

RESEARCH ARTICLE

Chain-Networked Micro-Silicon Electrodes Inducing Internal Isostatic Compressive Stress for High-Energy and High-Power Solid-State Batteries

 Seokjin Kim¹ | Kiran Raj^{2,3} | Weijiang Xue⁴  | Hyoung Jun Lim²  | Ju Li⁵  | Jaekyung Sung¹ 

¹Department of Materials Engineering and Convergence Technology, Gyeongsang National University, Jinju, Republic of Korea | ²School of Mechanical and Aerospace Engineering, Gyeongsang National University, Jinju, Republic of Korea | ³Department of Mechanical Engineering, Sree Buddha College of Engineering, Alappuzha, Kerala, India | ⁴State Key Laboratory For Mechanical Behavior of Materials, Center For Advancing Materials Performance from the Nanoscale (CAMP-Nano), Xi'an Jiaotong University, Xi'an, China | ⁵Department of Nuclear Science and Engineering and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

Correspondence: Hyoung Jun Lim (hj.lim@gnu.ac.kr) | Ju Li (liju@mit.edu) | Jaekyung Sung (juzhang@wiley.com)

Received: 9 July 2026 | **Revised:** 11 September 2026 | **Accepted:** 18 September 2026

Keywords: anode | carbon black | carbon nanotube | cathode | electrode | energy storage | materials science | nanotechnology | power density

ABSTRACT

Micron-sized silicon (μ -Si) offers a scalable pathway to high-capacity anodes, and its application in solid-electrolyte-free systems has garnered attention as a strategy to maximize energy density. However, achieving both high energy and power densities in such configurations remains challenging due to the lack of internal ionic conduction pathways and stress-accommodation mechanisms. Here, we report a Chain-based Networking (CN)-Si electrode architecture that overcomes these limitations and maximizes energy and power densities without incorporating solid electrolytes within the electrode. In this design, μ -Si particles are tightly wrapped and interconnected by single-walled carbon nanotubes (CNTs), forming a mechanically robust conductive network. The CNT wrapping imposes compressive stress during lithiation, distributing internal strain and preventing crack and void formation, mimicking the stress-dissipation principle of Prince Rupert's drop. As a result, the CN-Si electrode delivers superior electrochemical performance, with 78% capacity retention at 3C, significantly outperforming conventional Si electrodes using polymer or carbon black binders. In full-cell configurations with $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NCM811) cathodes, the CN-Si electrode retains 78.8% capacity after 3000 cycles at a high C-rate (5C). These findings demonstrate that stress-engineered micro-Si architectures can simultaneously overcome kinetic limitations and maximize both energy and power densities in solid-state battery systems, advancing practical high-performance All-Solid-State Batteries (ASSBs).

1 | Introduction

As the demand for electric vehicles and energy storage systems continues to rise, the development of Li-ion batteries (LIBs) with high energy density and enhanced safety has become increasingly critical [1–3]. All-solid-state batteries (ASSBs) are gaining attention as a promising solution, primarily because the thermal and mechanical stability of solid electrolytes not only

enables the use of high-capacity anode materials (such as Si and Li) but also suppresses the risk of battery explosion [4–7]. In particular, Si anode exhibits several advantages, including a high theoretical capacity (3579 mAh g^{-1}), natural abundance, low raw material cost, and a low electrochemical potential (0.4 V vs. Li/Li^+) [8–11]. In the ASSBs system, Si anodes demonstrate intrinsically high chemical and thermodynamic stability with solid electrolyte and they also show mechanical stability. This

All rights reserved, including rights for text and data mining and training of artificial intelligence technologies or similar technologies.

© 2026 Wiley-VCH GmbH

is because the surrounding solid electrolyte phase suppresses the volume expansion of Si anode, and the solid electrolyte interphase (SEI) forms only at the specific contact points where the solid electrolyte meets the Si [8, 9, 12–14]. This localized SEI formation is beneficial because it prevents continuous and uncontrolled growth of unstable SEI layers, leading to a reduction in the consecutive loss of Li source [15, 16]. In contrast, liquid-based electrolytes in traditional LIBs behave differently. The fluid of liquid electrolyte continuously percolates and interacts with all of the exposed surfaces derived from the cracked Si, causing continuous and unstable SEI formation. This repeated SEI growth consumes Li and damages battery performance [17–20]. Therefore, the combination of Si anodes and solid electrolytes holds tremendous potential.

In ASSBs, solid electrolytes are typically based on oxides, polymers, and sulfides [21, 22]. Among these, sulfide-based solid electrolytes are considered the most promising for practical applications due to their high ionic conductivity ($\sim 3 \text{ mS cm}^{-1}$) and excellent processability [23–25]. Because of the ductile nature of sulfide-based electrolytes, the electrode can be easily fabricated by mixing active materials with solid electrolytes and compressing them. However, the existence of solid electrolytes within the electrodes can lead to some issues: 1) The large amount ($> 30 \text{ wt\%}$) and high density of solid electrolytes in the electrodes make it challenging to achieve high energy density compared to conventional LIBs [26, 27]. 2) The high reactivity between sulfide-based solid electrolytes and conductive additives raises the irreversible capacity [25, 28, 29]. 3) A large amount of the boundary between the solid electrolyte and Si within the electrode causes the interfacial gap because of the volume expansion of Si during cycling, resulting in a severe increase in interfacial resistance [5, 30–32]. Therefore, recent research has focused on Diffusion-Dependent Si electrodes without solid electrolytes [13, 30, 33]. In this electrode system, low-cost and abundant pure micro-Si can be used, and it enables the achievement of sufficient ionic conductivity within the electrode even without solid electrolytes. Specifically, the transformation of Si into a Li-Si alloy during lithiation gives high Li-ion and electronic conductivity as is, and the soft nature of Li-Si allows the electrode to be a dense thin-film form, which minimizes interfacial contact losses [34, 35]. Moreover, the formation of SEI occurs at the interface between the solid electrolyte separator and the electrode, rather than within the electrode itself [13, 30]. Interestingly, these electrodes can achieve even higher volumetric energy density than anode-free systems (i.e. Li metal anode) (Figure 1a, b; Note. S1).

On this account, recent studies have proposed the pure Si electrodes (including low-cost micron-sized Si with a small amount of binder, etc.), which have shown significantly stable cycling performance [13, 36, 37]. However, it is noted that the vertical crack propagates within the electrode after cycling (de-lithiation state) [38–40]. This is because pre-formed Li-Si alloy contracts under stack pressure with vertically applied one-directional force, which leads to the development of high unidirectional tensile stress in the horizontal direction during delithiation. Such destroyed electrode structures cause the loss of Li-ion (dead particle) and electron pathways, resulting in the degradation of electrochemical performance. When considering the solid electrolyte free electrode, such phenomena are a more

serious situation from the viewpoint of the power density (rapid delithiation process). Rapid Li-ion extraction accelerates locally severe contraction during the Li-Si to Si phase transition, which not only reduces interfacial contact but also disrupts continuous pathways for Li-ion and electron transport within the electrode. Moreover, under such high-rate conditions, the limited diffusion kinetics of Li can lead to pronounced local Li depletion, inducing stress concentration and intensifying structural damage beyond that caused by uniform, slower delithiation [41–43]. The intrinsically low electrical conductivity of the Si ($\sim 3 \times 10^{-5} \text{ S cm}^{-1}$) aggravates the properties of the fast (dis)charging. Such poor power density could present a significant barrier to practical applications. Therefore, to achieve high-energy- and high-power-density ASSBs, there is strong motivation to propose an enhanced design that preserves the structural stability of Si in solid-electrolyte-free electrodes.

Having noted that enormous mechanical strength is achieved by the management of stress distribution (i.e., external compressive stress on the surface and tensile stress inside) in the principle of Prince Rupert's drop (Figure 1c), we considered whether a similar balance of stresses—external compression and internal tension—could serve as a mechanical reinforcement mechanism for Si anodes. In this study, we designed a Chain-based Networking (CN)-Si electrode using μ -Si, inspired by this stress-distribution concept. To realize this CN structure, carbon nanotubes (CNTs) were employed as the chain material, owing to their high mechanical strength and excellent electrical conductivity ($\sim 10^6 \text{ S cm}^{-1}$). During lithiation (charging), the CNT chains redistribute internal stress and suppress localized expansion [44], while during delithiation (discharging), the CNT confinement induces surface compressive stress and internal tensile stress, forming an internal stress configuration analogous to that of a Prince Rupert's drop. This dual-stress equilibrium enhances structural robustness and prevents crack and void formation. Furthermore, the highly conductive CNTs alleviate localized stress concentrations, promote uniform lithiation/delithiation, and facilitate efficient electron transport, thereby contributing to excellent high-rate performance. As a result, CN-Si shows a capacity retention of 78% ($\sim 2560 \text{ mAh g}^{-1}$) at 3C ($\sim 9.9 \text{ mA cm}^{-2}$) compared to the reference electrode containing polyvinylidene difluoride (PVDF) binder or styrene-butadiene rubber (SBR)/sodium carboxymethyl cellulose (CMC) binders with conductive agent (47% and 43%). The CN-Si/ $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NCM₈₁₁) full-cell exhibits strong durability in ASSBs, retaining 78.8% of its capacity after 3000 cycles at a current density of 11.5 mA cm^{-2} at room temperature.

2 | Results and Discussion

2.1 | CNT wrapping Creates a Stress-Managed CN-Si Architecture

To fabricate CN-Si electrodes, μ -Si was mixed with single-walled CNTs (material characterization is shown in Figure S1, and detailed fabrication is described in the Methods section). Two comparison electrodes were prepared to evaluate the efficacy of CNTs in forming electrically conductive and mechanically robust chain-like networks: a polymer-based Si electrode (P-Si) using PVDF binder, and a carbon and polymer-based Si

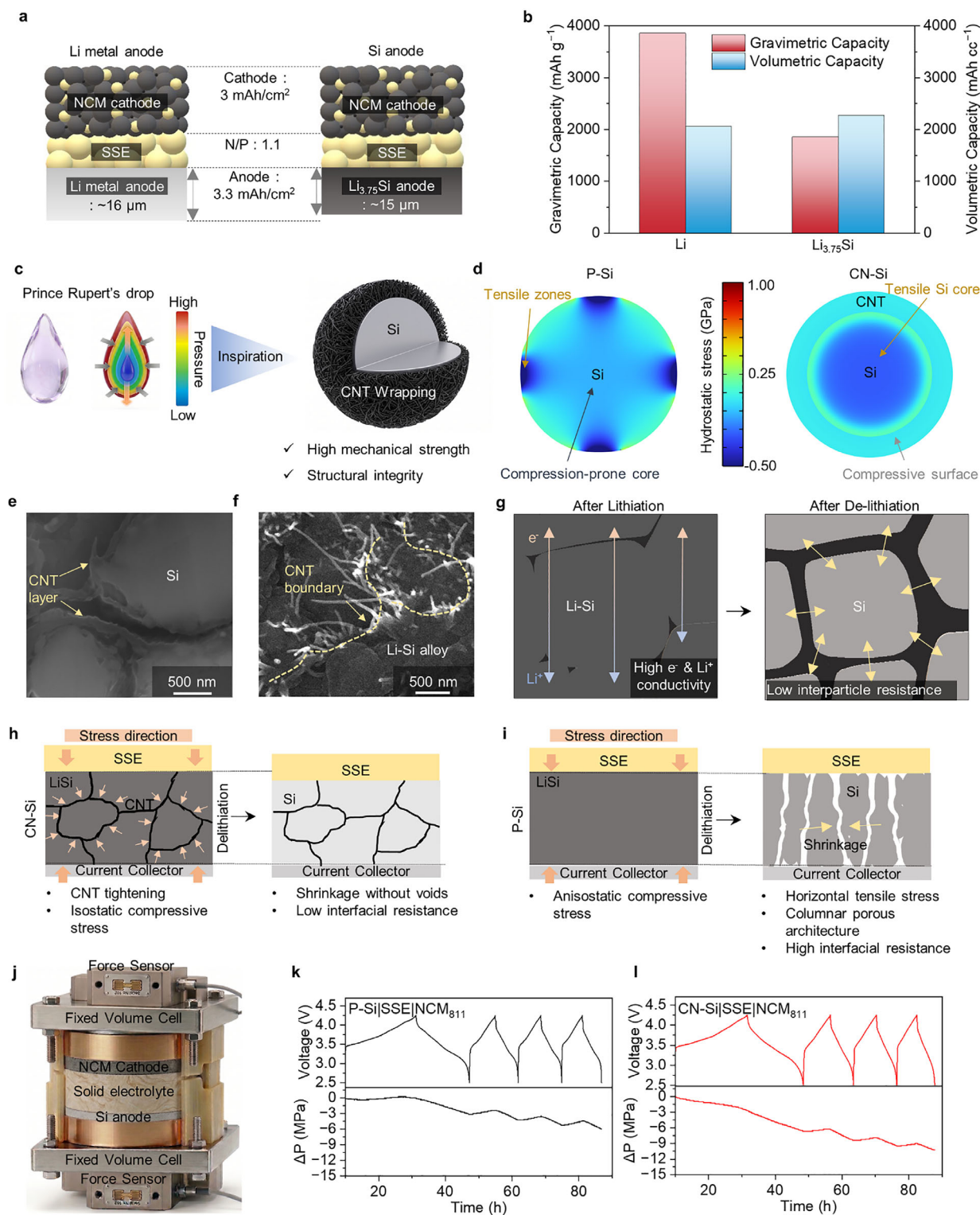


FIGURE 1 | Structural design concept and properties of the CN-Si electrode. a, Schematic comparison of full-cell configurations in ASSBs using Li metal (anode-free) and lithiated Si anodes, highlighting the cell thickness for each case at identical areal capacities. b, Gravimetric and volumetric capacities of Li metal (anode-free) and Si anodes. c, Schematic representation of the CN-Si electrode architecture, inspired by the fracture-resistant properties of Prince Rupert's drop. d, Hydrostatic stress (compression positive) during delithiation of a single-particle model for P-Si and CN-Si. e, Cross-sectional SEM image of the CN-Si electrode after fabrication. f, Top-view SEM images of the CN-Si electrode after lithiation. g, Schematic representation of the self-mitigating internal stress mechanism at the particle level in the CN-Si electrode throughout the charge–discharge process. h, i, Schematic comparison of mechanical responses of the CN-Si (h) and P-Si (i) electrodes at the electrode level during delithiation, respectively. j, Schematic image of the in situ pressure measurement system for CN-Si and P-Si electrodes during cycles. k, l, Graphs showing pressure variation during cycling for P-Si (k) and CN-Si (l) electrodes. To minimize the influence of the counter electrode pressure, full cells with NCM811 cathodes were employed.

electrode (CP-Si) using carbon black and SBR/CMC. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were conducted to examine the structure and morphology of materials within electrodes. XRD analysis confirms that Si crystal peaks were observed in all electrodes (Figure S2), but no other peaks were detected. This is because carbon and polymers exhibit amorphous structures, and single-walled CNTs have few graphene stacking layers. To investigate how stress redistribution within the CN-Si architecture—inspired by Prince Rupert's drop—contributes to mechanical reinforcement, multiphysics finite-element simulations were performed using COMSOL Multiphysics (Figure 1d). The 2D single-particle model used for this comparative simulation is illustrated in Figure S3, and further details are provided in Note S2. During delithiation, CN-Si develops a compression-dominated outer Si region while retaining tensile stress toward the particle interior. The compliant CNT layer accommodates the particle-volume change and redistributes interfacial loading, creating a Prince Rupert's-drop-inspired stress environment with a shell-core-like stress topology [45], thereby effectively suppressing mechanical degradation. Sign-resolved hydrostatic-stress analysis further supports this tensile-interior/compressive-outer-region configuration (Figure S4 and Table S8). In the cross-sectional SEM images, the fabricated CN-Si electrode shows that the Si particles are encapsulated by a bundle layer of CNTs (Figure 1e). This layer of CNTs forms a network structure within the electrode (Figures S5 and S6). After lithiation, the layer of CNTs exists as a boundary in the gap between Si particles (Figure 1f). Previous carbon-based Si anode strategies have mainly aimed to enhance electronic transport, stabilize SEI/interphase formation, or accommodate Si volume changes [12, 46, 47]. In contrast, the CN-Si electrode uses CNTs as a continuous chain-wrapping framework that goes beyond conventional conductivity enhancement or passive volume buffering by regulating stress evolution and providing a confining environment around Li-Si domains. The retained CNT boundary provides conductive pathways while maintaining this confinement after lithiation. Upon delithiation, contraction of the Li-Si domains within this confined structure can generate a shell-core-like stress environment, similar to the strengthening concept of Prince Rupert's drops (Figure 1g). At the electrode level, the structural evolution of the CN-Si electrode upon delithiation is shown in Figure 1h. Since the isostatic compressive stress derived from CNT wrapping is applied to Li-Si upon delithiation, the electrode shrinks without void formation and preserves its morphological integrity. Additionally, the structure where the CNT layer surrounds the Si particles leads to excellent electronic conductivity at both the particle and electrode levels. Such phenomena promote uniform lithiation and de-lithiation of Si particles within the electrode, preventing localized volume expansion and contraction. These mechanisms suppress the formation of cracks and voids upon cycling, maintaining high structural stability with low interfacial resistance. In contrast, the P-Si and CP-Si electrodes have a relatively weaker mechanical strength (the tensile strengths of PVDF and SBR are approximately 50 and 17.5 MPa, respectively) than that of CNTs (the tensile strength of single-walled CNTs is >100 GPa). The delithiation of Li-Si results in significant volume contraction under cell stack pressure (i.e. vertical stack pressure) without the benefit of isostatic compressive stress. This anisotropic shrinkage often leads

to the formation of a columnar porous architecture and structural discontinuities (Figure 1i). Consequently, the electrode suffers from morphological degradation, including particle pulverization and interfacial delamination, which compromise mechanical stability and electrochemical performance. It is also seen that the dot-shaped carbon structures of CP-Si are partially connected (see the cross-sectional and top view of the SEM image regarding various electrodes in Figures S5 and S6, respectively), leading to an overall non-uniform delithiation process. To substantiate this claim, we prepared a fixed-volume cell to measure the stack pressure changes that are affected by the internal stress change within the electrode derived from massive Si volume variation (The schematic diagram of the cell and the results are shown in Figure 1j, and detailed conditions are described in the Method section). During the charging process, P-Si exhibits a slight increase in stack pressure, which is attributed to the expansion of Si (Figure 1k). However, the pressure increase remains moderate, as the porous electrode (μ -Si particles with interparticle gaps as shown in Figure S5) gradually compacts into a denser structure (a Li-Si thin film as shown in Figure S7), thereby mitigating the direct transmission of expansion force into stack pressure. In contrast, the CN-Si electrode exhibits a pressure decrease, attributed to the constraining effect of CNT wrapping. As supported by the simulation in Figure 1d, this CNT-wrapped structure provides a compression-dominated stress environment during Li-Si contraction upon delithiation, thereby suppressing void formation and stabilizing the electrode structure. Notably, the CN-Si electrode maintains a substantial pressure drop (−11.4 MPa), particularly during delithiation in subsequent cycles, suggesting that volume contraction occurs without the formation of cracks or voids—likely due to the compressive environment sustained within the electrode (Figure 1h). The P-Si electrode exhibited a relatively smaller stack pressure change of −7 MPa. This is likely due to the formation of cracks and voids within its columnar structure during cycling, which limited the extent of electrode thickness contraction compared to CN-Si (Figure 1k), resulting in a less pronounced pressure decrease. It should be noted that the stack-pressure evolution in a fixed-volume cell does not directly measure internal compressive stress, but represents a cell-level chemo-mechanical response reflecting electrode structural evolution during lithiation/delithiation. Therefore, the distinct pressure responses of P-Si and CN-Si are interpreted as the macroscopic manifestation of different electrode behaviors caused by the presence or absence of CNT-mediated isostatic compressive confinement. This interpretation is consistent with the mechanism proposed in Figure 1h, as supported by first-cycle FIB-SEM observations showing thickness retention of CN-Si ($\sim 10\ \mu\text{m}$, Figure 2c) and crack formation with larger thickness in P-Si ($\sim 12\ \mu\text{m}$, Figure S10). The particle-level simulation in Figure 1d further supports CNT-mediated compression-dominated stress redistribution. This pressure behavior is also distinct from that commonly observed in conventional liquid-electrolyte LIBs. In conventional LIBs, Si-based anodes typically exhibit a continuous increase in stack pressure, primarily due to excessive SEI formation caused by the repeated exposure of Si to the liquid electrolyte. In contrast, the ASSB system described here significantly suppresses SEI formation by eliminating liquid electrolytes within the electrode, which likely contributes to a reduction or stabilization of stack pressure.

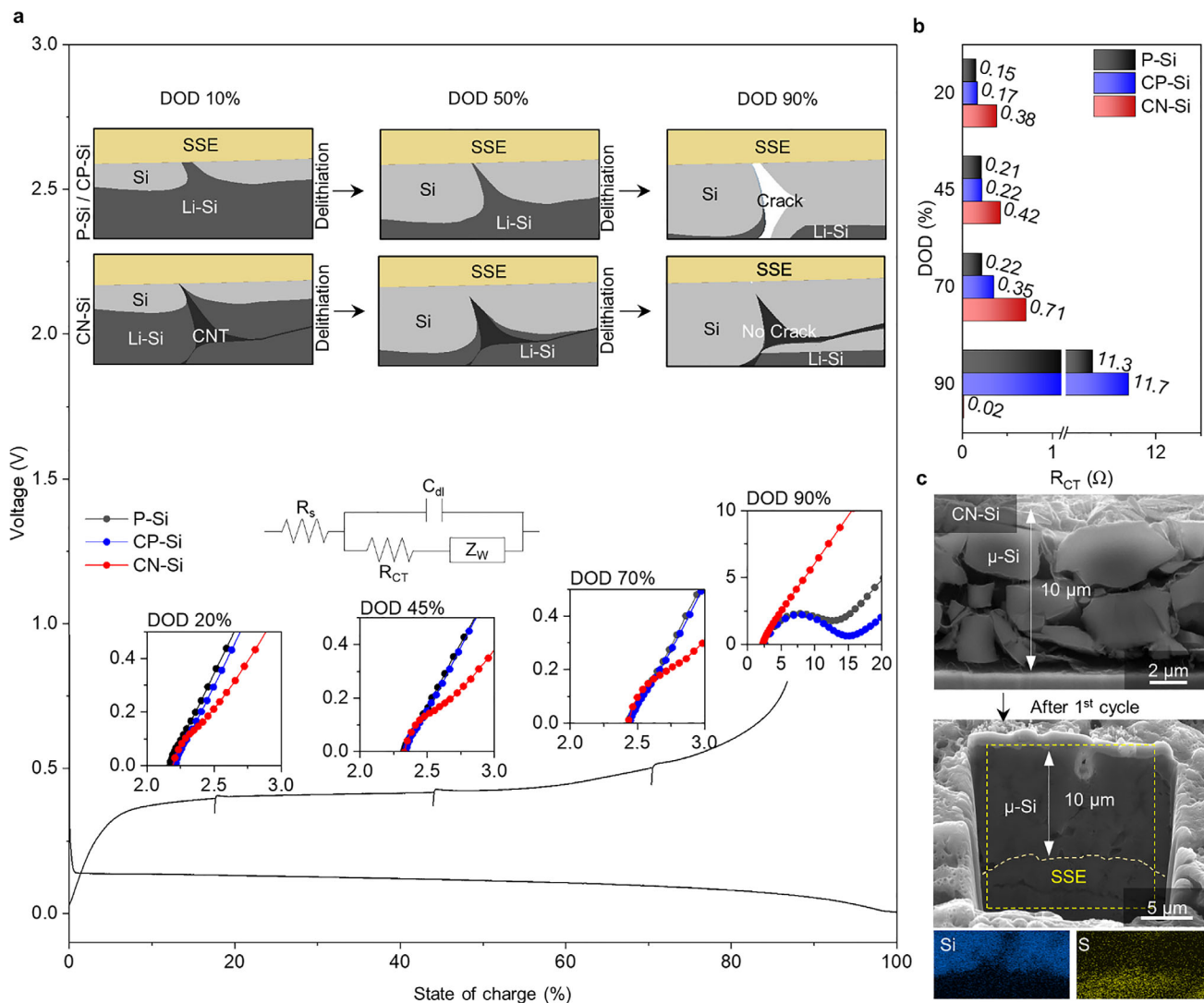


FIGURE 2 | Working mechanism of each electrode during the charging and discharging process. a, Voltage profile of each electrode with inset images showing morphological evolution at various DODs, and corresponding in situ EIS data in the high-frequency range with the fitted equivalent circuit. b, R_{CT} values of each electrode depending on DOD. c, Cross-sectional SEM and FIB-SEM/EDS images of the CN-Si electrode before and after the first cycle, showing no observable thickness change.

2.2 | CN-Si Preserves Interfacial kinetics and Structural Integrity During Delithiation

To elucidate the electrochemical behavior of each electrode, in situ Electrochemical Impedance Spectroscopy (EIS) measurements were performed at various depths of discharge (DOD) of 20%, 45%, 70%, and 90% (Figures 2a and S8). The extracted fitting parameters, including R_s , R_{CT} , and Z_w , are summarized in Table S1. P-Si and CP-Si electrodes exhibited low impedance during the early discharge stages but showed a pronounced increase in charge-transfer resistance ($R_{CT} = 11.3 \Omega$ and 11.7Ω , respectively) at 90% DOD (Figure 2b), which is attributed to Li/e^- transport loss caused by crack and void formation during delithiation. In contrast, the CN-Si electrode maintained stable impedance behavior up to 70% DOD, though with slightly higher R_{CT} than the other two. This apparent resistance arises from the intermediate CNT interlayer between adjacent Li-Si domains, which acts as an additional interfacial element in EIS and effectively facilitates uniform charge transport and

mechanical stress redistribution within the electrode. A consistent trend was observed in the corresponding Distribution of Relaxation Times (DRT) analysis (Figure S9). The DRT analysis was performed based on a regularized deconvolution approach for EIS spectra, and the peak assignments were made tentatively according to the relaxation-time ranges and their evolution with DOD (Table S2) [48, 49]. Up to 70% DOD, CN-Si exhibited higher DRT peak intensities than P-Si and CP-Si, which can be attributed to additional CNT-related interfacial responses while maintaining stable impedance evolution. At 90% DOD, however, P-Si and CP-Si displayed a dramatic rise in R_{CT} due to structural degradation, whereas CN-Si showed less pronounced interfacial resistance growth with peaks continuously shifting toward shorter relaxation times, reflecting enhanced reaction dynamics. An additional peak appeared around 10^{-7} s exclusively for P-Si, which may be associated with a high-frequency contact/interfacial response arising from structural heterogeneity and electrolyte-side microcrack formation (inset of Figure 2a). Furthermore, an SEI-related peak ($10^{-6} \sim 10^{-5}$ s range), indistinct

in earlier cycles, became prominent at 90% DOD for all electrodes, suggesting the formation or growth of decomposition-derived interphase layers at exposed Si/SSE interfaces during deep delithiation. Notably, the CN-Si electrode exhibited the smallest R_{SEI} and a uniform, left-shifted low-intensity peak profile, indicating that CNT encapsulation mitigates interphase-related resistance growth and preserves intimate electrical contact throughout cycling. To further validate these electrochemical interpretations, cross-sectional SEM and FIB-SEM analyses were performed to examine the structural evolution of the electrodes after first cycling. The CN-Si electrode exhibited no discernible change in thickness, maintaining approximately 10 μm before and after the first cycle (Figure 2c). In contrast, the P-Si electrode showed a larger thickness of approximately 12 μm with clear crack formation after the first cycle (Figure S10). This comparison supports that CNT wrapping helps preserve electrode integrity and suppress crack/void formation during Si volume change, consistent with the stress-dissipation mechanism described in Figure 1h. These observations suggest that the improved interfacial kinetics of CN-Si arise not only from enhanced electronic conductivity but also from the stress-regulation effect of the CNT chain network, which preserves electrode integrity and active reaction pathways during delithiation-induced contraction.

2.3 | CN-Si Sustains High-Rate Kinetics by Suppressing Delithiation-Induced Cracking

Based on these electrochemical analyses, we next evaluated the overall performance of the CN-Si electrode under practical half-cell conditions and compared it with that of the reference electrodes (CP-Si and P-Si). As shown in Figure 3a, the P-Si electrode exhibited the highest discharge capacity of 3563.1 mAh g^{-1} and an initial coulombic efficiency (ICE) of 91.9%. The CP-Si and CN-Si electrodes demonstrated discharge capacities of 3183.4 mAh g^{-1} and 3210.4 mAh g^{-1} , with ICE values of 87.7% and 89.3%, respectively. The slightly lower ICEs of the CP-Si and CN-Si electrodes may be associated with additional carbon-containing interfaces and increased initial polarization. For CN-Si, this ICE decrease is more likely associated with the lithiation overpotential introduced by the CNT network rather than with pronounced CNT-accelerated LPSCl decomposition. This interpretation is supported by the planar-interface control test: Cu/LPSCl exhibited a pronounced decomposition-associated voltage response above 0.8 V, whereas CNT-coated SUS/LPSCl showed a voltage profile similar to SUS/LPSCl without such a response (Figure S11). Nevertheless, the C-rate test revealed that the CN-Si electrode exhibited higher capacity retention at all rates compared to the P-Si and CP-Si electrodes (Figure 3b). Particularly at a high rate of 3C (9.9 mA cm^{-2}), the CN-Si electrode retained 78% of its original capacity at 0.3C (0.99 mA cm^{-2}), while the P-Si and CP-Si electrodes retained only 47% and 43%, respectively. Compared with representative Si-based anode half-cells reported for all-solid-state batteries, CN-Si delivers a high reversible capacity of approximately 2560 mAh g^{-1} even at 3C (9.9 mA cm^{-2}), highlighting its excellent high-rate capability (Figure S12 and Table S3). In P-Si and CP-Si electrodes, the Li-Si film undergoes structural changes during delithiation as it reverts to Si, forming columnar cracks and voids (As schematically depicted in Figure 1h,i). This effect could be more pronounced at high current densities, where the rapid contraction of Si

may lead to uneven Li-ion and electron reactions, resulting in localized delithiation. To further investigate the rate capability, we quantitatively analyzed the lithiation capacity derived from galvanostatic and potentiostatic stages at different current densities upon lithiation (Figure 3c–e). As shown in Figure 3f, the CN-Si electrode exhibited the lowest lithiation capacity from the potentiostatic region across all C-rates compared to the other electrodes. At a rate of 3C, the P-Si and CP-Si electrodes reach the cut-off voltage with severe overpotential, finally leading to the lithiation capacity of 5.2% and 6.7% at the potentiostatic region, respectively. Such an increased capacity contribution from the potentiostatic stage indicates the high overpotential of the P-Si and CP-Si electrodes during the charging process. This is because the lower structural stability of the P-Si and CP-Si electrodes leads to the formation and growth of cracks and voids as the current density increases. Such a phenomenon significantly damages the electrode structure and creates resistance to Li-ion and electron transport. On the other hand, the CN-Si electrode showed only about 3% of its capacity from the potentiostatic region. This reduced potentiostatic contribution is attributed to the combined effects of CNT-mediated crack/void suppression and enhanced electrode-level electronic conductivity. Four-point probe measurements showed that CN-Si exhibits an electronic conductivity of 9010 S cm^{-1} , which is much higher than those of CP-Si (13.9 S cm^{-1}) and P-Si (0.141 S cm^{-1}) (Figure S13). To verify that the superior performance of CN-Si is not simply due to enhanced electronic conductivity, a Super P-rich CP-Si electrode containing 10 wt% Super P was prepared as a high-conductivity control. SEM analysis shows that Super P does not encapsulate Si particles or form a continuous wrapping network, unlike the CNT layer in CN-Si (Figure S14). Despite the increased amount of conductive carbon additive, the Super P-rich CP-Si electrode exhibited poorer cycling performance than CN-Si (Figure S15). These results indicate that high electronic conductivity alone is insufficient to achieve the electrochemical stability of CN-Si, and that the CNT chain network plays an additional mechanical role by confining Si/Li-Si domains and suppressing crack/void formation. To verify the fast-delithiation properties of the CN-Si electrode, P-Si, CP-Si, and CN-Si electrodes were fully lithiated at 0.1C and then delithiated at 2C, corresponding to 6.6 mA cm^{-2} (Figure 3g; voltage profiles are shown in Figure S16a). Here, fast delithiation is defined as delithiation at 2C; because the DOD was limited to 50%, the effective delithiation time was approximately 15 min. This condition was selected to focus on the early-stage structural response and crack initiation under high-rate conditions, avoiding excessive mechanical deformation that may obscure subtle degradation mechanisms. Upon lithiation, Si particles in all the electrodes (CN-Si, P-Si, and CP-Si) are transformed into a thin Li-Si film without any pores within the electrode (Figure 3h and S7). The results demonstrate that the CN-Si electrode showed no formation of columnar cracks and voids (Figure 3i). In contrast, significant cracks and voids were observed in the P-Si and CP-Si electrodes as shown in Figures 3j and S16b, respectively.

2.4 | Optimized CNT Loading Stabilizes Cycling by Preserving Active Reaction Pathways

In the cycle test, the P-Si and CP-Si electrodes showed a severe capacity drop with discharge capacities of 609.8 mAh g^{-1} and

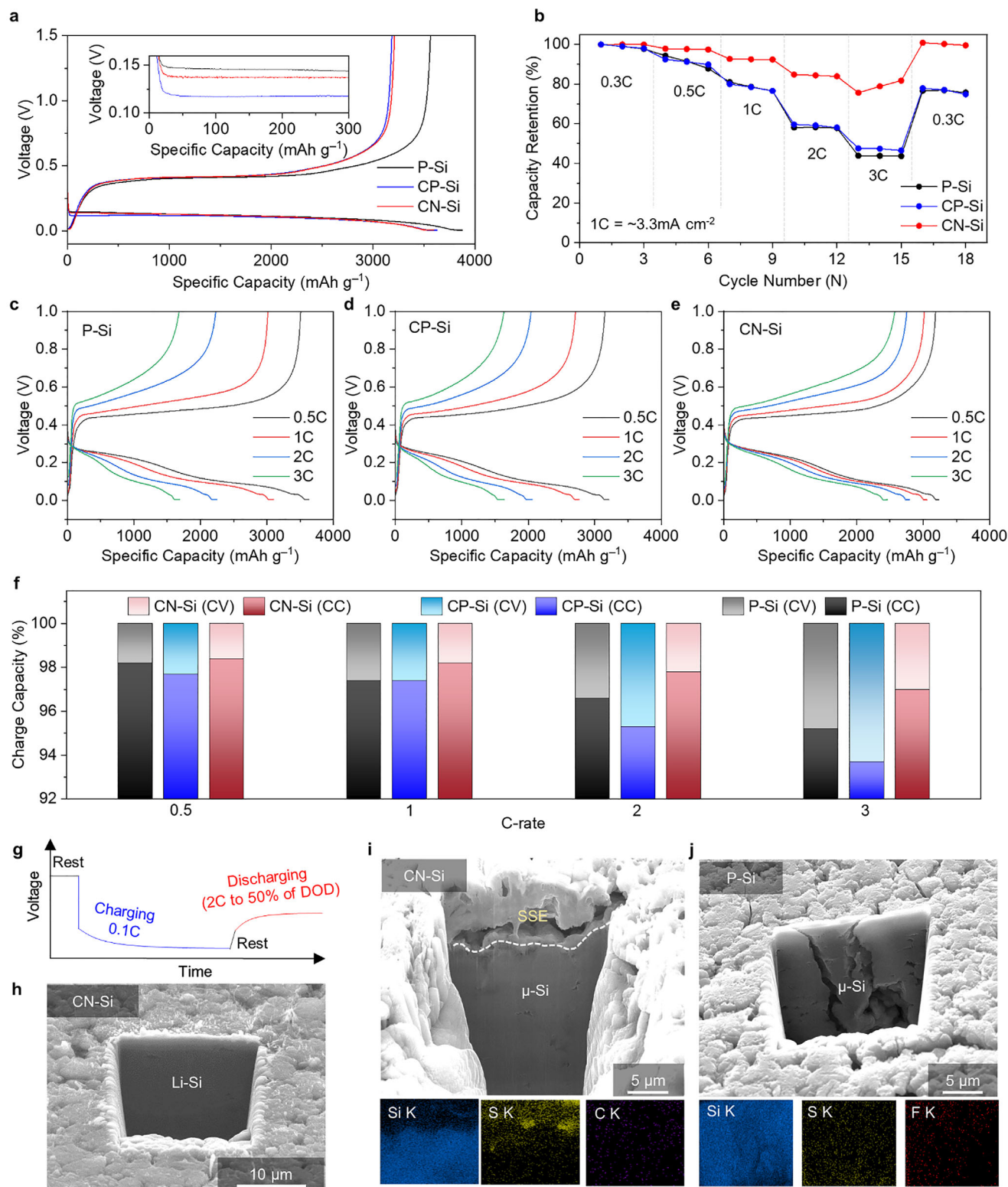


FIGURE 3 | Electrochemical Rate Capability of Comparative Electrode Systems. a, Voltage profiles of each electrode during the first cycle, with an inset showing a magnified view of the profile. b, Rate capability of P-Si, CP-Si, and CN-Si electrodes during delithiation from 0.3C to 3C, with the lithiation rate fixed at 0.3C. c-e, Voltage profiles of P-Si (c), CP-Si (d), and CN-Si (e) electrodes during rate testing from 0.5C to 3C. f, Quantitative analysis of lithiation capacity obtained from galvanostatic and potentiostatic steps at 0.5, 1, 2, and 3C rates. g, Graphical voltage profile showing electrochemical operating conditions for the post-mortem analysis of the fast-discharging test. h, Cross-sectional SEM image of the CN-Si electrode after the first lithiation. i, j, Cross-sectional SEM and EDS analysis of CN-Si (i) and P-Si (j) electrodes after formation (100% lithiation at 0.1C ($1\text{C} = 3.3\text{ mA cm}^{-2}$) and 50% delithiation at 2C).

524.3 mAh g⁻¹ (capacity retentions of 17.8% and 17.7%) after 50 cycles, respectively. The CN-Si electrode demonstrated a discharge capacity of 1932.8 mAh g⁻¹ and the highest capacity retention of 59.2%, which is 42% higher than those of the other two electrodes, along with an improved average coulombic efficiency (Figure 4a). To investigate the effect of CNT content on the electrochemical performance of CN-Si electrodes, a series of compositions with varying CNT loadings (0.5 wt% to 4 wt%) were evaluated. The initial discharge capacities for CN-Si electrodes with 0.5, 1, and 4 wt% CNT were measured to be 3025.0, 3492.4, and 1872.2 mAh g⁻¹, respectively, with corresponding initial coulombic efficiencies (ICEs) of 88.2%, 87.9%, and 81.1% (Figure S17a). Upon subsequent cycling, the electrodes with 0.5 wt% and 1 wt% CNT exhibited poor capacity retention of only 19.2% and 25.6%, respectively (Figure S17c). These results suggest that the low CNT content is insufficient to effectively wrap the Si particles and exert the necessary compressive stress for structural stabilization (Figure S18). In contrast, the electrode containing 4 wt% CNT experienced short-circuiting after only the second cycle (Figure S17b). Post-mortem optical/SEM/EDS analysis of the 4 wt% CNT electrode after micro-short behavior revealed localized Li metal deposits near the Si electrode/LPSCl region and deposit-like features on the electrode surface (Figure S19). The corresponding EDS maps showed O-rich and Si-poor regions around these deposits, consistent with oxidized Li-derived products associated with localized Li deposition. In addition, a CNT-only control experiment confirmed that Li can be plated and stripped on the CNT network (Figure S11), supporting the electrochemical feasibility of Li deposition on CNT-rich electronically conductive domains. These observations support the proposed mechanism shown in Figure S18c, where excessive CNT loading forms highly percolated electronic pathways while relatively limiting ionic transport. Such electronic/ionic transport imbalance can promote local electron accumulation at the electrode/solid-electrolyte interface, inducing localized Li deposition and electronically driven side reactions, eventually leading to premature short-circuiting. To further rationalize the optimized CNT content, the theoretical dense-film volumetric capacity of CN-Si electrodes was estimated at the fully lithiated Li₁₅Si₄ state (Note S3 and Table S4). The 2 wt% CNT electrode retained 99.2% of the volumetric capacity of pure Li₁₅Si₄, indicating that CNT incorporation at this level introduces only a negligible volumetric-capacity penalty while providing sufficient network formation for structural stabilization. Based on these observations, the CN-Si electrode with 2 wt% CNT was found to exhibit the most balanced and stable electrochemical performance among the tested compositions. To further investigate the effect of binder content on electrode performance, we also evaluated a P-Si electrode incorporating an excessive amount (2 wt%) of PVDF. Despite the increased polymer content, no improvement in cycling stability was observed (Figure S20). This result indicates that PVDF, owing to its relatively low mechanical strength, fails to generate sufficient compressive stress even at higher concentrations, thereby limiting its effectiveness in structural stabilization. EIS analysis was conducted to compare the electrochemical resistance caused by the structural evolution of each optimized electrode upon cycling (Figure 4b–d). The P-Si and CP-Si electrodes exhibited charge-transfer resistance (R_{CT}) values of approximately 17 Ω and 14 Ω , respectively, after the first cycle. These values increased significantly to 40 Ω and 52 Ω after 50 cycles. On the other hand, the CN-Si electrode

demonstrated an R_{CT} value close to 0 Ω after the first cycle and the lowest R_{CT} value of approximately 30 Ω after 50 cycles. The corresponding DRT analysis further supports the suppressed interfacial degradation of CN-Si (Figure S21). Based on the DRT peak assignments discussed above, the peak in the 10⁻⁶–10⁻⁵ s range can be associated with an interphase/SEI-related response. After 50 cycles, CN-Si exhibited the smallest peak intensity in this region among the three electrodes, suggesting suppressed interphase-related resistance growth during cycling. This trend is consistent with previous carbon-coated Si anode studies showing that carbonaceous surface layers can stabilize SEI/interphase formation and suppress interfacial resistance growth [50–52]. For CN-Si, the CNT network appears to further support this behavior by preserving electrode integrity and limiting newly exposed Si/SSE interfaces during cycling. The cycle-dependent voltage profiles normalized by SOC further support that the CNT network does not significantly accelerate electrolyte decomposition during cycling (Figure S22). In the first cycle, P-Si and CN-Si exhibited nearly similar Si lithiation/delithiation voltage behavior, indicating that CNT incorporation did not introduce a distinct additional decomposition-related voltage feature at the initial stage. As cycling progressed, P-Si showed pronounced overpotential and distorted voltage profiles, which are associated with structural degradation and loss of reaction pathways. In contrast, CN-Si maintained voltage profiles similar to its initial behavior, without a distinct additional high-potential plateau or abnormal voltage response. These results suggest that CNT-induced LPSCl decomposition or interfacial side reactions are not significantly accelerated during cycling. Subsequently, the potential behavior during the delithiation of Si was analyzed using differential capacity (dQ/dV) plots for the P-Si, CP-Si, and CN-Si electrodes at the fifth, 30th, and 50th cycles to investigate the underlying charge and discharge mechanisms (Figure S23). The dQ/dV plots revealed that all electrodes exhibited a peak at ~0.4 V in the fifth cycle, corresponding to the delithiation of the fully lithiated Li₁₅Si₄ phase (Figure 4e–g). However, as cycling progressed, the ~0.4 V peak was almost absent in the P-Si and CP-Si electrodes, while the CN-Si electrode consistently maintained a strong peak at ~0.4 V, after the 50th cycle (Figure 4g). These results indicate that in the P-Si and CP-Si electrodes, the formation of cracks and voids during cycling leads to a loss of electrical and ionic pathways within the electrode. This prevents reaching the fully lithiated state of the Li₁₅Si₄ phase. Conversely, the CN-Si electrode maintained its morphological integrity because the CNT network ensures uniform electrochemical reactions and superior performance upon cycling. It should be noted that the half-cell configuration employs Li metal as the counter electrode, where the Li/LPSCl interface can form decomposition-derived interphases and increase interfacial impedance during cycling [53]. Thus, the half-cell cycling result represents a conservative evaluation of the CN-Si electrode under additional interfacial constraints associated with the Li metal counter electrode. To investigate the practical applicability of the CN-Si electrode without relying on a Li metal counter electrode, a full cell comprising a CN-Si anode, SSE, and LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NCM₈₁₁) cathode was fabricated and evaluated at room temperature (Figures 4h–j). Detailed full-cell parameters, including cathode loading, cathode areal capacity, N/P ratio, solid-electrolyte thickness, voltage window, C-rate definition, and capacity-balancing method, are summarized in Table S5. The full cell delivered an initial specific

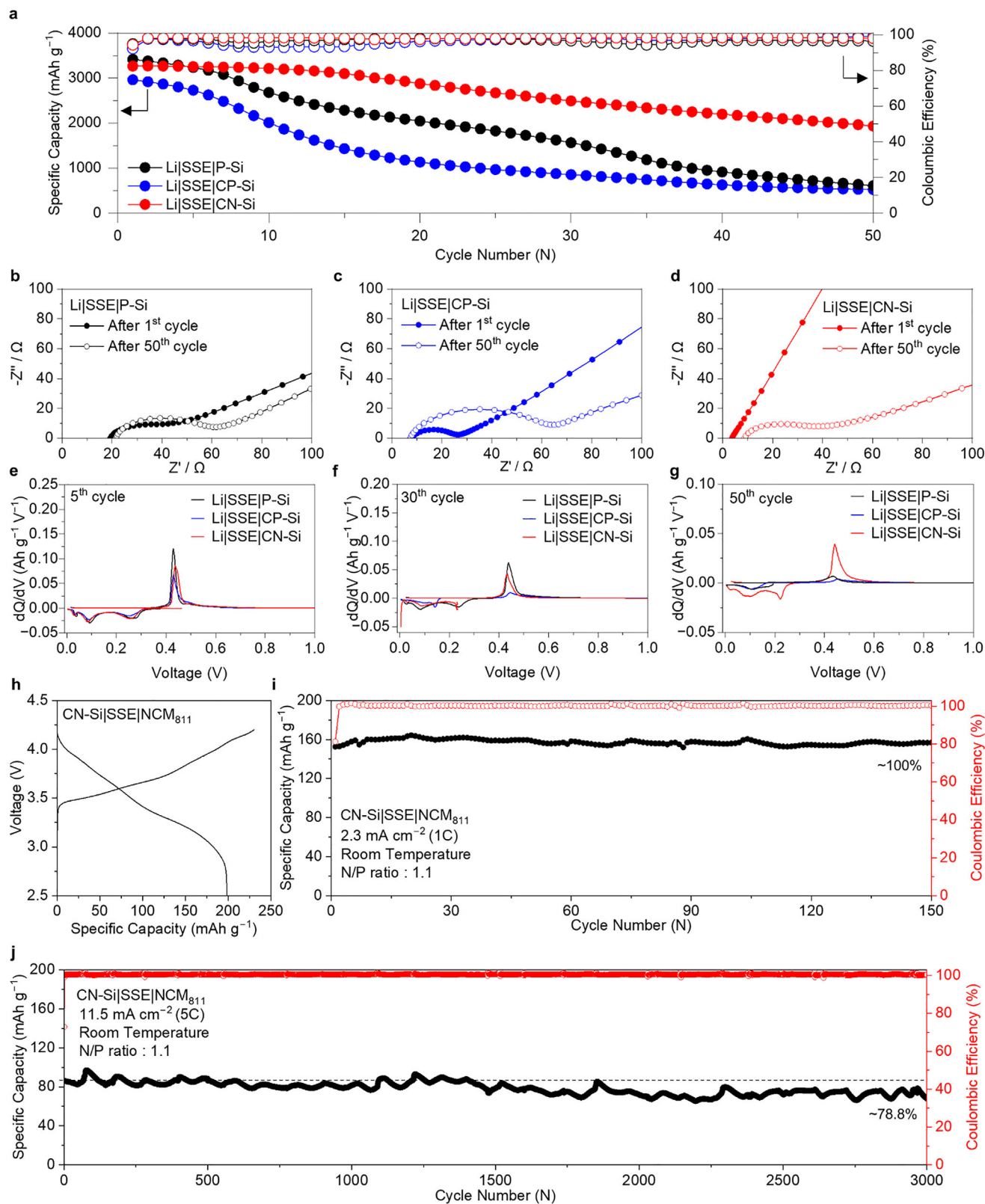


FIGURE 4 | Electrochemical characterization of various electrodes. a, Cycling performance of Li|SSE|P-Si, Li|SSE|CP-Si, Li|SSE|CN-Si electrodes operated at 0.3C during 50 cycles. b-d, Electrochemical impedance spectra of Li|SSE|P-Si, Li|SSE|CP-Si, and Li|SSE|CN-Si cells after the first and 50th cycles. The EIS spectra were analyzed using the same equivalent circuit shown in Figure 2a. e-g, Differential capacity plots of Li|SSE-based cells with P-Si, CP-Si, and CN-Si electrodes at the fifth, 30th, and 50th cycles. h-j, Electrochemical performance of the CN-Si|SSE|NCM₈₁₁ full cell including voltage profiles (h), cycling stability at 1C (i) and 5C (j) under a stack pressure of 250 MPa.

capacity of 198.6 mAh g⁻¹ with an initial Coulombic efficiency (ICE) of 86.3% (Figure 4h). Furthermore, it exhibited nearly 100% capacity retention over 150 cycles at 1C (Figure 4i), corresponding to 2.3 mA cm⁻², and retained 78.8% of its capacity after 3000 cycles at 5C (Figure 4j), corresponding to 11.5 mA cm⁻². These results demonstrate that the high-rate capability observed in the half-cell is successfully maintained in the practical full-cell configuration. Compared with previously reported NCM811|Si-based full cells, the CN-Si full cell shows competitive long-term cycling stability (Figure S24 and Table S6). To further distinguish the intrinsic contribution of the CN-Si architecture from the effects of Li metal counter-electrode instability and high external stack pressure, P-Si|SSE|NCM811, CP-Si|SSE|NCM811, and CN-Si|SSE|NCM811 full cells were additionally evaluated under a reduced stack pressure of 65 MPa, identical to that used for the half-cell tests. Under this condition, the CN-Si full cell exhibited superior cycling stability compared with the P-Si and CP-Si full cells, confirming that the improved full-cell performance originates from the CN-Si architecture rather than solely from the absence of Li metal or the use of high stack pressure (Figure S25).

2.5 | Post-Mortem Microscopy Confirms Crack and Void Suppression in CN-Si

The post-mortem characterization identifying structural degradation of the P-Si, CP-Si, and CN-Si electrodes was conducted using Focused Ion Beam (FIB)-SEM and EDS mapping. All electrodes were tested in half-cells employing lithium metal as the counter electrode, which served as an unlimited Li source. This configuration ensured full lithiation of the Si electrodes in every cycle, thereby enabling the evaluation of their structural stability under rigorous cycling conditions. Cross-sectional SEM images show the significant cracks and voids observed in the P-Si and CP-Si electrodes (Figure 5a,b). Such mechanical degradation is also observed on the electrode surface along the solid-electrolyte direction (Figure 5d,e), disrupting pathways for both Li ions and electrons. On the other hand, both the inside and surface of the CN-Si electrode exhibited suppressed formation and growth of cracks and voids (Figure 5c,f), which implies that CNT effectively maintained its morphological integrity. To further examine the wrapping effect of CNTs, we used an ion milling machine (dedicated equipment separated from the SEM machine) to cut a large area of the CN-Si electrode and obtained high-resolution cross-sectional SEM images along with EDS mapping. Using an integrated FIB-SEM machine can sometimes make it more challenging to obtain high-resolution or well-focused SEM images than with a dedicated SEM system due to beam alignment and stage tilt issues. The analysis confirmed that CNTs effectively encapsulated the Si particles, indicating that the wrapping and tightening action of CNTs imposes compressive stress on the Si. This compressive confinement contributes to enhanced structural integrity by preventing crack and void formation. Combined with the high electronic conductivity of the continuous CNT network, the preserved electrode architecture maintains Li-ion/electron transport pathways and active reaction interfaces during cycling. This synergistic structural/electronic stabilization is responsible for the excellent cycling stability and superior rate capability of CN-Si.

2.6 | Multiparticle Simulations Reveal CNT-Mediated Stress Redistribution and Hotspot Suppression

To further support these experimental observations, multiparticle-scale simulations were conducted to model stress interactions between adjacent Si particles during lithiation-induced swelling (Figure 6). In this model, a square domain containing randomly distributed Si particles of varying sizes was analyzed using the eigenstrain method to impose matched isotropic swelling (Figure S26) and the mechanical properties of the materials used in the simulation are summarized in Table S7. The spring-foundation stabilization used to suppress initial rigid-body motion was ramped down to a negligible stiffness as interparticle contact became dominant, ensuring numerical convergence without affecting the final stress distributions (Figure S27). The von Mises stress distributions for P-Si and CN-Si at different states of charge (SOC, 23%, 85%, and 100%) are illustrated in Figure 6. At a low lithiation state of 23%, stresses in P-Si remain below the model-defined yield strength, though local stress concentrations already appear at particle contacts (Figure 6a). As lithiation progresses (SOC = 85% and 100%), these stresses increase markedly, exceeding the compressive strength of crystalline Si (~950 MPa) (Figure 6b,c) [54]. In contrast, the CN-Si configuration exhibits a consistently lower overall von Mises stress magnitude, while the degree of stress uniformity depends on the lithiation state (Figure 6d-f). This reduction arises from the compliant CNT coating, which acts as a mechanical buffer that redistributes contact stresses between neighboring particles. Area-weighted post-processing shows that the mean von Mises stress in CN-Si is reduced by 21.43%, 12.80%, and 8.64% relative to P-Si at SOC = 23%, 85%, and 100%, respectively (Table S9). The equivalent-core mean, standard deviation (SD), and coefficient of variation (CV) further show that the stress-uniformity effect depends on the lithiation state. Notably, at SOC = 85%, the lower mean stress in CN-Si is accompanied by higher equivalent-core SD and CV, indicating stress reduction and redistribution rather than global homogenization (Table S10). The equivalent-core 95th-percentile von Mises stress is also lower in CN-Si, decreasing from 91 to 81 MPa, 951 to 921 MPa, and 870 to 805 MPa at the corresponding SOC (Table S11). The magnified view at SOC = 23% (Figure 6g) shows that CNT wrapping effectively alleviates local von Mises stress at particle contacts, while at SOC = 100% (Figure 6h), the hydrostatic stress map shows compression-dominated regions around the particle exteriors in the CN-Si configuration. These complementary findings indicate that CNT wrapping reduces the overall stress magnitude and suppresses high-stress regions, while redistributing the stress field as lithiation progresses. The degree of stress uniformity is SOC-dependent rather than uniform throughout the lithiation process. To further elucidate the buffering role of CNT, the maximum principal stress and stress triaxiality distributions at full lithiation (SOC = 100%) were analyzed (Figures S28 and S29). The P-Si configuration exhibits localized σ_1 hot spots and uniformly high triaxial compression across the particle bed, reflecting severe contact-stress concentration. In contrast, the CN-Si configuration shows a smoother distribution of principal stress and stress triaxiality near particle interfaces, further supporting redistribution of interparticle contact loads. These results further support the stress-redistribution and

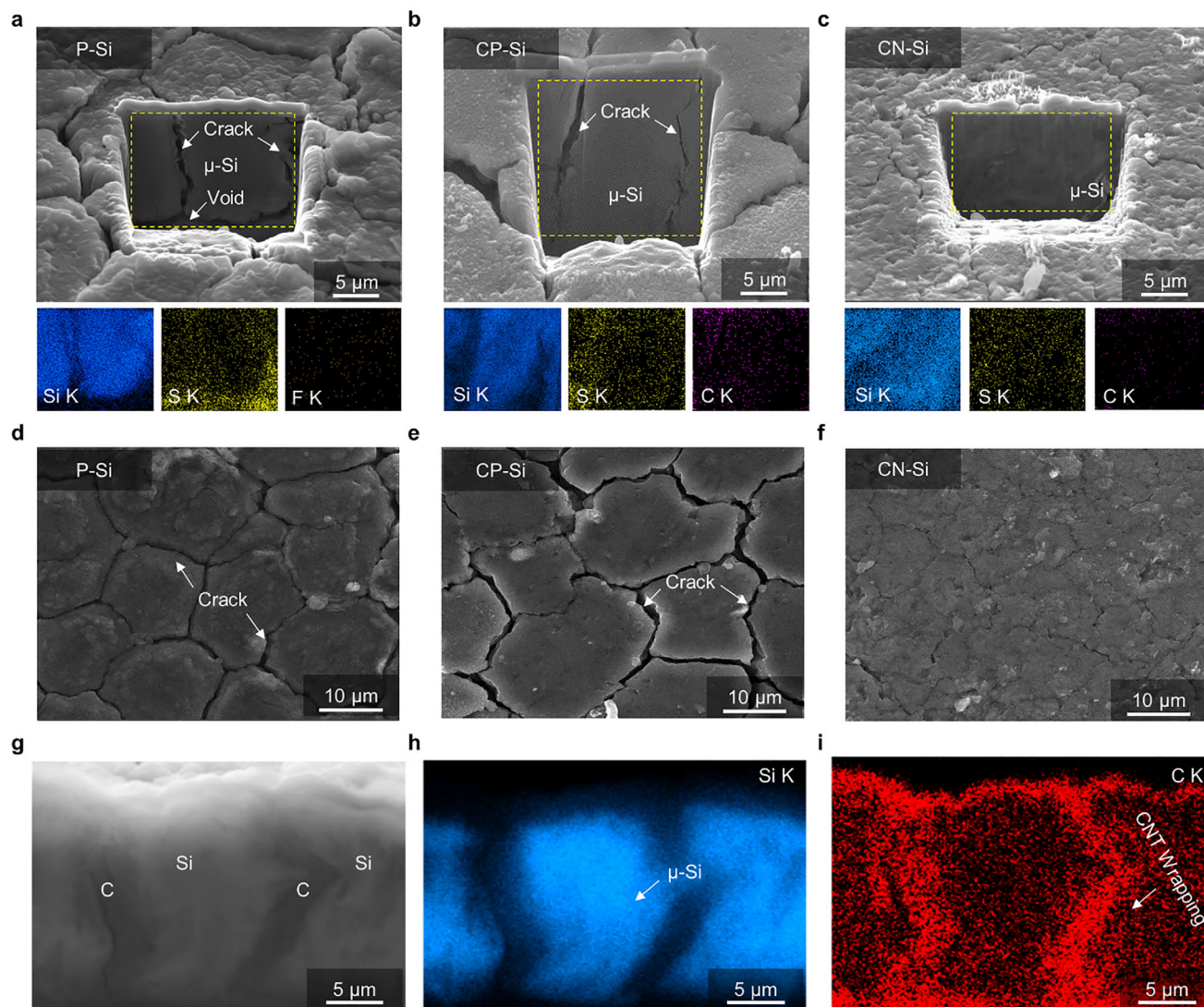


FIGURE 5 | Post-mortem analysis of various electrodes. a-c, Morphological and compositional analysis via cross-sectional SEM and EDS of each electrode in a half-cell configuration after 50 cycles under delithiated conditions. The images correspond to the electrode region adjacent to the solid electrolyte interface, and the yellow dashed boxes indicate the regions selected for EDS mapping. d-f, Top-view SEM images of Si electrodes in the delithiated state after 50 cycles, obtained from disassembled half-cells. g-i, Cross-sectional SEM image and corresponding EDS elemental maps of the CN-Si electrode after 50 cycles, prepared by FIB milling across the entire electrode width to visualize large-area structural and compositional features.

hotspot-suppression effect of CNT wrapping observed experimentally and in the von Mises/hydrostatic stress analyses.

3 | Conclusion

In this study, we demonstrated a novel Chain-based Networking (CN)-Si electrode architecture that significantly improves the structural and electrochemical stability of Si anodes in all-solid-state batteries (ASSBs) without the need for solid electrolytes within the electrode itself. By employing single-walled carbon nanotubes (CNTs) as mechanically robust and highly conductive chains, individual μ -Si particles were encapsulated and interconnected, forming a continuous, stress-managing network that is functionally analogous to the stress-reinforcing principle of Prince Rupert's drops. This CNT-mediated stress redistribution effectively mitigated volume-change-induced degradation during

lithiation/delithiation, suppressing the formation of cracks and voids while maintaining continuous interparticle contact and electrochemically accessible reaction pathways. Finite-element simulations further verified that CNT wrapping redistributes both von Mises and hydrostatic stresses, alleviating contact-stress concentrations and forming a smoother compression-dominated stress field around Si particles. As a result, the CN-Si electrode exhibited exceptional rate capability, retaining 78% of its capacity at 3C, and improved half-cell cycling stability, retaining 59.2% after 50 cycles, significantly outperforming conventional polymer- and carbon black-based Si electrodes. More importantly, in a CN-Si/NCM811 full-cell configuration, the CN-Si electrode retained 78.8% of its capacity after 3000 cycles at 5C, demonstrating robust long-term cell-level stability. Our findings highlight a scalable and cost-effective strategy for realizing structurally resilient, high-energy-density Si anodes by engineering internal stress distribution at the particle and electrode levels. The CN-Si

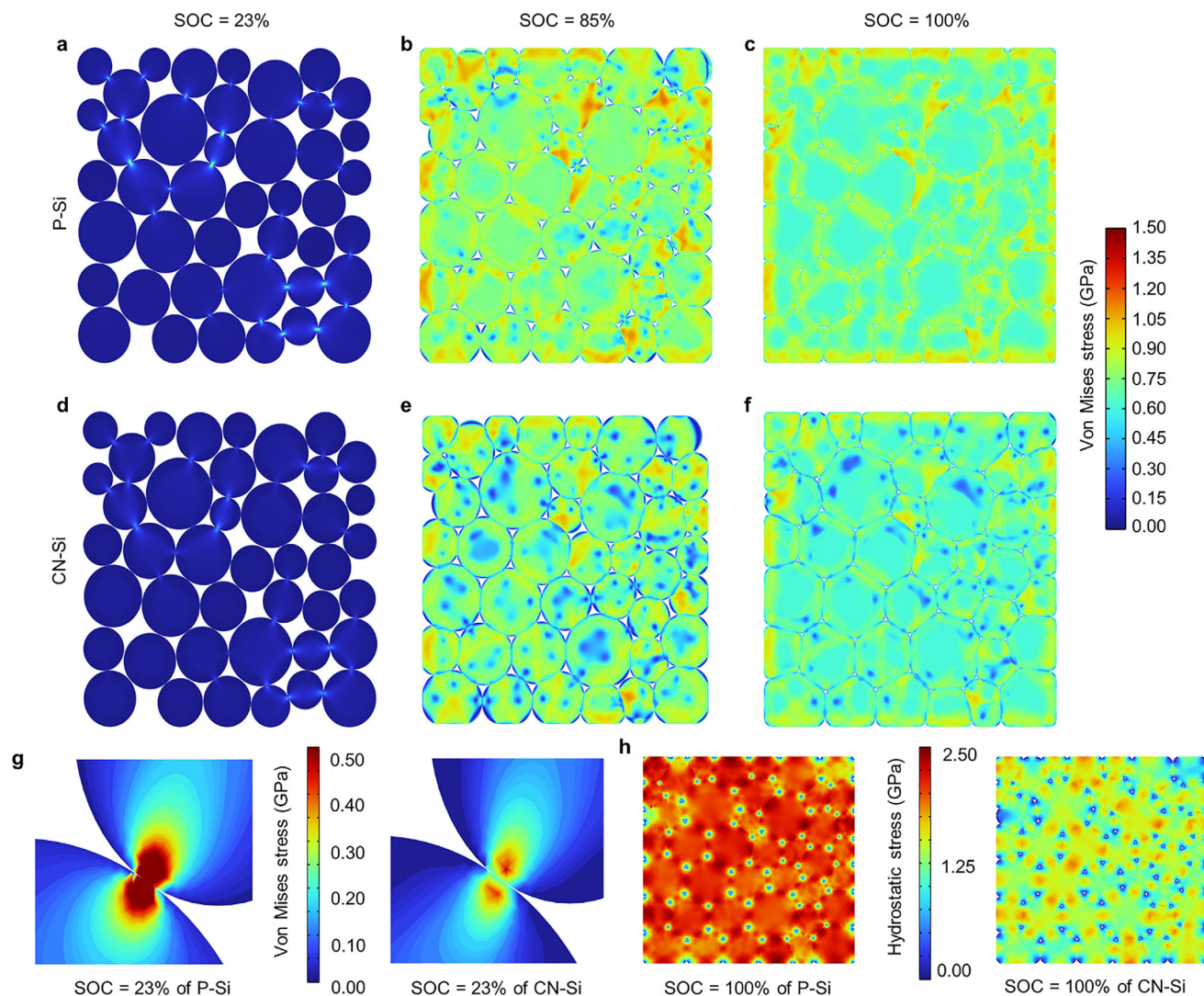


FIGURE 6 | Snapshots of the von Mises stress distribution in randomly dispersed Si particles during lithiation. a-h, Subplots (a–c) show the stress distribution in P-Si particles at States of Charge (SOC) of 23%, 85%, and 100%, respectively. Subplots (d–f) present the corresponding results for CN-Si particles. Subplot (g) provides a magnified view of the particle contact at SOC = 23%, highlighting the pronounced difference in stress concentrations between P-Si and CN-Si particles. h, Hydrostatic stress (compression positive) at SOC = 100% for P-Si and CN-Si particles.

design paves the way for the next generation of high-performance ASSBs that meet both energy and power demands without sacrificing mechanical integrity.

4 | Experimental Section

4.1 | Materials Preparation

The Si particles (μ -Si, 1–10 μ m) were dried in vacuum oven at 80°C overnight before use. Polyvinylidene fluoride binder used for the P-Si anode was obtained from Sigma-Aldrich. Super P (C65) was obtained from Alfa-Aesar and dried in vacuum oven at 80°C overnight before use and SBR/CMC were obtained from MTI Corp. using for the CP-Si anode. SWCNTs (H_2O , 0.4wt% CMC) used for the CN-Si anode was obtained from OCSIAI. Li metal foil was punched to obtain electrode discs (Φ = 13 mm) and used as the counter electrode in half-cell. Li_6PS_5Cl was used as a solid electrolytes.

4.2 | Preparation of Si Electrode

To fabricate the P-Si electrodes, a slurry was prepared using 99.9 wt% of Si, 0.1 wt% of PVdF and NMP (N-methyl-2-pyrrolidone) solvent before casting on a current collector. For CP-Si electrodes, a slurry was prepared using 94 wt% of Si, 3wt% of SuperP, 1.5 wt% of SBR, 1.5 wt% of CMC, and D.I water solvent before casting on a current collector. For the Super P-rich CP-Si control electrode, a slurry was prepared using 87 wt% Si, 10 wt% Super P, 1.5 wt% SBR, 1.5 wt% CMC, and D.I. water solvent. In the case of the CN-Si electrode, a slurry was prepared using 98 wt% of Si, 2 wt% of CNT, and D.I water solvent before casting on a current collector. All slurries were mixed using for a Thinky mixer (Thinky Corporation, AR-100). STS foil was used as a current collector and Doctor blade was using for casting on a current collector. All electrodes were dried in a vacuum oven 80°C overnight and punched to obtain electrode discs (Φ = 13 mm and 10 mm, $\sim 3.3\text{mAh cm}^{-2}$) before use. For evaluating the full-cell, Si electrodes were punched to obtain

electrode discs ($\Phi = 13$ mm and 10 mm, $\sim 2.5\text{mAh cm}^{-2}$) before use.

4.3 | Preparation of Cathode Electrode

Single-crystal NCM_{811} particles were obtained from SMLAB and we coated the LiNbO_3 on NCM particles. To fabricate the NCM electrode, we mixed the NCM_{811} , VGCF, $\text{Li}_6\text{PS}_5\text{Cl}$, and Nitrile Butadiene Rubber (NBR) (70:3:25:2 (wt%)) using Hexyl butyrate (HB) as solvent for casting on STS foil. After that, we cast the slurry on STS foil, dried the resulting electrode in vacuum oven with 80°C overnight and rolled it. We punched the electrode to obtain electrode discs ($\Phi = 13$ mm and 10 mm, $\sim 2.3\text{mAh cm}^{-2}$)

4.4 | Preparation of SWCNT-Coated SUS Electrodes

To prepare the SWCNT-coated SUS electrode, an SWCNT slurry was cast onto a SUS foil using a doctor blade. The thickness of the SWCNT coating layer was approximately 300 nm. The coated SUS foil was dried in a vacuum oven at 80°C overnight and then punched into disks ($\Phi = 13$ mm) before use.

4.5 | Cell Assembly

To fabricate cells for obtaining electrochemical performance, 153 mg of LPSCl was pressed as separator layer at 100 MPa. Then, the Si anode ($\Phi = 13$ mm) was pressed together with the LPSCl layer at 650 MPa. In the half-cell system, Li metal foil of the same size was pressed at 20 MPa, and a stack pressure of 65 MPa was applied. For the full-cell configuration, the NCM composite cathode was pressed at 400 MPa instead of lithium metal, followed by the application of a stack pressure of 250 MPa. For measuring the stress change during cycling, 90 mg of LPSCl was pressed at 60 MPa. Then, Si anode ($\Phi = 10$ mm) was pressed together with LPSCl layer at 400 MPa, and the NCM cathode ($\Phi = 10$ mm) was pressed at 350 MPa. Subsequently, a stack pressure of 50 MPa was applied. We defined the N/P ratio to 1.1 based on the theoretical capacities $\text{Si} = 3,300\text{ mAh g}^{-1}$ and $\text{NCM} = 220\text{ mAh g}^{-1}$. All processes were conducted in an Ar-filled glove box.

4.6 | Materials Characterization

X-ray diffraction (D8 advance A25, Bruker) was used to analysis the crystal structures of particles and electrodes using $\text{Cu K}\alpha$ radiation with 2θ in the range from 20.00° to 80.00° . The particle size distribution was measured by a particle size analyser (CILAS, 1090LD shape Analyzer). The SEM and EDS instrument (Apreo S, Thermo) was used to investigate the surface morphology of powders and electrodes. The FIB-SEM instrument (AMBER G, Tescan) was used to examined micro-structure of electrode. The stress change were measured using Digital Press (TPU-040, Teraleader). The impedance was measured by a Biologic (VSP-300), The amplitude of the input signal was 10 mV, and the frequency range was from 1 MHz to 0.1 Hz. The cell tester was used by a WonATech (WBCS 3000).

4.7 | Electrochemical Performance Tests

In the Li|SSE|Si system, we applied CC (Constant Current) /CV (Constant Voltage) and CC processes during charge/discharge. During the first cycle, the process was conducted at a rate of 0.1C ($1\text{C} = 3.3\text{ mA cm}^{-2}$) within a voltage range of 0.005–1.5 V. For subsequent cycles, the process was performed at a rate of 0.3C with a cut-off voltage of 1 V. In the rate test, we applied the current from 0.3C to 3C. In the Si|SSE|NCM_{811} system, CC was conducted at 0.1C for the initial cycle and at 1C for the subsequent cycles. The voltage window was set to 2.5–4.2 V for the first cycle, while the following 1C cycles were operated within 2.8–4.2 V. For measuring the stress change, we applied CC (0.05C for the first cycle and 0.1C for subsequent cycles) process and the range of cut-off voltage is between 2.5 and 4.2 V. The electrochemical stability of SWCNT against LPSCl was evaluated using planar-interface cells in which Cu, SUS, or SWCNT-coated SUS was used as the working electrode. The cells were tested in CC/CV mode at a constant current of 0.00015 A to 0.005 V, followed by a CV hold at 0.005 V with a current cutoff of 0.01C. The upper cutoff voltage was set to 1.5 V.

Author Contributions

Seokjin Kim: conceptualization, methodology, writing – original draft, visualization, investigation, validation. **Kiran Raj:** methodology. **Wei-jiang Xue:** methodology, validation, investigation. **Hyoung Jun Lim:** methodology, writing – review and editing, writing – original draft, supervision. **Ju Li:** supervision, methodology, conceptualization, writing – review and editing, validation. **Jaekyung Sung:** conceptualization, methodology, supervision, validation, investigation, visualization, writing – original draft, writing – review and editing.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (IRIS RS2024-00352303). This work was supported by the Technology Innovation Program (RS-2024-00432013 and RS-2025-02315167) funded by the Ministry of Trade, Industry & Energy (MOTIE, South Korea). This research was supported by Learning & Academic research institution for Master's PhD students, and Postdocs (LAMP) Program of the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education (RS-2023-00301974).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

References

1. Y. Jin, B. Zhu, Z. Lu, N. Liu, and J. Zhu, "Challenges and Recent Progress in the Development of Si Anodes for Lithium-Ion Battery," *Advanced Energy Materials* 7, no. 23 (2017): 1700715, <https://doi.org/10.1002/aeem.201700715>.
2. X. Zhan, M. Li, S. Li, et al., "Challenges and opportunities towards silicon-based all-solid-state batteries," *Energy Storage Materials* 61 (2023): 102875.

3. X. Zhang, D. Wang, X. Qiu, et al., "Stable high-capacity and high-rate silicon-based lithium battery anodes upon two-dimensional covalent encapsulation," *Nature Communications* 11, no. 1 (2020): 3826, <https://doi.org/10.1038/s41467-020-17686-4>.
4. M. Grandjean, M. Perrey, X. Randrema, et al., "Low pressure cycling of solid state Li-ion pouch cells based on NMC—Sulfide—Nanosilicon chemistry," *Journal of Power Sources* 585 (2023): 233646.
5. M. So, S. Yano, A. Permatasari, T. D. Pham, K. Park, and G. Inoue, "Mechanism of silicon fragmentation in all-solid-state battery evaluated by discrete element method," *Journal of Power Sources* 546 (2022): 231956.
6. L. Peng, C. Yu, Z. Zhang, et al., "Tuning Solid Interfaces via Varying Electrolyte Distributions Enables High-Performance Solid-State Batteries," *Energy & Environmental Materials* 6, no. 2 (2022): e12308, <https://doi.org/10.1002/eem.2.12308>.
7. M. Ko, S. Jayasubramanian, J. Kim, et al., "Modulating Conductivity and Porosity of Interlayer for Long-Cycling All-Solid-State Lithium Metal Batteries," *Advanced Materials* 38, no. 16 (2026): 15640, <https://doi.org/10.1002/adma.202515640>.
8. S. Cangaz, F. Hippauf, F. S. Reuter, et al., "Enabling High-Energy Solid-State Batteries With Stable Anode Interphase by the Use of Columnar Silicon Anodes," *Advanced Energy Materials* 10, no. 34 (2020): 2001320, <https://doi.org/10.1002/aenm.202001320>.
9. H. Huo and J. Janek, "Silicon as Emerging Anode in Solid-State Batteries," *ACS Energy Letters* 7, no. 11 (2022): 4005–4016.
10. H. A. Lee, M. Shin, J. Kim, J. W. Choi, and H. Lee, "Designing Adaptive Binders for Microenvironment Settings of Silicon Anode Particles," *Advanced Materials* 33, no. 13 (2021): 2007460, <https://doi.org/10.1002/adma.202007460>.
11. S. Jayasubramanian, S. Kim, M. Ko, and J. Sung, "The Pursuit for High Power Density in Silicon-Based ASSBs: Insights Into Limitations and Perspectives," *Advanced Energy Materials* 14, no. 16 (2026): e05061.
12. L. Hu, X. Yan, Z. Fu, et al., "A "Reinforced Concrete" Structure of Silicon Embedded Into an In Situ Grown Carbon Nanotube Scaffold as a High-Performance Anode for Sulfide-Based All-Solid-State Batteries," *ACS Applied Energy Materials* 5, no. 11 (2022): 14353–14360, <https://doi.org/10.1021/acsaeem.2c02890>.
13. D. H. S. Tan, Y.-T. Chen, H. Yang, et al., "Carbon-free high-loading silicon anodes enabled by sulfide solid electrolytes," *Science* 373, no. 6562 (2021): 1494–1499, <https://doi.org/10.1126/science.abg7217>.
14. S. Kim, S. Jayasubramanian, Y. Kim, et al., "Evaluating the efficacy of strategies for silicon/graphite anodes in Li-ion batteries," *Chemical Engineering Journal* 500 (2024): 157371.
15. S.-Y. Ham, E. Sebti, A. Cronk, et al., "Overcoming low initial coulombic efficiencies of Si anodes Through prelithiation in all-solid-state batteries," *Nature Communications* 15, no. 1 (2024): 2991, <https://doi.org/10.1038/s41467-024-47352-y>.
16. B. Ajdari, P. Asghari, and A. Molaei Aghdam, "Silicon Solid State Battery: The Solid-State Compatibility, Particle Size, and Carbon Compositing for High Energy Density," *Advanced Functional Materials* 34, no. 30 (2024): 2314822.
17. Z. Li, G. Wu, Y. Yang, et al., "An Ion-Conductive Grafted Polymeric Binder With Practical Loading for Silicon Anode With High Interfacial Stability in Lithium-Ion Batteries," *Advanced Energy Materials* 12, no. 29 (2022): 2201197, <https://doi.org/10.1002/aenm.202201197>.
18. B. Chen, D. Xu, S. Chai, Z. Chang, and A. Pan, "Enhanced Silicon Anodes With Robust SEI Formation Enabled by Functional Conductive Binder," *Advanced Functional Materials* 34, no. 34 (2024): 2401794, <https://doi.org/10.1002/adfm.202401794>.
19. B. Sreenarayanan, D. H. S. Tan, S. Bai, W. Li, and W. Bao, "Quantification of lithium inventory loss in micro silicon anode via titration-gas chromatography," *Journal of Power Sources* 531 (2022): 231327.
20. Y. Li, K. Yan, H.-W. Lee, Z. Lu, N. Liu, and Y. Cui, "Growth of conformal graphene cages on micrometre-sized silicon particles as stable battery anodes," *Nature Energy* 1, no. 2 (2016): 15029.
21. S. Chen, D. Xie, G. Liu, et al., "Sulfide solid electrolytes for all-solid-state lithium batteries: Structure, conductivity, stability and application," *Energy Storage Materials* 14 (2018): 58–74, <https://doi.org/10.1016/j.ensm.2018.02.020>.
22. S. Li, Z. Yang, S.-B. Wang, et al., "Sulfide-based composite solid electrolyte films for all-solid-state batteries," *Communications Materials* 5, no. 1 (2024): 44.
23. Z. D. Hood, A. U. Mane, A. Sundar, et al., "Multifunctional Coatings on Sulfide-Based Solid Electrolyte Powders With Enhanced Processability, Stability, and Performance for Solid-State Batteries," *Advanced Materials* 35, no. 21 (2023): 2300673, <https://doi.org/10.1002/adma.202300673>.
24. P. Adeli, J. D. Bazak, K. H. Park, et al., "Boosting Solid-State Diffusivity and Conductivity in Lithium Superionic Argyroditites by Halide Substitution," *Angewandte Chemie International Edition* 58, no. 26 (2019): 8681–8686, <https://doi.org/10.1002/anie.201814222>.
25. D. H. S. Tan, E. A. Wu, H. Nguyen, et al., "Elucidating Reversible Electrochemical Redox of Li6PSSCl Solid Electrolyte," *ACS Energy Letters* 4, no. 10 (2019): 2418–2427, <https://doi.org/10.1021/acsenergylett.9b01693>.
26. J. Wu, L. Yuan, W. Zhang, Z. Li, X. Xie, and Y. Huang, "Reducing the thickness of solid-state electrolyte membranes for high-energy lithium batteries," *Energy & Environmental Science* 14, no. 1 (2021): 12–36, <https://doi.org/10.1039/D0EE02241A>.
27. D. Li, H. Liu, Y. Liang, C. Wang, and L. Z. Fan, "Challenges and Developments of High Energy Density Anode Materials in Sulfide-Based Solid-State Batteries," *ChemElectroChem* 9, no. 24 (2022): 202200923, <https://doi.org/10.1002/celec.202200923>.
28. J. H. Choi, K. Ko, S.-J. Won, et al., "Important consideration for interface engineering of carbon-based materials in sulfide all-solid lithium-ion batteries," *Energy Storage Materials* 71 (2024): 103653.
29. J. Lee, D. Jin, J. Y. Kim, et al., "Dry Pre-Lithiation for Graphite-Silicon Diffusion-Dependent Electrode for All-Solid-State Battery," *Advanced Energy Materials* 13, no. 25 (2023): 2300172.
30. H. Huo, M. Jiang, Y. Bai, et al., "Chemo-mechanical failure mechanisms of the silicon anode in solid-state batteries," *Nature Materials* 23 (2024): 543–551, <https://doi.org/10.1038/s41563-023-01792-x>.
31. S. Y. Han, C. Lee, J. A. Lewis, et al., "Stress evolution During cycling of alloy-anode solid-state batteries," *Joule* 5, no. 9 (2021): 2450–2465, <https://doi.org/10.1016/j.joule.2021.07.002>.
32. J. A. Lewis, F. J. Q. Cortes, Y. Liu, et al., "Linking void and interphase evolution to electrochemistry in solid-state batteries using operando X-ray tomography," *Nature Materials* 20, no. 4 (2021): 503–510, <https://doi.org/10.1038/s41563-020-00903-2>.
33. J. Y. Kim, S. Jung, S. H. Kang, et al., "Graphite-Silicon Diffusion-Dependent Electrode With Short Effective Diffusion Length for High-Performance All-Solid-State Batteries," *Advanced Energy Materials* 12, no. 3 (2022): 2103108, <https://doi.org/10.1002/aenm.202103108>.
34. F. Shi, Z. Song, P. N. Ross, G. A. Somorjai, R. O. Ritchie, and K. Komvopoulos, "Failure mechanisms of single-crystal silicon electrodes in lithium-ion batteries," *Nature Communications* 7 (2016): 11886, <https://doi.org/10.1038/ncomms11886>.
35. Z. Wang, Q. Su, H. Deng, and Y. Fu, "Composition Dependence of Lithium Diffusion in Lithium Silicide: A Density Functional Theory Study," *ChemElectroChem* 2, no. 9 (2015): 1292–1297, <https://doi.org/10.1002/celec.201500201>.
36. I. Na, H. Kim, S. Kunze, et al., "Monolithic 100% Silicon Wafer Anode for All-Solid-State Batteries Achieving High Areal Capacity at Room Temperature," *ACS Energy Letters* 8, no. 4 (2023): 1936–1943, <https://doi.org/10.1021/acsenergylett.3c00496>.

37. J. Tao, J. Han, Y. Wu, et al., "Unraveling the performance decay of micro-sized silicon anodes in sulfide-based solid-state batteries," *Energy Storage Materials* 64 (2024): 103082.
38. D. L. Nelson, S. E. Sandoval, J. Pyo, et al., "Fracture Dynamics in Silicon Anode Solid-State Batteries," *ACS Energy Letters* 9, no. 12 (2024): 6085–6095, <https://doi.org/10.1021/acseenergylett.4c02800>.
39. W. Yan, Z. Mu, Z. Wang, et al., "Hard-carbon-stabilized Li-Si anodes for high-performance all-solid-state Li-ion batteries," *Nature Energy* 8 (2023): 800–813, <https://doi.org/10.1038/s41560-023-01279-8>.
40. L. Yang, H. S. Chen, H. Jiang, Y. J. Wei, and W. L. Song, "Failure mechanisms of 2D silicon film anodes: In situ observations and simulations on crack evolution," *Chemical Communications* 54, no. 32 (2018): 3997–4000, <https://doi.org/10.1039/C7CC09708E>.
41. C. Gan, X. Ye, S. Zhang, et al., "Current density induced growth of Li₁₅Si₄ alloy in silicon-carbon anodes During first lithiation process," *Journal of Energy Storage* 41 (2021): 102930.
42. W. Ai, L. Kraft, J. Sturm, A. Jossen, and B. Wu, "Electrochemical Thermal-Mechanical Modelling of Stress Inhomogeneity in Lithium-Ion Pouch Cells," *Journal of The Electrochemical Society* 167, no. 1 (2019): 013512, <https://doi.org/10.1149/2.0122001JES>.
43. M. Pharr and Z. Suo, "Variation of stress With charging rate due to strain-rate sensitivity of silicon electrodes of Li-ion batteries," *Journal of Power Sources* 270 (2014): 569–575, <https://doi.org/10.1016/j.jpowsour.2014.07.153>.
44. N. Wang and Z. Suo, "Long-distance propagation of forces in a cell," *Biochemical and Biophysical Research Communications* 328, no. 4 (2005): 1133–1138, <https://doi.org/10.1016/j.bbrc.2005.01.070>.
45. H. Aben, J. Anton, M. Öis, K. Viswanathan, S. Chandrasekar, and M. M. Chaudhri, "On the extraordinary strength of Prince Rupert's drops," *Applied Physics Letters* 109, no. 23 (2016): 231903, <https://doi.org/10.1063/1.4971339>.
46. Y. Chen, L. Li, J. Huang, et al., "Synergy of Si, Sn, and SWCNT Enables a Superior Mixed-Conductive Slurry-Coated Anode for All-Solid-State Lithium Batteries," *ACS Applied Energy Materials* 7, no. 19 (2024): 8658–8668, <https://doi.org/10.1021/acsaem.4c01615>.
47. D.-H. Kim, S.-H. Noh, Y.-C. Ha, et al., "Efficient Fabrication of High-Capacity Silicon Composite Anodes for All-Solid-State Lithium-Ion Batteries," *ACS Materials Letters* 7 (2025): 1211–1218, <https://doi.org/10.1021/acsmaterialslett.5c00068>.
48. P. Iurilli, C. Brivio, and V. Wood, "Detection of Lithium-Ion Cells' Degradation Through Deconvolution of Electrochemical Impedance Spectroscopy With Distribution of Relaxation Time," *Energy Technology* 10, no. 10 (2022): 2200547, <https://doi.org/10.1002/ente.202200547>.
49. S. Kim, J. Kim, and J. Sung, "Interfacial Degradation Electrochemistry of Micro-Silicon Anodes in Solid-State and Liquid Electrolytes," *Advanced Science* (2026): e76445, <https://doi.org/10.1002/advs.76445>.
50. F. Yu, Y. Mu, M. Han, et al., "Synergistic Integration of Carbon Nanotubes and Vertically Aligned Graphene Enables Silicon as Stable and High-Rate Anodes in Lithium-Ion Batteries," *Batteries & Supercaps* 9, no. 4 (2025): e202500648, <https://doi.org/10.1002/batt.202500648>.
51. K. Ge, Z. Wang, J. Liu, et al., "Constructing LiF-Enriched Solid Electrolyte Interface on Graphene Arrays With Abundant Edges on Microscale Si-C Anodes Toward High-Energy Lithium-Ion Batteries," *Advanced Functional Materials* 35, no. 5 (2024): 2414384, <https://doi.org/10.1002/adfm.202414384>.
52. Z. Li, R. Zhang, P. Yu, et al., "Tip Effect-Driven Charge Transport Enhancement in Silicon-Carbon Anodes for All-Solid-State Lithium-Ion Batteries," *Advanced Energy Materials* 15, no. 47 (2025): e04241, <https://doi.org/10.1002/aenm.202504241>.
53. S. Narayanan, U. Ulissi, J. S. Gibson, Y. A. Chart, R. S. Weatherup, and M. Pasta, "Effect of current density on the solid electrolyte interphase formation at the lithium|Li₆PS₅Cl interface," *Nature Communications* 13, no. 1 (2022): 7237, <https://doi.org/10.1038/s41467-022-34855-9>.
54. L. Hu, X. Zhang, P. Zhao, et al., "Gradient H-Bonding Binder Enables Stable High-Areal-Capacity Si-Based Anodes in Pouch Cells," *Advanced Materials* 33, no. 52 (2021): 2104416, <https://doi.org/10.1002/adma.202104416>.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: aenm71650-sup-0001-SuppMat.docx.

Supporting File 1: aenm71650-sup-0002-S1.gif.