

The Origin of Improved Performance in Boron-Alloyed Silicon Nanoparticle-Based Anodes for Lithium-Ion Batteries

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Stabilizing the solid electrolyte interphase (SEI) remains a key challenge for silicon-based lithium-ion battery anodes. Alloying silicon with secondary elements like boron has emerged as a promising strategy to improve the cycle life of silicon anodes, yet the underlying mechanism remains unclear. To address this knowledge gap, how boron concentration influences battery performance is systematically investigated. These results show a near-monotonic increase in cycle lifetime with higher boron content, with boron-rich electrodes significantly outperforming pure silicon. Additionally, silicon-boron alloy anodes exhibit nearly three times longer calendar life than pure silicon. Through detailed mechanistic analysis, alternative contributing factors are systematically ruled out, and it is proposed that improved passivation arises from a strong permanent dipole at the nanoparticle surface. This dipole, formed by undercoordinated and highly Lewis acidic boron, creates a static, ion-dense layer that stabilizes the electrochemical interface, reducing parasitic electrolyte decomposition and enhancing long-term stability. These findings suggest that, within the SEI framework, the electric double layer is an important consideration in surface passivation. This insight provides an underexplored parameter space for optimizing silicon anodes in next-generation lithium-ion batteries.

active material for lithium-ion batteries (LIBs) in high-energy-density applications like electric vehicles (EVs).^[1–5] However, the large volume changes with lithiation/delithiation, as well as an unstable and nonpassivating solid electrolyte interphase (SEI) reduce the longevity of silicon anodes well below graphite, which thus far has precluded silicon from broad market adoption.^[6–8] Indeed, the challenge of stabilizing high-content silicon anodes in reversible lithium-ion batteries has existed since the emergence of LIBs themselves.^[9–11]

Nanoscaling silicon particles has been shown to alleviate many of the mechanical stresses associated with repeated lithiation and delithiation cycles.^[12–15] However, reducing particle size also increases the surface area-to-volume ratio, amplifying chemical reactivity and exacerbating side reactions. To address this, surface modification with functional materials or chemistries has been

extensively explored to passivate silicon and mitigate parasitic reactions.^[16–21] While these approaches have shown promise in extending cycle life and enhancing understanding of SEI formation, a key insight from this body of work is that the most effective

1. Introduction

With a theoretical energy density ten times higher than graphite, Silicon (Si) has demonstrated promise as a next-generation anode

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passivation occurs when the silicon surface is entirely isolated from the electrolyte. Consequently, the ideal silicon/electrolyte interface is one where silicon itself is entirely shielded from direct contact with the electrolyte.

An alternative strategy to passivate the silicon surface is to alter the silicon itself through doping or alloying.^[22–24] Si alloys (such as Si-Fe, Si-Mn, Si-Co),^[25–27] and inorganic electrolyte additives,^[28–31] which change the chemical identity of the silicon surface, have shown promise for passivating the reactive silicon surface.^[32] For example, multivalent electrolyte additives such as Mg^{2+} have been shown to incorporate into the silicon active material, which reduces parasitic losses from electrochemical lithiation/delithiation.^[28,32] These active material modifications have other material benefits, such as dopant-induced deformations that can lower energy barriers and facilitate solid-state Li-ion diffusion in silicon.^[33–35] We previously demonstrated that alloying silicon nanoparticles with boron (Si-B) significantly enhances cyclic stability and processability, outperforming even the most advanced pure silicon-based anodes in side-by-side comparisons.^[36] Our findings indicated that engineering the surface chemistry of silicon nanoparticles to mitigate parasitic reactions is more effective with ionic chemistries than with molecular coatings or carbon-based passivation. However, the precise mechanisms underlying the improved performance remained speculative.

In this study, we synthesized silicon-boron alloy nanoparticles with varying Si:B stoichiometries and incorporated them into composite anodes composed of active material, carbon nanotubes, and a polyimide binder. We conducted a systematic investigation of the electrochemical performance of these anodes, paired with capacity-matched NMC811 cathodes using a standard carbonate-based electrolyte. Our results reveal a clear correlation between boron content and electrochemical performance, with higher boron-content materials significantly outperforming lower boron-content materials.

To uncover the mechanisms driving this performance enhancement, we carried out a comprehensive study examining both electrode-level and material-level properties. These analyses demonstrate that the improved performance is largely attributable to enhanced interfacial passivity, which reduces electrolyte degradation. This stabilization effect translates to a nearly threefold increase in calendar lifetime compared to anodes composed of pure silicon.

2. Results and Discussion

2.1. Characterization and Battery Performance

Si nanoparticles (NPs) were prepared using a custom-built radio frequency (RF) plasma reactor and were used as the baseline material in this work, the details of which have been described elsewhere.^[36] The silicon-boron (Si-B) NPs alloys with varying Si:B stoichiometries ranging from 3% to 50% boron were synthesized by varying the flow rate of process gases SiH_4 and B_2H_6 in the presence of carrier gases (Ar, H_2 , and He). Full details of plasma growth parameters are shown in Table S1 (Supporting Information). From X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements in our

previous work, these particles are single crystals with the same structure as pure silicon, have a significantly shifted Si 2P orbital energy relative to pure Si, a high density of free carriers, and strong surface Lewis acidity.^[36–39] These measurements indicate that these particles form a substitutional solid solution with aliovalent-type doping and a strong surface dipole.

Scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS) mapping of Si-B NPs with varying proportions of Si and B is given in Figure 1a. The STEM-EELS maps in Figure 1a show boron homogeneously distributed throughout the bulk of the Si NPs. In addition to compositional analysis from STEM-EELS, we performed inductively coupled plasma optical emission spectroscopy (ICP-OES). Figure 1b shows the boron mass percent as measured by ICP-OES, as well as the nominal concentration of boron in the synthesis. From Figure 1b, the two sets of values nearly completely overlap with one another, indicating that the incorporation of boron into silicon during the synthesis is nearly stoichiometric. This could be expected for a highly non-equilibrium synthetic method since the available energy from the capacitively-coupled plasma far exceeds the kinetic barriers of alloying.^[40] From here forward, the varied Si-B particles will be referred to by their boron mass percent as determined by ICP-OES (i.e., B0 for pure silicon, B50 for 50% boron, etc.). We note that the Si NP sizes in this work varied from ≈ 6 to 14 nm (Figure 1c) – a limitation of our synthesis – but this size regime generally displays similar performance characteristics from PECVD Si NP electrodes.^[41] However, we cannot completely rule out the effects of particle size on electrode performance.

Composite Si NP anodes consisting of carboxyl functionalized single-walled carbon nanotubes (SWCNTs-COOH), lithium carbonate (Li_2CO_3), and a polyimide (PI) binder were printed onto a copper current collector (see Experimental Section for details). As described previously, Li_2CO_3 coordinates to the Si-B surface, which serves two purposes: 1) Li_2CO_3 acts as an engineered inorganic SEI, and 2) inhibits undesirable dative interactions with carbon nanotubes or the PI binder.^[36] The average total thickness of these composite anodes is $\approx 25 \mu m$ as measured with a micrometer over several points along the electrode print.

To evaluate the cycle aging of these anodes in a LIB configuration, we first assemble the Si-B NP anodes with Li metal in a half cell configuration ($Li_2CO_3@Si-BX||Li$ where X is the boron stoichiometric percent) in 1.2 M $LiPF_6$ in 3:7 ethylenecarbonate:ethylmethyl carbonate (EC:EMC) with 3 wt% fluoroethylene carbonate (GenF3). Here, three Galvanostatic charge/discharge cycles were performed at C/20 between 0.01 and 1.5 V versus Li. The first cycle voltage profiles of all the half cells, along with their corresponding Coulombic efficiency (CE) values, are shown in Figure 2a. From Figure 2a, the 1st cycle CEs of all the cells are ≈ 75 –80%. The total gravimetric capacity decreases with increasing boron content, where the largest difference in gravimetric capacity occurs between $Li_2CO_3@Si-B50||Li$ and $Si-B0||Li$ at 1771 and 1451 $mAh g^{-1}$, respectively. This is expected as boron does not contribute to lithium storage capacity.^[42] We do note that the Si-B0 electrode silicon utilization in this voltage range is lower than expected ($>2500 mAh g^{-1}$). Several factors, such as surface oxidation,^[42] or electrode morphology,^[43] can impact the utilization.

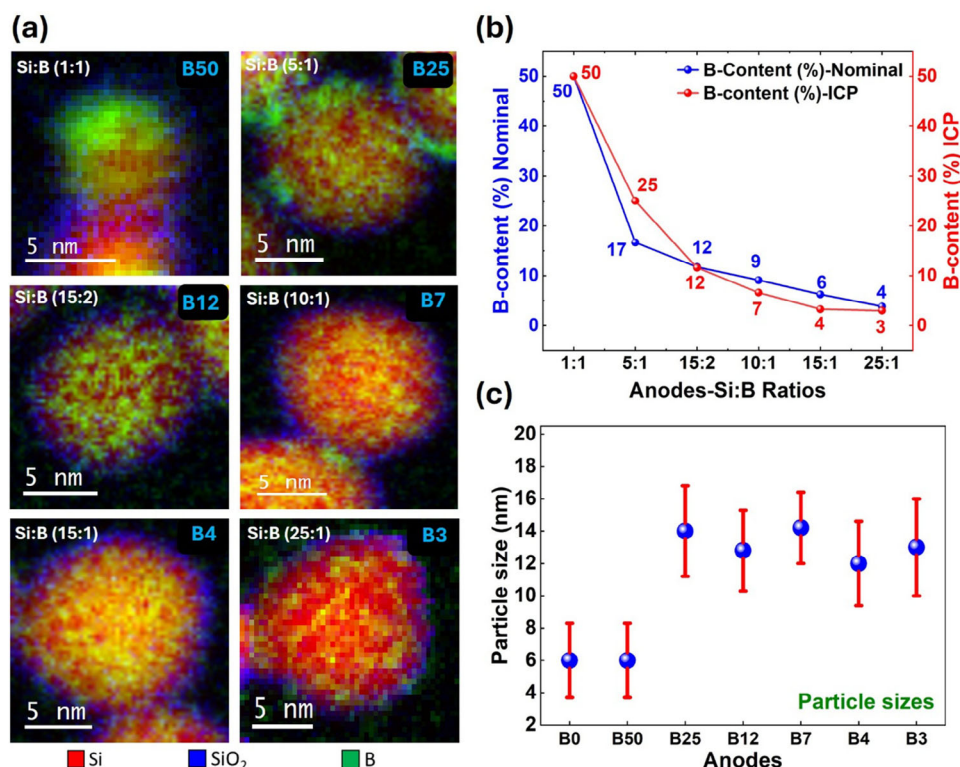


Figure 1. a) STEM-EELS images of Si-B NPs with varying boron concentrations and particle size,^[36] b) Inductively coupled plasma optical emission spectroscopy analysis of the Si-B NPs presented in percentage as the ratio of ICP-OES values to the nominal values in the synthetic mixture, and c) average particle sizes of the Si-B NPs with error bars (averages were taken from ten different particle sizes for each Si-B NPs studied in this work).

Voltage profiles of $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{Li}$ for all three cycles are shown in Figure S1 (Supporting Information). From Figure S1 (Supporting Information), this electrode displays a first cycle lithiation areal capacity of 2.96 mAh cm^{-2} and a CE of 75.90%. The second and third cycles deliver 2.28 and 2.25 mAh cm^{-2} with CEs of 98.30% and 99.01%, respectively. The first cycle voltage lithiation profile displays a steep capacity onset at $\approx 0.2 \text{ V}$ versus Li, but the second and third lithiation voltage profiles span a much broader range. This data shows that Si-B is crystalline in the first cycle, but upon delithiation, it becomes amorphous. During this phase transition, the boron appears to remain uniformly distributed within the structure without any sign of phase segregation (Figure S2, Supporting Information). Differential capacity (dQ/dV) curves of the second and third cycle for samples Si-B0||Li and $\text{Li}_2\text{CO}_3 @ \text{Si-B25} || \text{Li}$, provided in Figure S3 (Supporting Information), suggests that the silicon boron alloy has the same lithiation mechanism as Si, albeit with a slight increase in the overpotential. This behavior is consistent with our previous report.^[36]

C-Rate tests were performed on Si-B0||Li and $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{Li}$ within the same voltage window at 0.1C, 0.2C, 0.5C, 1C, 2C, and 5C (Figure S4, Supporting Information). At low C-rates, both $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{Li}$ and Si-B0||Li display similar capacity retention, but as the current increases, $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{Li}$ outperforms Si-B0||Li. As the electrode morphology and Li diffusivity are nearly identical between these two electrodes (vide infra), we attribute the improved rate capability to an improvement in electronic conductivity from the boron-induced free carriers.

Next, these anodes were removed from the half cell in a completely delithiated state (1.5 V vs Li) and reassembled into full cells against capacity-matched NMC811 (where X is the boron content in percentage unless $X = 0$) as the cathode and GenF3 as the electrolyte. As there is no electroactive Li remaining from the half-cell cycles, we do not consider these anodes as prelithiated. Rather, we consider them to simply have an *ex-situ* SEI where the majority of the early cycle losses were experienced in the half cell configuration and not in the full cell. The purpose of this procedure is to ensure that the early cycle losses in the full cells are not significant enough to impact the *n:p* ratio and keep the cathode operating voltage window close to its initial state.

Figure 2b presents voltage profiles for selected cycles (1–1000) of the $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$ cell. Additional voltage profiles for the 10th cycle of all full cells are provided in Figure S5 (Supporting Information) for comparison. The corresponding capacity retention of these full cells is shown in Figure 2c. For batteries with the highest boron-containing silicon nanoparticles ($\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$), 82.5% of their initial capacity is retained through 1000 cycles. In contrast, cells with lower boron content display a faster capacity fade. The cycle number at the end-of-life (EOL), defined as reaching 80% of the initial capacity, is shown in the table in Figure 2d and corroborates the trend of increasing cycle life with increasing boron content (Note that with an appropriate prelithiation protocol, Si-B0 electrodes do achieve 1000 cycles while retaining more than 80% of their capacity.^[43] Although the areal capacities of the samples vary due to

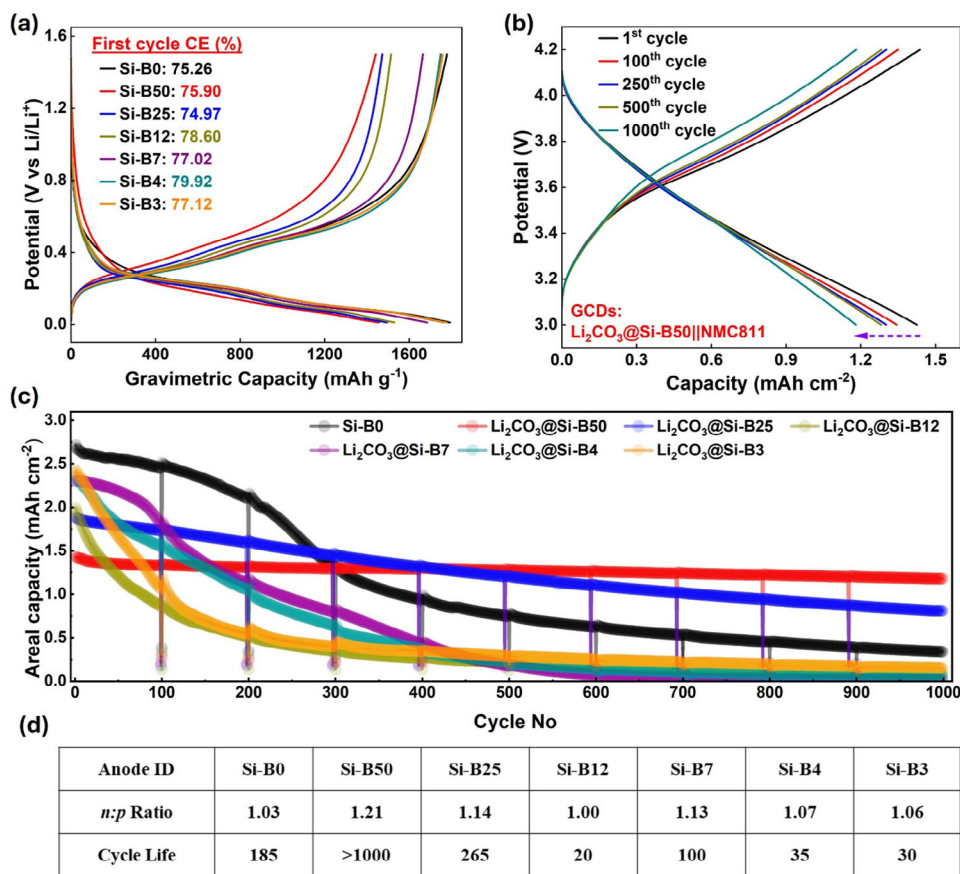


Figure 2. a) The first cycle voltage profiles of all the half cells expressed as gravimetric capacity of the total electrode mass ($\text{Li}_2\text{CO}_3@Si-BX + \text{CNT} + \text{PI}$) along with their corresponding Coulombic efficiency (CE), b) Galvanostatic charge/discharge (GCD) curves of selected cycles of $\text{Li}_2\text{CO}_3@Si-B50||NMC811$ full cell, c) a lifetime plot of cyclic data to the 1000th cycle of all the full cells, and d) A table displaying $n:p$ ratios and cycle life defined as 80% of full cell capacity during the first discharge cycles.

differences in hand-coated electrode preparation, the cathodes were selected to maintain a consistent $n:p$ ratio across all tests (table in Figure 2d). While the influence of areal capacity on anode cycle life cannot be entirely excluded, the consistent $n:p$ ratio ensures a uniform voltage operating window, allowing for a focused evaluation of boron content effects. Indeed, the anomalously low cycle life of $\text{Li}_2\text{CO}_3@Si-B12||NMC811$ in relation to the other boron content-based silicon batteries may be related to a poor $n:p$ electrode balance.

CE is a critical metric for assessing battery cycle stability, as it directly reflects the loss of lithium inventory (LLI) and loss of active material (LAM), particularly in flooded electrolyte systems like those used in this study.^[44] Figure 3a presents the CE for the first 100 cycles of all full cells, while Figure S6 (Supporting Information) provides CE data over 1000 cycles. The inset of Figure 3a plots the average CE during the first 100 cycles. The $\text{Li}_2\text{CO}_3@Si-B50||NMC811$ cell, with the highest boron content (B50), exhibits the highest CE among the samples. Its first-cycle CE reaches 90%, surpasses 99.8% within five cycles, and remains steady thereafter. The next highest boron-content cell, $\text{Li}_2\text{CO}_3@Si-B25||NMC811$, shows similar CE performance, with an average CE over 100 cycles within the margin of error compared to $\text{Li}_2\text{CO}_3@Si-B50||NMC811$. As boron content decreases,

however, the average CE also declines, accompanied by a slower rise in CE during the initial cycles. For instance, the lowest boron-content cell, $\text{Li}_2\text{CO}_3@Si-B3||NMC811$, does not achieve a stable CE plateau until approximately cycle 40. This trend of slower CE stabilization for lower boron-content cells is evident in the decreasing average CE values shown in the inset of Figure 3a. Interestingly, the pure silicon cell, $Si-B0||NMC811$, displays an average CE higher than that of the low boron-content $\text{Li}_2\text{CO}_3@Si-B12||NMC811$ cell but lower than the $\text{Li}_2\text{CO}_3@Si-B25||NMC811$. This could suggest that low boron concentrations may adversely affect cycle stability, or more likely, is an effect of the $Si-B0$ having a smaller diameter.^[41] Despite these nuances, the general trend is clear: the capacity retention improves with increasing boron content. To clearly illustrate this, we plot the capacity retention after 400 cycles alongside the boron content in these silicon electrodes as shown in Figure 3b. Cycle 400 is chosen to capture the effect of the “knees” in the cycle data.

Our previous work showed that the impedance gain of electrochemically cycled $\text{Li}_2\text{CO}_3@Si-B50$ is negligible, with almost no SEI accumulation over 1000 cycles.^[36] In this study, we observe that the cycle performance of $Si-B$ anodes consistently decreases as the boron content is reduced. To investigate whether cell impedance correlates with boron content, we calculated

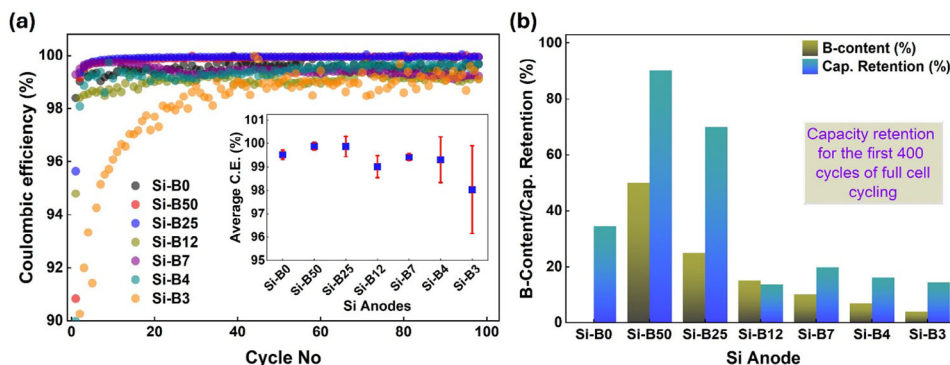


Figure 3. a) Coulombic efficiencies (%) in the first 100 cycles of all the full cell cycling and average coulombic efficiencies (%) with error bars in the inset. b) Side-by-side comparison of capacity retention (%) with boron content of all the full cells at cycle 400.

the area-specific impedance (ASI) over the course of the 1000-cycle experiment. This was achieved through hybrid pulse power characterization (HPPC) measurements conducted every 100 charge/discharge cycles, as shown in **Figure 4**.

Figure 4 plots the average discharge Δ ASI where Δ ASI is:

$$\Delta ASI_n = ASI_n - ASI_0 \quad (1)$$

here, n is the n^{th} cycle (100, 200, etc.) at which the average ASI (averaged over all current pulses for one cycle) was calculated, and ASI_0 is the ASI at cycle 0. For cells that reached their EOL prior to 1000 cycles, the Δ ASI data is not plotted beyond the last ASI measurement after EOL. From Figure 4, most cells have a sharp initial rise from $n = 0$ to $n = 100$. The magnitude of Δ ASI at cycle 100 generally follows the boron concentration, where Δ ASI is larger for samples with lower boron content, however, the sample with no boron content (Si-B0||NMC811) displayed the lowest initial Δ ASI. From cycle 100 to 200, Δ ASI does not increase for Li_2CO_3 @Si-B50||NMC811 but does for Si-B0||NMC811 and Li_2CO_3 @Si-B25||NMC811. The overall increase is the highest for Si-B25||NMC811. Si-B0||NMC811 reaches its EOL prior to 1000 cycles but displays a continuous ASI gain of $6 \Omega\text{cm}^2/100$

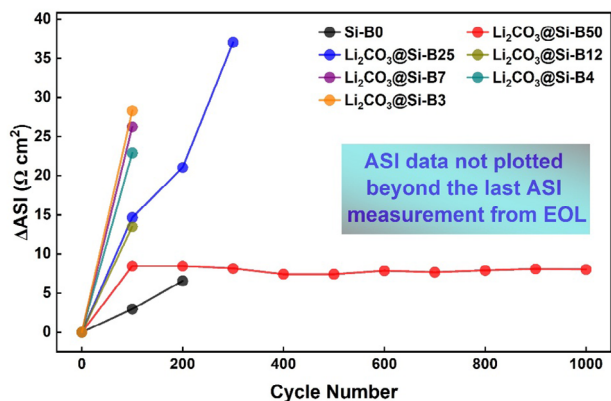


Figure 4. Change in the area-specific impedance (Δ ASI) for all the Li_2CO_3 @Si-BX||NMC811 cells. These data were derived from hybrid pulse power characterization (HPPC) steps every 100 cycles. Note: The cells with lower boron concentration have almost no capacity beyond 300th cycles and therefore the ASI of these cells are not shown beyond 300th cycle.

cycles. Similarly, Si-B25||NMC811 reaches its EOL prior to 1000 cycles, but displays a faster gain in ASI of $11 \Omega\text{cm}^2/100$ cycles. As cycling continues, the only cell to reach 1000 cycles before its EOL is Li_2CO_3 @Si-B50||NMC811, which shows almost no impedance gain after the first few cycles. The dQ/dV profiles presented in Figures S7 and S8 (Supporting Information) corroborate these measurements. Where the dQ/dV profile for Li_2CO_3 @Si-B50||NMC811 is almost perfectly overlapping for cycle 1, 100, and 200, the lower boron content alloy anodes display both a decrease in peak intensity (loss of capacity) and a feature shift to higher potentials (increasing cell impedance). While the ASI of the Si-B0||NMC811 and Li_2CO_3 @Si-B50||NMC811 samples follow our previous reports,^[36] the intermediate boron content anodes have a more unclear relationship with impedance rise.

2.2. Mechanistic Analysis

To understand why the presence of boron in silicon appears to improve the electrochemical performance of composite silicon anodes, we consider the relevant material-level and electrode-level property differences between Si-B and pure Si. We consider four different possibilities:

- The volume expansion of Si-B is lower than pure Si:* The volumetric changes of silicon upon repetitive lithiation/delithiation cycling are a central obstacle for extended lifetimes in silicon-containing anodes. Boron, however, does not alloy with Li, which reduces the possible Li storage capacity in Si-B by the molar equivalent of B in Si. Therefore, the Si-B volumetric expansion/contraction upon lithiation/delithiation is proportionally smaller than pure Si. Indeed, the improved performance in our Si-B electrodes may simply be the result of reduced overall mechanical strain.
- The surface dipole of Si-B increases the ionic density at the Si-B surface:* The strong Lewis acidity of surface boron in a diamond cubic lattice creates a large surface dipole. The addition of salts like Li_2CO_3 tightly coordinates to the boron at the surface to passivate the dipole. The high density of ions at the surface has the combined effect of creating an engineered SEI, a physical barrier between the electrolyte and the

electrode, that screens the electric field within the electrolyte to mimic an electrochemical double layer (EDL). Such an interface layer could provide chemical passivation between Si-B and the electrolyte.

- (c) *Si-B NPs are more electronically conductive:* Boron is an aliovalent *p*-type dopant in crystalline silicon. The free charge carriers increase the conductivity by many orders of magnitude. The enhanced conductivity reduces electron transport resistance across the depth of the electrode which could result in fewer electronically isolated regions and lower Li trapping (i.e., reduces loss of active material as a capacity loss mechanism).
- (d) *Si-B has better slurry properties:* The ionic nature of the Si-B surface creates a thermodynamic driving force for spontaneous colloidal suspension.^[37] This property enables ideal slurry suspensions by creating a highly dispersed colloid. To create dispersibility in pure silicon NPs, we covalently functionalize the surface with polar molecular coatings.^[43,45] While this coating does indeed suspend the NPs, the mechanism of action is completely different from the Si-B NPs and can easily be overcome if the surface coating is too thin. Indeed, the electrode dispersion may be different between Si-B and pure Si. The improved dispersion may then result in a macroscopic improvement in the structure of the composite electrode itself, which would enable more ideal electrode performance.

Any one or combination of these differences can be envisioned to affect the anode performance.

Isolating the root cause of improved performance in composite electrodes with different active materials is challenging. Several intersecting phenomena from electrode-level (ion transport, electron transport, homogeneity, particle dispersion, etc.) to material-level (charge transfer resistance, surface reactivity, diffusivity, etc.) convolute analyses that can lead to incorrect mechanistic assignments. Therefore, it is imperative that both electrode-level and material-level properties be understood and accounted for in order to gain true insight into the mechanisms that govern performance properties. To this end, we characterize the microstructural properties of the electrode and interfacial properties of the active material.

2.2.1. Electrode Microstructure

The microstructure of lithium-ion battery electrodes significantly impacts ion transport, electronic conductivity, and mechanical stability, which in turn influence capacity, cycle life, and Coulombic efficiency. To understand how the different Si-B active materials change the electrode microstructure, we first characterize the tortuosity. Here, we use the blocking electrolyte method to calculate the MacMullin number (N_M), which quantifies the ratio of ionic resistivity of a porous material relative to the electrolyte itself. N_M is given by Equation (2).

$$N_M = \frac{\kappa_0}{\kappa_e} = \frac{\tau}{\epsilon} \quad (2)$$

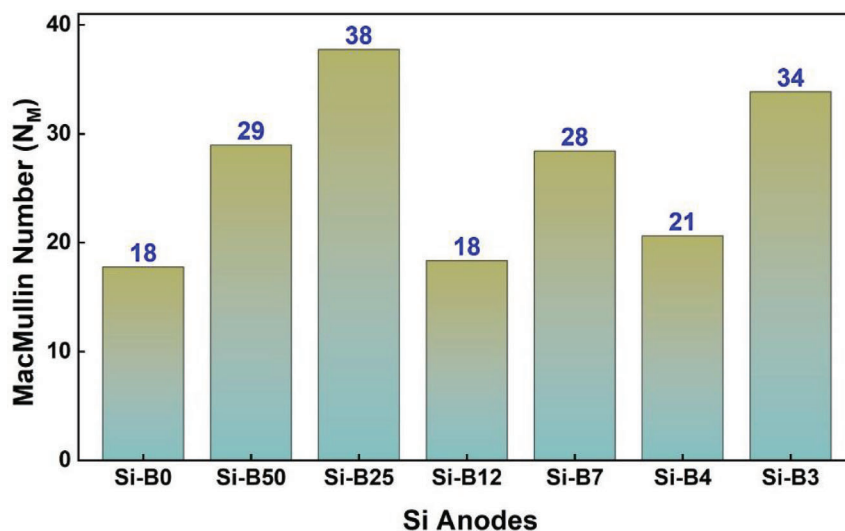
where κ_e is the effective ionic conductivity through the depth of the electrode, κ_0 is the intrinsic ionic conductivity of the elec-

trolyte, τ is the tortuosity factor, and ϵ is the electrode porosity (see Section S1 and Figure S9, Supporting Information, and associated discussion for details).^[46,47] In the ideal limit, $N_M = 1$, but in composite electrodes with porous structure, $N_M > 1$. For context, graphite anodes with 50 μm thicknesses have N_M values ≈ 10 .^[46] Figure 5 shows the measured N_M values for these electrodes, and Table S2 (Supporting Information) shows the values for the input parameters.

The data in Figure 5 reveal that most electrodes exhibit exceptionally high MacMullin numbers ($N_M > 20$), indicating a highly tortuous ion transport pathway. This is expected for electrodes made from nanoparticles with radii in the single-nanometer range, as these small particle sizes create pores much smaller than those in electrodes with larger particle sizes (>100 nm).^[48] Importantly, no consistent trend or value for N_M is observed across samples with varying boron concentrations, and the values vary greatly from sample to sample. We believe this is due to incomplete electrolyte wetting throughout the electrode volume (vide infra). As a result, assumptions underlying N_M calculations using the ion-blocking electrolyte method – such as complete saturation of the electrode by the electrolyte – are not satisfied, rendering these N_M values unreliable.

Next, to evaluate the key length scales within our electrodes and understand the likelihood of electrolyte wetting throughout the electrode, we conducted N_2 physisorption measurements on Si-B0 and Li_2CO_3 @Si-B25 electrodes. The specific surface area of each electrode was calculated from the measured isotherms using the Multi-point Brunauer–Emmett–Teller (MBET) theory (Figures S10 and S11, Supporting Information). As a control, N_2 physisorption measurements were also performed on the bare copper current collector (i.e., without a composite electrode), confirming, as expected, negligible porosity and minimal surface area (Figure S12, Supporting Information). The table in Figure 5 shows surprisingly strong agreement between the measured and calculated theoretical surface area (assuming isolated spheres). However, we estimate an error margin of up to 20%, as the measured electrode area – used to calculate the electrode mass in these physisorption experiments – was subject to variability, and the actual electrode surface area is less than our calculation.^[45]

To quantify the pore volume and pore size, we model the adsorption isotherms with non-local density functional theory (NLDFT, see Experimental section for details). Plots of the isotherms, pore size distribution, NLDFT fit to the sorption data, and T-tests are also provided in the Figures S10 and S11 (Supporting Information). The results show that the surface area extracted from NLDFT is similar to the MBET measurements for both Si-B0 and Li_2CO_3 @Si-B25. This agreement gives us confidence that the interpretation of the NLDFT model is valid. The porosities of Si-B0 and Li_2CO_3 @Si-B25 are 44% and 27%, respectively, suggesting that total pore volume does not limit ion or mass transport. However, the average pore diameters of 3.8 and 5.3 nm for Si-B0 and Li_2CO_3 @Si-B25, respectively, present a significant challenge for mass and ion transport within the electrode voids. A solvated Li-ion in ethylene carbonate (EC), with, depending on its solvation structure,^[49–51] a diameter of ≈ 1 nm, would face restricted movement given that the largest interparticle pore volumes are only 3–4 times larger. The voids at the contact points between NPs are likely smaller than 1 nm. Evidence of this mass transport limitation can be seen in the



Particle Size	Theoretical Surface area	Surface area from BET	Surface area from NLDFT	Porosity (%) from NLDFT	Pore size from NLDFT
Si-B0 (6 nm diameter)	429 m ² g ⁻¹	430 m ² g ⁻¹	306 m ² g ⁻¹	44%	3.8 nm
Si-B25 (12 nm diameter)	275 m ² g ⁻¹	161 m ² g ⁻¹	138 m ² g ⁻¹	27%	5.3 nm

Figure 5. MacMullin numbers (N_M) of the varied boron-content composite anodes measured from the ion-blocking method. The table includes surface area and porosity, both theoretical and measured from nitrogen physisorption.

desorption branch of both electrode isotherms. The steep desorption between relative pressures 0.4 and 0.5 P/P_0 indicates cavitation – a phenomenon induced by pore necks on the order of the N_2 size. In agreement, SEM images of these electrodes (Figures S13 and S14, Supporting Information) with a resolution of <50 nm display a dense brick-like structure with no clear pore morphology, indicating that the pore sizes are well below the resolution limit. These small pore sizes, therefore, inhibit electrolyte permeation throughout the electrode volume, and full electrode wetting is likely inhomogeneous and incomplete.

The combined findings from electrochemical and physisorption measurements suggest that ion transport is predominantly constrained by the small pore sizes in the electrodes. Moreover, as complete electrolyte wetting is improbable across all samples, the primary mass transport mechanism shifts to solid-state lithium diffusion through silicon. Thus, while the electrodes are highly tortuous for liquid phase ion transport, this property is consistent across samples and does not explain the variations in electrochemical performance.

To understand how boron impacts the solid-state Li-ion diffusion – the dominant mode of mass transport – we quantify the solid-state diffusivity in these Si-B anodes with Galvanostatic intermittent titration test (GITT) measurements in a half-cell configuration.^[52] The results are presented in Figure 6. The protocol consists of a short-duration constant current pulse of low

magnitude followed by a sufficiently long rest for electrode equilibration, applied in a repetitive fashion between the cell operating voltage window (Figure 6a). A description of the diffusion coefficient calculation and other relevant details is provided in Section S2 (Supporting Information) and associated Figures S15 and S16 (Supporting Information).

Figure 6b,c plots the lithium-ion diffusivity during the lithiation and delithiation half-cycles, respectively, as functions of the state of charge (SOC). The GITT measurements show that lithium diffusivity during lithiation is up to 10 times slower than delithiation diffusivity, consistent with previous studies.^[53,54] While a reduction in lithium diffusivity might be expected for Si-B nanoparticle alloys due to lattice contraction from shorter Si–B bonds compared to Si–Si bonds (1.92 vs 2.23 Å, respectively),^[55] the diffusivity values for lithiation and delithiation are nearly identical across all materials, except for minor deviations in the mid-SOC range in B-containing silicon. These results are consistent with previous reports, albeit at much lower boron concentrations.^[56] Given the challenges of performing GITT on compact electrodes (discussed further in Supporting Information), we consider these differences to fall within the uncertainty of our analysis. Thus, the presence of boron in silicon does not appear to significantly impact solid-state lithium-ion diffusivity. This suggests that intraparticle diffusion is not the rate-determining step; rather, interparticle lithium-ion transfer across

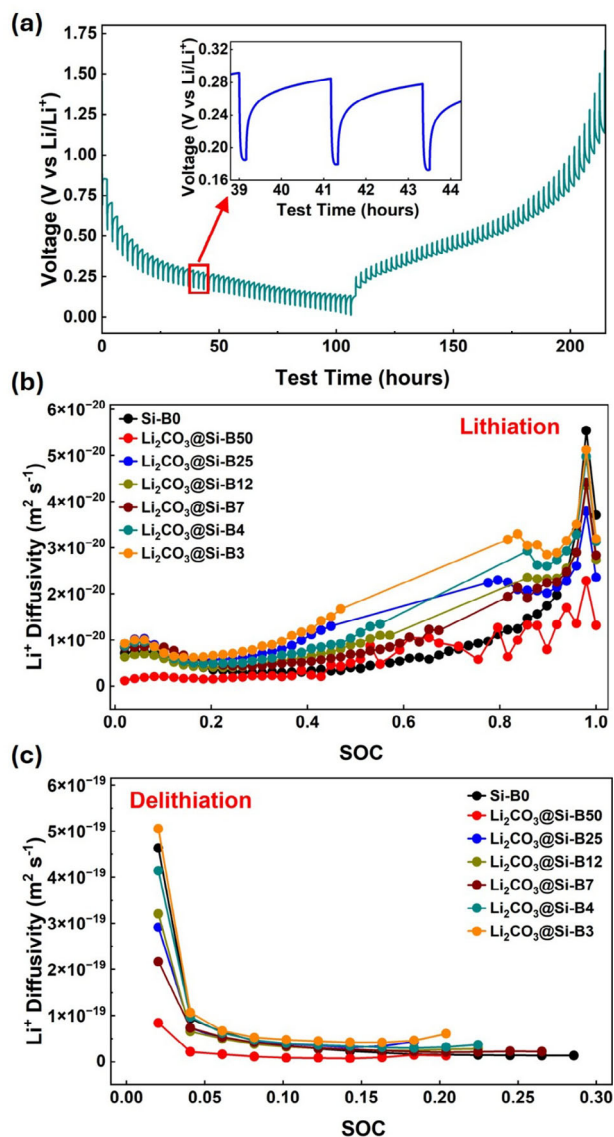


Figure 6. a) Full GITT voltage profile of Si-B50 anode (inset shows magnified view of the charge/discharge profiles during current pulses and rest periods). State-of-charge (SOC) versus Lithium-ion diffusivity of all the Si/Si-B electrodes during: b) Lithiation and c) Delithiation.

particle interfaces within the dense, brick-like monolithic electrode structure is the likely reason for identical diffusivities across all samples.

These measurements enable us to eliminate certain performance enhancement mechanisms. Specifically, we can rule out conductivity differences as the dominant mechanism: the lithium-ion transport mechanism is concentration gradient-driven solid-state diffusion, not conductivity-driven processes. Moreover, small amounts of boron (<12%) in Si-B result in decreased Coulombic efficiency compared to pure Si, further supporting that electrical conductivity is not the dominant factor. Similarly, since N_M is extremely high in all Si-B anodes and solid-state diffusion is the dominant mass transport mechanism, differences in particle dispersion are unlikely to account for perfor-

mance variations. Indeed, the electrode microstructure is likely not different enough between these anodes to affect any significant performance characteristics.

2.2.2. Material Interface Characterization

As is often the case, the passivity of the material interface and/or the strained SEI mechanics of growth, fracture, and regrowth during continuous cycling are at the center of the enhanced battery performance with Si-B alloy NPs. To isolate the effects of interfacial reactivity on electrolyte degradation from volumetric changes during cycling, we perform a calendar aging experiment. These experiments attribute capacity loss and impedance growth predominantly to the reactivity of Li_xSi interfaces, as volumetric changes occur only during the reference performance tests (RPT). Our calendar aging experiments are performed in single-layer pouch cells under reduced electrolyte conditions, where the electrolyte volume is four times the total pore volume of the battery.

The anodes are paired with initially oversized cathodes (NMC811 or LFP) and preconditioned by electrochemically cycling the cells three times to form an SEI over a full cell voltage range 3.0–4.2 V (NMC811) or 2.7–3.44 V (LFP). Following initial formation cycles, the $n:p$ ratio adjusts due to initial losses, resulting in cathode-limited cells with an $n:p$ ratio of $\approx 1.2:1$. The pouch cells are then degassed, resealed, and subjected to aging protocols as described in a recent project review meeting presentation and based on the United States Advanced Battery Consortium (US-ABC) calendar aging test.^[57]

During aging, the cells rest for 30 days at the top-of-charge under open-circuit conditions at 30 °C. To maintain a consistent state of charge, we apply daily “top-off” pulses. After the 30-day rest, an RPT is conducted, including three full cycles to measure capacity and HPPC tests to evaluate the ASI. This process repeats until the cells reach less than 80% of their initial capacity, at which point they are deemed to have reached the EOL. The voltage profile of an example of the aging protocol is illustrated in Figure 7a.

Figure 7b shows the average capacity retention as a percent of the initial capacity for Si-B0||NMC811 and Li_2CO_3 @Si-B50||NMC811 from monthly RPTs (only one set of triplicate single-layer pouch cells for Si-B50 anodes was measured due to resource constraints). The areal capacity at the beginning of life is $\approx 1.5 \text{ mAh cm}^{-2}$ for both Si-B0||NMC811 and Li_2CO_3 @Si-B50||NMC811 after the initial formation and degassing steps. Once these electrodes begin aging, however, there is a clear difference between them; the Li_2CO_3 @Si-B50||NMC811 retains much more capacity than Si-B0||NMC811 throughout the duration of the measurement. While neither crosses the 80% EOL threshold in the duration of the measurement, by month 14, Si-B0||NMC811 is at 83% while Li_2CO_3 @Si-B50||NMC811 is at 90%.

To extrapolate the calendar lifetime for each set of cells, we fit our capacity data to Equation (3).

$$C_n = C_0 - mt^p \quad (3)$$

where C_n is the capacity at time, t , and m and p are the slope and power, respectively. For our fitting, m and p are floating

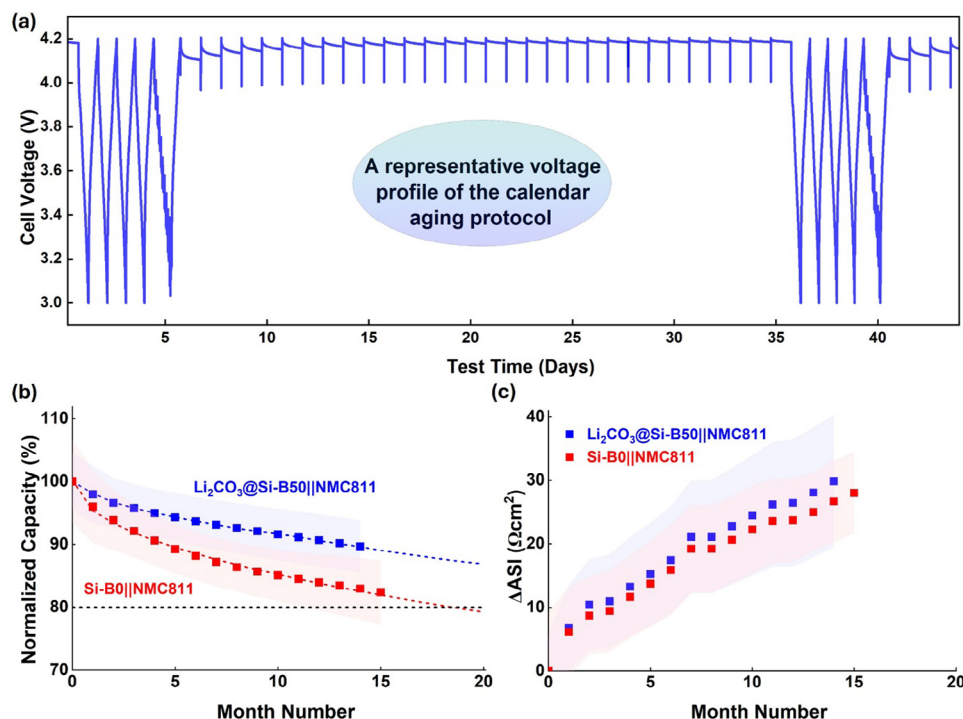


Figure 7. a) Voltage profile of the calendar aging protocol for $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$ in GenF3 electrolyte. b) Normalized average capacity retention over the period of 15 months as measured by reference performance tests. These values are the average of three independent pouch cell triplicates. The shadow region is $\pm 1\sigma$ from the mean value. The dashed lines are power functions fit to the data. c) Area-specific impedance for each of the reference performance tests calculated from the HPPC measurements. The error bars are $\pm 1\sigma$ from the mean value.

parameters. Capacity retention during calendar aging has broadly been observed to follow a square root dependence on time.^[58–65] As a free-floating parameter for fitting these data, $p = 0.55$ for $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$ and $p = 0.48$ for $\text{Si-B0} || \text{NMC811}$, indicating that the capacity retention in these electrodes does appear to follow the same square root dependence on time. From these fits, we project that $\text{Si-B0} || \text{NMC811}$ will have a calendar lifetime of 17.5 months (which is visible from the fit line crossing the 80% threshold line in Figure 7b), and $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$ will have a lifetime of 44 months. While we do not place high confidence in the absolute value of these projections (especially for $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$ with a much longer lifetime than the measured data), the differences between the two anodes are clear; $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$ has a significantly longer calendar life than $\text{Si-B0} || \text{NMC811}$. When these experiments are performed with lithium iron phosphate (LFP) cathodes instead of NMC811, we find similar results; capacity retention in $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{LFP}$ is higher than $\text{Si-B0} || \text{LFP}$ (see Section S3 (Supporting Information), Figures S17 and S18 (Supporting Information), and associated discussion for details). These findings indicate that the $\text{Li}_2\text{CO}_3 @ \text{Si-B50}$ interface is significantly more passivated than the Si-B0 interface, as these measurements reflect the only reactivity of the active material at the top of charge (TOC).

In an attempt to understand how power is affected during calendar aging, we show ΔASI over time in Figure 7c, where ΔASI is the difference between month 0 and the n^{th} month. From Figure 7c, ΔASI is nearly equal for both $\text{Si-B0} || \text{NMC811}$ and $\text{Li}_2\text{CO}_3 @ \text{Si-B50} || \text{NMC811}$, suggesting that the power loss over

time may not originate from the same mechanism that impacts capacity retention. However, we note that power loss derives not solely from an increase in the SEI resistance, but also loss of electrolyte components like solvent and anions and increasing cathode resistance. While we calculated the electrolyte volume to be relatively minimal, those calculations are based on the total pore volume of the anode (in addition to the separator and cathode pore volume). As we show above, it appears that electrolyte may not penetrate into the anode volume, which would manifest in these experiments as extra electrolyte. Thus, the nearly identical ΔASI values we observe in these experiments may not truly reflect power loss in minimal electrolyte conditions and may instead arise from impedance gain at other parts of the battery, such as the cathode.^[66] A more rigorous study on the relationship between electrolyte volume and our silicon-based anodes is necessary.

To understand how the environment at the Si-B0 and $\text{Li}_2\text{CO}_3 @ \text{Si-B}$ interfaces differs, we quantify the electrical double layer capacitance (EDLC). In the classical Guoy–Chapman–Stern–Grahame picture of electrode interfaces, the EDLC is composed of four distinct layers: the inner Helmholtz plane (adsorbed ions), the outer layer (partially desolvated ions), the diffuse layer (solvated ions in an electrostatic field), and the bulk electrolyte. The EDLC reflects the local ionic structure and ion density in the Helmholtz and diffuse layer at the active material interface. Because boron creates such a large dipole at the Si-B interface, we hypothesize that the EDLC, and thus the density of ions, increases with increasing boron content. To probe this hypothesis, we performed cyclic

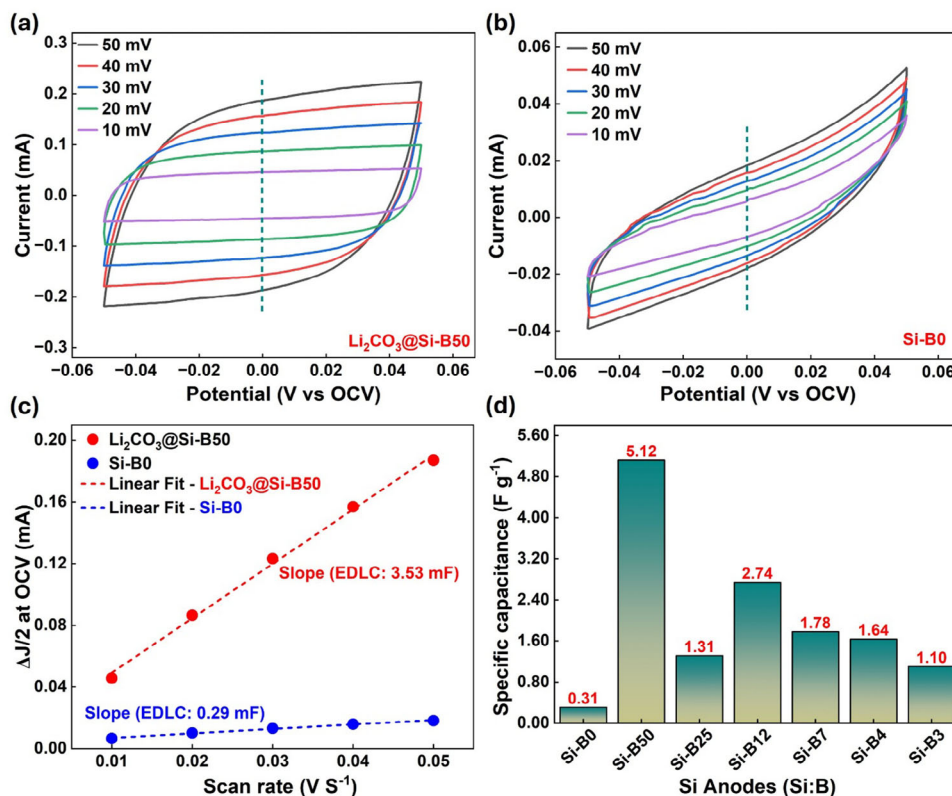


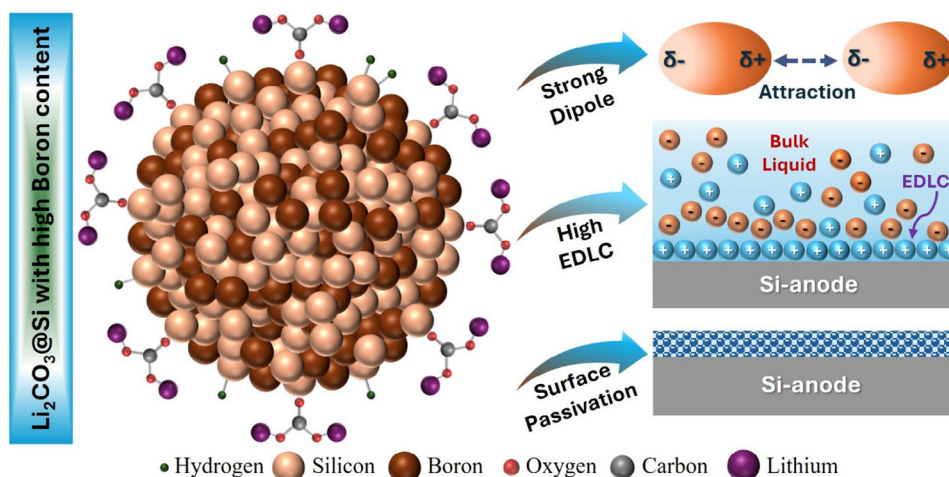
Figure 8. a) Cyclic voltammetry curves for the $\text{Li}_2\text{CO}_3@\text{Si-B50}$ anode at different scan rates within the voltage range of -0.05 – 0.05 V (vs OCV), b) Cyclic voltammetry curves for the Si-B0 anode at different scan rates within the voltage range of -0.05 – 0.05 V (vs OCV), c) Corresponding currents of $\text{Li}_2\text{CO}_3@\text{Si-B50}$ and Si-B0 at open circuit voltages as a function of the scan rate, and d) a comparative summary of the mass normalized EDLCs of all the anodes. All electrochemical data in the figure were conducted under ion-blocking electrolyte conditions with 0.5 M TBAPF₆ in Acetonitrile.

voltammetry (CV) measurements in a non-Faradaic region with a 100 mV voltage window centered on the open-circuit potential (V_{OC}). These measurements were performed on uncycled composite anodes in a three-electrode cell configuration under ion-blocking conditions as described above. The data is displayed in Figure 8.^[47]

From Figure 8a, the shape of the CVs of $\text{Li}_2\text{CO}_3@\text{Si-B50}$ is a fairly symmetric rectangle with no features located in the voltage window. The CVs of Si-B0 (Figure 8b) similarly contain no redox features in the scan window, but the CV shape is clearly not symmetric (for reference, CV curves for the remaining Si-B NP anodes are given in Figure S19, Supporting Information). The shape of these CVs is indicative of the uniformity of the EDLC. A planar electrode with a homogeneous surface (an ideal polarizable electrode) has a perfectly symmetric rectangular shape for CVs in a non-Faradaic voltage range. In the ideal case, the only time-dependent process is the charging and discharging of the double layer. A nonsymmetric CV indicates that the EDLC has a distribution of time constants. In the absence of redox chemistry, this distribution is mass or ion transport, which indicates a non-uniform or dynamic surface. Such asymmetries are common in very rough, inhomogeneous electrodes. Here, the difference in CV shape clearly indicates that the chemical environment of the $\text{Li}_2\text{CO}_3@\text{Si-B50}$ electrode has a complete and homogeneous distribution of ions at the surface, and the Si-B0 does not.

To quantify the EDLC, we plot half of the difference in current between forward and reverse voltage sweeps ($\Delta J/2$) at $V = 0$ against the scan rate (Figure 8c). Mass-normalized EDLCs were derived from the slopes of these plots and are plotted in Figure 8d.^[48] This method is described in detail elsewhere.^[67–69] The data in Figure 8d shows an obvious dependence of the EDLC on boron content; as the boron content in silicon increases, so too does the EDLC where the highest boron content silicon electrode is 16 times larger than the pure silicon with the lowest EDLC at 5.12 and 0.31 F g^{-1} , respectively. With the exception of the $\text{Li}_2\text{CO}_3@\text{Si-B25}$ electrode, the EDLC reliably tracks the boron content.

From our morphology analysis, we conclude that the pore sizes of the electrodes are too small for the electrolyte to penetrate into the bulk electrode. This limitation applies to both pure Si and Si-B alloy electrodes, meaning that electrolyte ions interact only with the electrode's geometric surface. We note, however, that because the boron-containing silicon electrodes also have Li_2CO_3 at their interface, it is possible that Li_2CO_3 contributes to the EDLC capacities where pure Si electrodes only contain the blocking TBA⁺ cation. This is an unlikely possibility as the Li_2CO_3 is not solvated and therefore will not have double layer capacitance (Li_2CO_3 will behave as a static dielectric in this case), but as an extra precaution, we performed these same EDLC measurements for pure Si with a supporting electrolyte of 0.5 M LiPF₆ (Figure S20, Supporting Information). From this measurement, the EDLC is within



Scheme 1. Illustration of a silicon-boron alloy material with a strong permanent dipole. This dipole forms an ion-dense layer between the active material and the electrolyte, which passivates the active material surface.

the error of the measurement of the TBAPF₆ electrolyte at 0.26 and 0.29 mF, respectively, which indicates that the simple presence of Li⁺ in the electrolyte does not increase the EDLC to the same degree as Si-B electrodes. Indeed, the increased EDLC is the result of a strong dipole, a material property of the Si-B nanoparticles.

Our mechanistic analyses reveal that the surface of Li₂CO₃@Si-B50 is more effectively passivated than that of pure silicon, with this enhanced passivation being the primary driver for the improved longevity of Si-B alloy anodes. We hypothesize that this superior passivation arises from the static ionic surface created by the strong surface dipole of Si-B alloys, as illustrated in **Scheme 1**. This ion-rich interface acts as both a physical and electrostatic barrier, shielding the reactive Li_xSi interface from the bulk electrolyte. From our EDLC measurements, we observe that the surface of Li₂CO₃@Si-B alloy anodes becomes increasingly ion-dense with higher boron content. This behavior mimics the function of an SEI passivating the surface across all SOC. The critical distinction between EDLC-derived passivation and the classical SEI on pure silicon lies in their static versus dynamic nature. In Li₂CO₃@Si-B, the surface dipole is an inherent material property, remaining constant regardless of SOC. By contrast, the SEI on pure silicon is highly dynamic, with its composition and structure varying significantly with SOC. These SEI dynamics, well-documented through various techniques,^[70–75] are known to affect cell performance. In the case of Si-B alloys, the ion-dense SEI mitigates such dynamics, as the interfacial Si-B dipole remains unchanged across all SOC. This stability underpins the improved passivation observed in Si-B nanoparticle-derived composite anodes and is key to their enhanced performance and cycle life.

3. Conclusion

In conclusion, we successfully synthesized silicon-boron alloy nanoparticles with varying Si:B ratios using plasma-enhanced chemical vapor deposition. The nanoparticles were surface-

functionalized with Li₂CO₃ by immersing them in an N-methyl-2-pyrrolidone-based electrolyte solution containing Li₂CO₃. This suspension was then used to prepare slurries for printing composite anodes, which were integrated into Li-ion batteries. Our results demonstrate a nearly monotonic relationship between the Si:B ratio and electrochemical cycling performance, with higher boron-content anodes exhibiting improved cycle lifetimes. These findings suggest the existence of an optimal Si:B alloy composition that balances gravimetric capacity with enhanced cycle life. Identifying this optimum, as well as understanding the LIB parameter space (i.e., electrolytes, cathodes, etc.) will be the topic of future communications.

To identify the origin of the improved cycle performance, we conducted a mechanistic analysis, systematically ruling out potential contributing factors. Our investigation showed that the morphology of all electrodes is densely packed with very small pore sizes (<5 nm). Based on this, we conclude that the electroactive surface area is predominantly limited to the geometric electrode surface, and electrode architecture is not the primary mechanism driving the performance enhancement. To explore differences in interfacial passivation, we performed a long-term calendar aging experiment using single-layer pouch cells with triplicate samples. The results demonstrate significantly improved capacity retention in Li₂CO₃@Si-B50 anodes compared to pure Si anodes, with an extrapolated calendar lifetime nearly three times longer for the Si-B alloy. These findings reveal that the enhanced performance of Si-B alloys originates from increased surface passivation, rather than being merely an effect of reduced volumetric changes during cycling. Finally, we demonstrate a clear scaling relationship between the EDLC and the boron content in Si-B nanoparticles. We reason that the origin of the improved passivity in Li₂CO₃@Si-B50 is the result of this ion-dense interfacial layer and its static nature across all SOC. If indeed this is the case, the design principles derived from addressing static versus dynamic SEIs extend to all interfaces (not just LIBs) that have some version of an SEI. Having identified this unique passivation mechanism, future efforts will be put forward to identify an optimal

composition of Si-B that balances the stability gain from boron inclusion with the loss in capacity from reduced silicon content.

4. Experimental Section

Radio Frequency Nonthermal Plasma Synthesis of Hydride-Terminated Si-B NPs: Si-B NPs with particle sizes ≈ 6.5 –14 nm (measured by X-ray diffraction and Scherrer analysis) were produced by a nonthermal plasma method using a capacitively coupled 13.56 MHz RF plasma. Process gas parameters are listed in Table S1 (Supporting Information), which were flowed through a 25 mm OD and 19 mm ID quartz reactor tube. The 250 W power was supplied to the electrode using an Advanced Energy Cesar 136 generator through an Advanced Energy VM1000 matching network. Si-B nanoparticles were collected downstream from the plasma on a 400-mesh stainless steel filter and transferred air-free to an inert-atmosphere glovebox for subsequent processing. Note that the air oxidation of B-Si nanoparticles generates highly toxic B_2H_6 gas and requires proper handling. Pure silicon NPs (Si-B0) were synthesized through the PECVD process as well. The details of which are described in the prior work.^[43]

Electrode Slurry Preparation: $Li_2CO_3@Si-BX$: 40 mg SWCNTs-COOH (purchased from Cheap Tubes) were dispersed in 3 mL NMP and sonicated for 30 min. Next, 20 mg lithium carbonate was added to the solution, followed by vortex mixing. Sequentially, 290 mg Si-BX NPs were added, and the solution was stirred on a hot plate at room temperature for 1 h. Finally, 20 mg of Ensinger polyimide P84 binder was added to the mixture, and the resultant slurry was left magnetically stirred at room temperature overnight. The slurry was then carefully sealed inside the glovebox and brought out for planetary mixing using a dual-axis Kurabo KK-250s. Pure silicon slurry preparation has been described elsewhere.^[43] Briefly, silicon nanoparticles with diethylene oxide (PEO) covalently bound to the surface as the silicon source material were used. The PEO provides colloidal stability to the Si to enable a homogeneous slurry. The silicon nanoparticles are suspended in NMP followed by the addition of SWCNT and then a PI/NMP solution. The slurry was magnetically stirred 16 h in an Ar atmosphere.

Anode Fabrication: Anodes were fabricated in an inert Ar-filled glovebox. After the completion of several slurry mixing steps, the slurry was blade casted onto a copper foil current collector using a step height of 250 μm at a speed of 1 cm s^{-1} . The electrodes were first dried at 150 °C for 4 h under a low-pressure vacuum and annealed thereafter at 450 °C for 4 h in a quartz tube furnace under flowing N_2 . For the pure silicon electrodes, the PEO volatilizes above 350 °C, which leaves a silicon surface with a native oxide layer.^[43]

Coin Cell Fabrication: Si NP composite anodes were tested using 2032-coin cells. Composite anodes were initially formed in a half-cell arrangement against Li metal foil and subsequently disassembled and reassembled into a full configuration against capacity matching NMC811. The fully prelithiated Si anodes were assembled into full cell against the 14 mm diameter punch of lithium nickel manganese cobalt oxide (NMC811) cathodes, which were provided by the CAMP facility at Argonne National Laboratory. Coin cells were assembled by attaching each electrode to a 16 mm diameter, 1 mm thick stainless-steel spacer with a stainless-steel wave spring positioned behind it. The electrodes were separated by a 19 mm diameter circular punch of porous polypropylene separator (Celgard 2325). Each coin cell was injected with 2 aliquots of 20 μL GenF electrolyte (1.2 M $LiPF_6$ in 3:7 ethylene carbonate:ethylmethyl carbonate with 3 wt% fluoroethylene carbonate by weight) onto either side of the separator before cells were sealed with a hydraulic crimper. The full cells were cycled between 3.0 and 4.2 V for 1000 cycles with 10 hybrid pulse power characterization (HPPC) cycles every 100 cycles. The HPPC technique was performed to evaluate the area-specific impedance (ASI) as a function of state of charge (SOC), measured at 10% intervals. The procedure pulsed the current in discharge for 10 s, followed by a pause to allow the voltage to relax. The current pulse in charge was 75% of the discharge in the next step. The discharge ASI is determined by dividing the discharge pulse voltage by the applied current.

CV and EIS: Electrical double layer capacitance (EDLC) of the electrodes was estimated by measuring cyclic voltammetry (CV) using a Biologic VMP3 potentiostat. CV measurements were performed in a three-electrode cell configuration against a stainless steel reference and counter electrode. The voltage range was set to scan from -0.05 to 0.05 V (vs OCV), and the electrolyte used was 0.5 M TBAPF₆ in acetonitrile (ACN) to avoid lithiation/delithiation during the CV measurements. A symmetric cell was fabricated using two equivalent Si/Si-B electrodes to measure electrochemical impedance spectroscopy (EIS). EIS was measured using a Biologic VMP3 potentiostat over the frequency range of 100 mHz–400 kHz at the open circuit voltage with an alternate amplitude of 10 mV. The sloping line in the most magnified Nyquist plot was fitted for x-axis intercept to evaluate R_{ion} to further determine tortuosity (τ) and MacMullin numbers (N_M).

Materials Characterization—STEM/EELS: Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) were performed on a monochromated FEI Titan TEM with a probe aberration corrector and a Gatan Image Filter (Quantum Spectrometer). For the STEM images, the electron dose rate was $\approx 4.5 \times 10^7 - 2 \times 10^8 e\text{\AA}^{-2} s^{-1}$. For EELS measurements, the Si $L_{2,3}$ -edge and the B K-edge were measured with a dispersion of 0.1 eV ch^{-1} , an energy resolution of ≈ 1 eV, a pixel size of 0.3 nm, an exposure time of 10 ms, and a collection semi-angle of 44 mrad. The Si, SiO₂, and B EELS maps were calculated from a model using Gatan Digital Micrograph software. The model used a power law background and was corrected for plural scattering. The cross-section model used Hartree-Slater for boron and standard reference spectra for Si and SiO₂.

Materials Characterization—ICP-OES: Inductively coupled plasma – optical emission spectroscopy (ICP-OES) (Thermo Scientific iCAP 7400 ICP-OES Duo) was performed to quantitatively characterize the Si:B ratio. Briefly, samples were weighed out in an argon-filled glove box to avoid spontaneous ignition in air. Samples were removed from the glove box and immediately quenched by adding 18 M Ω DI water, followed by 2 mL of nitric acid (Fisher Chemical, Trace metal grade) to oxidize the silicon nanoparticles. Approximately 2 mL of 5% hydrofluoric acid (diluted from concentrated HF solution – Sigma Aldrich, Trace metal) was added and allowed to complete the dissolution of the B-Si sample. Unreacted HF was observed to skew the silicon signal from etching the glass nebulizer of the HF. The error was estimated to increase the silicon content by 20 ppm, which was accounted for in the data analysis.

Porosity Measurements: Porosity measurements were carried out on a Quantachrome QuadraSorb station. For these measurements, 1" x 6" electrode strips were carefully cut from the prepared electrode. The mass of the electrode material was quantified based on the mass measurements of the prepared sample and subtraction of the copper mass. The total mass for each measurement was set to at least 20 mg of silicon, resulting in total surface areas of $>3 m^2$. The Cu strips were then rolled into a $\frac{1}{2}$ " length to fit inside a measurement tube. The sample in the tube was degassed for 24 h at 100 mTorr and 200 °C. N_2 physisorption measurements were carried out at 77.4 K at various partial pressures (P/P_0) with an equilibration time of 300 s and an equilibration timeout of 900 s. The sorption data were analyzed in two ways. First, the BET surface area was calculated. Next, the data were modeled from NLDFT using an N_2 /silica absorption branch kernel at 77 K based on a cylindrical pore model. The MBET, raw isotherm, NLDFT fit, and pore size histogram are shown in Table S3 (Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from corresponding author upon reasonable request.

Keywords

calendar aging, cycle life, energy storage, lithium-ion battery, nanoparticle alloys, silicon anodes

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