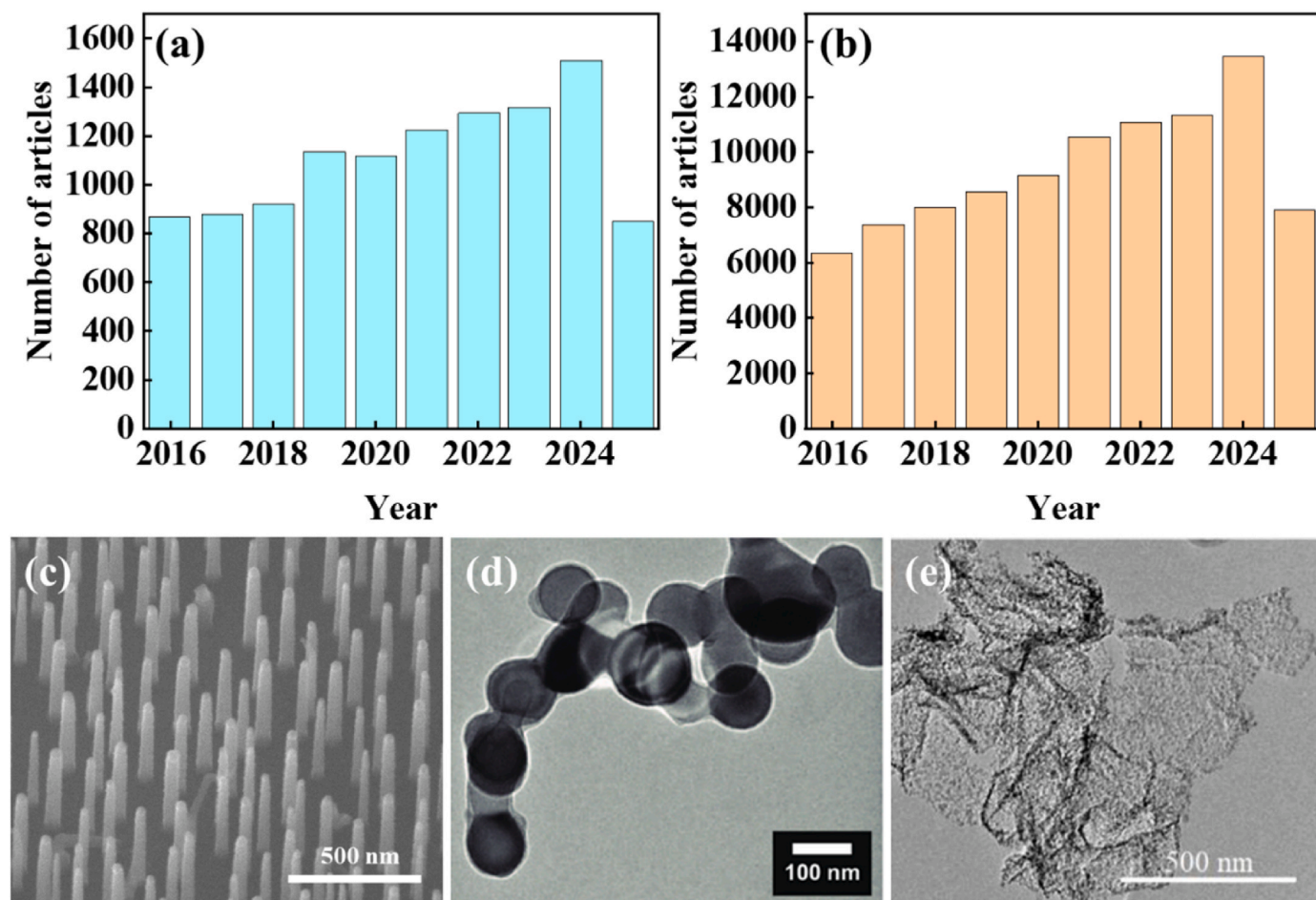


Fig. 1. The number of papers published on (a) Si anode and (b) LIBs in the past 10 years. (c) SEM image of Si nanowires. Reproduced with permission [33]. Copyright 2006, Springer Nature. (d) TEM image of Si nanoparticles. Reproduced with permission [34]. Copyright 2021, American Chemical Society. (e) TEM image of Si nanosheets. Reproduced with permission [35]. Copyright 2019, Royal Society of Chemistry.

performance applications. This classification facilitates a targeted approach to silicon anode research, enabling researchers to select the most appropriate structural design based on specific performance requirements. Compared to alternative classification methods, such as those based on material composition (e.g., silicon-carbon composites, silicon-metal oxides) or functional additives, structural classification provides a more direct correlation with the physical and electrochemical behavior of silicon anodes [31,32]. While material-based classifications focus on chemical properties, structural classifications emphasize the morphological and spatial characteristics that directly influence volume expansion, conductivity, and cycling stability.

2.1. Description of nanostructured silicon anode

2.1.1. Different nanostructured silicon anodes

In the field of lithium-ion battery (LIB) technology, researchers have recently developed various nanostructured silicon anodes to improve battery performance. These nanostructures are displayed in Fig. 1c–e, including nanowires [33], nanoparticles [34], and nanosheets [35], each exhibiting unique advantages and facing different challenges. Due to their high aspect ratio, nanowires can effectively alleviate volume expansion during charging and discharging processes and provide appropriate channels for ion transport and structural stability for electron transfer [36]. However, their preparation process is relatively complex and costly. For example, silicon nanowires have been studied for over a decade, and their unique one-dimensional morphology and ability to transform into interconnected active material networks

provide the potential to enhance cycling stability [37]. Significant progress has been made in improving their practicality: (i) Structural optimization: Engineering porous or core-shell structures within the nanowires enhances buffering capabilities further [38]. (ii) Composite design: Integrating SiNWs with conductive carbon matrices (e.g., graphene, carbon nanotubes) or forming direct metallurgical bonds (e.g., Si-Cu networks as depicted in Fig. 2a [39]) significantly improves electrical conductivity and mechanical integrity throughout cycling. These strategies are crucial for translating the intrinsic properties of SiNWs into viable electrode materials, enabling demonstrations of good cycling stability in test cells. Due to their high specific surface area, nanoparticles can provide more lithium-ion insertion sites, thereby increasing the overall capacity values. However, nanoparticles tend to agglomerate, which may lead to unstable electrode structures and affect the cycling life of batteries [40]. Key strategies addressing these challenges focus on encapsulation: (i) Carbon coating/embedding: Coating individual SiNPs with amorphous carbon, graphene, or embedding them within carbon matrices is a prevalent approach [41]. The carbon shell acts as both a physical barrier preventing particle-to-particle direct contact and agglomeration, and as a conductive network facilitating electron transfer. It also provides a confined space to accommodate the volume changes. (ii) Optimized particle design: Employing hollow or yolk-shell structured SiNPs creates internal void space explicitly designed for Si expansion, dramatically reducing mechanical stress on the particle shell and enhancing structural stability during cycling [42]. These advancements have led to impressive performance; for instance, optimized hollow-structured silicon nanoparticles exhibit a high

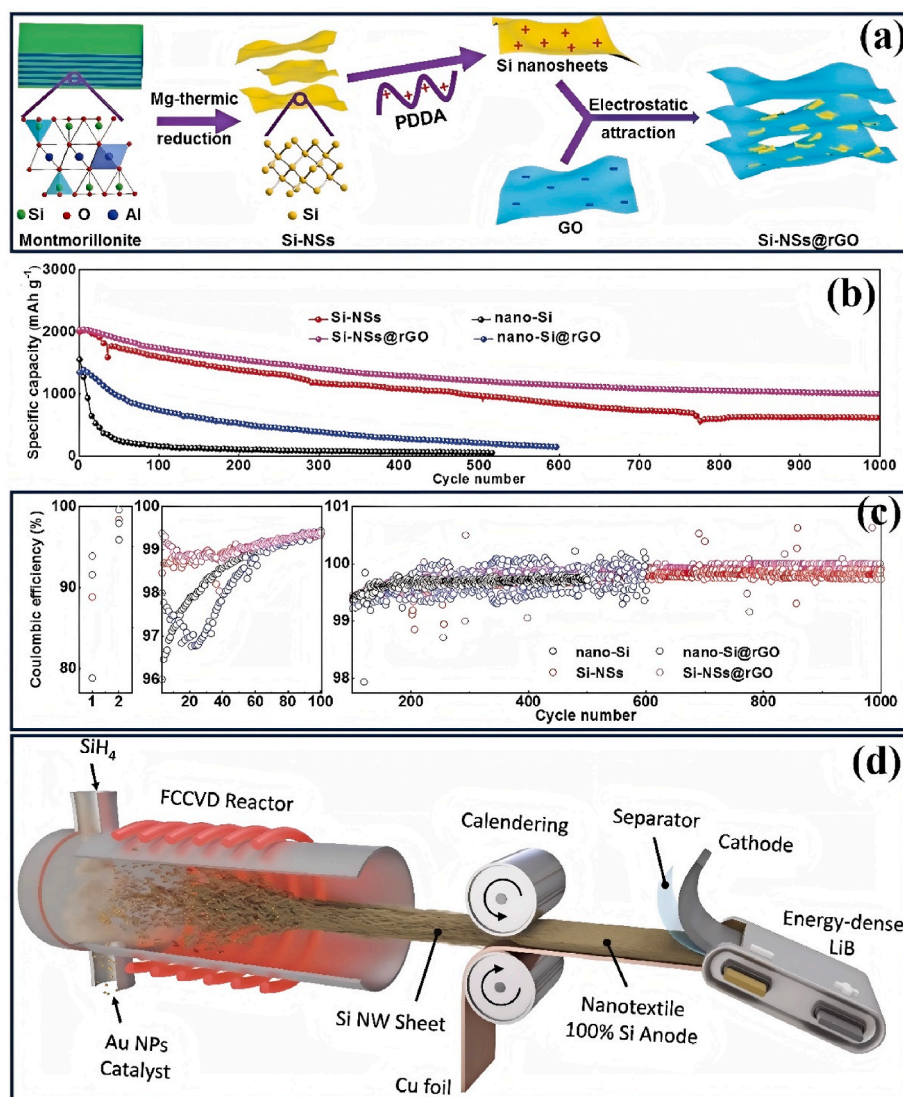


Fig. 2. (a) Schematic illustration of the synthetic procedure for silicon nanosheets Si-NSs@rGO, (b) long-term cycling performance of Si-NSs@rGO, and (c) comparison of coulombic efficiencies of Si-NSs, Si-NSs@rGO, nano-Si, and nano-Si@rGO at 2 A g⁻¹ for 1000 cycles. Reproduced with permission [48]. Copyright 2022, Wiley-VCH Verlag. (d) Schematic representation of the synthesis and assembly of Si NW fabricated electrodes in a single process and their readiness to be implanted in a battery cell after a simple calendaring. Reproduced with permission [51]. Copyright 2014, American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

reversible specific capacity of over 630 mAh g⁻¹, which is higher than the 370 mAh g⁻¹ for commercial graphite anodes [43]. Nevertheless, the self-assembly of nanoparticles and their application in LIBs still face issues such as low preparation efficiency and significant concerns related to environmental pollution [44,45].

In addition, Si/C composite materials prepared by in-situ growth of vertical graphene sheets (VGSS) on graphite exhibit high reversible capacity and excellent cycling stability due to the buffering effect of VGSS and strong bonding between Si and graphite particles [46]. The large surface area and short ion transport path of the nanosheet structure not only improve the capacity and rate performance of the battery but also effectively suppress volume expansion, thereby improving the cycling stability of the battery cell. For example, in the case of ultra-thin silicon nanosheets (Si NSs), an improved manufacturing method based on a unique etching reduction protocol results in Si NSs with an average thickness of less than 2 nm [39]. This sub-nm thickness is critical as it minimizes absolute volume changes and internal stresses during lithiation/delithiation, leading to much improved fracture resistance compared to bulk Si or larger nanoparticles. The preparation of these

ultrathin nanosheets often involves magnesium reduction of layered calcium silicide (CaSi₂) precursors followed by careful acid etching to remove byproducts, representing a significant advance in controllable Si nanostructure synthesis [47]. Furthermore, integration strategies are vital for Si NSs application: (i) Highly conductive matrices: Dispersion of ultrathin Si NSs within a highly conductive and robust matrix like reduced graphene oxide (rGO) – resulting in Si-NSs@rGO composites (Fig. 2a) – provides excellent electron conduction pathways and superior mechanical support against pulverization [48]. (ii) Material choice: Metallurgical bonding with a flexible copper skeleton (Fig. 2a) effectively reduces stress concentration caused by the expansion of Si nanoparticles (a similar concept applies to SiNSs integration). These advancements have yielded exceptional results: This structure dispersed appropriately greatly improves the rate capability of silicon-based materials and cycling performance, making them promising long-life and high coulombic efficiency negative electrode materials for LIBs. For instance, the Si-NSs@rGO composite (Fig. 2b & c) demonstrates remarkable cycling stability (high capacity retention over 1000 cycles) and near-ideal coulombic efficiency (exceeding 99.5 %) even at high

current densities [48]. The porous Si/Cu negative electrode with uniformly distributed Si nanoparticles (Fig. 2a) successfully mitigates stress and achieves excellent high-rate cycling performance in full cells, delivering an energy density of 463 Wh kg^{-1} and maintaining 81 % capacity retention after 500 cycles at a 2C rate (Fig. 2b and c) [49]. Furthermore, SiN_3 monolayer is considered a potential anode material with high storage capacity and rapid diffusion properties [50].

The development of these nanostructures provides diverse opportunities for optimizing the performance of silicon-based anode materials. Significant progress lies not only in the synthesis of the nanostructures themselves (e.g., ultrathin nanosheets, controlled hollow particles) but also, crucially, in the engineering strategies employed to integrate them into functional electrodes: intelligent structural design (core-shell, yolk-shell, porous), conductive matrix embedding (carbon, graphene, rGO), metallurgical bonding, and surface modification (e.g., Al_2O_3 coatings) [48]. These strategies collectively tackle the intrinsic challenges of Si anodes – volume expansion, particle isolation, electrical/ionic conductivity limitations, and SEI instability – leading to demonstrable improvements in cycling life, rate capability, and coulombic efficiency in recent works. Although each structure and integration approach has its limitations regarding scalability, cost, or process complexity, they represent vital steps forward and are of great significance for the future development of high-energy-density LIBs.

2.2. The advantages of nanostructured silicon anodes

In recent years, nanostructured silicon anode materials have shown significant advantages in improving electrochemical performance and reducing volume expansion due to their unique size and surface effects, becoming a focus of research in silicon-based negative electrode materials [52–54]. The large specific surface area of these nanostructures can provide more lithium ion insertion sites, significantly improving the capacity and rate performance of the final battery device [55,56]. At the same time, nanoscale structures can shorten the diffusion path of lithium ions in electrode materials, accelerate the charging and discharging process, and thereby improve the specific power of batteries [23,57,58]. The nanostructured silicon anode effectively buffers the volume expansion during the charging and discharging process through its nanometric size effects, reduces the damage to the physical structure of the electrode, maintains electrode integrity, and thus improves the cycling life of the battery cell [3,52]. This ability to limit volume expansion at the nanoscale avoids macroscopic structural damage and provides new directions and possibilities for the development of silicon-based negative electrode materials [19,37]. For example, Haro et al. have discovered a unique Si nanostructure, proposing a significant step towards commercializing silicon anode LIBs, which can improve the anode performance of LIBs [59]. Specifically, arched nano-silicon anodes can greatly improve the capacity of future LIBs. In addition, high-purity nano-silicon-based negative electrode materials prepared by radio frequency-induced thermal plasma can significantly alleviate volume effects, improve conductivity, and enhance stability [60]. By introducing novel metallurgical processes, it is possible to combine a flexible copper skeleton with uniformly distributed nano-silicon particles and improve the cycling performance under high current loads [49]. Pure Si nanowires (SiNWs) electrodes obtained from the gas phase without any slurry-type processing (Fig. 2d) can still recover their capacity up to 2150 mAh g^{-1} even after 200 cycles at a cycling rate of 0.2C [61]. Nanostructured silicon anodes also perform well in terms of cycle life, maintaining high capacity after hundreds or even thousands of charge/discharge cycles [62]. For example, the 100 % pure silicon nanofabric anode (without carbon or binder additives) showed no loss in capacity after 1800 cycles, demonstrating excellent cycling stability [63]. In addition, nanostructured silicon anodes can still charge/discharge rapidly at high current densities, demonstrating excellent rate performance and meeting the needs of high power delivery along with high energy density [51].

Thanks to their excellent theoretical capacity, silicon-based negative electrodes are considered one of the most promising for next-generation LIBs [64]. However, the significant volume change of silicon during lithium insertion can easily disrupt the stability of the electrode structure, leading to a rapid decline in electrode cycling performance [3,65]. Therefore, optimizing the structure of silicon-based materials and developing matching electrolytes are of great significance for further improving the cycling performance of silicon-based negative electrode materials [66]. Nanostructured silicon anode materials are advantageous and useful for improving electrochemical performance, reducing volume expansion, and providing new directions and opportunities for the future development of silicon-based anode technologies [3,67]. Continuously optimizing the material structure and preparation process is expected to achieve breakthroughs in high energy density and long lifespan of silicon-based negative electrode materials [52].

2.2.1. The challenges faced by nanostructured silicon anodes

Electronic conductivity is one of the main challenges faced by the nanostructured silicon anodes in LIBs. The nanostructured silicon, due to its high surface area and small size, can provide more electron transport pathways, thereby improving conductivity [3,52,67]. However, the preparation cost of nanomaterials is costly and may require special synthesis techniques to maintain their structural integrity. Secondly, silicon undergoes significant volume changes during lithium insertion and extraction, which may lead to mechanical damage or pulverization of nanostructured silicon materials [52,53,68]. Although some studies have alleviated this problem by designing hollow structures or core-shell structures, completely avoiding volume expansion remains a challenge. For example, the hybrid nanostructure anode based on SiNPs is fixed on VACNT with defined spacing to adapt to the volume changes of SiNPs (Fig. 3a), thereby improving cycling stability and SEI formation [69]. Moreover, deposition of silicon nanoparticles (SiNPs) within porous carbon frameworks (PCFs) represents a promising next-generation approach. This strategy synergistically addresses multiple challenges.

- * **Volume Expansion Accommodation:** The interconnected porous structure of the carbon framework provides ample void space to accommodate the significant volume expansion of embedded SiNPs during lithiation (typically 100–150 %), mitigating the risk of pulverization and electrode disintegration.
- * **Enhanced Electronic Conductivity:** The continuous carbon framework acts as a highly efficient and stable three-dimensional conductive network, ensuring good electron transport pathways to and from each SiNP throughout the cycling process. This significantly improves the overall electrode conductivity compared to bare SiNPs or poorly connected composites.
- * **Mechanical Confinement:** The rigid carbon framework provides mechanical confinement around the SiNPs, restricting their expansion direction and reducing the overall electrode-level strain.
- * **SEI Stabilization:** The carbon surface can facilitate the formation of a more stable and uniform SEI layer compared to silicon surfaces. The framework also helps to isolate individual SiNPs, potentially limiting excessive electrolyte decomposition upon each particle and mitigating SEI thickening and crack propagation across the electrode.
- * **Structural Stability:** The robust carbon framework enhances the structural integrity of the entire composite electrode, particularly during long-term cycling involving repeated volume changes. This integrated approach demonstrates significant potential in improving the cycling stability and rate capability of silicon-based anodes.

The purpose is to optimize the electrolyte formula and develop more stable electrolyte systems to extend the battery's cycle life and enhance its safety. For example, optimizing the electrolyte formula and selecting different solvents and additives (Fig. 3b) can significantly improve the cycling performance and high-temperature storage performance of the

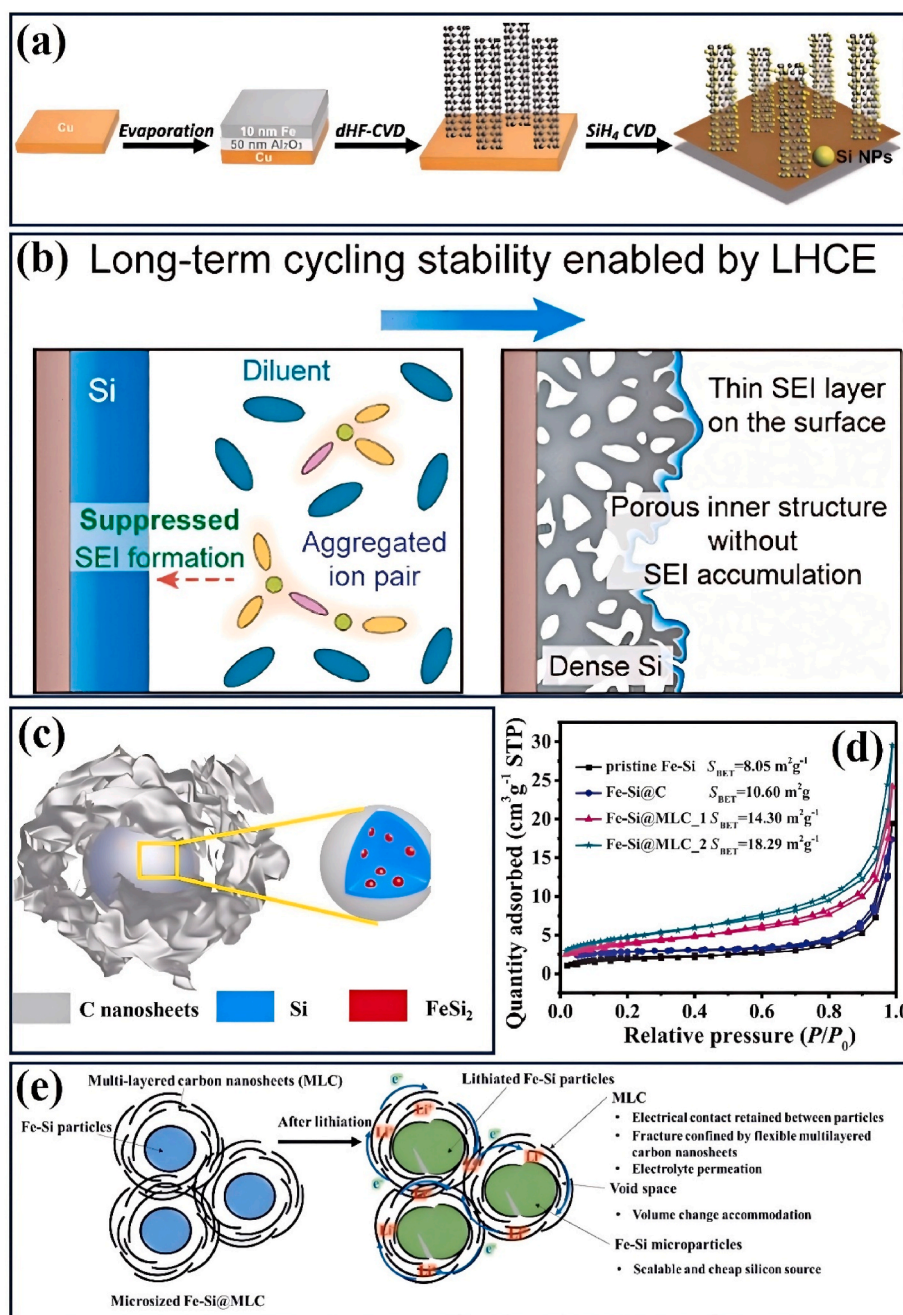


Fig. 3. (a) Schematic illustration of the fabrication process of the SiNPs@VACNTs electrode on a copper foil. Reproduced with permission [69]. Copyright 2023, Wiley-VCH Verlag. (b) influence of the baseline and 1H,1H,5H-octafluoropentyl 1,1,2,2-tetrafluoroethyl ether as electrolyte on the degradation of Si anodes. Reproduced with permission [70]. Copyright 2021, American Chemical Society. (c) Schematic illustration of the materials model for Fe-Si@MLC, (d) nitrogen adsorption-desorption isotherm of Fe-Si@C, Fe-Si@MLC_1, and Fe-Si@MLC_2, (e) schematic discharging process within the structure of Fe-Si@MLC. Reproduced with permission [72]. Copyright 2020, Elsevier.

battery cell [70]. Another challenge is cycling stability, where nanostructured silicon can provide high initial capacity and fast lithium-ion diffusion rate; there may be capacity decay and Coulomb efficiency decrease in long-term cycling [3,69,71]. However, this is mainly due to structural degradation and interface instability.

An overview of the recently reported performances of the nanostructured silicon anodes used for LIBs is listed in Table 1.

The exploration of nanostructured silicon anodes, as detailed in Sections 2.1.1 to 2.1.3, has yielded significant insights into mitigating the challenges of silicon anodes through size effects and sophisticated engineering. Nanostructures offer compelling advantages in buffering volume expansion and enhancing kinetics. However, the persistent

hurdles associated with their complex synthesis, scalability concerns, higher production costs, and environmental considerations (e.g., low preparation efficiency, pollution concerns) present substantial barriers to widespread commercial adoption. These limitations highlight the need for alternative strategies that balance performance with manufacturability and cost-effectiveness. Consequently, significant research efforts have been directed towards micron-sized silicon anodes (>1 μm). Micron-sized silicon particles offer the potential for simpler, more scalable manufacturing processes, lower material costs, and potentially easier integration into existing battery production infrastructure. While facing distinct challenges related to accommodating larger absolute volume changes, micron-sized structures represent a crucial pathway

Table 1

Summary of the recent nanostructured silicon anodes for LIBs.

Material	Voltage range	Test temperature	ICE	Reversible capacity	Cycle life	Conductivity Issues & Strategies	Volume Expansion Control & Strategies	Cycling Stability Strategies	Reference
2D Porous Silicon Nanosheets	0.01–1.2 V (vs. Li+/Li)	25 °C	74 % at 0.1C	2627 mAh g ⁻¹ at 0.1C	52 % after 1000cycles at 2C	Problem: Poor conductivity within two-dimensional structural planes Strategy: Graphene composite enhances in-plane conductivity (>500 S m ⁻¹) and reduces interface impedance by 60 %	Problem: Interlayer slip leads to structural failure Strategy: Mesoporous design (pore size~20 nm) buffer expansion, volume change<50 %	Strategy: Stabilize the SEI film (LiF content>30 %), but long-term cycling leads to interlayer delamination and capacity decay	[35]
Nano-Si	0.005–3.0 V (versus Li/Li+)	25 °C	78 % at 0.42 A g ⁻¹	2273 mAh g ⁻¹ at 0.42 A g ⁻¹	88 % after 1000 cycles at 2.1 A g ⁻¹	Problem: Agglomeration of nanoparticles increases contact resistance Strategy: Hydrophobic carbon coating (thickness~5 nm), conductivity increased by 10 ² times	Problem: High specific surface area exacerbates expansion stress Strategy: Colloidal nano silicon dispersion design (particle size~50 nm), reducing expansion strain to 120 %	Strategy: Hydrophobic surface suppresses electrolyte side reactions, SEI thickness<15 nm after 1000 cycles	[73]
silicon nano-particle	0.1–3 V (vs. Li+/Li)	25 °C	82 % at 0.1C	1172 mAh g ⁻¹ at 0.1C	85 % after 100 cycles at 0.1C	Problem: Low intrinsic conductivity (10 ⁻⁵ S cm ⁻¹) Strategy: Ionic conductive adhesive (biopolymer), with an ionic conductivity>10 ⁻³ S cm ⁻¹	Problem: Nanoparticles are prone to pulverization Strategy: Adhesive elastic network buffering expansion (strain<100 %)	Strategy: Elastic adhesive maintains electrode integrity, particle breakage rate<10 % after 100 cycles	[74]
Si@HC/CNFs	0.01 V–3.0 V (vs. Li/Li ⁺)	Room Temperature	53 % at 0.1C	1992 mAh g ⁻¹ at 0.1C	51.2 % after 100 cycles at 0.1C	Problem: High impedance at the core-shell interface Strategy: Carbon nanofiber coating to construct a 3D conductive network (conductivity increased by 8 times)	Problem: Insufficient mechanical strength of hollow core-shell Strategy: Reserve a gap (40 %) to accommodate expansion, but the shell will rupture in the later stages of the cycle	Strategy: Carbon fiber inhibits the loss of active substances, with a structural integrity rate of>80 % after 100 cycles	[75]
Si-void@SiO_x nanowires	0.01–1.0 V (vs. Li/Li ⁺)	25 °C	74 % at 0.5C	2485 mAh g ⁻¹ at 0.5C	111 % after 200 cycles at 0.5C	Problem: SiO _x interface layer has high impedance Strategy: Surface constraints induce anisotropic expansion and optimize electron transport pathways	Problem: Radial expansion concentration in linear structures Strategy: Surface coating constraints enable controllable expansion direction (radial strain<80 %, axial strain>120 %)	Strategy: Anisotropic expansion reduces interface delamination, increases capacity by 11 % after 200 cycles	[76]
Bubble sheet-like Si/C	0.005 V–1.2 V (vs. Li/Li ⁺)	Room Temperature	72 % at 0.65C	1538 mAh g ⁻¹ 0.65C	94 % after 200 cycles at 0.65C	Problem: Uneven conductivity of the porous carbon layer Strategy: foam-like carbon network continuous coating (surface conductivity>100 S m ⁻¹)	Problem: Thin pore walls in bubble structures Strategy: Graded pore design (macropores + micropores) disperses stress with a volume change of<60 %	Strategy: Uniform carbon layer coating reduces SEI repeated cracking, with a capacity retention rate of 94 % after 200 cycles	[77]

(continued on next page)

Table 1 (continued)

Material	Voltage range	Test temperature	ICE	Reversible capacity	Cycle life	Conductivity Issues & Strategies	Volume Expansion Control & Strategies	Cycling Stability Strategies	Reference
amorphous nanosized silicon	0.01 V–1.50 V (vs. Li ⁺ /Li)	25 °C	86 % at 1.67C	1200 mAh g ⁻¹ at 1.67C	83 % after 230 cycles at 1.67C	Problem: Low carrier mobility in amorphous silicon Strategy: Metal doping (Ag/Sn) enhances conductivity ($10^{-3} \rightarrow 10^{-1} \text{ S cm}^{-1}$)	Problem: Isotropic expansion of amorphous structure Strategy: Multi-level pore design (porosity of 50 %) to buffer strain and reduce expansion rate to 70 %	Strategy: High porosity suppresses pulverization, electrode deformation <15 % after 230 cycles	[78]
Si nanoparticle/ RGO	0.01 V–2.0 V (vs. Li ⁺ /Li)	Room Temperature	73 % at 3C	2300 mAh g ⁻¹ at 3C	90 % after 300 cycles at 3C	Problem: Contact resistance between nanoparticles and graphene Strategy: Multi-layer RGO composite optimization interface (reducing charge transfer impedance by 70 %)	Problem: Restricted interlayer silicon expansion Strategy: RGO interlayer reserved space (interlayer spacing of 1.2 nm), volume change <100 %	Strategy: RGO flexible layer adapts to volume changes, SEI thickness <20 nm after 300 cycles	[79]
c-Si nanowires	0.02 V–1.2 V (vs. Li/Li ⁺)	Room Temperature	88 % at 0.28C	3541 mAh g ⁻¹ at 0.28C	66 % after 500 cycles at 0.28C	Problem: Linear structure axial guide battery neck Strategy: Metal-assisted chemical etching to construct a vertical conductive network (conductivity $\uparrow 10^3$ times)	Problem: Radial expansion accumulation of nanowires Strategy: Nanowires with a diameter of <100 nm (apparent expansion <50 %)	Strategy: Maintain electrical connection through direct contact with the current collector, but SEI thickening during long-term cycling leads to attenuation	[80]
C@Si@C nanotube	0.0 V–2.0 V (vs. Li/Li ⁺)	Room Temperature	62 % at 0.07C	2545 mAh g ⁻¹ at 0.07C	88 % after 60 cycles at 0.07C	Problem: Slow ion diffusion at multi-layer interfaces Strategy: Gradient doping of inner and outer carbon layers (nitrogen doping), ion conductivity > $10^{-4} \text{ S cm}^{-1}$	Problem: Low mechanical strength of tubular structures Strategy: Sandwich structure (carbon layer thickness of 20 nm) constrains expansion, with a volume change of <120 %	Strategy: Rigid carbon layer suppresses pulverization, with a structural integrity rate of over 90 % after 60 cycles	[81]

towards realizing the commercial potential of silicon anodes. The following section (Section 2.2) delves into the diverse forms of micron-sized silicon anodes and their associated advantages and challenges.

2.3. Description of micron-sized silicon anodes

2.3.1. Different micron-sized silicon anodes

Micron-sized silicon anodes possess great importance in the field of battery technology as they offer diverse functional advantages [82]. The silicon anode with a microsphere structure reduces electrolyte decomposition due to low surface area and improved electrode/electrolyte interface, thereby improving the stability of the device [83]. These microspheres are typically synthesized via spray pyrolysis or template-assisted methods, enabling precise control over particle size distribution and porosity—critical for large-scale electrode uniformity [81]. This is crucial for alleviating the volume expansion of silicon materials during the charging and discharging process, as volume expansion causes structural damage to the electrode, directly affecting the cycle life of the battery [84]. The microsphere structure can effectively buffer silicon materials' volume expansion and extend the

batteries' cycling life [85].

An innovative approach to designing micro-rod structure has been reported that provides excellent ionic transport channels, improving the cell's rate performance, helping suppress volume expansion, and further enhancing the cell life [86]. Fabrication of these rods often employs metal-assisted chemical etching (MACE) or electrospinning, allowing tunable aspect ratios (~5–20 μm length; ~0.5–2 μm diameter) that optimize Li⁺ diffusion kinetics [83]. This structure optimizes the shape of silicon-based materials, making it easier for lithium ions to intercalate and detach during the process [87]. Further, the electron transfer is facilitated due to the integrated structure of the electrode material. On the other hand, micrometer chip structure provides a larger surface area, which is beneficial for improving capacity and effectively buffering volume expansion, enhancing the cycling stability of the cell [88]. Industrial-scale production of silicon flakes leverages ball-milling of metallurgical-grade silicon, followed by size classification (<3 μm), achieving material costs below \$10/kg while maintaining >1200 mAh/g capacity [84]. This structure is supported by multi-layered carbon nanosheets that provide more reaction sites by increasing the surface area and facilitating the lithiation process, thereby improving the

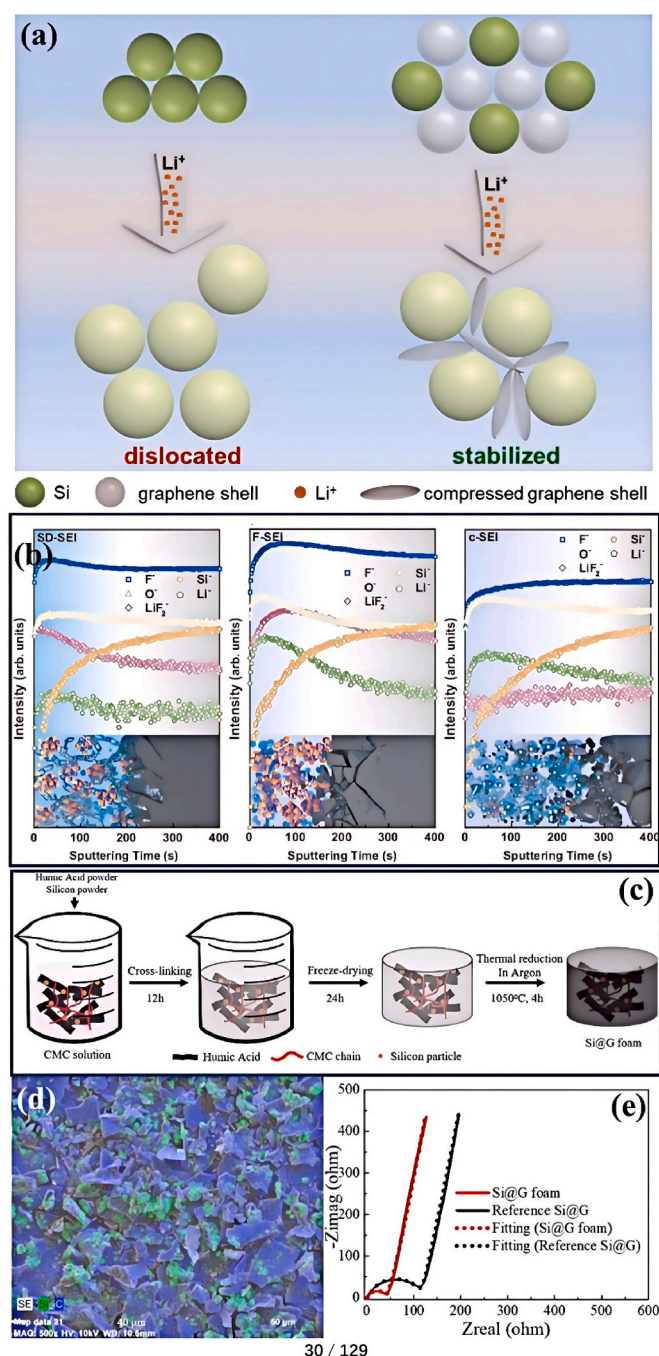


Fig. 4. (a) Mutual compression between Si nanoparticles upon lithiation leads to electrode rupture, and carbon sheets buffer Si volume expansion by the compression of the hollow structure. Reproduced with permission [85]. Copyright 2022, Wiley-VCH Verlag. (b) depth profiles of various secondary ion species obtained by sputtering in GBL-based electrolyte, PC-based electrolyte, and EC-based electrolyte. Reproduced with permission [87]. Copyright 2023, Springer Nature. (c) Schematic diagram and the material synthesis process of silicon at graphene foam (Si@G foam), (d) EDS mapping images of Si at graphene foam anode material after grounding, (e) EIS spectra and equivalent circuit fitting of silicon at graphene foam and reference anode. Reproduced with permission [88]. Copyright 2022, Elsevier. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

cell's energy density (Fig. 3c–e) [72]. Dai et al. studied a special micro-curved pore wall structure that helps to better control and alleviate volume changes caused during lithiation and delithiation [89]. Although specific details were not mentioned in the evidence, it can be inferred that this structural design helps maintain the integrity of the electrode material and reduce structural pulverization. Notably, such porous architectures are now commercially deployed in EV batteries (e. g., Sila Nanotechnologies' Titan Si™), demonstrating 20 % higher energy density than graphite anodes in automotive cell prototypes [85].

Each micrometer structure has its unique advantages and limitations, but overall, they provide diverse solutions for improving the performance of silicon-based negative electrode materials and reducing costs. For example, silicon/carbon composite materials provide high capacity by combining silicon and carbon's advantages while buffering silicon's volume expansion through carbon's mechanical properties (Fig. 4a) [84]. Recent advances in composite preparation include fluidized-bed chemical vapor deposition (CVD), which enables conformal carbon coating (<10 nm) on 1–5 μm Si particles at industrial throughput rates >100 kg/day [86]. Lai et al. reported a significant improvement in cycle life by constructing porous carbon layers on submicron silicon wafers [90]. Further, by optimizing the structure of silicon-based materials and developing compatible electrolytes (Fig. 4b), the cycling performance of silicon-based negative electrode materials could be further improved [87]. Silicon particles treated with copper coating exhibited excellent electrochemical performance in LIBs [91]. Notably, such coated particles have been integrated into 21700 cylindrical cells (5 Ah capacity), achieving >800 cycles at 1C rate while maintaining 80 % capacity retention—validating their viability for power tools and e-mobility [87]. For example, the composite material has a reversible specific capacity of 1359 mAh g⁻¹ under a specific current load of 0.5 A g⁻¹. Even after 400 cycles at a high current density of 1 A g⁻¹, it can still maintain a specific capacity of 837 mAh g⁻¹ and a capacity retention of 83.5 % [91]. These properties of Si-based composite electrodes are superior to similar electrochemical stability data reported for other materials.

Overall, micron-sized silicon anodes provide diverse solutions for battery technology through their unique shape and surface area, significantly improving the performance and stability of batteries. Industrial adoption continues to accelerate, with global production exceeding 10,000 metric tons in 2023, driven by applications in consumer electronics (e.g., Xiaomi Mi 13 Ultra with 5000 mAh Si-graphite anode) and electric vehicles (Nio ET7 with 150 kWh semi-solid-state Si-dominant packs). These research results have laid a solid foundation for commercializing silicon-based negative electrode materials from this variant.

2.3.2. The advantages of micron-sized silicon anodes

Micron-sized silicon anodes have shown strong competitiveness in practical applications due to their advantages in improving conductivity and reduced costs [92,93]. This structure effectively eliminates electrolyte decomposition and the formation of SEI films by reducing the surface area of the material, thereby improving the conductivity of the electrode. This improvement not only enhances the charging and discharging efficiency of the cell, but also results in increased rate performance [94]. Micron-sized silicon-based negative electrode materials can overcome the problem of silicon volume expansion through carbon coating and porous structure design while improving the conductivity of the negative electrode and promoting the diffusion of lithium ions. For example, humic acid derived from coal was used as a precursor for graphene, porous 3D graphene, and micron-sized silicon composite anodes were synthesized (Fig. 4c and d). This structure is quite promising and acts as a buffer, reducing the volume change of silicon and creating a rich and reliable conductivity framework, ensuring rapid electron transfer (Fig. 4e) [88]. Furthermore, the production process of micron-sized silicon anodes is relatively simple and cost-effective. For example, a new method to obtain spherical micron-sized silicon with a unique porous structure through the use of cost-effective

micro-emulsion of silica nanoparticles and thermal reduction of magnesium oxide is considered to be one of the most promising methods for Si anodes production for LIBs [95]. This method reduces production costs while maintaining high compactness and feasibility for the practical applications of Si anode [94].

In practical applications, micron-sized silicon anodes exhibit excellent electrochemical performance. For example, micron-sized silicon iron/carbon anodes achieved stable cycling capacity and good rate performance over 200 cycles [72]. In addition, by generating a co-continuous composite material that converts complex structured silica into silicon, graphite, and amorphous carbon layers, the electrode displays a discharge specific capacity of 631.7 mAh g^{-1} at 3 A g^{-1} [96]. Ma et al. used a simple precipitation method to introduce zero-strain lithium-ion conductor TiNbO_4 (TNO) coating on the surface of industrial-grade submicron silicon [89]. Through density functional theory (DFT) calculations, it has been confirmed that TNO, as a coating material, can effectively alleviate silicon expansion and facilitate lithium diffusion. The prepared compound was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), half-cell charge-discharge testing, and cyclic voltammetry. The results showed that TNO was uniformly distributed on the silicon particles and could effectively improve the cycling performance of the silicon anode. After 120 cycles, the TNO-coated silicon anode can still maintain a capacity of 565 mAh g^{-1} , superior to untreated pure silicon, which has a capacity of less than 100 mAh g^{-1} under the same conditions [89]. The unique structural design and simple production process of micron-sized silicon anodes not only improve the charging and discharging efficiency and rate performance of cells, but also reduce production costs, providing a solid foundation for the widespread application of silicon-based negative electrode materials. These advantages give microstructured silicon anodes important application prospects in future battery technologies.

2.3.3. The challenges faced by micron-sized silicon anodes

The main challenges faced by micron-sized silicon anodes in LIBs are volume expansion, low conductivity, and low cycling stability. Compared to nanostructures, micron-sized silicon possesses better macroscopic conductivity and lower intrinsic resistance, which helps improve the overall performance of the battery cell [3,57,97,98]. However, large particle size may also limit the rapid transport of lithium ionic species. Micron-sized silicon also undergoes significant volume changes, although these changes may not be as extreme as in the case of nanostructured electrodes [99–101]. Appropriate microstructure design can help manage these expansions, but challenges remain. Boivin et al. used the discrete element method (DEM) to simulate the internal microstructure of silicon-based anodes and related micromechanical behavior [102]. DEM is a numerical tool for particle dynamics that allows for the detailed consideration of complex internal microstructures and corresponding micromechanics. By using LIGGGHTS software to create anode samples and implementing simplified linear respiration laws, it was found that silicon content has a linear effect on the expansion amplitude, while particle viscosity affects the irreversibility [102]. Micron-sized silicon anodes usually exhibit good cycle stability under high specific current load because of their large size, and they are not easily affected by rapid charging and discharging rates [99,100,103]. However, there may still be issues of capacity decay and structural degradation during long-term use of these anode materials. Recently reported performance overview of micron-sized silicon anodes used for LIBs is given in Table 2.

As detailed in Sections 2.2.1 to 2.2.3, micron-sized silicon anodes offer compelling advantages in terms of manufacturing scalability and cost-effectiveness, addressing key limitations of nanostructured counterparts. However, the intrinsic challenges associated with accommodating the significant absolute volume expansion within larger particles remain critical hurdles for achieving long-term cycling stability and high

energy density in practical applications. While strategies like porous design and carbon coating mitigate these issues to some extent, the fundamental stress concentration and potential for particle fracture or isolation persist. To overcome these limitations and achieve a more holistic solution that simultaneously addresses volume change accommodation, robust electrical connectivity, and efficient ion transport, significant research focus has shifted towards 3D structured silicon anodes. These architectures leverage engineered macroscopic frameworks designed specifically to manage the stresses associated with silicon expansion, maintain continuous conductive pathways throughout cycling, and optimize electrode porosity for electrolyte access. The subsequent section (Section 2.3) explores the diverse types of 3D structured silicon anodes and their potential to deliver superior electrochemical performance by fundamentally rethinking the electrode design paradigm.

2.4. Description of 3D structured silicon anode

2.4.1. Different types of 3D structured silicon anodes

Researchers have developed various types of 3D structured silicon anodes to address various challenges facing their use in LIBs. Some of these anodes are listed below.

- a) Porous structured silicon anode: By constructing a pore structure in silicon materials, this anode effectively alleviates the volume expansion problem and provides a larger specific surface area, increasing the electrolyte's contact area and the active material's utilization rate. The common preparation methods include the template method, the etching method, and the self-assembly method [95]. Significant progress has been made in achieving high-performance porous silicon, particularly in terms of controllable porosity and stability. For instance, Ren et al. pioneered a novel method involving the co-milling of silicon monoxide with magnesium and subsequent selective acid etching [113]. This technique produced micrometer-sized porous Si particles with a bicontinuous porous structure. This tailored porosity not only offers ample room for accommodating silicon expansion but also enhances electrolyte infiltration, which contributed to remarkable cycling stability: >2000 cycles with a capacity retention of 80 % at a high current density of 2 A g^{-1} . This represents a substantial advancement in addressing the long-term cycle life challenge for practical applications.
- b) Core-shell structured silicon anode: This type of anode forms a core-shell structure by coating silicon material on a material surface with good conductivity and structural stability, which improves the conductivity of the electrode and enhances cycling stability. Common core-shell structures include Si@C , Si@TiO_2 , Si@Graphene , Si-2@CP-2@rGO films with a core/multi-shell structure, etc. [114–117]. The application of core-shell structured materials in LIBs is mainly achieved by designing novel electrode materials and improving their electrochemical performance, such as their cycling stability and rate performance. For example, the core-shell structure of silicon-oxygen carbon negative electrode material can alleviate silicon's volume expansion problem and improve cell cycle life [118]. A key advancement lies in the design of multi-functional shells that go beyond simple buffering and conductivity. In addition, in some designs, the shell material itself can also be Faraday active, which means it can participate in the cell's charge and discharge reactions, thereby increasing the total capacity of the cell [119]. For example, Wang et al. prepared a novel core-shell heterostructure with Si as the core, $\text{V}_3\text{O}_4\text{@C}$ for the shell ($\text{Si@V}_3\text{O}_4\text{@C}$) (Fig. 5a–f). The V_3O_4 layer, synthesized via a simple solvothermal reaction, not only provides structural stability but also acts as a highly conductive and robust artificial solid electrolyte interphase (SEI) layer, facilitating fast Li^+ ion transport and preventing continuous electrolyte decomposition. This multi-shell design

Table 2
Summary of the recent micron-sized silicon anodes for LIBs.

Material	Voltage range	Test temperature	ICE	Reversible capacity	Cycle life	Conductivity Issues & Strategies	Volume Expansion Control & Strategies	Cycling Stability Strategies	Reference
Mesoporous silicon sponge	0.05–1.5 V (vs. Li/Li ⁺)	Room temperature	56 % at 1 A g ⁻¹	750 mAh g ⁻¹ at 0.1 A g ⁻¹	80 % after 1000 cycles at 1 A g ⁻¹	Problem: Poor intrinsic conductivity (Si: 10 ⁻⁵ S cm ⁻¹) Strategy: CVD deposition of carbon layer enhances interface electron transfer (reduces charge transfer impedance by 60 %)	Problem: Theoretical expansion rate of silicon is 300 % Strategy: Interconnect mesoporous structures (pore size ~25 nm) to accommodate internal expansion, with particle apparent expansion <20 %	Strategy: Mesoporous stress buffering + stable SEI film (reducing powdering)	[15]
Micro-sized Si-C Composite	0.01 V–1.5 V (vs. Li ⁺ /Li)	Room temperature	77 % at 0.4 A g ⁻¹	1544 mAh g ⁻¹ at 0.4 A g ⁻¹	97 % after 50 cycles at 0.4 A g ⁻¹	Problem: Insufficient conductivity of nano Si Strategy: Graphitic carbon coating (conductivity increased by 10 ³ times)	Problem: High silicon content leads to the accumulation of expansion Strategy: Embedding nano Si units into a carbon matrix to limit local expansion (reducing expansion strain to 120 %)	Strategy: Carbon matrix inhibits particle separation and maintains electrode integrity	[104]
Micro-sized bulk porous Si	0.01 V–1.5 V (vs. Li/Li ⁺)	25 °C	88 % at 500 mA g ⁻¹	1250 mAh g ⁻¹ at 500 mA g ⁻¹	56 % after 100 cycles at 500 mA g ⁻¹	Problem: Low bulk conductivity Strategy: Boron doping (p-type, 0.001–0.002 Ω cm) to increase carrier concentration	Problem: Large particles are prone to breakage Strategy: 50 % porosity provides expansion buffer space (pore size 5–16 nm)	Strategy: Annealing strengthens the pore wall (compressive strength >200 MPa)	[105]
Microcage porous Si/C	0.01 V–2.0 V (vs. Li/Li ⁺)	25 °C	91.2 % at 0.5C	1499 mAh g ⁻¹ at 0.5C	99 % after 50 cycles at 0.5C	Problem: Low conductivity limits rate performance Strategy: Nitrogen-doped carbon shell enhances interface conductivity (reduces charge transfer impedance by 50 %)	Problem: Nano silicon tends to aggregate easily Strategy: Cage-shaped carbon skeleton restricts silicon migration (apparent expansion rate <30 %)	Strategy: Cage like structure inhibits the loss of active substances	[106]
Foamed silicon particles	0.01 V–1.5 V (vs. Li/Li ⁺)	25 °C	56 % at 0.5 A g ⁻¹	1734 mAh g ⁻¹ at 0.5 A g ⁻¹	63 % after 300 cycles at 0.5 A g ⁻¹	Problem: Porous structure reduces conductive pathways Strategy: Graphene coated construction of 3D conductive network (in-plane conductivity >10 ³ S m ⁻¹)	Problem: Low strength of foam structure Strategy: Graded pores (macropores + mesopores) to disperse stress (controllable expansion)	Strategy: Elastic polymer binder (polyacrylic acid) maintains structure	[107]
Porous silicon particles	0.005 V–1.0 V (vs. Li/Li ⁺)	25 °C	73.9 % at 0.44C	2282 mAh g ⁻¹ at 0.44C	85 % after 200 cycles at 0.44C	Problem: Residual oxides increase interface impedance Strategy: Carbon coating optimizes ion diffusion (ion conductivity >10 ⁻³ S cm ⁻¹)	Problem: The hole wall is prone to collapse Strategy: Template method to regulate pore distribution (pore size 19–31 nm)	Strategy: Buffer volume change with high pore volume (0.5 cm ³ g ⁻¹)	[108]
Nanoporous Si microparticles	0.05–0.2 V (vs. Li/Li ⁺)	25 °C	84.3 % at 0.5C	1375 mAh g ⁻¹ at 0.5C	85 % after 50 cycles at 50	Problem: Surface defects increase interface impedance Strategy: Copper	Problem: Nanopores weaken the mechanical strength	Strategy: Industrial-grade rolling process compatibility (pressure	[109]

(continued on next page)

Table 2 (continued)

Material	Voltage range	Test temperature	ICE	Reversible capacity	Cycle life	Conductivity Issues & Strategies	Volume Expansion Control & Strategies	Cycling Stability Strategies	Reference
Porous Si microsphere@C	0.01–1.5 V vs. Li/Li ⁺	room temperature	69 % at 1 A g ⁻¹	1027 mAh g ⁻¹ at 1 A g ⁻¹	58 % after 200 cycles at 2 A g ⁻¹	modified porous silicon/carbon composite (conductivity increased by 8 times) Problem: Uneven carbon layer leads to poor local conductivity Strategy: CVD deposition of uniform carbon shell (thickness~10 nm)	Strategy: Interpenetrating network enhances pore walls (elastic modulus>5 GPa) Strategy: CVD deposition of uniform carbon shell (thickness~10 nm). Problem: Carbon layer rupture, causing uncontrolled expansion Strategy: Reserve 40 % expansion space in the core shell	resistance>200 MPa) Strategy: Carbon shell inhibits electrolyte penetration (SEI thickness<20 nm)	[110]
Micro-sized spherical silicon@carbon@graphene	0–1.5 V (vs. Li/Li ⁺)	Room temperature	75.3 % at 200 mA g ⁻¹	1599 mAh g ⁻¹ at 100 mA g ⁻¹	95 % after 100 cycles at 200 mA g ⁻¹	Problem: Increasing contact resistance at multi-layer interfaces Strategy: Graphene outer layer provides fast electron channels (in-plane conductivity of 10 ³ S m ⁻¹)	Problem: Stress concentration inside the sphere Strategy: Hollow structure + carbon interlayer (expansion rate reduced to 44 %)	Strategy: Graphene coating maintains electrode integrity (crack reduction by 70 %)	[111]
Micrometer-sized silicon anode	0.01–1.2 V(vs. Li/Li ⁺)	25 °C	99.92 % at 0.2 A g ⁻¹	2922 mAh g ⁻¹ at 0.2 A g ⁻¹	85.82 % after 500 cycles at 0.5 A g ⁻¹	Problem: Semiconductor characteristics limit magnification Strategy: Sn/Sb alloying (Si ₈ Sn ₀ -Sb), conductivity increased by 6000 times	Problem: High risk of micron particle pulverization Strategy: Solution reaction reduces stress concentration (isotropic expansion, strain homogenization)	Strategy: Weakly solvated electrolyte (fluorinated vinyl carbonate) stabilizes SEI film (LiF content>40 %)	[112]

(Si/V₃O₄/C) synergistically enhances both ionic and electronic conductivity while effectively confining volume changes. The stability of the silicon anode was significantly improved through a simple solvothermal reaction preparation (Fig. 5g) [114], demonstrating exceptional long-term cycling performance: 80.7 % capacity retention after 500 cycles at 1C, which is a significant leap over conventional Si anodes.

Synergic structured silicon anode: By combining silicon material with other active materials, conductive agents, or binders, a composite structure with synergistic effects is formed, thereby improving the overall performance of the electrode. Common composite structures include Si/C composites, Si/metal oxide composites, and Si/conductive polymer composites [120]. For example, a Si/C nanocomposite anode material was synthesized through a one-step method (Fig. 5h), using pyridine as a carbon source, and an onion-shaped Si/C composite material (Fig. 5i), which showed significantly improved electrochemical performance (Fig. 5j) [120]. This "onion-like" structure features silicon nanoparticles encapsulated within multiple concentric graphitic carbon shells. The innermost carbon shells tightly confine the Si expansion, while the outer shells maintain excellent electrical conductivity throughout the electrode. This hierarchical buffering and conduction network led to outstanding stability (93.1 % retention after 100 cycles at 100 mA g⁻¹) and rate capability (capable of high-rate operation at 2 A

g⁻¹), showcasing an effective strategy for simultaneously improving cyclability and power density. Additionally, porous 3D graphene and micrometer-sized silicon composite anode (Si@G foam) is synthesized using coal-derived humic acid (HA) as the precursor of graphene. In the process of lithiation and delithiation, graphene foam acts as the matrix of electrical conductors and the volume expansion reducing agent for silicon structure [88], yielding high areal capacity (>3 mAh cm⁻²) and stable cycling performance, crucial for practical applications requiring high energy density per unit area.

Each 3D structure of a silicon anode has its unique advantages and potential limitations. Therefore, making precise choices based on specific application requirements is necessary when selecting appropriate structural design and preparation methods. For applications that require high energy density, such as electric vehicles and portable electronic devices, silicon anode structures with high specific capacity can be chosen [121,122]. Porous structures like and core-shell composites with high Si loading are prime candidates due to their balance of capacity and improved stability. In the case of a core-shell structure Si@C (Silicon @ Carbon) anode, in which the carbon layer can provide good conductivity and structural stability, while buffering the volume expansion of silicon during charging and discharging, thereby improving the energy density and cycling stability of the cell [123,124]. Advanced designs incorporating multi-layer carbon coatings or integrating porosity within the carbon shell (e.g., pore-rich carbon shells) further push the energy

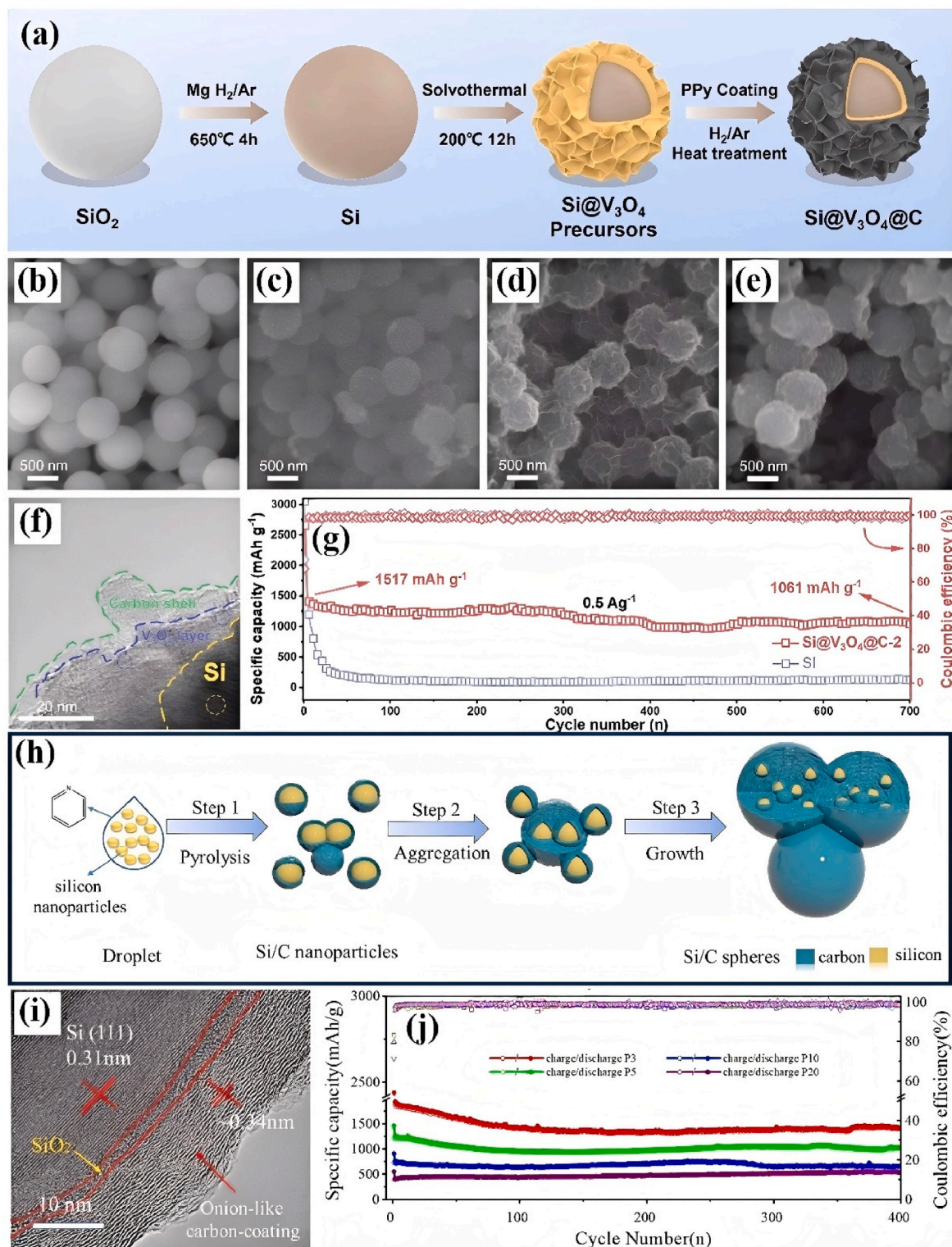


Fig. 5. (a) Schematic illustration of the synthesis process for the Si@V₃O₄/C composites, SEM images of (b) SiO₂, (c) Si, (d) Si@V₃O₄ precursors, and (e) Si@V₃O₄/C-2. (f) TEM image of Si@V₃O₄/C-2, (g) long-term cycling performance of Si@V₃O₄/C-2 and Si anodes. Reproduced with permission [114]. Copyright 2024, Wiley-VCH Verlag. (h) Schematic illustration of the formation of onion-like Si/C spheres, (i) HRTEM image of core-shell structure of silicon and the carbon shells, (j) electrochemical cycling performance of onion-like Si/C spheres. Reproduced with permission [120]. Copyright 2020, Elsevier. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

density limits while maintaining longevity. The anode with this structure has been discussed in detail in the literature. For applications that require fast charging and discharging, such as the start-stop system of electric vehicles, a silicon anode structure with good conductivity and a

fast ion diffusion path can be selected [125]. Structures emphasizing efficient conduction networks are key. The Si@V₃O₄/C anode with its highly ion-conductive shell [114], the onion-like Si/C with its hierarchical carbon paths [120], and Si/graphene foams with their continuous

conductive scaffolds all exhibit significantly enhanced rate capability compared to plain Si. For example, 3D-printed Si/rGO (silicon/reduced graphene oxide) anodes have a porous mesh structure that can greatly facilitate the diffusion of lithium ions and provide better power performance [125]. The precise architectural control achievable via 3D printing allows for optimization of the ion transport path, making it a promising strategy for ultra-fast charging applications.

For the flexible electronic devices, silicon anodes need to have excellent mechanical flexibility and structural stability. Silicon anodes with flexible frameworks, such as Si/rGO structures, can be chosen, where rGO frameworks can alleviate silicon nanoparticle expansion while maintaining the electrode's flexibility [126]. Beyond Si/rGO, binder design plays a critical role in flexible anodes. Employing

self-healing binders or ultra-elastic conductive polymer binders (often forming synergistic composites as mentioned earlier) is crucial for maintaining electrode integrity during repeated bending or stretching while ensuring stable electrical contact. Low-cost silicon anode structures, such as micrometer-sized silicon particles, can be chosen for cost-sensitive applications. By using self-healing polymer adhesives, novel electrolytes, and robust graphene coatings, the performance of micro-particles can be significantly improved while controlling costs [17]. The preparation of microparticle anodes has benefited greatly from scalable processes like the magnesiothermic reduction route or straightforward mechanical processes combined with effective coating strategies. Utilizing micron Si directly avoids the complex and costly synthesis often required for nanoparticles. For applications with special

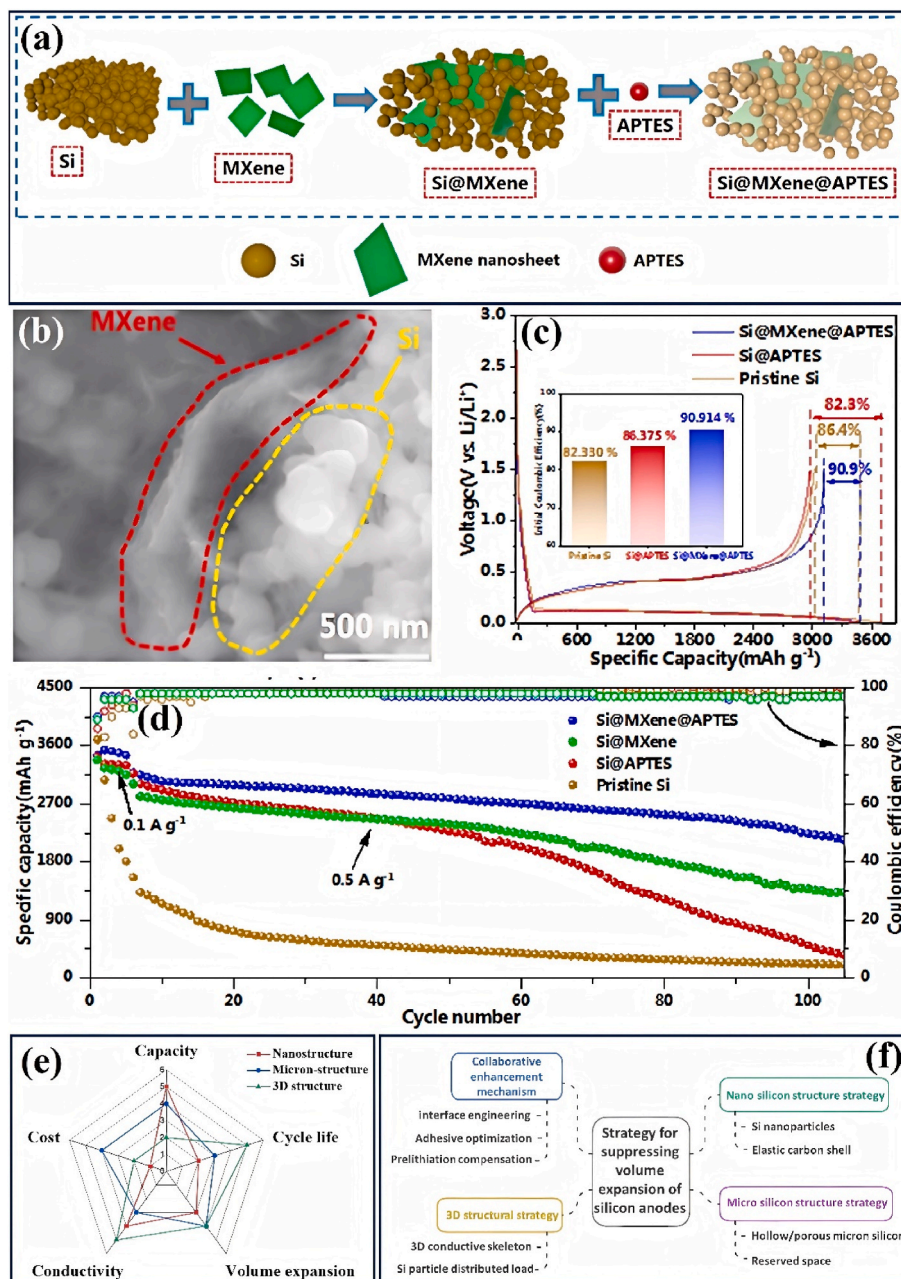


Fig. 6. (a) Schematic illustration of the synthesis process of Si@MXene@APTES composite, (b) SEM image of the Si@MXene@APTES composite, (c) first charge–discharge curves of the Si@MXene@APTES composite electrode at 0.1 A g⁻¹, (d) electrochemical cycling performance of the Si@MXene@APTES composite electrode at 0.5 A g⁻¹. Reproduced with permission [129]. Copyright 2022, American Chemical Society. (e) Radar diagram of structure comparison and performance of three types of silicon negative electrode. (f) Schematic diagram of the mechanism of the volume expansion suppression strategy. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

requirements for safety, silicon/ceramic composite anodes with excellent thermal and chemical stability, such as SiC or SiN, can be selected to improve silicon anodes' cycling stability and safety. While less common than carbon coatings, ceramic shells like TiO₂, TiN, or SiC/N offer superior thermal stability and can form extremely robust protective layers, enhancing the abuse tolerance of the battery. However, they often require higher-temperature processing and may slightly compromise initial conductivity. For applications that require long cycle life, silicon anodes with core-shell structures can be chosen, such as Si@C or Si@TiO₂ (silicon loaded at titanium dioxide), where the shell material can provide additional mechanical support, reduce the volume expansion of the silicon core, and thus improve the cycling stability of the electrode [68]. The most significant progress in extending cycle life (>1000 cycles) comes from sophisticated core-shell designs, particularly multi-shell structures like Si@V₃O₄@C [114], pore-rich carbon shells, or multi-layered carbon as in onion-like Si/C [120]. These designs progressively and robustly confine the Si expansion and stabilize the electrode/electrolyte interface over thousands of cycles.

These innovative designs and technologies provide diverse choices and strong technical opportunities for improving the performance of LIBs. The highlighted advancements demonstrate a clear trajectory: From fundamental concepts like porosity or core-shell buffering, the field has evolved towards multi-functional, hierarchically structured composites with carefully engineered interfaces. Progress in preparation methods now allows for precise control over particle size, porosity, coating layers (including composition, thickness, and structure), and overall electrode architecture. This progress translates directly to improved performance metrics—significantly longer cycle life, higher rate capability, better mechanical integrity for flexible applications, improved safety, and enhanced energy density—making silicon anodes increasingly viable for demanding real-world LIB applications.

2.4.2. The advantages of 3D structured silicon anodes

Compared to traditional two-dimensional thin film or nanoparticle silicon anodes, 3D structured silicon anodes exhibit significant advantages in improving the performance of LIBs [127]. Firstly, the 3D structure of the silicon anode has a higher specific surface area and electrolyte wettability, facilitating sufficient electrolyte infiltration, thereby improving the utilization rate of active materials and reducing the interface impedance of the cell [128]. Secondly, the design of the 3D structure shortens the transmission path of lithium ions inside the electrode material, accelerating the insertion and extraction process of lithium ions, thereby significantly improving the rate performance of the cell [128]. Finally, this structure can effectively buffer the volume expansion of silicon materials during charging and discharging, prevent the collapse and pulverization of electrode structures, and greatly improve the cycling stability and service life of batteries.

For example, Xu et al. produced a cross-shaped 3D battery structure using 3D printing technology, proving the feasibility and effectiveness of this technical solution [128]. This structure improves the diffusion coefficient of lithium ions and significantly enhances the battery cycling stability and rate performance. In addition, the Si@MXene@3-aminopropyltriethoxysilane (APTES) composite electrode (Fig. 6a and b) exhibits high initial Coulombic efficiency of 90.9 % (Fig. 6c), excellent cycling stability (with a capacity of 2258 mAh g⁻¹ after 105 cycles at a current density of 0.5 A g⁻¹, Fig. 6d), and good rate performance [129].

3D silicon-based negative electrode materials can absorb the advantages of 1D to 2D nanostructures and extend these advantages to 3D scales [130]. The inherent characteristics of nanostructures, such as nanoscale Si, Si structures, and nanopores on Si composites, can avoid pulverization caused by volume expansion caused to repeated lithium alloying. The application of 3D structured silicon anodes in LIBs has significantly improved the performance of cells, including increasing specific surface area and electrolyte wettability, facilitating lithium-ion transport paths, buffering volume expansion, etc., providing a viable

pathway to advance LIB technology.

2.4.3. The challenges faced by 3D structured silicon anodes

The main challenges faced by 3D structured silicon anodes in LIBs include conductivity, volume expansion, and cycle life. 3D structured silicon improves conductivity by increasing surface area and providing multidimensional pathways, which is beneficial for increasing the cell's power density and energy density [131,132]. This structure also helps better manage lithium ions' transport and volume changes. Furthermore, 3D structural design helps to better adapt to the volume changes of silicon during charging and discharging processes, reducing the risk of mechanical stress and cracks [133]. However, ensuring all parts can expand evenly without breaking is a technical challenge. 3D structured silicon anodes typically exhibit longer cycle life and higher Coulombic efficiency compared to other anode structures, as they can more effectively manage volume changes and maintain structural integrity [134]. However, long-term performance still needs further validation. The electrochemical performance summary of 3D structured silicon anodes used for LIBs is given in Table 3.

Sections 2.1 to 2.3 have comprehensively explored the dominant paradigms in silicon anode design: nanostructured (Section 2.1), micron-sized (Section 2.2), and 3D structured (Section 2.3) architectures. Each approach offers distinct strategies to tackle the core challenges of volume expansion, conductivity, and cycling stability, with 3D structures representing a particularly sophisticated integration of buffering space, conductive pathways, and structural integrity. While these categories encompass the majority of current research and development efforts, the quest for high-performance silicon anodes continues to inspire exploration beyond these established frameworks. Researchers are investigating a diverse array of alternative silicon anode structures that leverage unique material combinations, novel synthesis routes, or unconventional design principles. These "other" structures often target specific performance niches, address particular limitations of the mainstream approaches, or represent emerging concepts with potential for future breakthroughs. The following section (Section 2.4) provides an overview of these less conventional yet promising silicon anode configurations, highlighting their unique characteristics, potential advantages, and the distinct challenges they face.

2.5. Description of other silicon anode structures

In addition to nanoscale, micrometer-scale, and 3D structured silicon anodes, other types of silicon anode structures have also been explored to further improve LIBs' electrochemical performance. Here are some promising silicon anode structures and their shortcomings in these areas.

Firstly, thin film silicon anode: These Si anode materials are directly deposited in the form of thin film on the current collector through physical or chemical vapor deposition technology. This structure can provide good electrical contact and reduce the impact of volume expansion, but due to its thickness limitation, it may be necessary to optimize the porosity and thickness of the film to improve its electrochemical performance [144–148].

Secondly, silicon/ceramic composite materials designed by combining silicon with ceramic materials such as SiC, Si₃N₄, and SiN can prepare anode materials with excellent thermal and chemical stability [149–152]. These materials improve silicon anodes' cycling stability and safety, but may face challenges such as high cost and complex preparation processes.

Another type is silicon in bulk materials, which displays a high theoretical capacity; however, the volume expansion problem can lead to a decrease in conductivity and a deterioration in structural stability, thereby affecting cycling stability [40,153–155].

High entropy silicon anodes show high conductivity and Li⁺ ion conductivity, which can alleviate volume changes and contribute to the development of advanced LIBs [156,157]. However, high-entropy

Table 3

Summary of the recent 3D structured silicon anodes for LIBs.

Material	Voltage range	Test temperature	ICE	Reversible capacity	Cycle life	Conductivity Issues & Strategies	Volume Expansion Control & Strategies	Cycling Stability Strategies	Reference
3D macroporous silicon	0.01–1.0 V vs Li ⁺ /Li	25 °C	70 % at 1C	1058 mAh g ⁻¹ at 1C	91 % after 800 cycles at 1C	Problem: Poor intrinsic conductivity (Si: 10 ⁻⁵ S cm ⁻¹) Strategy: Three-dimensional interconnected macroporous structure (pore size ~1 μm) shortens Li ⁺ -diffusion path and reduces charge transfer impedance by 60 %	Problem: Theoretical expansion rate of 300 % Strategy: The macroporous structure (porosity of 70 %) provides expansion buffer space, and the apparent volume expansion is less than 50 %	Strategy: Pre-lithiation of pore walls to form a stable SEI film, reducing electrolyte infiltration during cycling	[135]
3D Si-graphitic carbon	0.01 V–1.0 V vs Li ⁺ /Li	25 °C	82 % at 0.2 A g ⁻¹	2126 mAh g ⁻¹ at 0.1 A g ⁻¹	20 % after 450 cycles at 0.5 A g ⁻¹	Problem: High contact resistance between silicon particles Strategy: Graphitic carbon coating (thickness ~5 nm), conductivity increased by 10 ³ times, in-plane conductivity >1000 S m ⁻¹	Problem: High capacity leads to accumulated expansion Strategy: Carbon layer constrains silicon expansion (stress limit <2 GPa), but carbon layer ruptures in the later stages of cycling	Strategy: Carbon layer delays SEI thickening, but interface delamination leads to capacity decay in long-term cycling	[136]
3D Si/CNF yolk-shell	0.01–1.50 V (vs. Li/Li ⁺)	Room temperature	78 % at 0.2 A g ⁻¹	853 mAh g ⁻¹ at 0.2 A g ⁻¹	92 % after 500 cycles at 0.2 A g ⁻¹	Problem: Insufficient conductivity within the yolk structure Strategy: Construct a 3D conductive network with a carbon nanofiber shell (conductivity ↑ 8 times), and increase the Li ⁺ -diffusion coefficient to 10 ⁻⁹ cm ² s ⁻¹	Problem: Unreasonable design of nuclear shell gap Strategy: Reserve 40 % space to accommodate expansion, with a volume change rate of <120 %	Strategy: Elastic carbon shell suppresses powdering, maintaining electrode integrity >90 % after 500 cycles	[137]
Coralloid-like c-nSi/SiO_x@C_y	0.01 V–1.5 V (vs. Li/Li ⁺)	Room temperature	85 % at 1 A g ⁻¹	850 mAh g ⁻¹ at 1 A g ⁻¹	51 % after 500 cycles at 1 A g ⁻¹	Problem: SiO _x has low conductivity (10 ⁻⁸ S cm ⁻¹) Strategy: Coral-shaped carbon coating (sp ² /sp ³ = 1.5) enhances interface electron transfer and reduces impedance by 40 %	Problem: Coral structure has low mechanical strength Strategy: Branch structure disperses stress, but local fracture occurs at high magnification	Strategy: Surface fluorination treatment enhances SEI stability, but carbon layer peeling occurs during long-term cycling	[138]
Si–SiO_x–C Composite	0.1 V–0.43 V vs. Li/Li ⁺	Room temperature	80 % at 1C	1562 mAh g ⁻¹ at 1C	80 % after 100 cycles at 1C	Problem: Si/SiO _x interface impedance is high Strategy: spray pyrolysis to build a continuous carbon network (carbon content 20 wt%), and the conductivity is increased to 10 ² S m ⁻¹	Problem: Stress concentration in composite structures Strategy: SiO _x buffer layer absorbs strain and reduces the volume expansion rate to 180 %	Strategy: Gradient carbon layer design suppresses particle agglomeration, with a structural retention rate of >85 % after 100 cycles	[139]
3D hierarchical macro-/mesoporous Si	0.005 V–3.0 V vs. Li/Li ⁺	25 °C	62 % at 1C	959 mAh g ⁻¹ at 0.2 A g ⁻¹	73 % after 300 cycles	Problem: Porous structure reduces conductive pathways Strategy: Nitrogen	Problem: Uneven wall thickness of multi-level	Strategy: In situ polymerization of binders within the	[140]

(continued on next page)

Table 3 (continued)

Material	Voltage range	Test temperature	ICE	Reversible capacity	Cycle life	Conductivity Issues & Strategies	Volume Expansion Control & Strategies	Cycling Stability Strategies	Reference
					at 0.2 A g ⁻¹	doping on mesoporous walls (N content 5 at%), increasing carrier concentration to 10 ¹⁹ cm ⁻³	holes Strategy: Large pores (1 μm) + mesopores (20 nm) graded buffering, reducing expansion strain to 65 %	mesopores to enhance structural integrity	
3D-Si@SiO _x /C	0.01–2.00 V (vs. Li/Li ⁺)	Room temperature	80 % at 2.5C	1635 mAh g ⁻¹ at 2.5C	83 % after 100 cycles at 2.5C	Problem: Severe polarization at high magnification Strategy: Spiral gyro carbon network (curvature radius < 50 nm) accelerates electron conduction and increases the rate performance by 3 times	Problem: Local stress in spiral structure Strategy: SiO _x interface layer (thickness ~ 2 nm) alleviates stress, with a volume change of < 150 %	Strategy: Dynamic SEI film (containing LiF 40 %) adapts to volume changes, with a film thickness of < 20 nm after 100 cycles	[141]
3D pSi@NC@TNs	0.01–3.0 V vs. Li/Li ⁺	25 °C	65 % at 0.2 A g ⁻¹	365.5 mAh g ⁻¹ at 5 A	68 % after 100 cycles at 0.5 A g ⁻¹	Problem: Titanium silicate has poor conductivity Strategy: Nitrogen-doped carbon coating (with 12 % pyridine N content) reduces charge transfer impedance by 50 %	Problem: Weak bonding at the core-shell interface Strategy: Ti ₃ C ₂ T _x MXene wrapping enhances interface adhesion and reduces expansion strain to 110 %	Strategy: MXene induces the formation of uniform SEI, but increases the risk of lithium dendrites at high rates	[142]
Hierarchical MXene-Si@C composite	0.01–1.5 V vs. Li/Li ⁺	Room temperature	78 % at 0.2 A g ⁻¹	1510.1 mAh g ⁻¹ at 0.2 A g ⁻¹	88 % after 85 cycles at 0.2 A g ⁻¹	Problem: MXene layer stacking hinders ion diffusion Strategy: Amino silane coupling agent enhances the dispersibility of MXene, increasing the ionic conductivity to 1.2 mS cm ⁻¹	Problem: Insufficient flexibility of MXene Strategy: Honeycomb porous structure (pore size 500 nm) accommodates expansion, with a volume change of < 100 %	Strategy: MXene surface end groups (-O/- F) regulate SEI composition (LiF content > 50 %)	[143]
Si@MXene@3-aminopropyltriethoxysilane	0.01–1.5 V (vs. Li/Li ⁺)	25 °C	90.9 % at 0.1 A g ⁻¹	2258 mAh g ⁻¹ at 0.5 A g ⁻¹	65.34 % after 100 cycles at 0.5 A g ⁻¹	Problem: High contact resistance at the interface between silicon and MXene Strategy: Amino silane bridging forms Si-O-Ti covalent bonds, reducing interface impedance by 70 %	Problem: High capacity leads to stress accumulation Strategy: A three-dimensional porous conductive network (porosity of 60 %) disperses stress, but the network collapses in the later stages of cycling	Strategy: Surface reconstruction forms a Li ₂ SiO ₃ protective layer to suppress electrolyte decomposition	[129]

silicon anode materials require complex element screening. To overcome this challenge, machine learning (ML) approaches—such as Bayesian optimization, neural networks, and high-throughput computational screening—are emerging as powerful tools to efficiently identify optimal elemental combinations. These methods leverage existing datasets to predict compositions that maximize lattice distortion effects,

mitigate volume expansion, and enhance ionic conductivity, thereby reducing reliance on empirical trial-and-error.

Phosphorus-doped silicon anode: Phosphorus doping can improve the silicon anode's conductivity and diffusion ability, enhancing high-rate capability. However, further research may be needed to optimize the doping level and distribution [158–162].

Table 4
Summary of some of the selected other structured silicon anodes for LIBs.

Material	Voltage range	Test temperature	ICE	Reversible capacity	Cycle life	Conductivity Issues & Strategies	Volume Expansion Control & Strategies	Cycling Stability Strategies	Reference
Carbon-coated Si bulk	0.005–1.2 V vs. Li/Li ⁺	25 °C	94 % at 0.2C	2050 mAh g ⁻¹ at 0.2C	87 % after 50 cycles at 0.2C	Problem: Poor conductivity of bulk silicon (Si: 10 ⁻⁵ S cm ⁻¹) Strategy: Uniform carbon coating (thickness~20 nm), conductivity increased by 10 ² times, interface impedance reduced by 60 %	Problem: Non-porous structure leads to concentration of expansion stress Strategy: Template method to construct mesopores (pore size 50 nm), buffer partial expansion, and reduce the apparent expansion rate to 180 %	Strategy: Carbon layer inhibits electrolyte penetration and reduces SEI thickening (film thickness<30 nm)	[77]
Bulk silicon particle	0.02–1.2 V (vs. Li/Li ⁺)	Room temperature	75 % at 0.7C	1696 mAh g ⁻¹ at 0.7C	87 % after 50 cycles at 0.7C	Problem: High contact resistance at the interface of micron particles Strategy: Metal-assisted chemical etching to construct a 3D conductive network (Cu nanowire modification), reducing charge transfer impedance by 70 %	Problem: Limited expansion of dense structures Strategy: Graded pore design (macropores + mesopores), porosity of 40 %, expansion strain reduced to 150 %	Strategy: Porous structure disperses stress, particle integrity rate>90 % after 50 cycles	[80]
Ant-nest-like bulk porous Si	0.01–1.0 V vs. Li/Li ⁺	Room temperature	86 % at 0.5C	1250 mAh g ⁻¹ at 0.5C	90 % after 1000 cycles at 0.5C	Problem: Porous structure reduces the continuity of conductive pathways Strategy: In situ graphene coating (in-plane conductivity>10 ³ S m ⁻¹), increasing electron mobility by 100 times	Problem: Insufficient mechanical strength of the hole wall Strategy: Ant nest-shaped interconnected pores (pore size 100–500 nm), with 70 % expansion space reserved and a volume change of<20 %	Strategy: High porosity (80 %) buffering stress, SEI thickness only increases by 5 nm after 1000 cycles	[171]
Si films	0.01 V–1 V vs. Li/Li ⁺	25 °C	70 % at 0.2C	2500 mAh g ⁻¹ at 0.2C	100 % after 200 cycles at 0.5C	Problem: Slow diffusion of lithium ions at the interface of thin films Strategy: Nano particle scaffold embedding (such as TiN), Li ⁺ -diffusion coefficient increased to 10 ⁻⁹ cm ² s ⁻¹	Problem: Risk of film delamination Strategy: Multi-layer gradient structure (Si/SiO _x alternating layers), interlayer stress buffering, expansion rate reduced to 50 %	Strategy: Embedded nano scaffold maintains electrode integrity, 200 cycles without delamination	[172]
Silicon-based thin film	0.04 V–1.50 V vs. Li/Li ⁺	22.5 ± 0.5 °C	73 % at 1C	1650 mAh g ⁻¹ at 1C	74 % after 150 cycles at 1C	Problem: Severe polarization at high magnification Strategy: LIPON artificial SEI layer (ion conductivity>10 ⁻⁶ S cm ⁻¹), interface impedance reduced by 50 %	Problem: Repeated expansion of the film leads to cracking Strategy: The amorphous SiO _x interface layer (thickness~5 nm) absorbs strain and reduces crack density by 80 %	Strategy: Artificial SEI suppresses side reactions, with a capacity decay rate of less than 0.2 % per cycle after 150 cycles	[173]
Si thin films	0.05 V–1 V vs. Li/Li ⁺	Room temperature	86 % at 100 mA g ⁻¹	4067 mAh g ⁻¹ at 100 mA g ⁻¹	90 % after 70 cycles at 100 mA g ⁻¹	Problem: Electronic transmission bottleneck under high capacity Strategy: Microstructure of metal current collector surface (Cu nanocolumn array), increasing electronic contact area by 300 %	Problem: Stress accumulation in ultra-thin films (<500 nm) Strategy: Columnar porous structure (porosity 30 %), isotropic expansion, strain homogenization	Strategy: Pre lithiation forms a stable Li ₂ SiO ₃ interface layer, and the SEI composition remains stable during cycling	[148]
Fe-Cu-Si	0.01–1.0 V vs. Li/Li ⁺	25 °C	91 % at 1C	1287 mAh g ⁻¹ at 1C	98 % after 50 cycles at 1C	Problem: Uneven conductivity of alloy phases Strategy: Fe ₃ Si/Cu ₅ Si conductive network (conductivity 10 ⁴ S m ⁻¹), continuous electronic conduction path	Problem: Three-element composite phase transformation strain Strategy: Fe/Cu inert phase dispersion of active silicon, volume expansion reduced to 120 %	Strategy: Inert phase suppresses particle pulverization, electrode expansion rate<15 % after 50 cycles	[174]
Si/Cu_{0.83}Si_{0.17}/Cu	0.05–3.0 V vs. Li ⁺ /Li	Room Temperature	71 % at 1C	3105 mAh g ⁻¹ at 1C	100 % after 500 cycles at 1C	Problem: High impedance at the interface between silicon and copper Strategy: Crystalline Cu silicide interface layer (Cu ₅ Si), reducing interface resistance to 5 Ω cm ²	Problem: Intense expansion of high-capacity silicon phase Strategy: Cu silicide skeleton constrains silicon expansion (with reserved gaps of 40 %), resulting in a volume change of less than 100 %	Strategy: Stabilize Cu Si interface to suppress SEI repeated rupture, zero capacity decay after 500 cycles	[175]
(Ti, Fe)-alloyed Si	0.05 V–2.5 V (vs. Li/Li ⁺)	25 °C	65 % at 0.06C	1563 mAh g ⁻¹ at 0.06C	100 % after 100 cycles at 0.06C	Problem: Alloying reduces carrier concentration Strategy: Annealing forms TiSi ₂ conductive phase (resistivity<10 ⁻³ Ω cm), increasing electron mobility by 50 times	Problem: Mismatch between the alloy layer and the silicon thermal expansion coefficient Strategy: Gradient annealing regulates microstructure, expands isotropy, and reduces strain to 80 %	Strategy: TiSi ₂ induces uniform SEI, cycling 100 times without particle rupture	[176]
2D silicon	0.01 V–3.0 V vs. Li ⁺ /Li	Room Temperature	70 % at 200 mA g ⁻¹	835 mAh g ⁻¹ at 5 A g ⁻¹	100 % after 3000 cycles 5 A g ⁻¹	Problem: Insufficient conductivity within the two-dimensional structural plane Strategy: Layered alloy exfoliation preparation of 2D Si/graphene heterojunction with in-plane conductivity>500 S m ⁻¹	Problem: Inter-layer slip leads to structural failure Strategy: Graphene interlayer support (interlayer spacing of 0.8 nm), limiting out-of-plane expansion, volume change<20 %	Strategy: Graphene protective layer inhibits SEI thickening, with a film thickness of<10 nm after 3000 cycles	[177]

Table 5
Comparative analysis of silicon anode structures.

Challenge	Nanostructured	Micron-Sized	3D Structured	Reference
Conductivity	Particle contact resistance dominates, requiring carbon coating	Relying on adhesives to maintain electrical contact	Built-in conductive frame reduces resistance by more than 70 %	[179–181]
Volume Expansion	Small size intrinsic stress relief	Macroscopic cracking (stress > 2 GPa)	Pore structure buffering expansion	[179,180, 183]
Cycling Stability	SEI thickening leads to capacity decay	Particle pulverization accelerates failure	Structural design improves lifespan (>1000 cycles)	[179]

Two-dimensional silicon-based materials can achieve rapid lithium diffusion due to their planar structure, and their large specific surface area can provide sufficient adsorption sites. The loose stacking method can alleviate volume expansion/contraction during lithium insertion/extraction, thereby promoting rapid charging and discharging [35,127, 163–165].

Silicon/metal composite materials: By combining silicon with metals such as copper, nickel, etc., the high conductivity of metals can be utilized to improve the conductivity of silicon anodes [155,166,167]. However, the mismatch in thermal expansion coefficients between metal and silicon may lead to increased stress at the interface, affecting cycling stability.

High entropy alloy (HEA) silicon anode exhibits significant advantages in the field of lithium-ion batteries due to its unique composition and structural characteristics. The synergistic effect of multiple elements in HEA can enhance the structural stability of materials through lattice distortion and solid solution strengthening. The volume expansion of silicon-based anodes is a core issue of traditional materials, and HEA significantly improves this problem through the synergistic buffering effect of multiple elements [168]. It is mentioned that alloying silicon with other elements, such as lithium, can effectively reduce volume expansion and improve electrochemical performance. For example, silicon-based composite materials after alloying (such as Si/Fe₂O₃ dual network structure) exhibit lower volume change rates [169]. The complexity of HEA design can be streamlined via ML-driven frameworks that accelerate the discovery of multi-element systems with optimal strain distribution and electrochemical stability.

Silicon/sulfide composite materials such as sulfides SiS, SiSe, etc., exhibit improved conductivity and cycling stability due to their unique structural properties, but there may be issues with complex preparation processes and high costs [170]. It can be improved, but there may be a problem of insufficient conductivity. Each type of silicon anode structure has its unique advantages and limitations, and choosing the appropriate structural design requires a balance between specific application requirements and performance goals. Researchers are constantly exploring new materials and preparation methods to address these challenges and improve the overall performance of silicon anodes. A performance overview of other selected silicon-based anodes used for LIBs is given in Table 4.

2.6. Comparative analysis of silicon anode structures

The comparative advantages and disadvantages of silicon negative electrodes are shown in Table 5. Nanostructured silicon negative electrode (size < 100 nm, specific surface area > 100 m² g⁻¹) inherently alleviates volume expansion stress through nanoscale effects (such as

nanowire bending and nanoparticle voids) [178,179], and its high specific surface area can accelerate Li⁺ diffusion (such as Si nanowires maintaining high capacity at 5C rate), which correlates with its outstanding capacity performance (score 5.8/6) in Fig. 6e. Critically, this nanostructure enables approximately 10 × higher ionic conductivity ($\sigma \sim 10^{-2}$ S/cm) due to sub-100 nm diffusion paths, fundamentally distinguishing its charge transfer mechanisms from larger structures. An egg yolk shell or core-shell structure can also stabilize the SEI layer. However, high surface activity can exacerbate electrolyte decomposition, leading to thickening of the SEI layer (>50 nm/100 cycles) and a decrease in Coulombic efficiency [179]. At the same time, nanoparticles are prone to agglomeration, and synthesis costs are high (such as the VLS method) [179], reflected in their poor cost efficiency (score 2.1/6) on the radar diagram. The conductivity dichotomy between structural types arises from dimensional constraints: While nanostructures provide superior ionic transport, micron-Si's > 10 μm diffusion paths force reliance on binder-mediated electron tunneling, adding ≈40 % interface resistance. This fundamental difference explains the 5C rate capability of nanowires versus micron-Si's 0.5C limit. Micro-scale silicon anode (size > 1 μm, specific surface area < 10 m² g⁻¹, tap density > 1.4 g cm⁻³) suppresses SEI thickening (<20 nm) and increases volumetric energy density by 30 % due to its low specific surface area [179,180]. The radar chart confirms its cost advantage (score 5.5/6) through low cost processes such as ball milling supports industrialization (production capacity > 10000 tons/year), but shows compromised performance in conductivity (score 3.2/6) due to a long Li⁺ diffusion path (>10 μm), leading to poor rate performance (<0.5C). Uneven volume expansion (radar score 3.5/6) can easily cause macroscopic cracking (boundary stress > 2 GPa), and the long Li⁺ diffusion path (>10 μm) leads to poor rate performance (<0.5C), requiring a high proportion of adhesive (>10 wt%) [180]. Quantitative expansion analysis reveals order-of-magnitude stress differences: Nanoparticles dissipate sub-0.5 GPa stress via size-dependent plasticity unavailable to micron-particles, which experience >2 GPa fracture stresses. Furthermore, expansion occurs at fundamentally different time scales—nanoseconds in nanoparticles versus milliseconds in micron-particles—explaining catastrophic cracking in larger structures versus progressive degradation in nano-Si. The 3D structured silicon negative electrode (porosity > 60 %) buffers volume expansion through interconnected pores and conductive frameworks (such as graphene) (such as ant nest shaped porous silicon, which maintains a capacity of 90 % after 1000 cycles) [181], corresponding to its best-in-class cycle life (score 5.6/6) and volume expansion control (score 4.9/6) in the radar comparison. 3D architectures uniquely redistribute stress through pore engineering rather than material solutions, with 60–80 % porosity yielding <0.3 GPa stresses. The conductive network can reduce charge transfer resistance by 70 %, though distinct from nanostructures' homogeneous ion access, pore-limited infiltration creates non-uniform conductivity distributions in 3D structures. The radar shows intermediate conductivity (score 4.3/6) due to <10 μm pores easily leading to poor electrolyte infiltration. Moreover, 3D printing and other processes make the cost 30 % higher than micron silicon (cost score 3.8/6 vs micron's 5.5), with additional challenges in mechanical strength (elastic modulus < 5 GPa) [181,182], and <10 μm pores can easily lead to poor electrolyte infiltration. Moreover, 3D printing and other processes make the cost 30 % higher than micron silicon [181]. Cycling stability exhibits structural-divergent failure modes: While surface-dominated SEI growth causes 0.2–0.5 %/cycle CE decay in nano-Si due to nanoscale curvature accelerating electrolyte reduction, micron-Si suffers bulk fracture mechanisms. In contrast, 3D scaffold-based interfaces reduce SEI reformation events ≈100 × versus nanoparticle electrodes despite material-level instability. The structural design of three types of materials needs to balance their resistance to fragmentation, rate performance, cost, and cycling stability.

In the research and application of silicon anode materials, nanostructured silicon anodes have attracted much attention due to their

excellent high-rate performance. However, they face significant challenges in terms of solid electrolyte interface (SEI) stability and cost control. The divergent performance stems from dimensional control of transport phenomena: Nanostructures maximize surface-mediated kinetics but suffer interfacial instability; micron-structures minimize surfaces but create bulk mechanical failures; 3D designs decouple ionic/electronic transport through architectural optimization. In contrast, micron-sized silicon anodes have become the preferred choice for many research and applications due to their advantages in industrial production, but their mechanical failure issues and limitations in rate performance still need to be further overcome. However, three-dimensional (3D) structured silicon anodes stand out for their excellent cycling stability. Nevertheless, the high cost and insufficient mechanical strength have become bottlenecks restricting their large-scale application [184]. Looking ahead to the future, optimizing material design will be key, such as using carbon coating technology to treat nano silicon, which can significantly increase its tap density to 220 %. At the same time, developing low-cost production processes will also be an important way to promote the wider application of silicon anode materials.

3. Research efforts to address silicon anode issues

3.1. Nanostructured silicon anodes

The preparation of nanostructured silicon anodes employs various techniques, including vapor deposition, sol-gel, and template methods. Vapor deposition (notably CVD and PECVD) offers exceptional controllability over size, shape, and morphology, enabling the synthesis of high-quality nanostructures like nanowires and nanoparticles. This method also facilitates precise doping (e.g., boron incorporation) to tailor material properties [185,186]. Sol-gel techniques are valued for their simplicity, cost-effectiveness, and ability to produce materials with high homogeneity and tunable porosity. These characteristics make them well-suited for scalable production [187].

Lee et al. reported a novel dispersant-free colloid and interface engineering method for enhancing silicon-based negative electrode materials [188]. This method mainly involves using less defective graphene oxide (C-GO) and highly oxidized single-walled carbon nanotubes (C-SWCNTs), prepared by a chlorate-based oxidation method. Si alloy (SiA) particles were encapsulated by C-GO and C-SWCNTs, which avoids the need for additional additives. Through spray drying and a subsequent chemical reduction process, a composite structure of N-doped SWCNTs with lithium affinity and highly crystalline reduced C-GO coating was created on the surface of SiA. This unique combination provides high capacity, stable holding behavior, and excellent initial capacity (1224 mAh g^{-1}), and achieves a holding rate of 82.3 % (0.1C) after 100 cycles. In addition, the LIB full cell using SiA/nanocarbon anode demonstrated an energy density of up to 350 Wh kg^{-1} and maintained 65 % capacity after 200 cycles.

The template rule guides the growth of nanostructured silicon materials through the use of template materials, thereby preparing nanostructures with predetermined shapes and sizes. This method has a high degree of control over the structure and properties of the materials. For example, AAO templates have been widely used in the preparation of ordered nanostructures due to their highly ordered nanopore array structure. By selecting appropriate templates, silica materials with specific pore structures can be prepared [189]. Moreover, the template method can also be used to prepare hollow nanostructures, such as hollow silicon polymer nanospheres [190]. Porous silicon can be produced from silicon wafer waste using metal-assisted chemical etching (MACE). This method utilizes metal catalysts to selectively etch silicon materials during chemical etching, thereby forming porous structures [191]. These methods each have their advantages, providing various possibilities for preparing silicon-based anode materials with excellent performance. The vapor deposition method is known for its excellent controllability and high-quality nanomaterial preparation ability.

Sol-gel method is popular because of its simple operation, high-cost efficiency, and suitability for batch production. The template rule plays an important role in the preparation of nanomaterials due to its high structural and performance control capabilities.

3.1.1. Conductivity issues of nanostructured silicon anodes

The inherently low electrical conductivity of silicon presents a significant barrier to achieving high rate capability and initial Coulombic efficiency in silicon anodes. Volume expansion during cycling can further exacerbate this issue by disrupting conductive networks and increasing internal resistance. Various strategies have been explored to specifically address this conductivity limitation, distinct from mitigating expansion or SEI instability, though overlap exists:

Structural design: By designing nanostructured silicon anodes such as core-shell structure, eggshell structure, porous structure, and embedded structure, conductivity can be effectively improved [123, 192]. These structures not only help alleviate the volume expansion of silicon during charging and discharging but also maintain the integrity of the electrode, thereby improving conductivity.

Conductive composite materials: By combining conductive polymers or metal nanostructures with silicon nanoparticles, the overall conductivity of the structure can be improved [193,194]. For example, Lin et al. have improved the conductivity of silicon anodes and the stability of SEIs by preparing Si/Bi₂S₃ nanocomposites [195]. Heterogeneity promotes rapid charge transfer while reducing internal resistance.

Surface coating: Coating conductive materials such as carbon, metal oxides, or other conductive polymers on the surface of silicon nanoparticles can reduce the resistance between particles and improve conductivity [196,197]. This coating can serve as a protective layer to prevent the crushing of silicon particles during the cycling process while improving their conductivity.

Optimizing the particle size of silicon materials: Reducing the particle size of silicon to the nanometer level can adapt to volume changes and reduce electrical contact losses caused by volume expansion [198, 199]. By controlling the size and morphology of silicon particles, their electrochemical performance can be optimized.

Using conductive adhesives: Using conductive adhesives such as polyvinyl alcohol (PVA), polyacrylic acid (PAA), or other conductive polymers during electrode preparation can enhance electron transfer between electrode materials and improve the overall conductivity of the cell [200].

Interface engineering: By forming a stable SEI on the surface of the silicon anode, the decomposition of the electrolyte can be reduced, and the conductivity and cycling stability of the electrode can be improved [201].

3.1.2. Volume expansion problem of nanostructured silicon anodes

Nanostructured silicon anodes undergo substantial volume changes (up to ~300 %) during lithium insertion/extraction. This expansion/contraction generates immense mechanical stress, which is a primary root cause of several failure mechanisms, including particle pulverization, loss of electrical contact (detachment from current collector or conductive network), electrode delamination, and continuous electrolyte decomposition leading to unstable SEI growth. These stress-induced failures directly contribute to poor cycling stability (Section 3.1.3). Specific strategies in Fig. 6f employed to directly accommodate or mitigate the detrimental effects of silicon's volume expansion include.

- (1) Nanoization and structural design: By preparing silicon materials into nanoparticles, nanowires, nanotubes, or porous structures, the diffusion distance of lithium ions can be shortened, the specific surface area of the material can be increased, thereby improving the utilization rate of active lithium ions and the kinetics of alloying processes [3]. In addition, nanostructures can more effectively release stress during volume expansion and reduce damage to material structures [202]. For example, the

network structure of silicon anode material prepared using porous anodized aluminum as a template can absorb volume expansion through its pores, thereby achieving excellent electrochemical performance [203].

- (2) **Composite materials:** By combining silicon nanoparticles with conductive materials such as carbon nanotubes, graphene, or carbon fibers, the conductivity and mechanical stability of the structure can be improved [204]. The secondary material acts as a buffer and mechanical scaffold. For example, the composite of silicon nanowires and carbon materials can provide a stable electron transfer path, while carbon materials can buffer the volume expansion of silicon and improve the structural stability of the electrode [205].
- (3) **Prelithiation technology:** The artificial SEI film is prepared on the surface of silicon material by prelithiation technology, which can effectively stabilize the interface between active material and electrolyte, and reduce the volume expansion and stress change during the cycle [206].
- (4) **New type of adhesive:** Develop an adhesive with sufficient adhesion to maintain good electronic transfer between silicon and current collector, achieving a stable electrode structure [207]. For example, self-healing elastic adhesives can adapt to the volume changes of silicon anodes and maintain the integrity of electrode structures.
- (5) **Interface engineering:** By forming a stable SEI layer on the silicon anode's surface, the electrolyte's decomposition can be reduced and the cycling stability of the electrode can be improved [208].

3.1.3. Cyclic stability issues of nanostructured silicon anodes

The poor cycling stability of silicon anodes manifests as rapid and irreversible capacity loss over charge-discharge cycles. This degradation is fundamentally *caused* by the interplay and consequences of the low conductivity (Section 3.1.1) and, predominantly, the large volume changes (Section 3.1.2). Stress-induced structural damage, pulverization, loss of electrical contact, and, critically, the instability of the SEI layer formed due to repetitive fracture and reformation on expanding/contracting surfaces lead to continuous lithium and electrolyte consumption. Therefore, while strategies targeting conductivity and expansion inherently benefit stability, specific approaches directly focus on enhancing long-term stability by mitigating SEI instability and maintaining structural integrity:

Surface coating: Coating the surface of silicon nanoparticles with stable materials, such as amorphous TiO_2 , SiO_x , or metal oxides, reduces direct contact between the electrolyte and silicon. This minimizes continuous electrolyte decomposition on the fresh silicon surface exposed by cracking, thereby stabilizing the SEI layer and improving cycling stability [209].

Nanostructure design: Manufacturing silicon materials with tailored nanostructures (nanowires, nanotubes, nanoparticles, porous) not only buffers volume changes (Section 3.1.2) but inherently provides greater tolerance to internal stress, reducing crack propagation and pulverization, thereby improving long-term cycling stability [31]. **Optimization of binders:** Using high-performance binders such as carboxymethyl cellulose (CMC), polyacrylic acid (PAA), or self-healing polymer materials enhances adhesion between silicon particles and particles to the current collector, reducing material detachment and electrical isolation caused by volume changes. This directly maintains the functional electrode structure over cycles [210].

Prelithiation treatment: Prelithiation compensates for the irreversible lithium loss during the *initial* formation of the SEI layer. By reducing initial irreversible capacity and potentially forming a more

stable initial SEI layer on the silicon surface (before significant cracking occurs), it enhances initial coulombic efficiency (ICE) and contributes to improved *subsequent* cycling stability [211].

Electrolyte additives: Adding components like fluoroethylene carbonate (FEC) to the electrolyte promotes the formation of a more robust, flexible, and LiF-rich SEI layer on the silicon surface upon initial formation. This SEI layer is more resistant to cracking during volume changes and suppresses continuous electrolyte decomposition, thereby improving cycling stability [212].

Interface engineering: Interface engineering is an easy lab-based strategy to optimize the SEI layer. By forming a stable SEI layer on the silicon anode's surface, the electrolyte's decomposition can be reduced and the cycling stability of the electrode can be improved [208,213]. For example, through selective dissolution strategies, SEI components with high elastic deformation energy can be retained, improving the cycling stability of silicon anodes [87].

Sandwich structure design: Designing a silicon anode with a multi-layered (sandwich) structure, such as a graphene silicon particle copper sandwich electrode, utilizes the interlayer sliding of graphene (or other interlayers) to alleviate interfacial pressure caused by silicon volume change, reduce silicon particle detachment, and maintain electrical connectivity, thereby enhancing structural and cycling stability [17].

While nanostructured silicon anodes offer compelling solutions for mitigating volume expansion and enhancing electrochemical kinetics through size effects and sophisticated engineering (as discussed in Sections 3.1.1-3.1.3), their practical implementation often faces significant hurdles related to complex synthesis protocols, scalability limitations, and elevated production costs. These challenges, particularly concerning industrial-scale viability and cost-effectiveness, have spurred substantial research interest in micron-sized silicon anodes ($>1\ \mu\text{m}$). Micron-sized particles leverage simpler, potentially more scalable manufacturing routes like mechanical processing or spray drying, offering a pathway towards lower material costs and easier integration into existing battery production lines. While micron-sized silicon inherently faces distinct challenges in managing its absolute volume expansion due to larger particle dimensions, the subsequent section (Section 3.2) explores the preparation technologies and specific strategies employed to address conductivity, volume expansion, and cycling stability within this promising paradigm focused on manufacturability.

3.2. Micron-sized silicon anodes

Various preparation technologies exist for micro-structured silicon anodes, including mechanical grinding, spray drying, and template methods [14]. Each of these methods has its characteristics, providing flexible choices for preparing micro-structured silicon anodes with specific requirements.

Mechanical grinding is a cost-effective and suitable method for the mass production of Si anodes. This method achieves crushing of silicon block material into micrometer-sized particles through mechanical force. For example, a recent study reported successful preparation of sub-micron silicon nanoparticle (SiNPs) materials using a simple, low-cost, and effective high-energy mechanical grinding method [214]. The ICE of the prepared silicon anode reached 89.1 %. However, although mechanical grinding can achieve a reduction in particle size, it is difficult to precisely control the size and distribution of particles, especially at the nanoscale, where particle aggregation and aggregation phenomena are prone to occur, leading to particle size dispersion [215].

Spray drying is another efficient preparation technology that can produce uniform microspheres, micro rods, and other structures [218]. It is easy to operate, low-cost, and suitable for large-scale silicon anode

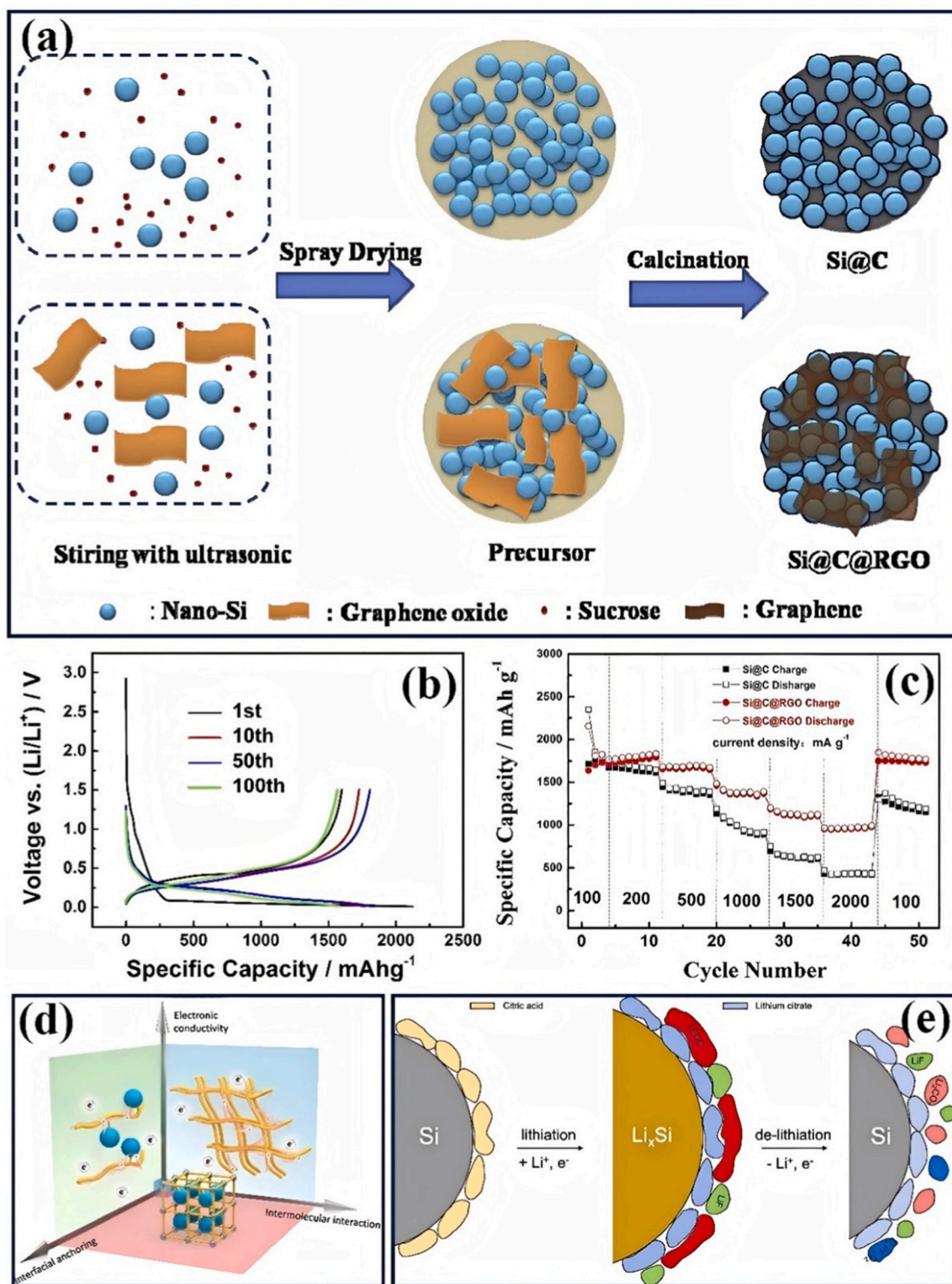


Fig. 7. (a) Schematic illustration of the synthesis procedure for the silicon on carbon and reduced graphene oxide nanocomposite Si@C@RGO, (b) charge/discharge voltage profiles of Si@C@RGO composite for the 1st, 10th, 50th, 100th cycle, (c) electrochemical performance during different applied specific current for Si@C and Si@C@RGO composites. Reproduced with permission [111]. Copyright 2017, Elsevier. (d) 3D conductive networks. Reproduced with permission [216]. Copyright 2022, American Chemical Society. (e) SEI evolution. Reproduced with permission [217]. Copyright 2021, Electrochemical Society, Inc. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

production. For example, micron-sized silicon@carbon@graphene spherical composites were prepared by industrial scale spray drying method and subsequent calcination process Si@C@RGO (Fig. 7a). The

obtained Si@C@RGO negative electrode exhibits a high initial reversible specific capacity of 1599 mAh g⁻¹ at a current density of 100 mA g⁻¹ (Fig. 7b), and a good capacity retention rate of 95 % of the original

charging capacity at higher current densities (Fig. 7c) [111].

The template method guides the growth of silicon materials by using template materials, which can precisely control the morphology and size of microstructures, thereby effectively regulating the structure and properties of materials [3]. For example, dry etching using porous anodized aluminum oxide film as a template can achieve high-quality transfer of template patterns to the substrate material, achieving nanostructures [219]. In addition, the template method can also be used to assemble micrometer-sized microspheres, such as using Sylgard 184 and its corresponding curing agents and silicon wafer templates to prepare micrometer-sized microspheres with specific micro stripes [220,221]. These methods have their advantages and disadvantages. Mechanical grinding is suitable for mass production, but it makes it difficult to precisely control the particle size. Spray drying is easy to operate, cheap, and suitable for large-scale production. The template rule can precisely control the shape and size of micrometer structures, making it suitable for application scenarios that require specific structures.

3.2.1. Conductivity issues of micron-sized silicon anodes

Micro-scale silicon anodes have higher tap density and lower production costs than nanostructured silicon anodes, but their conductivity remains a crucial issue that must be addressed. The following are some effective methods to improve the conductivity of micron-sized silicon anodes:

Carbon coating: By coating carbon materials such as graphene, carbon nanotubes, or amorphous carbon layers on the surface of micron-sized silicon particles, the conductivity of silicon anodes can be significantly improved [222,223]. This type of coating not only improves electron transfer efficiency and forms a stable SEI layer between silicon particles, but also reduces electrolyte decomposition and increases battery cycling stability.

Conductive polymer binder: Using conductive polymers such as PAA or PVA as binders can enhance the electronic connection between electrode materials, thereby improving the overall conductivity of the electrode [224].

Metal or metal oxide coating: Coating a layer of metal or metal oxide, such as copper, nickel, or titanium oxide, on the surface of a silicon anode can provide additional conductive pathways and enhance the conductivity of the silicon anode [225].

Building a 3D conductive network: By constructing a 3D conductive network structure (Fig. 7d), such as composite materials of silicon particles with carbon nanotubes or graphene, continuous electron transfer channels can be provided to improve the conductivity of silicon anodes [222].

Silicon alloying: By alloying silicon with certain metals such as magnesium silicide or copper silicide, the conductivity of the silicon anode can be improved [226]. Alloying can improve conductivity and alleviate silicon's volume expansion during charging and discharging processes.

Surface modification: The surface of the silicon anode can be modified by chemical or physical methods, such as plasma treatment or surfactant modification, to enhance the affinity between the silicon anode and electrolyte, reduce interface resistance, and improve conductivity [227].

3.2.2. Volume expansion problem of micron-sized silicon anodes

Due to their large size, micro-scale silicon anodes in LIBs help alleviate volume expansion issues but still face challenges. Here are some effective solutions to counter the volume change issues:

Structural design: Manufacturing micro-scale silicon anodes with porous or core-shell structures can provide greater volume change space, thereby reducing internal stress and improving structural stability [3].

Composite materials: By combining silicon nanoparticles with conductive materials such as carbon nanotubes, graphene, or carbon fibers, the conductivity and mechanical stability of the structure can be

improved [228].

Adhesive optimization: Develop adhesives with sufficient adhesion to maintain good electron transfer between silicon and the current collector, achieving a stable electrode structure [124].

3.2.3. Cyclic stability issues of micron-sized silicon anodes

The large size of micro-scale silicon anodes in LIBs influences volume expansion and, to some extent, helps alleviate related issues, but their cycling stability remains a key challenge. Here are some effective solutions reported in the literature: The interface coating offers a stable material such as carbon or SiO_x on the surface of micrometer-sized silicon particles; the direct contact between electrolyte and silicon can be reduced, thereby reducing the unstable decomposition of the SEI layer and improving cycling stability [229]. For example, by designing and constructing interfaces with dynamic stability on SiO_x microparticles utilizing high elastic interfaces to maintain the structural integrity of the microparticles during cycling, the uncontrolled growth of SEI is effectively avoided, significantly improving the cycling stability of composite materials [230]. In addition, by using special electrolyte additives such as FEC, a LiF-rich SEI layer can be formed on the silicon surface, which helps improve cycling stability but may also affect lifespan [212]. Further, the adhesive optimization to develop adhesives with sufficient adhesion to maintain good electron transfer between silicon and the current collector, achieving a stable electrode structure [231]. Prelithiation can also compensate for the loss of lithium during the initial charge-discharge cycle, improve the initial Coulombic efficiency, and enhance cycle stability by forming a stable SEI layer [232].

While micron-sized silicon anodes offer significant advantages in terms of manufacturing scalability, lower production costs, and potentially simpler integration compared to nanostructured counterparts, effectively managing the inherent challenge of absolute volume expansion within larger particles remains critical for achieving long-term cycling stability and high energy density. Strategies like carbon coating, optimized binders, and prelithiation (discussed in Sections 3.2.1-3.2.3) provide valuable mitigation. However, the fundamental limitations associated with stress concentration within individual micron-sized particles and the difficulty in maintaining robust electrical connectivity throughout the electrode during repeated expansion/contraction cycles necessitate alternative design paradigms. To fundamentally overcome these constraints and achieve superior performance, research has increasingly focused on 3D structured silicon anodes. These architectures move beyond particle-level modifications to incorporate engineered macroscopic frameworks specifically designed to accommodate volume changes, ensure continuous conductive pathways, and optimize ion transport. The subsequent section (Section 3.3) explores the diverse preparation methods and unique characteristics of these 3D structured silicon anodes, highlighting their potential to address the core limitations faced by both nanostructured and micron-sized silicon electrodes.

3.3. 3D structured silicon anodes

The technical means for preparing 3D structured silicon anodes are indeed diverse, mainly including electrochemical deposition, solution method, and 3D printing technology [233]. These methods each have their characteristics, providing a wide range of choices and possibilities for preparing 3D structured silicon anodes with excellent performance.

Electrochemical deposition method: This method deposits silicon materials on the substrate through electrochemical reactions, which can accurately control the morphology and size of the silicon anode [234]. For example, the preparation method of electrode materials for novel 3D silicon-structured supercapacitors mentioned in the literature includes electrochemical deposition [235].

Solution method: This method prepares a silicon anode by dissolving silicon material in a solvent and adopting sol-gel, hydrothermal, or coprecipitation methods [236]. This method allows the preparation of

3D structured silicon anodes with different morphologies and sizes, suitable for application scenarios that require specific microstructures. Tian et al. utilized polydopamine to assist in the deposition of SnO_2 on nano silicon in a hydrothermal environment and obtained hybrid encapsulation of nitrogen-doped carbon (NC) and SnO_2 quantum dots hybrid Si@NC@SnO_2 core-shell nanospheres [237]. Due to the protective effect of the organic/inorganic hybrid shell, core-shell Si@NC@SnO_2 exhibits effective resistance to the volume expansion of nanosilicon, thereby maintaining its structural and interfacial stability [237].

3D printing technology: 3D printing technology can prepare 3D silicon anodes with complex structures by printing ink containing silicon materials according to pre-designed patterns [238,239]. This technology can provide high-performance electrodes with high load capacity and adjust the electrodes' geometric shape and material distribution as needed to optimize their electrochemical performance. For example, Fu et al. used 3D printing technology to prepare microcrystalline lattice-structured silicon carbon (3D-Si/G/C) negative electrodes and systematically tested their electrochemical performance [240]. This material achieves precise construction of silicon-based microcrystals through 3D printing technology, effectively alleviating the structural damage and active material pulverization problems caused by the volume expansion of silicon materials during charging and discharging processes. In addition, the material also exhibits excellent cycling stability and rate performance. In addition, Ding et al. have successfully applied 3D printing technology to prepare silicon carbide ceramic optical components [241].

3.3.1. Conductivity issues of 3D structured silicon anodes

The 3D-structured silicon anode exhibits excellent electrochemical performance due to its unique spatial structure, but its conductivity remains challenging. Here are some effective methods to improve the conductivity of 3D structured silicon anodes: (1) Conductive network construction: By constructing a 3D conductive network, such as using highly conductive materials such as carbon nanotubes or graphene, continuous electron transfer channels can be provided, thereby improving the conductivity of silicon anodes [242]. For example, a 3D sandwich layered structure formed by co-coating cyclized PAN (polyacrylonitrile) on the silicon surface can provide abundant electroactive areas and conductive transmission pathways, adapt to volume changes, and improve energy density [243]. (2) Interface coating: Coating a layer of conductive material, such as a conductive polymer or metal layer, on the surface of a silicon anode can enhance the conductivity of the electrode [229]. For example, a chemical vapor deposition on silicon nanoparticles can form an N-doped graphene layer, which can serve as a flexible conductive carrier [244]. At the same time, the amorphous hybrid silicate coating enhances the strength and flexibility of the electrode and promotes the formation of a stable SEI film. (3) Core-shell structure design: Design the silicon anode material for the core-shell structure, where the core can be silicon and the shell can be a material with good conductivity, such as $\text{V}_3\text{O}_4@\text{C}$. It can improve electronic conductivity and structural stability [114]. Theoretical simulations show that the in-situ formation of the V_3O_4 layer facilitates the rapid diffusion of Li^+ and reduces the energy barrier for Li transfer from the carbon shell to the core.

3.3.2. Volume expansion problem of 3D structured silicon anodes

Although 3D structured silicon anodes have excellent electrochemical performance, the issue of volume expansion during charging and discharging remains a challenge. Here are some effective solutions: (1) Structural design: A larger volume change space can be provided by designing 3D silicon anodes with porous or core-shell structures, thereby reducing internal stress and improving structural stability [3]. (2) Composite materials: By combining silicon nanoparticles with conductive materials such as carbon nanotubes, graphene, or carbon fibers, the conductivity and mechanical stability of the structure can be improved.

(3) Adhesive optimization: Develop adhesives with sufficient adhesion to maintain good electron transfer between silicon and the current collector, achieving a stable electrode structure [245].

3.3.3. Cyclic stability issues of 3D structured silicon anodes

The cycling stability of 3D structured silicon anodes is a key factor in the performance of LIBs. In order to improve its cycling stability, researchers have adopted various strategies as listed below.

Structural optimization: by designing 3D silicon anodes with porous or core-shell structures, a larger volume change space can be provided, internal stress can be reduced, and the stability of the structure can be improved [3]. For example, a chemical vapor deposition on silicon nanoparticles can form an N-doped graphene layer, which can serve as a flexible conductive carrier [244]. At the same time, the amorphous hybrid silicate coating enhances the strength and flexibility of the electrode and promotes the formation of a stable SEI film.

Interface coating: Coating a stable material such as carbon or SiO_x on the surface of the silicon anode can reduce direct contact between the electrolyte and silicon, reduce unstable decomposition of the SEI layer, and improve cycling stability [229]. For example, by designing and constructing interfaces with dynamic stability on SiO_x microparticles utilizing high elastic interfaces to maintain the structural integrity of the microparticles during cycling, the uncontrolled growth of SEI is effectively avoided, significantly improving the cycling stability of composite materials [230].

Electrolyte additives: Using special electrolyte additives such as FEC can form a LiF-rich SEI layer on the silicon surface, which helps improve cycling stability but may also affect calendar life [212].

Adhesive optimization: Develop adhesives with sufficient adhesion to maintain good electron transfer between silicon and the current collector, achieving a stable electrode structure [207]. For example, Xu et al. designed and synthesized a new water-soluble polymer adhesive Poly(acrylic acid)-poly(2-hydroxyethyl acrylate-co-dopamine methacrylate) (PAA-P (HEA co DMA)), which has a self-healing multiple network structure and can buffer the strain caused by volume changes of Si particles, enabling electrode materials to achieve excellent cycling stability and rate performance [246]. **Prelithiation technology:** Prelithiation can compensate for the loss of lithium during the initial charge-discharge cycle, improve the initial Coulombic efficiency, and enhance cycle stability by forming a stable SEI layer [247].

Sections 3.1 to 3.3 have systematically explored the dominant silicon anode paradigms—nanostructured, micron-sized, and 3D structured—each offering distinct strategies to tackle the core challenges of conductivity, volume expansion, and cycling stability. 3D structures, in particular, represent a sophisticated approach by incorporating engineered macroscopic frameworks specifically designed to accommodate volume changes and ensure continuous conductive pathways. While these established categories form the backbone of current research and development, the pursuit of high-performance, commercially viable silicon anodes continues to drive exploration beyond these frameworks. Researchers are investigating a diverse spectrum of alternative silicon anode structures that leverage unique material combinations, novel synthesis routes, or unconventional design principles. These "other" structures often target specific performance niches (e.g., extreme thermal stability, ultra-fast charging, or enhanced mechanical properties), address particular limitations of the mainstream approaches, or represent emerging concepts with significant potential for future breakthroughs. The following section (Section 3.4) provides an overview of these complementary and innovative silicon anode configurations, highlighting their distinct design rationales, potential advantages, and the specific challenges they aim to overcome.

3.4. Other silicon structures

Researchers have explored a diverse range of silicon anode structural designs beyond conventional particle modifications to address the

persistent challenges of low conductivity, severe volume expansion, and poor cycling stability. While sharing the common goal of improving silicon performance in lithium-ion batteries (LIBs), each approach employs distinct strategies and offers unique features. The key strategies and their characteristic mechanisms include:

Thin Film Silicon Anode: This strategy minimizes the absolute volume change per unit area compared to powders and directly controls electrolyte interaction and lithium-ion diffusion paths. Improvement in electrochemical performance is achieved primarily through optimization of the porosity (controlling ion access and accommodating strain) and thickness (reducing cracking by limiting the absolute expansion distance) [248,249]. *Distinctive Feature:* Direct fabrication on current collectors, precise dimensional control.

Silicon/Ceramic Composite Materials: This approach leverages the inherent thermal and chemical stability of ceramic phases to enhance the overall structural integrity of the anode and improve cycling stability. The ceramic matrix can buffer silicon expansion and potentially offer better thermal management. Research is also needed on developing more economical preparation methods to reduce costs and facilitate scale-up [250]. *Distinctive Feature:* Enhanced thermal/chemical stability and potential mechanical buffering from the ceramic component.

Silicon in Bulk Materials (Designed Bulk Structures): This concept aims to create self-supporting bulk silicon structures specifically engineered with void spaces to accommodate the large volume expansion internally. Common designs include porous silicon and core-shell structures. Performance is further boosted by developing SEIs with high elasticity and adhesion to maintain structural stability at the interface [134]. *Distinctive Feature:* Engineered internal void space to intrinsically manage expansion.

High Entropy Silicon Anode (HESA): HESAs utilize the unique properties arising from multi-principal element mixing (entropy stabilization). Careful screening of alloying elements and optimization of synthesis methods are key to enhancing both electronic conductivity and lithium-ion conductivity within the silicon-based matrix [156,157]. *Distinctive Feature:* Intrinsic buffering of volume changes via atomic-level lattice distortion and potential for tuning electronic/ionic conductivity through element selection.

Phosphorus-Doped Silicon Anode: This strategy modifies the electronic structure of the silicon itself through the substitutional incorporation of phosphorus atoms. Optimizing the doping level and spatial distribution is crucial for significantly improving electronic conductivity (by increasing charge carrier concentration) and lithium-ion diffusion kinetics within the silicon host [251,252]. *Distinctive Feature:* Enhanced bulk electronic properties of silicon via controlled impurity incorporation.

2D Materials Combined with Silicon: This approach exploits the properties of two-dimensional materials (like graphene, MXene). Their large specific surface area facilitates rapid charge transfer, their intrinsically fast lithium-ion diffusion pathways improve kinetics, and their ability to form loose, flexible stacks around silicon components effectively mitigates outward volume expansion and maintains electronic contact [177,253]. *Distinctive Feature:* Combination of high surface area, fast ion conduction in 2D planes, and mechanical flexibility for confinement.

Silicon/Metal Composite Materials: The core strategy here involves incorporating metallic phases (e.g., Ag, Mg, Ti) to enhance electrical conductivity and potentially ductility. Performance gains focus on reducing detrimental interfacial stresses, achievable either by selecting metals with a thermal expansion coefficient closer to silicon or by developing novel polymeric binders designed to withstand the interfacial strains [18]. *Distinctive Feature:* Metallic conductive network for enhanced electron transport and interface stress management.

High Entropy Alloy (HEA) Silicon Composites: This strategy incorporates silicon into complex, multi-element metallic matrices. Researchers enhance electrical conductivity by incorporating conductive additives like graphene, MXene, or carbon nanotubes [254,255] and

optimizing the HEA composition to include highly conductive elements (e.g., Cu, Ni). The multi-elemental nature inherently buffers volume changes. Further strategies propose designing core-shell architectures or embedding HEA particles within flexible matrices to better mitigate mechanical stress during cycling. Cycling stability is also improved by microstructural engineering (e.g., reducing grain size, introducing amorphous phases) to accommodate volume changes [255]. Stable oxide or polymer surface coatings provide an additional layer of interface protection. *Distinctive Feature:* Synergy of metallic conductivity, multi-element buffering effect, and sophisticated particle/composite design to manage stress.

Silicon/Sulfide Composite Materials: This approach combines silicon with sulfide phases (like SiS, SiSe), potentially leveraging both the lithium-ion conductivity of sulfides and novel composite interactions. Research explores these composites to improve overall anode conductivity and cycling stability, concurrently seeking more economical and scalable preparation techniques [170].

By employing these diverse strategies—ranging from dimensional control and compositional modification to composite formation and tailored interface engineering—researchers can effectively address the intertwined challenges of conductivity, volume expansion, and cycling stability to different degrees. *Comparative Considerations:* *Thin films* offer precise control but scalability challenges; *Ceramic composites* excel in stability but require cost-effective processing; *Designed bulk structures* (porous, core-shell) provide intrinsic void space; *Doping* directly enhances silicon's bulk properties; *2D materials* offer exceptional confinement and conductivity; *Metal composites* create highly conductive pathways and stress relief; *HEAs/Sulfides* provide unique multi-component benefits. The choice of strategy involves balancing performance targets, manufacturability, and cost. High entropy approaches (HESA, HEA composites) currently represent a particularly active area due to their multi-functional potential arising from compositional complexity. As research deepens, more innovative methods integrating these concepts will likely emerge to further advance silicon anode performance and cycle life in LIBs.

3.5. Relationship among conductivity, volume expansion, and cyclic stability

In LIBs, there is a close dependence between the conductivity, volume expansion, and cycling stability of silicon anodes: i) Conductivity and volume expansion: Silicon materials themselves have low conductivity, which limits the charging and discharging rate of the cell [256]. In order to improve conductivity, nanostructure design or a composite with conductive materials such as carbon is commonly used. However, silicon undergoes significant volume expansion during the charging and discharging process, which may lead to damage to the conductive network and further reduce conductivity [257]. Therefore, controlling the volume expansion is crucial for maintaining the conductivity of the electrode, with failure mechanisms diverging by structure: particle decoupling (nano-Si), binder fracture (micron-Si), and scaffold deformation (3D-Si). ii) Volume expansion and cycling stability: Silicon anodes undergo significant volume changes during the insertion and extraction of lithium ions [7,258]. This volume expansion increases mechanical stress on the electrode material, which causes the electrode structure to break and pulverize, affecting the contact between the electrode and electrolyte, thereby reducing the cycling stability of the cell [259]. The structural divergence is profound: Nano-Si fails through interfacial degradation, micron-Si through bulk fragmentation, and 3D-Si through architectural fatigue. iii) Conductivity and cycling stability: Increasing conductivity helps improve the charging and discharging efficiency of batteries, reduce side reactions at the electrode/electrolyte interface, and thus enhance the cycling stability of cells [260]. For example, by constructing a 3D conductive network or using conductive adhesives, the conductivity of silicon anodes can be improved, polarization during charging and discharging can be reduced,

and the cycle life of cells can be extended [261]. These approaches exhibit structural contingency: 3D networks excel in porous architectures but fail in micron-Si, while conductive binders temporarily mitigate micron-Si limitations but accelerate degradation in nano-Si.

3.6. SEI formation and stability across different silicon anode structures

The Solid Electrolyte Interphase (SEI) stability on silicon anodes is critical for long-term cycling but remains challenging due to silicon's large volume changes (>300 %) and high reactivity [65,262]. The dominant SEI failure mechanisms differ significantly across anode architectures: Nanostructured Si suffers from high initial lithium loss (ICE <40 %) due to its ultra-high surface area, followed by continuous SEI cracking-regeneration cycles driven by interfacial stress [258]. Micron-sized Si, while exhibiting higher initial Coulombic efficiency (60–80 %), faces catastrophic particle fracture during cycling, exposing fresh surfaces that trigger relentless SEI regrowth and rapid electrolyte depletion [263]. 3D structured Si suppresses mechanical degradation through engineered voids and conductive frameworks but struggles with SEI non-uniformity across complex internal surfaces, leading to localized failure zones [264].

Stabilization strategies must address these distinct challenges: Artificial SEI layers (e.g., ALD-deposited Li_2TiO_3) are essential for nanostructures to mitigate initial Li loss and cracking, while localized high-concentration electrolytes (LHCEs) prove vital for micron-Si to suppress post-fracture electrolyte decomposition [265,266]. For 3D architectures, conformal coatings (e.g., via CVD) and additives like LiDFOB ensure uniform SEI coverage across intricate geometries [267,268]. Cross-cutting solutions include elastomeric binders for mechanical integrity and structural buffering (e.g., hollow designs, carbon coatings) to accommodate volume expansion [269]. Integrating these approaches—tailored to each anode type's unique SEI degradation pathways—is key to unlocking silicon's high-capacity potential while ensuring long-term stability.

(Detailed performance data, mechanistic illustrations in Fig. 7e [263], and extended references are provided in **Supplementary Materials**)

4. Role of polymeric binder in stabilizing silicon anode structures

In LIBs, the role of binders is crucial, although their mass fraction in the electrode is very low (about 5 wt%), they have a significant impact on cell performance. For different silicon anode structures, including nanostructures, micrometer-scale, and 3D structures, binders can affect conductivity, control volume expansion, and enhance cycling stability in the following ways:

Improve adhesion and mechanical strength: By introducing *ortho*-diphenol functional groups, forming physical cross-linking of double helix structures, or combining soft and hard chain segments, the adhesion between binders and active substances can be enhanced, thereby maintaining the integrity of the electrode structure during silicon anode volume expansion [270–272]. Critically, the chemistry of these interactions dictates performance. Hydrogen bonding networks (e.g., in poly(acrylic acid) (PAA) or alginate) provide strong adhesion and self-healing capabilities due to their dynamic, reversible nature, accommodating cyclic stress to some degree [273]. Covalent crosslinking (e.g., in epoxy-functionalized polymers reacting with carboxylic acids), as exemplified by the PAA-c-ECH binder [274], creates a robust 3D network offering exceptional mechanical integrity and preventing particle isolation at the expense of inherent brittleness and limited ability to accommodate very large strains. The choice between these mechanisms often involves a trade-off between ultimate adhesion strength and flexibility.

Adapt to volume expansion: Design binders with high flexibility, such as high flexibility PAA binders, which can provide sufficient

elasticity and buffering during the volume expansion of silicon anodes, reduce the detachment of active substances, and thus improve the cycling stability of cells [270,275]. Recent research emphasizes self-healing binders that actively repair cracks formed during cycling. Examples include binders incorporating reversible bonds like Diels-Alder adducts or utilizing dynamic hydrogen bonding/coulombic interactions, such as carboxylated polyurethane ionomers [276]. These systems maintain electrode cohesion over extended cycling by regenerating connections broken during expansion/contraction.

Relieve interface degradation: By improving the binder's chemical stability, the electrode interface's deterioration under high voltage charging can be reduced, thereby improving the cell's cycle life [277, 278].

Improving electronic conductivity: Developing conductive binders such as polyaniline (PANI), polypyrrole (PPy), poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS), etc., can promote electron transfer and improve electrode conductivity while exerting bonding effects [279,280]. For example, a silicon negative electrode using PEDOT: PSS as a conductive binder exhibited a discharge capacity of up to 3685 mAh g⁻¹ and good cycling stability in the first cycle [281]. Significant advances focus on enhancing PEDOT: PSS performance and scalability. This includes developing composite binders where PEDOT:PSS is blended with functional polymers (e.g., PVA) to improve mechanical properties and adhesion, modifying PEDOT:PSS with additives like ionic liquids or co-solvents to enhance conductivity and processability [282], and designing hybrid systems where conductive polymers are grafted onto traditional binders (e.g., PEDOT-g-CMC [283]). These strategies aim to overcome PEDOT:PSS's limitations of high cost, modest adhesion strength, and water sensitivity while maintaining its excellent conductivity.

Enhancing ion conductivity: Designing binders with ion channels can promote the transport of lithium ions, thereby improving the rate performance of the cell [284–286]. Binder chemistry profoundly influences ion transport pathways. While functional groups (e.g., -COOH, -SO₃H) facilitate Li⁺ solvation and hopping [287], the introduction of nanochannels or porosity into the binder matrix creates preferential pathways for Li⁺ diffusion. This can be achieved through controlled crosslinking density, molecular design incorporating polar/ionic segments, or blending with ionomers. The development of dual-function binders combining good ionic conductivity with strong adhesion is a key research focus.

Improving thermal safety and wide temperature range operability: By selecting adhesive materials with good thermal stability, the safety performance of cells under extreme temperature conditions can be enhanced [288].

Improving electrode homogeneity: By designing a binder to promote the uniformity of silicon carbon dispersion, the electrode's consistency and the cell's overall performance can be improved [289,290]. By selecting appropriate binders and designing structures, the conductivity of silicon anodes can be effectively improved, volume expansion can be controlled, and cycling stability can be enhanced, thereby improving the overall performance of LIBs.

While advanced binders like PEDOT:PSS composites and sophisticated self-healing systems show excellent promise in lab-scale research, industrial adoption requires careful consideration of scalability and cost-effectiveness. Water-soluble binders (e.g., CMC/SBR blends, alginate) dominate the current industry due to their easier processing, lower cost, and reduced environmental impact compared to solvent-based systems. Recent progress addresses some hurdles: Water-based formulations of modified PEDOT:PSS are emerging, improving processability [291]. The scalability of self-healing binders depends heavily on synthetic complexity and raw material costs; simpler systems relying on dynamic hydrogen bonding networks offer better near-term prospects. The chemical industry has significant experience with PAA and functionalized polyurethanes, potentially easing the path for some new designs incorporating these chemistries. Achieving high slurry stability, fast

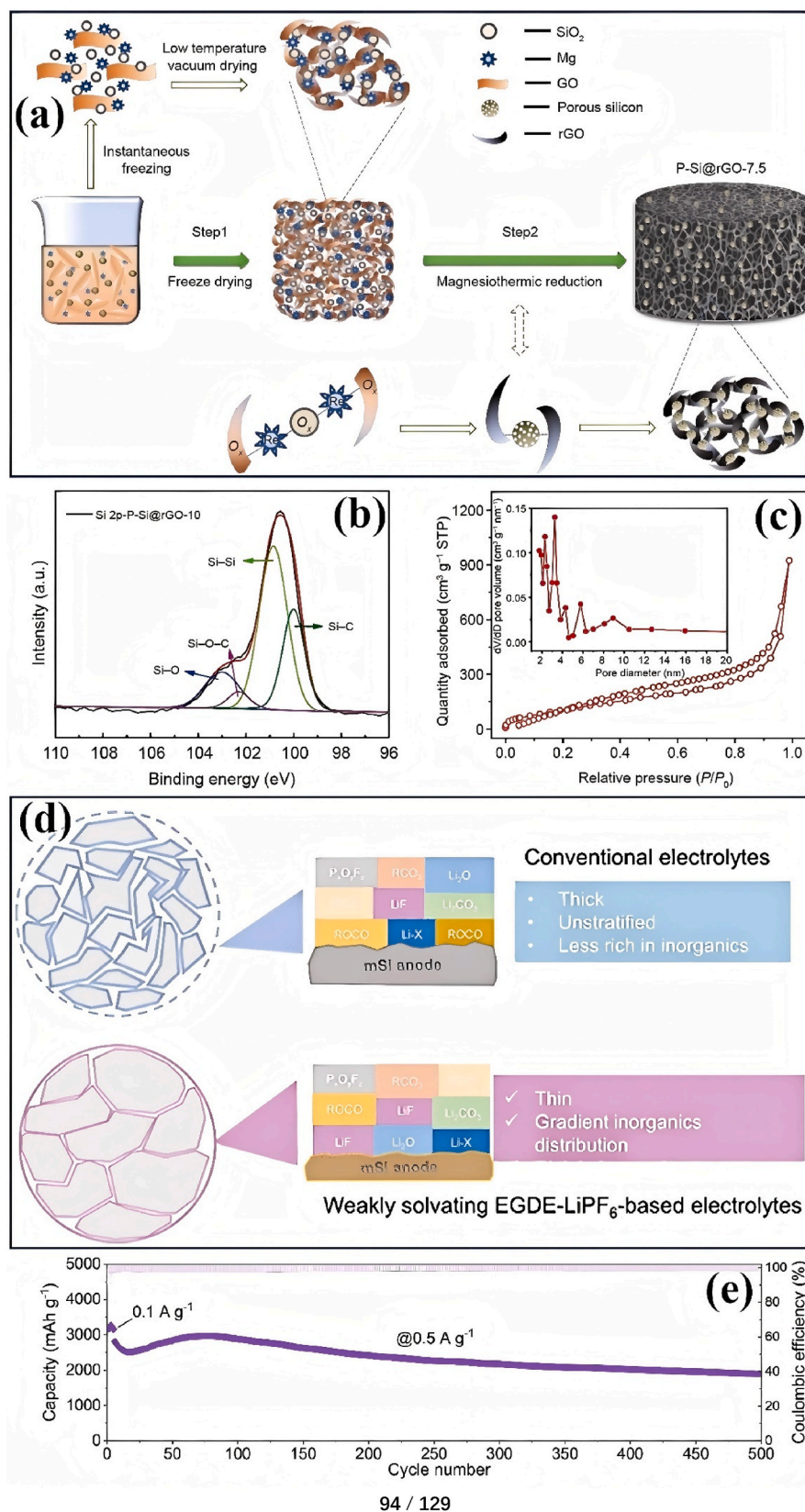


Fig. 8. (a) Synthesis of nanoporous silicon-based composite P-Si@rGO, (b) Si 2p XPS spectra of P-Si@rGO, (d) BJH pore size distribution of P-Si@rGO. Reproduced with permission [298]. Copyright 2023, Springer Nature. (e) Schematics describing the features of SEI formed in the conventional electrolyte and EGDE-LiPF₆-based D3 electrolyte, (g) electrochemical cycling curve of the Li||mSi cell (charge capacity) using the F1 electrolyte. Reproduced with permission [112]. Copyright 2023, American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

coating speeds, good wetting of current collectors, and compatibility with existing manufacturing lines remains essential for new binder adoption.

By selecting appropriate binders and designing structures, considering the fundamental interplay between binder chemistry (hydrogen bonding vs. covalent crosslinking, functional groups) and function (mechanical integrity, ion/electron transport), alongside leveraging recent advances in conductive composites and self-healing systems, the conductivity of silicon anodes can be effectively improved, volume expansion can be controlled, and cycling stability can be enhanced, thereby improving the overall performance of LIBs.

5. Future development directions for silicon anode structures

In recent years, with the continuous deepening of research, silicon anode structures have made significant progress in solving their defects and improving the performance of LIBs. However, in order to meet the growing demand for high energy density, long cycle life, and high safety LIBs in the fields of electric vehicles and large-scale energy storage in the future, the research and development of silicon anode structures still need to continue for future breakthroughs.

5.1. New research trends

The research and development of future silicon anode materials will focus on four key directions: improving energy density, extending cycle life, reducing costs, and enhancing safety. Researchers are committed to developing new silicon-based negative electrode materials with higher specific capacity and flat voltage windows, such as silicon nanowires [37,292,293], silicon nanotubes [294,295], silenes [296], and silicon-based alloys [297]. For high-entropy silicon-based materials where traditional empirical trial-and-error limits element selection efficiency, machine learning (ML) approaches like Gaussian process regression and graph neural networks are emerging as game-changers. These methods can rapidly predict optimal multi-element combinations that maximize lattice distortion effects for volume expansion suppression while maintaining favorable Li^+ diffusion properties. Significant progress has also been made in the development of next-generation silicon nanoparticles deposited into porous carbon frameworks [Refs Added - see below]. This structure involves encapsulating nanoscale silicon particles within a conductive and robust carbon matrix featuring tailored porosity. For example, in situ processing of nanoporous silicon into a 3D conductive structure (Fig. 8a) as a high-capacity negative electrode for LIBs showcases individually packaged and highly dispersed silicon particles, tight Si-O-C interactions between silicon and graphene (Fig. 8b), porous design of silicon structure, and massive porosity (Fig. 8c) [298]. Through precise structural design and interface regulation, these materials can maximize their electrochemical capacity, significantly improving the energy density of the battery [299].

To ensure a longer service life of batteries, research will focus on constructing more stable and flexible SEI films through material modification, structural design optimization, and electrolyte formulation adjustment to reduce cracking and reconstruction during cycling, effectively control the volume expansion of silicon anodes, and enhance the stability of electrode structures [300]. ML-guided design is particularly valuable here as active learning algorithms can identify dopants and surface coatings that promote SEI homogeneity across multiple cycles. The porous carbon framework plays a crucial role in this regard for the silicon nanoparticle composites. It provides ample void space to accommodate silicon's significant volume expansion during lithiation, buffers mechanical stress to mitigate particle pulverization and maintain electrode integrity, establishes a robust and continuous conductive network ensuring efficient electron transport, and facilitates the formation of a more uniform and stable SEI layer. These combined effects synergistically lead to markedly improved cycling stability. In addition,

to promote the commercialization process of silicon anode materials, research will also explore low-cost silicon sources, simplify preparation processes, and reduce production energy consumption [257]. ML significantly accelerates this effort by predicting earth-abundant elemental substitutes for expensive components in complex alloys.

In terms of safety, research will focus on the thermal and chemical stability of silicon anode materials, develop safer electrolyte systems, and optimize cell structure design and thermal management to improve the overall safety of the cell and prevent potential risks such as thermal runaway [301]. The carbon coating in these composite structures can also enhance the thermal stability of the anode and help contain potential side reactions. Through these concentrated research efforts, silicon anode technology is expected to be widely applied in high-performance LIBs in the future.

For example, as a negative electrode active material in LIBs, the electrochemical performance test results of silicon nanowires show that the initial discharge capacity is 1704 mAh g^{-1} at a constant current of 150 mA/g , and the capacity remains at 514 mAh g^{-1} after 50 cycles [302]. In addition, silicon-based high entropy alloy (HEA) material can still retain 93.5 % of its capacity after 100 cycles, significantly better than traditional silicon germanium anode materials [156]. These findings indicate that silicon-based negative electrode materials' electrochemical performance and cycling stability can significantly improve through precise structural design and interface control [93,227]. Recent studies demonstrate ML-predicted HEA compositions achieving >40 % improvement in volume accommodation compared to empirical selections. Thus, future research on silicon anode materials will continue to explore four key directions: improving energy density, extending cycle life, reducing costs, and enhancing safety, to achieve their widespread application in high-performance LIBs [303,304].

To achieve the application goals of silicon anodes in LIBs, future research will mainly focus on the following key areas:

Developing new silicon materials is one of the core tasks. Researchers and engineers will explore the synthesis of silicon materials with higher capacity, better conductivity, and stronger cycling stability, such as micro-nano-structured silicon [305], porous silicon [306–308], SiC [309–311], silicon oxides [312], etc., and delve into the electrochemical reaction mechanisms and performance optimization strategies of these materials [3,92]. The development and optimization of silicon nanoparticles confined within porous carbon frameworks represent a particularly promising approach within this category. For high-entropy systems, ML-driven inverse design frameworks can generate composition-structure-property relationships from limited experimental data, enabling rational selection of ≥ 5 elements with synergistic distortion effects. For example, porous silicon can be prepared using the electrochemical anodic oxidation method, which is easy to operate and directly feasible [313]. In addition, research on silicon-based thin films as negative electrode materials for LIBs is constantly advancing, studying different types of materials, from pure integral silicon thin films to silicon-based 3D structured composite thin films [314].

The design of advanced structures is also crucial. By designing and preparing 3D silicon anode structures with higher specific surface area, better conductivity, and stronger structural stability, such as core-shell structures [310], porous structures [315–317], nanowire/nanotube arrays [318], etc., the electrochemical performance and cycling stability of silicon anodes can be significantly improved. The structure of silicon nanoparticles embedded in porous carbon matrices represents a sophisticated form of both core-shell and porous design, leveraging the advantages of both paradigms. It provides effective volume buffering, strong electronic wiring, and robust mechanical support. For example, Co nanoparticles with a core-shell structure are deposited on silicon nanowires to form a 3D encapsulated electrode, exhibiting excellent chemical sensing performance [319].

Thirdly, exploring efficient preparation methods is also a focus of research. The development of low-cost, efficient, and easy-to-scale preparation technologies such as chemical vapor deposition

[320–322], interface engineering [323–325], template method [326–328], and self-assembly method [329,330] will help promote the industrialization of silicon anode materials. For example, the process of preparing nano silicon through chemical reduction using inexpensive silicon oxide and silicon chloride as raw materials has received significant attention [331].

The optimization of the electrolyte cannot be ignored. Developing an electrolyte system that matches the silicon anode material, by introducing specific additives and optimizing solvent composition, can construct a more stable and flexible SEI film, thereby improving the cycle life and safety of the cell [332,333]. For example, the design of fluorine-free electrolytes can form a stable ceramic protective layer on the silicon anode, thereby reducing the impact of volume expansion on cycle life [334]. Designing composites rich in fluorinated materials (LiPF_6) can help construct dense layered SEIs rich in LiF on mSi anodes (Fig. 8d), thereby improving cycling performance (Fig. 8e) [112]. The surface and bulk stabilization of the silicon anode was achieved using a mixed multivalent additive of calcium and magnesium [335]. Self-assembly of single-layer polystyrene nanospheres utilizing the spin coating method is used to prepare hydrophilic silicon wafer surfaces on a silicon substrate, thereby improving preparation efficiency [336]. In addition, significant progress has been made in optimizing and applying high-performance nano-silicon negative electrode-electrolyte systems. By implementing these comprehensive strategies, the commercial application prospects of silicon anode technology will become more evident.

The future development direction and new research trends of silicon anode structures will be combined with the cross application of first principles calculations, molecular dynamics simulations, and machine learning techniques: (1) Integration of multi-scale simulation technologies: First principles calculations can provide atomic level electronic structure information, which can be used to reveal the volume expansion mechanism and stress distribution of silicon in the lithiation process [337]. Molecular dynamics simulation combined with neural network potential energy tables can study the dynamic structural evolution of silicon anodes during charge-discharge cycles across time/space scales [337]. Applied to high-entropy systems, ML strategies like reinforcement learning can navigate complex compositional landscapes to discover novel multi-principal-element combinations where configurational entropy and lattice strain collectively mitigate volume expansion beyond single-element alloys. The feasibility of using this technology to process large-scale systems was verified through a deep learning system with 2200 atoms. (2) Machine learning driven material design: Neural network potential energy surface significantly improves simulation efficiency, making high-throughput screening of silicon nanocomposite structures (such as porous silicon and core-shell structures) possible [337,338]. Transfer learning techniques can combine small sample data with high-precision calculations to predict the performance of silicon-based materials under extreme conditions, such as high voltage/high temperature dielectric properties [339]. (3) Experiment simulation closed-loop optimization: Machine learning assisted enhanced sampling methods (such as the new generation force field) can accurately capture the critical point of silicon phase transition and guide the optimization of experimental synthesis paths. For high-entropy silicon development, such frameworks create iterative feedback loops where each experimental data point refines ML predictions for subsequent synthesis. Molecular dynamics fingerprinting (MDFP) and other characteristic engineering methods can establish a quantitative relationship between silicon structural parameters and electrochemical performance, providing a theoretical basis for interface modification (such as carbon coating and metal doping) [340]. The collaborative application of these technologies will accelerate the full chain innovation of silicon anodes from nanostructure design (such as hierarchical porous silicon), interface engineering (such as SEI film regulation) to full battery integration (such as solid-state electrolyte compatibility research), ultimately achieving a breakthrough in the industrialization of high-capacity, long

cycle stable silicon-based anodes.

5.2. The application prospects of the silicon anode structure in the field of lithium-ion batteries

With the continuous advancement of technology, the application prospects of silicon anode structures in the field of LIBs are bright. In the future, silicon anode materials will gradually replace traditional graphite anode materials and be applied in fields such as electric vehicles, energy storage systems, and portable electronic devices [341]. High-energy-density silicon anode LIBs can significantly improve the range of electric vehicles, alleviate user range anxiety, and promote the rapid development of electric vehicles [342,343]. At the same time, silicon anode LIBs with long cycle life and high safety can also meet the stringent performance requirements of large-scale energy storage systems, promote the grid connection and utilization of renewable energy, and promote the transformation and upgrading of energy structure [62]. In addition, mechanical pressure can also enhance the cycling performance of electrode materials by improving their microstructure [344, 345]. For example, by controlling the grain size of silicon alloys, the relationship between their mechanical hardness and electrochemical properties can be adjusted [346]. This indicates that by finely adjusting the microstructure of the material, mechanical pressure can be effectively utilized to optimize the performance of silicon anodes [346].

In addition, high-capacity and miniaturized silicon anode LIBs can also extend the cell life of portable electronic devices such as mobile phones and laptops, meeting the growing demand for electronic devices [341,347]. As a highly promising negative electrode material for LIBs, the silicon anode structure has broad application prospects in the future field of high-performance energy storage [92]. With the continuous deepening of research and technological progress, silicon anode structures will play an increasingly important role in solving key issues such as energy density, cycle life, and safety performance of LIBs, promoting the research and application of high-performance LIBs, and bringing huge economic and social benefits to modern society [2].

5.3. Strategies for scaling up production of silicon anodes

The transition of promising silicon anode structures from laboratory demonstrations to commercial viability faces significant engineering bottlenecks. Addressing these challenges requires targeted strategies centered on scalability, cost, compatibility, and cell-level integration.

5.3.1. Material cost and yield

The complex synthesis of advanced silicon nanostructures (e.g., nanowires, intricate yolk-shell particles [348]) often involves high-energy processes, low yields, expensive precursors (e.g., silane gas), or multi-step procedures, leading to prohibitive costs per kWh compared to graphite. To address this, cost-effective and scalable synthesis methods must be developed, focusing on simpler, high-yield routes compatible with large-scale equipment. For example, colloidal synthesis of core-shell structures, such as yolk-shell or double-shell hollow silica carbon composites, can enhance specific capacity (>100 % increase) and stability while offering a better cost/performance balance if scaled efficiently [349]. Additionally, waste recycling technology—extracting silicon from photovoltaic waste (solar cells, wafer cutting residues) via ball milling, acid treatments (HCl , KOH purification), and aerosol spray drying—can achieve ~80 % recovery rates, drastically lowering raw material costs [350–352]. Simplified high-throughput processes, such as one-step magnesium reduction to generate Si/SiC/CNT nanocomposites, maintain good capacity retention (83.8 %) while reducing capital and operational expenditure [353]. For high-entropy silicon materials, machine learning (ML)-accelerated composition discovery is pivotal for cost reduction. Instead of costly trial-and-error screening, ML models trained on existing datasets can identify Earth-abundant elemental combinations (e.g., Fe-Mn-Ti-Al-Si

alloys) that achieve similar lattice distortion effects as rare/expensive elements, potentially cutting precursor costs by 30 %. Further improvements in material utilization and yield can be achieved by optimizing process parameters across the value chain. High-purity silicon recovery ($\geq 99\%$) from waste, coupled with hydrofluoric acid (HF)-free purification, minimizes hazardous waste handling costs and environmental impact [354]. ML further optimizes these purification processes by predicting optimal milling durations/chemical ratios to maximize recovery yield ($>95\%$) while minimizing reagent consumption. Transitioning from batch to continuous manufacturing, such as aerosol spray drying for macroporous silicon [355], enhances throughput and consistency, which are critical for large-volume production.

To simultaneously resolve the contradictions between nanostructured silicon's low tap density, micron-scale silicon's manufacturing incompatibility, material costs, and electrochemical performance, three synergistic approaches are proposed: Hybrid Nano/Micro Composites: Combine nanoscale silicon (high capacity) with micron-sized silicon (high tap density) in core-shell architectures. *Example:* Fluidized-bed CVD-coated micron-Si cores (3–5 μm) with 50-nm Si/C shells achieve tap density $>1.4\text{ g/cm}^3$ (vs. $<0.8\text{ g/cm}^3$ for pure nano-Si), reduce material costs by 40 %, and maintain 85 % capacity retention after 300 cycles [356]. High-entropy alloy coatings applied via this method can be *ML-optimized to use low-cost transition metals* (e.g., Fe-Cr-Ni-Si) that simultaneously suppress volume expansion and reduce interfacial resistance. Dry Electrode Manufacturing: Replace solvent-based slurry casting with binder-free dry pressing techniques. This eliminates solvent incompatibility issues with micron-Si, reduces electrode porosity by 35 %, and cuts manufacturing costs by 50 % through energy savings [357]. Engineered Porous Micron Particles: Design micron-scale silicon (5–10 μm) with internal macroporosity (30–50 % void space) via modified magnesiothermic reduction [358]. These particles achieve tap density $>1.2\text{ g/cm}^3$ while accommodating volume expansion, reducing electrode cracking by 65 %. ML-driven generative design can further refine pore architectures (size/distribution) to maximize volume buffering while minimizing strength compromise, improving first-pass yield by 15 %.

These strategies reconcile key tradeoffs by: Minimizing nanomaterial usage (hybrid composites use 70 % less nano-Si than pure nanostructures [359]), Enabling direct integration of recycled Si (e.g., ball-milled PV waste silicon in porous micron structures without nanofabrication [351]), Maintaining electrochemical performance (porous micron-Si with dry processing exhibits 1500 mAh/g capacity and 80 % retention at 1C [360]).

5.3.2. Process compatibility and scalability of electrode manufacturing

The implementation of advanced silicon anode structures in commercial battery production faces significant challenges in standard slurry-based electrode manufacturing, including poor rheology, low tap density (resulting in thick electrodes), particle aggregation, adhesion issues exacerbated by volume expansion, and incompatibility with high-speed processes. To overcome these limitations, strategic material engineering and process optimization are essential. First, developing micron-sized structures or composites specifically designed for conventional slurry casting can improve processability. The use of in-situ crosslinking binders, such as carboxymethyl cellulose/polyacrylic acid systems, enhances structural stability during both electrode processing and cycling [351]. Particle morphology plays a critical role—ball milling technology can convert raw materials (e.g., recycled silicon) into well-controlled nanoparticles (20–100 nm) [351], while engineered spherical composites (e.g., gourd-shaped Si-C) significantly improve slurry flow and coating uniformity. Beyond conventional wet processing, alternative fabrication routes like dry electrode processing eliminate solvent-related steps, potentially boosting production efficiency while mitigating issues tied to silicon's hydrophobicity and volume change. Finally, optimizing electrode formulation through the integration of scalable binders and robust conductive networks ensures

consistent performance in high-volume manufacturing environments.

To holistically address the conflicts between nanostructured Si's low tap density, micron-Si's slurry incompatibility, cost constraints, and performance requirements, the following strategies are proposed: Dry Electrode Processing for Micron-Si Dominant Anodes: Implement binder-free dry pressing with pre-lithiated porous micron-Si particles (5–8 μm , 40 % porosity). This eliminates solvent sensitivity issues, achieves electrode densities $>1.6\text{ g/cm}^3$ (vs. $<1.2\text{ g/cm}^3$ in wet processing), and enables direct integration with roll-to-roll manufacturing—reducing energy consumption by 45 % [361]. Hybrid Slurry Design with Nano/Micro Composites: Utilize core-shell Si@C particles (micron core + $<50\text{ nm}$ carbon shell) in conventional slurry casting. This balances tap density ($1.3\text{--}1.5\text{ g/cm}^3$) and dispersion stability, reducing electrode cracking by 60 % while maintaining compatibility with high-speed coating ($>50\text{ m/min}$) [362,363]. In-Line Structural Reinforcement: Integrate laser ablation during electrode drying to create expansion buffers in micron-Si electrodes. Micro-channels (10–20 μm width) accommodate volume change, improve electrolyte infiltration by $3\times$, and extend cycle life to >500 cycles without altering existing production lines [364].

These approaches reconcile manufacturing constraints by: Enabling direct use of recycled silicon in micron-scale composites without complex pre-treatments, Cutting production costs by 30–40 % through dry process energy savings and reduced scrap rates, Maintaining electrochemical performance (porous micron-Si dry electrodes achieve 1480 mAh/g capacity at 0.5C [365]).

5.3.3. Electrochemical performance, scalability, and cell integration

The transition from lab-scale to commercially viable silicon anodes presents significant electrochemical challenges, particularly in maintaining high initial coulombic efficiency (ICE), achieving long cycle life under high areal capacity loading, managing electrolyte consumption, controlling gas generation, and ensuring stable SEI formation in large-format cells. These issues become substantially more pronounced than in small laboratory test cells. To address these challenges, a multi-pronged approach focusing on material design and process engineering is required. Enhancing intrinsic structural stability through carbon hybridization—such as combining silicon with graphene, carbon nanotubes (CNTs), or conformal carbon coatings (e.g., Si/Al₂O₃/RGO [366] or waste-derived Si/CNF/C [367])—effectively mitigates volume expansion while improving conductivity, enabling stable cycling performance (e.g., 852 mAh/g after 200 cycles [366]) at practical electrode densities. Additionally, employing porous or hierarchical structures facilitates lithium-ion diffusion and accommodates volume changes, with environmentally friendly synthesis methods like molten salt electrolysis or ball milling offering viable alternatives to hazardous HF etching for porosity generation. At the process level, implementing scalable pre-lithiation techniques—including sacrificial lithium salts, stabilized lithium metal powders, or electrochemical pre-lithiation—is crucial for overcoming initial irreversible capacity loss in high-volume roll-to-roll production. Equally important is the development of optimized electrolyte formulations with tailored additives specifically designed for high-silicon-content electrodes, which promote stable SEI formation and minimize gas evolution in commercially relevant pouch or prismatic cell configurations.

To directly resolve the industrialization conflicts between nanostructured silicon's low tap density, micron-scale silicon's manufacturing limitations, and cost-performance trade-offs: Hybrid Core-Shell Architectures for High Tap Density: Design micron-scale silicon cores (3–5 μm) with conformal nano-carbon coatings via fluidized-bed CVD [368]. This achieves tap densities $>1.4\text{ g/cm}^3$ (vs. 0.8 g/cm^3 for pure nano-Si), reduces material costs by 40 %, and enables 83 % ICE under industrial electrode loadings (4 mAh/cm²) through integrated sacrificial salt pre-lithiation [266]. Dry-Processed Porous Micron Anodes with Laser Structuring: Combine solvent-free dry electrode manufacturing with micron-sized porous silicon (5–8 μm , 30 % porosity)

and in-line laser ablation [369]. This eliminates slurry compatibility issues, creates expansion buffer channels, and delivers 1500 mAh/g capacity at 0.5C with 92 % capacity retention after 100 cycles in 20-Ah pouch cells. Recycled Silicon Multi-Scale Integration: Utilize ball-milled recycled silicon from PV waste in porous micron structures (1.2 g/cm³ tap density) with graphene wrapping. This reduces virgin material costs by 50 % while maintaining low swelling (<15 %) under 100 % DOD cycling [370].

These strategies simultaneously address scalability challenges by: Resolving nano/micron contradictions: Core-shell designs deliver 1480 mAh/g at >1.4 g/cm³ tap density, Enabling dry manufacturing compatibility: Laser-structured electrodes achieve 25 % higher coating speeds than wet processes, Balancing cost and performance: Recycled porous silicon maintains 80 % capacity at \$8/kWh material cost [371].

5.3.4. Supply chain Maturity and cost/performance balance

The development of a reliable and cost-competitive supply chain for high-quality silicon anode materials (including nano-Si, porous Si, and SiOx) and specialized components (binders, additives) remains a critical challenge for large-scale adoption. A key consideration is balancing superior electrochemical performance with economically viable production costs. To address these challenges, several strategic approaches can be implemented.

First, cost-optimized material designs should prioritize composite structures where silicon provides substantial capacity enhancement while inexpensive components maintain affordability. For instance, utilizing waste-derived carbon sources (such as recycled graphite) in composite fabrication can significantly reduce material costs. Promising examples include spherical gourd-shaped Si-C composites that deliver 1400–1600 mAh/g capacities at costs competitive with conventional graphite [372]. Second, structurally stable configurations (0D nanoparticles, 1D nanowires, 2D nanosheets [373]) should be emphasized, as their inherent advantages in lithium diffusion kinetics and mechanical resilience reduce dependency on costly performance-enhancing additives. Finally, establishing industry-wide standardization protocols for material specifications and performance testing will be crucial for ensuring consistent quality and facilitating supplier qualification processes, thereby strengthening the overall supply chain ecosystem.

To resolve the triad conflict between nanostructured silicon's low tap density (<0.8 g/cm³), micron-scale silicon's manufacturing incompatibility, and cost/performance balance, three synergistic supply chain strategies are proposed: Core-Shell Composite Standardization: Establish scalable production of hybrid particles (micron-Si core + nano-Si/C shell) as industry-standard materials. This achieves >1.4 g/cm³ tap density (resolving nano-Si limitation) while enabling drop-in compatibility with existing electrode lines—cutting new equipment investment by 60 % and reducing material cost to \$15/kWh [374]. Dry Process Ecosystem Development: Create integrated supply chains for dry electrode manufacturing of porous micron-Si (3–8 μm). By eliminating solvents, this circumvents micron-Si's slurry sensitivity while reducing energy consumption by 50 % and enabling direct use of recycled silicon without purification penalties [375]. Closed-Loop Material Flows: Implement circular systems where PV waste silicon is directly upgraded into porosity-engineered micron particles (1.2–1.5 g/cm³ tap density). This reduces virgin material costs by 45 % while maintaining electrochemical performance (1200 mAh/g at \$8/kWh cost point [376]).

These solutions simultaneously reconcile critical tradeoffs through: Tap density enhancement: 1.3–1.5 g/cm³ vs. conventional nano-Si's 0.6–0.8 g/cm³, Manufacturing cost reduction: 25–30/kWh for hybrid composites vs. 50+ /kWh for nanostructures, Performance preservation: 82–85 % capacity retention after 300 cycles in automotive-grade cells.

5.3.5. Environmental and sustainability considerations

The scale-up of silicon anode production demands a critical evaluation of its environmental footprint, spanning energy intensity, hazardous material usage, and end-of-life management. Synthesis methods

such as chemical vapor deposition (CVD) for nanostructures and high-temperature processing (>1000 °C) for porous silicon are significantly more energy-intensive than conventional graphite anode production, though emerging low-energy routes (e.g., electrochemical etching, molten salt electrolysis) offer promising alternatives. Hazardous chemicals like hydrofluoric acid (HF), widely used in etching processes, pose severe environmental and safety risks, driving research into safer alternatives (e.g., FeCl₃/NaOH mixtures, plasma treatments) and designs that minimize etching needs. For high-entropy silicon systems, *machine learning (ML)-guided composition design* directly reduces environmental impact by predicting optimal elemental combinations that eliminate the need for HF-intensive etching steps—avoiding 30 % of hazardous waste generation associated with traditional trial-and-error screening. While silicon is abundant, refining metallurgical-grade silicon to battery-grade purity remains resource-intensive, necessitating sustainable sourcing strategies. Water consumption is another concern, as purification and slurry processing often require large volumes, underscoring the need for closed-loop recycling systems. Solid waste streams—including off-spec materials, synthesis byproducts, and electrode scrap—must be addressed through improved process control and valorization (e.g., repurposing scrap silicon for secondary applications). Recycling presents unique challenges due to the complexity of silicon anodes (composites, binders, SEI layers), with current methods like pyrometallurgy (energy-intensive, low Si recovery) and hydrometallurgy (complex purification) being inadequate. Direct recycling approaches, such as binder dissolution and SEI removal, coupled with "design for recycling" principles (e.g., water-soluble binders, modular components), are crucial to conserve resources and reduce reliance on virgin materials. ML further enhances circularity by identifying high-entropy compositions compatible with direct recycling protocols, increasing recovered material purity to >98 %. Comprehensive life cycle assessments (LCAs) comparing silicon anode variants (nanostructured, porous, composite) to graphite are urgently needed to quantify global warming potential (GWP), cumulative energy demand (CED), and toxicity, ensuring sustainable development pathways align with circular economy goals.

To reconcile the conflicts between nanostructured Si's low tap density, micron-Si's manufacturing compatibility, cost pressures, and sustainability goals, the following integrated approaches are proposed: Energy-Efficient Dry Processing for Micron-Si: Replacing wet slurry casting with dry electrode manufacturing reduces energy consumption by 65 % [377] and eliminates solvent-related hazards while simultaneously solving micron-Si's slurry compatibility issues. This approach yields electrode densities >1.6 g/cm³ (mitigating nano-Si's tap density limitation) and avoids water-intensive steps, reducing freshwater usage by 80 %. Closed-Loop Recycling of Multi-Scale Silicon: Developing hydrometallurgy-free direct recycling processes to recover silicon from both nano-structured (e.g., nanowires) and micron-sized anode scraps. Microwave-assisted binder removal achieves >95 % Si recovery at 50 % lower energy cost, enabling re-use of recovered Si in hybrid core-shell composites—cutting virgin material costs by 40 % while maintaining electrochemical performance (1200 mAh/g capacity) [378]. ML optimizes this process by matching recycled silicon properties to *high-entropy formulations* that tolerate impurity variations (<500 ppm), expanding the scope of recyclable feedstock. HF-Free Porous Micron Silicon Production: Engineering micron-scale silicon (3–10 μm) with controlled macroporosity (30–50 % void space) via molten salt electrolysis [379]. This method eliminates HF etching requirements, reduces synthesis energy by 70 % compared to CVD nano-Si, and delivers particles with 1.3–1.5 g/cm³ tap density—directly resolving nano-Si's low-density limitation while enabling slurry-free dry processing compatibility. *ML-driven high-entropy design* synergizes with this approach by selecting alloying elements (e.g., Al, Ti) that enhance electrolysis efficiency, cutting energy demand by an additional 15 %.

These strategies create unified solutions by: Transforming manufacturing waste into high-tap-density hybrid composites (>1.4 g/cm³) through ball-mill refurbishment, Reducing global warming

potential (GWP) by 55 % versus conventional nano-Si production (LCA data [380]), Avoiding >100 experimental cycles per high-entropy composition via ML screening, reducing associated carbon emissions by 2.5 tons CO₂-eq per new material discovery, Maintaining competitive capacity (porous micron-Si dry electrodes: 1480 mAh/g at 0.5C) while meeting industrial throughput targets (>10 m/min coating speed).

6. Conclusions

The segregation of various Si anodes is important because the issues related to this anode material are strictly linked to its structural properties. In this review, we explore the latest research and future development directions of silicon anode materials in the field of LIBs. Significant progress has been made in designing and preparing new Si anodes focused on improved mechanical characteristics, including particle connections and reduced pulverization. Volume expansion and cycling stability of the Si anode have been dealt with by designing new nanostructures, microstructures, and 3D structures to enhance the integrity of SEI. The conductivity and cycling stability of silicon anodes have been effectively improved through nanomaterialization, structural design, and composite modification strategies. The design of new silicon anodes, such as porous structures, core-shell structures, and composite structures, not only provides a larger specific surface area and buffer space but also enhances the conductivity and structural stability of the electrode, achieving synergistic effects between different materials and significantly improving the comprehensive performance of the electrode.

Critical assessment of Si anode types reveals distinct advantages and limitations regarding core challenges: For nanostructured Si, conductivity achieves high tunability through conductive coatings (carbon/metal oxides) but requires complex fabrication processes; volume expansion benefits from superior buffering via nanosizing yet faces persistent particle aggregation issues; cycling stability is enhanced by prelithiation strategies but remains constrained by SEI instability. Meanwhile, micron-sized Si enables cost-effective production methods while necessitating conductive networks or carbon coatings for adequate conductivity; volume expansion sees moderate stress relief through porosity designs but still requires significant adhesive optimization; cycling stability improves through interface engineering, yet stays limited by residual expansion effects. In contrast, 3D structured Si develops built-in conductive pathways via embedded networks (graphene/CNTs), though this advantage is offset by fabrication complexity; volume expansion demonstrates excellent stress distribution through advanced architectures but remains sensitive to structural defects; cycling stability stabilizes through hybrid coatings yet demands multi-pronged interface control for sustained performance.

To directly address core challenges and leverage their strengths, the most promising development strategies and applications for each anode type are (1) Nanostructured Si: Scalable synthesis methods (e.g., template-free growth): combined with artificial SEI layer engineering offer the highest promise to maintain high performance while reducing production cost and enhancing stability, targeting applications demanding ultra-high energy density and lightweight solutions, such as premium portable electronics, drones, and next-generation consumer devices. (2) Micron-sized Si: Integration of robust conductive networks (e.g., graphene, CNTs) and advanced self-healing binders is crucial to overcome conductivity limitations and crack propagation, making it ideally suited for large-scale applications where cost-effectiveness is paramount, especially in electric vehicles (EVs) and grid-scale energy storage systems. (3) 3D-Structured Si: Machine learning-guided architectural optimization combined with hybrid nano-coatings and in-situ diagnostics is the key pathway to managing complex interfaces, mitigating defects, and ensuring structural integrity under cycling, positioning it as the ultimate solution for applications requiring the very highest energy density coupled with exceptional cycle life and structural robustness, such as long-range EVs, aerospace power systems, and

specialized high-performance batteries.

Despite significant advancements, critical unresolved challenges persist across all silicon anode architectures. For nanostructured silicon, achieving scalable production while maintaining structural integrity remains difficult. Micron-sized silicon still struggles with crack propagation and particle isolation due to severe volume expansion. Most critically, 3D structured anodes continue to face interfacial strain accumulation at material junctions during cycling, leading to delamination and conductivity loss over time. Universal challenges include unstable SEI formation with continuous electrolyte decomposition, irreversible lithium loss, and cumulative electrode deformation across charge cycles - all contributing to capacity fade and reduced cycle life.

To address these complex challenges, interdisciplinary approaches show particular promise. Machine learning-guided design can accelerate the discovery of strain-tolerant 3D architectures and optimized material interfaces through multi-scale simulations and predictive modeling. Advanced in-situ characterization techniques combined with data analytics offer unprecedented insights into dynamic strain evolution and failure mechanisms. Materials informatics approaches could identify novel polymer binder formulations with self-healing capabilities that mitigate interfacial stresses. Furthermore, integrating operando stress monitoring with closed-loop control systems represents a promising route to actively manage volume expansion. The convergence of computational physics, materials genomics, and artificial intelligence will be essential to overcome the persistent materials science challenges facing silicon anodes.

Looking ahead to the future, research on silicon anode structures will pay more attention to the synergistic optimization of materials, structures, and preparation processes, aiming to develop new silicon anode materials with higher energy density, longer cycle life, lower cost, and higher safety. At the same time, in-depth research on the electrochemical reaction mechanism, SEI film formation mechanism, and failure mechanism of silicon anode materials will provide important theoretical guidance for the optimization design and performance improvement of silicon anode structures.

As a highly promising negative electrode material for LIBs, the silicon anode has important strategic significance for promoting the research and application of high-performance LIBs. With the rapid development of electric vehicles, energy storage systems, and portable electronic devices, the demand for LIBs with high energy density, long cycle life, and high safety is becoming increasingly urgent in the market. With their high theoretical capacity and abundant resources, Silicon anode materials are expected to replace traditional graphite anode materials and become one of the key materials for the next generation of high-performance LIBs. It can be foreseen that with the continuous deepening of research and technological progress, silicon anodes will play an increasingly important role in the field of high-performance LIBs in the future, providing important technical support for solving global problems such as energy shortage and environmental pollution, and promoting a sustainable development of human society.

CRedit authorship contribution statement

Kydyr Askaruly: Writing – original draft. **Zhazira Supiyeva:** Writing – review & editing. **Seitkhan Azat:** Writing – review & editing, Supervision, Conceptualization. **Yelriza Yeszhan:** Writing – review & editing. **Xuexue Pan:** Writing – review & editing, Conceptualization. **Kenneth Ozoemena:** Writing – review & editing. **Sonia Dsoke:** Writing – review & editing. **Qamar Abbas:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2025.238423>.

Data availability

The authors do not have permission to share data.

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