

Silicon Nanoparticles for Battery Electrodes: From Synthesis to Solid-State Integration

Abhijit V. Bachute

Department of Chemistry, Sambhaji Kendre Mahavidyalaya, Jalkot, Latur, MS, India-413532

Corresponding Author: abhijitbachute327@gmail.com

Abstract

Silicon nanoparticles are widely regarded as the most viable near-term route to high-capacity anodes for both liquid-electrolyte lithium-ion batteries (LIBs) and emerging all-solid-state batteries (ASSBs). This review traces the silicon anode research pipeline from the bottom up: beginning with nanoparticle synthesis, moving through electrode-level composite integration and liquid-electrolyte interphase behavior, and concluding with the distinct set of challenges that arise when silicon nanoparticles are integrated into solid-state cells. We compare the major synthesis routes — ball milling, magnesiothermic and aluminothermic reduction, chemical/electrochemical etching, chemical vapor deposition, and hydrothermal synthesis — in terms of scalability, cost, and the nanostructures they yield. We then discuss how particle size, morphology, and surface chemistry govern solid electrolyte interphase (SEI) formation in conventional liquid electrolytes, and how the same design variables govern solid–solid contact stability when silicon is paired with sulfide, oxide, or polymer solid electrolytes. Recurring engineering strategies — carbon/oxide coatings, composite architectures, artificial interphases, and stack-pressure management — are examined across both electrolyte classes to identify where solutions transfer directly and where solid-state integration demands fundamentally different design rules. The review closes with an assessment of remaining scalability, safety, and manufacturing barriers and identifies research directions most likely to accelerate commercial adoption of silicon nanoparticle anodes.

Keywords: *silicon nanoparticles; anode synthesis; solid electrolyte interphase; all-solid-state battery; lithium-ion battery; electrode integration*

1. Introduction

Graphite has served as the dominant lithium-ion battery (LIB) anode material for over three decades, but its theoretical capacity of 372 mAh g⁻¹ is now widely viewed as a ceiling that cannot meet the energy-density demands of electric vehicles, aviation, and grid storage. Silicon offers a theoretical specific capacity of approximately 3579 mAh g⁻¹ — nearly ten times that of graphite — together with natural abundance, low cost, and a low lithiation potential, making it the most extensively studied next-generation anode candidate [1], [2].

The obstacle to commercialization is not silicon's chemistry but its mechanics: lithiation drives volumetric expansion exceeding 300%, and the resulting stress fractures particles, degrades electrical percolation within the electrode, and continuously exposes fresh silicon surface to the electrolyte [3]. Nanoparticle engineering — controlling particle size, morphology, porosity, and surface chemistry — has become the primary lever for managing this mechanical problem, and a large body of synthesis literature has emerged around producing silicon nanostructures that are simultaneously performant and manufacturable at scale.

2. Why Nanoscale Silicon: Electrochemical and Mechanical Rationale

Silicon stores lithium through an alloying reaction rather than the layered intercalation used by graphite. Upon lithiation, crystalline silicon converts through an amorphous Li_xSi intermediate before reaching the Li₁₅Si₄ phase near full capacity, a transformation that is intrinsically more disruptive to the host lattice than intercalation [4], [5]. Because the resulting mechanical stress scales with particle size, reducing at least one particle dimension below approximately 150 nm keeps the absolute (rather than fractional) strain within a range that avoids fracture, while simultaneously shortening lithium-diffusion paths and adding lithium-storage sites at grain boundaries [2].

This size effect is well documented at the electrochemical level: studies correlating particle size with cycling performance report that excessively large silicon nanoparticles tend to form the crystalline Li₁₅Si₄ phase and undergo

electrochemical sintering, both of which accelerate capacity fade, whereas appropriately sized particles better tolerate repeated volume change [6]. At the same time, smaller particles present more surface area to the electrolyte, so nanostructuring inevitably trades improved mechanical tolerance against increased parasitic surface reactivity [7] — a tension that motivates much of the interphase-engineering discussion in Sections 5 and 6.

3. Synthesis of Silicon Nanoparticles

Table 1 summarizes the principal synthesis routes used to produce silicon nanoparticles and nanostructures for battery electrodes, compared by feedstock, resulting morphology, and scalability.

Table 1. Comparison of silicon nanoparticle synthesis routes for battery electrodes.

Route	Precursor Feedstock	Resulting Nanostructure	Scalability	Representative Outcome
High-energy ball milling	Metallurgical Si, ferrosilicon, PV kerf waste	Irregular 0D particles, <150 nm	High — industrially proven	Low cost, feedstock-flexible; requires carbon co-milling to limit agglomeration
Magnesiothermic / aluminothermic reduction	SiO ₂ (engineered, diatomite, rice-husk ash, clay)	Porous 0D/3D sponge-like Si	Medium — batch, exothermic control needed	Retains templated porosity; ~1500 mAh g ⁻¹ reversible capacity reported
Chemical / electrochemical etching	Bulk Si wafers	Porous Si, mesoporous spheres	Low	Precise pore-size control; hazardous HF chemistry limits throughput
CVD / vapor-phase growth	SiH ₄ , Si ₂ H ₆	Nanowires, thin films, Si@C core-shell	Low–Medium	Excellent morphology/adhesion control; high capital cost
Hydrothermal/solvothermal	Silicates, organosilanes	Mesoporous/low flow nanospheres	Low	Mild conditions; long reaction times limit scale-up

3.1 Mechanical (Top-Down) Synthesis: Ball Milling

High-energy ball milling is the most industrially mature route to silicon nanoparticles, converting bulk or metallurgical-grade silicon — including low-cost and waste-derived feedstocks such as photovoltaic kerf waste and ferrosilicon — into particles below roughly 150 nm through repeated mechanical impact [1]. The approach is attractive because it is inexpensive, scalable, and feedstock-agnostic, but it produces a broad particle-size distribution and can promote agglomeration if over-milled; co-milling with carbon precursors or dispersing agents is commonly used to control both effects and to build in a conductive matrix from the outset [1].

3.2 Reduction-Based Synthesis: Magnesiothermic and Aluminothermic Routes

Magnesiothermic and aluminothermic reduction convert silica precursors — including engineered nanoporous SiO₂ and natural feedstocks such as rice-husk ash, diatomite, and clay minerals — into porous nanostructured silicon that inherits the pore architecture of the parent template [8], [9]. Because the reduction reaction is strongly exothermic, uncontrolled heat release can collapse the intended porosity; recent work has addressed this by regulating magnesium particle size to moderate the reaction rate, and by combining ball milling with magnesiothermic reduction to eliminate the need for external heating altogether, improving both process safety and scalability [8]. Reported reversible capacities for porous nano-silicon produced by these routes reach on the order of 1500 mAh g⁻¹ after extended cycling, though post-synthesis acid leaching to remove magnesium oxide and silicide by-products remains a processing bottleneck [10].

3.3 Chemical/Electrochemical Etching and Hydrothermal Synthesis

Chemical and electrochemical etching, typically using hydrofluoric-acid-based chemistries on bulk silicon wafers, allows fine control over pore size and porosity but is constrained by reagent hazard and poor scalability. Hydrothermal and solvothermal synthesis, using silicate or organosilane precursors under mild aqueous conditions, offers complementary morphological control — particularly for mesoporous or hollow nanospheres — at the cost of long reaction times that limit throughput [11].

3.4 Vapor-Phase Synthesis: Chemical Vapor Deposition

Chemical vapor deposition (CVD), typically from silane or disilane precursors, provides the most precise control over nanostructure morphology and coating conformality, enabling silicon nanowires, thin films, and core-shell Si@C architectures with strong adhesion to current collectors or scaffold materials [12]. This precision comes at the cost of high capital equipment expense, low throughput, and the flammability and toxicity of silane-based precursors, which together confine CVD largely to laboratory-scale architecture development and specialized thin-film applications rather than bulk electrode manufacturing.

3.5 Toward Scalable and Sustainable Feedstocks

A consistent trend across recent synthesis literature is the move toward abundant, low-cost, or waste-derived silicon sources processed through simple mechanochemical routes. Ball-milling-assisted magnesiothermic reduction of natural clay minerals has been demonstrated as a universal, scalable strategy that avoids clay pretreatment and external heating entirely [8], while controlled magnesiothermic reduction of engineered SiO₂ continues to refine yield and morphology control at moderate temperatures [9]. Recycled and bio-derived binder chemistries applied to silicon kerf-waste anodes extend this sustainability focus from the particle level into electrode formulation, improving cycling stability while reducing reliance on virgin materials [13]. Collectively, these developments suggest that the field is converging on synthesis strategies that balance electrochemical performance against the cost, safety, and throughput requirements of commercial-scale manufacturing.

4. From Particles to Electrodes: Composite Integration

Nanoparticle synthesis alone does not resolve silicon's degradation modes; electrode-level composite design is equally important. The dominant strategy pairs silicon nanoparticles with a conductive, mechanically buffering carbon phase — carbon coatings, graphene wrapping, or reduced-graphene-oxide encapsulation — that maintains electronic percolation as particles fracture or reorganize and that partially isolates the silicon surface from direct electrolyte contact, reducing parasitic interphase growth. Two-step processing routes, in which micron-scale silicon is first mechanically reduced to sub-micron particles and then coated with oxide or graphene-oxide layers, exemplify this approach, and hierarchical architectures embedding silicon nanoparticles within carbon honeycomb scaffolds or high-entropy alloy matrices have reported improved initial Coulombic efficiency and multi-hundred-cycle capacity retention [12]. Binder chemistry and prelithiation strategies further compound these particle- and coating-level effects at the composite-electrode scale, and are discussed further in Section 5.

5. Interphase Behavior in Liquid-Electrolyte Systems

In conventional carbonate-based electrolytes, the solid electrolyte interphase (SEI) that forms on silicon nanoparticles is compositionally similar to that on graphite — comprising inorganic LiF and Li₂CO₃ alongside organic lithium alkyl carbonates — but is mechanically far less stable, because the underlying particle continuously changes volume [14]. Each lithiation/delithiation cycle can crack the existing SEI and expose fresh silicon, so the interphase thickens and its composition drifts progressively rather than stabilizing, consuming both active lithium and electrolyte over time [4]. Because this parasitic reactivity scales with surface area, initial Coulombic efficiency is closely tied to nanoparticle size and specific surface area, creating an explicit design trade-off between mechanical robustness (favoring smaller particles) and interphase stability (favoring larger particles or protected surfaces) [2].

Several complementary strategies mitigate this instability: conductive or protective surface coatings that physically separate silicon from the electrolyte while accommodating volume change; electrolyte additives such as fluoroethylene

carbonate that promote thinner, more flexible, LiF-rich SEI layers; functional binders that maintain strong yet reversible adhesion to the silicon surface; and prelithiation methods, including mixed-conducting approaches, that compensate for first-cycle irreversible lithium loss [11]. Together, these measures have brought silicon-dominant and silicon–graphite blended anodes substantially closer to commercial deployment in liquid-electrolyte LIBs.

6. Integration into Solid-State Batteries

6.1 A Fundamentally Different Interfacial Problem

All-solid-state batteries (ASSBs) replace the liquid electrolyte with a solid ion conductor, improving safety and enabling pairing with higher-energy cathode chemistries. However, because the electrode–electrolyte contact in an ASSB is solid–solid rather than solid–liquid, silicon's volumetric breathing risks not only particle fracture but outright physical separation from the ion-transport pathway — a failure mode with no direct analogue in liquid systems [15]. Mechanistic studies of silicon anodes under realistic, low stack-pressure conditions have shown that minimizing expansion alone is insufficient if intimate solid–solid contact with the electrolyte cannot be maintained throughout cycling [15].

6.2 Electrolyte-Class-Dependent Interfacial Behavior

Table 2 compares the three principal solid electrolyte classes used with silicon anodes.

Table 2.: Solid electrolyte classes and their characteristic interfacial behavior with silicon nanoparticle anodes

Electrolyte Class	Conductivity (RT)	Mechanical Character	Dominant Interfacial Issue
Sulfide (e.g., Li6PS5Cl, LGPS)	10^{-3} – 10^{-2} S cm ⁻¹	Soft, deformable	Reactive interphase (Li2S/SiS2/P2S5); moisture sensitivity
Oxide (e.g., LLZO, NASICON)	10^{-4} – 10^{-3} S cm ⁻¹	Rigid, brittle	Poor conformal contact with expanding Si; high interfacial impedance
Polymer (e.g., PEO, PVDF-HFP composites)	10^{-5} – 10^{-4} S cm ⁻¹ (RT)	Compliant	Lower conductivity; narrower electrochemical stability window

Sulfide electrolytes (e.g., Li6PS5Cl, Li10GeP2S12) provide the highest room-temperature ionic conductivities but react with silicon to form an interfacial layer, only nanometers to tens of nanometers thick, composed of Li2S, SiS2, and P2S5-derived glass phases that functions as a Li-conductive, electronically insulating interphase analogous in role to the conventional SEI [16]. In situ characterization of silicon/sulfide composite electrodes has identified multiple distinct crack-formation mechanisms — including through-thickness channel cracks and delithiation- or relithiation-driven interfacial fracture — with thicker electrodes disproportionately prone to the latter [17].

Oxide electrolytes (e.g., garnet-type LLZO, NASICON-type conductors) offer superior chemical and electrochemical stability but are rigid and brittle, making conformal contact with an expanding silicon anode intrinsically difficult to sustain; consequently, interfacial impedance driven by poor and evolving physical contact dominates performance limitations in oxide-based silicon ASSBs [18].

Polymer electrolytes (e.g., PEO- and PVDF-HFP-based composites) are mechanically compliant and can chemically anchor to the silicon surface, actively regulating interphase chemistry and stress accommodation rather than serving as a passive separator [15]. Composite polymer electrolytes integrated with silicon nanosheet electrodes through in situ secondary coating processes have demonstrated lower charge-transfer resistance and more stable cycling than

mechanically stacked cells, by maximizing solid–solid contact area; LiF-rich and Li₂SO_x-rich interphase chemistries, along with chemically anchored interfaces, have proven particularly effective in this regard [15].

6.3 Mechanical–Electrochemical Coupling

A distinguishing feature of silicon nanoparticle anodes in ASSBs is the tight coupling between mechanics and electrochemistry: applied stack pressure, particle-level stress fields, and interphase evolution jointly determine performance. Multiphysics modeling of silicon/carbon composite anodes in ASSBs has identified spatially distinct failure modes — shear-driven failure at the anode–electrolyte interface versus tension-driven failure at particle–coating interfaces — indicating that adhesion and coating strategies developed for liquid-electrolyte systems cannot be transferred to solid-state cells without modification [19].

6.4 Transferable and Non-Transferable Design Lessons

Several interphase-engineering lessons from liquid-electrolyte systems transfer directly to solid-state integration: carbon and oxide coatings that buffer stress and limit direct electrolyte contact remain beneficial across both platforms, and composite/hierarchical particle architectures that distribute mechanical stress improve cycling stability regardless of electrolyte class [20]. However, stack-pressure management, electrolyte-class-specific interphase chemistry (LiF-rich versus sulfide-derived interphases), and processing methods that maximize initial solid–solid contact area are unique to ASSB integration and have no counterpart in liquid-electrolyte cell design [18].

7. Characterization Approaches Across Platforms

Progress in both liquid-electrolyte and solid-state silicon anode research increasingly depends on operando and in situ characterization capable of resolving structural and chemical evolution during cycling. In situ electrochemical impedance spectroscopy tracks the growth of interfacial resistance associated with SEI or solid-electrolyte-interphase evolution and contact loss. In situ X-ray computed tomography visualizes crack initiation and propagation within composite silicon electrodes at the particle and electrode scale, while in situ thin-film X-ray diffraction resolves structural evolution at electrode/electrolyte interfaces in ASSBs [17]. Complementary ex situ methods — transmission electron microscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy — remain essential for resolving interphase composition, while chemo-mechanical models coupling particle-level stress to interphase formation provide a framework for interpreting these observations and guiding synthesis and electrode design [4].

8. Challenges and Future Directions

Despite substantial progress across the synthesis-to-integration pipeline, several challenges remain before silicon nanoparticle anodes achieve broad commercial deployment:

- Scalable, low-hazard synthesis: translating porous or composite nanostructure benefits into simple, safe, high-throughput processes — particularly for magnesiothermic and CVD-based routes — remains an open manufacturing problem.
- First-cycle efficiency versus mechanical tolerance: the intrinsic trade-off between nanoscale surface area and irreversible interphase formation is only partially resolved by current coating and additive strategies.
- Solid–solid contact under realistic stack pressure: results obtained at high laboratory-scale applied pressures often do not translate to the lower pressures achievable in commercial pack designs.
- Electrolyte-specific interphase control: sulfide electrolytes in particular require interphases or coatings that suppress continued reactive interdiffusion without compromising ionic conductivity.
- Thick, high-mass-loading electrodes: most demonstrations use thin electrodes; extending nanostructuring and interphase-engineering benefits to commercially relevant mass loadings remains a key scale-up gap.
- Sustainable feedstocks: continued development of waste- and bio-derived silicon sources, paired with recycled binder chemistries, is needed to align performance gains with economically and environmentally viable manufacturing.

Promising directions include hierarchical architectures that combine carbon or high-entropy-alloy matrices with nanoscale silicon, polymer and composite solid electrolytes engineered to actively regulate interphase chemistry, machine-learning-guided optimization of synthesis parameters, and continued valorization of low-cost silicon feedstocks such as photovoltaic kerf waste and natural clay minerals.

9. Conclusion

Silicon nanoparticle synthesis has matured substantially, with ball milling, magnesiothermic reduction, etching, CVD, and hydrothermal methods now offering a broad toolkit for tailoring particle size, morphology, and porosity to specific performance and manufacturing requirements. These synthesis-level advances have meaningfully improved mechanical tolerance to volumetric cycling, but the interfacial problem — SEI instability in liquid electrolytes and the combined chemical and mechanical fragility of solid–solid contact in ASSBs — remains the central bottleneck to commercialization. Critically, solid-state integration introduces design requirements that are not simply inherited from liquid-electrolyte engineering: stack-pressure management, electrolyte-class-specific interphase chemistry, and processing methods that preserve solid–solid contact area is unique to ASSBs and demand dedicated research attention. Continued integration of scalable nanoparticle synthesis, tailored interphase engineering, and cell-level mechanical design — supported by operando characterization and multiphysics modeling — offers the clearest path toward silicon nanoparticle anodes that are viable in both liquid-electrolyte and solid-state battery platforms.

Conflict of interest

The author affirms that he has no conflicts of interest related to this work's publication. The research, analysis, findings interpretation, and paper preparation were not impacted by any financial, personal, or professional interactions.

REFERENCES

- [1] A. A. Pavlovskii, K. Pushnitsa, A. Kosenko, P. Novikov, and A. A. Popovich, "Nanostructured silicon anodes for lithium-ion batteries: Advances, challenges, and future prospects," *Materials*, vol. 19, no. 2, p. 281, 2026, doi: 10.3390/ma19020281.
- [2] Z. Zhang, Y. Wu, Z. Mo, X. Lei, X. Xie, X. Xue, H. Qin, and H. Jiang, "Research progress of silicon-based anode materials for lithium-ion batteries," *RSC Adv.*, vol. 15, no. 14, pp. 10731–10753.
- [3] K. Askaruly, Z. Supiyeva, S. Azat, Y. Yeszhan, X. Pan, K. Ozoemena, S. Dsoke, and Q. Abbas, "From electrochemical performance to mechanical issues: A review on silicon anode architectures for advanced lithium-ion batteries," *J. Power Sources*, vol. 659, p. 238423, 2025.
- [4] L. Köbbing, A. Latz, and B. Horstmann, "Voltage hysteresis of silicon nanoparticles: Chemo-mechanical particle-SEI model," *Adv. Funct. Mater.*, vol. 34, no. 7, Art. no. 2308818, 2024.
- [5] X. Zuo, J. Zhu, P. Müller-Buschbaum, and Y.-J. Cheng, "Silicon based lithium-ion battery anodes: A chronicle perspective review," *Nano Energy*, vol. 31, pp. 113–143, 2017.
- [6] H. Nomura and K. Sato, "Cycle life improvement of lithium-ion batteries using particle size controlled silicon nanoparticle anodes," *Jpn. J. Appl. Phys.*, vol. 64, p. 09SP09, 2025, doi: 10.35848/1347-4065/adfb83.
- [7] C. Zhang, F. Wang, J. Han, S. Bai, J. Tan, J. Liu, and F. Li, "Challenges and recent progress on silicon-based anode materials for next-generation lithium-ion batteries," *Small Struct.*, vol. 2, p. 2100009, 2021.
- [8] T. Xiong, Q. Chen, S. Wei, J. Xie, J. Du, J. Zhu, and R. Zhu, "Ball-milling-assisted magnesiothermic reduction of clay minerals to nano-Si as high-performance lithium-ion battery anodes," *Nano Lett.*, vol. 26, no. 1, pp. 341–350, 2026.
- [9] P. A. Sánchez, K. Thangaian, O. A. Øie, A. Gaarud, M. Rodríguez Gomez, V. Diadkin, J. Campo, F. H. Cova, and M. V. Blanco, "Toward the controlled synthesis of nanostructured Si and SiO_x anodes for Li-ion batteries via SiO₂ magnesiothermic reduction reaction," *ACS Appl. Energy Mater.*, vol. 8, no. 4, pp. 2249–2259, 2025, doi: 10.1021/acsaem.4c02836.

- [10] M. Yan, S. Martell, S. V. Patwardhan, and M. Dasog, "Key developments in magnesiothermic reduction of silica: Insights into reactivity and future prospects," *ChemRxiv*, 2024.
- [11] Z. Xiao, C. Wang, L. Song, Y. Zheng, and T. Long, "Research progress of nano-silicon-based materials and silicon-carbon composite anode materials for lithium-ion batteries," *J. Solid State Electrochem.*, vol. 26, pp. 1125–1136, 2022.
- [12] G. Zhu, D. Chao, W. Xu, M. Wu, and H. Zhang, "Microscale silicon-based anodes: Fundamental understanding and industrial prospects for practical high-energy lithium-ion batteries," *ACS Nano*, vol. 15, no. 10, pp. 15567–15593, 2021.
- [13] A. Hennessy, A. Sankaran, A. Hannon, M. Cornago, T. Kennedy, H. Geaney, and K. M. Ryan, "Unlocking stable cycling in silicon kerf waste anodes with recycled polyacrylamide-based binders for lithium-ion battery applications," *ACS Appl. Mater. Interfaces*, vol. 17, no. 51, pp. 69541–69550, 2025.
- [14] M. Kim, Z. Yang, and I. Bloom, "Review—The lithiation/delithiation behavior of Si-based electrodes: A connection between electrochemistry and mechanics," *J. Electrochem. Soc.*, vol. 168, p. 010523, 2021.
- [15] X. Liu, X. Li, Y. Yu, and N. H. Jamadon, "Polymer-regulated silicon–electrolyte interfaces in solid-state lithium-ion batteries: Interphase chemistry, stress accommodation, and contact stability," *Front. Mech. Eng.*, vol. 12, Art. no. 1836323, 2026.
- [16] S. Asano, J.-I. Hata, K. Watanabe, K. Shimizu, N. Matsui, N. L. Yamada, K. Suzuki, R. Kanno, and M. Hirayama, "Formation processes of a solid electrolyte interphase at a silicon/sulfide electrolyte interface in a model all-solid-state Li-ion battery," *ACS Appl. Mater. Interfaces*, vol. 16, no. 6, pp. 7189–7199, 2024.
- [17] F. Liang, L. Yang, R. Hu, B. Yuan, M. Zhu, and J. Liu, "Mechanisms, development, and applications of silicon-based anodes in solid state batteries," *Chem. Sci.*, vol. 17, no. 2, pp. 738–771, 2026.
- [18] D. Wang, X. Wu, Y. Ren, Y. Li, X. Xie, X. Ma, I. Razanau, X. Chen, J. Lu, and K. Pan, "A review of interface optimization strategies for solid electrolytes and anode materials," *Nanoscale Adv.*, vol. 7, no. 15, pp. 4535–4550, 2025.
- [19] X. Gao, L. Jia, and X. Zhang, "Interface engineering for silicon/carbon composite anode in all-solid-state batteries," *Energy Mater. Devices*, vol. 3, no. 3, p. 9370067, 2025.
- [20] B. Li, Z. Chen, M. Sun, K. Xie, X. Yang, C. Zhang, X. Cheng, X. Wan, J. Chai, Z. Liu, and Y. Zheng, "Advances in silicon-based anodes for all-solid-state lithium batteries: Material modification and structural design," *J. Energy Storage*, vol. 135, Art. no. 118309, 2025.