

Self-Healing SA@Borax Binder for In Situ Tuning of the Solid Electrolyte Interfaces for Silicon Anodes

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dimensional network. This network enhances mechanical stability, accommodates the volume changes of silicon nanoparticles, and maintains electrode integrity during cycling. Furthermore, the SA@Borax binder efficiently regulates the SEI film composition, promoting beneficial components that stabilize the SEI film and improve the lithium-ion diffusion rates. Electrochemical tests demonstrate that the Si anode with SA@Borax binder maintains a discharge specific capacity of 1655.80 mAh g^{-1} after 500 cycles at a current density of 0.5 A g^{-1} , showcasing excellent long-term cycle stability. This research presents a viable strategy for developing high-performance binders for the next generation of lithium-ion batteries.

KEYWORDS: self-healing, solid electrolyte Interface, binder, silicon anode, lithium-ion battery

1. INTRODUCTION

With the growing interest in high-performance energy storage systems, lithium-ion batteries (LIBs) have garnered significant attention. Graphite, a commonly used LIB anode, offers excellent electrochemical and cycle stability in the anode of LIBs but is limited by its low theoretical capacity (372 mAh g⁻¹).^{1,2} To meet the urgent demand for high-capacity energy storage systems, researchers are focusing on silicon (Si) as a potential anode material for the next generation of LIBs.^{3,4} Silicon, which is abundant and environmentally friendly, has a relatively low potential (around 0.4 V vs Li⁺/Li) with a high theoretical capacity of 4200 mAh g^{-1 5,6} However, despite its advantages, Si faces challenges due to its significant volume change (approximately 300%) during lithiation and dilithiation, leading to particle pulverization, electrode structure damage, and an unstable solid electrolyte interphase (SEI).^{7–10} These issues severely limit the cycling life and practical application of Si anodes in LIBs.

To address the challenges associated with silicon (Si) anodes in lithium-ion batteries (LIBs), several strategies have been proposed, with a significant focus on modifying Si anode binders.^{11–16} Polymer binders are crucial for stabilizing the internal structure of electrode materials and enhancing Li-ion transport.^{17–21} Beyond the commonly used ones such as poly(vinylidene fluoride) (PVDF) and styrene–butadiene rubber (SBR), binders with functional groups such as hydroxyl (–OH) or carboxyl (–COOH), like poly(acrylic acid) (PAA), carboxymethyl cellulose (CMC), and alginate, have shown promise in improving the cycling life of Si anodes by bonding with Si particles.^{22,22,22–25} However, these linear binders often lack ideal mechanical properties and electrochemical stability during lithiation and delithiation processes.^{22,22,26–28} Conductive polymers like polyaniline (PANI),²² polypyrrole (PPy),²⁹ and polythiophene (PTH)^{30–32} have been adopted to improve ionic conductivity but struggle to maintain the integrity of Si particles under significant volume changes.^{33,34} Alternatively, aqueous polymer binders, which form hydrogen

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bonds with Si and use water as a solvent, offer ecofriendliness and improved mechanical properties. Examples include poly(acrylic acid) (PAA),³⁵⁻³⁷ poly(acrylamide) (PAM),^{22,38,39} poly(vinyl alcohol) (PVA),^{22,40,41} and various polysaccharides like sodium alginate^{42,43} and carboxymethyl cellulose.^{44,45} These binders enhance adhesion and cycle stability, and their functionalization has been extensively researched to further improve performance.⁴⁶

To enhance the interaction between silicon (Si) and binders, researchers have developed various cross-linked polymer binders, such as PAA-PVA47 and CMC-PAA,48 which feature a three-dimensional (3D) cross-linking network with high mechanical and adhesion strength, better accommodating the significant volume changes of Si anodes. These cross-linked polymer binders, forming a three-dimensional network, effectively suppress excessive volume expansion and improve mechanical and electrochemical performance, thus maximizing the overall efficacy of Si anodes.⁴⁹ While most studies focus on organic-organic polymer binders, organic-inorganic polymer binders, like PVA with sodium borate (SB),⁵⁰ have shown promise in improving conductivity and stability.⁵¹ Building on this research, advanced binders like alginate (SA), cross-linked with borax through an esterification reaction, might show enhanced mechanical robustness and peel strength, preserving the Si anode's integrity over long cycling periods. Furthermore, the dynamic boronate ester (B-O) bonds provide self-healing and deformability, which are crucial for addressing the structural deterioration of electrodes.⁵² Designing a polymer binder that integrates these self-healing properties with efficient energy dissipation and strong adhesion could be a promising approach for the development of high-performance binder materials. Specifically, binders utilizing dynamic boronate ester (B-O) bonds formed between boronic acid and diols or between borax and diols have shown significant potential.53 Borax, hydrolyzed in water to form boric acid and borate ions, creates B-O bonds with diols, enhancing the binder's ability to accommodate volume changes and maintain structural integrity.⁵⁴ These dynamic B-O bonds allow the binder to effectively divert stress and prevent the accumulation of damage, maintaining electrical contact during the Si anode's repeated swelling and shrinking.¹¹ Despite these advancements, the electrochemical performance of polymeric binders still requires improvement, and the mechanisms for stress and energy dissipation remain unclear, necessitating further research to guide the design of next-generation Si anode binders.

In this study, a novel SA@Borax composite material was prepared by introducing sodium tetraborate (borax) into sodium alginate, serving as a self-healing binder for the highperformance Si anode. The two substances spontaneously form a boro-oxygen bond using the -OH group rich in silicon to construct a dynamic cross-linking network. This results in a three-dimensional network structure with high mechanical properties, improving the mechanical properties, stability, and structural integrity of the binder. Sodium alginate is widely used as a binder for anode materials of lithium-ion batteries due to its excellent adhesion, electrical conductivity, and environmental friendliness. The combination of sodium tetraborate and sodium alginate produces the boro-oxygen bond that effectively holds silicon nanoparticles together, preventing them from breaking apart or detaching during cycling and thereby improving the cycle stability of silicon anode material. Additionally, the boron-oxygen bond exhibits

strong thermal and chemical stability, maintaining integrity under harsh temperatures and corrosive conditions, which enhances the battery's longevity and safety. Electrochemical tests demonstrate that the Si anode retains a discharge specific capacity of 1655.80 mAh g^{-1} after 500 cycles at the current density of 500 mAh g^{-1} , indicating excellent cyclic stability.

2. RESULTS AND DISCUSSION

The SA@Borax binder was synthesized through a one-step process that simultaneously incorporates boronate ester bonds and cross-linking. The synergistic effect of SA and borax creates a three-dimensional network structure with a high mechanical strength. Due to the strong interfacial interaction between the sodium alginate and the particles, this binder effectively binds with silicon nanoparticles.⁵⁵ The boron– oxygen bond represents a strong interaction with good chemical and thermal stability,⁵⁶ which can effectively withstand the large volume effect of silicon nanoparticles and ensure the integrity of the electrode structure during the cycle. In addition, chain sliding and hydrogen bond recombination between sodium alginate molecules give the binder self-healing and plasticity properties. As shown in Figure 1, the



Figure 1. Schematic diagram of the SA@Borax binder.

combination of SA and borax, linked by boronate ester and hydrogen bonds, creates a healable binder with strong adhesion to the silicon nanoparticles. This structure can better accommodate the significant volume changes and pressure during the anode's cycling life. SEM images (Figure S1A,B) of SA@Borax and SA electrodes show that the spherical silicon nanoparticles are closely connected with certain void spaces, which can help the electrode release the internal stress caused by the volume effect. The corresponding EDS images further prove that the silicon nanoparticles are in close contact with the conductive carbon black, and the electron transport channels formed by the two ensure the electrochemical stability in the charging and discharging process.⁵⁷

Figure 2A shows an FTIR comparison between pure SA and SA@Borax binders. The diffraction peaks at 3425, 2921, 1618, 1415, and 1033 cm⁻¹ correspond to the O–H stretching vibration, $-CH_2$ symmetric stretching vibration, C=O stretching vibration, $-CH_2$ deformation vibration, and C–O stretching vibration, respectively. When borax is added, a peak of the stretching vibration of B–O–C can be observed at 1351 cm⁻¹, indicating the formation of the boron–oxygen bond.⁴⁹ This boron–oxygen bond can also be identified by the XPS. Figure 2B demonstrates the B 1s spectrum of the as-prepared SA@Borax binder. The characteristic peak of the B 1s fine spectrum at 186.74 eV corresponds to the B–B bond, while the characteristic peak at 193.49 eV corresponds to the B–O



Figure 2. (A) FTIR of the pure SA complex and SA@Borax complex. (B) High-resolution XPS spectra of B 1s. (C) DRIFTS results of the SA@ Borax complex. (D) Thermogravimetric curves of composites. (E) Nitrogen adsorption desorption curves and pore size distribution of composites.

bond. The existence of the boron-oxygen bond confirms the successful cross-link reaction. The chemical and thermal stability of the B-O bond enhances the structural integrity of the electrode sheet and the strain resistance to the volume change of silicon nanoparticles. These properties make the binder better adapt to the volume expansion of the siliconbased negative electrode and enhance the bond between the binder and the electrode material, thus improving the integrity and stability of the electrode sheet.¹¹ Figure S2 presents the XPS full spectrum and detailed fine spectrum of the SA@Borax complex. The full spectrum of XPS (Figure S2A) reveals that SA@Borax mainly consists of five elements: Na, O, C, B, and Si. The elemental composition, detailed in Table S1, indicates that boron (B) comprises 2.62% of the total composition. The fine spectrum of C 1s (Figure S2B) shows that there are four characteristic peaks at 284.80, 285.60, 287.51, and 289.13 eV, representing C-C, C-O-C, C=O, and O-C=O chemical bonds, respectively. Figure S2C is a fine spectrum of O 1s, showing that the characteristic peaks at 532.38, 533.17, 533.96, and 537.69 eV correspond to B-O, C-O, Si-O, and C=O chemical bonds, respectively. The characteristic peak at 100.00 eV in the Si 2p fine spectrum (Figure S2D) corresponds to the Si-Si bond, and the Si-O bond at 104.01 eV illustrates the interaction between the Si nanoparticle and the binder.²⁰ Figure S3 presents the solid-state ¹¹B NMR spectroscopic analysis of the SA@Borax complex. The spectrum reveals two distinct peaks: one at 4.61 ppm, attributable to unbound tetrahedrally coordinated (BO₄) boron atoms in borax, and another at 0.16 ppm, corresponding to mono- and diesterbound signals from boron atoms that form coordination bonds with the hydroxyl and carboxyl groups in SA.^{58,59} The presence of this bound boron peak links SA and borax.

To characterize the dynamic behavior of the cross-linked SA@Borax binder, Figure 2C demonstrates the in situ temperature-changing infrared results of the SA@Borax complex. Similar to the FTIR results, the diffraction peak at 3437 cm⁻¹ corresponds to the elongated O-H stretching vibration. As the temperature rose from 30 to 100 °C, the stretching vibration of the O-H complex gradually shifted from 3435 to 3415 cm⁻¹, indicating that as the temperature increased, the hydrogen bond association formed a stable supramolecular polymer network,⁶⁰ which harmoniously interacted with the boron-oxygen bonds and established a thermally and chemically stable three-dimensional network with high mechanical strength. This network guarantees the strain resistance and structural stability of the Si anode. As a sacrificial bond, hydrogen bond gradually dissociated from the weakest bond to the strongest bond when subjected to the stress from Si volume expansion. This process endows the binder with energy dissipation properties,²⁰ giving the SA@ Borax compound excellent self-healing capabilities. It effectively transfers the stress caused by repeated changes in the volume of silicon nanoparticles when it is used as a binder for electrode sheets.¹⁷ Consequently, it effectively prevents the rupture and regeneration of the SEI film caused by the volume expansion of the silicon-based anode, reducing the consumption of active lithium and electrolyte.⁶¹

As revealed in Figure 2D, thermogravimetric analysis (TGA) was performed on the SA and SA@Borax materials to evaluate their thermal stability by tracking mass changes in a precisely controlled temperature environment. The results indicate that the SA material displayed its first significant weight loss peak at 48.12 °C as the temperature gradually increased, likely corresponding to the initial decomposition of low-molecular-weight components within the material. As the temperature continued to increase to 189.99 °C, the rate of weight loss of SA increased significantly, signaling the onset of decomposition of the primary components of the material. A second peak weight loss occurred at 249.08 °C, after which the rate of weight loss slowed and stabilized, reaching the residual mass of 88.10% by 800 °C.

In comparison, the SA@Borax composite demonstrated greater thermal stability. The beginning of rapid weight loss in SA@Borax was delayed until the temperature increased to 159.66 °C, indicating an elevated decomposition temperature likely due to the incorporation of the borax component. The peak weight loss of the composite occurred at 227.24 °C followed by a rapid reduction in the weight loss rate, eventually stabilizing at 800 °C with the residual mass of 92.28%. This improved thermal stability suggests that the SA@Borax composite contains more thermally stable components likely due to the formation of B–O bonds between borax and SA. The formation of these chemical bonds alters the thermal decomposition mechanism of the material, thereby enhancing its overall thermal stability.

Figure S4 demonstrates the heat transfer characteristics of CMC, SA, and SA@Borax binders exposed to an alcohol lamp flame at varying time intervals, as captured through thermal imaging. The experimental setup utilized a tripod to secure both the binder and the infrared camera, with quartz cotton positioned beneath the binder to prevent direct flame contact. As the exposure time increased, the three binders exhibited distinct heat transfer patterns. Notably, at both 120 and 360 s, the SA@Borax binder maintained significantly lower temperatures compared to SA and CMC binders. This reduced heat

transfer rate effectively mitigates the risk of localized overheating within the battery, thereby enhancing its safety performance.⁶² The improved thermal stability and slower heat propagation characteristics offer dual benefits: they reduce thermal runaway risk in Li-ion batteries during overheating or short-circuit events while preserving structural and functional integrity throughout extended charge/discharge cycling.^{63,64}

The nitrogen adsorption–desorption curves, pore size distributions, and specific surface areas of the composites are shown in Figure 2E and Table S2. Both materials exhibit nitrogen adsorption–desorption curves with prominent hysteresis loop, characteristic of type IV curves. Notably, the specific surface area of the SA@Borax anode material increased significantly from 120.675 m² g⁻¹ for SA to 315.595 m² g⁻¹. This larger specific surface area enhances the active sites available for lithium ion insertion and extraction, significantly enhancing the capacity of the batteries.⁶⁵ The incorporation of borax also enhanced the pore structure of the composite, offering greater storage capacity for lithium ions, and provided sufficient buffer space to accommodate the volume expansion of silicon, thereby improving the cycling stability of the anode.⁶⁶

The self-healing behavior of the SA@Borax binder plays a crucial role in managing the significant volume expansion that occurs during the cycling of lithiation and delithiation. This behavior can be demonstrated by observing the morphological evolution of a given cut polymer membrane. To visualize the self-healing capability of the SA@Borax binder, we dyed the two sections of the binder with white and red colors, respectively. As shown in Figure 3A, when these two dyed sections were placed close together, the contact area between them spontaneously formed a new, dense bond within 5 min.



Figure 3. (A) Digital photo of self-healing test of SA@Borax binder. (B) Peeling experiment of the electrodes. (C) The digital photos of peeling experiment. (D) The weight-bearing test of SA@Borax before (left) and after (right) healing at 25 °C for 2 h.



Figure 4. Electrochemical properties of SA@Borax, SA, borax, and PVDF composite electrode: (A) cycle stability; (B) constant current charge and discharge curve; (C) CV curves at different sweep speeds; (D) relationship between Log(peak current) and Log(scan rate); (E) contribution rate of pseudocapacitance corresponding to different sweep speeds; (F) Nyquist curve of the composite electrode and the relationship between Z' and $\omega^{-1/2}$ in the low-frequency region; (G) GITT curve and lithium-ion diffusion coefficient for the SA@Borax composite electrode; and (H) comparison of cycle properties between SA@Borax binders and previously reported binders.

The healed SA@Borax binder could then be stretched to a high degree of deformation without cracking, demonstrating its excellent self-healing ability. This remarkable self-healing property enables the binder to adapt effectively to significant volume changes in the silicon nanoparticles and transfer stress

by forming alternative hydrogen bonds in the branch chains to prevent stress accumulation, thereby maintaining the stability of electrical contact during repeated expansion and contraction of the silicon anode.²² Figure 3B,C shows the mechanical property test of the electrode sheet.⁶⁷ The strength of the binder was characterized by attaching the tape between the electrode sheet and the sensor to record the force applied when the tape is pulled out at different displacements. Due to the strong adhesion of the binder, almost no active substance is removed from the SA@Borax electrode sheet at a stripping force of 2.56 N, while the underlying copper foil can be seen from the SA electrode sheet (0.12 N). The rigidity of SA@ Borax was assessed using a weight-bearing test (Figure 3D). A sample measuring $46 \times 18 \times 3$ mm and weighing 4.2 g was placed on a Petri dish. Incremental weights were added to the sample, which successfully supported a load of 500 g without breaking-more than 119 times its own weight. The deformation increased with added weight and decreased upon removal of the weights, until the sample fully recovered. Even after healing (the healed part was colored red), the samples could still support 500 g with minimal deformation and returned to their original shape without any cracks once the weights were removed. These results indicate that introducing the boron-oxygen bond not only strengthens the interaction between the binder and the active materials, enhancing the adhesion between the electrode component and the copper foil, but also aids in forming a three-dimensional, double-cross-linked network structure within the electrode material. This network provides a more stable and robust framework that tightly anchors the silicon nanoparticles. It effectively releases volumetric stress on silicon particles during multiple charge-discharge cycles, stabilizing the SEI layer. Simultaneously, it ensures close contact between the active material and the current collector, preventing electrical isolation and electrode delamination.⁶

To evaluate the electrochemical performance of the SA@ Borax binder in the silicon-based anode, a series of characterizations were performed in this work by using the CR2032 coin cell. Figure S5A plots the CV curves of the SA@ Borax silicon anode in the voltage range from 0.01 to 1.0 V with a scan rate of 0.1 mV s^{-1} . For the first lithiation of the anode, the small current increasing from 0.7 V is related to the formation of SEI between the silicon nanoparticles and the electrolyte. After that, two peaks occur at 0.22 and 0.03 V corresponding to the formation of the Li_xSi ($0 \le x \le 4.4$). These two peaks are also observed in the subsequent cycles, implying a similar reaction of two-stage lithiation processes for the silicon anode. In the anodic scan, two oxidation peaks (0.48 and 0.30 V) were observed, which were attributed to the delithiation of Li_xSi to form Si. The cycling performance of the SA@Borax silicon anode under the current density of 0.5 A g^{-1} is shown in Figure 4A. The electrode was activated at a current density of 0.1 A g^{-1} in the first five cycles. After the first five cycles of the activation, the sixth cycle demonstrated a discharge capacity of 2839.27 mAh g^{-1} with a Coulomb efficiency (CE) of 97.57% and retained a capacity of 1655.80 mAh g^{-1} with a CE of 99.73% after 500 cycles. Compared with the cyclic performance of SA (438.96 mAh g^{-1} after 500 cycles), borax (3.61 mAh g^{-1} after 500 cycles), and PVDF (518.50 mAh g^{-1} after 200 cycles) electrodes, the SA@Borax composite electrode has excellent cyclic stability. This is attributed to the chemical and thermal stability of the boronoxygen bond cross-linked network in the SA@Borax complex and the excellent self-healing ability of the binder. The charge and discharge curves of the SA@Borax composite electrode under different cycles are shown in Figure 4B. The anode shows the classical electrochemical characteristics of the silicon nanoparticles. Two voltage plateaus around 30 and 220 mV are

measured on the discharge curve, corresponding to the lithiation of silicon nanoparticles in the anode. On charge curves, voltage plateaus around 300 and 480 mV are observed, consistent with the peaks shown on the CV graph in Figure S5A. The initial charge-discharge specific capacities were 3080.77 and 4342.52 mAh g^{-1} (ICE = 70.94%), respectively. During the charging and discharging processes, the continuous volume change of silicon leads to the rupture and regeneration of the SEI film, resulting in the loss of a large amount of lithium and electrolyte, which leads to the low initial Coulomb efficiency of silicon anode and the deterioration of its electrochemical stability.⁶⁹ The high ICE of the SA@Borax composite electrode is attributed to the fact that the SA@ Borax binder effectively regulates the composition of the SEI film and forms a stable and thin solid electrolyte interface. At the same time, the high mechanical properties of the binder boron-oxygen bond cross-linking network can alleviate the internal stress caused by the volume expansion of the negative silicon electrode. With the progress of the cycle, the coincidence degree of charge and discharge curve gradually increases, the electrochemical performance becomes stable, the capacity attenuation decreases, the charging and discharge platform changes little, and the polarization degree is weak, reflecting the excellent cyclic stability and reversibility of the SA@Borax composite electrode.⁷⁰

To further explore the electrochemical kinetics of the SA@ Borax binder used with the silicon anode in lithium-ion batteries, various CV curves at scan rates ranging from 0.1 to 1 mV s⁻¹ are presented in Figure 4C. By correlating the scan rate to the peak current response, it is possible to distinguish between diffusion behavior and pseudocapacitance during the battery's charging and discharging process. Specifically, if the peak current *i* varies with the square root of the scan rate v (b = 0.5), the process is controlled by diffusion. Conversely, if the peak current *i* varies linearly with the scanning rate v (b = 1), the behavior is pseudocapacitive, indicating capacitive control. Therefore, the current (*i*) versus scan rate (v) should follow eqs 1 and 2:⁷¹

$$i = av^b \tag{1}$$

$$\log(i) = b\log(v) + \log(a)$$
⁽²⁾

To quantify this behavior, parameter b is calculated from the slope of the log(v)-log(i) plot, as illustrated in Figure 4D, to determine whether there is a pseudocapacitance behavior in the charging and discharging process. A *b* value of 0.5 suggests diffusion-controlled kinetics typical of battery materials. If the b value is between 0.5 and 1, the electrode material exhibits characteristics of a dual-model energy storage (DMES) system, combining properties of both batteries and capacitors. A bvalue ≥ 1 indicates dominant pseudocapacitive properties. The calculated b values for the anode and cathode peaks are 0.70 and 0.62, respectively, indicating that the SA@Borax electrode engages in DMES behavior. This behavior is beneficial for the rapid transport of lithium ions and enhances cycle stability by combining the advantageous properties of both battery-like and capacitive energy storage mechanisms. According to the following formula:

$$i = k_1 v + k_2 v^{1/2} \tag{3}$$

Further analysis involves calculating the capacitance current k_1v for each voltage value to determine the overall capacitance contribution at different sweep speeds, as shown in Figure



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Figure 5. (A) In situ EIS during charge and discharge of the first cycle; SA@Borax relaxation time (DRT) function $\gamma(\tau)$ and intensity plot of DRT function $\gamma(\tau)$ for (B) discharging and (C) charging; (D) 3D schematic of FTIR of the SA@Borax composite electrode at different voltages; and (E) 2D schematic of FTIR of the SA@Borax composite electrode at different voltages.

SSB-F. Figure 4E reveals that the pseudocapacitance effect intensifies with increasing scan rates, finally reaching 71% of the total capacitance at 0.9 mV s⁻¹. The excellent capacitance characteristic indicates that SA@Borax significantly improves the reaction kinetics during electrode cycling.⁷³

The electron/ion transport within the electrode was analyzed by using electrochemical impedance spectroscopy (EIS). As shown in Figure 4F, the Nyquist diagram features a semicircle in the high-frequency region, indicative of the charge transfer process, and a straight line in the low-frequency region, corresponding to the solid diffusion of lithium ions within the silicon particles. The charge transfer resistances (R_{ct}) of SA, borax, and SA@Borax composite electrodes are 114, 113, and 47.3 Ω , respectively, as determined by the diameter of the semicircle. These results indicate a significant reduction in the interfacial impedance of the composite electrode attributed to the boron-oxygen cross-linked network.⁷¹ Furthermore, the electrochemical AC impedance method not only elucidates the reaction kinetics at the interface but also facilitates the calculation of the lithium-ion diffusion coefficient D_{Li}^{+} , thereby assessing the ion diffusion performance of the electrode. The D_{Li}^{+} is calculated using following formula:⁷⁴

$$Z = R_{\rm S} + R_{\rm ct} + \sigma \omega^{-1/2} \tag{4}$$

$$D_{\rm Li^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$
(5)

Here, *R* is the gas reaction constant (8.314 J mol⁻¹ K⁻¹); *T* represents the absolute temperature (298.15 K); *A* represents the electrode reaction area approximated by the surface area of the electrode in this experiment; *n* is the number of electrons transferred per molecule in the electrode reaction (for lithium ions, *n* is 1); *F* is the Faraday constant; *C* is the concentration of Li⁺ in the electrode; ω is the angular frequency; and σ is the Warburg coefficient, which is determined as the slope of the line after a linear fit of Z' vs $\omega^{-1/2}$. As shown in Figure 4F, the lithium-ion diffusion coefficients of the SA, borax, and SA (ω) Borax composite electrodes are 3.0959 × 10⁻¹⁶, 4.3389 × 10⁻¹⁶, and 7.2539 × 10⁻¹⁶, respectively, demonstrating the superior lithium-ion diffusion performance of the SA (ω) Borax composite.

In order to gather more precise information on the reaction kinetics and the lithium-ion diffusion coefficient of the research anode. After stabilizing the activated electrode by cycling for five cycles at a low current density of 100 mA g^{-1} , the SA@ Borax composite electrode was tested using the galvanostatic

intermittent titration technique (GITT) technology, as shown in Figure 4G. GITT calculations are based on Fick's second law of diffusion, which can be expressed as follows:⁷⁵

$$D_{\mathrm{Li}^{+}} = \frac{4L^2}{\pi\tau} \left(\frac{\Delta E_{\mathrm{s}}}{\Delta E_{\mathrm{t}}}\right)^2 \tag{6}$$

Here, D_{Li}^{+} represents the lithium-ion diffusion coefficient $(cm^2 s^{-1})$; L denotes the diffusion distance (cm) of Li⁺, equivalent to the thickness of the electrode; τ is the relaxation time (s); ΔE_s represents the steady-state potential change (V) induced by the current pulse; and ΔE_t refers to the potential change during the relaxation time (V) after the constant current pulse. Figure 4G, Figure S6, and Table S3 reveal that the lithium-ion diffusion coefficient under varying degrees of lithiation and delithiation follows the "W"-shaped distribution during the lithium removal. In the discharge process, the diffusion coefficient ranges from 2.15731×10^{-13} to $1.96004 \times$ 10^{-10} , peaking when the lithium insertion reaches 25% $(3.22283 \times 10^{-12} - 7.49867 \times 10^{-11})$ for the SA anode material). During the charging process, the lithium-ion diffusion coefficient ranges from 1.02509×10^{-11} to 1.07257 \times 10⁻¹⁰, achieving a maximum of 50% delithiation (3.00975 \times 10^{-14} –2.04134 × 10^{-10} for the SA anode material). Compared to the SA anode, the SA@Borax anode demonstrates superior lithium-ion diffusion coefficients, suggesting that lithium ions in SA@Borax can be quickly alloyed with silicon nanoparticles, thereby significantly enhancing its electrochemical performance. As shown in Figure 4H and Table S4, the SA@Borax binder exhibits superior cyclic performance compared with other reported binders,^{15,17,20,22,56,76-80} attributed to the synergistic action of B-O bond and hydrogen bonding.

Tto elucidate the transport mechanism of lithium ions within the SA@Borax electrode, in situ electrochemical impedance spectroscopy (EIS) was conducted during the first lithium removal/insertion cycle. The corresponding Nyquist curve is shown in Figure 5A and compared with the results of SA electrodes (Figure S7). It reveals that the charge transfer resistance of the electrode initially stabilizes and then increases, while the slope of the low-frequency region decreases during the discharge process, indicative of the formation of a solid electrolyte interphase (SEI) film. The discharge initiates as silicon particles make contact with the electrolyte, triggering a reaction where the lowest unoccupied molecular orbital (LUMO) of the electrolyte is lower than the electrochemical potential of the anode, leading to electron transfers from the anode to the electrolyte and consequent reduction and formation of the SEI film on the anode surface.^{18,81} Initially, the SEI film forms as an inorganic layer, primarily composed of LiF and Li2CO3 that provides high toughness and excellent stability. This toughness accommodates volume changes in the electrode material, while the stability helps prevent further electrolyte decomposition.⁸² Additionally, Li₂CO₃ acts as an ionic conductor, enhancing the lithium ion diffusion within the SEI layer.⁸³ During the discharge process, ethylene carbonate (EC) decomposes extensively to form the organic outer layer of the SEI film extensively. The instability of the organic outer layer leads to an increase in charge transfer and lithium-ion diffusion resistance, aligning with the observations from the Nyquist curve. The SA electrode has a greater charge transfer resistance compared with the SA@Borax electrode. This is not only because the cross-linked network imparts superior structural

properties to the SA@Borax electrode but also because during the lithiation process, the SA electrode forms more unstable organic SEI layers, which increase the charge transfer resistance. Conversely, during the charging phase, the scenario reverses: the active material adjusts with the deintercalation of lithium ions, and the unstable SEI organic layer disintegrates, which diminishes the charge transfer resistance and enhances the lithium-ion diffusion coefficient. Toward the end of the charging cycle, a stable and compact SEI film, predominantly composed of LiF and Li₂CO₃, forms, ensuring stable charge transfer resistance and an increased rate of lithium-ion diffusion.^{84,85} In contrast, the SA electrode demonstrated a distinctive behavior throughout the delithiation process. During the predelithiation stage, its charge transfer resistance decreases. However, this resistance progressively increases during the middle and late stages primarily due to the SEI layer instability. During the later stages of delithiation, the SEI layer experiences rupture, exposing the underlying Si negative electrode. This exposure triggers additional electrolyte decomposition, leading to the formation of an SEI layer. The consequent thickening of the SEI layer not only elevates charge transfer resistance but also potentially compromises overall battery performance through continued degradation.

To delve deeper into the dynamics of the lithium storage process, the distribution of relaxation time (DRT) function graph $\gamma(\tau)$ (Figure 5B,C, Figure S8) was calculated using the DRT tool on the MATLAB platform developed by Ciucci's team.^{86,87} These DRT function graphs, along with FTIR analysis performed on the SA@Borax and SA electrode at various voltages during cycling (Figure 5D,E, Figure S9), were used to investigate the lithium storage mechanism. The highfrequency region, located at $\tau < 10^{-3}$ s, is associated with the formation of the SEI; the intermediate-frequency region, located at 10^{-2} s < τ < 1 s, is associated with the charge transfer between the SEI membrane and the active material; and the low-frequency area, ranging from 1 to 10 s, corresponds to the solid phase diffusion process in the SEI membrane of silicon electrode.⁸⁸ In the FTIR analysis, the characteristic peak at 751.62 cm⁻¹ was identified as a signal for Li₂CO₃, while peaks at 894 and 943 cm⁻¹ corresponded to the out-of-plane deformation vibrations of the olefins. The broad peak at 1118.51 cm⁻¹ matched the organic components in the SEI layer and the stretching vibrations of the C-O bond in the electrode material. The peak at 1274 cm^{-1} was attributed to the presence of LiPF₆. The peak at 1385 cm^{-1} corresponded to the characteristic C-F bond vibration, while the peak at 1442 cm⁻¹ matched the characteristic vibration of LiF. The appearance and disappearance of peaks in the FTIR spectra effectively map the dynamic transitions of lithium-ion embedding and detachment to the SEI layer at various voltages. Observation during the first lithium-ion embedding (first discharge) of the SA@Borax electrode reveals that the peak at $\tau < 10^{-3}$ s correlates with the decomposition of electrolytes. As the discharge reaches 1 V vs Li^+/Li , decomposition of FEC and LiPF₆ occurs, forming Li₂CO₃dominated sediments on the surface of Si particles and forming an inorganic inner layer with high fracture toughness.⁸⁹ Li₂CO₃ primarily functions as an ionic conductor, facilitating lithiumion transport and thereby enhancing charge transfer efficiency.90 Therefore, the Li2CO3 generation process effectively reduces the lithium ion diffusion resistance. When further discharged to 0.8 V vs Li⁺/Li, large-scale decomposition of EC occurs, with products like ROCOOLi and

LiOR emerging and forming the organic outer layer of the initially established SEI film by Si. This formation is consistent with the Nyquist curve during the discharge process, where the charge transfer resistance increases gradually during discharge. Additionally, the FTIR spectra reveal shifts in peaks associated with organic components, along with the emergence of olefinrelated peaks. Continuous discharge to 0.1 V vs Li⁺/Li leads to the formation of a double-layer SEI film.⁹¹ In the 1 s < τ < 10 s range, the peak decreases alongside the reduction of lithiumion diffusion resistance. There is a notable peak value at the open circuit voltage that rapidly decreases during discharge to 0.75 V due to the initial high diffusion impedance from a low concentration of lithium ions in the silicon nanoparticles. When the discharge proceeds to 0.1 V, the higher concentration of lithium ion in the silicon particles lowers the diffusion impedance. In the SA electrode, the relaxation time peaks demonstrate notable shifts compared to the SA@ Borax electrode, specifically in two regions: the electrolyte decomposition peaks (around 10^{-3}) and the charge transfer peaks $(10^{-2} < \tau < 1)$. This shift toward larger relaxation times primarily results from SEI layer instability. FTIR analysis near the discharge platform provides additional evidence, revealing that SA generates a higher proportion of organic component SEI layers compared to SA@Borax. The progressive thickening of the SEI layer extends the charge transport pathway, resulting in substantially increased relaxation times. This extended pathway indicates that charge transfer during electrolyte decomposition becomes more challenging in SA electrodes, necessitating longer periods to complete the charge transfer process.

During the subsequent charging process (Li-ion removal), when the voltage rises from 0.01 to 1.2 V vs Li^+/Li , the peak resistance of $\gamma(\tau)$ in the high-frequency region decreases and shifts to a higher frequency, potentially due to the volume shrinkage of Si particles during the dealloying process. The easily fractured organic outer layer of SEI film breaks and falls off from the Si particle surface under compressive stress, leaving a more stable and tougher inorganic inner layer. This coincides with the attenuation and eventual disappearance of the characteristic olefin peaks in the FTIR spectra. Meanwhile, significantly enhanced peaks observed at around 0.5 V are attributed to the transformation of the Li_xSi alloy into amorphous silicon during delithiation accompanied by the decomposition and the formation of organic components in the SEI layer. This observation is consistent with the Nyquist curve during the charging cycle. In the range of 1 s < τ < 10 s, the increase of lithium-ion diffusion resistance with the charging is attributed to the decreasing lithium-ion concentration, thereby increasing diffusion resistance. By transforming the DRT function gamma (τ) diagram into the intensity diagram, as shown in the inset of Figure 5C, the migration pattern of lithium ions within the negative electrode material can be observed more directly. In the range of 1 s < τ <10 s, the electrode exhibits a sustained peak period from 1.15 to 0.75 V attributed to the growth of SEI film, which destabilizes the mass transfer process. However, the peak intensity of the SEI film from 0.75 to 0.01 V is small, indicating that the SEI film of the electrode quickly reaches a stable state during the cycle. In contrast, the SA electrode exhibits a distinctive behavior in the charging plateau region, where the peak intensity associated with SEI formation initially remains low but experiences rapid elevation toward the plateau's end. This behavior stems from structural alterations during the

delithiation process that compromise SEI layer stability, ultimately resulting in layer rupture during late-stage delithiation. The subsequent exposure of the Si negative electrode catalyzes additional electrolyte decomposition. This sequential process aligns with the FTIR patterns, which demonstrate consistent peaks corresponding to various SEI layer components.

As shown in Figure S10, XPS tests were performed on the negative electrode material after different numbers of cycles. The total spectrum revealed that the electrode material primarily consists of seven elements: F, O, C, B, P, Si, and Li. The high-resolution XPS spectra of C 1s, Si 2p, B 1s, P 2p, O 1s, F 1s, and Li 1s at different cycle numbers are illustrated in Figure S11 and Figure 6A–C. The C 1s fine spectrum



Figure 6. Fine XPS spectra of the SA@Borax composite electrode with different cycles: (A) O 1s, (B) Li 1s, and (C) F 1s. (D) SEM images of the SA@Borax composite electrode at the 1st, 100th, and 500th cycle. (E) SEM cross-section images of the SA@Borax composite electrode at the 1st, 100th, and 500th cycle. (F) Schematic diagram of SEI composition regulated by the binder SA@Borax.

remains consistent with that before cycling, with characteristic peaks near 284.8, 286.59, 288.53, and 289.53 eV, corresponding to the chemical bonds C–C, C–O, C=O, and RO–CO₂Li, respectively. In the Si 2p fine spectrum, the peak at 98.62 eV corresponds to the Si–Si bond, while the peak at 102.81 eV corresponds to the Si–O bond. The O 1s fine spectrum shows peaks attributed to the Si–O bond (532.02 eV) and the –COOLi bond (532.81 eV). For Li 1s, peaks at 55.26 and 55.88 eV correspond to the Li₂CO₃ and LiF chemical bond, respectively. The F 1s fine spectrum displays high-intensity LiF peaks (684.87 eV) and lower-intensity Li_xPF_y/Li_xPO_yF_z peaks (687.78 eV), indicating that fewer electrolytes decompose and are consumed during the cycling. In addition, LiF plays a crucial role in regulating Li⁺

transformation and deposition in the SEI layer.²¹ The B–O peak in the B 1s fine spectrum demonstrates the stability of the 3D boron–oxygen bond network through cycling, enhancing the electrode sheet's structural integrity and improving the electrochemical performance of SA@Borax complex. In the P 2p fine spectrum, a new PO_xF_y peak appears with the continued cycling,⁹² indicating reduced electrolyte decomposition and consumption and a decrease in organic SEI film components.

Table S5 shows the contents of each chemical bond under different cycles. The data indicate that from the 1st cycle to the 10th cycle, the content of RO-CO₂Li and other organic components in the electrode increases, while the proportion of $Li_x PF_y/Li_x PO_y F_z$ -LiF also increases. These component changes are related to the SEI film's evolution. The SEI has a doublelayer structure; the inner layer at the electrode cross section and silicon nanoparticle edges contains more inorganic components, such as LiF. Its compact structure and fewer pores confer high fracture toughness and mechanical stability, preventing further electrolyte decomposition.93,94 The SEI surface on silicon nanoparticles contains more organic mixture generated by electrolyte decomposition, forming a porous layer prone to fracture.⁸¹ The increase in organic and inorganic components represents the formation of an organic-inorganic double-layer SEI film. This SEI film accommodates electrode volume changes, synergizes with the binder, buffers electrode contraction/expansion, and prevents further direct contact between the electrolyte and Si, enhancing battery Coulomb efficiency.¹⁸ After the 10th cycle, the organic component content decreases, while the inorganic component content increases, suggesting that the SA@Borax binder effectively regulates the SEI film's composition. This regulation establishes a robust SEI film on the silicone-based negative electrode, crucial for improving the performance of lithium-ion batteries.⁹⁵ Table S6 details the elemental content changes across different cycle numbers.

The SEI film is an interfacial layer that possesses the properties of a solid electrolyte and is an excellent conductor of Li^+ ions. The formation of the SEI film consumes active lithium and increases the irreversible capacity during the first charge and discharge. However, its insolubility in organic solvents makes it stable in organic electrolytes, preventing direct contact between solvent molecules and the negative electrode. This avoids irreversible damage to the electrode material caused by the solvent molecules coembed-ding.^{22,96–100}

To further analyze the morphological evolution and failure mechanisms of the SA@Borax electrode during cycling, we characterized the electrode surface and cross section after 1, 100, and 500 cycles. Initially, the electrode demonstrated a smooth, uniform surface and a well-preserved internal structure (Figure 6D, Figures S12 and S13). After the first cycle, while the SA electrodes displayed fine surface cracks, the SA@Borax electrode sheet remained intact, which can be attributed to the boron-oxygen bond cross-linking network that provides structural stability. After 100 cycles, the SA@Borax electrode surface exhibited only minor cracks, whereas the SA electrodes developed denser and larger surface cracks, demonstrating that the SA@Borax binder effectively accommodates the volume expansion of silicon nanoparticles, thus preventing large-scale structural collapse. After 500 cycles, both electrodes displayed noticeable cracks resulting from the stress of repeated silicon nanoparticle expansion and contraction, leading to structural

damage and capacity attenuation. Prior to cycling, the SA@ Borax electrode exhibited closer contact with the copper foil compared to the SA electrode (Figure S14), contributing to its superior electrochemical performance. The SA@Borax electrode thickness increased from an initial average of 7.425 to 8.575, 8.514, and 15.827 µm after 1, 100, and 500 cycles, respectively (Figure 6E), corresponding to expansion rates of 15.48, 14.67, and 113.16%. In comparison, the SA electrode exhibited more substantial growth, with thickness increasing from an initial average of 8.033 to 12.346, 29.270, and 37.191 μ m after 1, 100, and 500 cycles, respectively (Figure S15), corresponding to significantly higher expansion rates of 53.69, 264.37, and 362.97%. The relatively low expansion rate in the first 100 cycles is attributed to the hydrogen-bonded supramolecular polymer network, which interacts with the boron-oxygen bond to create a stable, high-strength threedimensional network, ensuring the strain resistance and structural stability of the Si anode. The electrode maintained strong adhesion to the copper foil, showing no significant cracking or damage, indicating a stable structural adhesion between the Si and the binder.

Figure 6F illustrates the regulatory mechanism of the SA@ Borax binder on the SEI film, summarized from characterization data before and after the cycling. The reactions on the negative electrode surface, likely caused by electrolyte decomposition, result in the formation of lithium methyl carbonate (LMC), lithium ethylene monocarbonate (LEMC), dilithiated ethylene monocarbonate (DLEMC), Li₂CO₃, and LiF, which coat the negative electrode surface with the SEI film. This process also produces gases such as ethylene, carbon monoxide, and others.¹⁰¹ The widely accepted 3D "mosaic model" shows that the SEI film's interior consists of various inorganic lithium salts, while the outer layer comprises porous organic components.^{81,102,103}

The addition of the SA@Borax binder results in a gradual decrease in organic components within the SEI film, while the contents of LiF and Li₂CO₃ gradually increase during the delithium/lithium process. LiF, with its excellent Young's modulus, can withstand significant strains during cycling and plays a crucial role in regulating the transport and uniform deposition of Li⁺ ions.^{94,99,100,103} The reduction in electrolyte consumption and decomposition leads to a decrease in the level of Li_xPF_y/Li_xPO_yF_z inorganic chemicals. Additionally, Li₂B₄O₇, known for its stability, reduces the erosion of the SEI film by electrolyte decomposition products and provides more migration channels as a lithium ion conductor.^{104–106} The SEI layer becomes more robust and stable due to the rise of high-toughness inorganic components. This effectively isolates the electrolyte and negative electrode, reducing electrolyte loss and enhancing the battery's overall performance.

3. CONCLUSIONS

The SA@Borax binder was developed as an innovative solution for silicon-based negative electrodes in lithium-ion batteries. Its design leverages the synergistic interaction between sodium alginate and boron—oxygen bonds, forming a robust threedimensional network with a high mechanical strength and chemical stability. This network accommodates the substantial volume changes of silicon nanoparticles during cycling while maintaining the structural integrity of the electrode. The chain sliding and hydrogen bond recombination properties of sodium alginate confer deformability and self-healing characteristics to the binder, ensuring long-term stability and performance. Furthermore, the SA@Borax complex effectively regulates the SEI film composition, promoting the formation of beneficial components and creating a strong, stable SEI film. This regulation reduces the consumption of silicon and electrolyte while enhancing the diffusion rate of lithium ions. Experimental results demonstrate the exceptional long-term cycle stability of the SA@Borax binder, with a discharge specific capacity of 1655.80 mAh g⁻¹ maintained after 500 cycles at a current density of 0.5 A g⁻¹. This research presents a viable and effective strategy for developing advanced binders for the next generation of high-performance lithium-ion batteries.

4. EXPERIMENTAL SECTION

4.1. Synthesis of the SA@Borax Binder. To prepare the composite binder material, 0.2 g of sodium alginate was added to 10 mL of deionized water, and the mixture was stirred at 400 rpm using a mechanical mixer until completely dissolved. Subsequently, 0.1 g of anhydrous borax was added to the solution, which was then stirred at 90 °C and 300 rpm for 6 h. After the stirring process, the achieved binder material was cooled for further use.

4.2. Structure and Electrochemical Characterization. 4.2.1. Structure Characterization. The microstructures and morphologies of the prepared samples were examined by using fieldemission scanning electron microscopy (FE-SEM, ZEISS Gemini 300). The X-ray photoelectron spectroscopy (XPS) patterns were measured by a Thermo scientific K-Alpha with an Al K α X-ray source. A Fourier transform infrared spectroscopy (FTIR, ThermoFisher iS20) was used to detect functional groups inside materials. Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS, ThermoFisher iZ10) was used to dynamically demonstrate the change of functional groups with temperature. The peeling test was carried out on a Suns Technology UTM4203 tensile test machine to detect the bond strength of the binder. Thermogravimetric analysis (TGA, Hitachi 7200) was performed in an argon atmosphere with a temperature ramp rate of 10 °C/min and over a range of 30 to 800 °C. Specific surface area and pore size analysis (BET, Autosorb iQ) was conducted by heating the material to 100 $^\circ$ C at a rate of 10 $^\circ$ C/ min, holding for 10 min, and then further heating to 200 °C followed by degassing for 6 h. After degassing, a full pore-size analysis was preformed under a pressure of 1.0×10^{-5} Pa. The test results were derived using the BET computational model to analyze the specific surface area and pore size distribution of the material.

4.2.2. Electrochemical Characterization. The electrochemical performance of the SA@Borax binder was evaluated by using CR2032-type coin cells. To prepare the electrodes, Si nanoparticles were mixed with different binders and the conductive additive Super-P in a weight ratio of 8:1:1, using deionized water as the solvent. The resulting slurry was coated onto a copper foil and dried at 60 °C for 12 h. Electrodes with a 12 mm diameter were punched from the dried slurry/copper foil. Lithium metal served as the negative electrode. The coin cells were assembled in an argon-filled glovebox (H₂O, O₂ < 0.01 ppm). Each cell comprised the prepared electrode, Celgard 2400 separator, lithium metal negative electrode, and electrolyte consisting of 1 M LiPF₆ in a 1:1 volume mixture of dimethyl carbonate (DEC) and ethylene carbonate (EC) with additives 2% vinylene carbonate (VC) and 10% fluoroethylene carbonate (FEC).

Galvanostatic charge and discharge (GCD) tests were conducted using a Neware BTS-4008 system to intuitively evaluate the electrochemical performance of the materials. The voltage range for the tests was 0.01-1.0 V. The batteries were activated for five cycles at a low current density (0.1 A g⁻¹) followed by charge–discharge cycles at a higher current density of 0.5 A g⁻¹. Cyclic voltammetry (CV) tests were performed by using a Zahner Zennium-XC electrochemical workstation to study the reaction mechanisms and reversibility of the electrodes during charging and discharging. The CV tests were conducted within a scanning voltage range of 0.01-1.0 V at various scanning rates: 0.10, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, and

0.90 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was used to obtain information about the kinetic mechanisms and interface structure of the electrodes. EIS tests were performed on batteries that had been resting for 24 h in potentiostatic mode, with a disturbance amplitude of 5 mV, across a frequency range of 10 mHz to 100 kHz. The distribution of relaxation time (DRT) was utilized to deconvolute the coupled EIS data into a continuous curve with multiple specific peaks representing dynamic parameters of different electrochemical processes. In situ EIS testing was conducted by using the Zennium XC electrochemical workstation. A constant current of 0.1 A g^{-1} was applied to discharge the battery from 1.15 to 0.01 V, with EIS measurements taken at 0.05 V intervals. These processes were analyzed using the DRT tool on the MATLAB platform to reveal the electrode's interface adjustment mechanisms. The galvanostatic intermittent titration technique (GITT) was employed to accurately characterize the lithium-ion diffusion capacity. The GITT tests were performed using the Neware BTS-4008 system with a constant current density of 0.1 A g^{-1} , a pulse duration of 20 min, and a relaxation time of 30 min.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.4c10154.

SEM and EDS images showing the morphology and elemental distribution of SA@Borax and SA electrodes; XPS spectra revealing chemical states of the SA@Borax complex; solid ¹¹B NMR spectrum demonstrating the structural composition of SA@Borax; time-resolved infrared thermal imaging comparing CMC, SA, and SA@Borax binders; CV curves with capacity contribution analysis at different scan rates; GITT measurements showing the lithium ion diffusion behavior; in situ EIS data during electrochemical cycling; relaxation time distribution analysis of impedance response; in situ FTIR spectra tracking structural evolution; comprehensive XPS analysis before and after cycling; surface and cross-sectional SEM images tracking morphological changes through cycling; elemental composition from XPS analysis; specific surface area and pore structure parameters; quantitative lithium-ion diffusion coefficients from GITT; comparative cycling performance with state-of-the-art binders; detailed chemical bond evolution during cycling; and atomic concentration changes throughout electrochemical cycling (PDF)

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Author Contributions

T.H., H.Z., and C.L. conceived and designed the study. T.H., Y.D., and H.Z. carried out experiments and statistical analysis. S.Z., X.Y., H.B., and L.Y. assisted with the data analysis. T.H., H.Z., and C.L. wrote and edited the manuscript. H.Z. and C.L. administered and supervised all the experiments and analyses. The authorship order was assigned based on the degree of contribution. All the authors have read and approved the manuscript.

Notes

The authors declare no competing financial interest.

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