

Enhanced Lithium Storage in Micro-Si-Based Anode Materials through Low-Temperature Interface Engineering with an Ultrathin Phenolic Interlayer

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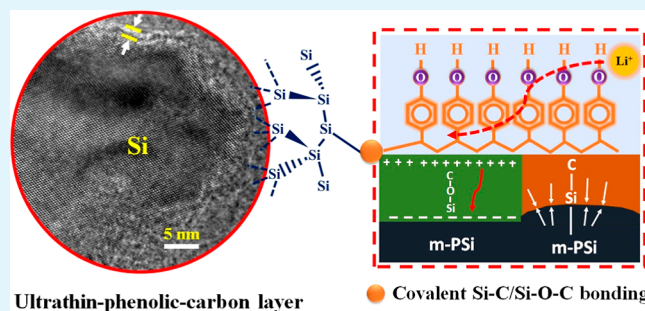
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ABSTRACT: Silicon (Si) anode materials show tremendous potential for high-energy Li-ion batteries (LIBs) due to their excellent theoretical capacity. However, critical issues like initial capacity loss, unstable solid electrolyte interface (SEI) formation, and volume changes during cycling have hindered their practical application. To address these challenges, we have developed a resilient Si interface for rapid Li^+ ion transport while maintaining Si structural integrity. Herein, we utilized micro-sized porous silicon (m-PSi) coated with an ultrathin phenolic interlayer from low-temperature thermolysis of poly(4-vinylphenol) (PVP). This PVP-derived phenolic carbon is covalently linked to the Si surface, creating a strong Si interface and a pathway for Li^+ ion transport. The grafted m-PSi (m-GPSi) anode shows an impressive initial capacity of 3134 mA h g^{-1} with a capacity retention of 80.0% after 100 cycles at 0.1 A g^{-1} . Moreover, it demonstrated a superior rate performance of 1270 mA h g^{-1} at 4 A g^{-1} with a recovery rate of 96% at 0.1 A g^{-1} . These results surpass state-of-the-art micro-sized Si anodes, primarily due to the covalently interfaced ultrathin phenolic interlayer, consequently enhancing Li^+ ion conductivity, mechanical strength, and stable SEI formation during the LIB operation. This research offers a convenient interface engineering strategy to enhance the Si anode performance for next-generation LIBs.

KEYWORDS: poly(4-vinylphenol), low-temperature thermal grafting, porous silicon microparticles, phenolic interlayer, nanoscale interface engineering



1. INTRODUCTION

Silicon has emerged as a promising contender for next-generation anode materials owing to its high theoretical capacity of 4200 mA h g^{-1} ($\text{Li}_{3.75}\text{Si}$), moderate working potential, and high natural abundance.^{1,2} However, there are several prominent challenges that impede its widespread commercial adoption, including significant volume expansion ($\sim 400\%$), limited electrical conductivity, formation of an unstable solid electrolyte interface (SEI) layer, and a sluggish Li^+ ion diffusion rate.³ To overcome these obstacles, porous silicon (PSi) has been identified as an alternative solution that exhibits exceptional ability to accommodate volume changes and enhance Li^+ ion diffusion, leading to improved cyclic performance.⁴ However, the stability of the PSi interface remains paramount for mitigating side reactions and unlocking the full capacity. This understanding has led to advancements in the nanoscale interface design aimed at reinforcing the enhanced mechanical structural integrity, enhancing lithium-ion storage, and ensuring efficient charge transport during an extended cyclic process.^{5–7} Various hybrid nanomaterials⁸

(such as two- or three-dimensional nanostructures,⁸ core-shell structures,⁹ double core-shell structures,¹⁰ and alloys¹¹) are frequently paired with carbon-based materials (such as carbon nanotubes,¹² carbon nanosheets,¹³ graphite,¹⁴ and conductive polymers¹⁵). Despite these combinations, issues such as inadequate cyclic stability and poor rate capability persist.^{12,16}

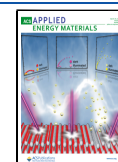
Si/C composites harness nanosized Si to alleviate pronounced volume changes and boost conductivity.^{17,18} Nonetheless, their large surface areas are at a high risk of oxidation in corrosive electrochemical environments, leading to rapid capacity degradation after limited cycles.^{19–21} Further complicating matters, intricate, and high-temperature techniques (e.g., thermal pyrolysis, magnesiothermic reduction,

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mechanical milling, and chemical vapor deposition) have traditionally been used to improve the electrochemical performance of Si anodes.^{7,22,23} Furthermore, most Si/C composites contain a dominant carbonaceous layer (often exceeding a 60 wt % C content).²⁰ This layer typically manifests weak adhesion to the active Si materials due to limited intermolecular interactions, such as van der Waals forces, π - π stacking, and electrostatic forces.^{21,24} Consequently, Si/C composites often exhibit compromised cycling stability and poor rate capability.²⁵ To fortify the physicochemical integrity of Si-based anodes, it is essential to introduce durable covalent bonds between the C matrices and the Si interface. Among the various C matrices explored, phenolic carbon stands out because of its ability to store significant Li⁺ ions per unit mass, resulting in high specific capacities and commendable rate capabilities.^{30–32}

In this study, we developed a novel micro-sized PSi (m-PSi)-based anode material covalently attached to a phenolic-rich ultrathin interlayer via facile one-pot thermolysis of a poly(4-vinylphenol) (PVP) polymer at a low temperature. Specifically, PVP-loaded m-PSi underwent thermal depolymerization at 360 °C, leading to the generation of phenolic carbon fragments that were grafted onto the porous channels. Consequently, phenolic carbon-grafted m-PSi (m-GPSi) showed a remarkable initial capacity of 3496 mA h g⁻¹ and maintained an exceptional rate capability of 96% from its initial capacity at 0.1 A g⁻¹. The enhanced performance of m-GPSi is primarily attributed to the para-substituted hydroxy phenolic carbon. This phenolic interlayer not only offered a robust protective barrier against corrosive electrolytes but also established efficient pathways for the rapid transport of Li⁺ ions in the anode.

2. EXPERIMENTAL SECTION

2.1. Chemical Materials. Si powder (99% purity, ~325 mesh), PVP ($M_w \sim 25$ kDa) powder, and hydrofluoric acid solution (48%, 7664-39-3) were obtained from Sigma-Aldrich, Korea. Silver nitrate powder was purchased from Duksan Pure Chemicals (South Korea). Nitric acid solution (70 wt %, 7697-37-2) and anhydrous ethanol (99.9% purity) were obtained from Daejung Chemicals and Metals Co., Ltd., South Korea. All the chemicals were used directly without additional purification.

2.2. Synthesis of Microsized Porous Silicon Particles (m-PSi). A metal-assisted chemical etching (MACE) process was used to synthesize m-PSi.³³ To prepare the etchant, a solution was formed by mixing 0.06 mol L⁻¹ AgNO₃ with a 5 M HF solution in a 1:3 v/v ratio. Initially, 2 g of micro-sized silicon powder (~325 mesh) was dispersed in 50 mL of deionized (DI) water and stirred at a rate of 250 rpm. Subsequently, 200 mL of the etchant solution was gently introduced into the Si dispersion, and the mixture was stirred for 1 h. The resulting Ag-deposited Si powder was then placed in the bottom of a plastic conical tube. The sediment was collected and repeatedly rinsed with DI water to eliminate the residual etchant solution. To remove Ag residues from m-PSi, the Ag-deposited Si powder was immersed in 200 mL of 70 wt % HNO₃ and stirred for 2 h. Subsequently, the solution was filtered through filter paper attached to a vacuum aspirator. The final product, i.e., silver-removed PSi powder, was thoroughly rinsed with DI water/ethanol, and the resultant powder was dried overnight in a vacuum oven set at 60 °C.

2.3. Synthesis of PVP-Grafted Porous Silicon Microparticles (m-GPSi). The as-synthesized m-PSi powders were treated with a 0.8% HF solution (containing 10 vol % ethanol) to remove native silicon oxides of m-PSi, which were adventitiously formed under ambient conditions. Subsequently, HF-treated m-PSi was rinsed with ethanol three times and subsequently dried overnight under vacuum at 60 °C. The dried samples were finely ground using a mortar and

pestle to obtain fine powdered samples. Further, 0.5 g of this m-PSi powder was then heated to 70 °C on a hot plate for 5 min, followed by the addition of 10% (w/v) PVP in 1 mL of ethanol. The PVP-loaded m-PSi was then heated for another 5 min at 70 °C to evaporate the ethanol. Subsequently, the temperature was raised to 110 °C and maintained there for 10 min to ensure that PVP effectively penetrated the porous channels of m-PSi. Finally, this mixture was transferred to a tube furnace, maintained under a N₂ atmosphere for 30 min, and heated to 360 °C at a ramping rate of 5 °C/min and maintained there for 1 h. The resulting PVP-grafted m-PSi (m-GPSi) was cooled to an ambient temperature under a steady N₂ flow. Any unreacted polymer residue was eliminated by soaking m-GPSi in ethanol for 2 h. Finally, it was washed thrice with ethanol and dried overnight in a vacuum oven set at 60 °C. Similarly, 5 and 15% (w/v) PVP-grafted samples are synthesized following the same procedures. Specifically, the m-GPSi obtained from grafting with 10% (w/v) PVP, with a PVP to m-PSi weight ratio of 1:5, is denoted as m-GPSi-10. The other m-GPSi samples grafted with 5 and 15% (w/v) PVP are referred to as m-GPSi-5 and m-GPSi-15, respectively. In reference, m-GPSi-10 is simply referred to as m-GPSi throughout the main text.

2.4. Electrochemical Measurements. The anode materials were prepared by mixing 60 wt % active materials, 20 wt % Super-P C as the conductive agent, and 20 wt % poly(acrylic acid) (Aldrich) as the binder and dispersed in ethanol. This slurry was thoroughly mixed and spread onto a copper foil via a doctor blade. The resulting electrodes were air-dried and subsequently placed in a vacuum oven at 60 °C for 12 h. The electrodes had a mass loading of the active materials between 0.90 and 1.00 mg cm⁻² and a thickness of $\sim 10 \pm 0.5$ μ m. They were then tailored to a diameter of 1.2 cm. The electrochemical performance of the anode material was assessed by using a half-coin cell (CR2032) constructed in an Ar-filled glovebox. Further, Li metal (Welcos Co.) was used as the counter electrode, a Celgard 2400 polypropylene membrane was used as the separator, and an electrolyte consisting of 1.0 M LiPF₆ in the mixture of ethylene carbonate:diethyl carbonate (5:5 v/v) was enhanced with 5.0 wt % fluoroethylene carbonate. The cyclic performance was evaluated using a WonATech battery tester (WBCS3000L Model) in a voltage range of 0.01–1.5 V (relative to Li/Li⁺). The initial two cycles ran at a C-rate of 0.01C, with subsequent cycles at C/44 (1C equivalent to 4400 mA g⁻¹), later translating to 0.1 A g⁻¹. The cyclic performance of the m-PSi and m-GPSi specimens was also examined at a higher current density of C/8 (i.e., 0.5 A g⁻¹). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a ZIVE SP1 single-channel potentiostat. The CV data were obtained in the voltage window of 0.0–1.5 V at a scan rate of 0.2 mV s⁻¹, while EIS analysis was performed in the frequency range of 10⁵ to 10⁻³ Hz with an amplitude perturbation signal of 5 mV using the Smart Manager software. The Nyquist plots for equivalent circuit modeling were fitted by using Z-view software (Scribner Associates). Rate tests were conducted at varying current densities: 0.1, 0.2, 1, 2, and 4 A g⁻¹, with each density maintained for 5 cycles. The capacities of all the coin cells were computed based on the mass of PSi present in the active materials.

2.5. Postmortem SEI Layer Analysis by ATR-FTIR. Postmortem SEI layer characterization of the cycled electrodes was performed by ex situ attenuated total reflection (ATR) FTIR spectroscopy. The PerkinElmer Spectrum Two FTIR Spectrometer (using a LiTaO₃ detector) equipped with a single reflection PIKE Technologies Miracle Universal ATR sampling accessory is utilized to record the ATR-FTIR spectra as described elsewhere.²⁶ The cycled coin cells are disassembled to separate electrodes in the Ar-filled glovebox (M. O. Tec., MOGV2SSP, H₂O, O₂ < 0.1 ppm) and washed with the dimethyl carbonate (Daejung Chemicals and Metals Co., LTD, South Korea) for 30 s to remove the remaining electrolyte, followed by drying it at room temperature inside the glovebox to avoid direct exposure in the ambient condition. The dried electrodes are mounted on the ATR unit to record FTIR spectra in the glovebox to protect the SEI from atmospheric adulteration.²⁷

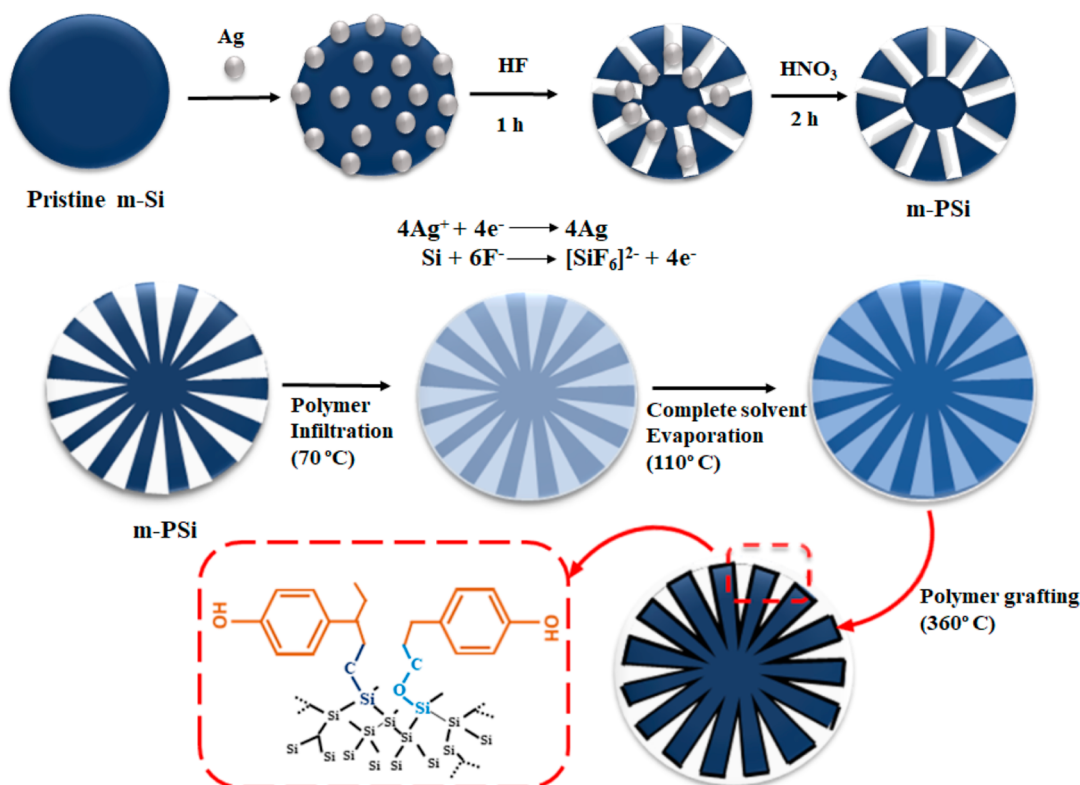


Figure 1. Schematic depicts the synthesis of porous micro silicon (m-PSi) and polymer-grafted PSi (m-GPSi).

3. RESULTS AND DISCUSSION

Based on the synthesis procedures shown in Figure 1, MACE²⁸ was used to fabricate highly fibrous PSi particles. These were subsequently impregnated with a 10% (w/v) PVP solution for the thermolytic grafting process.²⁹ The choice of PVP is advantageous because of its excellent solubility in the nontoxic ethanol solvent, which enhances the environmental compatibility of the grafting process. Specifically, m-PSi underwent a low-temperature thermolysis after PVP loading. Subsequently, phenolic-rich C moieties were uniformly grafted onto m-PSi through the defragmentation of PVP via chain scission and intermolecular transfer mechanisms at 360 °C.³⁰ These carbon moieties were securely bonded to the Si interface via dual linkages of the Si–O–C/Si–C grafts. The m-PSi grafted with PVP is hereafter referred to as m-GPSi. The prepared samples were then characterized and tested as anode materials of Li-ion batteries (LIBs).

3.1. Characterization of As-Synthesized Samples. The FE-SEM images of the unaltered m-Si as shown in Figure 2a clearly show the smooth morphological characteristics of the Si surface. Post the Ag-assisted chemical etching of m-Si, Figure 2b presents the fibrous-looking porous structure of m-PSi. After the thermolytic grafting process, the fibrous morphology of m-PSi was mostly preserved, although some rounded edges of the fibers were still apparent in PVP-grafted m-PSi (m-GPSi), as indicated in the magnified inset of Figure 2c. The transmission electron microscopy (TEM) images in Figure 2d–g clearly depict the dimple-scale-like fibrous nature of m-PSi. Similarly, Figure 2h,i shows the well-retained porous morphology of m-GPSi with some smooth edges. Importantly, the high-resolution (HR)-TEM images in Figure 3a,b show the delicate boundary of crystalline Si, which is enveloped by an ultrathin phenolic interlayer of ~2 nm thick, delineated by red

arrows. Additionally, the EDS mapping of Figure 3d–3,4 confirms the presence of high C and O contents in m-GPSi, which is attributed to the interfacial phenolic carbon coating. Notably, the EDS mapping in Figure 3d–1 shows faint traces of Ag residue in m-PSi, which were not completely removed by the HNO₃ rinsing process. The high-angle annular dark-field (HAADF) image in Figure 3d indicates that the process of PVP grafting onto m-PSi successfully preserved the holocrystalline phase of PSi in m-GPSi.

Figure S1a shows the X-ray diffraction (XRD) analysis of the m-Si, m-PSi, and m-GPSi samples. In the XRD patterns for all three samples, distinct peaks emerge at specific 2θ angles: 28.4, 47.29, 56.11, 69.12, 76.36, and 88.02°. These angles correspond to the (111), (220), (311), (400), (331), and (422) crystallographic planes of cubic-phase Si, respectively (JCPDS card no. 27-1402).³¹ This finding indicates that the crystalline phase of the pure Si remains intact after the thermolytic grafting process at 360 °C. Notably, m-GPSi did not display discernible C peaks, likely owing to the amorphous nature of the grafted C species. Also, there were no apparent peaks of residual Ag in the XRD patterns of the m-PSi and m-GPSi samples.³²

Figure S1b shows the Fourier transform infrared (FTIR) spectra of the prepared samples, confirming the successful grafting of amorphous carbonaceous materials containing phenolic moieties onto m-PSi. The FTIR spectrum of m-PSi features a Si–O–Si stretching band at 1050 cm^{−1}, suggesting the incidental formation of adventitious silicon oxide in m-PSi during its storage in an atmospheric environment.³³ By contrast, the lack of a Si–O–Si band in m-GPSi suggests that Si–O bonds were transformed, yielding a new peak at 1180 cm^{−1}, associated with Si–O–C grafts.^{34,35} However, a pronounced band around 3700 cm^{−1} in m-GPSi indicates

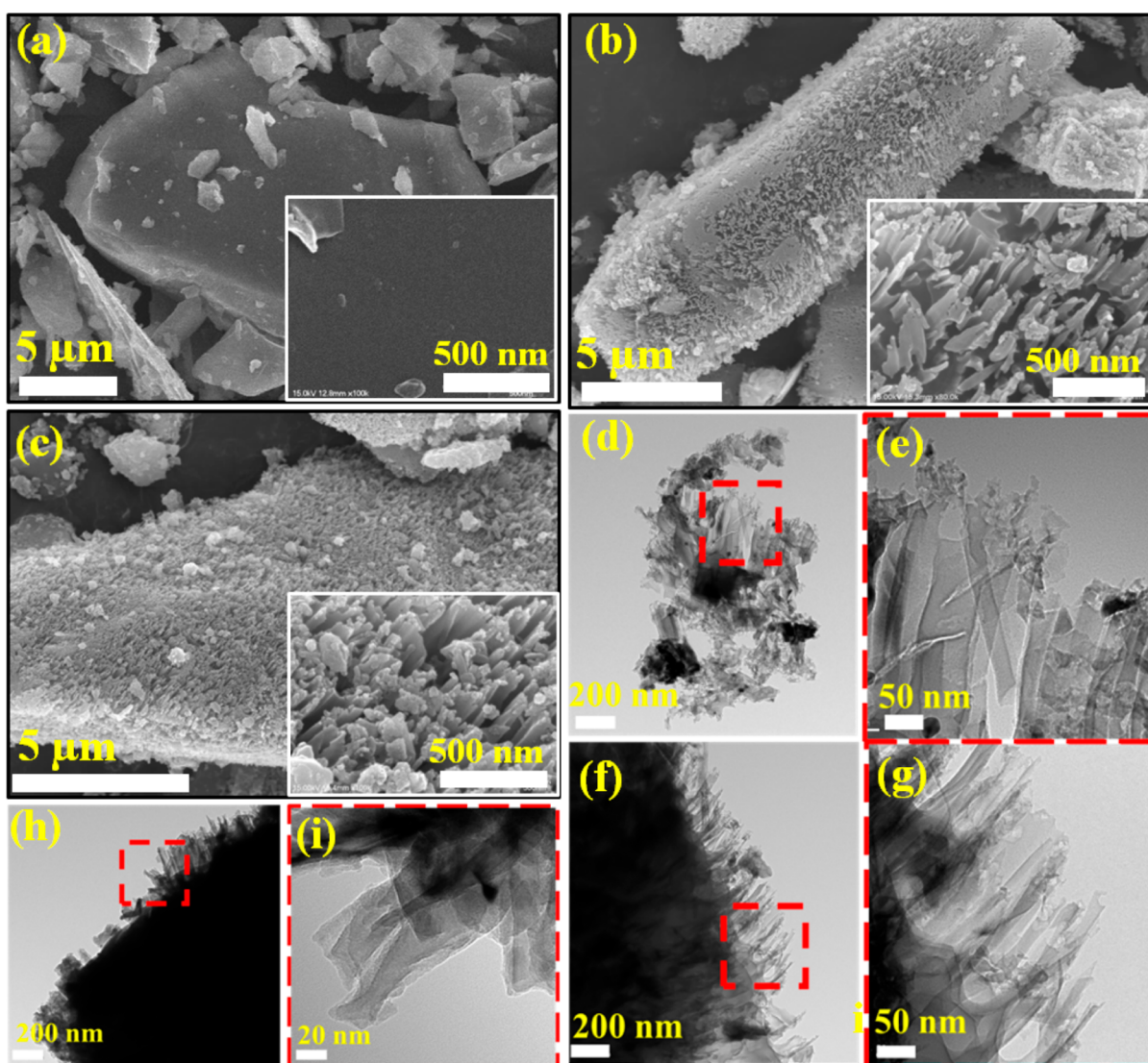


Figure 2. FE-SEM images of (a) m-Si, (b) m-PSi, and (c) m-GPSi with magnified inset views. TEM images of (d–g) m-PSi and (h,i) m-GPSi with magnified view (red dotted).

phenolic carbon grafts.³⁶ The FTIR spectra of m-PSi show three minor peaks near 2141, 2115, and 2090 cm^{-1} , which are attributed to Si–H_{*x*} (where *x* = 3, 2, and 1, respectively).⁴⁰ This band is absent in m-GPSi, suggesting that Si–H bonds have transitioned into Si–C linkage, to give a subsequent peak at 815 cm^{-1} , which was further corroborated by subsequent X-ray photoelectron spectroscopy (XPS) analyses. Moreover, both m-PSi and m-GPSi exhibited a strong Si–Si stretching peak at $\sim 650 \text{ cm}^{-1}$, signifying a consistent crystalline Si structure throughout the interface engineering process.

The nature of the PSi composites was investigated using Raman spectroscopy (Figure S1c). The m-PSi and m-GPSi samples exhibited three distinct characteristic peaks. The primary intense peak at 519 cm^{-1} was assigned to crystalline Si because of its transverse optical vibrational mode.³⁷ Among the two minor peaks, the first peak at 295 cm^{-1} corresponds to Si oxide, and the second broad peak at 950 cm^{-1} corresponds to the Si–Si stretching mode. No distinguishable D or G bands appeared in the Raman spectra of m-GPSi, probably because of the amorphous nature of the ultrathin carbonaceous layer. Figure 4a–f shows the core-level deconvoluted XPS spectra for C 1s, O 1s, and Si 2p of the as-prepared samples (m-PSi and

m-GPSi). The primary C 1s spectrum at 284.39 eV (as seen in Figure 4a) splits into the sp^2 and sp^3 hybridization states of the C–C bond in m-GPSi at 284.40 and 285.81 eV, respectively.³⁸ Conversely, the C 1s spectrum of m-PSi in Figure 4d predominantly features C–C in the sp^2 hybrid state. Furthermore, the m-GPSi C 1s spectrum contains peaks representing Si–O–C (283.80 eV) and Si–C (284.50 eV), verifying the presence of phenolic carbon moieties grafted on the m-PSi.^{39,40} The O 1s spectrum in Figure 4b highlights the dominant Si–O–Si peak at 532.78 eV and the Si–O–C peak at 531.52 eV. Conversely, the O 1s spectra of m-PSi (Figure 4e) primarily indicated the presence of silicon oxide and chemisorbed water at 532.79 and 531.51 eV, respectively.^{35,41} In Figure 4c, the Si 2p spectrum of m-GPSi is divided into primary peaks, Si 2p_{3/2} at 99.5 eV and Si 2p_{1/2} at 99.12 eV, indicating the oxidation states of the Si material. Crucially, two noticeable peaks at 102.11 and 103.01 eV denote Si–C and Si–O–C species on the Si interface, likely formed during the thermolytic grafting.^{42–44} A negligible Si–O–Si peak at 103.12 eV in m-GPSi's Si 2p suggests that nonatmospheric grafting reduced the formation of silicon oxide on the PSi.^{2,40,43} In contrast, the Si 2p spectrum of m-PSi in Figure 4f features a

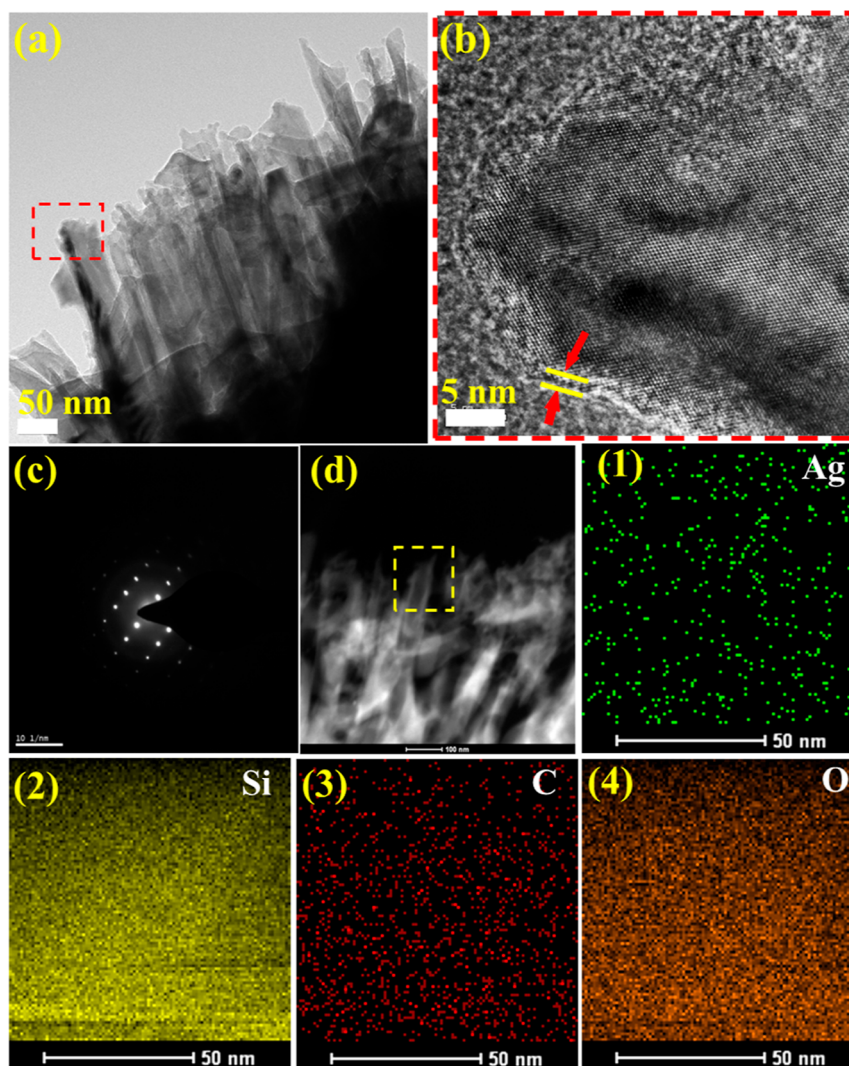


Figure 3. (a) TEM, (b) HR-TEM of m-GPSi showing an ~ 2 nm ultrathin phenolic carbon interface. (c) SAED image, (d) HAADF image of m-GPSi. TEM-EDS of m-GPSi (1–4).

pronounced Si–O–Si peak at 103.45 eV, indicating an oxidized Si surface before polymer grafting.⁴⁵ Finally, the survey scan of m-GPSi in Figure 4g–h highlights above-discussed intense peaks for C 1s, O 1s, and Si 2p at bonding energies of 284.39, 532.38, and 99.15 eV, respectively.⁴⁶ A minor F 1s peak at 686.69 eV arises from negligible HF residuals in the m-PSi. As shown in Figure 4i, the m-GPSi surface primarily comprises Si–O–C (85%) and Si–C (15%) fractions with a minor fraction of $\sim 2\%$ Si–O–Si. By contrast, the surface of m-PSi mainly contained Si–O–Si species. Surface composition fractions were determined by evaluating the areas within the deconvoluted XPS spectra. These observations indicate that nanointerface engineering via PVP thermolysis facilitates the formation of dual Si–O–C/Si–C covalent linkages.⁴⁴

A plausible mechanism for the PVP thermolysis is proposed in Figure S2, forming a phenolic-carbon-grafted Si surface. The para-substituted hydroxyl groups in PVP promote the formation of phenolic carbon radicals during thermal depolymerization.⁴⁷ This phenomenon can be explained by the increased stability of carbocation moieties at the benzylic sites and bolstered by the resonance effects of the lone electron pairs of the oxygen atom at the para position.⁴⁸ Consequently,

the phenolic radicals formed during the thermal depolymerization of PVP were readily converted into covalent linkages of Si–O–C/Si–C species. This conversion is supported by previous XPS analyses of the grafted PSi. In conclusion, phenolic carbon moieties facilitate the efficient conversion of Si–O/Si–H groups into Si–O–C/Si–C bonds by stabilizing the benzylic carbocations during the thermolytic grafting process.³¹

Thermogravimetric analysis (TGA) was used to assess the carbon content of m-GPSi, which is also represented by m-PSi TGA (Figure 5a). The initial weight loss of 0.048% (up to 250 °C) can be attributed to water evaporation from m-GPSi, whereas the subsequent weight loss between 250 and 620 °C is primarily due to the degradation of the ultrathin phenolic interlayer at high temperatures. Surprisingly, the C content of m-GPSi was estimated as 0.98 wt %, just below 1.0 wt %. The increase in weight by 4.94 wt % beyond 620 °C is primarily attributed to bulk Si-oxidation (indicated by the shaded area), which is caused by residual/adventitious presence of oxygen, despite N₂ purging.⁴⁹ In contrast, m-PSi exhibits a 4.26 wt % weight gain around 450 °C, probably due to the early oxidation of bulk Si.

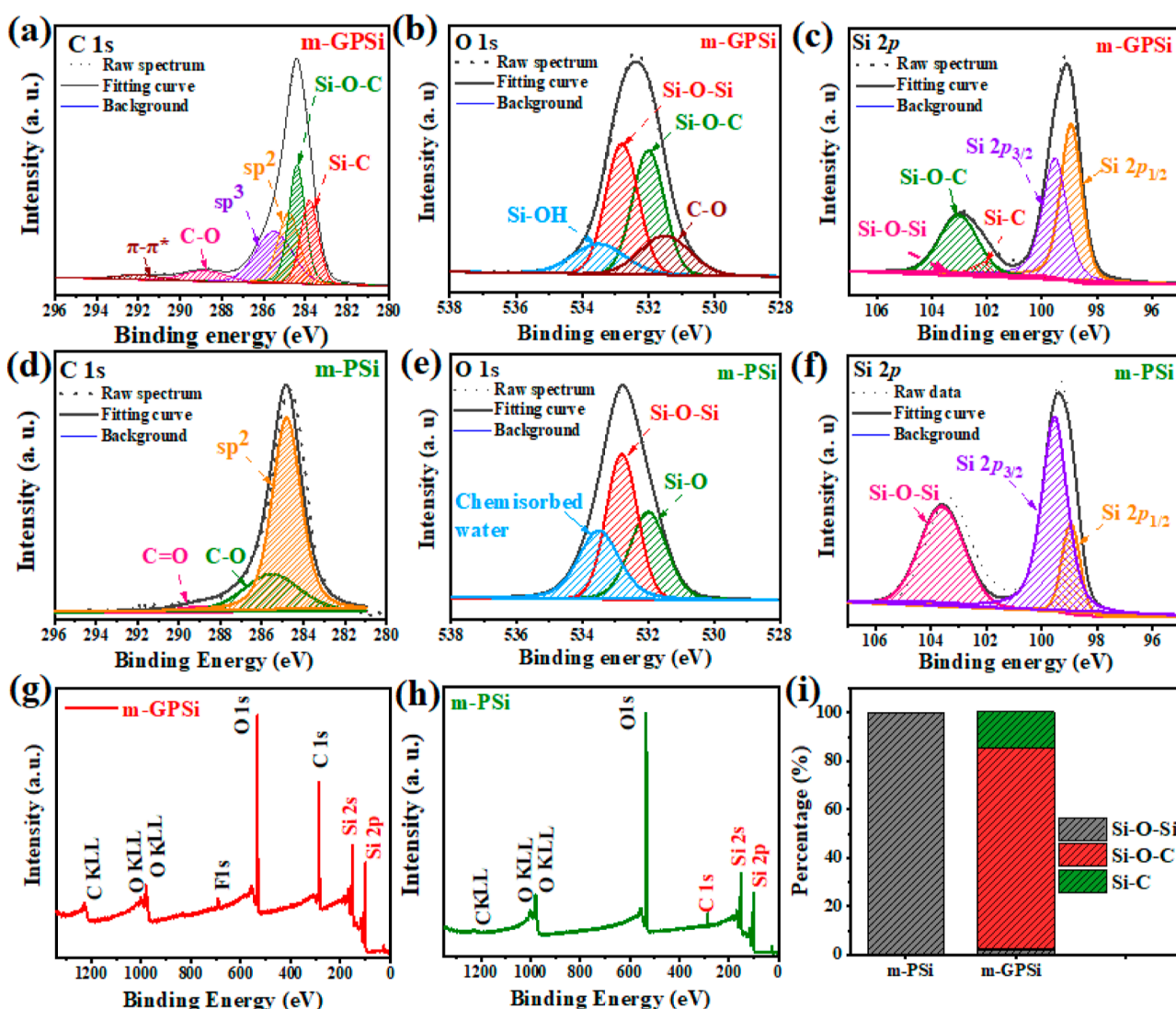


Figure 4. Deconvoluted XPS core spectra (a) C 1s, (b) O 1s, and (c) Si 2p of m-GPSi. XPS (d) C 1s, (e) O 1s, and (f) Si 2p of m-PSi. XPS survey scan of (g) m-GPSi and (h) m-PSi. (i) Surface composition comparison of the samples obtained by deconvoluted XPS Si 2p core spectra.

Brunauer–Emmett–Teller (BET) analysis was performed to investigate the impact of grafting on the porosity and surface area of the m-Si, m-PSi, and m-GPSi samples. The N₂ adsorption/desorption isotherms in Figure 5b reveal that PSi attained almost six times larger surface area (Langmuir = 20.80 m² g^{−1}, BET = 14.78 m² g^{−1}) than that of m-Si (Langmuir = 3.72 m² g^{−1}, BET = 2.60 m² g^{−1}). The m-GPSi experienced a further improvement in the surface area (Langmuir = 26.86 m² g^{−1}, BET = 17.61 m² g^{−1}), probably due to the formation of amorphous phenolic interlayer that can provide the additional voids.⁵⁶ According to the pore-size distribution in Figure 5c, m-PSi and m-GPSi have two different pore size range of mesopores (~3.5 nm and 45–75 nm). By contrast, m-Si has no actual porosity as it is evident from the nearly horizontal line in the pore size distribution curve. In summary, Figure 5d shows the comparison of surface area and pore size of the samples obtained from the BET and Barrett–Joyner–Helenda (BJH) analysis methods. m-GPSi showed a significant increase in surface area compared with the m-PSi and m-Si samples, and the pore size of m-GPSi was reduced after grafting, indicating the successful integration of the phenolic interlayer onto the porous channels of m-PSi. The recorded BET data are

utilized to calculate the porosity of all materials (Table S1) using the following formula.⁵⁰

$$\text{Porosity} = \frac{\text{BET pore volume}}{\text{BET pore volume} + \text{volume of sample}}$$

The calculated porosity values for m-Si, m-PSi, and m-GPSi are 5.81, 68.98, and 61.45%, respectively, indicating a significant improvement in porosity for both m-PSi and m-GPSi as compared to that for m-Si. However, m-GPSi exhibits a slight decrease in porosity relative to m-PSi, possibly due to the decrease in pore diameter after polymer grafting onto the porous walls of m-PSi, as noticed by the BET data.

3.2. Electrochemical Evaluation of the Active Materials. The redox mechanism of the synthesized samples was investigated using CV in the voltage window 0.0–1.5 V at the scan rate of 0.2 mV s^{−1}. Figure S3a–c shows the voltammograms of m-Si, m-PSi, and m-GPSi, respectively. All the samples demonstrated a distinct peak at 0.19 V in their cathodic curves, representing the insertion of Li⁺ ions into crystalline Si to form an amorphous Li_xSi phase.⁵¹ This lithiation peak was more pronounced in the voltammograms of m-PSi and m-GPSi than in that of m-Si, suggesting enhanced

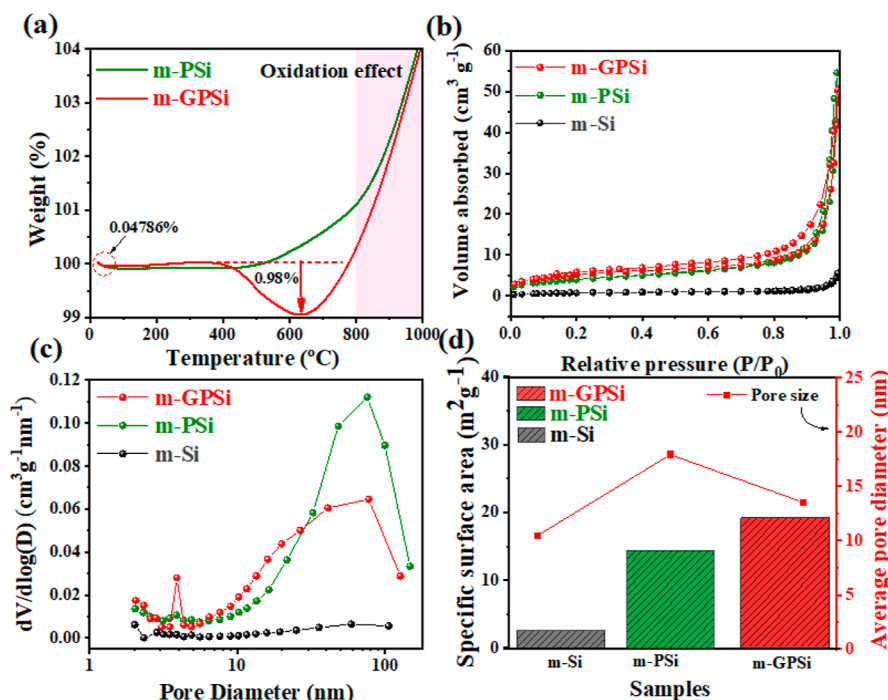


Figure 5. (a) Overlapped TGA curve for m-GPSi with m-PSi. (b) N_2 adsorption/desorption isotherms of m-Si, m-PSi, and m-GPSi samples. (c) BJH pore-size distribution obtained from adsorption isotherm. (d) Surface area and pore size comparison of samples obtained from the Brunauer–Emmett–Teller (BET) method.

lithiation in the PSi samples. The anodic curves of the samples exhibit two peaks at ~ 0.40 and 0.50 V corresponding to the delithiation of amorphous Li_xSi to α -Si.⁵² In contrast, m-Si is unable to produce the characteristic two delithiation peaks, which can be attributed to the formation of a thick and unstable SEI layer, leading to increased resistance at the working electrode.^{53,54} As the scan number increases, there is a gradual intensification in the voltammogram peak, making the oxidation and reduction peaks more discernible, which confirms the electrochemical reversibility of Si anodes.⁵⁵ The peak currents of m-PSi and m-GPSi were substantially higher than that of bulk m-Si, probably because of the improved surface activation of the PSi materials.⁵⁴ The m-GPSi voltammogram showed no additional peaks, indicating the absence of side reactions between the Li^+ ions and the grafted phenolic interlayer during the charge/discharge process. This suggests that the ultrathin phenolic interlayer passivates the Si interface and provides a better diffusion path for Li^+ ions. Additionally, there was no significant difference in the CV curves of m-PSi and m-GPSi, indicating that the grafted phenolic interlayer did not restrict the lithiation/delithiation reactions in the cyclic process.⁵⁶

Further electrochemical investigations were performed to understand the Li^+ ion storage mechanism. In this study, CV curves of the samples (m-Si, m-PSi, m-GPSi) are taken at different scan rates ranging from 0.02 to 0.2 $mV s^{-1}$, as shown in Figure S4a–c. In these voltammograms, both the anodic and cathodic peak intensities show a notable increase in proportion to the scan rate, indicating the activation of the native silicon surface.⁵⁷ With the increasing scan rate, the anodic and cathodic peaks moved to higher and lower potentials, respectively, reflecting the increased polarization of the active Si materials.⁵⁸ The kinetics of the anodic and cathodic processes were examined (Figure S4(d–i)) using eqs S1 and S2, which are explained in the calculation Section S1.2 of the

Supporting Information. Subsequently, the fractional capacitive contributions of the samples (m-Si, m-PSi, and m-GPSi) were determined by evaluating the peak current (i) at various scan rates (v) and inserting these values into eqs S5 and S6. Figure 6a–c illustrates the specific capacitive contributions for each sample at their respective scan rates. In m-GPSi, the Li^+ ion storage mechanism is prominently capacitive controlled, especially evident as the scan rate increases from 0.02 to 0.2 $mV s^{-1}$ (Figure 6c). Remarkably, the capacitive contribution of Li storage reached $\sim 60\%$ at the highest scan rate of 0.2 $mV s^{-1}$. The pronounced capacitive contribution of m-GPSi was primarily attributed to the abundance of active sites within the amorphous phenolic interlayer for Li^+ ion storage and the absorption reactions of Li^+ ions with phenyl rings.⁵⁹ Conversely, a diffusion-controlled process dominated the m-PSi anode with capacitive contributions restricted to $\sim 20\%$ at all scan rates (Figure 6b). For bulk m-Si, diffusion-controlled processes were even more accentuated. Even at the modest scan rate of 0.02 $mV s^{-1}$, the diffusion storage contribution is $\sim 95\%$, and it rises to 98% at the elevated scan rate of 0.2 $mV s^{-1}$. This unequivocally indicates that Li^+ storage in m-Si is predominantly governed by diffusion processes (Figure 6a). Meanwhile, the substantial adsorption and desorption of Li^+ ions at the electrode–electrolyte interface of the m-GPSi anode amplified the capacitive contribution.⁵⁸ This predominant capacitive charge storage (i.e., double-layer capacitance) mechanism in m-GPSi is responsible for the superior rate capability; data are shown in Figure 6g.⁶⁰

Furthermore, the diffusion coefficients of Li^+ ions were measured using the Randles–Sevcik equation⁶¹

$$I_p = 0.4463 \times AF \left(\frac{F}{RT} \right)^{1/2} C_{Zn^{2+}} D_{Li^+}^{1/2} \nu^{1/2} \quad (1)$$

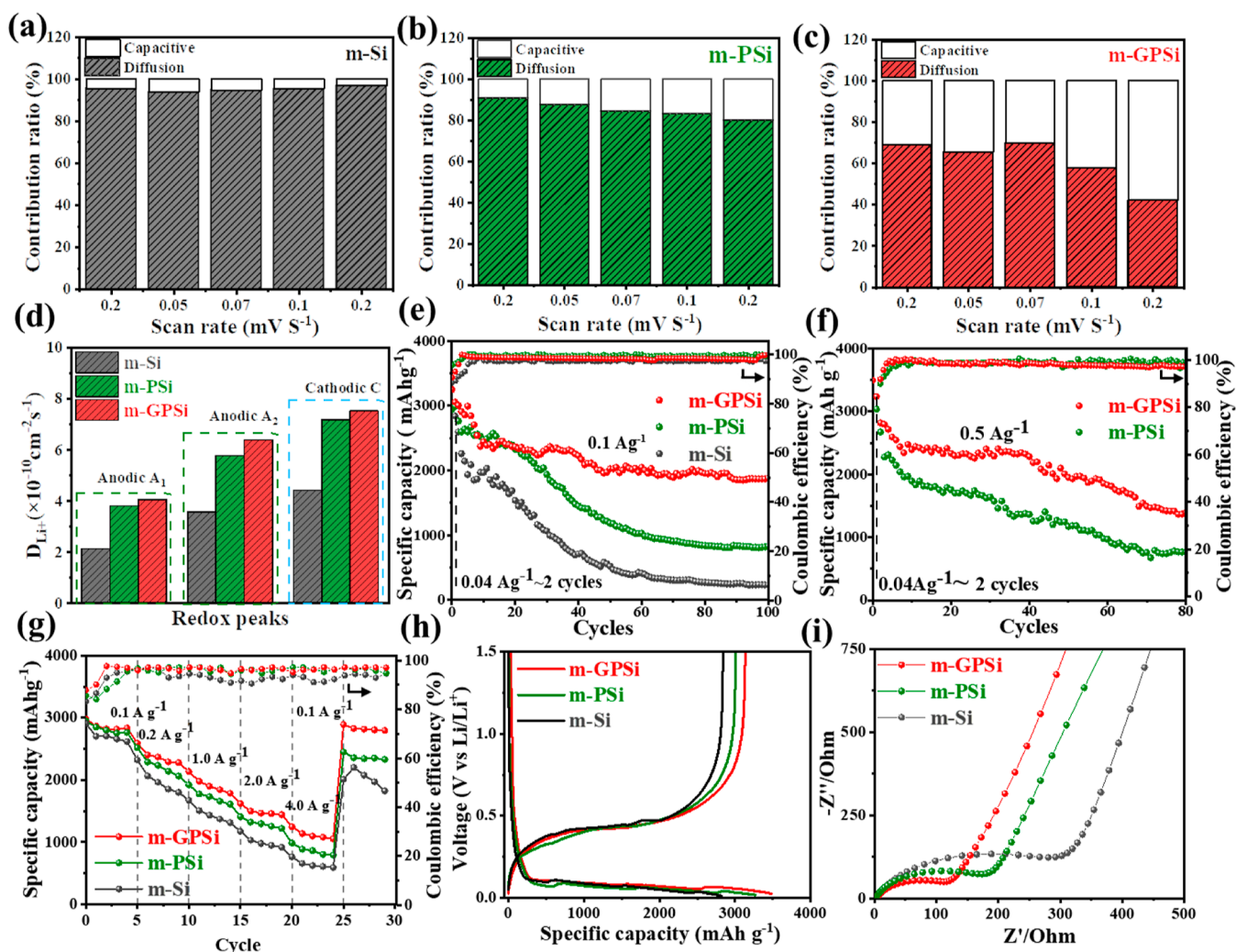


Figure 6. Diffusion contribution at different scan rates for (a) m-Si, (b) m-PSi, and (c) m-GPSi. (d) Comparison of the diffusion coefficients obtained from CV curves at different scan rates for all three samples. Cyclic performance of m-Si, m-PSi, and m-GPSi at (e) 0.1 A g⁻¹ and (f) 0.5 A g⁻¹. (g) Rate capability of m-Si, m-PSi, and m-GPSi. (h) Voltage profile of the initial charge–discharge cycle of active materials. (i) Nyquist plot of m-Si, m-PSi, and m-GPSi.

Here, I_p represents the peak current value, A is the effective area of the electrode (1.13 cm²), F is the Faraday constant (96,485 s A mol⁻¹), R represents the gas constant (8.314 J K⁻¹ mol⁻¹), T denotes the absolute temperature in Kelvin, C is the concentration of Li⁺ ions (1.0 mol cm⁻³), D_{Li^+} is the diffusion coefficient of Li⁺ ions (cm² s⁻¹), and ν is the scan rate (mV s⁻¹). Figure 6d compares the diffusion coefficients of the Li⁺ ions in the m-Si, m-PSi, and m-GPSi anode samples, which were calculated using eq 1. Among them, m-GPSi demonstrated the highest Li⁺ ion diffusion coefficient of 7.52×10^{-10} and 7.17×10^{-10} cm² s⁻¹ in the cathodic and anodic regions, respectively, highlighting the remarkable enhancement in Li⁺ ion transport in the grafted Si anode materials. Meanwhile, m-Si shows a lower diffusion coefficient of 2.13×10^{-10} and 4.05×10^{-10} cm² s⁻¹ for anodic and cathodic regions, respectively. Owing to its porous structure, m-PSi displayed a notable increase in the Li⁺ ion diffusion coefficient in both anodic (3.80×10^{-10} cm² s⁻¹) and cathodic (6.38×10^{-10} cm² s⁻¹) regions.

3.3. Cyclic Performance of As-Prepared Si-Based Anodes. Figure 6e presents the cyclic performances of the prepared samples, with initial capacities of 2840, 2942, and

3134 mA h g⁻¹ for m-Si, m-PSi, and m-GPSi, respectively, at a current density of 0.04 mA h g⁻¹. The initial Coulombic efficiencies of m-Si, m-PSi, and m-GPSi were calculated to be 88, 92, and 90%, respectively. Impressively, all samples reached a high Coulombic efficiency (CE) of 99% after 10–15 cycles. For the capacity retention calculation, the fifth cycle capacity was used as a reference, given the stable formation of SEI in Si-based anodes.⁶² Among the samples, 10% (w/v) grafted m-GPSi exhibits the highest initial capacity, retaining 80% of its initial capacity after 100 cycles. By contrast, m-PSi and m-Si exhibit retentions of 31.97% and 11.85%, respectively, at a current density of 0.1 A g⁻¹. At the higher current density of 0.5 A g⁻¹, m-GPSi had a reversible capacity of 1400.5 mA h g⁻¹ (54.0% retention), while m-PSi showed a much lower capacity of 757.4 mA h g⁻¹ (28% retention) after 80 cycles (Figure 6f).

Among the as-prepared samples (m-GPSi-5, m-GPSi-10, and m-GPSi-15), the 5% (w/v) PVP-grafted m-GPSi-5 exhibits a retention of 36.2% after 80 cycles at 0.5 A g⁻¹, which is not satisfactory (Figure S5a). Furthermore, m-GPSi-15 with the highest PVP concentration performs even worse than m-PSi, retaining only 21.7% with a capacity of 555.3 mA h g⁻¹. These optimization data clearly indicate that 10% (w/v) PVP grafting

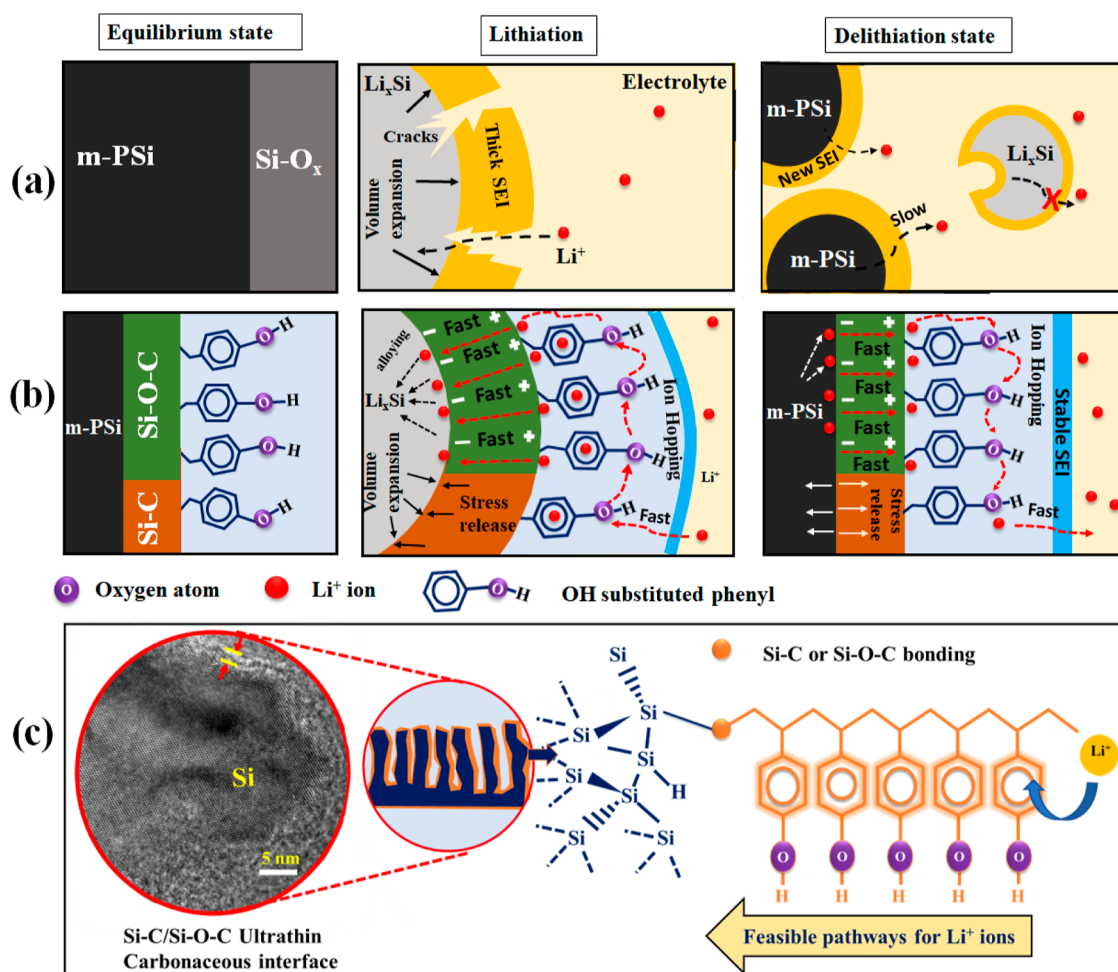


Figure 7. Plausible Li^+ ion storage mechanism for Si-based anode materials. (a) m-PSi: pulverization of PSi due to massive volume expansion. (b) Robust Si-C/Si-O-C interface of the micro-sized m-GPSi providing rapid transport of Li^+ ions and formation of the stable SEI layer during the charge–discharge cycle. (c) Feasible pathways for Li^+ ion transport.

is beneficial and sufficient to significantly improve the cyclic performance of m-GPSi-10, as shown in Figure S5b.

Rate capabilities of the m-Si, m-PSi, and m-GPSi samples were evaluated across a current density ranging from 0.1 to 4.0 A g^{-1} , with measurements taken every 5 cycles for each sample (Figure 6g). Notably, m-GPSi exhibited the specific discharge capacities of 3012.09, 2588.56, 2134.69, 1617.43, and 1250.70 mA h g^{-1} at the equivalent current densities of 0.1, 0.2, 1.0, 2.0, and 4.0 A g^{-1} , respectively. It also displayed an impressive 95.97% recovery rate, with a capacity of 2891.90 mA h g^{-1} at 0.1 A g^{-1} after 25 cycles. On the contrary, m-Si and m-PSi achieved capacities of 752 and 973.40 mA h g^{-1} at 4 A g^{-1} and showed inferior recovery rates of 83 and 69% at 0.1 A g^{-1} after 25 cycles, respectively.

Figure 6h illustrates the initial charge–discharge voltage profiles of the m-Si, m-PSi, and m-GPSi samples. m-GPSi had an initial discharge capacity of 3134 mA h g^{-1} and a charge capacity of 3482 mA h g^{-1} , leading to a CE of 90% at 0.04 A g^{-1} . The 10% irreversible efficiency loss is primarily attributed to the cumulative effects of SEI layer formation and the irreversible insertion of Li^+ ions into the Si active material during the charge–discharge process. Similarly, m-PSi and m-Si exhibited initial discharge capacities of 2942 and 2840 mA h g^{-1} , with respective charge capacities of 3268.87 and 3227.28 mA h g^{-1} , respectively. The average CEs for m-Si, m-PSi, and

m-GPSi were determined to be 97.8, 99.2, and 98.2%, respectively. The relatively lower CE of m-GPSi than that of m-PSi may be attributed to increased electrolyte consumption and irreversible reactions during SEI formation owing to its enlarged specific surface area of m-GPSi compared to that of m-PSi.⁶³

Prior to cycling, the electrochemical processes of the fabricated Si anode materials were investigated via impedance measurements by using EIS. Figure 6i shows the impedance spectra for the m-Si, m-PSi, and m-GPSi samples, covering a frequency range of 10^5 to 10^{-3} Hz with an amplitude signal of 5 mV. In the Nyquist plot, the initial resistance, denoted as R_e , represents the electrolyte solution in the coin cell, which is typically termed electrolyte resistance. The semicircle in the high-frequency domain, marked as R_{SEI} , suggests impedance from SEI layer formation. R_{ct} characterizes the resistance from the charge-transfer reactions at the electrolyte–active material interface.⁶⁴

Figure S6a depicts the fitted equivalent circuit and the resulting resistance values for all three materials. Notably, the m-GPSi anode presented the lowest R_e value of 2.22 Ω , validating the efficient redox kinetics of the grafted materials. m-GPSi also showed the smallest R_{ct} value of 79.30 Ω , underlining the proficient charge-transfer reaction of Li^+ ions between the active materials and the electrolyte.⁶⁵ Hence, this

Table 1. Cyclic Performance of the m-GPSi in Comparison to that of State-of-the-Art Micro-Si/C Composites

anode materials	synthesis method	carbonization temp. (°C)/time (h)	Si wt %	ICE ^a	rate capability ^b	cyclability ^c	refs
m-GPSi	thermolytic grafting	360°C/1	99.02	90.0	1250.7/4	1905@100	this work
N-Si/C	thermal annealing	1000°C/2	65.38	91	877/1	1238@100	75
MFG/PNSi@C composite	pyrolysis	900°C/3	29.41	82.8	450/1.6	1141@200	76
Si/C-HF	calcination	800°C/4	30.0	63.3	69/1.0	710@300	77
Si@C-G	ball milling and pyrolysis	1000°C/4	10.0	83.8	1117.1/2.0	80@250	17
Si@C/CNTs@GS	calcination	700°C/2	75	87.6	1016.2/1.6	1524@130	78
Si-CNT	chemical dealloying	600°C/3	47.3	60.2	510/5	1275@100	79
P2-1050-Si@V@C	pyrolysis	850–1150°C/2	23.0	79	743/2	755@200	18
Si@C _{MR}	pyrolysis	700°C/2	5.26	~71	1628.7/2	1279@500	34
p-Si@C	freeze-drying-annealing	600°C/3	45	58	946/4	1990@100	80
Si@3DC	calcination	800°C/1	70.7	68.8	658/20	1588@1000	81
pitch-Si-0.5/C	electro spraying and calcination	800°C/2	60	83.3	406/2	929@200	82
C@pSi-I	pyrolysis	800°C/3	50	82.5	1226.9/2	1116.7@200	22
MSN@C@void@N-C	calcination	800°C/3	66.6	70	816/4	1372@150	83

^aICE is initial coulombic efficiency, %. ^bRate capability obtained as the specific capacity at the highest current density, mA h g⁻¹/A g⁻¹. ^cCyclability obtained as a final specific capacity versus the cycle number, mA h g⁻¹@Cycle.

effect can be attributed to the ion migration mechanism boosted by the attached phenolic interlayer, which is enriched with highly electronegative O atoms.⁶⁶ In the initial plot, m-GPSi exhibited a smaller semicircle compared to the bare m-PSi and m-Si samples, highlighting the influence of the ultrathin phenolic interlayer in establishing a stable SEI interface with reduced resistance.⁶⁷ Furthermore, the R_{SEI} values for m-PSi and m-GPSi were estimated as 175.16 and 128.19 Ω , respectively. The lower R_{SEI} value for m-GPSi signifies that its ultrathin phenolic interlayer promotes the formation of a robust SEI layer with minimal resistance. Ultimately, m-GPSi showed reduced impedance and superior conductivity, contributing to improved Li⁺ ion charge-transfer kinetics throughout the cycling. Table S2 summarizes the retention capacities of the samples at both the 5th and 100th cycles, and Figure S6b shows a comparison of the samples. The data clearly indicate the superior retention capacity of m-GPSi (80.01%) compared with those of m-PSi (31.97%) and m-Si (11.85%). In addition, m-GPSi exhibited excellent rate capability and cyclic performance.

3.4. Enhanced Performance of Si-Based Anodes by Thermolytic Grafting. Figure 7 shows the Li⁺ ion storage mechanism in the m-PSi and m-GPSi anode samples, highlighting the pivotal role of the covalently grafted phenolic interlayer at the Si interface. Specifically, m-PSi with its Si–O–Si interface experiences severe volume stress stemming from the enormous volume change of active Si materials during cycling. The repeated volume expansion and contraction led to the fracturing of the m-PSi core structure (Figure 7a), inducing the creation of an unstable SEI layer and significant capacity loss over repeated cycles.⁶⁸ By contrast, m-GPSi possesses a Si–O–C/Si–C covalent interface, which introduces a dual storage mechanism (Figure 7b). Within this diffusion-controlled mechanism, the Si–C linkage serves as a protective shield for the internal structure of m-GPSi, imparting enhanced mechanical and chemical stabilities to the active material. Additionally, in the capacitive storage process, the polarized Si–O–C linkage increases the adsorption of Li⁺ ions on the grafted layer, elevating the Li⁺ ion storage capacity of m-GPSi.⁴⁵ Furthermore, the para-substituted hydroxy phenolic interlayer offers expedited pathways for the transport of Li⁺

ions. Specifically, the para-substituted oxygen atom functions as a transfer hub for the swift movement of Li⁺ ions, providing an excellent rate capability (Figure 7c).⁶⁹

To emphasize the effect of para-substituted OH groups on the enhanced transport of Li ions, m-PSi was grafted with poly(4-styrenesulfonic acid) (m-PSi@PSSA), and its rate capability was compared with that of m-GPSi (similarly referred to as m-PSi@PVP) (Figure S7). The sulfonic functional group (SO₃H) in the PSSA can react with the Li⁺ ions through neutralization reactions, leading to the irreversible loss of Li ions during the cyclic process. Moreover, the resultant SO₃[−]–Li⁺ ionic moieties can hinder the pathways for the easy movement of Li ions in the grafted interlayers.⁷⁰ As projected, m-PSi@PSSA exhibited a poor rate capability of 605 mA h g⁻¹ with the lower recovery rate of 68% of the initial capacity at 0.1 A g⁻¹. In contrast, the oxygen atom in the phenolic carbon in m-GPSi serves as a hopping site for Li⁺ ions to swiftly transport the Li ions, thereby demonstrating high-rate capability compared to other materials.

To be summarized, the ultrathin phenolic interlayer provided additional capacitive storage, streamlined rapid Li⁺ ion transport, and reinforced the structural integrity of the material. The phenolic carbon components within the grafted layer can accommodate up to six Li⁺ ions per phenyl ring, allowing efficient insertion and extraction from the structure.⁷¹ Table 1 compares the electrochemical performance of recently documented micro-sized Si/C composites. Interestingly, our m-GPSi demonstrated superior specific capacity and rate capability, highlighting a significant Si content of 99.02%, which differs from other recent studies, in which the Si content was below 30–40%. Furthermore, our low-temperature interface engineering with an ultrathin phenolic interlayer offers a simple and one-pot process for creating a resilient Si interface under mild conditions, distinguishing it from most studies that employ harsh reaction conditions like high temperatures, high pressures, and/or vacuum environments.

3.5. Postmortem Analysis of the Cycled Anodes. A thorough postmortem analysis of the cycled coin cells was performed to better understand the advantages of PVP grafting on PSi in terms of its performance enhancement. Figure 8a–d shows the cross-sectional SEM images obtained before and

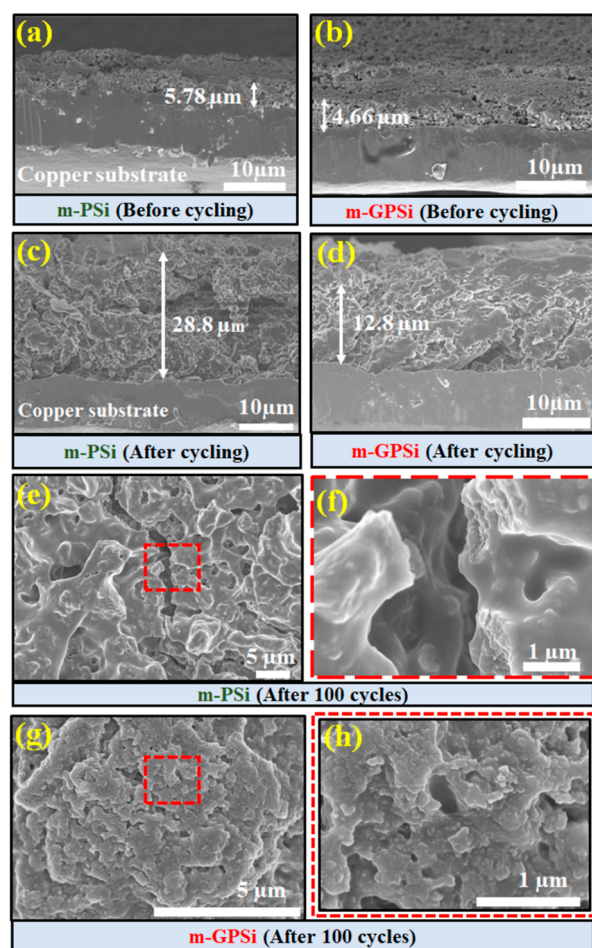


Figure 8. Cross-sectional SEM images of (a) m-PSi, (b) m-GPSi before cycling, (c) m-PSi, and (d) m-GPSi after cycling. Postmortem FE-SEM surface analysis after 100 cycles for (e,f) m-PSi and (g,h) m-GPSi.

after 100 cycles for both the pristine and grafted PSi anodes. The ultrathin phenolic interlayer distinctly minimized the linear expansion of the grafted sample, restricting the expansion to $\sim 200\%$. This is in stark contrast to the untreated counterpart, which displayed an expansion rate of $\sim 400\%$, as shown in Figure 8c. Furthermore, the ungrafted sample displayed considerable deformation, and multiple voids were evident in its structure, which eventually caused its detachment from the current collector. By contrast, the grafted sample effectively maintained its morphology and electrical connections, as shown in Figure 8d. Further insights were provided by the top-view FE-SEM images of the cycled anode materials featured in Figure 8e–h. The ungrafted sample underwent extreme cracking and displayed the formation of large holes, as shown in Figure 8e,f. These drastic morphological alterations inevitably led to capacity fading in several cycles. By contrast, the surface morphology of the grafted sample remains largely unchanged, with minimal small holes and the absence of cracks, as depicted in Figure 8g,h.⁷²

SEI layer composition was investigated by performing ATR-FTIR analysis (Figure 9) for the cycled anodes to evaluate the significance of the grafted phenolic interface in SEI layer formation. As summarized in Table S3, the SEI layer of the m-GPSi anode mainly consists of highly Li^+ ion conducting carboxylic acid salts, RCOOLi , to give a broad intense peak in

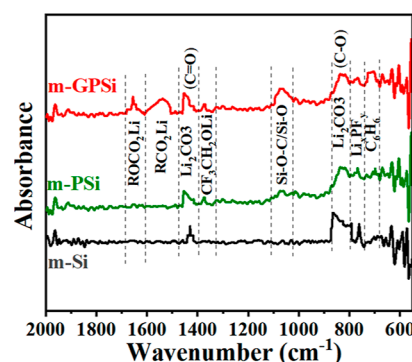


Figure 9. ATR-FTIR spectra of the cycled anodes.

the range of $1542\text{--}1500\text{ cm}^{-1}$.^{45,73,74} Moreover, m-GPSi shows the clear presence of Si-O-C/Si-O entities in the spectral range of $1100\text{--}1050\text{ cm}^{-1}$, whereas these entities are notably absent in both m-PSi and m-Si, probably due to the formation of a thick SEI layer. To be conclusive, ultrathin phenolic interlayer in m-GPSi promoted the formation of the stable and high ionic conductive SEI layer to give high-rate capability and stable cyclic performance. The superior electrochemical performance of both m-PSi and m-GPSi in comparison to that of m-Si is attributed to their pronounced mesoporosity and substantial surface area, which is confirmed by the BET analysis.⁵⁰ The combination of the porous structure and the ultrathin phenolic carbon coating plays a crucial role in shortening Li -ion diffusion pathways and mitigating mechanical stress within m-GPSi. This synergy effect not only preserves the structural integrity but also reduces charge-transfer resistance, consequently delivering high-rate capability and strong cyclic stability.

In this work, efforts have been made to improve Li^+ ion storage in micro-sized PSi via nanointerface engineering. The highly porous nature and covalently bonded phenolic interface (through Si-O-C/Si-C linkages) of m-GPSi effectively streamlined the access and storage of Li^+ by shortening the diffusion pathway. Moreover, the covalent linkages at the Si interface significantly restricted the linear expansion of the anodes throughout charge–discharge cycling. Although micro-sized Si has inherent challenges, such as low intrinsic capacity and restricted rate capability owing to its larger size, the presence of an ultrathin phenolic interlayer significantly improves the initial capacity of m-GPSi (3012 mA h g^{-1}) and maintains an impressive rate capability of 96% following a current density recovery from 4 to 0.1 A g^{-1} . Notably, those outcomes are achieved by utilizing a high Si content of 99% and sidestepping complex and costly procedures, such as multiphase CVD and high-temperature pyrolysis exceeding 700°C . Ultimately, this research underscores the potential of nanointerface engineering via low-temperature thermolysis to enhance Li^+ ion storage in micro-sized Si.

4. CONCLUSIONS

A nanoscale engineered interface was developed through a simple thermolytic grafting process using a unique para-hydroxyl-substituted styrene polymer executed at low temperature ($\leq 360^\circ\text{C}$). A pivotal achievement was the covalent attachment of an ultrathin phenolic interlayer to the surface of m-PSi, which enhanced the performance of the Si-based anode materials. The para-substituted-hydroxy-phenyl interlayer ensured an efficient Li^+ ion transfer and optimized ion

migration, consequently producing a notable Li^+ ion diffusion coefficient in m-GPSi. Specifically, the dual covalent linkages via Si–O–C/Si–C grafts not only increased the capacitive storage of Li^+ ions but also served as a deterrent to the marked volume expansion during the charge/discharge process. This design enabled the m-GPSi anode to achieve an impressive capacity retention of 80.01% at 0.1 A g^{-1} . Moreover, it exhibited a remarkable rate capability of $1250.70 \text{ mA h g}^{-1}$ at 4 A g^{-1} and demonstrated an admirable 96% recovery of its initial capacity, setting the stage for the fabrication of advanced LIB anodes.

■ ASSOCIATED CONTENT

Data Availability Statement

The authors confirm that all underlying data are available in the article and its [Supporting Information](#). Raw data supporting the findings of this study are available from the corresponding author upon request.

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.3c03002>.

XRD, FTIR, and Raman spectra of the samples; proposed thermolytic grafting mechanism; CV curves of the samples for five cycles; CV curves of the samples at different scan rates; photographic images and cyclic performance of the samples with different polymer concentrations; equivalent circuit for EIS spectra and retention comparison of the samples; rate capability of the samples; cyclic performance and retentions of the samples; porosity values of the samples; and FTIR spectra of postcycled composites ([PDF](#))

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Notes

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■ REFERENCES

- (1) Zhang, C.; Wang, F.; Han, J.; Bai, S.; Tan, J.; Liu, J.; Li, F. Challenges and Recent Progress on Silicon-Based Anode Materials for Next-Generation Lithium-Ion Batteries. *Small Struct.* **2021**, *2* (6), 210019.
- (2) Li, W.; Ma, Q.; Liu, X.; Chen, A.; Wang, J.-H.; Min, D. H.; Xiong, P.; Liu, M.; Park, H. S. Enhanced reaction kinetics enabled by a bi-element co-doping strategy for high-performance ternary Si-based anodes of Li-ion batteries. *Chem. Eng. J.* **2023**, *453*, 139567.
- (3) Kim, H.; Shin, S.; Jung, D. S.; Kim, J. H. Fabrication of Si/N-doped carbon nanotube composite via spray drying followed by catalytic chemical vapor deposition. *J. Alloys Compd.* **2023**, *939*, 168743.
- (4) Guo, R.; Zhang, S.; Ying, H.; Yang, W.; Wang, J.; Han, W. Q. New, Effective, and Low-Cost Dual-Functional Binder for Porous Silicon Anodes in Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11* (15), 14051–14058.
- (5) Luo, W.; Chen, X.; Xia, Y.; Chen, M.; Wang, L.; Wang, Q.; Li, W.; Yang, J. Surface and Interface Engineering of Silicon-Based Anode Materials for Lithium-Ion Batteries. *Adv. Energy Mater.* **2017**, *7* (24), 1701083.
- (6) Jiang, C.; Xiang, L.; Miao, S.; Shi, L.; Xie, D.; Yan, J.; Zheng, Z.; Zhang, X.; Tang, Y. Flexible Interface Design for Stress Regulation of a Silicon Anode toward Highly Stable Dual-Ion Batteries. *Adv. Mater.* **2020**, *32*, 1908470.
- (7) Mei, S.; Guo, S.; Xiang, B.; Deng, J.; Fu, J.; Zhang, X.; Zheng, Y.; Gao, B.; Chu, P. K.; Huo, K. Enhanced ion conductivity and electrode-electrolyte interphase stability of porous Si anodes enabled by silicon nitride nanocoating for high-performance Li-ion batteries. *J. Energy Chem.* **2022**, *69*, 616–625.
- (8) Anh Tran, V.; Huu Do, H.; Duy Cam Ha, T.; Hyun Ahn, S.; Kim, M.-G.; Young Kim, S.; Lee, S.-W. Metal-organic framework for lithium and sodium-ion batteries: Progress and perspective. *Fuel* **2022**, *319*, 123856.
- (9) Xue, X.; Liu, X.; Lou, B.; Yang, Y.; Shi, N.; Wen, F.; Yang, X.; Liu, D. The mitigation of pitch-derived carbon with different structures on the volume expansion of silicon in Si/C composite anode. *J. Energy Chem.* **2023**, *84*, 292–302.
- (10) Xing, Y.; Shen, T.; Guo, T.; Wang, X.; Xia, X.; Gu, C.; Tu, J. A novel durable double-conductive core-shell structure applying to the synthesis of silicon anode for lithium ion batteries. *J. Power Sources* **2018**, *384*, 207–213.
- (11) Zheng, P.; Sun, J.; Liu, H.; Wang, R.; Liu, C.; Zhao, Y.; Li, J.; Zheng, Y.; Rui, X. Microstructure Engineered Silicon Alloy Anodes for Lithium-Ion Batteries: Advances and Challenges. *Batteries Supercaps* **2023**, *6* (1), No. e202200481.
- (12) Chen, Y.; Du, N.; Zhang, H.; Yang, D. Facile synthesis of uniform MWCNT@Si nanocomposites as high-performance anode materials for lithium-ion batteries. *J. Alloys Compd.* **2015**, *622*, 966–972.

- (13) Li, Y.; Xiao, P.; Xiong, J.; Luo, J.; Zhou, P.; Xie, X.; Li, Y.; Chen, M. Scalable fabrication of nano/porous Fe-Si coated by 2D carbon nanosheets composite anode for high-performance lithium-ion batteries. *J. Alloys Compd.* **2023**, *945*, 169331.
- (14) Li, P.; Hwang, J.-Y.; Sun, Y.-K. Nano/Microstructured Silicon-Graphite Composite Anode for High-Energy-Density Li-Ion Battery. *ACS Nano* **2019**, *13* (2), 2624–2633.
- (15) Wang, F.; Chen, G.; Zhang, N.; Liu, X.; Ma, R. Engineering of carbon and other protective coating layers for stabilizing silicon anode materials. *Carbon Energy* **2019**, *1* (2), 219–245.
- (16) Zhang, C.; Cai, X.; Chen, W.; Yang, S.; Xu, D.; Fang, Y.; Yu, X. 3D Porous Silicon/N-Doped Carbon Composite Derived from Bamboo Charcoal as High-Performance Anode Material for Lithium-Ion Batteries. *ACS Sustainable Chem. Eng.* **2018**, *6* (8), 9930–9939.
- (17) Zhang, W.; Fang, S.; Wang, N.; Zhang, J.; Shi, B.; Yu, Z.; Yang, J. A compact silicon-carbon composite with an embedded structure for high cycling coulombic efficiency anode materials in lithium-ion batteries. *Inorg. Chem. Front.* **2020**, *7* (13), 2487–2496.
- (18) He, Y.; Han, F.; Wang, F.; Tao, J.; Wu, H.; Zhang, F.; Liu, J. Optimal microstructural design of pitch-derived soft carbon shell in yolk-shell silicon/carbon composite for superior lithium storage. *Electrochim. Acta* **2021**, *373*, 137924.
- (19) Zuo, X.; Zhu, J.; Müller-Buschbaum, P.; Cheng, Y.-J. Silicon based lithium-ion battery anodes: A chronicle perspective review. *Nano Energy* **2017**, *31*, 113–143.
- (20) Wang, F.; Lin, S.; Lu, X.; Hong, R.; Liu, H. Poly-dopamine carbon-coated stable silicon/graphene/CNT composite as anode for lithium ion batteries. *Electrochim. Acta* **2022**, *404*, 139708.
- (21) Song, J.; Chen, S.; Zhou, M.; Xu, T.; Lv, D.; Gordin, M. L.; Long, T.; Melnyk, M.; Wang, D. Micro-sized silicon-carbon composites composed of carbon-coated sub-10 nm Si primary particles as high-performance anode materials for lithium-ion batteries. *J. Mater. Chem. A* **2014**, *2* (5), 1257–1262.
- (22) Tang, X.; Wen, G.; Song, Y. Novel scalable synthesis of porous silicon/carbon composite as anode material for superior lithium-ion batteries. *J. Alloys Compd.* **2018**, *739*, 510–517.
- (23) Zhang, Y.; Qin, X.; Liu, Y.; Chen, Y.; Lei, C.; Wei, T. Novel Si@C/P anode materials with improved cyclability and rate capacity for lithium-ion batteries. *J. Alloys Compd.* **2022**, *899*, 163237.
- (24) Shen, X.; Tian, Z.; Fan, R.; Shao, L.; Zhang, D.; Cao, G.; Kou, L.; Bai, Y. Research progress on silicon/carbon composite anode materials for lithium-ion battery. *J. Energy Chem.* **2018**, *27* (4), 1067–1090.
- (25) Dou, F.; Shi, L.; Chen, G.; Zhang, D. Silicon/Carbon Composite Anode Materials for Lithium-Ion Batteries. *Electrochem. Energy Rev.* **2019**, *2* (1), 149–198.
- (26) Nguyen, C. C.; Song, S.-W. Interfacial structural stabilization on amorphous silicon anode for improved cycling performance in lithium-ion batteries. *Electrochim. Acta* **2010**, *55* (8), 3026–3033.
- (27) Song, S.-W.; Baek, S.-W. Surface layer formation on Sn anode: ATR FTIR spectroscopic characterization. *Electrochim. Acta* **2009**, *54* (4), 1312–1318.
- (28) Han, H.; Huang, Z.; Lee, W. Metal-assisted chemical etching of silicon and nanotechnology applications. *Nano Today* **2014**, *9* (3), 271–304.
- (29) Wang, J.; Joo, J.; Kennard, R. M.; Lee, S.-W.; Sailor, M. J. Thermolytic Grafting of Polystyrene to Porous Silicon. *Chem. Mater.* **2016**, *28* (1), 79–89.
- (30) Fan, S.; Wang, H.; Qian, J.; Cao, Y.; Yang, H.; Ai, X.; Zhong, F. Covalently Bonded Silicon/Carbon Nanocomposites as Cycle-Stable Anodes for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2020**, *12* (14), 16411–16416.
- (31) Wahab, R.; Ahmad, N.; Alam, M. Silicon nanoparticles: a new and enhanced operational material for nitrophenol sensing. *J. Mater. Sci.: Mater. Electron.* **2020**, *31* (19), 17084–17099.
- (32) Xuan Tran, M.; Woo, J.-Y.; Nguyen, T.-A.; Lee, S.-W.; Kee Lee, J. Thermolytically grafted silicon particles with ultrathin carbonaceous coating rich of phenyl moieties as lithium-storage anode material. *Chem. Eng. J.* **2020**, *395*, 125169.
- (33) Martin-Palma, R. J. Biomedical applications of nanostructured porous silicon: a review. *J. Nanophotonics* **2010**, *4* (1), 042502.
- (34) Ma, Q.; Xie, H.; Qu, J.; Zhao, Z.; Zhang, B.; Song, Q.; Xing, P.; Yin, H. Tailoring the Polymer-Derived Carbon Encapsulated Silicon Nanoparticles for High-Performance Lithium-Ion Battery Anodes. *ACS Appl. Energy Mater.* **2020**, *3* (1), 268–278.
- (35) Tou, M.; Michalsky, R.; Steinfeld, A. Solar-Driven Thermochemical Splitting of CO(2) and In Situ Separation of CO and O(2) across a Ceria Redox Membrane Reactor. *Joule* **2017**, *1* (1), 146–154.
- (36) Su, X.; Wu, Q.; Li, J.; Xiao, X.; Lott, A.; Lu, W.; Sheldon, B. W.; Wu, J. Silicon-Based Nanomaterials for Lithium-Ion Batteries: A Review. *Adv. Energy Mater.* **2014**, *4* (1), 1300882.
- (37) Senez, V.; Armigliato, A.; De Wolf, I.; Carnevale, G.; Balboni, R.; Frabboni, S.; Benedetti, A. Strain determination in silicon microstructures by combined convergent beam electron diffraction, process simulation, and micro-Raman spectroscopy. *J. Appl. Phys.* **2003**, *94* (9), 5574–5583.
- (38) Kozakov, A. T.; Kochur, A. G.; Kumar, N.; Panda, K.; Nikolskii, A. V.; Sidashov, A. V. Determination of sp² and sp³ phase fractions on the surface of diamond films from C1s, valence band X-ray photoelectron spectra and CKVV X-ray-excited Auger spectra. *Appl. Surf. Sci.* **2021**, *536*, 147807.
- (39) Bashouti, M. Y.; Paska, Y.; Puniredd, S. R.; Stelzner, T.; Christiansen, S.; Haick, H. Silicon nanowires terminated with methyl functionalities exhibit stronger Si-C bonds than equivalent 2D surfaces. *Phys. Chem. Chem. Phys.* **2009**, *11* (20), 3845–3848.
- (40) Zeng, S.; Feng, W.; Peng, S.; Teng, Z.; Chen, C.; Zhang, H.; Peng, S. Dual-functional SiOC ceramics coating modified carbon fibers with enhanced microwave absorption performance. *RSC Adv.* **2019**, *9* (53), 30685–30692.
- (41) Shi, J.; Gao, H.; Hu, G.; Zhang, Q. Interfacial self-assembled Si@SiO₂@C microclusters with high tap density for high-performance Li-ion batteries. *Mater. Today Energy* **2022**, *29*, 101090.
- (42) Agyeman, D. A.; Song, K.; Lee, G.-H.; Park, M.; Kang, Y.-M. Carbon-Coated Si Nanoparticles Anchored between Reduced Graphene Oxides as an Extremely Reversible Anode Material for High Energy-Density Li-Ion Battery. *Adv. Energy Mater.* **2016**, *6* (20), 1600904.
- (43) Zeng, Y.; Huang, Y.; Liu, N.; Wang, X.; Zhang, Y.; Guo, Y.; Wu, H. H.; Chen, H.; Tang, X.; Zhang, Q. N-doped porous carbon nanofibers sheathed pumpkin-like Si/C composites as free-standing anodes for lithium-ion batteries. *J. Energy Chem.* **2021**, *54*, 727–735.
- (44) Khung, Y. L.; Ngali, S. H.; Scaccabarozzi, A.; Narducci, D. Formation of stable Si–O–C submonolayers on hydrogen-terminated silicon(111) under low-temperature conditions. *Beilstein J. Nanotechnol.* **2015**, *6*, 19–26.
- (45) Tran, M. X.; Nguyen, T.-A.; Lee, J. K.; Lee, S.-W. Porous silicon covalently-grafted with chloro-styrenic carbons for fast Li⁺ diffusion and durable lithium-storage capability. *J. Power Sources* **2023**, *554*, 232326.
- (46) Li, Y.; Liu, W.; Long, Z.; Xu, P.; Sun, Y.; Zhang, X.; Ma, S.; Jiang, N. Si@C Microsphere Composite with Multiple Buffer Structures for High-Performance Lithium-Ion Battery Anodes. *Chemistry* **2018**, *24* (49), 12912–12919.
- (47) Saito, T. The Solution Behavior of Polystyrene Derivatives: Poly-*p*-chlorostyrene. *Bull. Chem. Soc. Jpn.* **1962**, *35* (9), 1580–1584.
- (48) Kuo, S.-W.; Chen, C.-J. Functional Polystyrene Derivatives Influence the Miscibility and Helical Peptide Secondary Structures of Poly(γ -benzyl L-glutamate). *Macromolecules* **2012**, *45* (5), 2442–2452.
- (49) Li, C.; Liu, C.; Ahmed, K.; Mutlu, Z.; Yan, Y.; Lee, I.; Ozkan, M.; Ozkan, C. S. Kinetics and electrochemical evolution of binary silicon-polymer systems for lithium ion batteries. *RSC Adv.* **2017**, *7* (58), 36541–36549.
- (50) Liu, Y.; Zhong, Y.; Zeng, Z.; Zhang, P.; Zhang, H.; Zhang, Z.; Gao, F.; Ma, X.; Terrones, M.; Wang, Y.; et al. Scalable Synthesis of a Porous Micro Si/Si-Ti Alloy Anode for Lithium-Ion Battery from

Recovery of Titanium-Blast Furnace Slag. *ACS Appl. Mater. Interfaces* **2023**, *15* (47), 54539–54549.

- (51) Ren, W.-F.; Li, J.-T.; Zhang, S.-J.; Lin, A.-L.; Chen, Y.-H.; Gao, Z.-G.; Zhou, Y.; Deng, L.; Huang, L.; Sun, S.-G. Fabrication of multi-shell coated silicon nanoparticles via in-situ electroless deposition as high performance anodes for lithium ion batteries. *J. Energy Chem.* **2020**, *48*, 160–168.
- (52) Tesfaye, A. T.; Gonzalez, R.; Coffey, J. L.; Djenizian, T. Porous Silicon Nanotube Arrays as Anode Material for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7* (37), 20495–20498.
- (53) Choi, M.; Kim, J. C.; Kim, D. W. Waste Windshield-Derived Silicon/Carbon Nanocomposites as High-Performance Lithium-Ion Battery Anodes. *Sci. Rep.* **2018**, *8* (1), 960.
- (54) Schroder, K. W.; Celio, H.; Webb, L. J.; Stevenson, K. J. Examining Solid Electrolyte Interphase Formation on Crystalline Silicon Electrodes: Influence of Electrochemical Preparation and Ambient Exposure Conditions. *J. Phys. Chem. C* **2012**, *116* (37), 19737–19747.
- (55) Zhang, Z.; Ying, H.; Huang, P.; Zhang, S.; Zhang, Z.; Yang, T.; Han, W.-Q. Porous Si decorated on MXene as free-standing anodes for lithium-ion batteries with enhanced diffusion properties and mechanical stability. *Chem. Eng. J.* **2023**, *451*, 138785.
- (56) Qi, C.; Li, S.; Yang, Z.; Xiao, Z.; Zhao, L.; Yang, F.; Ning, G.; Ma, X.; Wang, C.; Xu, J.; et al. Suitable thickness of carbon coating layers for silicon anode. *Carbon* **2022**, *186*, 530–538.
- (57) Ashuri, M.; He, Q.; Liu, Y.; Shaw, L. L. Investigation towards scalable processing of silicon/graphite nanocomposite anodes with good cycle stability and specific capacity. *Nano Mater. Sci.* **2020**, *2* (4), 297–308.
- (58) Lee, Y. S.; Ryu, K. S. Study of the lithium diffusion properties and high rate performance of TiNb(6)O(17) as an anode in lithium secondary battery. *Sci. Rep.* **2017**, *7* (1), 16617.
- (59) Wang, M.-S.; Fan, L.-Z. Silicon/carbon nanocomposite pyrolyzed from phenolic resin as anode materials for lithium-ion batteries. *J. Power Sources* **2013**, *244*, 570–574.
- (60) Scaravonati, S.; Sidoli, M.; Magnani, G.; Morengi, A.; Canova, M.; Kim, J.-H.; Riccò, M.; Pontiroli, D. Combined capacitive and electrochemical charge storage mechanism in high-performance graphene-based lithium-ion batteries. *Mater. Today Energy* **2022**, *24*, 100928.
- (61) Leftheriotis, G.; Papaefthimiou, S.; Yianoulis, P. Dependence of the estimated diffusion coefficient of Li_xWO₃ films on the scan rate of cyclic voltammetry experiments. *Solid State Ionics* **2007**, *178* (3–4), 259–263.
- (62) Ni, B.; Jiang, H.; Guo, W.; Xu, Q.; Min, Y. Tailoring the oxidation state of metallic TiO through Ti³⁺/Ti²⁺ regulation for photocatalytic conversion of CO₂ to C₂H₆. *Appl. Catal., B* **2022**, *307*, 121141.
- (63) Bärmann, P.; Mohrhardt, M.; Frerichs, J. E.; Helling, M.; Kolesnikov, A.; Klabunde, S.; Nowak, S.; Hansen, M. R.; Winter, M.; Placke, T. Mechanistic Insights into the Pre-Lithiation of Silicon/Graphite Negative Electrodes in “Dry State” and After Electrolyte Addition Using Passivated Lithium Metal Powder. *Adv. Energy Mater.* **2021**, *11* (25), 2100925.
- (64) Lozhkina, D. A.; Rumyantsev, A. M.; Astrova, E. V. Impedance Spectroscopy of Porous Silicon and Silicon-Carbon Anodes Produced by Sintering. *Semiconductors* **2020**, *54* (3), 383–391.
- (65) Nulu, A.; Nulu, V.; Moon, J. S.; Sohn, K. Y. Unified NCNT@rGO bounded porous silicon composite as an anode material for Lithium-ion batteries. *Korean J. Chem. Eng.* **2021**, *38* (9), 1923–1933.
- (66) Xue, C.; Liu, Y.; Zhao, J.; Li, X.; Zhang, J.; Zhang, J. Nitrogen-doped carbon nanofibers derived from phenolic-resin-based analogues for high-performance lithium-ion batteries. *Solid State Ionics* **2022**, *376*, 115854.
- (67) Ma, L.; Fu, X.; Zhao, F.; Yu, L.; Su, W.; Wei, L.; Tang, G.; Wang, Y.; Wu, F.; Guo, X. Microsized Silicon/Carbon Composite Anodes through In Situ Polymerization of Phenolic Resin onto Silicon Microparticles for High-Performance Lithium-Ion Batteries. *ACS Appl. Energy Mater.* **2023**, *6* (9), 4989–4999.
- (68) Jia, H.; Li, X.; Song, J.; Zhang, X.; Luo, L.; He, Y.; Li, B.; Cai, Y.; Hu, S.; Xiao, X.; et al. Hierarchical porous silicon structures with extraordinary mechanical strength as high-performance lithium-ion battery anodes. *Nat. Commun.* **2020**, *11* (1), 1474.
- (69) Dokko, K.; Watanabe, D.; Ugata, Y.; Thomas, M. L.; Tsuzuki, S.; Shinoda, W.; Hashimoto, K.; Ueno, K.; Umebayashi, Y.; Watanabe, M. Direct Evidence for Li Ion Hopping Conduction in Highly Concentrated Sulfolane-Based Liquid Electrolytes. *J. Phys. Chem. B* **2018**, *122* (47), 10736–10745.
- (70) Lu, Y.; Gu, S.; Guo, J.; Rui, K.; Chen, C.; Zhang, S.; Jin, J.; Yang, J.; Wen, Z. Sulfonic Groups Originated Dual-Functional Interlayer for High Performance Lithium–Sulfur Battery. *ACS Appl. Mater. Interfaces* **2017**, *9*, 14878–14888.
- (71) Lei, Z.; Yang, Q.; Xu, Y.; Guo, S.; Sun, W.; Liu, H.; Lv, L. P.; Zhang, Y.; Wang, Y. Boosting lithium storage in covalent organic framework via activation of 14-electron redox chemistry. *Nat. Commun.* **2018**, *9* (1), 576.
- (72) Li, C.; Lou, X.; Shen, M.; Hu, X.; Guo, Z.; Wang, Y.; Hu, B.; Chen, Q. High anodic performance of Co 1, 3, 5-benzenetricarboxylate coordination polymers for Li-ion battery. *ACS Appl. Mater. Interfaces* **2016**, *8* (24), 15352–15360.
- (73) Lu, W.; Xiong, S.; Xie, K.; Pan, Y.; Zheng, C. Identification of solid electrolyte interphase formed on graphite electrode cycled in trifluoroethyl aliphatic carboxylate-based electrolytes for low-temperature lithium-ion batteries. *Ionics* **2016**, *22* (11), 2095–2102.
- (74) Eshetu, G. G.; Figgemeier, E. Confronting the Challenges of Next-Generation Silicon Anode-Based Lithium-Ion Batteries: Role of Designer Electrolyte Additives and Polymeric Binders. *ChemSusChem* **2019**, *12* (12), 2515–2539.
- (75) Hsieh, C.-C.; Liu, W.-R. Effects of nitrogen doping on Si/carbon composite anode derived from Si wastes as potential active materials for Li ion batteries. *J. Alloys Compd.* **2019**, *790*, 829–836.
- (76) Chen, H.; Hou, X.; Chen, F.; Wang, S.; Wu, B.; Ru, Q.; Qin, H.; Xia, Y. Milled flake graphite/plasma nano-silicon@carbon composite with void sandwich structure for high performance as lithium ion battery anode at high temperature. *Carbon* **2018**, *130*, 433–440.
- (77) Zuo, X.; Wang, X.; Xia, Y.; Yin, S.; Ji, Q.; Yang, Z.; Wang, M.; Zheng, X.; Qiu, B.; Liu, Z.; et al. Silicon/carbon lithium-ion battery anode with 3D hierarchical macro-/mesoporous silicon network: Self-templating synthesis via magnesiothermic reduction of silica/carbon composite. *J. Power Sources* **2019**, *412*, 93–104.
- (78) Chen, H.; Shen, K.; Hou, X.; Zhang, G.; Wang, S.; Chen, F.; Fu, L.; Qin, H.; Xia, Y.; Zhou, G. Si-based anode with hierarchical protective function and hollow ring-like carbon matrix for high performance lithium ion batteries. *Appl. Surf. Sci.* **2019**, *470*, 496–506.
- (79) Yi, Z.; Lin, N.; Zhao, Y.; Wang, W.; Qian, Y.; Zhu, Y.; Qian, Y. A flexible micro/nanostructured Si microsphere cross-linked by highly-elastic carbon nanotubes toward enhanced lithium ion battery anodes. *Energy Storage Mater.* **2019**, *17*, 93–100.
- (80) Gao, R.; Tang, J.; Zhang, K.; Ozawa, K.; Qin, L.-C. A sandwich-like silicon-carbon composite prepared by surface-polymerization for rapid lithium-ion storage. *Nano Energy* **2020**, *78*, 105341.
- (81) Wu, F.; He, Z.; Wang, M.; Huang, Y.; Wang, F. Construction of three-dimensional carbon framework-loaded silicon nanoparticles anchored by carbon film for high-performance lithium-ion battery anode materials. *Nano Res.* **2022**, *15* (7), 6168–6175.
- (82) Chen, C.-Y.; Liang, A.-H.; Huang, C.-L.; Hsu, T.-H.; Li, Y.-Y. The pitch-based silicon-carbon composites fabricated by electro-spraying technique as the anode material of lithium ion battery. *J. Alloys Compd.* **2020**, *844*, 156025.
- (83) Luo, J.; Ma, B.; Peng, J.; Wu, Z.; Luo, Z.; Wang, X. Modified Chestnut-Like Structure Silicon Carbon Composite as Anode Material for Lithium-Ion Batteries. *ACS Sustainable Chem. Eng.* **2019**, *7* (12), 10415–10424.