



Improving the porous carbon matrix to suppress the formation of surface silicon for improved cycling stability

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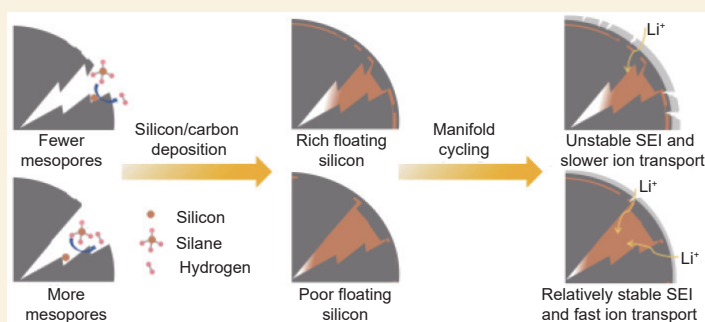
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Abstract: Silicon-carbon composites prepared by chemical vapor deposition (CVD) are highly promising anode materials for high-energy-density lithium-ion batteries. However, the influence of the pore structure of the porous carbon (PC) carrier on the silicon deposition behavior, as well as the influence of surface silicon on its outer surface on cycling stability, remain unclear, which severely hinders the development and practical application of these anodes. Nitrogen adsorption-desorption analysis, X-ray photoelectron spectroscopy, and thermogravimetric analysis were used to investigate the effect of the pore structure of the porous carbon on the silicon deposition, especially the formation of surface silicon. Research shows that too much surface silicon hinders lithium-ion diffusion kinetics and decreases the stability of the solid electrolyte interphase layer, thereby leading to decreased cycling stability of the anode. Porous carbon with an increased mesopore content allows silicon to deposit deeper into the pores, thereby reducing the formation of surface silicon and extending the cycle life. Electrochemical results show that the optimized silicon-carbon composite maintains a high specific capacity of 693.1 mAh/g after 150 cycles at 0.5 C (900 mA/g). This work provides new insights into the development and failure mechanisms of CVD-derived silicon-carbon composite anodes.

Key words: Chemical vapor deposition; Silicon deposition behavior; Silicon-carbon anode; Floating silicon; Lithium-ion battery



1 Introduction

Driven by the demand for extended driving range in new energy vehicles, lithium-ion batteries (LIBs) are currently evolving toward high energy density and long cycle life^[1]. However, graphite anodes, with their limited theoretical specific capacity (372 mAh/g), can hardly meet such heightened requirements^[2]. Owing to their abundant resources, low operating potential, and high theoretical capacity (3579 mAh/g), silicon anode has emerged as one of the promising alternatives to graphite anodes^[3]. However, pure silicon anodes can hardly be directly used in LIBs due to their drawbacks of low electronic conductivity and significant volume expansion (up to 300%)^[4]. Currently, modification strategies such as silicon nanosizing^[5], graphite

blending^[6] and silicon-carbon compositing^[7] are commonly employed. Among these, silicon-carbon anode materials prepared by chemical vapor deposition (CVD) have emerged as promising candidates for next-generation high-capacity anodes, owing to their high electronic conductivity and effective buffering for volume expansion^[8].

The preparation of silicon-carbon anode materials by CVD is based on delivering silane gas to a carbon substrate (typically including graphite^[9], porous

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hard carbon^[10], etc.). At elevated temperatures, the silane undergoes pyrolysis to form silicon and hydrogen, after which silicon deposits onto the carbon substrate, yielding a silicon-carbon composite. Among them, porous carbon rich in micropores has thus become a prominent focus in silicon-carbon composite research, owing to its robust mechanical strength, abundant pore structure that provides ample accommodation space for silicon vapor deposition, and excellent ability to suppress volume expansion^[11]. For instance, Mu et al.^[12] prepared porous carbon rich in micropores by CO₂ etching of phenolic resin-based carbon microspheres, deposited silicon through CVD into the pores, and then conducted carbon coating through acetylene cracking. The resulting Si/ASC composite exhibited a capacity retention of 93.3% after 800 cycles in half-cells and a capacity retention of 46.7% after 500 cycles in full-cells. Currently, modification strategies for CVD-derived silicon-carbon materials are primarily focused on tailoring the porous carbon substrate. The pore structure of porous carbon is one of the most critical factors influencing silicon deposition behavior and the electrochemical performance of the resulting silicon-carbon composites. For example, Yang et al.^[13] obtained porous carbons with distinct pore-size distributions by employing different precursors. Their results indicated that, due to the stronger physisorption force in micropores compared to mesopores or the material surface, the deposition rate of silicon from silane is faster within micropores. While larger mesopores can facilitate higher silicon loading, they may also lead to the formation of localized crystalline silicon domains. Furthermore, studies have revealed that both the micropore/mesopore ratio^[14] and the total pore volume^[15] of porous carbon significantly influence silicon deposition behavior, thereby altering the rate capability and cycling performance of the resulting silicon-carbon composites. These studies indicate that the pore structure of porous carbon is one of the most critical factors influencing both the silicon deposition behavior and the electrochemical performance of silicon-carbon composites.

However, CVD-derived silicon cannot be fully deposited within the internal pores of porous carbon. A portion of the silicon inevitably deposits on the external surface of the porous carbon, forming so-called surface floating silicon^[16]. Current studies indicate that such surface floating silicon significantly affects the cycling performance of CVD-derived silicon-carbon composite anodes. For example, Guo et al.^[17] suggested that floating silicon significantly amplifies the kinetic hysteresis within the 0.01–0.8 V window, thereby effectively suppressing deep lithiation of Si and contributing positively to cycling stability. In contrast, Yu et al.^[18] argued that the presence of surface floating silicon results in excessive electrode expansion, which is detrimental to cycling stability. However, the influence of the pore structure of porous carbon on the formation of such floating silicon remains unclear. Therefore, there is an urgent need to further investigate the influence of the porous carbon's pore structure on silicon deposition behavior and the influence of surface floating silicon on cycling failure mechanisms, in order to improve the cycle life of CVD-derived silicon-carbon composite anodes.

In this study, porous carbons with different pore structures are prepared using KOH activators at varying mass ratios (1.75 : 1, 2.00 : 1, 2.25 : 1). Nano-silicon and a carbon coating are deposited into the porous carbons via CVD, yielding CVD-derived silicon-carbon materials with different contents of surface floating silicon. N₂ adsorption-desorption analysis is employed to investigate the influence of pore structure on silicon deposition behavior. Further characterization, including conductivity measurements, X-ray photoelectron spectroscopy (XPS) analysis, and thermogravimetry analysis, is conducted to evaluate the relative amount of surface floating silicon. Finally, the electrochemical performance and post-cycling electrode morphology of the 3 materials (PC_{1.75}@Si@C, PC_{2.00}@Si@C and PC_{2.25}@Si@C) are compared. The results reveal that surface floating silicon hinders ion diffusion kinetics and deteriorates the stability of the solid electrolyte interphase (SEI), thereby leading to degradation of cycling stability of the silicon-carbon

anode. Porous carbon with lower porosity or a moderately higher mesopore proportion can reduce the formation of surface floating silicon, thus extending cycle life. These findings provide new insights into the failure mechanisms and structural optimization of CVD-derived silicon-carbon anodes.

2 Experiment

2.1 Preparation of PC_x , $PC_x@Si$ and $PC_x@Si@C$

A predetermined amount of resin-based carbon microspheres (obtained from the Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences) is mixed with KOH at different mass ratios (1.75 : 1, 2.00 : 1, 2.25 : 1) and ball milled for 30 min to ensure homogeneity. The mixed powder is placed in a tubular furnace, heated to 800 °C at 2 °C/min under an argon atmosphere, and held for 2 h. After activation, the powder is washed three times with deionized water and dried to remove residual ions. The dried powder is then transferred again to the tubular furnace, heated to 900 °C at 2 °C/min and maintained for 2 h to remove most oxygen-containing functional groups. The resulting material is designated as PC_x , where x denotes the mass ratio of carbon microspheres to KOH.

Approximately 1 kg of PC_x is placed in a fluidized-bed reactor, purged with argon to clean the internal atmosphere, and then heated to 470 °C at 2 °C/min. To investigate the effects of total pore volume on silicon loading and the formation of surface floating silicon, silane is introduced into $PC_{1.75}$ and $PC_{2.00}$ at flow rates of 850 and 950 L/kg, respectively, with a volume ratio of carrier gas (argon) to silane of 5 : 1 (different silane volumes are used to fully utilize the nano pores and avoid the formation of a surface silicon shell). To explore the effect of an increased mesopore proportion under high microporosity on surface floating silicon, the same amount of silane (950 L/kg) is introduced into $PC_{1.75}$ and $PC_{2.00}$ to ensure identical silicon loading. A small amount of carbon is deposited on the surface using acetylene as the carbon source to prevent silicon from coming into contact with air and causing danger. The resulting

product after deposition is labeled $PC_x@Si$. Then the $PC_x@Si$ material is transferred to a rotating furnace, where an equal amount of acetylene is introduced at 600 °C to deposit a uniform carbon coating. The final coated product is designated as $PC_x@Si@C$.

2.2 Cell assembly

The silicon-carbon material ($PC_x@Si@C$) prepared by CVD is used as the active material. A slurry is prepared by uniformly mixing the $PC_x@Si@C$, conductive additive (Super P), and lithium polyacrylate (PAA-Li, 4%) binder in a mass ratio of 8 : 1 : 1. The slurry is then cast onto carbon-coated copper foil and dried under vacuum at 80 °C for 12 h. After drying, the electrode is cut into circular discs with a diameter of 10 mm to serve as working electrodes, with an active material loading of approximately 1.0 mg/cm². CR2032 coin-type cells are assembled in an argon-filled glove box ($\varphi_{O_2} \leq 0.01 \times 10^{-6}$, $\varphi_{H_2O} \leq 0.01 \times 10^{-6}$) for electrochemical evaluation. In a half-cell configuration, lithium metal foil is used as the counter electrode, and a polypropylene (PP) separator is placed between the working and counter electrodes. The electrolyte consists of 1 mol L⁻¹ LiPF₆ in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DEC) (volume ratio 3 : 4 : 3), with 5% (mass fraction) fluoroethylene carbonate (FEC) as an additive. All cells are rested for 12 h after assembly and tested at room temperature (25 °C).

2.3 Electrochemical measurement

Galvanostatic charge/discharge (GCD) and galvanostatic intermittent titration technique (GITT) measurements are conducted on a LAND battery test system (LAND, Wuhan, China) over a voltage range of 0.01–2.0 V (vs. Li/Li⁺). Prior to cycling, all cells are activated for 2 cycles at a current density of 0.05 C before proceeding with constant-current charge/discharge cycles at other rates (1 C = 1800 mA/g). The trapped active lithium content is determined by holding the cell at 1.5 V for 12 h, and the amount of lithium extracted during this step corresponds to the trapped active lithium content^[19]. For the GITT test, the pulse duration is 30 min followed by a relaxation

period of 1 h. Cyclic voltammetry (CV) is performed between 0.01 and 2.0 V at scan rates ranging from 0.1 to 1.0 mV/s. Electrochemical impedance spectroscopy (EIS) is carried out over a frequency range of 100 kHz to 10 mHz with an alternating current perturbation amplitude of 5 mV. Both EIS and CV tests are conducted using a Bio-Logic VSP electrochemical workstation. Cycle counting starts from first cycle after the pre-cycling.

2.4 Characterization

The morphology and elemental composition of the samples are characterized using a scanning electron microscope (SEM, FEI Phenom) equipped with energy-dispersive spectroscopy (EDS). The microstructure of the sample is analyzed with a high-resolution transmission electron microscope (HRTEM, JEM-2100F) equipped with EDS. The particle size distribution is evaluated with a laser diffraction particle size analyzer (Bettersize 2600). The average electrical conductivity is measured using a powder resistivity meter (Suzhou Jingge, China, ST2742). The crystal structure and phase composition are examined by X-ray diffraction (XRD, MiniFlex) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Raman spectroscopy is performed on a Raman spectrometer (Japan, Horiba Lab-RAM HR Evolution) with a 532 nm laser. The relative silicon content in the samples is calculated from the mass difference before and after oxygen combustion at 900 °C. Nitrogen adsorption-desorption experiments are carried out on a gas physisorption analyzer (BEL SORP-MAX) to determine the specific surface area and pore structure parameters. The oxygen combustion behavior and relative silicon content of the silicon-carbon composite are evaluated by a simultaneous thermal analyzer (TGA, Mettler TGA/DSC 3+). The surface elemental states are characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Possible functional groups are identified using Fourier-transform infrared spectroscopy (FT-IR, Bruker TENSOR 27). After cycling, the cells are disassembled in an argon-filled glove box. The electrodes are rinsed three times with dimethyl carbonate (DMC) and dried before characterization.

Cross-sections of the electrodes are prepared by fracturing in liquid nitrogen with a blade, with minimal exposure to air throughout the process.

3 Results and discussion

3.1 Material preparation process

Fig. 1a illustrates the preparation process of the CVD-derived silicon-carbon anode. First, resin-based carbon microspheres are activated using KOH at different mass ratios. To eliminate the influence of surface functional groups, the material is further carbonized at 900 °C to remove oxygen-containing functional groups, thereby obtaining porous carbon materials with distinct pore structures (PC_x). Then, nano-silicon is deposited through silane pyrolysis onto the PC_x substrates, yielding the $\text{PC}_x@\text{Si}$ materials (Equation S1). The $\text{PC}_x@\text{Si}$ material is then placed in a rotary furnace, where a uniform carbon coating is deposited by acetylene pyrolysis (Equation S2), ultimately yielding the $\text{PC}_x@\text{Si}@\text{C}$ composite. The protective carbon layer serves a dual purpose: on one hand, it minimizes direct contact between silicon and the electrolyte, thereby mitigating excessive SEI growth. On the other hand, it also provides a degree of buffering against silicon expansion. Fig. 1b–d and Fig. S1 show the SEM images of PC_x , $\text{PC}_x@\text{Si}$ and $\text{PC}_x@\text{Si}@\text{C}$ respectively. SEM images reveal that all three PC_x materials exhibit spherical morphology. After silicon deposition and carbon coating, the overall spherical shape remains largely intact, but the surface pores of the porous carbon become less discernible following deposition. Moreover, no discernible nanoparticles are observed on the surface of $\text{PC}_x@\text{Si}$, indicating the absence of substantial silicon particle deposition (Fig. S2). Table S1 presents the variation in median particle size (D50) before and after silicon deposition. As the KOH ratio increases, the particle size of PC_x gradually decreases, which may be attributed to more extensive carbon etching by KOH. The particle size of $\text{PC}_x@\text{Si}@\text{C}$ increases slightly, likely due to the deposited carbon coating. Fig. 1e shows the XRD patterns of PC_x . The broad diffraction peak appearing around 43° corresponds to the (100) crystal plane of hard car-

bon^[20]. These broad and low-intensity diffraction features indicate that all three porous carbons possess a disordered structure^[12]. The peak appearing around 26° is attributed to the (002) crystal plane of hard carbon. However, this peak is often overshadowed by the intense low-angle diffraction caused by the micropore structure, making it difficult to identify clearly^[11]. Compared with $PC_{2.00}$ and $PC_{2.25}$, $PC_{1.75}$ exhibits a stronger and sharper (100) diffraction peak. This indicates that $PC_{1.75}$ possesses longer graphene-like domains and a higher degree of structural ordering, which is more favorable for electrical conductivity. This evolution in microcrystalline structure arises because increasing KOH concentration accelerates the etching rate of carbon layers, preferentially thinning and fragmenting them into smaller graphene-like sheets^[21]. It should be noted that, considering that an

excessively high KOH ratio would cause excessive pore etching and thus be detrimental to mechanical strength, a higher KOH ratio was not adopted in this study^[21–22]. Elemental analysis (Fig. 1f) shows that the chemical compositions of the 3 porous carbons (PC_x) are similar, consisting primarily of carbon with trace amounts of oxygen. Additionally, the conductivities of $PC_{1.75}$, $PC_{2.00}$ and $PC_{2.25}$ are 20.68, 19.99 and 20.58 S/cm, respectively (Fig. 1g). The minor differences in conductivity likely originate from variations in their microcrystalline and pore structures. In summary, the similar morphology and chemical structure of the 3 porous carbon materials do not interfere with silicon deposition.

3.2 Analysis of silicon deposition behavior

To analyze the influence of the pore structure of porous carbons on silicon deposition behavior, nitro-

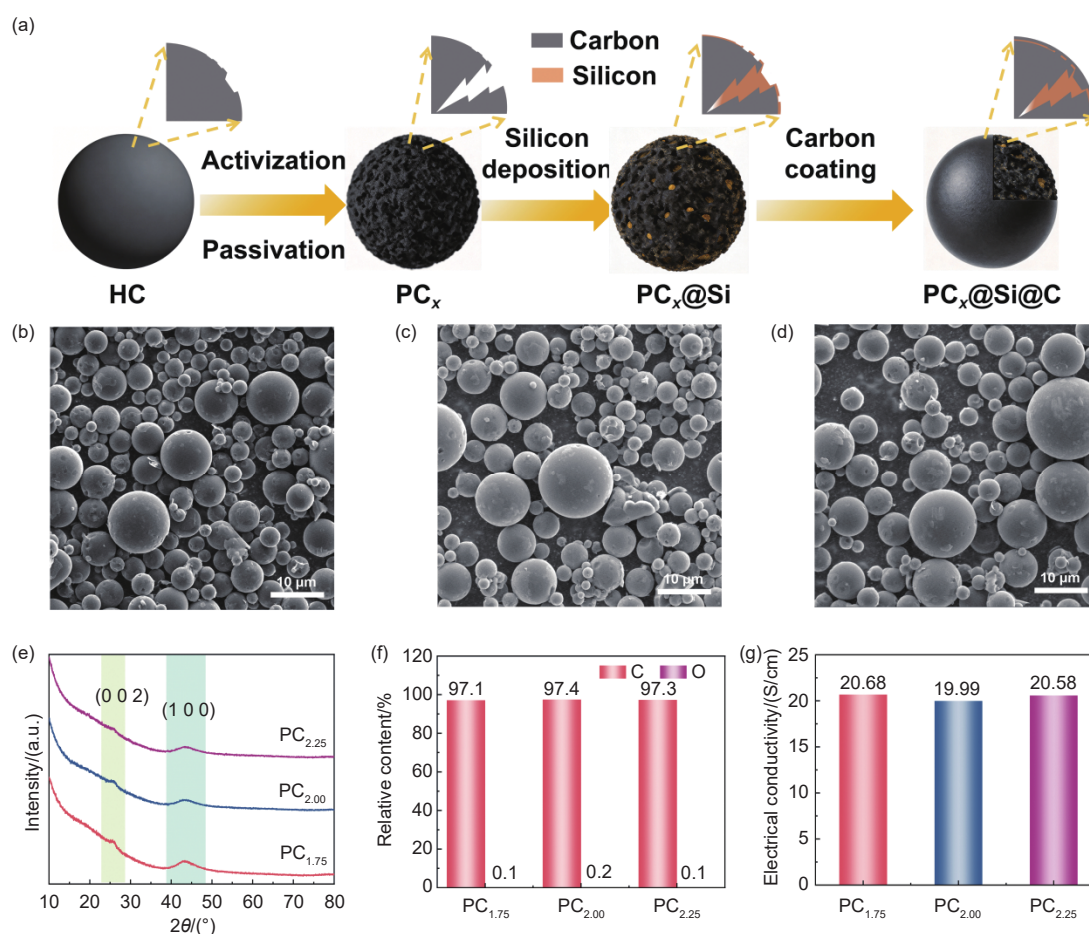


Fig. 1 Preparation of CVD-derived silicon-carbon materials and structural analysis of porous carbons (PC_x). (a) Schematic diagram of the $PC_x@Si@C$ preparation process. (b–d) SEM images of $PC_{1.75}$, $PC_{2.00}$ and $PC_{2.25}$, respectively. (e) XRD patterns of PC_x . (f) Elemental composition (C, O) of PC_x . (g) Powder conductivity of PC_x .

gen adsorption-desorption measurements are performed on the PC_x , $PC_x@Si$, and $PC_x@Si@C$ samples. Fig. 2a shows the adsorption-desorption isotherms of the 3 PC_x materials. All nitrogen adsorption-desorption isotherms conform to Type I isotherms, indicating that the pore structure of the 3 porous carbons is predominantly composed of micropores. Table S2 summarizes the specific surface area and pore structure parameters of PC_x . As the KOH ratio increases, both the specific surface area and total pore volume of PC_x increase. The change from $PC_{1.75}$ to $PC_{2.00}$ is primarily attributed to an increase in micropores, which is likely due to the higher KOH ratio providing more activation sites for pore etching. The significant overlap of interaction potentials between the pore walls in micropores typically results in a stronger

physical adsorption force compared to mesopores or the material surface, thereby favoring a higher silicon deposition rate^[13]. From $PC_{2.00}$ to $PC_{2.25}$, the specific surface area changes only slightly while the total pore volume increases further. This may be attributed to excessive KOH etching causing the breakdown of micropore walls, which subsequently merge to form more mesopores. The mesopores with larger pore volumes may facilitate the loading of silicon into the pores^[13]. Fig. 2b presents the nitrogen adsorption-desorption isotherms of the $PC_x@Si$ materials. After silicon deposition, the isotherms remain Type I, but the adsorption quantity decreases, indicating that silicon primarily deposits into the micropores of the porous carbon without completely filling them (Table S3). Following carbon coating on the surface of $PC_x@Si$,

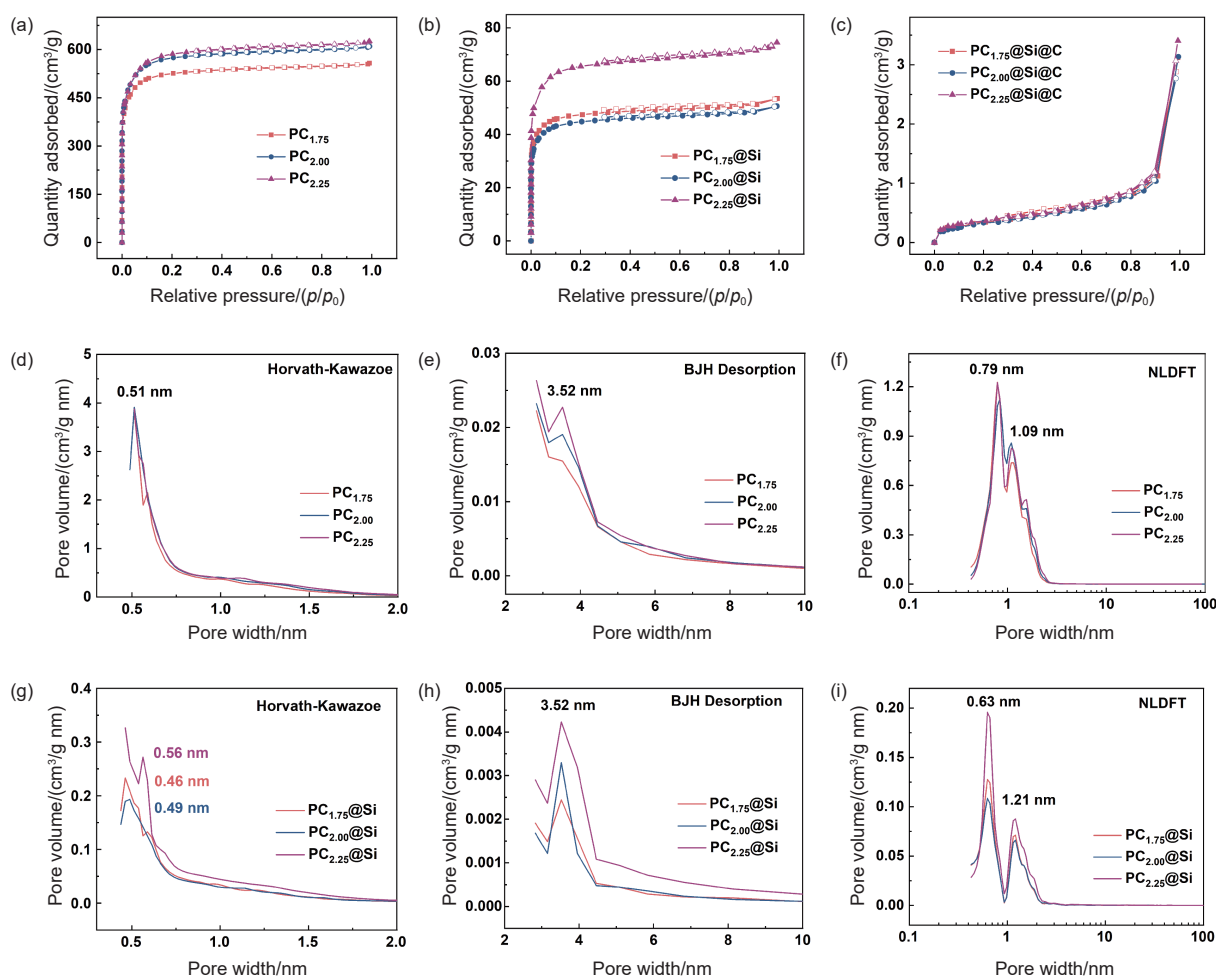


Fig. 2 Pore structure analysis before and after deposition. (a–c) Nitrogen adsorption-desorption isotherms of PC_x , $PC_x@Si$, and $PC_x@Si@C$, respectively. (d–f) Micropore size distribution, mesopore size distribution, and full pore size distribution of PC_x , respectively. (g–i) Micropore size distribution, mesopore size distribution, and full pore size distribution of $PC_x@Si$, respectively

the isotherms shift to Type II (Fig. 2c), suggesting that the carbon layer covers the surface of $\text{PC}_x\text{@Si}$ and blocks the remaining pores (Table S4).

To investigate the relationship between Si deposition behavior and the pore structure of porous carbon, the micropore size distribution, mesopore size distribution, and full pore size distribution of the materials before and after Si deposition were analyzed using the Horvath-Kawazoe (HK) model, the Barrett-Joyner-Halenda (BJH) model, and non-local density functional theory (NLDFT), respectively (Fig. 2d–i). The pore size distribution of PC_x is concentrated mainly within 0.7–3 nm (Table S5). Since silicon does not form a silicon shell layer on the surface, constrained by the micro/mesopores, the deposited silicon can be considered predominantly nanoscale silicon particles or clusters (< 3 nm). Table S3 presents the specific surface area and pore structure parameters of $\text{PC}_x\text{@Si}$. After silicon deposition, the total pore volume of the porous carbon decreases while a certain pore structure remains, indicating that silicon primarily deposits into the micropores. Moreover, compared to $\text{PC}_{1.75}$, a larger volume of silane is introduced for $\text{PC}_{2.00}$, resulting in more nanoscale silicon deposition in $\text{PC}_{2.00}\text{@Si}$ and a correspondingly greater reduction in its total pore volume. To examine the effect of mesopores on silane deposition, $\text{PC}_{2.25}$ is subjected to the same silane volume as $\text{PC}_{2.00}$. Fig. 2g–i and Table S3 show that the increased proportion of mesopores in the porous carbon leads to a higher specific surface area and pore volume in $\text{PC}_{2.25}\text{@Si}$. This may be because $\text{PC}_{2.25}$, which has more mesopores, causes silicon to deposit deeper inside the pore channels, leaving greater accessible pore volume.

In Fig. 3a, the XRD patterns of $\text{PC}_x\text{@Si}$ indicate that $\text{PC}_{1.75}\text{@Si}$, $\text{PC}_{2.00}\text{@Si}$ and $\text{PC}_{2.25}\text{@Si}$ primarily deposit amorphous or small-sized crystalline silicon. The attenuation of the low-angle peak further confirms that silicon mainly deposits into the micropores^[18]. The retention of the (002) and (100) peaks demonstrates that the carbon matrix retains its microcrystalline structure after deposition. To further investigate the deposition location of silicon, HRTEM

and HRTEM-EDS were employed to analyze the edge of $\text{PC}_x\text{@Si}$. As shown in Fig. S3 and S4, no silicon shell layer is formed on the external surface of PC, further demonstrating that silicon is deposited within the pores of the porous carbon. Fig. 3b shows the FT-IR spectra of $\text{PC}_x\text{@Si}$. The absorption peak at 1110 cm^{-1} is attributed to the stretching vibration of Si—O bonds^[23], while the peak at 762 cm^{-1} corresponds to amorphous Si—C bonds^[24–25]. The FT-IR results indicate that the chemical bonding at the silicon-carbon interface is similar after silicon deposition. Fig. 3c shows the Raman spectra of $\text{PC}_{1.75}\text{@Si}$, $\text{PC}_{2.00}\text{@Si}$ and $\text{PC}_{2.25}\text{@Si}$. Typically, the Raman peak around 520 cm^{-1} corresponds to crystalline silicon, while the peak near 480 cm^{-1} is attributed to amorphous silicon. The silicon peaks for all 3 materials appear near 480 cm^{-1} , further confirming that the deposited nano-silicon is primarily amorphous^[12]. Compared with $\text{PC}_{1.75}\text{@Si}$ and $\text{PC}_{2.00}\text{@Si}$, $\text{PC}_{2.25}\text{@Si}$ exhibits a weaker silicon signal and a stronger carbon signal. This may be attributed to the increased proportion of mesopores, which facilitates the transport and deposition of silicon into deeper micropores, thereby reducing the silicon signal detected from the surface while enhancing the carbon signal. The oxidation behavior and approximate silicon content of $\text{PC}_x\text{@Si}$ were analyzed by TGA in an oxygen atmosphere (Fig. 3d). The identical weight change behavior of $\text{PC}_{2.00}\text{@Si}$ and $\text{PC}_{2.25}\text{@Si}$ confirms their similar chemical structures. The lower final mass of $\text{PC}_{1.75}\text{@Si}$ is attributed to its lower silicon content.

To quantitatively analyze the relative silicon content, the $\text{PC}_x\text{@Si}$ are subjected to combustion in a muffle furnace at 900 °C under an oxygen atmosphere^[18]. The relative silicon content is calculated using Equation S3–S5 based on the mass change before and after combustion. As can be observed in Fig. 3e, $\text{PC}_{2.00}\text{@Si}$ exhibits the highest silicon content. Compared with $\text{PC}_{1.75}\text{@Si}$, this difference may be attributed to the greater abundance of micropores in $\text{PC}_{2.00}$, which provide stronger adsorption capacity for silane, thereby promoting more extensive silane pyrolysis and deposition. The relative silicon content of

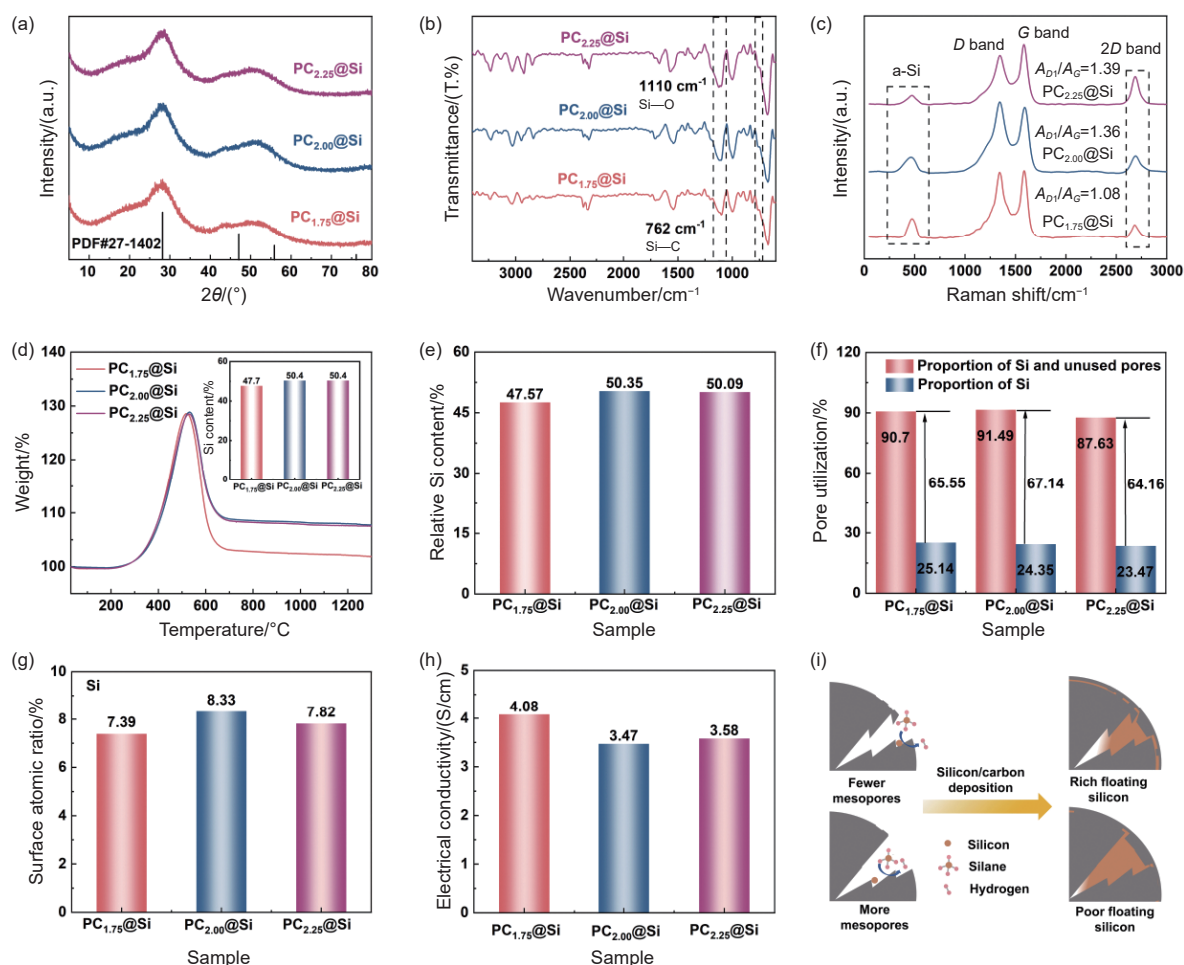


Fig. 3 Analysis of silicon deposition behavior. (a) XRD patterns of $PC_x@Si$. (b) FT-IR spectra of $PC_x@Si$. (c) Raman spectra of $PC_x@Si$. (d) TGA curves of $PC_x@Si$, with the inset showing the calculated relative silicon content. (e) Relative silicon content of $PC_x@Si$. (f) Pore volume occupancy of $PC_x@Si$. (g) Surface Si atomic percentage of $PC_x@Si$. (h) Powder conductivities of $PC_x@Si$. (i) Schematic of the silicon deposition behavior

$PC_{2.25}@Si$ is similar to that of $PC_{2.00}@Si$, indicating that the slightly increased proportion of mesopores does not enhance silane pyrolysis and deposition. Since silane cannot enter all micropores and premature pyrolysis may block pore channels, CVD-silicon deposition inevitably leaves a portion of the internal pore space in porous carbon incompletely utilized. To analyze the utilization efficiency of the pore volume by deposited silicon, the pore volume occupancy and the silicon-volume occupancy are calculated using the volumetric method (Equation S6) and the gravimetric method (Equations S7–S8), respectively. The difference between these 2 occupancy values represents the proportion of internally unoccupied pores (Equation S9). As shown in Fig. 3f, $PC_{2.00}@Si$ exhibits the largest fraction of unoccupied internal pores. This suggests that silicon in $PC_{2.00}@Si$ is deposited pre-

dominantly in the outer and middle regions of the pore channels. Compared with $PC_{2.25}@Si$, $PC_{2.00}@Si$ possesses a similar silicon content but a higher proportion of unoccupied pores, implying that some silicon may not be deposited within the pores.

Indeed, in current CVD processes for depositing nano-silicon, it is impossible to entirely avoid partial deposition of silane on the external surface of the porous carbon, which inevitably results in a certain amount of floating silicon on the surface of the silicon-carbon composite^[17]. The surface atomic composition of $PC_x@Si$ is analyzed by XPS. As shown in Fig. 3g and Table S6, $PC_{2.00}@Si$ exhibits the highest relative atomic percentage of silicon on its surface, confirming a greater amount of surface floating silicon compared to $PC_{1.75}@Si$ and $PC_{2.25}@Si$. The Si 2p XPS spectra (Fig. S5) indicate that silicon on the sur-

face of $\text{PC}_x\text{@Si}$ exists primarily as Si—Si bonds. The presence of Si—C bonds demonstrates successful composite formation between the deposited silicon and the porous carbon. The appearance of Si—O bonds is attributed to inevitable surface oxidation occurring during material preparation and storage^[14]. Fig. 3h presents the powder conductivity of $\text{PC}_x\text{@Si}$ after nano-silicon deposition. The average conductivity values of $\text{PC}_{1.75}\text{@Si}$, $\text{PC}_{2.00}\text{@Si}$ and $\text{PC}_{2.25}\text{@Si}$ are 4.08 S/cm, 3.47 S/cm and 3.58 S/cm, respectively. A lower powder conductivity corresponds to a higher number of exposed silicon particles on the surface of the silicon-carbon material. Therefore, the lowest conductivity of $\text{PC}_{2.00}\text{@Si}$ further confirms its higher content of surface floating silicon^[16]. In Fig. S4, the silicon signals at the edges of $\text{PC}_{1.75}\text{@Si}$ and $\text{PC}_{2.25}\text{@Si}$ are relatively weaker, while that of $\text{PC}_{2.00}\text{@Si}$ is relatively stronger. This further proves that $\text{PC}_{2.00}\text{@Si}$ has more surface floating silicon. Regrettably, the actual content of surface floating silicon has not been precisely quantified.

In summary, as shown in Fig. 3i, nano-silicon generated from silane pyrolysis primarily deposits in the form of amorphous silicon within the micropores of porous carbon, yet it cannot fully utilize the internal micropores. An increase in the micropores of porous carbon enhances its adsorption capacity for silane, thereby enabling the deposition of a higher relative content of nano-silicon. However, the increased silane supply also prolongs the exposure of the external surface to silane, further leading to the formation of more floating silicon. Increasing the proportion of mesopores in porous carbon with high microporosity facilitates deposition of silicon into the deeper pores, reduces the proportion of unoccupied internal pores, and thus decreases the formation of surface floating silicon.

To minimize direct contact between silicon and the electrolyte, a carbon coating is deposited onto $\text{PC}_x\text{@Si}$. Fig. S6 further shows the XRD patterns after carbon deposition. The results indicate that the carbon deposition does not significantly alter the crystalline form of silicon. Fig. 2c and Table S4 present the pore structure parameters of $\text{PC}_x\text{@Si@C}$ after carbon

coating. The comparable specific surface area and pore volume indicate that the carbon layer covers the residual pores of $\text{PC}_x\text{@Si}$. The chemical structure of the surface coating is analyzed by XPS (Fig. S7 and Table S7). The study reveals that the surface chemical states of $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$ are similar. Notably, compared with $\text{PC}_x\text{@Si}$, the relative content of Si—C bonds on the surface of $\text{PC}_x\text{@Si@C}$ exceeds that of Si—Si bonds, confirming the successful formation of the carbon coating. Given the similar specific surface areas of the three materials, the influence of the coating structure on initial SEI formation is largely minimized.

3.3 Analysis of electrochemical behavior

To investigate the effects of silicon deposition in porous carbons with different pore structures on electrochemical performance, half-cells of $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$ are assembled and tested. Fig. 4a shows the initial charge/discharge curves of $\text{PC}_x\text{@Si@C}$. The first-cycle discharge specific capacities of $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$ are 1747.93, 1846.81 and 1798.70 mAh/g, respectively, with corresponding initial Coulombic efficiencies (ICE) of 89.74%, 90.27% and 89.76%. The highest initial discharge capacity and slightly superior ICE of $\text{PC}_{2.00}\text{@Si@C}$ can be attributed to its highest relative silicon content^[21]. Fig. 4b presents the differential capacity (dQ/dV) curves of $\text{PC}_x\text{@Si@C}$ at 0.05 C. The similar reaction peaks indicate that $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$ share identical electrochemical reaction pathways during the initial charge/discharge. Fig. 4c and 4d show the cycling performance of $\text{PC}_x\text{@Si@C}$ at 0.1 and 0.5 C, respectively. It is evident that $\text{PC}_{2.00}\text{@Si@C}$ exhibits the poorest cycling stability, delivering a remaining capacity of 446.2 mAh/g after 150 cycles at 0.5 C. In contrast, $\text{PC}_{1.75}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$ demonstrate relatively superior cycling stability, with remaining capacities of 606.6 and 693.1 mAh/g, respectively, after 150 cycles at 0.5 C. Compared with other silicon-carbon anodes prepared by the CVD method, $\text{PC}_{2.25}\text{@Si@C}$ exhibits comparable initial discharge capacity, ICE, and cycling stability (Table S8). Compared with

PC_{2.00}@Si@C, the relatively higher cycling stability of PC_{1.75}@Si@C may be attributed to its lower silicon content and lower amount of surface floating silicon, as both factors facilitate the carbon framework in buffering volume changes during lithiation/delithiation. Compared to PC_{2.25}@Si@C, since both have the same silicon content, the inferior stability of PC_{2.00}@Si@C is likely related to its higher surface floating silicon content. Surface floating silicon is only partially constrained by the carbon coating, which is less effective than the carbon framework in suppressing volume expansion during cycling. Furthermore, the lower surface floating silicon content in PC_{2.25}@Si@C contributes to higher conductivity, promoting more efficient ion/electron transport. Fig. 4e and Fig. 4f display the differential capacity (dQ/dV) curves before and after cycling at a rate of 0.5 C. At the initial stage of cyc-

ling, PC_{1.75}@Si@C exhibits the highest low-potential lithiation capacity. Its lower silicon content and longer graphene-like microcrystalline domains result in higher conductivity, which is more favorable for lithium-ion diffusion into the bulk phase. The lower lithiation capacities of PC_{2.00}@Si@C and PC_{2.25}@Si@C are likely due to their higher silicon content leading to relatively lower charge transfer ability compared to PC_{1.75}@Si@C, thus hindering the lithium-ion diffusion within the bulk material. Compared with PC_{2.00}@Si@C, PC_{2.25}@Si@C shows a relatively lower low-potential lithiation capacity. This may be attributed to the greater amount of surface floating silicon in PC_{2.00}@Si@C, which facilitates the formation of more Li₁₅Si₄^[18], thereby contributing to its higher differential capacity in the low-potential region. After 150 cycles, both the high-potential and low-potential

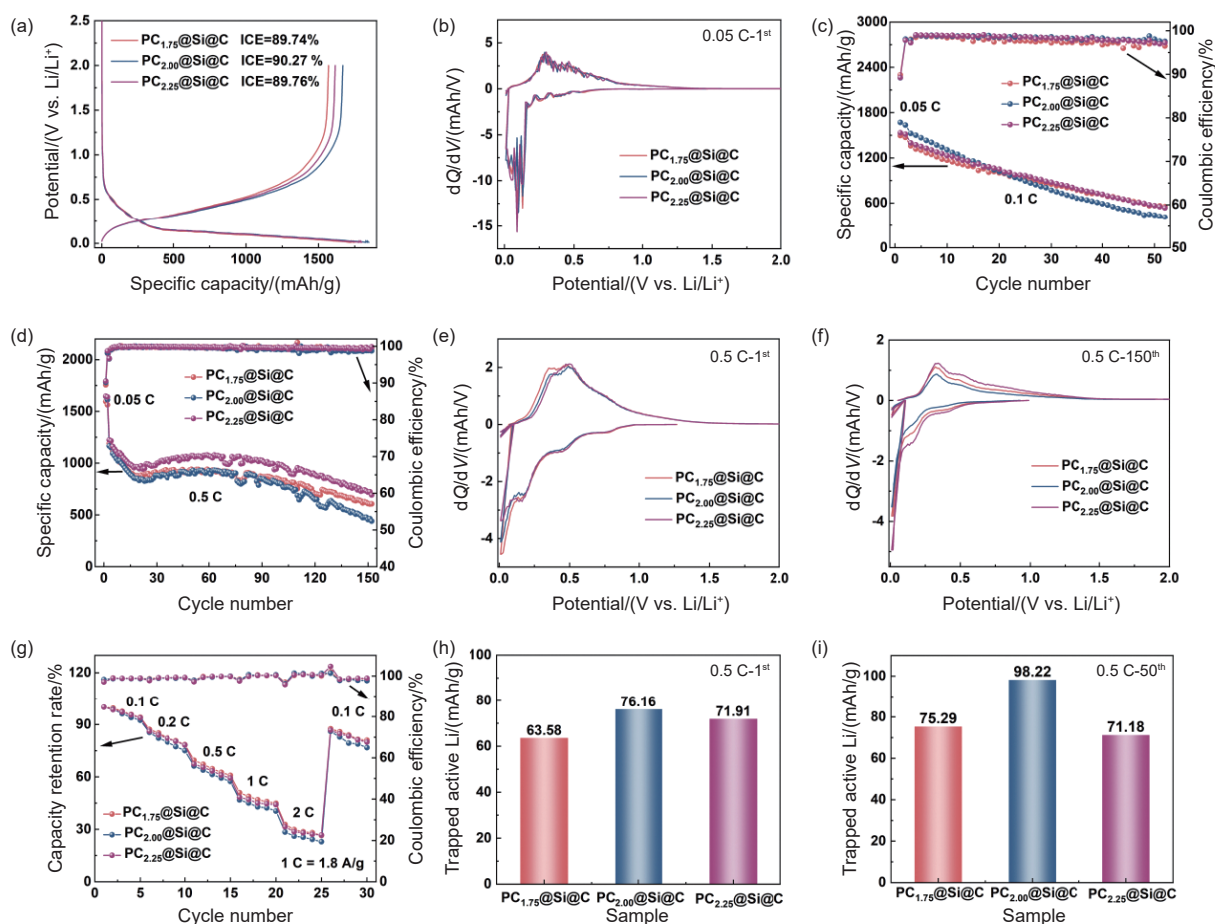


Fig. 4 Electrochemical performance analysis of PC_x@Si@C in half-cells. (a) Initial charge/discharge curves. (b) First-cycle differential capacity (dQ/dV) curves at 0.05 C. (c) Cycling performance at 0.1 C. (d) Cycling performance at 0.5 C. (e) Differential capacity (dQ/dV) curves for the first cycle at 0.5 C. (f) Differential capacity (dQ/dV) curve for the 150th cycle at 0.5 C. (g) Rate capability of PC_x@Si@C. (h) Content of trapped active lithium in the first cycle at 0.5 C. (i) Content of trapped active lithium in the 50th cycle at 0.5 C

peaks show significant attenuation, indicating that the trapped active lithium may occupy a portion of the active sites^[26].

Fig. 4g and Fig. S8 present the capacity retention of $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$ at different current rates. It can be observed that the capacity retention among the three materials is comparable at low rates, while at high rates, $\text{PC}_{1.75}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$ exhibit superior capacity retention compared to $\text{PC}_{2.00}\text{@Si@C}$. The best rate performance of $\text{PC}_{1.75}\text{@Si@C}$ is likely attributed to its lower silicon loading. A lower silicon loading not only prevents uncontrolled volume expansion associated with excessive silicon but also leverages the higher conductivity of the silicon-carbon matrix for more efficient electron transport. Compared to $\text{PC}_{2.00}\text{@Si@C}$, the reduced surface floating silicon in $\text{PC}_{2.25}\text{@Si@C}$ likely facilitates ion transport, thereby contributing to its better rate capability. To investigate changes in ion transport behavior, the content of captured active lithium at different cycle numbers is further analyzed. As shown in Fig. 4h and Fig. 4i, $\text{PC}_{2.00}\text{@Si@C}$ exhibits the highest amount of trapped active lithium, and this amount increases more rapidly with cycling. The accumulation of trapped active lithium is associated with sluggish kinetics in silicon-based anodes^[27]. This indicates that $\text{PC}_{2.00}\text{@Si@C}$ suffers from inferior kinetics, and its kinetic degradation progresses faster than that of $\text{PC}_{1.75}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$ ^[28].

3.4 Lithium-ion storage kinetic analysis

To further analyze the kinetic behavior of $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$, CV measurements were performed. Fig. 5a displays the first-cycle CV curves at a scan rate of 0.1 mV/s. The peak observed at 0.9-1.5 V appears only in the first cycle and disappears in subsequent cycles (Fig. S9), thus it is ascribed to electrolyte decomposition and the formation of the SEI^[29]. The similar peak currents for SEI formation suggest that $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$ exhibit comparable SEI-formation kinetics in the initial cycle, which may be related to their similar specific surface areas and

surface chemical structures. The reduction and oxidation peaks correspond to the lithiation and delithiation processes of $\text{PC}_x\text{@Si@C}$, respectively. Generally, the lower the oxidation peak potential and the higher the reduction peak potential, the more favorable it is for electrode kinetics^[30]. The CV results demonstrate that $\text{PC}_{2.25}\text{@Si@C}$ possesses the most favorable electrochemical kinetics among the 3 materials. As the scan rate increases, the peak currents gradually rise, and the reduction/oxidation peaks show a slight shift in potential (Fig. 5b-d). To quantify the kinetic contributions, the power-law relationship between the peak current (i) and the scan rate (v) can be expressed by the following Equation (1):

$$i = av^b \quad (1)$$

where a and b are adjustable parameters. The b value close to 0.5 indicates diffusion-controlled behavior, while b value close to 1 suggests capacitive (surface-controlled) behavior.^[31] The b value can be fitted using Equation (2):

$$\log i = \log a + b \log v \quad (2)$$

Fig. 5e presents the b value fitting for the delithiation peak. The results show that the b values for $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$ are 0.62, 0.60 and 0.59, respectively. All values are close to 0.5, indicating that the delithiation process in all three materials involves a mixed mechanism of diffusion and pseudocapacitance, but remains predominantly diffusion-controlled. For the lithiation peak, the b values are 0.59, 0.58 and 0.60 for $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$, respectively (Fig. S10), consistent with the delithiation peaks and confirming diffusion-dominated lithiation behavior. The CV results demonstrate that the primary limitation for the lithiation/delithiation reactions in these materials is the diffusion of ions within the bulk phase^[32]. Fig. 5f presents the Nyquist plots of the 3 silicon-carbon materials after pre-cycling. In these plots, the intercept of the EIS plot with the real axis corresponds to the internal resistance (R_s); the first semicircle corresponds to the SEI resistance (R_{SEI}); the second semicircle represents the charge transfer resistance (R_{CT}), and the sloping line reflects the diffusion

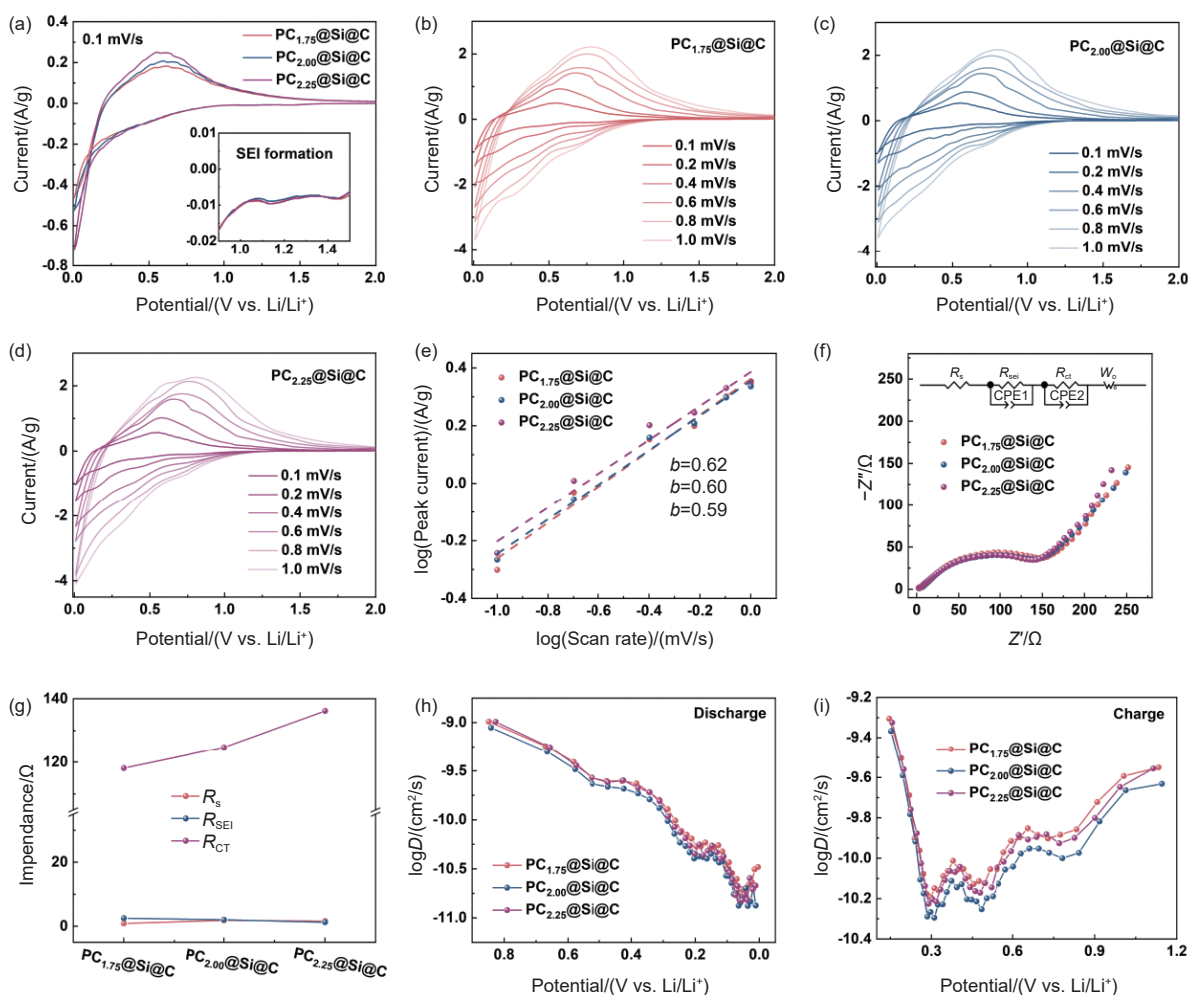


Fig. 5 Kinetic analysis of $PC_x@Si@C$. (a) First-cycle CV curves at a scan rate of 0.1 mV/s, with the inset showing a magnified view of the 0.95–1.5 V region; (b–d) CV curves of $PC_{1.75}@Si@C$, $PC_{2.00}@Si@C$, and $PC_{2.25}@Si@C$, respectively, at various scan rates (0.1–1.0 mV/s). (e) b -value fitting for the delithiation peak of $PC_x@Si@C$. (f) Nyquist plots of $PC_x@Si@C$. (g) EIS resistances of $PC_x@Si@C$ in the first cycle. (h) Lithium-ion diffusion coefficients during the discharge process of $PC_x@Si@C$. (i) Lithium-ion diffusion coefficients during the charge process of $PC_x@Si@C$

impedance^[33]. The values of R_s , R_{SEI} and R_{CT} are obtained by fitting the data using the equivalent circuit. As shown in Fig. 5g, the R_{SEI} and R_s values of $PC_{1.75}@Si@C$, $PC_{2.00}@Si@C$, and $PC_{2.25}@Si@C$ are similar, which may be attributed to their comparable SEI formation. The lowest R_{CT} value of $PC_{1.75}@Si@C$ is likely related to its higher electrical conductivity. Compared with $PC_{2.25}@Si@C$, the lower R_{CT} of $PC_{2.00}@Si@C$ may be associated with its higher content of trapped active lithium.

To further investigate the ion diffusion kinetics during lithiation/delithiation in $PC_{1.75}@Si@C$, $PC_{2.00}@Si@C$, and $PC_{2.25}@Si@C$ electrodes, GITT measurements were performed. The lithium-ion diffusion coefficient (D_{Li^+}) is determined using Equation (3):

$$D_{Li^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (3)$$

where τ is the relaxation time constant, M_B and V_M are the molar mass and molar volume of the active material, m_B is the mass of the active material, A is the electrochemically active surface area of the electrode, ΔE_s is the steady-state voltage change after the current pulse, and ΔE_t is the voltage change during the pulse after removing the iR drop^[8]. Fig. S11 presents the potential-time profile obtained from the GITT measurement. Fig. 5h and Fig. 5i show the lithium-ion diffusion coefficients during the discharge and charge processes, respectively. It can be observed that both $PC_{1.75}@Si@C$ and $PC_{2.25}@Si@C$ exhibit higher D_{Li^+} values than $PC_{2.00}@Si@C$ during both lithiation and delithiation, indicating the poorest ion diffusion kinet-

ics for $\text{PC}_{2.00}\text{@Si@C}$. This can be attributed to 2 main factors: First, its higher silicon content inherently slows ion transport^[15]. Second, the lower intrinsic conductivity of silicon, combined with the greater amount of surface floating silicon in $\text{PC}_{2.00}\text{@Si@C}$, results in reduced overall conductivity, which further hinders lithium-ion diffusion^[18]. The inferior ion diffusion kinetics of $\text{PC}_{2.00}\text{@Si@C}$ limits its lithiation/delithiation behavior at high rates, consequently leading to increased accumulation of trapped active lithium that occupies active sites and reduces reversible capacity.

In summary, the lithiation/delithiation behavior of all three materials is diffusion-controlled. In the ini-

tial cycles, their R_{SEI} values are similar, which is consistent with their comparable surface chemical structures. The gradually increasing R_{CT} values, however, show an opposite trend to the cycling performance, indicating that R_{CT} is not the primary limiting factor. However, $\text{PC}_{2.00}\text{@Si@C}$, which possesses the highest surface floating silicon content, exhibits the lowest lithium-ion diffusion coefficient. This suggests that a high content of surface floating silicon likely hinders bulk ion-diffusion kinetics.

3.5 Electrode failure analysis

To further investigate the results of $\text{PC}_x\text{@Si@C}$ with different structures on the cycled electrodes, cells

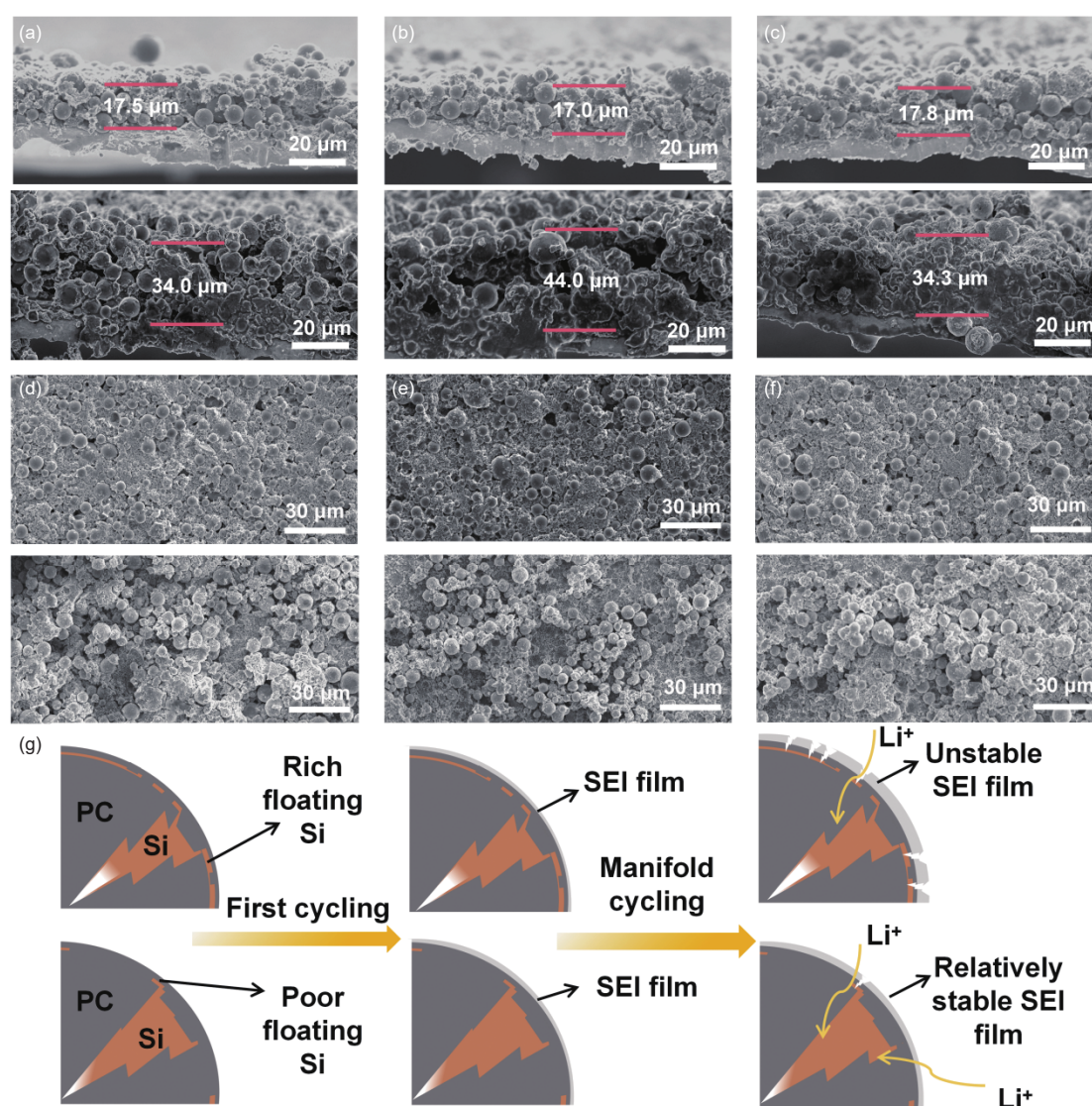


Fig. 6 Cycling failure mechanism of $\text{PC}_x\text{@Si@C}$. (a–c) Thickness comparison of fresh and cycled electrodes for $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$, respectively. The upper images show fresh electrodes, and the lower images show electrodes after 50 cycles. (d–f) Top-view comparison of fresh and cycled electrodes for $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$, respectively. The upper images show fresh electrodes, and the lower images show electrodes after 150 cycles. (g) Schematic diagram of the cycling failure mechanism of $\text{PC}_x\text{@Si@C}$

after 50 and 150 cycles were disassembled for analysis. Fig. 6a–c show cross-sectional SEM images of the $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$ electrodes after 50 cycles, respectively. The electrode thicknesses after 50 cycles are 34.0, 40.0 and 34.3 μm , respectively. Compared with the pristine electrodes, all three materials exhibit a certain degree of volume expansion, and $\text{PC}_{2.00}\text{@Si@C}$ shows the highest expansion ratio. This is likely related to the expansion of surface floating silicon and excessive growth of the SEI layer. Fig. 6d–f present top-view SEM images of the $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$ and $\text{PC}_{2.25}\text{@Si@C}$ electrodes after 150 cycles, respectively. Compared with the uniform and relatively smooth pristine electrodes, all 3 cycled electrodes display uneven surfaces with localized rough regions, and some active material has even detached from the current collector. This effect is most pronounced for the $\text{PC}_{2.00}\text{@Si@C}$ electrode, likely due to deteriorated electrode adhesion caused by SEI growth. Furthermore, EIS measurements are performed on cells after 150 cycles (Fig. S12). The EIS results show that the R_{SEI} values for $\text{PC}_{1.75}\text{@Si@C}$, $\text{PC}_{2.00}\text{@Si@C}$, and $\text{PC}_{2.25}\text{@Si@C}$ after 150 cycles are 5.43, 7.97 and 4.01 Ω , respectively. Compared with the cells at the beginning of the cycle, all 3 exhibit an increase in R_{SEI} , confirming continuous SEI growth. $\text{PC}_{2.00}\text{@Si@C}$ shows the highest growth rate, indicating the faster growth of SEI layer that is more detrimental to ion/electron transport.

Fig. 6g illustrates the cycling failure mechanism of $\text{PC}_x\text{@Si@C}$ electrodes. After pre-cycling, similar SEI layers form on all 3 electrodes. During cycling, silicon confined within the pores is strongly constrained by the porous carbon matrix, whereas surface floating silicon is only covered by a relatively thin carbon coating and experiences less restriction. Consequently, surface floating silicon undergoes significant expansion, which may even fracture the carbon coating. This repeated expansion and contraction of the floating silicon leads to continuous disruption and re-formation of the SEI, promoting further electrolyte decomposition and additional SEI growth. The combined effects of excessive SEI growth and the expansion

of surface floating silicon cause overall electrode swelling, which deteriorates electrode adhesion and results in active-material detachment. Moreover, surface floating silicon hinders ion-diffusion kinetics, leading to increased accumulation of captured active lithium that occupies active sites and reduces reversible capacity.

4 Conclusion

This study prepares porous carbons with different pore structures by varying the KOH activator ratios, investigating the influence of pore architecture on silicon deposition behavior and reaction kinetics, and further exploring the impact mechanism of surface floating silicon on cycling failure. The results indicate that an increased micropore volume facilitates a higher silicon mass loading. However, the corresponding larger silane amount increases its exposure to the external carbon surface, thereby elevating the content of surface floating silicon. Moderately increasing mesopores in high-microporosity porous carbon promotes deeper deposition of silicon into the pore channels, thereby reducing the formation of surface floating silicon. Excessive surface floating silicon hinders lithium-ion diffusion kinetics, leading to increased accumulation of captured active lithium, which occupies active sites and accelerates capacity fading. Furthermore, excessive surface floating silicon causes severe electrode expansion, accelerates SEI growth, promotes active material detachment, and ultimately accelerates electrode degradation. This study suggests that future performance improvements may be achieved by optimizing the pore structure and silane deposition duration to alleviate floating silicon formation, or by employing more effective binders to suppress volume expansion. These conclusions provide valuable insights for the future research and development of CVD-derived silicon-carbon composite anodes.

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