



Silicon deposition in the pores of a microporous carbon enables stable high-performance silicon/carbon anodes

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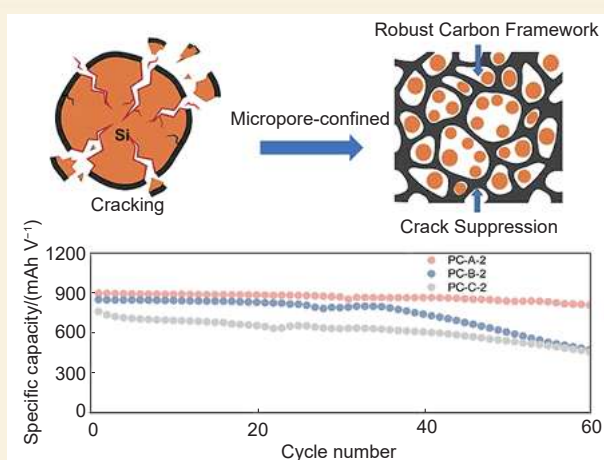
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Abstract: Silicon/carbon composites are promising anode materials for lithium-ion batteries because of the high capacity of silicon and the structural stability of the carbon frameworks. However, achieving a uniform distribution and high silicon loading while limiting severe volume expansion remains a critical challenge. We have shown that a carbon host with a high microporosity has a strong confinement, enabling the fabrication of silicon/carbon composites with high silicon loading. More importantly, the microporosity is found to govern both the silicon deposition behavior and the resulting electrochemical performance. A high micropore content (92%) promotes preferential silane adsorption and directs silicon nucleation within micropores, producing uniformly dispersed amorphous silicon domains with a high mass loading of 51%. The confinement mechanism simultaneously buffers volume expansion during lithiation and suppresses the formation of the detrimental crystalline $\text{Li}_{15}\text{Si}_4$ phase. Consequently, the composite with 92% microporosity delivers a high initial Coulombic efficiency of 91.2% and improved cycling stability, retaining 82.42% of its capacity ($814.93 \text{ mAh g}^{-1}$) after 60 cycles. This work establishes micropore-induced confinement as an effective design principle for high-performance silicon/carbon anodes, enabling high silicon loading while maintaining structural stability.

Key words: Microporous carbon; Chemical vapor deposition; Confinement effect; Silicon/carbon anode; Lithium-ion battery



1 Introduction

In recent years, the rapid development of electric vehicles (EVs), hybrid vehicles, and consumer electronics has driven continuous increases in the demands for lithium-ion batteries regarding energy density and rate performance^[1]. With a theoretical capacity of only 372 mAh g^{-1} , conventional commercial graphite anodes are increasingly inadequate for meeting the demands of future high energy battery systems^[2–3]. Silicon anode materials have garnered significant attention due to their exceptionally high theoret-

ical capacity ($\sim 4200 \text{ mAh g}^{-1}$), low lithiation/delithiation potential, natural abundance and relatively low cost^[4–5].

However, silicon-based materials suffer from severe volume expansion of approximately 300% during lithiation, which results in particle pulverization,

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electrode disintegration, continuous rupture and reformation of solid electrolyte interphase (SEI), low initial Coulombic efficiency, and rapid capacity decay. These intrinsic issues greatly hinder the practical application of silicon in commercial lithium-ion batteries. Recently, Solution mixing and thermal annealing have been widely used to prepare Si-based composite anodes, such as Si-ZnO composites synthesized by Liu et al.^[6]. However, the introduction of metal-based components tends to increase material costs and complicate scalable preparation. The construction of silicon/carbon (Si/C) composites has been widely accepted as an effective approach to alleviate these difficulties. In such composites, the carbon matrix can accommodate the volume changes of silicon, enhance electronic conductivity, and improve the structural stability of the electrode. A variety of carbon architectures, including porous carbon frameworks, carbon nanotubes, graphene networks, hollow carbon structures, and Sn-composite silicon anode^[7], have been employed to host silicon. Among these, porous carbon hosts are especially promising because their internal pore structures can buffer silicon expansion and confine silicon deposition within the micropore spaces, thereby reducing mechanical stress and stabilizing the electrode-electrolyte interface. Nevertheless, achieving high silicon loading together with uniform dispersion and long-term structural integrity remains a significant challenge. In many cases, silicon deposition occurs preferentially on the external surface of the carbon host, leading to particle aggregation, poor interfacial contact, and accelerated electrode degradation during cycling. Recent investigations have indicated that the pore structure of the carbon host, particularly the proportion of micropores, plays a critical role in determining silicon deposition behavior and the resulting electrochemical performance. Despite growing recognition of these effects, the detailed relationship between microporosity and key aspects such as silicon distribution, structural evolution during cycling, and overall stability has not been systematically elucidated. This knowledge gap motivates the present

study^[8–9].

Currently, Si/C anode preparation technology has undergone several modification strategies. One common approach is to reduce silicon particle size to the nanoscale, which can effectively alleviate mechanical stress during volume expansion^[10–11]. However, nano-sized silicon generally suffers from low tap density and high surface reactivity, leading to increased side reactions and reduced initial Coulombic efficiency. Another widely investigated strategy involves the construction of Si/C composite structures, where conductive carbon frameworks buffer volume variation and enhance electrical conductivity. In particular, porous carbon materials have been widely explored as effective hosts for silicon due to their tunable pore structures, high electronic conductivity, and structural robustness^[12]. Among various fabrication approaches, chemical vapor deposition (CVD) has emerged as a key technique to address uneven coating and to strengthen interfacial bonding in such composites^[13]. In a typical CVD process, silanes serve as the silicon source and acetylene or other hydrocarbons as the carbon source. Under controlled temperature and pressure, these precursors were pyrolyzed to deposit silicon and carbon layers within the pores of the carbon substrate^[14]. The resulting composites exhibit uniform structures, excellent cycling stability, and high initial coulombic efficiency^[15–17]. Moreover, CVD presents moderate equipment requirements and high production efficiency, making it suitable for industrial-scale manufacturing of Si/C anodes. Compared to composites using silicon or siloxane, the pore structure of porous carbon not only confines silicon domains growth by providing buffer space but also traps fractured silicon domains within the pores, preventing their direct contact with the electrolyte and thus reducing side reactions^[18–20]. Although porous carbon substrates are crucial for enhancing the performance of Si/C anodes, the influence of micropore fraction on silane deposition pathways and the resulting electrochemical performance of Si/C anodes remains insufficiently understood^[21–23].

Herein, we systematically investigate how the micropore structure of porous carbon substrates regulates silane deposition behavior and the electrochemical performance of Si/C anodes. Porous carbon hosts with different microporous ratios (92%, 84% and 59%) were employed to study the relationship between pore structure and silicon deposition characteristics. The results indicate that a high microporous content (92%) creates a strong confinement environment, significantly promoting silane adsorption and directing silicon nucleation within confined pores. This confined growth ensures uniform silicon distribution, provides mechanical restraint during lithiation of Si and effectively suppresses the formation of detrimental crystalline $\text{Li}_{15}\text{Si}_4$ during lithiation. Consequently, the optimized composite achieves enhanced structural stability, delivering a high initial Coulombic efficiency (ICE) of 91.2%, with capacity retention rate of 82.42% after 60 cycles. This study clarifies the critical role of microporous design and provides an effective strategy for fabricating high-performance Si/C anodes by CVD.

2 Experiment

2.1 Material synthesis

Si/C composites were synthesized by a two-step CVD process. In the first stage, pre-treated carbon substrates were heated to 500 °C (5 °C min⁻¹) under Ar flow. A silane/Ar mixture (100 mL min⁻¹) was introduced for 120 min, enabling silane to diffuse into the carbon pore network and thermally decompose into Si deposition. Subsequently, the temperature was ramped to 700 °C (5 °C min⁻¹) under Ar, followed by the introduction of acetylene (50 mL min⁻¹) for 60 min. The resulting pyrolysis generated a uniform amorphous carbon coating encapsulating the Si-loaded particles, strategically designed to buffer Si volume expansion during lithiation and enhance the overall electronic conductivity.

2.2 Characterization and measurement

Details of battery assembly and material characterization methods are provided in the Supporting Information.

3 Results and discussion

3.1 Mechanism of silane deposition regulated by porous carbon substrates

To systematically investigate the influence of carrier structure on Si loading, four progressively increasing silane fluxes (denoted 1-4) were applied to three distinct porous carbon substrates (PC-A, PC-B, and PC-C), yielding samples labeled PC-X-Y (where $X = \text{A/B/C}$ and $Y = 1-4$). Fig. 1a presents a schematic representation of the predicted structural outcomes following silane deposition on the three porous carbons. This diagram visually illustrates how variations in the initial microporosity of the substrate influence the morphology and spatial distribution of the deposited silicon. The high microporosity of PC-A provides strong adsorption ability, enabling uniform silicon deposition with high loading. In contrast, the higher mesopore fraction in PC-C is less favorable for silane chemisorption and uniform nucleation, and its open pore structure exerts weaker control over silicon deposition behavior. The calculated average pore diameters for the post-deposition structural models are 1.77 nm for PC-A, 1.94 nm for PC-B, and 3.48 nm for PC-C, indicating that the 3 substrates will provide distinct ionic transport environments.

The nitrogen adsorption-desorption isotherms in Fig. 1b provide structural evidence for these predictions. The three carbon substrates show distinct adsorption behaviors^[24]. PC-A exhibits a typical Type I isotherm with steep uptake at low pressures, indicating abundant micropores. The adsorption reaches a plateau with no obvious hysteresis, confirming its predominantly microporous structure. PC-C displays a mixed Type I/IV isotherm. A distinct H4-type hysteresis loop appears at $p/p_0 > 0.45$ with continuous uptake at high pressures, indicating the presence of mesopores and macropores. PC-B shows characteristics similar to PC-A with high micropore uptake and weak hysteresis at $p/p_0 > 0.4$ and specific surface area (1892.54 m² g⁻¹) is slightly lower than that of PC-A (1992.92 m² g⁻¹).

Quantitative analysis of the pore structure

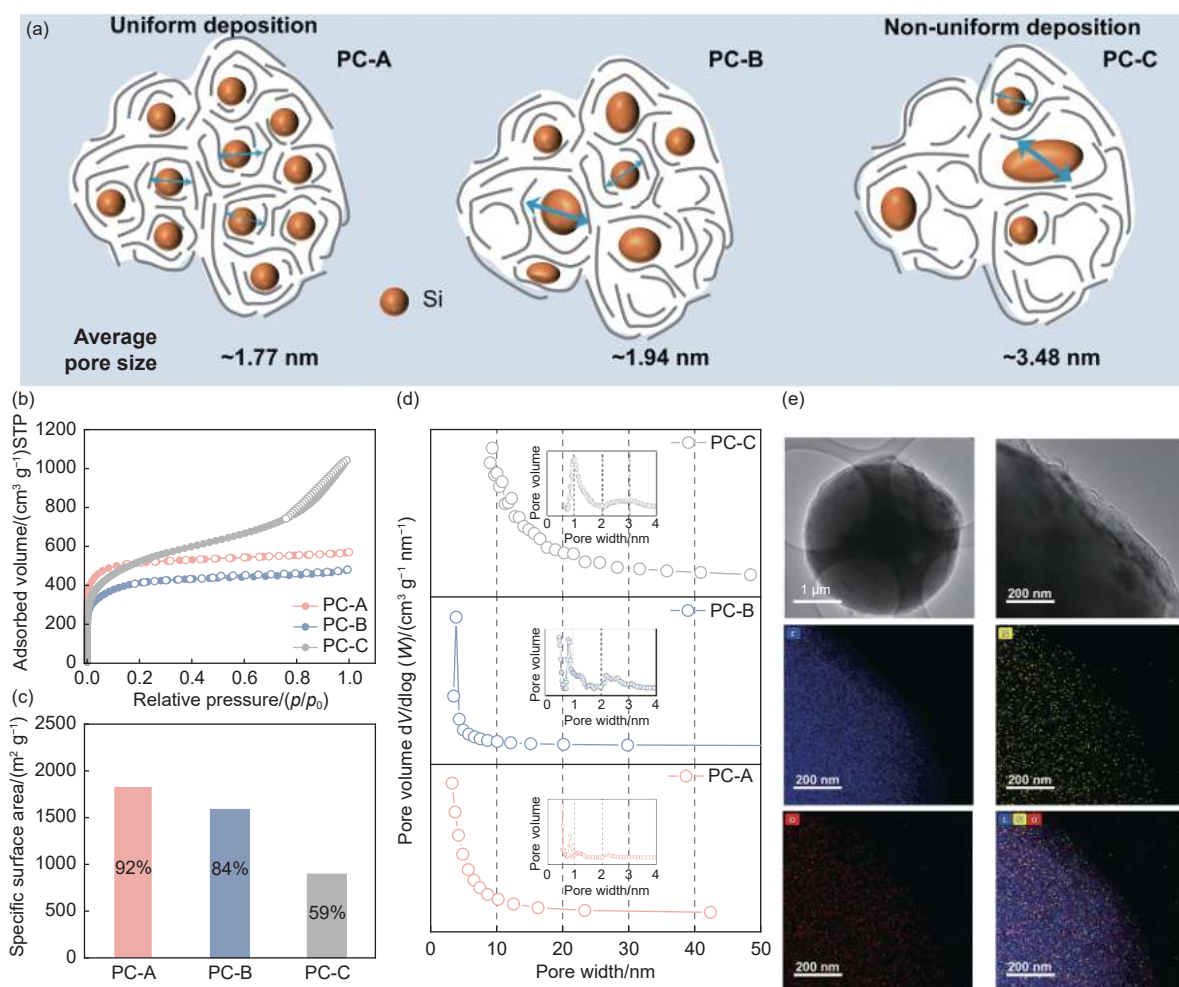


Fig. 1 Structural characterization of porous carbon substrates. (a) Schematic illustration of silane deposition behavior within porous carbon. (b) N₂ (77 K) adsorption-desorption isotherms. (c) Micropore fraction. (d) Pore size distribution curves of PC-A, B and C. (e) TEM image and elemental distribution mappings (C, N, O) for PC-A

through model calculations further clarifies the differences among the three materials. The bar chart in Fig. 1c reveals that micropores account for 92% of the total pore volume in PC-A, 84% in PC-B, and 59% in PC-C, forming a distinct gradient from a microporous-dominated to a multi-level pore structure. The pore size distribution curves in Fig. 1d provide more detailed structural information. PC-A exhibits a sharp distribution peak with exceptionally high intensity in the ultramicropore region below 1 nm, indicating a highly concentrated pore size distribution dominated by sub-nanometer micropores. In contrast, PC-C displays a broad and intense distribution signal across the 2-50 nm range, consistent with the mesoporous and macroporous features suggested by its mixed Type I/IV isotherm.

Fig. 1e presents the representative microstruc-

ture and elemental distribution of PC-A. Transmission electron microscopy (TEM) images reveal that the PC-A material consists of uniform spherical particles. The corresponding elemental mapping confirms that carbon, nitrogen, and oxygen are homogeneously distributed throughout the particles. The uniform dispersion of these elements suggests a homogeneous surface chemistry, which is well-suited for subsequent uniform silicon deposition. Scanning electron microscopy (SEM) images (Fig. S1) reveal distinct morphological differences among the pristine carbon substrates. While PC-A and PC-B exhibit intact, micrometer-scale block-like structures with well-defined edges and relatively smooth surfaces, PC-C displays a highly fragmented, smaller, and stacked morphology. The robust conductive network and mechanical integrity of PC-A, combined with the ef-

fects of microporous confinement, determine the final electrochemical behavior. In addition, the FTIR spectrum in Fig. S2 verifies the existence of —OH surface functional groups which provides strong interfacial anchoring effects helping to promote the process of silane adsorption and deposition. Through this systematic characterization, carbon carrier models with microporous volume fractions of 92% (PC-A), 84% (PC-B), and 59% (PC-C) were successfully constructed. This distinct structural gradient, transitioning from predominant microporosity to a coexistence of multi-level pores, provides an ideal comparative platform for subsequent investigations of silicon deposi-

tion behavior.

3.2 Pore structure of composite materials after deposition

Fig. 2a illustrates the synthesis procedure for the Si/C composites by a two-step chemical vapor deposition strategy. Silicon was first deposited onto the porous carbon substrates through the thermal decomposition of silane, followed by a carbon coating process using acetylene pyrolysis^[23,25]. Evaluated by thermogravimetric analysis (TGA), the silicon contents of the three carbon substrates after different silane fluxes are summarized in Fig. 2b. At the same silane flow rate, the silicon loading consistently followed the order PC-

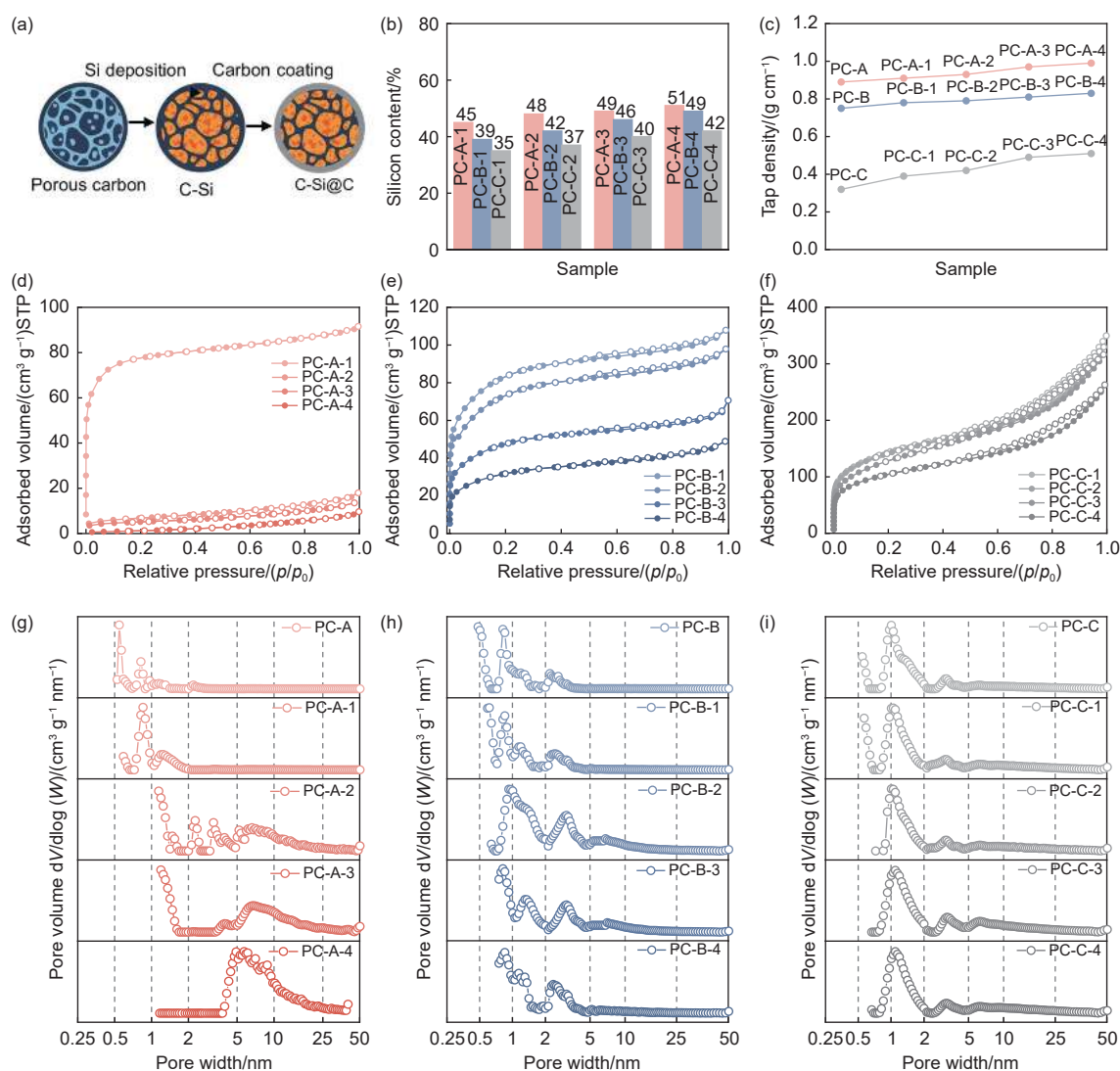


Fig. 2 Evolution of pore structure in materials after silane deposition. (a) Schematic illustration of the two-step chemical vapor deposition process for preparing Si—C composites. (b) Silicon content of PC-A, PC-B and PC-C after deposition with different silane fluxes. (c) Tap density of the 3 series after deposition. (d-f) N₂ (77 K) adsorption-desorption isotherms and (g-i) Pore size distribution curves of PC-A, PC-B and PC-C before and after deposition with different silane fluxes

A > PC-B > PC-C, which correlates directly with their initial microporosity. These results indicate that a high porosity can increase the amount of silane deposited. Tap density measurements (Fig. 2c) provided complementary evidence. The tap density of each series followed the same order PC-A > PC-B > PC-C. The particle size distributions of the composites (Fig. S3) showed no significant variation with increasing silicon loading. Tap density and the particle size distributions confirm that silicon was predominantly deposited within the internal pore network rather than on the external surface, thereby increasing the bulk density of the composite particles.

Fig. 2d-f present the nitrogen adsorption-desorption isotherms used to probe the pore structure evolution after silicon deposition. The sharp adsorption uptake at low relative pressures ($p/p_0 < 0.1$) confirms the presence of abundant micropores. With increasing silane flux, the nitrogen adsorption capacity of all deposited samples decreases substantially compared to the pristine substrates, showing a clear decreasing trend that aligns well with the increasing silicon content. For the PC-A series, the isotherm of PC-A-4 approaches the horizontal axis with extremely low adsorption, indicating that its originally accessible pore channels have been largely occupied by deposited silicon. Quantitative analysis reveals that after silicon deposition, the specific surface areas of PC-A-4, PC-B-4 and PC-C-4 decrease from their initial values of 1992.92, 1892.54 and 1530.31 $\text{m}^2 \text{g}^{-1}$ to 4.26, 112.64 and 364.20 $\text{m}^2 \text{g}^{-1}$, respectively. This significant reduction confirms that silane molecules effectively diffuse into the carbon particles and undergo in-situ thermal decomposition within the micropores. The most pronounced decrease in PC-A-4 is attributed to its high initial microporosity of 92%. The strong adsorption potential within micropores prolongs the residence time of silane molecules, enhancing in-situ pyrolysis efficiency and silicon loading. In contrast, PC-C, with an initial microporosity of 59%, retains a relatively high specific surface area after deposition with a final silicon content of 42%, reflecting incomplete pore filling.

The corresponding pore size distribution curves in Fig. 2g-i further reveal the confinement behavior of silicon within pores of different dimensions. After deposition, the characteristic micropore peaks below 2 nm are significantly attenuated or disappear completely across all samples, indicating that small silane molecules preferentially infiltrate and nucleate within micropores, leading to their closure. In the 2–50 nm mesopore region, peak intensities gradually decrease with increasing silicon loading. For the PC-A series, which possesses abundant and relatively well-ordered micropores, the pore size distribution across the full range becomes flattened after deposition, indicating effective and thorough pore filling. In contrast, the PC-C series retains some mesoporous features after deposition due to its higher initial proportion of mesopores and macropores, suggesting that wider pore channels are difficult to fully occupy with silicon. These differences reflect the significant influence of the initial pore size distribution of the carbon substrate on the deposition kinetics and spatial distribution of silicon.

Collectively, these gas adsorption results confirm that the CVD process employed in this study enables effective silicon filling within the internal pores of porous carbon. The dramatic reduction in specific surface area and the significant attenuation of characteristic pore peaks jointly demonstrate that silicon is not merely deposited on the carbon surface, but is deeply anchored within the carbon framework through a pore confinement effect. Carbon substrates with high microporosity exhibit superior silane adsorption thermodynamics and deposition kinetics, providing critical insights for the structural design of Si/C anode hosts. Following silane deposition and carbon coating, the surface morphology of the composites underwent noticeable changes (Fig. S4). Although the overall particles maintained their original micrometer-scale skeleton structure without obvious collapse or fragmentation, their surfaces became exceptionally smooth and dense. This surface evolution is primarily attributed to the amorphous carbon layer generated by acetylene pyrolysis, which effectively filled the mi-

croscopic defects on the particle surfaces. Furthermore, no obvious accumulation or agglomeration of external silicon particles was observed in the SEM field of view, confirming that the active material is predominantly confined within the internal carbon skeleton. The micropore network thus serves as the primary host for silicon immobilization, and its abundance directly dictates both the achievable silicon loading and the physical density of the resulting composite^[26–27].

3.3 Phase and microstructure analysis of the composites

To further investigate the deposition state of silicon within the porous carbon and its impact on the carbon framework, systematic phase and microstructural analyses were conducted on the PC-A series samples (from PC-A to PC-A-4). Fig. 3a displays the X-ray diffraction (XRD) patterns of PC-A and its post-deposition counterparts. The pristine PC-A exhibits only the broad diffraction peaks characteristic of amorphous carbon, located at approximately 24° and 44°. In all deposited samples, no distinct crystalline silicon features were detected, except for a faint, sharp peak near 27° in PC-A-4, which may correspond to either crystalline silicon or a silicate phase^[28].

Combined with the pore structure analysis discussed above, these results suggest that when internal

micropores become saturated, further silane cracking is forced onto the exterior surfaces or into macropores. Lacking spatial confinement, this external silicon freely nucleates and expands into large crystalline phases. This XRD-confirmed inward-to-outward deposition sequence dictates that practical material design must carefully balance silicon loading against pore capacity. Such optimization effectively mitigates surface bulk silicon formation, thereby safe-guarding the structural robustness of the composite.

Fig. 3b compares the Raman spectra of the PC-A series. All samples exhibit characteristic carbon *D* bands ($\sim 1350\text{ cm}^{-1}$) and *G* bands ($\sim 1580\text{ cm}^{-1}$). The I_D/I_G ratios for PC-A-1 to PC-A-4 remain within a narrow range of 1.12–1.21, showing no systematic variation with increasing silicon loading. Notably, despite the high silicon content (up to 51%), no distinct silicon signal is observed in any of the spectra. This is primarily attributed to two factors: the Raman scattering cross-section of carbon is significantly larger than that of silicon, allowing the carbon *D* and *G* bands to dominate even at high silicon loadings. Additionally, silicon deposited by low-temperature CVD exists highly dispersed amorphous Si confined within micropores, both of which lead to broadened and weakened Raman signals that are readily obscured by the carbon background. Therefore, the absence of detectable

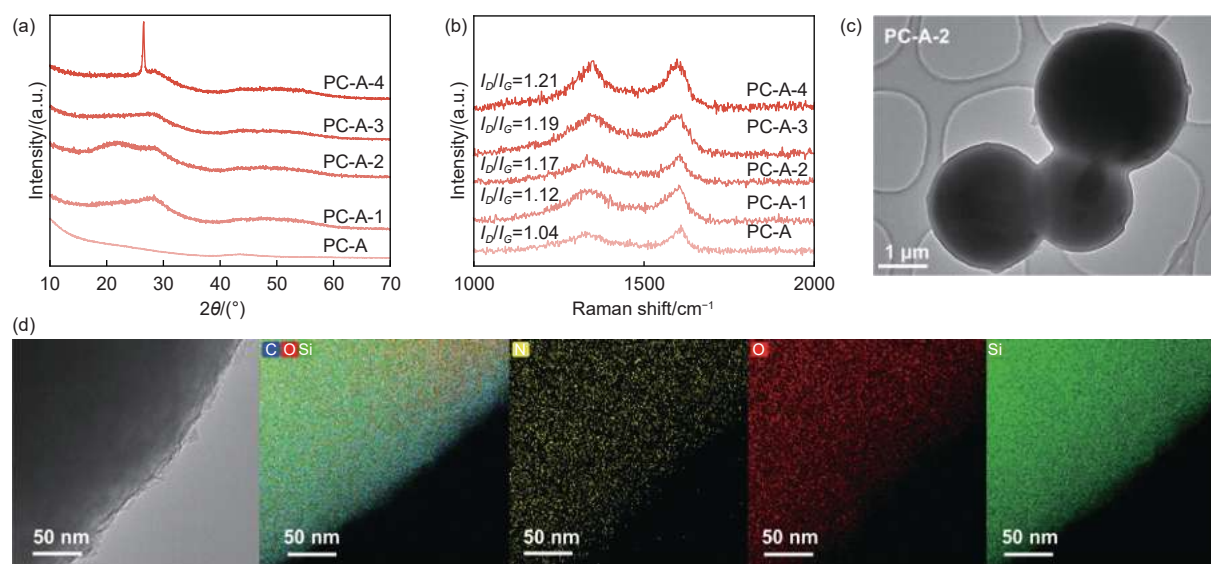


Fig. 3 Physical phases and microstructure of Si—C composites. (a) XRD patterns of and (b) Raman spectra of sample PC-A before and after silicon deposition on carbon. (c-d) Aberration-corrected TEM images and mappings of PC-A-2

silicon signals in the Raman spectra does not indicate the lack or abnormal distribution of silicon. Rather, it reflects that silicon is present in a highly dispersed nanoscale form effectively confined within the carbon framework, achieving a well-integrated composite structure^[29]. Raman spectra for the PC-B and PC-C series are provided in Fig. S5 and S6, respectively, showing similar trends in I_D/I_G evolution with increasing silicon loading.

Microscopic morphology and elemental distribution provide more direct evidence. The transmission electron microscopy image in Fig. 3c reveals that the material retains a uniform spherical morphology similar to that of pristine PC-A even after silicon deposition, with no apparent silicon agglomeration or structural disruption. The corresponding elemental distribution maps in Fig. 3d further confirm that silicon is uniformly distributed throughout the composite particles, exhibiting a high degree of spatial overlap with the substrate elements. This directly demonstrates the successful and homogeneous deposition of silicon within the three-dimensional pore network of the porous carbon, rather than accumulation on the external surface.

These results demonstrate that silicon has been successfully incorporated into the PC-A host, forming a highly dispersed and uniformly amorphous composite structure. This unique microstructure suggests potential electrochemical advantages: amorphous silicon can mitigate anisotropic stresses during lithium alloying, while the uniformly dispersed Si/C interfaces may facilitate rapid charge transport and provide stable mechanical support^[30]. These interactions may further impact the macroscopic conductivity and structural stability of the composite. Such deposition-regulated microstructural characteristics and interfacial states will be pivotal in determining the electrochemical performances of the material^[31].

3.4 Comparison of electrochemical performance of carbon composite anodes

Following the establishment of the material microstructures, we systematically evaluated the electrochemical performance of 3 composite materials (PC-

A-2, PC-B-2, PC-C-2) under an identical deposition amount to elucidate the influence of the carrier structure on electrode kinetics and cycling stability. Fig. 4a compares the cyclic voltammetry (CV) curves of the three materials at a scan rate of 0.9 mV s^{-1} . The CV curve of PC-A-2 exhibits the earliest onset potential for electrochemical reactions, the highest peak current, and the largest enclosed area. These features are less pronounced in PC-B-2, while PC-C-2 shows the latest onset potential and the weakest current response. This indicates that PC-A-2 possesses the most favorable electrochemical reactivity and the highest reversible capacity, which aligns with its highest silicon loading and uniform Si/C composite structure observed in prior characterization. The relatively poorer activity of PC-C-2 may be attributed to its lower silicon content and potentially less uniform silicon distribution within its more open pore structure.

To gain deeper insight into the reaction kinetics, the charge storage mechanism was further analyzed. Fig. 4b presents a stacked bar chart illustrating the pseudocapacitive contribution of PC-A-2 at different scan rates. As the scan rate increases from 0.1 to 0.9 mV s^{-1} , the contribution from the surface-driven pseudocapacitive process shows a significant and systematic enhancement. This trend indicates that charge storage in PC-A-2 is not solely controlled by diffusion; its well-developed pore structure and highly dispersed active interfaces facilitate rapid surface reactions, providing a key kinetic perspective for understanding its outstanding rate performance. Interfacial charge transfer resistance is a critical factor influencing rate performance. The Nyquist plots in Fig. 4c and the histogram of charge transfer resistance (R_{ct}) values in Fig. 4d provide quantitative results. Interfacial R_{ct} was evaluated by electrochemical impedance spectroscopy (EIS) measurements. Fitting analysis reveals that PC-A-2 exhibits the lowest R_{ct} value of 37.83Ω , followed by PC-B-2 (60.54Ω) and PC-C-2 (103.67Ω). The equivalent circuit diagram and parameter error table are presented in Fig. S7 and Table S1. The superior charge transfer kinetics of PC-A-2 stem from its high microporosity and the associated

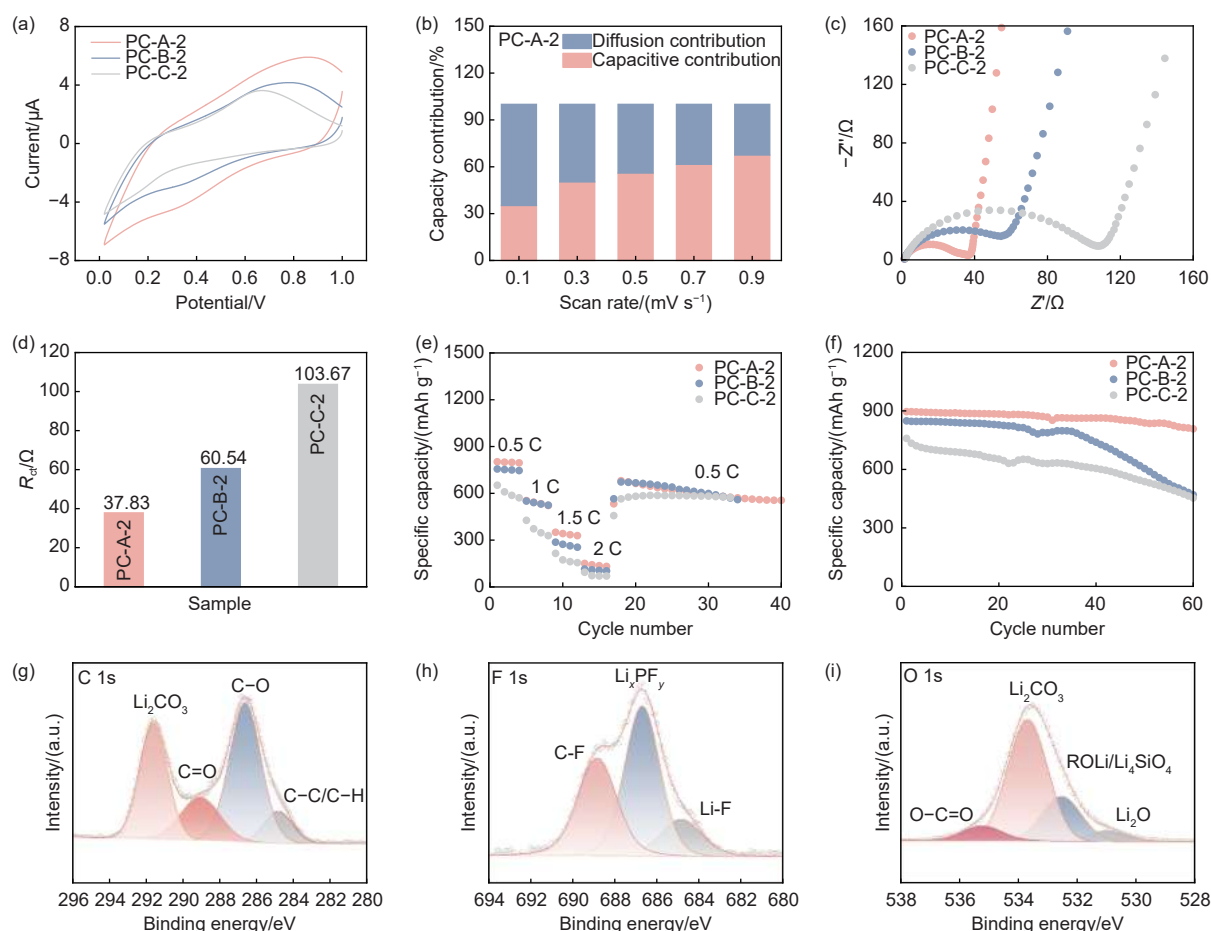


Fig. 4 Electrochemical performance of samples with different silicon deposition loads. (a) CV curves of PC-A-2, PC-B-2 and PC-C-2. (b) Pseudocapacitive contribution analysis of PC-A-2. (c) EIS and (d) Comparison of R_{ct} of PC-A-2, PC-B-2 and PC-C-2. (e) Rate performance and (f) Cycling performance at 0.5 C of half-cell. (g-i) XPS analysis of the SEI on the PC-A-2 electrode after 50 cycles

confinement effect. The abundant micropores enable highly dispersed Si within the carbon framework, creating extensive interfacial electron pathways and reducing contact resistance through intimate pore wall contact. In contrast, the higher R_{ct} value of PC-C-2 arises from its lower micropore fraction, where silicon aggregates into larger particles with poor confinement, compromising electrical contact during cycling. PC-B-2 exhibits intermediate behavior consistent with its moderate microporosity. In the low-frequency Warburg region, PC-A-2 shows the steepest slope, indicating the fastest lithium-ion diffusion due to shortened diffusion pathways from ultrasmall silicon domains. Conversely, PC-C-2 displays slower diffusion kinetics associated with larger silicon aggregates^[27,32–34].

The rate performance of the three medium-load samples (PC-A-2, PC-B-2 and PC-C-2) is com-

pared in Fig. 4e. PC-A-2 delivers the best rate performance. At 0.5 C, PC-A-2 delivers an initial discharge capacity of 802.6 mAh g⁻¹, significantly outperforming PC-B-2 and PC-C-2. The improved high-rate performance of the PC-A series is primarily attributed to its distinctive pore structure and high tap density. With 92% microporosity and a specific surface area of 1993 m² g⁻¹, PC-A features a well-developed three-dimensional micropore network that effectively confines silicon and shortens lithium-ion diffusion pathways. In addition, the conductive network and mechanical integrity of PC-A ensure stable electrochemical performance (Fig. S1). In contrast, PC-C, with only 59% microporosity and a substantial fraction of mesopores and macropores, fails to provide adequate confinement, resulting in longer diffusion paths, severe polarization, and poor particle contact due to its loose framework. Rate capabilities for low

and high loading samples are shown in Fig. S8 and S9, exhibiting similar trends of accelerated decay at higher rates, indicating that rate deterioration is governed mainly by the intrinsic properties of the Si/C composite rather than silicon loading alone. Comparative cycling performance in Fig. 4f further confirms these trends. The PC-A series, benefiting from its high microporosity, demonstrates the best cycling stability with $814.93 \text{ mAh g}^{-1}$ after 60 cycles at 0.5 C. By contrast, the PC-C series, contains abundant mesopores and macropores. In such structures, silane-derived silicon deposits not only within pore channels but also aggregates on pore walls or in larger voids. The insufficient spatial confinement in wider pores allows severe volume changes during cycling, leading to progressive loss of electrical contact and continuous SEI reconstruction, which consumes electrolyte and active lithium and accelerates capacity fade. Within each substrate series, increasing silicon deposition from low to medium loading markedly improves reversible capacity while preserving good stability. However, further increasing to high mass loading results in accelerated decay in later cycles, likely due to excessive silicon accumulation on external surfaces or overfilling of pore channels, which generates excessive internal stress and structural collapse. In addition, for carbon substrates with smaller pore sizes, the electrochemical performance cannot be further improved (Fig. S10). Among all samples, PC-A-2 achieves the optimal combination of high specific capacity and excellent cycling stability, owing to its well-engineered micropore confinement and balanced silicon loading^[35].

The cycling performance of PC-A, PC-B and PC-C at low, medium, and high silicon loadings is presented in Fig. S11-S13. For PC-A, the medium loading sample achieves the optimal balance between capacity and stability. Low loading provides stable but lower capacity, while high loading leads to rapid decay due to excessive silicon loading. We further assembled full cells to evaluate the electrochemical performance under medium areal loading conditions. The results demonstrate that a high capacity retention of

95.17% can be achieved at 0.5 C after 50 cycles, revealing the promising practical application potential of the as-prepared electrode (Fig. S14). For PC-B, a similar trend is observed, though capacities are slightly lower and high-loading decay is more severe. For PC-C, overall capacities are lower across all loadings. Medium loading delivers the highest capacity but decays earliest, while low loading shows the most stable performance. The open pore structure of PC-C provides weaker confinement, resulting in gradual capacity loss rather than abrupt failure. The structure of PC-B accommodates silicon well initially but may progressively fail under prolonged cycling stress, whereas the multi-level pore structure of PC-C offers the weakest constraint on silicon volume expansion, leading to rapid capacity decay.

To further understand this performance advantage from the perspective of interfacial chemistry, Fig. 4g-i shows the high-resolution C 1s, F 1s, and O 1s XPS spectra with peak fitting. The C 1s XPS spectrum displays peaks at 284.8 eV (C—C/C—H from carbon substrate), 286.6 eV (C—O), and 288.8 eV (C=O), indicating organic SEI components from electrolyte decomposition. The F 1s XPS spectrum shows a main peak at 686.7 eV, deconvoluted into LiF ($\sim 685 \text{ eV}$) and Li_xPF_y species ($\sim 687 \text{ eV}$), confirming inorganic constituents. The O 1s peak at 533.7 eV corresponds to Li_2CO_3 , ROLi , Li_4SiO_4 and $\text{O}=\text{C}=\text{O}$, further evidencing mixed composition. These results indicate that the SEI on PC-A-2 exhibits a hybrid organic-inorganic nature. The presence of LiF even on the unetched surface suggests inorganic enrichment, likely promoted by the microporous confinement effect. This SEI structure contributes to interfacial stability and fast Li^+ transport, underpinning the excellent cycling performance. The corresponding Si 2p, and Li 1s XPS spectra (Fig. S15) further support the SEI structure analysis. The Si 2p XPS spectrum shows both elemental silicon ($\sim 99.8 \text{ eV}$) and oxidized silicon ($\sim 102.0 \text{ eV}$), indicating structural integrity after cycling. The Li 1s peak near 55 eV corresponds to LiF and other inorganic SEI components, consistent with the inorganic-rich layer discussed in the main text.

3.5 Electrode stability analysis and volume expansion management

To further elucidate the differences in stability among materials with various carrier structures from thermodynamic and interfacial perspectives, we analyzed the first-cycle electrochemical behavior, aiming to establish a comprehensive mechanistic understanding. Fig. 5a displays the first-cycle galvanostatic charge-discharge profiles of the medium-deposition materials (PC-A-2, PC-B-2, PC-C-2) in a half-cell configuration. PC-A-2 exhibited the highest specific charge/discharge capacities and the most prolonged voltage plateau, alongside the high ICE of 91.2%. PC-B-2 demonstrated intermediate metrics, while PC-C-2 showed the lowest capacity and ICE. This trend aligns with the cycling performance results (Fig. 4f) and directly correlates high initial efficiency with superior improved cycling stability, as a higher ICE implies reduced irreversible lithium consumption and the formation of a more robust initial interface. The first-cycle charge-discharge profiles for low and high silicon loadings are presented in Fig. S16 and S17. With low silicon loading, the discharge specific capacities of

PC-A, PC-B, and PC-C are comparable, and PC-A samples exhibit a slight advantage. With high silicon loading, all samples show reduced capacities due to excessive silicon deposition obstructing ion transport pathways, with PC-A experiencing the most pronounced decline despite its initial loading advantage. The capacity retention of all samples after 60 cycles is summarized in Fig. S18. PC-A-2 exhibits the highest retention among all samples, maintaining over 90% of its initial capacity. For PC-A series, retention decreases progressively with increasing silicon loading, with PC-A-4 showing the most significant decay. The PC-B series displays moderate retention at low and medium loadings but substantial decline at high loading. The PC-C series shows the lowest retention across all loadings, with values consistently below 60%. These results further confirm that high microporosity combined with optimal silicon loading is essential for achieving improved cycling stability.

To gain deeper insight into the efficiency disparities, the electrochemical reaction pathways during the first cycle were analyzed. The differential capacity (dQ/dV) curves in Fig. 5b reveal crucial information.

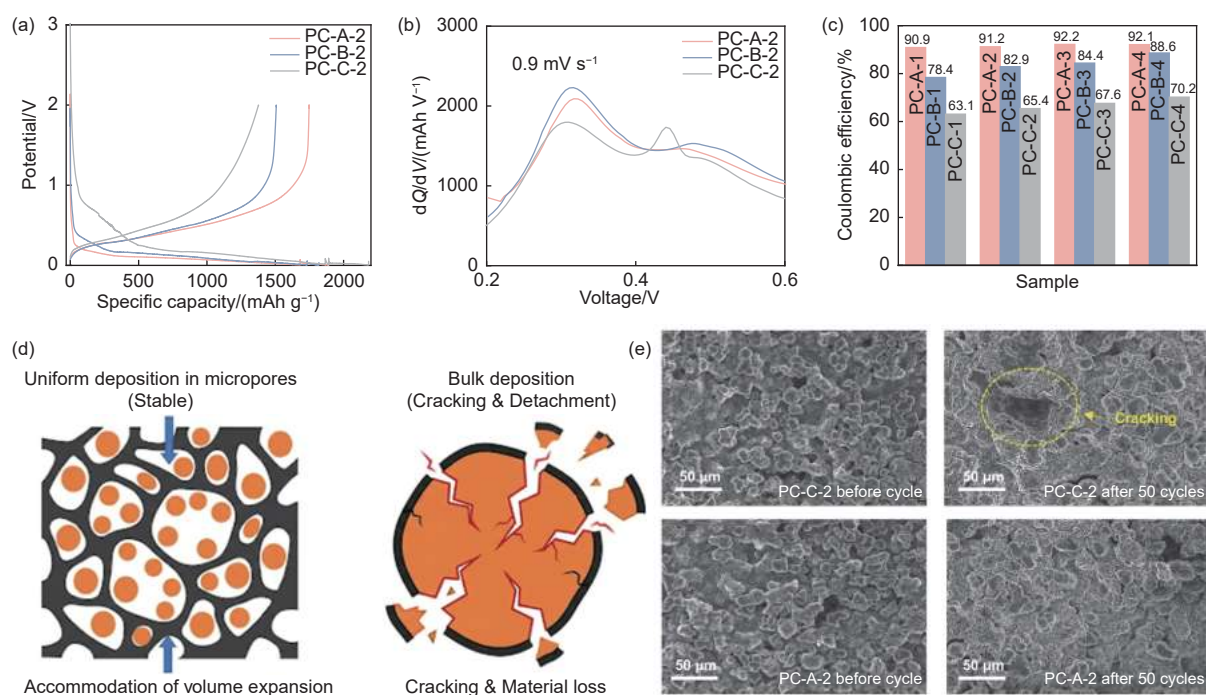


Fig. 5 Influence of microporous structure on electrode stability. (a) Charge-discharge curves of the first cycle and (b) Corresponding curves of dQ/dV versus voltage of PC-A-2, PC-B-2 and PC-C-2 based half-cell. (c) Comparison of ICE among different materials. (d) Schematic diagram illustrating the mechanism by which microporous structures restrict silicon volume expansion. (e) SEM images of PC-A-2 and PC-C-2 before and after cycle

All three materials exhibit a reduction peak around 0.3 V, corresponding to the lithiation of silicon. However, the peak positions for PC-B-2 and PC-C-2 are shifted toward lower potentials, with PC-C-2 displaying the lowest peak intensity. Such peak shifts typically indicate greater reaction polarization or slower kinetics. More significantly, only the curve for PC-C-2 shows a distinct oxidation peak near 0.43–0.45 V, which is associated with the delithiation of the detrimental crystalline $\text{Li}_{15}\text{Si}_4$ phase. The formation of crystalline $\text{Li}_{15}\text{Si}_4$ phase involves substantial volume change and mechanical stress, resulting in electrode structural degradation and electrochemical degradation. Furthermore, the corresponding XRD pattern shows peaks of $\text{Li}_{15}\text{Si}_4$, verifying its presence. (Fig. S19). The corresponding peaks for PC-A-2 and PC-B-2 are very weak or absent, indicating that their structural frameworks effectively suppress this detrimental phase transition.

Fig. 5c systematically presents the ICE for all samples across different deposition levels. A clear trend emerges: at any given deposition level, the efficiency consistently follows the order PC-A > PC-B > PC-C. This order aligns perfectly with their respective microporosity contents (PC-A: 92%, PC-B: 84%, PC-C: 59%). For the materials depicted, the ICE increases slightly with the deposition amount and microporosity content, which may be attributed to that the decreased specific surface area leads to a reduction in side reactions. Although the ICE of PC-A-2 is not the highest among the samples, it exhibits the most balanced electrochemical performance when cycle stability and rate capability are both taken into consideration.

To summarize these findings, we propose a mechanistic model, illustrated schematically in Fig. 5d. The model contrasts 2 scenarios: within a microporous confining environment, silicon deposition is restricted to narrow carbon channels. During subsequent lithiation, the volumetric expansion of silicon is uniformly constrained by the surrounding carbon walls, preventing particle fracture. In contrast, within larger pores or more open structures, silicon depos-

ition and growth occur more freely. The resulting agglomerates undergo severe anisotropic expansion during lithiation, readily leading to fracture of the carbon framework, detachment of silicon particles, and persistent interfacial side reactions. This model provides an intuitive explanation for why the PC-A series (particularly PC-A-2) achieves high silicon loading alongside high capacity and exceptionally improved cycling stability. Finally, direct post-cycling morphological evidence, to be presented, will further substantiate the aforementioned mechanism. Fig. 5e presents post-cycling SEM images of the PC-A-2 and PC-C-2 electrodes after 50 cycles. A direct comparison reveals a stark contrast in morphological integrity. The PC-C-2 electrode exhibits severe, large cracks, as circled in the corresponding image. Structural degradation mainly originates from the stresses induced by phase transformation during the formation of $\text{Li}_{15}\text{Si}_4$. Crack formation aggravates side reactions and further causes capacity loss. In contrast, the PC-A-2 electrode maintains its overall morphology without significant cracking. This distinct divergence in failure modes provides direct visual evidence that supports the microporous confinement stabilization mechanism^[36]. The absence of major cracks in PC-A-2 correlates with its high micropore content, which effectively constrains silicon expansion and preserves electrode integrity during repeated lithiation and delithiation^[37].

4 Conclusion

In this work, we established a highly effective design principle for high-performance Si/C anodes by precisely engineering the internal pore structure of the carbon carrier by chemical vapor deposition. A high content of micropores, specifically a sample with 92% microporosity, creates a strong confinement environment that directs preferential silane adsorption and uniform silicon nucleation. This micropore-induced confinement fundamentally buffers severe volume expansion and minimizes direct contact between the active silicon and the liquid electrolyte. Consequently, the robust structural framework prevents particle frac-

ture and successfully suppresses the formation of the detrimental crystalline $\text{Li}_{15}\text{Si}_4$ phase during repeated lithiation and delithiation. As a result, the optimized composite achieves a high amorphous silicon loading of 51% and delivers an outstanding initial Coulombic efficiency of 91.2%. By balancing capacity and reaction kinetics at a moderate silicon loading, this rational structural design overcomes the traditional trade-offs among high capacity, interfacial stability, and cycling life in silicon-based anodes. This micropore-confinement strategy presents a practical and scalable pathway, providing a clear direction for the development of commercially viable, high-energy-density lithium-ion batteries.

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