

Bridging microstructure and electrochemistry: Advanced modification strategies for hard carbon anode

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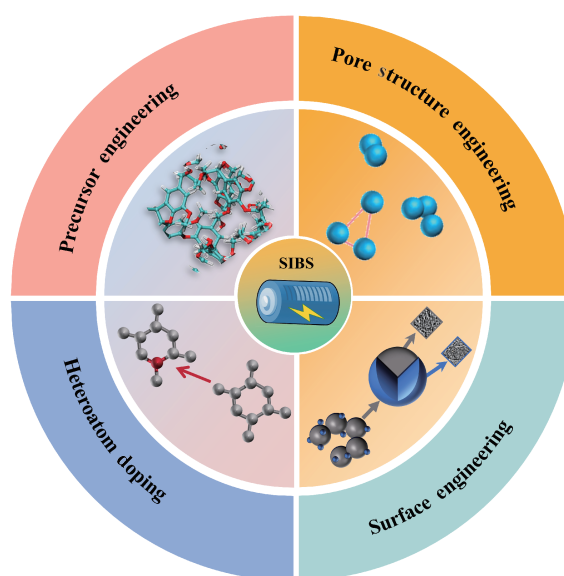


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ABSTRACT: Hard carbon is the most commercially viable anode for sodium-ion batteries, with low operating potential, high reversible capacity, abundant raw materials and low manufacturing cost. However, its intrinsic structural disorder, characterized by randomly stacked turbostratic graphene layers, nanopores and amorphous regions, has sparked long-standing debates on fundamental sodium storage mechanisms, significantly impeding rational electrode design and industrial translation. This review overviews sodium storage processes in hard carbon, analyzes synergistic contributions of intercalation, pore filling and surface adsorption, and establishes microstructural-electrochemical performance correlations. It focuses on four mainstream modification strategies: Precursor engineering, pore structure regulation, heteroatom doping and interface engineering, elucidating their enhancement mechanisms and discussing inherent limitations and trade-offs. Finally, it outlines key challenges and future directions, providing critical theoretical and technical guidance for next-generation hard carbon anodes and practical sodium-ion battery deployment.



KEYWORDS: sodium-ion batteries, hard carbon, sodium storage mechanisms, performance optimization

1 Introduction

As the global economy expands, energy security and environmental protection have become dual challenges for contemporary development. In the vigorous pursuit of the grand vision of “carbon peak” and “carbon neutrality”, reducing excessive reliance on traditional energy sources and seeking sustainable power alternatives has become an inevitable choice^{1–4}. Consequently, green energy technologies such as wind power, hydropower, and

solar energy as core pathways to achieving sustainable energy utilization have garnered widespread attention across society^{5–7}. Driven by the need to promote energy structure transformation and enhance grid stability, the energy storage industry is rapidly expanding in scale^{8–10}. Among these technologies, lithium-ion batteries (LIBs) stand as the most mature representative of electrochemical energy storage solutions^{11, 12}. Currently dominating market share, LIBs rank among the most widely applied energy storage technologies^{13, 14}.

However, the growing scarcity of lithium resources has become an industry consensus^{15–18}, primarily attributed to its extremely low crustal abundance (only about 0.0065%) and severely imbalanced geographical distribution: South America holds approximately 70% of the world's lithium reserves. Concurrently, LIBs production accounts for ~ 65% of global lithium consumption. This highly concentrated supply pattern, coupled with limited resource

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reserves, continuously elevates the strategic risk of lithium as a core raw material, making it difficult to fully meet future application demands^{19–23}. As an ideal alternative, sodium establishes its resource security advantage with a 2.83% crustal abundance and avoids issues of regional distribution imbalance. Since sodium and lithium belong to the same group in the periodic table^{24–27}, sodium-ion batteries (SIBs) exhibit strong similarities to LIBs in chemical behavior and energy storage mechanisms²⁸. During charging and discharging cycles, ions and electrons migrate in opposite directions through the internal electrolyte and external circuit connecting the cathode and anode, respectively^{20, 29–31}. Compared to lithium ions (Li^+), sodium ions (Na^+) exhibit higher ionic conductivity due to their smaller Stokes radius and weaker solvation. This characteristic results in relatively lower charge transfer resistance during charging and discharging, making SIBs more conducive to achieving high-rate fast charging. Although SIBs exhibit slightly higher internal resistance than LIBs, they generate lower instantaneous heat during short circuits, thereby reducing thermal runaway risks. Furthermore, since Na^+ do not alloy with aluminum, aluminum foil can be directly used as the anode current collector, effectively lowering manufacturing costs at the system level. Furthermore, SIBs can be transported in a 0 V state, whereas LIBs must maintain a certain charge to prevent current collector damage. This not only reduces potential fire hazards during transportation but also enhances the safety and applicability of SIBs for large-scale energy storage^{32–39}. With the rapid advancement of SIBs, their energy density and cycle stability have steadily approached and even surpassed traditional LIBs under certain application conditions, exhibiting considerable promise for next-generation large-scale energy storage^{40–45}.

SIBs impose extremely stringent requirements on anode materials, making structural design and material selection particularly critical. These materials must simultaneously deliver high energy storage capacity at low potential, excellent cycle stability, high initial Coulombic efficiency (ICE), and cost-effectiveness. Therefore, developing suitable anode materials is a pivotal step in constructing SIBs. To achieve rapid charge/discharge capability, electronic conductivity, and high sodium storage capacity, anode materials must exhibit rapid ion diffusion properties. The selected anode material must maintain minimal volume change and structural integrity over hundreds or even thousands of charge-discharge cycles, which is equally vital for electrode longevity and safety. Consequently, anode materials integrating high performance, reliability, and safety are urgently required. Compared to other anodes, carbon-based materials offer inherent advantages in conductivity, structural design, interface stability, cost-effectiveness, and environmental friendliness^{46–48}.

Among carbonaceous anode materials for SIBs, graphite features a highly ordered layered structure with an interlayer spacing of 0.334 nm and stores charge solely through interlayer intercalation. However, the relatively large ionic radius of Na^+ makes the formation of stable NaC_6 thermodynamically unfavorable, resulting in poor sodium-storage capability and limited practical applicability. Although soft carbon can adjust its interlayer spacing through high-temperature treatment, its graphitized microcrystals exhibit relatively regular arrangement, resulting in persistently small interlayer spacing and insufficient closed pores. While its rate performance is acceptable, its sodium storage specific capacity typically fails to meet high energy density requirements^{49–52}. In contrast, hard carbon is considered a more suitable anode material

for sodium-ion batteries because its unique disordered architecture, expanded interlayer spacing, and multiscale porosity, together with its superior electrical conductivity and cost-effectiveness, effectively accommodate sodium ions and enable high reversible sodium storage capacity, making it a highly promising candidate for anode applications^{53–55}. Importantly, the practical potential of hard carbon has begun to be reflected in the early-stage commercialization of sodium-ion batteries. Several prototype and commercial SIB systems employing hard carbon anodes have been demonstrated for stationary energy-storage systems, low-speed electric mobility, and compact transportation platforms, highlighting its feasibility for broader practical deployment. These emerging applications further emphasize the importance of optimizing hard carbon microstructure, ICE, and long-term cycling stability to satisfy practical performance requirements. To further optimize hard carbon performance, precursor selection plays a decisive role.

To further optimize hard carbon performance, precursor selection plays a decisive role. From the perspective of precursor selection, biomass-derived precursors are attractive due to their renewability, low cost, and inherent heteroatom content^{56, 57}, which facilitate the formation of expanded carbon frameworks after pyrolysis. Petroleum-derived precursors such as coal typically exhibit high carbon yield and low impurity content⁵⁸, enabling the construction of dense carbon structures with good cycling stability, suitable for large-scale applications. Polymer-derived precursors (e.g., phenolic resins) offer tunable molecular structures and high purity, allowing precise regulation of carbon microstructure and resulting in relatively homogeneous carbon materials with stable electrochemical behavior. Overall, the electrochemical performance of carbon anodes is strongly governed by precursor chemistry and the resulting microstructure; however, achieving a balanced optimization of capacity, stability, and safety remains a key challenge for practical SIB applications.

In recent years, numerous reviews have extensively summarized characterization methods for hard carbon microstructures^{59, 60}, pore regulation strategies, or individual modification pathways. However, most of these studies still discuss “microstructure construction” and “sodium storage behavior analysis” in isolation, lacking a systematic elucidation of the relationship between “structure construction, sodium storage mechanism, and enhancement of electrochemical performance”⁶¹. Concurrently, the mechanism governing sodium storage within the low potential plateau region is still a matter of ongoing debate. The relative contributions and evolutionary processes of multiple sodium storage mechanisms, including adsorption, intercalation, and pore filling, under different microstructures are not yet fully understood. Addressing these gaps, this review systematically summarizes recent research progress on hard carbon anodes in SIBs, concentrating on: (1) hard carbon’s performance benefits and structural features; (2) the intrinsic synergistic relationship between sodium storage mechanisms and microstructural evolution; (3) comprehensive optimization strategies and their mechanisms based on precursor control, pore structure design, heteroatom doping, and interfacial engineering. Furthermore, it analyzes the key bottlenecks hindering the achievement of excellent capacity, ICE, and cycle life in hard carbon anode. It concludes with a forward-looking discussion on future development paths, with the goal of offering engineering direction and theoretical assistance for building high-performance, affordable, and sustainable anode materials for SIBs.

2 Structural characteristics

As a common non-graphitizable carbon, hard carbon differs from soft carbon in that it usually starts at 800–2000 °C when thermosetting precursors carbonize, forming an amorphous carbon structure. During the early stages of carbonization, sp^3 hybridization creates a three-dimensional cross-linked structure⁶², which impedes the growth of carbon layers. Consequently, even when heated to 3000 °C, it remains difficult to convert into graphite^{63, 64}. In addition, its structure at the molecular scale is considerably more intricate than the long-range ordered layered configuration characteristic of graphite. This class of materials exhibits high defect density, disordered domains, and tunable multi-scale pore structures. Notably, its unique microstructure is closely linked to sodium storage behavior: surface adsorption, interactions between defects and functional groups, intercalation between disordered carbon layers, and pore filling processes collectively constitute the primary mechanisms contributing to Na^+ storage in hard carbon systems, significantly determining their electrochemical performance.

As shown in Fig. 1, the pyrolysis process of hard carbon is typically separated into three phases: the pyrolysis stage below 1000 °C, the carbonization stage between 1000 and 2000 °C, and the graphitization stage above 2000 °C⁶⁵. Aromatization and condensation processes cause the precursor to progressively change into amorphous carbon and nanographite microcrystals during the pyrolysis stage. Studies indicate^{66, 67} that approximately 600 °C represents a critical transition temperature: prior to this point, the formed graphite microcrystals are relatively dispersed and exhibit poor conductivity. Once temperatures exceed this threshold, the microcrystals continue to grow and interconnect, leading to enhanced conductivity. As temperatures further rise above 1000 °C,

the carbonization stage commences, characterized by the continuous evolution and cross-linking of the graphite interlayer structure, alongside the gradual collapse of open pores structures into closed pores. When processing temperatures exceed 2000 °C, graphite domains expand further, but excessively enlarged ordered regions become unfavorable for Na^+ storage. Considering structural evolution, electrochemical behavior, and adaptability, the optimal preparation temperature range for hard carbon materials typically lies between 1000 and 1600 °C. Within this characteristic carbonization temperature window, ideal hard carbon anode materials can be obtained^{68–71}.

3 Electrochemical sodium storage mechanism

Benefiting from the unique microstructure within hard carbon, including disordered graphite layers, abundant defects, and porous structures, it exhibits a characteristic sodium storage profile, featuring the coexistence of a high potential sloping region alongside a low potential plateau region. Achieving performance tunability and structural design requires a thorough understanding of the sodium storage processes controlling various potential regions. Based on systematic electrochemical analysis, *in situ/ex situ* characterization, and theoretical simulations in recent years, various explanations have been proposed for the high potential sloping region and the low potential plateau region observed in the charge-discharge profiles of hard carbon. Proposed sodium storage mechanisms can be summarized into the following four types^{72–75} (as shown in Fig. 2): insertion-adsorption model, adsorption-intercalation model, adsorption-filling model, and three-stage model⁷⁶.

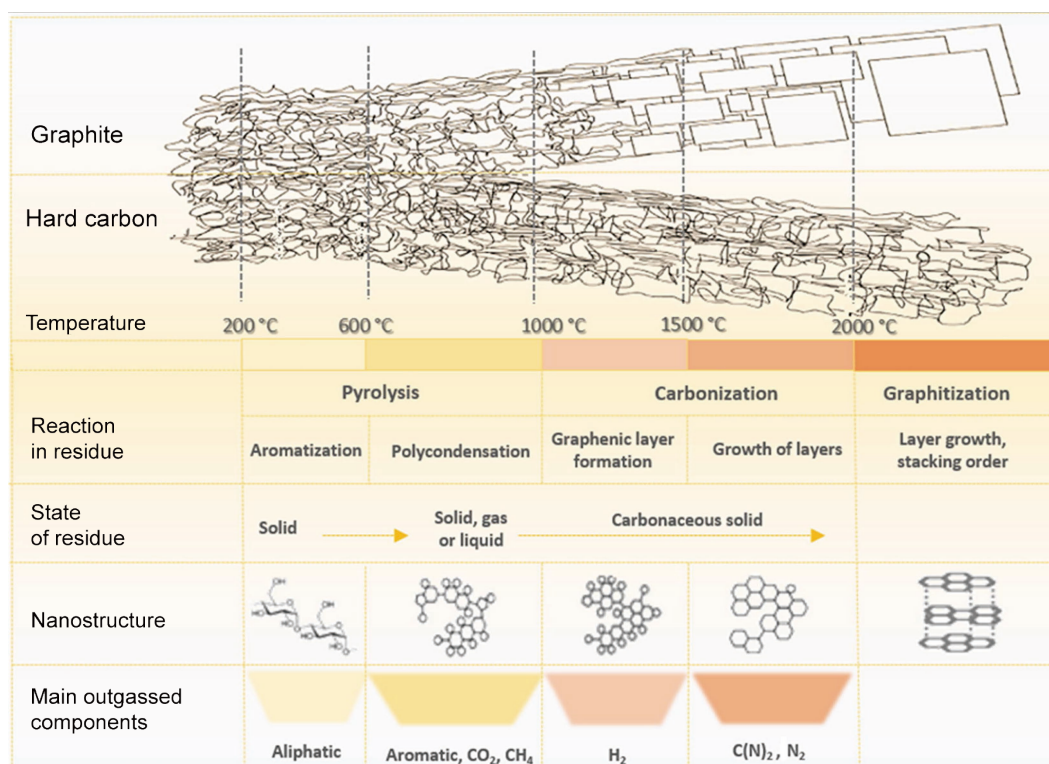


Fig. 1. The carbonization process as a function of temperature. Reproduced with permission from Ref.⁶³, © Elsevier Ltd 2018.

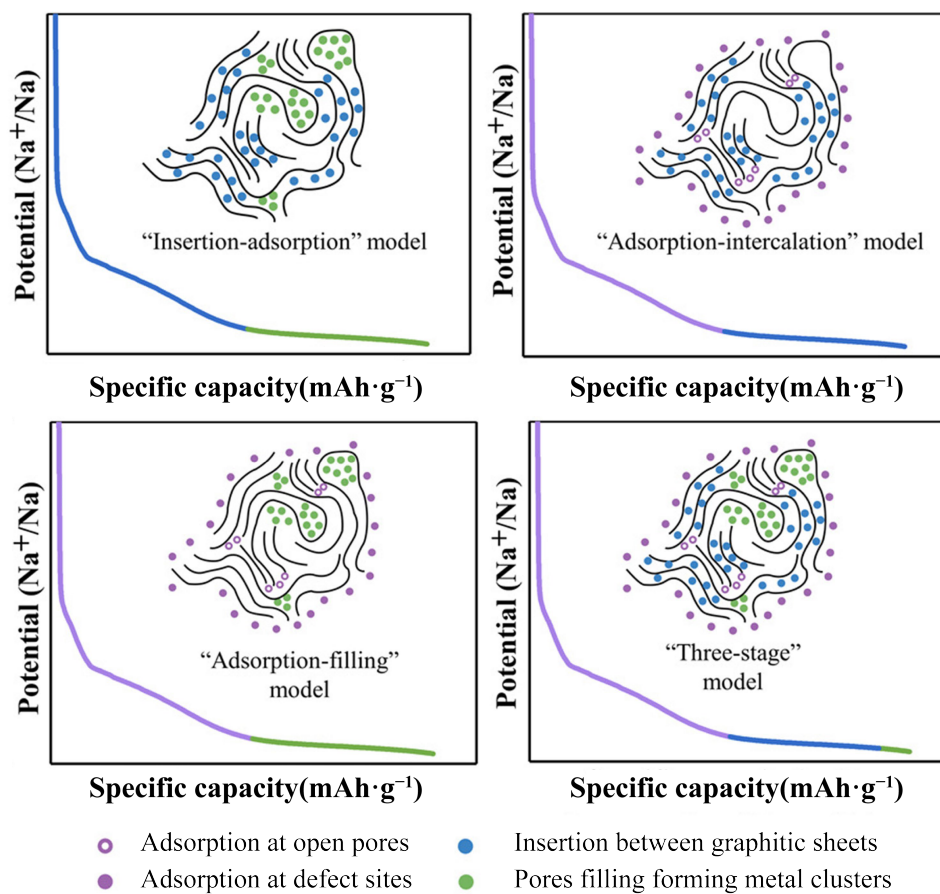


Fig. 2. The proposed sodium storage models. Reproduced with permission from Ref.⁷⁶, © Chen X. Y. *et al.* 2022.

3.1 Insertion-adsorption model

The sodium storage mechanism was initially derived from the “house of cards” model proposed by Stevens and Dahn *et al.*⁷⁷ in 2000, which led to the formulation of the “insertion-adsorption” theory. The theory points out that the high potential slope region is attributed to the intercalation of Na⁺ between the graphite layers, while the low potential plateau region is derived from the adsorption and filling of ions inside the porous structure. This mechanism has been strongly confirmed by precise characterization methods such as wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS)⁷⁸. Since then, Komaba *et al.*⁷⁹ used *ex situ* X-ray diffraction (XRD) and SAXS tests to further verify the intercalation-adsorption model. They observed that although hard carbon exhibited comparable reversible storage capacities in sodium- and lithium-based electrolyte systems, the corresponding voltage response profiles differed markedly. Specifically, Li⁺ storage was characterized by a sloping capacity contribution over a broad potential range, whereas Na⁺ displayed a more pronounced low-voltage plateau feature. These distinctions suggest that sodium and lithium follow different storage pathways within the hard-carbon framework, reflecting fundamental differences in their interaction mechanisms with the carbon microstructure (Fig. 3a). As shown in Fig. 3b, when the battery discharge is reduced to 0.2 V, the (002) diffraction peak shifts to a small angle, which means that the intercalation of Na⁺ leads to the expansion of the carbon layer spacing. Subsequently, as the potential rises to 2.0 V during the charging process, the diffraction peak can be accurately reset, which fully proves that the intercalation and extraction behavior of Na⁺

between the carbon layers has excellent reversibility in the slope potential region.

Moreover, as shown in Fig. 3c, a comparative investigation of Na⁺ and Li⁺ insertion in hard carbon reveals that, in the sloping region, both systems exhibit a gradual increase in interlayer spacing with increasing capacity, indicating that this stage is primarily governed by interlayer insertion. Owing to the larger ionic radius of Na⁺, a more pronounced lattice expansion is observed compared with Li⁺. In contrast, the evolution behavior of Li⁺ is consistent with that of lithium-graphite intercalation compounds. In the near-0 V plateau region, the interlayer spacing remains essentially unchanged, suggesting that the capacity contribution in this stage is no longer associated with further lattice expansion, thereby implying that a distinct insertion/storage mechanism operates in the low-voltage region. From the SAXS results of Fig. 3d, it is observed that as the potential decreases from 0.2 V to 0 V, the scattering intensity in the range of 0.03–0.07 Å⁻¹ diminishes, suggesting a reduction in electron density between the carbon framework and the pores. This variation is ascribed to the reversible insertion of sodium into the nanoporous structure.

3.2 Adsorption-intercalation model

According to the “adsorption-intercalation” mechanism, the total sodium capacity of hard carbon comprises two distinct contributions, as depicted in Fig. 4a: first, the adsorption of Na⁺ at defect sites within the high potential slope region; and second, the insertion of Na⁺ into turbostratic carbon layers in the low potential plateau region.

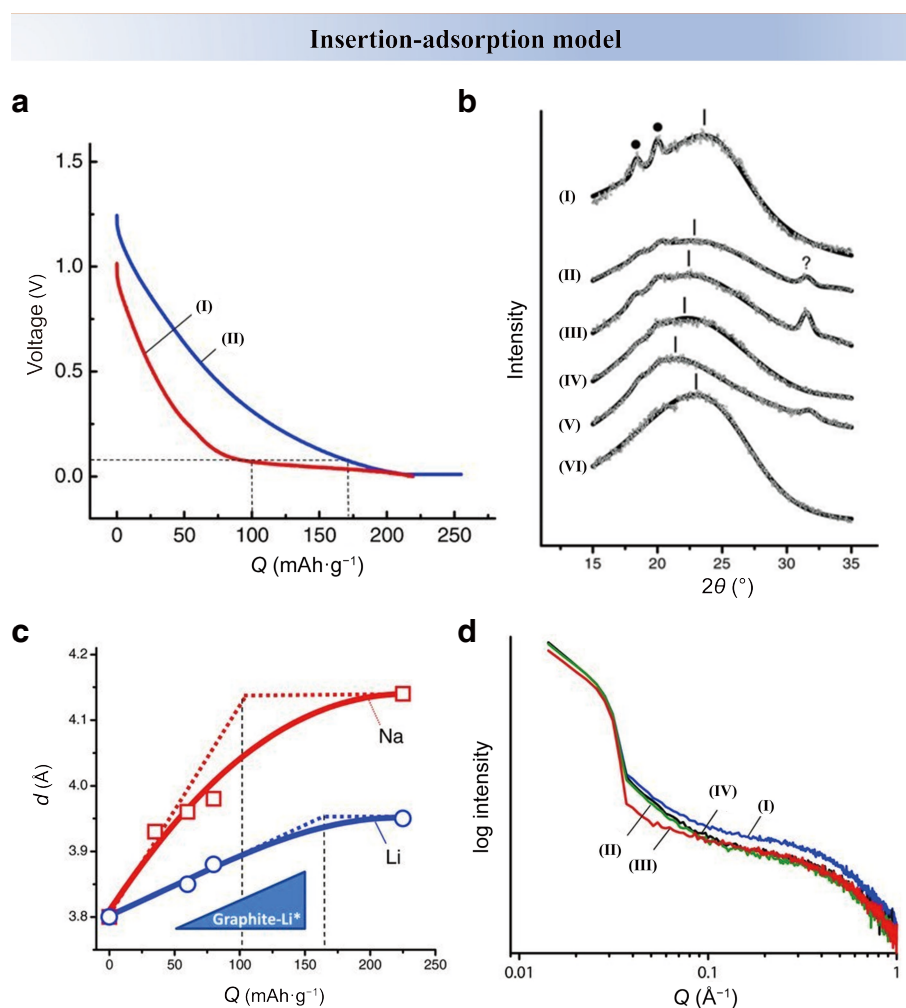


Fig. 3. Insertion-adsorption model of anode in Na and Li-based system. **a**, Second-cycle chronopotentiograms of hard-carbon electrodes in Na and Li-based electrolyte systems; **b**, *Ex situ* XRD patterns; **c**, Dependence of interlayer spacing estimated from XRD data on insertion capacity for hard-carbon electrodes tested in Na and Li cell; **d**, *Ex situ* SAXS patterns. Reproduced with permission from Ref.⁷⁹, © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2011.

The prototype of this mechanism originated from Cao's⁸⁰ study on polyaniline-based hollow carbon nanowires, whose core insight posits that Na⁺ adsorption and intercalation correspond to the slope region and plateau region of the potential curve, respectively. Concurrently, they theoretically analyzed the energy relationship between Na⁺ intercalation behavior and carbon layer spacing (Fig. 4b). The results indicate that when carbon materials exhibit a relatively regular layered structure with interplanar spacing slightly exceeding 0.37 nm, Na⁺ intercalation similar to Li⁺ formation of LiC₆ in graphite can be achieved. Qiu *et al.*⁸¹ synthesized a series of structurally controllable nanostructured hard carbon materials and further validated the “adsorption-intercalation” model for Na⁺ storage through advanced techniques such as *in situ* XRD and simulations.

Fig. 4c shows the *in situ* XRD changes of this hard carbon material during its first discharge-charge cycle. During Na⁺ intercalation into hard carbon, Na⁺ initially adsorbs at defect sites, resulting in a pronounced slope in the early potential curve. As the reaction progresses, Na⁺ subsequently inserts into graphite interlayers with suitable interlayer spacing, yielding a flat plateau region at low potential. This provides robust experimental support for the notion that “the slope region is primarily attributed to adsorption”, thereby enhancing the scientific understanding of

sodium storage mechanisms in hard carbon. Additionally, Zhao *et al.*⁸² successfully synthesized spherical hard carbon with pseudographitic characteristics using dichloromethane and benzidine as precursors via a specific process. To investigate its electrochemical reaction mechanism, *in situ* Raman spectroscopy was employed to monitor the microstructural evolution of the material during charging and discharging in real time. As shown in Fig. 4d, the G peak exhibits a distinct shift within the 0.2–0 V potential range, providing direct evidence for Na⁺ intercalation between the pseudographitic layers.

In contrast to the “insertion-adsorption” model, the “adsorption-intercalation” framework provides a more effective interpretation of Na⁺ storage differences across various potential regions, while also incorporating the influence of structural disorder and defect sites on the storage behavior of hard carbon. Nevertheless, the boundary between the “adsorption” and “intercalation” processes remains poorly defined. This is particularly evident in the intermediate potential region, where Na⁺ storage is likely governed by the concurrent contribution of both mechanisms. As a result, the interpretation of this transition zone often depends on specific experimental observations, which may restrict the model's broader applicability. In addition, its universality is further affected by the type of hard carbon and the synthesis route employed, as notable

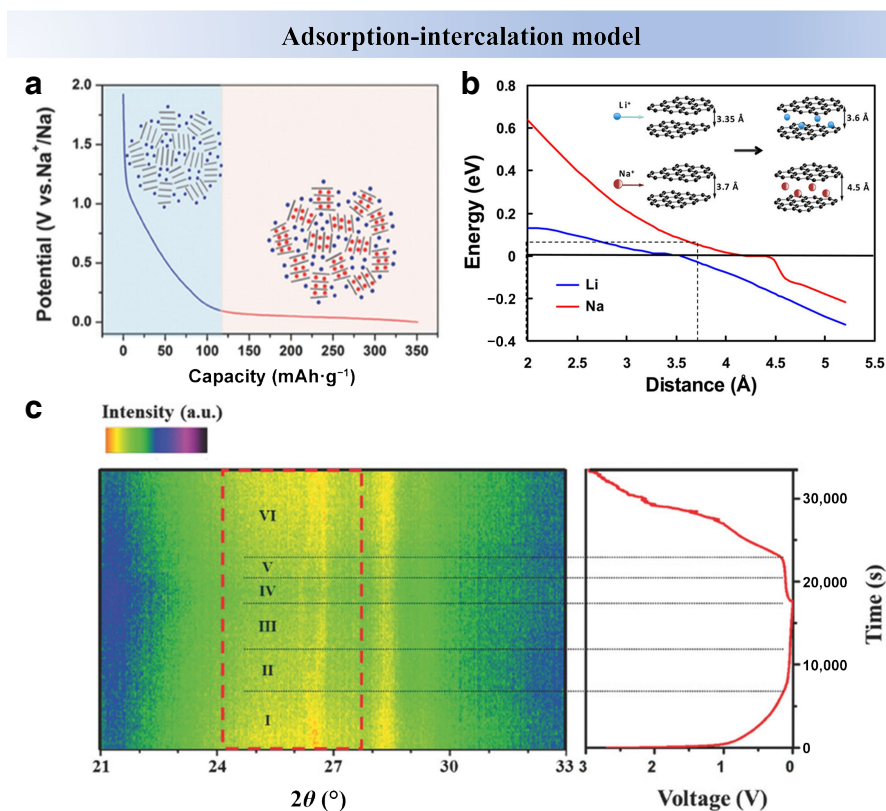


Fig. 4. Adsorption-intercalation model in Na-ion battery. **a**, Schematic illustration of the mechanisms: “adsorption-intercalation” mechanism, Reproduced with permission from Ref.⁸¹, © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017; **b**, Theoretical energy cost for Na⁺ and Li⁺ intercalation into carbon as a function of carbon interlayer distance, Reproduced with permission from Ref.⁸⁰, © American Chemical Society 2012; **c**, *In situ* XRD mapping during the first charge-discharge cycle, Reproduced with permission from Ref.⁸¹, © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017.

variations in sodium storage characteristics are frequently observed among different samples.

3.3 Adsorption-filling model

According to the “adsorption-filling” model, the sodium storage capacity of hard carbon originates from two stages: first, in the high potential slope region, Na⁺ is adsorbed by surface defects and disordered regions; as the potential decreases, Na⁺ further fills the pores within the hard carbon, thereby contributing capacity in the plateau region.

As early as 2016, Zhang *et al.*⁸³ prepared carbon nanofibers (CNFs) *via* electrospinning and proposed an “adsorption-filling” sodium storage mechanism by controlling surface and pore structure characteristics through carbonization at different temperatures. They deliberately triggered sodium deposition by discharging the electrode below 0 V. As shown in Fig. 5a, when the potential approached -0.015 V, the potential curve exhibited a characteristic “V”-shaped profile, typically regarded as a signature of sodium nucleation and growth. Concurrently, *in situ* XRD measurements detected a gradually intensifying weak diffraction peak at $2\theta \sim 29^\circ$, corresponding to the formation of metallic sodium. Combining these results, the capacitive contribution in the low potential region neither originates from Na⁺ intercalation nor resembles metallic sodium deposition. Furthermore, the pronounced low potential plateau exclusively appears in samples carbonized above 1000 °C, which exhibit abundant mesoporous structures whose electrochemical behavior strongly aligns with the “pore-filling” model. Subsequently, Li *et al.*⁸⁴ prepared structurally

uniform hard carbon microtubes using cotton as a precursor and investigated their structural evolution during discharge. *Ex situ* transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) revealed no significant interlayer intercalation during sodium intercalation: disordered carbon features persisted before and after discharge, with essentially unchanged interlayer spacing. In contrast, after sodium intercalation, the edges of carbon layers and nano pore regions gradually became blurred (Fig. 5b), indicating sodium enrichment at these structural sites. Fig. 5c displays *ex situ* XPS spectra of electrodes under different states. As the discharge potential decreased from 0.12 V to 0 V, the XPS signal intensity of Na 1s increased, and its binding energy progressively shifted toward the characteristic value of metallic sodium, reflecting the evolution of the sodium storage state. Based on these results, the sodium storage behavior of hard carbon can be divided into two stages (Fig. 5d): in the slope region above 0.12 V, sodium adsorption primarily occurs on the surface; whereas in the low potential plateau region near 0 V, filling of nanopores dominates.

The “adsorption-filling” model provides a crucial theoretical framework for elucidating the sodium storage mechanism in hard carbon materials, yet it exhibits certain limitations in practical applications. First, this model primarily focuses on the macroscopic description of physical adsorption and pore-filling processes, tending toward excessive simplification when applied to complex systems. Actual sodium storage behavior is profoundly influenced by the interplay of multiple factors, including surface chemistry, diverse pore structures, and ion migration dynamics. A purely

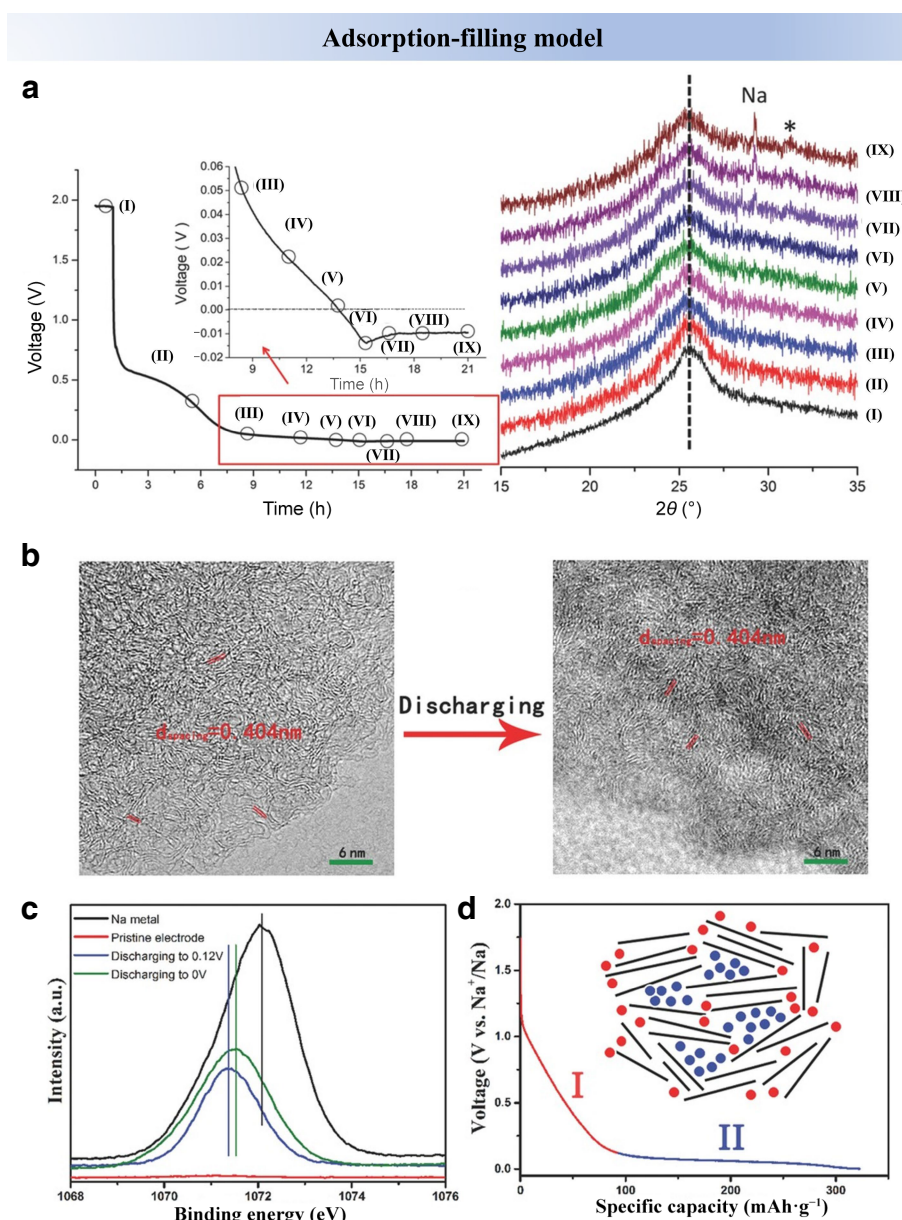


Fig. 5. Adsorption-filling model in Na-ion battery. **a**, XRD pattern recorded *in situ* on the first discharge, Reproduced with permission from Ref.⁸³, © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2015; **b**, *Ex situ* characterization: TEM images of the pristine sample and the sample discharged to 0 V; **c**, *Ex situ* XPS Na 1s spectrum profiles; **d**, Schematic of sodium storage mechanism, Reproduced with permission from Ref.⁸⁴, © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2016.

physical model struggles to comprehensively explain these underlying mechanisms. Second, hard carbon materials synthesized from different precursors and via distinct processes exhibit significant variations in microstructure. This leads to differing specific adsorption and filling mechanisms, thereby limiting the model's universality. Therefore, existing theoretical frameworks require validation and refinement through integration with more diverse experimental data and advanced characterization techniques. While the “adsorption-pore filling” model serves as a crucial theoretical starting point for understanding sodium storage in hard carbon, its applicability under complex operating conditions necessitates further exploration and refinement.

3.4 Three-stage model

According to the “three-stage” approach, adsorption, intercalation, and filling all work together to define hard carbon's capacity:

initially, Na⁺ is electrostatically driven to attach to surface defects; subsequently, it undergoes restricted interlayer intercalation in the middle stage; finally, Na⁺ enters the micropores or graphitic structure of hard carbon in a filling form, achieving high sodium storage capacity.

In 2018, Jin *et al.*⁸⁵ proposed a three-stage sodium storage model Galvanostatic Intermittent Titration Technique (GITT), *Ex situ* XRD, and atomic pair distribution function (PDF) analysis. This model clearly distinguishes the three mechanisms: “adsorption”, “intercalation”, and “filling”-based on structural changes and potential ranges (Fig. 6a).

To further elucidate the sodium storage behavior in hard carbon, *ex situ* PDF analysis was conducted at various discharge states (Fig. 6c). The corresponding PDF curves are presented in Fig. 6d, and the structural evolution between adjacent states was tracked using differential PDF (D-PDF) analysis (Fig. 6e). The results

Three-stage model

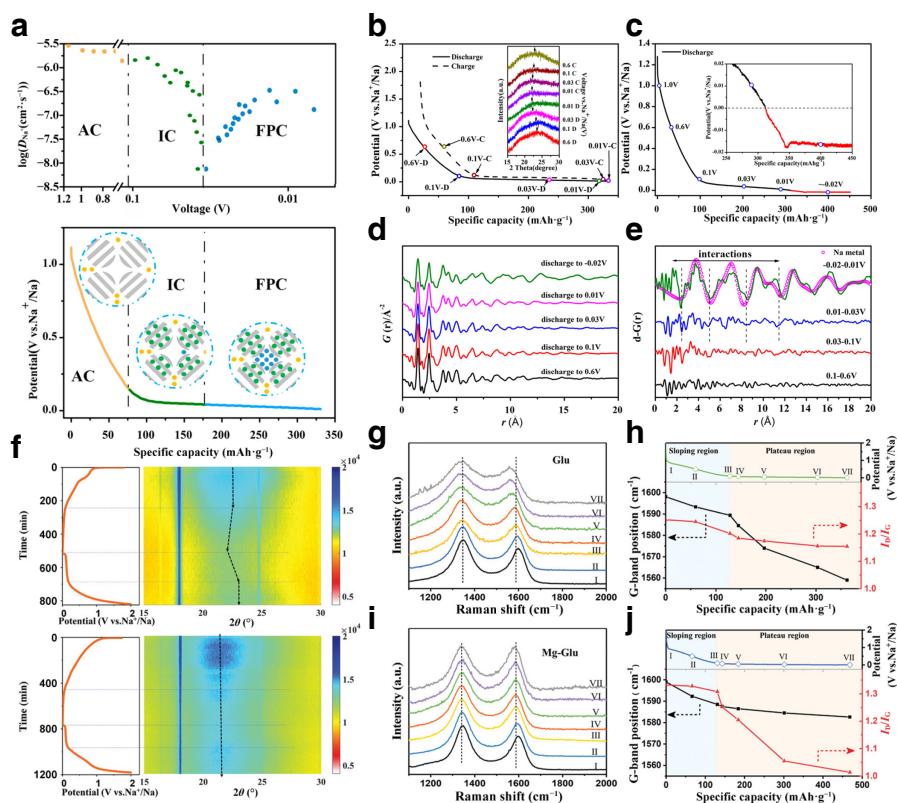


Fig. 6. Three-stage model. **a**, Na^+ diffusion coefficients and schematic illustration of the mechanisms for Na^+ storage in hard carbon: absorption capacity (AC), interlayer intercalation capacity (IC), and filling-pore capacity (FPC); **b**, *Ex situ* XRD mapping during the first discharge-charge at 20 mA g^{-1} ; **c**, Electrodes discharge at various stages; **d**, PDF data for electrodes discharging at the different stages; **e**, D-PDFs at various states of discharge. Reproduced with permission from Ref.⁸⁵, © American Chemical Society 2018; **f**, The operando XRD mappings during the initial discharge-charge process; **g**, **h**, *Ex situ* Raman spectra (g) and the evolution (h) of the G-band position and I_D/I_G as a function of discharge capacity; **i**, **j**, *Ex situ* Raman spectra (i) and the evolution (j) of the G-band position and I_D/I_G as a function of discharge capacity. Reproduced with permission from Ref.⁸⁶, © Wiley-VCH GmbH 2022.

indicate that the D-PDF between 0.6 V and 0.1 V exhibits negligible variation, suggesting that sodium storage in this potential region is dominated by adsorption, with minimal structural perturbation to the hard carbon framework. In contrast, within the range of 0.1–0.03 V, slight changes emerge in the low r region ($r < 5 \text{ Å}$). Combined with the *in situ* XRD results (Fig. 6b), these features can be attributed to local interlayer spacing adjustments associated with Na intercalation into turbostratic carbon nanodomains. When the potential further decreases to 0.03–0.01 V, the D-PDF displays pronounced variations extending to larger r values ($r < 10 \text{ Å}$), which resemble those observed between 0.01 and –0.02 V. This behavior implies the presence of Na clustering within confined environments, thereby substantiating the rationality of a three-stage sodium storage mechanism. Specifically, the high potential slope capacity primarily originates from the physical and/or chemical adsorption of Na^+ at surface sites and edge defects of hard carbon, where the storage contribution is highly sensitive to surface disorder, defect density, and functional group distribution, indicating that the sloping region is intrinsically governed by surface chemistry. Subsequently, during the early stage of the mid to low potential plateau, Na^+ intercalates into the interlayer gaps of locally ordered graphitic microdomains. The onset and magnitude of this contribution are closely related to microcrystallite length, stacking orientation, and local structural order, reflecting a transition from surface-dominated behavior to bulk structural

participation. Finally, in the ultralow potential region (0.03–0.01 V), sodium storage is attributed to Na^+ filling and clustering within closed or semi closed nanopores, a process constrained by the confined spatial environment induced by the surrounding carbon architecture.

In 2022, Cao *et al.*⁸⁶ reported the fabrication of two hard carbon materials featuring distinctly different microstructural characteristics, one primarily composed of pseudo-graphitic domains and the other dominated by microporous architectures. By jointly employing XRD, *in situ* Raman spectroscopy, electron paramagnetic resonance (EPR), and theoretical calculations, the authors systematically correlated microstructural features with sodium storage behavior, thereby providing further experimental support for the hybrid adsorption-intercalation-filling storage mechanism. As shown in Fig. 6f, the *in situ* XRD patterns obtained during the first sodiation-desodiation cycle are displayed together with the corresponding electrochemical profiles. For the glu-derived hard carbon, progressive sodiation leads to a gradual attenuation of the (002) reflection intensity, which is largely restored upon desodiation. This reversible intensity modulation persists across both the sloping and plateau regions, suggesting that Na^+ intercalation into the carbon layers induces transient structural disorder. Notably, during discharge within the plateau region, the (002) peak shifts toward lower diffraction angles, indicative of interlayer expansion, while the peak position reverses during

sodium extraction, consistent with interlayer contraction. In contrast, the Mg-Glu sample (Fig. 6f, bottom) exhibits comparable reversible changes in (002) peak intensity without an obvious peak shift, implying that Na^+ intercalation remains operative but proceeds without pronounced interlayer spacing variation, likely due to the reduced proportion of pseudo-graphitic domains in this material.

Raman spectroscopy was further employed to complement the XRD analysis (Figs. 6g and 6i). As revealed by the spectra, the intercalation or adsorption of alkali metal ions weakens C–C bonding interactions, manifested by a redshift of the G band, whereas ion adsorption at defect sites and within pores suppresses the vibrational modes of sp^2 -bonded carbon rings, leading to an attenuation of the D-band intensity. For the Glu electrode, progressive discharge induces a gradual redshift of the G band in the sloping region, suggesting that Na^+ storage is predominantly associated with adsorption in regions characterized by relatively large interlayer spacing. Upon entering the plateau region, the G band undergoes a more pronounced redshift accompanied by spectral broadening. In conjunction with the reference system, this behavior is attributed to Na^+ intercalation between carbon layers. Concurrently, a decrease in the I_D/I_G ratio is observed (Fig. 6h), reflecting the involvement of partial defect-related adsorption and limited pore filling, although their overall contribution remains minor. By comparison, the Mg-Glu electrode exhibits a G-band redshift and a reduced I_D/I_G ratio within the sloping region (Fig. 6j), indicative of sodium adsorption at defect sites. In the plateau region, a substantial decrease in I_D/I_G is detected while the G-band position shows only marginal variation, implying that sodium storage is primarily governed by adsorption and pore filling rather than interlayer intercalation.

The “three-stage” model offers a unified conceptual framework for interpreting sodium storage in hard carbon and effectively captures the intrinsic multistep nature of Na^+ uptake. By integrating surface adsorption, interlayer intercalation, and pore filling, this model highlights the coupled roles of surface chemistry, interlayer galleries, and internal porosity in governing sodium storage behavior. Nevertheless, several limitations remain when extending this model to practical systems. In particular, it does not fully account for the pronounced microstructural heterogeneity among hard carbon materials derived from different precursors or processing routes, nor does it explicitly incorporate the complex influences arising from electrolyte composition and electrode–electrolyte interfacial chemistry. Consequently, although this framework significantly advances the mechanistic understanding of sodium storage in hard carbon, further validation and refinement are required through the integration of advanced *in situ/operando* characterization techniques and complementary theoretical simulations.

4 Optimization strategies

Although hard carbon anodes exhibit considerable potential for Na^+ storage, their practical application is still restricted by several intrinsic limitations, including relatively low ICE, sluggish sodium-ion transport kinetics, and the trade-off between capacity and rate performance. To address these issues, various optimization strategies have been developed, mainly including precursor engineering, pore structure regulation, heteroatom doping, and surface modification. These approaches primarily focus on regulating the microstructure, electronic properties, and interfacial

characteristics of hard carbon, thereby improving sodium-storage behavior.

Precursor pretreatment influences the carbonization process by adjusting the composition and molecular structure of carbon sources, thereby affecting the formation of the final carbon framework. Pore structure engineering mainly aims to optimize pore distribution and interlayer spacing, which can improve ion transport pathways while providing additional sodium-storage sites. Heteroatom doping modifies the local electronic environment and introduces defect sites, which may improve electrical conductivity and provide additional active sites for sodium storage. Surface modification mainly regulates the electrode/electrolyte interface, contributing to improved interfacial compatibility and more stable solid electrolyte interphase (SEI) formation. Through the combined regulation of bulk structure and surface characteristics, these strategies can effectively optimize the physicochemical properties of hard carbon and improve its electrochemical performance. Such multidimensional structural design provides an important basis for enhancing reversible capacity, cycling stability, and rate capability, while offering useful guidance for the rational design of hard carbon anodes for sodium-ion batteries.

4.1 Precursor pretreatment

Given that the sodium storage behavior of hard carbon is highly dependent on its microstructure, which is largely inherited from the molecular configuration of the precursor and its carbonization pathway, precursor optimization represents the most fundamental means for enabling mechanism-oriented hard carbon design. For instance, molecular level engineering of precursor materials prior to carbonization, such as crosslinking treatments, hydrothermal processing, or chemically induced modifications: can predefine the orientation and crosslinking degree of carbon layers. In this way, the advantages introduced by precursor modification are translated from the surface into the bulk structure as intrinsic structural “genes”, thereby facilitating the synergistic coupling of high ICE, superior rate capability, and long-term cycling stability.

4.1.1 Acid washing

To elucidate the influence of acid treatment on the microstructural characteristics and electrochemical behavior of carbon materials, Huo *et al.*⁸⁷ employed hydrochloric acid to modify the precursor. This modification strategy enabled a dual regulation of the microstructure. On the one hand, the enlarged interlayer spacing provided a greater abundance of active sites for sodium storage; on the other hand, the specific surface area of the material was effectively reduced. As a result, the modified hard carbon anode delivered a high capacity of $382.3 \text{ mAh}\cdot\text{g}^{-1}$, markedly exceeding that of the untreated counterpart ($319.6 \text{ mAh}\cdot\text{g}^{-1}$). Meanwhile, the ICE increased from 62% to 67%, accompanied by a pronounced improvement in cycling stability. Tian *et al.*⁸⁸ effectively suppressed side reactions through acid-washing pretreatment, thereby achieving an improvement in sodium storage capacity. Comparative results of HC-1, HC-2, and HC-3 indicate that the sodium storage performance is progressively enhanced with increasing degrees of structural regulation (HC-1, HC-2, and HC-3 correspond to the optimal samples obtained from the orthogonal, single-factor, and response surface experiments, respectively). At a current density of $0.03 \text{ A}\cdot\text{g}^{-1}$, the reversible specific capacities increase sequentially (208.5 , 231.8 , and $245.1 \text{ mAh}\cdot\text{g}^{-1}$), while the ICE rises from 57.3% to 67%, suggesting a partial suppression of interfacial side reactions. Analysis of the galvanostatic charge-

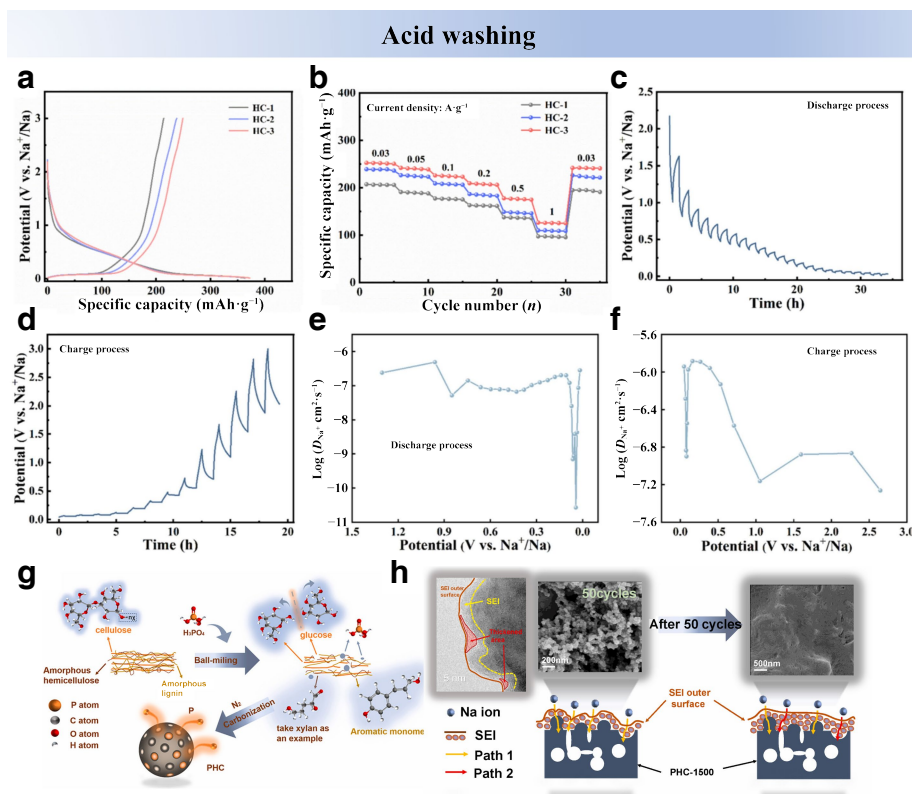


Fig. 7. Electrochemical performance and behavior of acid washing based hard carbon in Na-ion battery. **a, b**, Initial galvanostatic charge-discharge profiles (0.03 A·g⁻¹) and rate performance (0.03–1 A·g⁻¹) of HC-1, HC-2, and HC-3; **c, d**, GITT profiles of hard carbon; **e, f**, Corresponding Na⁺ diffusion coefficients derived from GITT analysis, Reproduced with permission from Ref.⁸⁸, © Elsevier Ltd 2025; **g**, Preparation principle of hard carbon; **h**, The SEI film formed during the first 50 cycle and the SEI film after 50 cycles, Reproduced with permission from Ref.⁸⁹, © Elsevier Ltd 2025.

discharge profiles (Fig. 7a) reveals that the optimized samples exhibit an increasingly extended low-voltage plateau, accompanied by a higher capacity contribution, indicating more effective utilization of sodium storage active sites. In the rate performance tests (Fig. 7b), when the current density is increased from 0.03 to 1 A·g⁻¹, HC-3 retains 50.1% of its capacity and delivers a reversible capacity of 126.4 mAh·g⁻¹. Upon returning to a lower current density, its capacity recovers to approximately 240 mAh·g⁻¹, demonstrating good structural robustness and electrochemical reversibility. Furthermore, GITT measurements and the corresponding diffusion coefficient analysis (Figs. 7c–7f) indicate that structural optimization facilitates faster Na⁺ diffusion kinetics, thereby enhancing the rate capability of the electrode.

Beyond impurity removal, acid washing also plays a critical role in regulating the precursor structure. In a similar vein, to elucidate the intrinsic relationship between biomass structural modulation and sodium storage performance, Zhan *et al.*⁸⁹ employed walnut shells as the precursor and developed a porous hard carbon featuring high capacity, a broad potential plateau, and excellent stability through phosphoric acid treatment. As illustrated in Fig. 7g, phosphoric acid exerts a dual function in this system, serving simultaneously as a dopant and a structural modifier. Specifically, it facilitates the disruption of microcrystalline cellulose domains and effectively etches the compact configurations of lignin and hemicellulose, thereby promoting the formation of a larger number of closed pores with increased dimensions. Experimental results indicate that the sample pyrolyzed at 1500 °C delivers an exceptionally high capacity of 422.0 mAh·g⁻¹ at 20 mA·g⁻¹, with the plateau region contributing as much as 322.0 mAh·g⁻¹. Owing to

the formation of a stable SEI film (Fig. 7h), the ICE reaches a remarkable 93.99%. Notably, the plateau capacity of the phosphoric-acid-assisted hard carbon is enhanced by 192 mAh·g⁻¹ compared with that of the directly carbonized counterpart, corresponding to an almost twofold improvement. Furthermore, when paired with a Na₃V₂(PO₄)₃ cathode in a full-cell configuration, the device achieves an energy density of 190.3 Wh·kg⁻¹ and retains 88.6% of its capacity after 350 cycles at a 1C rate.

4.1.2 Alkali washing

By proposing a two-stage regulation strategy centered on “component-directed removal followed by chemical etching”, Zhao *et al.*⁹⁰ achieved precise control over the evolution of pore architecture and nanostructure in hard carbon, thereby markedly enhancing its sodium storage capability. As illustrated in Fig. 8a, the strategy first constructs size-tunable core closed pores through the removal of soluble alkaline components, after which chemical etching is carried out using the residual *in situ* alkaline species to further refine the pore structure. The resulting hard carbon simultaneously features short-range disordered graphitic domains, which are favorable for Na⁺ intercalation/deintercalation kinetics, together with abundant micropores and closed pores. These characteristics give rise to structural units with appropriate pore sizes and ultrathin carbon layer encapsulation, leading to a substantial increase in the number of sodium storage (active sites). Consequently, the optimized material exhibits outstanding electrochemical and kinetic performance, delivering a reversible capacity of 389.6 mAh·g⁻¹, an ICE of 90.7%, and a high plateau capacity of 261.5 mAh·g⁻¹. Notably, even at a high areal mass

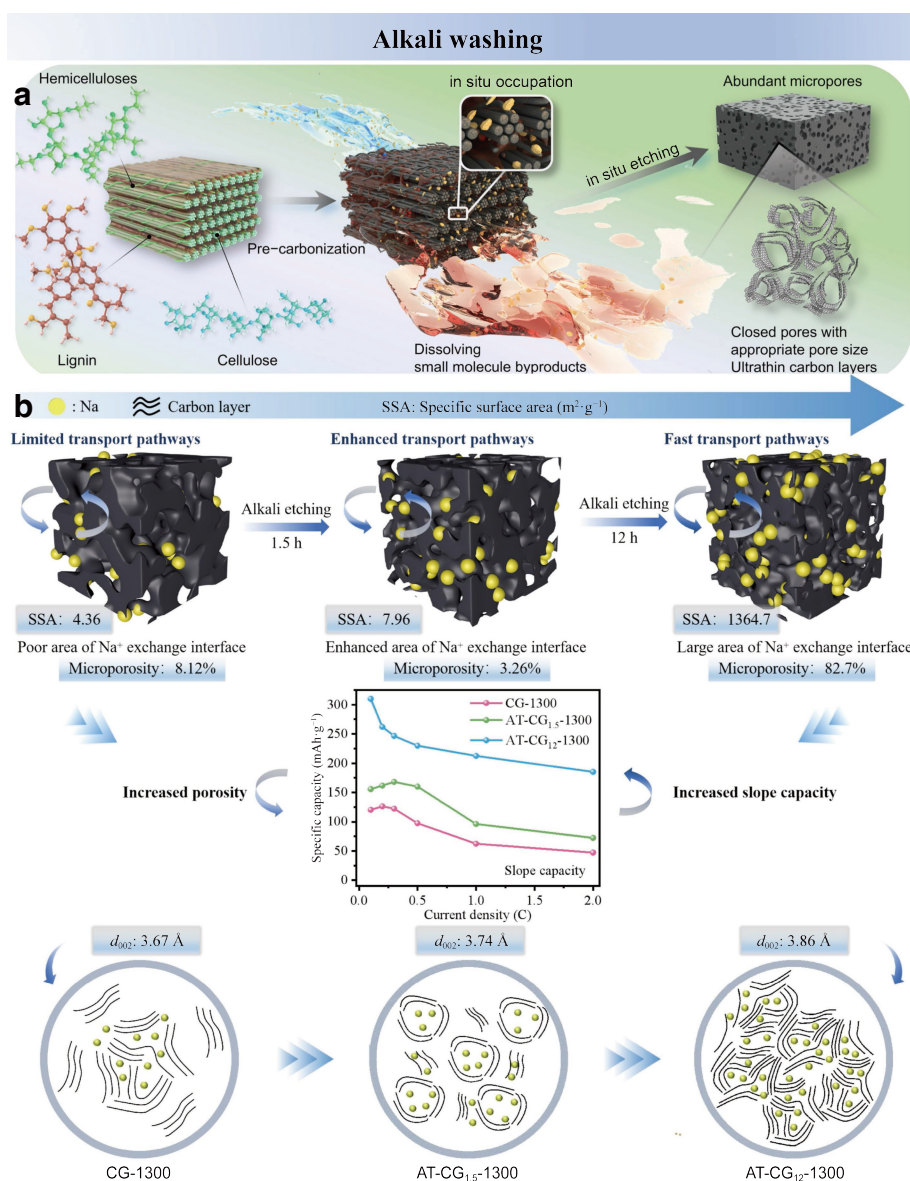


Fig. 8. Electrochemical performance and behavior of alkali washing based hard carbon in Na-ion battery. **a**, Schematic of the dual-phase pore engineering process for hard carbon synthesis, Reproduced with permission from Ref.⁹⁰, © Zhao W. *et al.* 2025; **b**, The schematic illustration for how alkali etching time effects the microstructure and sodium storage performance of coffee grounds-derived hard carbon, Reproduced with permission from Ref.⁹¹, © 2025 Elsevier B.V. 2025.

loading of $7.364 \text{ mg} \cdot \text{cm}^{-2}$, a reversible capacity of $377.0 \text{ mAh} \cdot \text{g}^{-1}$ is maintained, highlighting the excellent practical adaptability of this material. Liao *et al.*⁹¹ similarly proposed an “alkali etching-carbonization coupling” strategy (Fig. 8b), in which controllable alkali etching drives the directional degradation of hemicellulose and lignin, enabling a transition from randomly distributed pores to designable microporous architectures. Moreover, a clear correlation among etching time, micropore fraction, and kinetic performance was established, systematically elucidating the decisive role of pore structure in fast sodium storage behavior. A high micropore proportion ($> 80\%$), together with a large specific surface area, provides abundant active sites and efficient ion diffusion pathways, leading to pronounced improvements in reversible capacity ($294.38 \text{ mAh} \cdot \text{g}^{-1}$) and rate performance ($185.26 \text{ mAh} \cdot \text{g}^{-1}$ at 2 C). Building on this concept, Chen *et al.*⁹² further focused on the compositional regulation of lignocellulosic components to construct hard carbon enriched with closed pores. This strategy

markedly increased the fraction of crystalline cellulose in walnut shells, thereby inducing the formation of a large number of closed pores during carbonization. As a result, the optimized hard carbon delivers a reversible capacity of $341.8 \text{ mAh} \cdot \text{g}^{-1}$ with an ICE of 85.1% , accompanied by a plateau capacity enhancement of $53.5 \text{ mAh} \cdot \text{g}^{-1}$ compared with the untreated counterpart.

4.1.3 Hydrothermal

While regulating precursor composition to remove inorganic impurities, tune structural ordering, and reconstruct active sites, the introduction of additional pretreatment strategies aimed at deeper precursor structural modulation is likewise critical for the rational construction of hard carbon microstructures. Guided by this concept, Liu *et al.*⁹³ employed discarded mulberry branches as the starting material and successfully expanded the interlayer spacing of graphitic nanocrystallites through a hydrothermal modification strategy, while simultaneously establishing ion transport pathways

with hierarchical porosity. This structural design, in synergy with newly generated active sites such as nanopores and defects, substantially enhances charge-transfer kinetics and overall electrochemical performance of the hard carbon. As shown in Fig. 9a, the electrode delivers an initial charge-discharge capacity of 330.0 mAh g^{-1} and maintains an outstanding capacity of 175.5 mAh g^{-1} even at a high current density of 10 A g^{-1} (Fig. 9b). Remarkably, a sodium storage capacity of 155 mAh g^{-1} is retained under extremely low-temperature conditions (-50°C) (Fig. 9c), and no noticeable capacity fading is observed after 400 cycles at -20°C and 1 A g^{-1} . In a similar manner, Jia *et al.*⁹⁴ employed discarded peanut shells as the precursor and developed a high-performance hard carbon by integrating hydrothermal pretreatment with subsequent high-temperature pyrolysis. The hydrothermal step reinforces the nanostructure of the material, promoting the formation of a highly dispersed lamellar configuration, which simultaneously improves electrolyte penetration and enhances sodium storage capability. The resulting hard carbon exhibits a specific surface area of $7.1 \text{ m}^2 \text{ g}^{-1}$ and an enlarged interlayer spacing of 0.406 nm . When evaluated as an anode material for SIBs, it delivers a high reversible capacity of $357.55 \text{ mAh g}^{-1}$ at a current density of 30 mA g^{-1} , together with an ICE of 63.4%. In addition, GITT measurements confirm its favorable diffusion kinetics, enabling efficient Na^+ insertion/

extraction and thereby ensuring both excellent rate capability and structural stability. Guo *et al.*⁹⁵ further regulated the crosslinking degree of resorcinol–benzaldehyde resin through a hydrothermal reaction, thereby enabling precise control over the microstructure of the derived hard carbon. The results demonstrate that, compared with directly carbonized hard carbon (DHC), the sample prepared by hydrothermal treatment for 6 h (HHC6) exhibits more pronounced structural advantages. In this context, the strong molecular crosslinking induced during the hydrothermal process is considered a key factor in the construction of closed pores structures. Accordingly, it was proposed that a highly crosslinked three-dimensional network decomposes into randomly arranged short-range ordered microcrystallites during pyrolysis, giving rise to abundant closed pores. Figs. 9d and 9e present the cyclic voltammetry (CV) curves of HHC6 and DHC recorded at a scan rate of 0.1 mV s^{-1} , where HHC6 displays a distinct redox peak near 0.1 V , indicative of a higher plateau capacity. In addition, the high crosslinking characteristic endows the hard carbon microcrystallites with a unique spherical morphology and enlarged interlayer spacing, which markedly enhances the rate capability. As a result, the optimized carbon anode delivers a specific capacity of 372.7 mAh g^{-1} (Fig. 9f), with both plateau capacity and rate performance substantially outperforming those of the pristine sample (Figs. 9g–9i). Furthermore, GITT measurements (Figs. 9j–

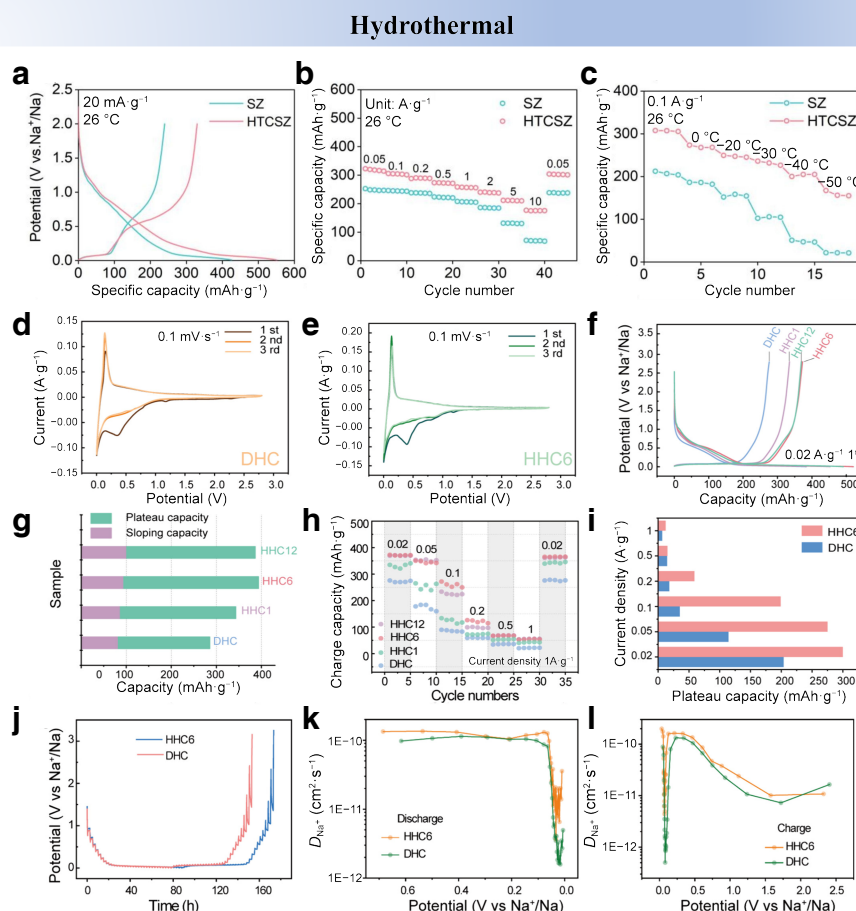


Fig. 9. Electrochemical performances: **a**, The first cycle of GCD curves; **b**, Rate performance; **c**, Cycle for three times at different temperatures and current density of 0.1 A g^{-1} . Reproduced with permission from Ref.⁹³, © Elsevier B.V. 2025; **d**, **e**, CV curves at 0.1 mV s^{-1} of DHC (**d**) and HHC6 (**e**); **f**, First cycle GCD curves; **g**, **h**, Specific capacity from sloping and plateau regions (**g**), and rate performance (**h**); **i**, Plateau capacity at different current densities; **j**, GITT curves; **k**, **l**, Na^+ diffusion coefficient. Reproduced with permission from Ref.⁹⁵, © American Chemical Society 2024.

9l) reveal a superior ion diffusion coefficient, accounting for the excellent rate performance of the HHC6 electrode.

4.1.4 Ball milling

Compared with approaches such as adjusting component ratios, regulating the precursor structure and the manner of carbon framework construction can more directly influence carbon layer rearrangement and pore evolution during carbonization. On this basis, Tang *et al.*⁹⁶ employed a ball milling strategy to tailor the carbon chain length of the precursor, thereby enabling effective regulation of the pore architecture in hard carbon (Fig. 10a). Experimental results demonstrate that variations in carbon chain length can substantially modulate the rearrangement behavior of carbon layers at high temperatures, giving rise to diverse pore configurations ranging from closed to open pores. Electrochemical measurements reveal that hard carbon enriched with closed pores exhibits superior performance, delivering a high specific capacity of $356.0 \text{ mAh}\cdot\text{g}^{-1}$ at a current density of $20 \text{ mA}\cdot\text{g}^{-1}$ (Fig. 10b) and a plateau capacity of $262.0 \text{ mAh}\cdot\text{g}^{-1}$ (Fig. 10c), both markedly exceeding those of the pristine sample and open pores dominated hard carbon. In addition, excellent rate capability (Fig. 10d) and long-term cycling stability are achieved, with 80% capacity retention maintained after 500 cycles at $500 \text{ mA}\cdot\text{g}^{-1}$ (Fig. 10e). Similarly, Yu *et al.*⁹⁷ precisely manipulated the crystallite characteristics and defect distribution of bamboo-derived hard carbon through mechanical activation. It was found that the high surface area intermediates generated by ball milling preferentially evolve into hard carbon featuring abundant closed pores, effective interlayer spacing, and appropriate defect density during subsequent carbonization, which collectively and substantially enhance sodium storage performance. As a result, the optimally milled hard carbon

delivers a reversible capacity of $315.2 \text{ mAh}\cdot\text{g}^{-1}$ at $17.5 \text{ mA}\cdot\text{g}^{-1}$, with an ICE of 79.3%, along with excellent rate capability and cycling stability.

In addition, as shown in Fig. 10f, Zhou *et al.*⁹⁸ applied a dry ball milling pretreatment to waste cotton fibers, which successfully induced a crystalline phase transition of cellulose from phase I to phase II. This transformation promoted the formation of a polycrystalline carbon layered structure with enlarged interlayer spacing during the subsequent pyrolysis process. Such microcrystalline carbon domains are favorable for Na^+ accommodation, thereby enhancing the sodium storage capability (Fig. 10g). Comparative experimental results indicate that the hard carbon subjected to ball milling pretreatment exhibits a substantially improved sodium storage performance. The reversible capacity increases from 166.76 to $270.00 \text{ mAh}\cdot\text{g}^{-1}$, while the ICE rises markedly from 65.03% to 85.34%. In addition, the ball milled hard carbon demonstrates excellent rate capability and cycling stability, maintaining a stable capacity of $193.85 \text{ mAh}\cdot\text{g}^{-1}$ after 1,300 cycles at a high current density of $2 \text{ A}\cdot\text{g}^{-1}$. Further kinetic investigations reveal that the pronounced performance enhancement primarily originates from the engineered multilayer carbon structure, which facilitates more efficient Na^+ intercalation.

4.2 Pore structure engineering

Pore structure regulation, as a natural extension of precursor optimization, aims to further enlarge, reconstruct, or precisely tailor the intrinsic porosity of precursors through chemical or physical activation strategies. Such controlled modulation of the pore architecture enables the targeted optimization of the hard carbon microstructure, thereby leading to additional improvements in electrochemical performance^{99,100}.

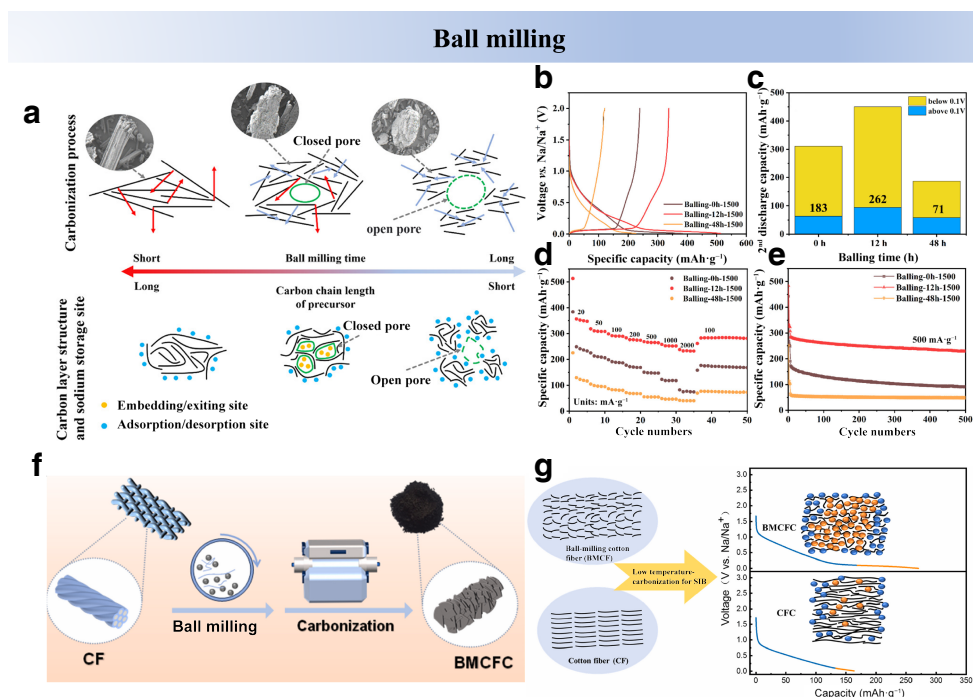


Fig. 10. Ball milling based hard carbon in Na-ion battery. **a**, Schematic diagram of the influence of precursor carbon chain length on the closed pores structure formation and sodium storage site; **b**, The first galvanostatic discharge/charge profile; **c**, Summary of the capacity potential distribution; **d**, Rate capability, and **e**, Long-term cycling performance, Reproduced with permission from Ref.⁹⁶, © American Chemical Society 2024; **f**, Illustration of converting waste cotton fibers with dry ball-milling method into hard carbon; **g**, Schematic illustration of electrochemical sodium storage mechanism, Reproduced with permission from Ref.⁹⁸, © Elsevier Ltd. 2025.

4.2.1 Chemical activation

By rationally tuning the pore size distribution, pore connectivity, and the cooperative architecture of closed and open pores, Na^+ transport kinetics can be substantially enhanced, accompanied by a pronounced increase in low potential plateau capacity. Nevertheless, limitations remain in terms of pore-shape controllability, dimensional precision, and regulation of the local chemical environment. To extend pore engineering into the chemical dimension, Sun *et al.*¹⁰¹ employed a reaction-induced, template-guided strategy using sodium acetate as a nanoporous template, enabling molecular level control over both pore-channel architecture and crystalline configuration, while simultaneously achieving *in situ* pre-sodiation. This template design constructs confined nanoscale spaces together with a hierarchical pore network, thereby effectively tailoring the carbon phase derived from phenolic resin and suppressing the growth of long-range ordered carbon layers (Fig. 11a). Density functional theory (DFT) calculations (Figs. 11b and 11c) reveal that, during high-temperature pyrolysis, the migration of residual sodium species (Na_2CO_3 and Na_2O) on the hard carbon surface modulates the composition and morphology of the SEI and induces its uniform

formation, resulting in a thin, compact, NaF -rich SEI film. As a result, the electrode delivers a reversible capacity of $456.0 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1 C , along with outstanding rate capability ($325.0 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C) and cycling stability, retaining approximately $300.0 \text{ mAh}\cdot\text{g}^{-1}$ after 600 cycles. Benefiting from the deposition of sodium clusters, a high ICE of 93% is achieved. Yuan *et al.*¹⁰² integrated carboxylate-mediated chelation chemistry with an ultrafine zinc acetate templating approach and phenolic resin interfacial encapsulation to engineer directionally confined closed pores architectures in bituminous coal-derived hard carbon. NaOH activation was employed to introduce abundant carboxyl functional groups onto the carbon surface, which facilitated the uniform anchoring of nanoscale domains and led to the formation of a dense network of enclosed nanocavities. Electrochemical evaluations demonstrate that the optimized hard carbon electrode delivers a high reversible capacity of $370.9 \text{ mAh}\cdot\text{g}^{-1}$ at a current density of $20 \text{ mA}\cdot\text{g}^{-1}$, together with an ICE as high as 92.5%. Notably, even under a high current density of $1 \text{ A}\cdot\text{g}^{-1}$, the electrode retains 80.6% of its capacity after 3,000 cycles. As shown in Fig. 11d, the full cell assembled with a $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode maintains 80.4% capacity retention after 100 cycles at $100 \text{ mA}\cdot\text{g}^{-1}$. Similarly, Ren *et al.*¹⁰³ employed a

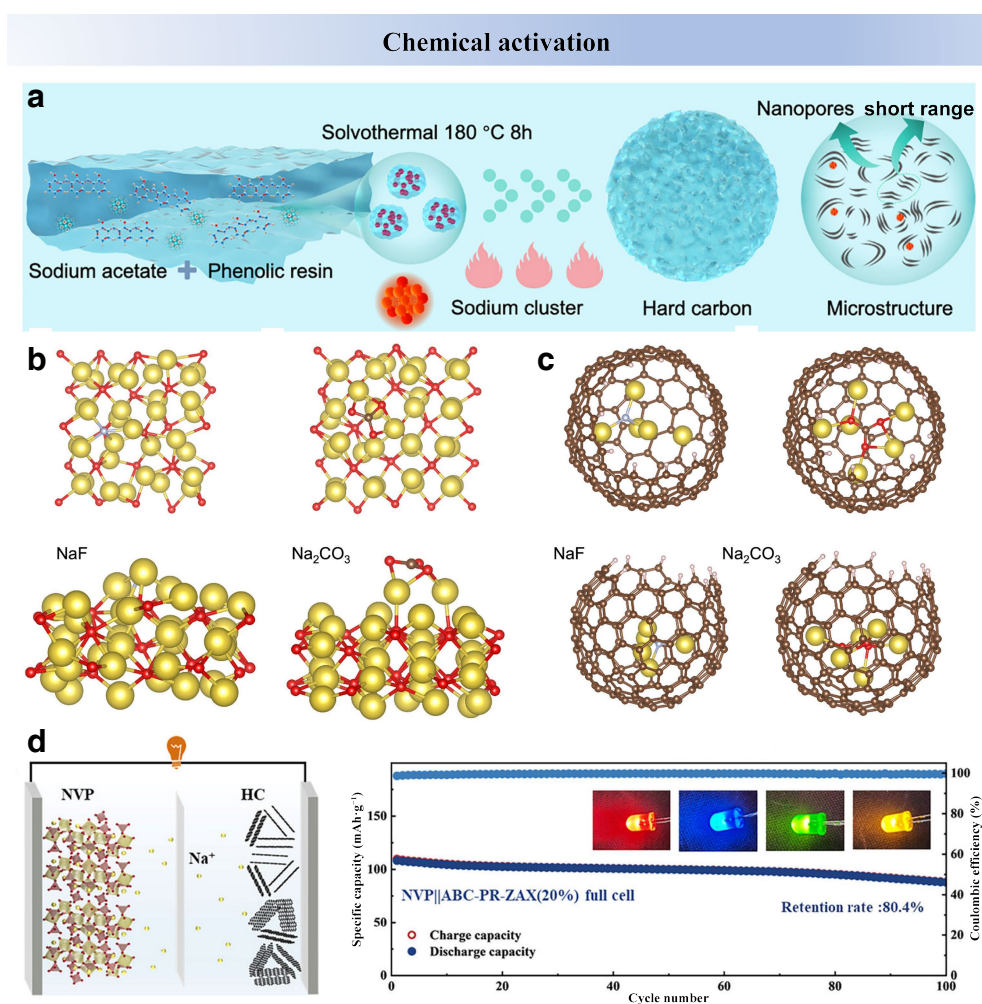


Fig. 11. Chemical activation based hard carbon in Na-ion battery. **a**, Schematic illustration for synthesis of hard carbon; **b**, Top and side views of simulated interaction configurations NaF and Na_2CO_3 ; **c**, Top and side views of simulated configurations that closed nanopores with sodium clusters, Reproduced with permission from Ref.¹⁰¹, © Elsevier Ltd. 2024; **d**, Schematic of SIBs and cyclability of the full cell at 1 C and the insert shows the optical photographs of the lighted LED bulbs, Reproduced with permission from Ref.¹⁰², © Yuan, J. L. *et al.* 2025.

magnesium oxide templating strategy to thermally treat a mixture of magnesium gluconate and walnut shell under an inert atmosphere, thereby constructing abundant closed pores with well-defined dimensions. This distinctive pore architecture not only provides sufficient storage space for Na^+ in the low potential plateau region but also markedly accelerates charge-transfer kinetics. As an anode material, the resulting hard carbon delivers an ICE of 89.8% together with a high sodium storage capacity of $366.0 \text{ mAh}\cdot\text{g}^{-1}$. In a related study, Wang *et al.*¹⁰⁴ developed a lignin-derived hard carbon using an *in situ* ZnO templating strategy. During carbonization, oxygen-containing functional groups within lignin adsorb Zn^{2+} , which are subsequently converted *in situ* into ZnO nanoparticles that act as sacrificial templates for structural modulation. This process effectively tailors both the closed pores characteristics and the microcrystalline arrangement of the hard carbon. As a consequence, the introduction of ZnO templates leads to pronounced increases in closed pores volume and interlayer spacing, enabling the obtained hard carbon to deliver a reversible capacity of $358.0 \text{ mAh}\cdot\text{g}^{-1}$ at a current density of $50 \text{ mA}\cdot\text{g}^{-1}$.

In addition, by introducing polyvinylpyrrolidone (PVP) as an additive, You *et al.*¹⁰⁵ successfully developed a waste wood-derived hard carbon with a more elaborated pore architecture. *In situ* SAXS and high-resolution transmission electron microscopy (HR-TEM) analyses revealed that the resulting material, characterized by an open pores structure and an enlarged interlayer spacing (d_{002}), effectively facilitates the reversible insertion and extraction of Na^+ . Meanwhile, *in situ* TEM and XRD investigations further confirmed the structural robustness of this hard carbon during electrochemical

operation. Electrochemical measurements showed that the material delivers a high reversible capacity of $350.7 \text{ mAh}\cdot\text{g}^{-1}$ at 0.05 C , together with an ICE of 94.9%. Moreover, the assembled 18,650 full-cell maintained a capacity retention of 94.5% after 400 cycles at a current of 1 A .

4.2.2 Physical activation

Although chemical templating enables precise tailoring of pore-size distribution and affords carbon materials with high specific surface areas, the subsequent template-removal process often compromises the integrity of the carbon framework and generates substantial chemical waste. In contrast, physical templating strategies can induce the formation of closed micropores without post-treatment, thereby preserving structural robustness while markedly improving the ICE. On this basis, Zheng *et al.*¹⁰⁶ employed a CO_2 etching strategy to generate abundant closed pores within starch-derived hard carbon, leading to a pronounced enhancement of the low potential plateau capacity. As illustrated in Fig. 12a, the CO_2 etching process initially creates open pores within the carbon matrix, which are subsequently transformed into sodium-favorable closed pores through *in situ* structural rearrangement under high-temperature conditions (Fig. 12b). Owing to this pore evolution, the resulting hard carbon anode exhibits outstanding electrochemical performance, delivering a total sodium storage capacity of $487.6 \text{ mAh}\cdot\text{g}^{-1}$, with a plateau contribution as high as $351 \text{ mAh}\cdot\text{g}^{-1}$ (Fig. 12c), together with an ICE of 90.56%. Fig. 12d further compares the differences in pore structure and pore-size distribution between the two materials. Wang *et al.*¹⁰⁷ further

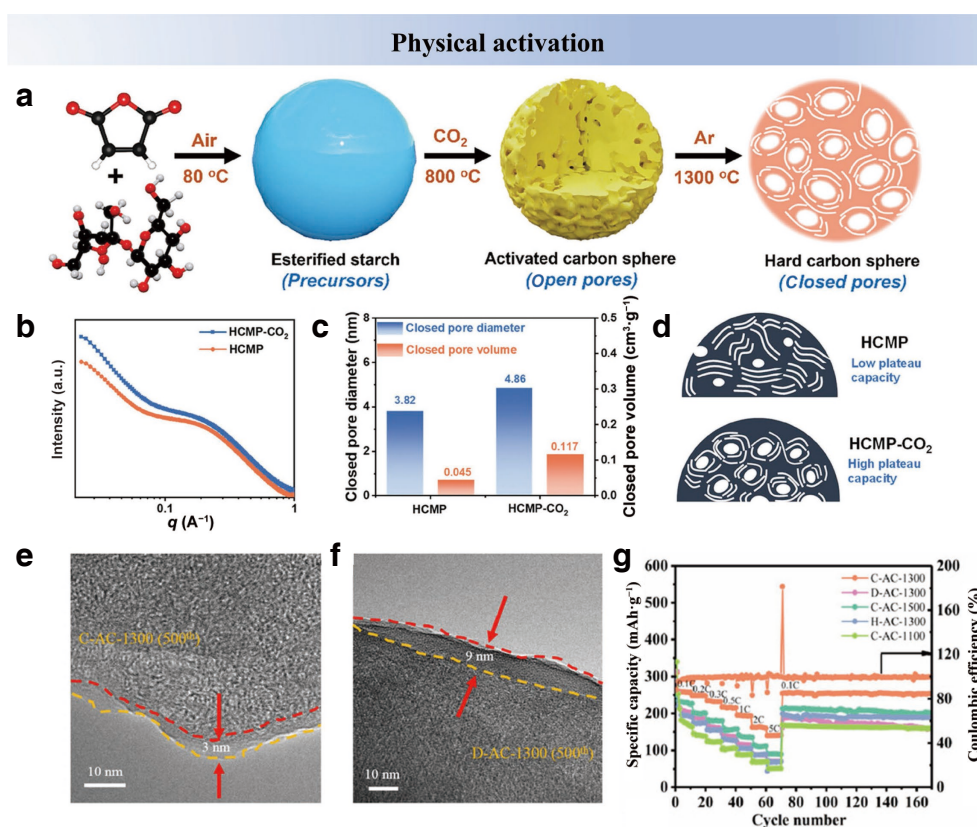


Fig. 12. Fabrication and structure of hard carbon with closed pores microspheres. **a**, Schematic of the synthesis; **b**, Small-angle X-ray scattering patterns; **c**, Closed pores diameter and closed pores volume; **d**, Schematic illustration of the pore structure evolution, Reproduced with permission from Ref.¹⁰⁶, © Wiley-VCH GmbH 2023; **e, f**, Comparison of SEI after 500 cycles in C-AC-1300 (e) and D-AC-1300 electrolytes (f); **g**, Rate capability, Reproduced with permission from Ref.¹⁰⁸, © Wiley-VCH GmbH 2025.

substantiated the above conclusions by activating bamboo-derived carbon precursors with CO₂ at 800 °C to tailor their pore architecture, followed by high-temperature carbonization at 1,300 °C to obtain hard carbon anodes for sodium ion batteries. The results indicate that the CO₂ activation process constructs a hierarchical pore structure within the carbon matrix, providing abundant Na⁺-accessible active sites while avoiding excessive pore corrosion. Subsequent high-temperature carbonization induces densification of the external surface and open pores, which is beneficial for achieving a high ICE. Meanwhile, the preservation of internal pores plays a positive role in enhancing sodium storage in the low potential plateau region. Electrochemical evaluations reveal that the optimized sample delivers a reversible specific capacity of 339.2 mAh·g⁻¹ at a current density of 30 mA·g⁻¹, together with an ICE of 86.3%.

Moreover, pore architecture in hard carbon can be controllably tuned by thermal treatment under different atmospheres, as convincingly demonstrated by Li *et al.*¹⁰⁸. By innovatively introducing an acetylene atmosphere during pyrolysis, hydrogen radicals released from acetylene decomposition react with heteroatoms (O, N, and S) present in the precursor, removing them in gaseous forms such as H₂O, NH₃, and H₂S. Concurrently, the generated carbon radicals deposit on the carbon surface, inducing defect structures that promote the transformation of pre-existing open pores into closed ones. This process effectively suppresses the formation of surface defects and gas-evolved pores during carbonization, and subsequent thermal treatment further stabilizes the pore configuration. As shown in Figs. 12e and 12f, owing to the formation of a thinner and more uniform SEI, the acetylene-mediated hard carbon (C-AC-1300) delivers a higher reversible capacity and superior rate capability at 0.3 C compared with the directly carbonized sample (D-AC-1300) (Fig. 12g), with the ICE increased to 88%. After 500 cycles at this current density, a reversible capacity of 210 mAh·g⁻¹ is retained. In addition, the optimized electrode exhibits favorable low-temperature performance, maintaining a reversible capacity of 247 mAh·g⁻¹ at -20 °C under 0.05 C. Meanwhile, Duan *et al.*¹⁰⁹ achieved precise pore regulation by coupling steam-assisted physical activation with reconstruction induced by high-temperature carbonization. By finely tuning the steam dosage at 800 °C, a controllable open pores network was first established. Subsequent high-temperature treatment efficiently transformed these open pores into ultramicropores and closed pores. The study revealed that both the volume and size of open pores formed during the pre-carbonization stage play a decisive role in the final pore evolution; excessive or oversized open pores impede pore closure during the high-temperature step. Benefiting from this synergistic regulation strategy, the optimized hard carbon anode delivers a reversible specific capacity of 377.6 mAh·g⁻¹ at a current density of 30 mA·g⁻¹, with a plateau contribution as high as 284.1 mAh·g⁻¹. Moreover, full cells assembled with this material retain 94.3% of their capacity after 400 cycles.

4.3 Heteroatom doping

Heteroatom doping is an effective functional modification strategy for hard carbon, primarily relying on the simultaneous regulation of electronic structure, surface chemistry, and sodium-storage sites to overcome its intrinsic limitations. In terms of electronic structure, the electronegativity difference between heteroatoms and carbon induces local charge redistribution, generating electron-rich and electron-deficient regions that facilitate charge transport pathways,

reduce charge-transfer resistance, and enhance coupled ion/electron transport kinetics. Regarding surface chemistry, doping introduces heteroatom-containing polar functional groups, thereby improving electrolyte wettability and promoting the formation of a stable SEI layer, which suppresses side reactions and contributes to higher ICE. With respect to sodium-storage-site regulation, heteroatom incorporation disrupts the structural ordering of carbon layers by expanding interlayer spacing, generating defect sites (e.g., vacancies and edge defects), and forming heteroatom-associated active sites. These structural modifications collectively enhance sodium-storage capability in both the sloping and plateau regions, thereby significantly improving the overall electrochemical performance of hard carbon anodes^{110–113}.

4.3.1 Nitrogen doping

The incorporation of nitrogen dopants into hard carbon effectively improves sodium storage performance through multi-level structural and electronic modulation. At the structural level, nitrogen incorporation generally induces lattice distortion and defect formation, leading to expanded interlayer spacing and increased accessible Na⁺ storage sites. At the electronic level, the presence of electronegative nitrogen atoms redistributes charge density within the carbon matrix, thereby improving electronic conductivity and facilitating coupled ion/electron transport kinetics. Different nitrogen configurations exhibit distinct roles in regulating electrochemical behavior. Pyridinic N and pyrrolic N, can serve as strong adsorption centers for Na⁺ and are therefore widely regarded as key contributors to pseudocapacitive charge storage. In contrast, graphitic N contributes less directly to Na⁺ adsorption but plays an important role in enhancing electrical conductivity and promoting rapid electron transport within the carbon framework. The synergistic effect of these configurations enables simultaneous improvement of capacity, rate performance, and structural stability^{114–116}. Li *et al.*¹¹⁷ successfully constructed a nitrogen-rich hard carbon skeleton by inducing condensation and cross-linking reactions under high-temperature and high-pressure conditions. Within this structure, nitrogen atoms predominantly exist as pyridine nitrogen, graphitic nitrogen, and pyrrole nitrogen. Their incorporation not only generates abundant defects and active sites within the carbon matrix but also effectively expands the interlayer spacing, thereby enhancing the material's Na⁺ adsorption capacity and closed pores sodium storage capacity. Furthermore, this doped structure significantly enhances electron and ion transport rates while stabilizing the structure during charge-discharge cycles, preventing carbon skeleton collapse and SEI film rupture. Benefiting from the synergistic effects of these properties, the material exhibits outstanding electrochemical performance: a high reversible capacity of 259 mAh·g⁻¹ at 0.1 A·g⁻¹, and maintains a specific capacity of 124.0 mAh·g⁻¹ with excellent cycling stability (95% capacity retention after 500 cycles) even at a high rate of 1 A·g⁻¹. Zeng *et al.*¹¹⁸ prepared nitrogen-doped hard carbon materials (denoted as CNHC-1200, CNHC-1400, and CNHC-1600) using starch as a precursor, graphitic carbon nitride (CN) as a crosslinker and dopant, and varying carbonization temperatures (1200, 1400, and 1600 °C). While suppressing melt foaming and structural collapse during starch pyrolysis, the introduced graphitic nitrogen (as shown in Figs. 13a–13f) provided additional active sites. This not only induced defect formation but also enhanced material dynamics. The synergistic effects of optimized interlayer spacing, hierarchical porous structure, and active sites significantly improved ion migration efficiency. Experimental results demonstrate that at a current density of 1,000 mA·g⁻¹, the material

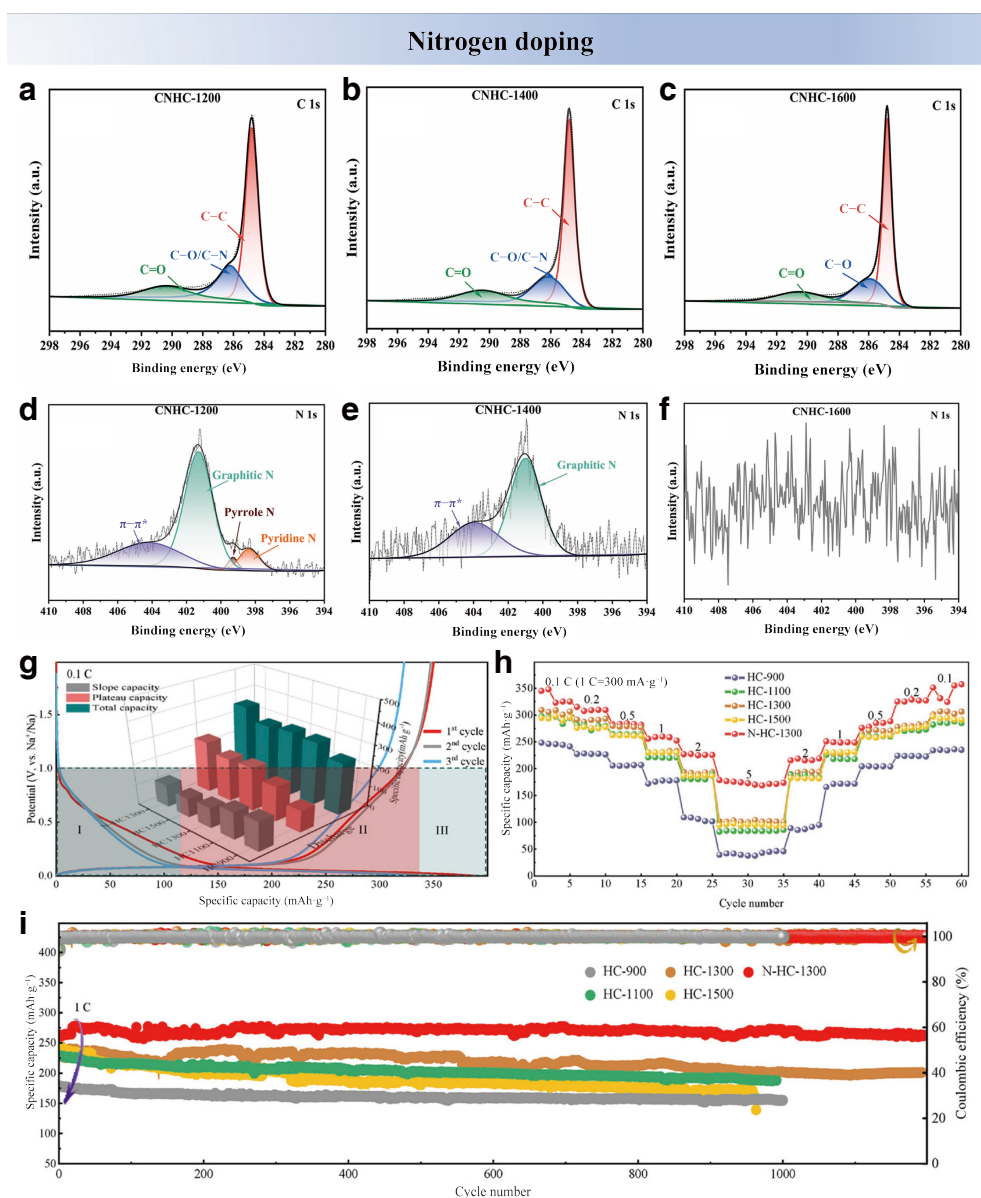


Fig. 13. XPS spectra. **a–f**, The C1 and N1s of CNHC-1200 (**a**, **d**), CNHC-1400 (**b**, **e**) and CNHC-1600 (**c**, **f**), Reproduced with permission from Ref.¹¹⁸, © Elsevier B.V. 2025; **g**, The specific capacity ratio of those secured from slopes and plateaus of initial discharge curve at 0.1 C; **h**, Rate capability. **i**, Long-term cycling performance at 1 C, Reproduced with permission from Ref.¹¹⁹, © Wiley-VCH GmbH 2025.

maintains a high reversible capacity of 254.9 mAh·g⁻¹. After 500 cycles, the capacity remains at 213.9 mAh·g⁻¹, achieving a capacity retention rate of 79.8%, exhibiting outstanding rate performance and cycling stability.

Huang *et al.*¹¹⁹ reported the successful preparation of nitrogen-doped hard carbon via annealing waste wood under a nitrogen atmosphere. This material demonstrates distinct structural advantages. In particular, the constructed hierarchical pore network facilitates rapid Na⁺ transport, while the enlarged interlayer spacing simultaneously increases Na⁺ insertion capacity and mitigates volume strain during repeated charge–discharge processes. Moreover, nitrogen incorporation markedly enhances electronic conductivity and introduces additional electrochemically active sites. As a result, the hard carbon delivers a high reversible discharge capacity of 350.1 mAh·g⁻¹ at 0.1 C, together with an ICE of 90.1% (Fig. 13g). As shown in Figs. 13h and 13i, it also exhibits excellent rate capability, maintaining capacities of 260.4 mAh·g⁻¹ at

1 C and 170.3 mAh·g⁻¹ at 5 C, as well as outstanding cycling durability, retaining 262.7 mAh·g⁻¹ after 1,200 cycles at 1 C with a capacity retention of 96.5%.

4.3.2 Phosphorus doping

Incorporating heteroatoms with larger atomic radii than carbon (e.g., phosphorus) into the carbon lattice induces distortion of graphitic layers and enlarges the interlayer spacing of hard carbon. This structural modulation effectively reduces the diffusion resistance of Na⁺ while markedly increasing the sodium storage capacity. In addition, the formation of stable P–C and P–O bonds not only reinforces the structural integrity of the electrode and participates in redox processes, but also lowers the ion diffusion energy barrier, thereby improving the long-term cycling durability and rate performance of hard carbon^{120, 121}. On this basis, Wang *et al.*¹²² introduced phosphorus into hard carbon, which triggered deformation of the molecular-layer framework within pseudo-

graphitic domains, expanded the interlayer distance, and increased the population of internal closed micropores, collectively enhancing the sodium storage capability of the carbon matrix. Compared with the undoped counterpart, the phosphorus-doped hard carbon exhibited a substantial increase in reversible capacity from 240.3 to 359.9 mAh·g⁻¹ during charge-discharge cycling at 0.05 C.

Furthermore, phosphate species possess stronger reducibility than adjacent carbon atoms, generating electron holes that partially compensate for the intrinsically limited electronic conductivity of hard carbon. As shown in Fig. 14a, Song *et al.*¹²³ demonstrated that phosphorus incorporation effectively tailored the interlayer spacing of local graphitic microcrystals while introducing abundant functional groups and active sites. As illustrated in Fig. 14b, the modified hard carbon (NOP-1400) delivered an ultrahigh capacity of 510.22 mAh·g⁻¹ at a current density of 0.1 A·g⁻¹, together with excellent rate performance and pronounced plateau capacity (Figs. 14c and 14d). Moreover, phosphorus doping facilitated the formation of a uniform and inorganic-rich SEI film. Consequently, the phosphorus-doped hard carbon exhibited markedly enhanced sodium storage capacity and cycling stability relative to the undoped sample, maintaining a high specific capacity of

445.65 mAh·g⁻¹ after 500 cycles at 0.1 A·g⁻¹. The sodium storage mechanism and the formation of sodium metal clusters were further corroborated by *in situ* Raman, XRD, and XPS analyses (Figs. 14e and 14f).

In addition, Liang *et al.*¹²⁴ successfully developed a high-performance phosphorus-doped porous hard carbon by modifying olive pit-derived carbon with soybean lecithin followed by phosphorus doping. At the microscopic level, phosphorus incorporation broadened the interlayer spacing and optimized the graphitization degree, ensuring rapid transport of both electrons and ions. Electrochemical evaluations highlighted the advantages of this coupled effect: the material delivered a high reversible capacity of 350 mAh·g⁻¹ at 0.1 A·g⁻¹ with an ICE of 89.6%, and exhibited outstanding long-term cycling stability over 1,000 cycles at 1 A·g⁻¹, with nearly negligible capacity decay.

4.3.3 Sulfur doping

Sulfur doping effectively enlarges the interlayer spacing of hard carbon by introducing sulfur atoms with relatively large atomic size, while simultaneously generating abundant edge defects. These effects increase the specific surface area, regulate the pore

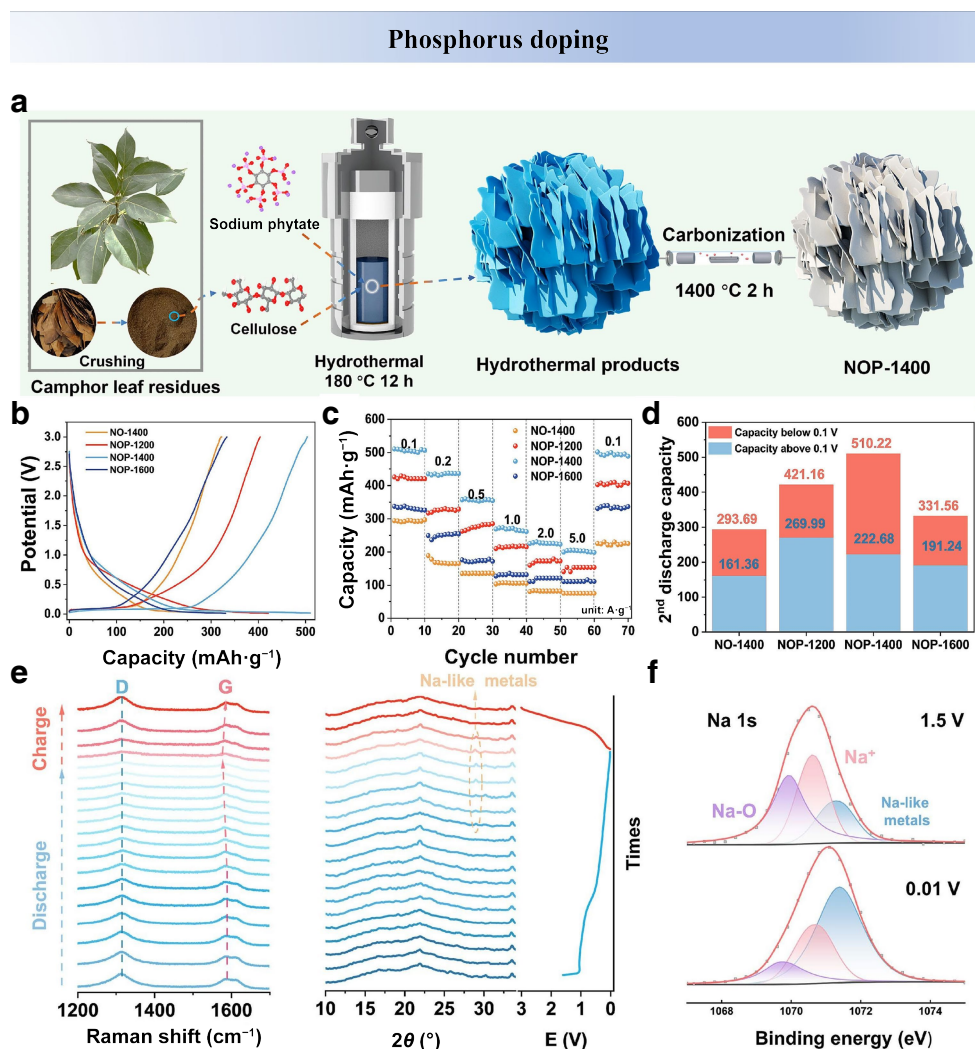


Fig. 14. Phosphorus doping based hard carbon in Na-ion battery. a, Schematic of material synthesis; b, The second GCD; c, Rate performance; d, Comparison of capacities above and below 0.1 V of the second cycle; Reaction mechanism of NOP-1400; e, *In situ* Raman and *in situ* XRD at the initial cycle; f, *Ex situ* XPS of Na 1s, Reproduced with permission from Ref.¹²³, © Elsevier Inc. 2025.

architecture, and promote the formation of additional micro and mesopores. Moreover, sulfur incorporation strengthens the affinity of hard carbon toward electrolyte ions; by facilitating rapid Na^+ transport and providing extra chemisorption sites and redox-active centers, it substantially enhances the specific capacity.^{125, 126} Wei *et al.*¹²⁷ introduced sulfur functional groups into hard carbon via an activation process and, to elucidate the influence of thiophene-type sulfur (C-S/C=S) on electron-transfer kinetics, performed differential charge density analyses on three model systems (Figs. 15a–15c). DFT results reveal that, in contrast to the relatively uniform charge distribution surrounding Na^+ on pristine graphene, pronounced charge accumulation emerges at sulfur sites in the doped structures. This interfacial charge redistribution lowers the interfacial transport resistance, markedly strengthens Na^+ adsorption, and accelerates electron migration (Figs. 15d–15f). In addition, density-of-states calculations (Figs. 15g and 15h) indicate that pristine graphene exhibits zero density of states at the Fermi level, characteristic of semiconducting behavior, whereas C-S/C=S doping introduces states crossing the Fermi level, imparting

metallic conductivity and thereby enhancing electrical conductivity and electron-transfer rates. Consequently, sulfur-doped hard carbon delivers a reversible capacity of up to $366.6 \text{ mAh}\cdot\text{g}^{-1}$ at a current density of $20 \text{ mA}\cdot\text{g}^{-1}$, together with favorable capacity retention and high-rate stability.

Liu *et al.*¹²⁸ employed coconut shell fibers as a precursor to synthesize carbon nanosphere anodes featuring small particle size, a highly developed pore network, and low structural ordering, characteristics that are particularly advantageous for efficient sulfur incorporation. The resulting material achieved a high reversible capacity of $536 \text{ mAh}\cdot\text{g}^{-1}$ and maintained $308 \text{ mAh}\cdot\text{g}^{-1}$ even at a high current density of $5 \text{ A}\cdot\text{g}^{-1}$; after 1,000 cycles, a capacity retention of 90.3% was retained. Such outstanding electrochemical performance is primarily attributed to the synergistic effect between the enlarged interlayer spacing induced by sulfur doping and the hierarchical porous architecture. These structural features not only expand the available Na^+ storage sites but also markedly accelerate ion diffusion and induce a pronounced pseudocapacitive contribution. Yan *et al.*¹²⁹ developed a sulfur-doped biomass-

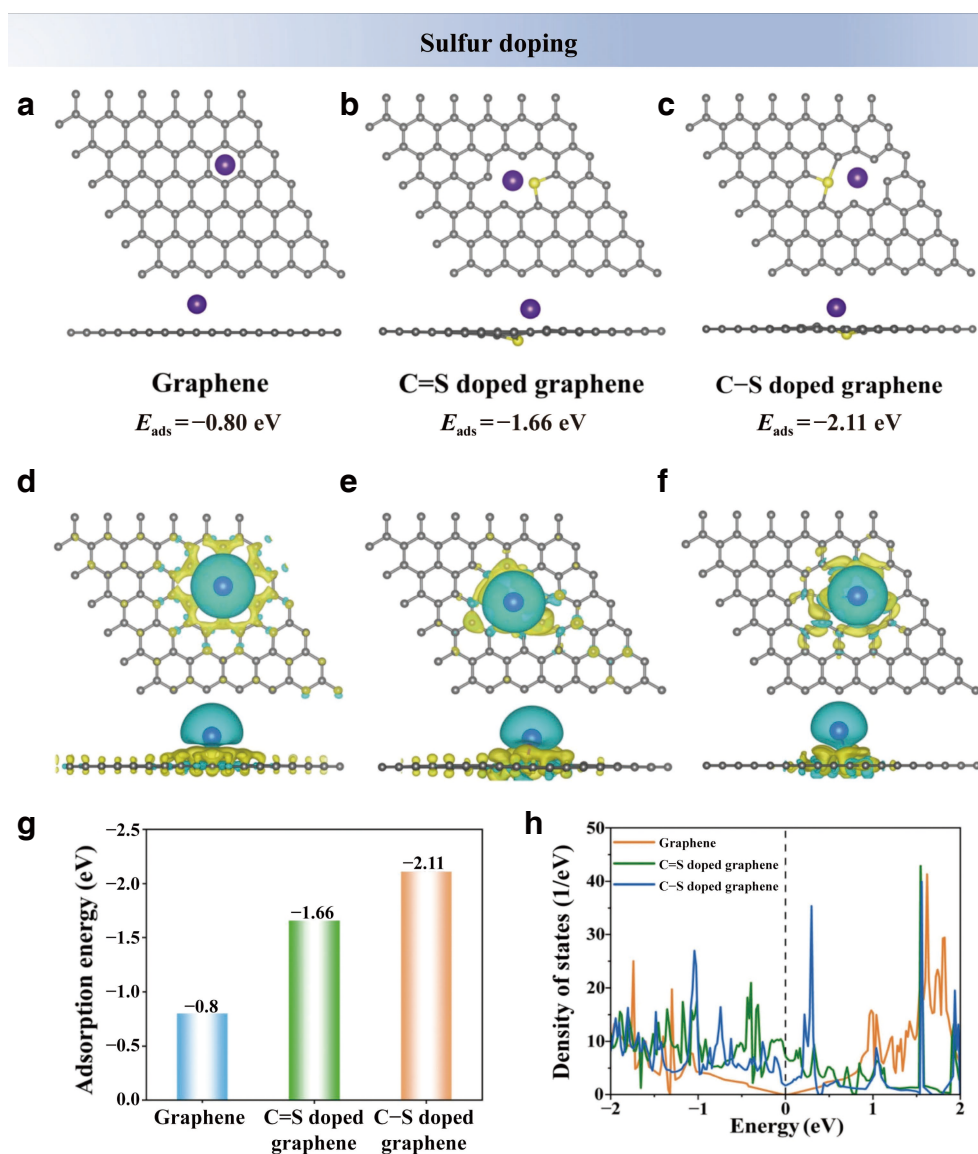


Fig. 15. First-principles calculations. **a–c**, Models; **d–f**, Charge density differences of the graphene, C=S doped graphene, and C-S doped graphene with defects, respectively; **g**, **h** Corresponding Total Density of States (The dashed line at 0 eV indicates the Fermi level), Reproduced with permission from Ref.¹²⁷, © Elsevier B.V. 2025.

derived carbon using a molten-salt strategy, achieving a relatively high sulfur content and pronounced modulation of the material's chemical characteristics. This modification improves electronic transport efficiency and, by introducing abundant electrochemically active sites, substantially enhances sodium storage capability. Electrochemical evaluations demonstrate excellent rate performance, with desirable specific capacities maintained even at elevated current densities. After 3,100 cycles, the capacity retention remains as high as 95%, highlighting the exceptional long-term cycling stability of the material.

4.3.4 Fluorine doping

Fluorine doping modifies the electronic structure of hard carbon by introducing highly electronegative fluorine atoms and optimizes ion-transport kinetics through the formation of semi-ionic C–F bonds. Its primary contribution lies in inducing a robust and uniform NaF-rich SEI film, which simultaneously enhances the ICE and cycling stability while effectively reducing interfacial resistance. Compared with other heteroatom dopants, fluorine plays a more pronounced role in deep modification of the electrode/electrolyte interface, making it an effective strategy for achieving long cycle life and high-rate performance in SIBs^{130, 131}. Meng *et al.*¹³² incorporated fluorine into resin-derived hard carbon, leading to expanded interlayer

spacing, the generation of additional reversible defect sites, optimized distributions of oxygen-containing functional groups, and the formation of a more compact pore structure, collectively improving sodium storage capability. In parallel, fluorine doping substantially refined the electrode/electrolyte interface by promoting the formation of a dense and homogeneous NaF-rich SEI, thereby markedly accelerating Na⁺ and electron transport. As a result, the modified hard carbon exhibited excellent durability, retaining 92% of its capacity after 1,000 cycles at 1 C, corresponding to a capacity of 301.0 mAh·g^{−1}.

Cai *et al.*¹³³ successfully prepared a fluorine-doped three-dimensional porous carbon composite via *in situ* fluoride ion exchange followed by carbonization. It was found that the C–F bonds and defect sites introduced by fluorine doping significantly enhanced Na⁺ adsorption and diffusion kinetics. Electrochemical measurements demonstrated that this material delivered a high reversible capacity of 357 mAh·g^{−1} at a current density of 0.1 A·g^{−1}, with a capacity retention exceeding 90% (180 mAh·g^{−1}) after 800 cycles at 2 A·g^{−1}. Notably, even under extremely low-temperature conditions of −30 °C, the material maintained outstanding electrochemical performance, achieving an ICE of 89% and preserving a specific capacity of 143 mAh·g^{−1} after 800 cycles. Accordingly, *in situ* electrochemical impedance spectroscopy (EIS)

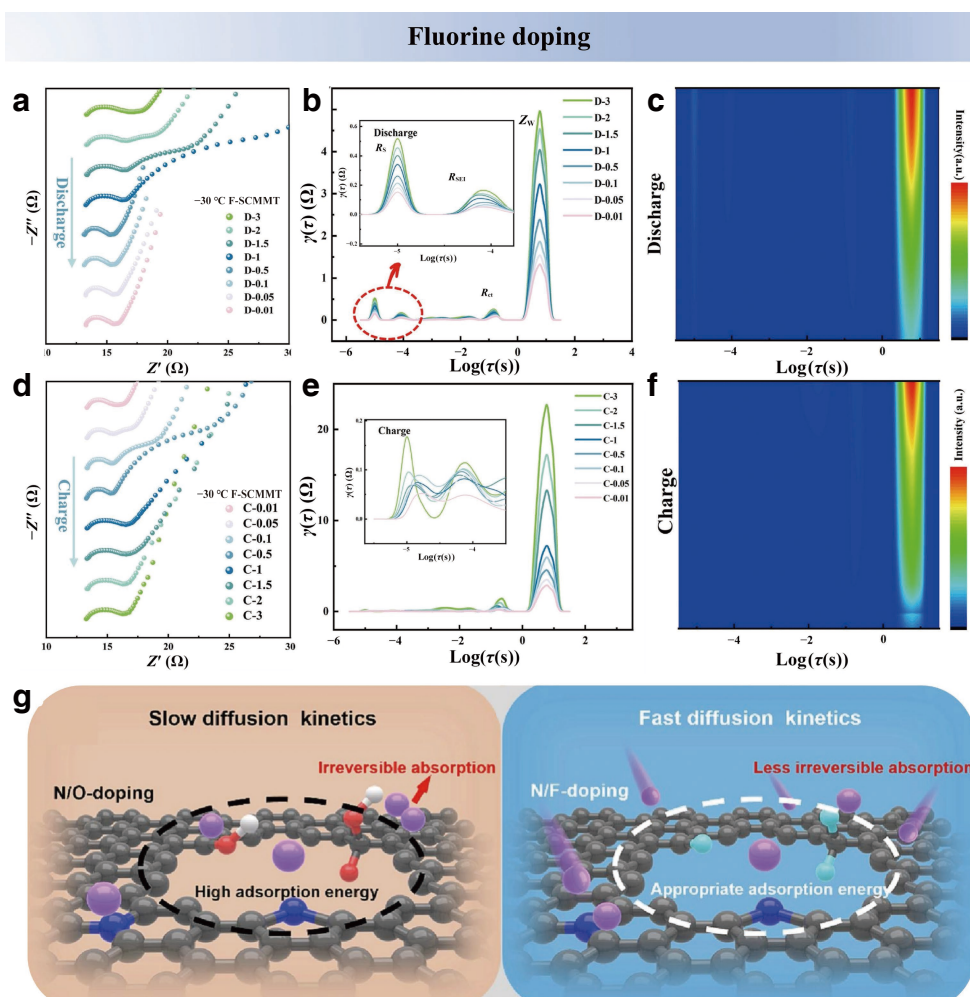


Fig. 16. Fluorine doping based hard carbon in Na-ion battery. **a**, *In situ* EIS during discharge of F-SCMMT at −30 °C; **a–d**, corresponding DRT curves (**b**) and Contour plots (**c**); **d**, *In situ* EIS during charge of F-SCMMT at −30 °C; **e, f**, corresponding DRT curves (**e**) and contour plots (**f**), Reproduced with permission from Ref.¹³³, © Elsevier Ltd. 2025; **g**, mechanism of regulating the E_{ads} on the kinetics of hard carbon, Reproduced with permission from Ref.¹³⁴, © Elsevier B.V. 2024.

combined with distribution of relaxation time (DRT) analysis was employed to accurately resolve the complex electrochemical processes (Figs. 16a–16f). These results confirmed the high stability of the interlayer framework, thereby indirectly validating a pore-dominated sodium storage mechanism. This conclusion further substantiates the pore-governed storage behavior of F-SCMMT and clarifies the Na^+ storage characteristics under low-temperature conditions.

By chemically substituting oxygen-containing functional groups with fluorine atoms, He *et al.*¹³⁴ prepared a fluorine-doped hard carbon enriched with C–F bonds. The well-developed microporous framework and abundant structural defects within the carbon matrix provide numerous fast pathways for ion transport. Consequently, outstanding electrochemical stability was achieved in SIBs, with a capacity of $372.2 \text{ mAh}\cdot\text{g}^{-1}$ retained after 1,000 cycles at a current density of $0.1 \text{ A}\cdot\text{g}^{-1}$. In addition, appropriate charge-transfer characteristics at the hard carbon/electrolyte interface effectively suppressed parasitic reactions, leading to the formation of a uniform inorganic/organic SEI. This interphase not only serves as a protective barrier to mitigate side reactions but also enhances kinetic performance owing to its favorable ionic conductivity. As illustrated in Fig. 16g, the doped hard carbon exhibits suitable adsorption energies (E_{ads}) for ions at defect sites, thereby alleviating irreversible ion adsorption. The reduced extent of side reactions between the electrolyte and the anode facilitates the development of a homogeneous and stable SEI, which further promotes diffusion kinetics during subsequent charge–discharge processes. Notably, even in potassium-ion storage, this inorganic-rich SEI layer plays a critical protective role, enabling the material to maintain an exceptionally high capacity of $214.2 \text{ mAh}\cdot\text{g}^{-1}$ after 5,000 cycles at a current density of $10 \text{ A}\cdot\text{g}^{-1}$.

Overall, although N, P, S, and F doping all contribute to improving the sodium-storage performance of hard carbon through regulation of the electronic structure and sodium-storage sites, their effects show clear differences. Nitrogen doping mainly improves electronic conductivity and provides defect-related adsorption sites, which is more favorable for enhancing surface-driven capacitive sodium storage and rate performance. In comparison, phosphorus and sulfur doping mainly influence the carbon framework by enlarging the interlayer spacing and introducing structural disorder, thereby facilitating Na^+ insertion and improving the plateau capacity. Among them, phosphorus doping is more often associated with reduced sodium-ion diffusion barriers through P-related bonding environments, while sulfur doping tends to introduce more defects and porous structures, which can provide additional active sites for sodium storage. Fluorine doping differs from the above dopants in that its main role is usually related to interfacial regulation. The formation of NaF-rich interphase products can help stabilize the electrode/electrolyte interface, thus improving the ICE and cycling stability.

These results indicate that different dopants regulate hard carbon through different dominant mechanisms, and each shows its own advantages in balancing conductivity, structural regulation, and interfacial stability. Therefore, future work should focus on clarifying the structure–property relationship of different dopants and exploring rational co-doping strategies to achieve more effective and coordinated regulation of sodium-storage behavior.

4.4 Surface modification

Surface modification enables deep regulation of the interfacial physicochemical properties of hard carbon by constructing dense

physical barrier layers or artificial SEI film on the carbon surface. Such interfacial engineering not only effectively suppresses irreversible electrolyte decomposition by sealing open pores and passivating surface defects, thereby markedly improving the ICE and cycling stability, but also accelerates Na^+ capture and transport through optimization of interfacial charge-transfer resistance. Consequently, surface modification is regarded as a pivotal processing strategy for translating hard carbon anodes from laboratory-scale demonstrations to commercially viable SIBs with high safety and long service life.

Owing to the insufficient stability of the SEI film, hard carbon anodes commonly suffer from a relatively low ICE. In contrast, soft carbon, benefiting from its smoother surface, tends to induce the formation of a more ordered SEI, although its intrinsic sodium storage capability is comparatively limited. To integrate the advantages of both materials, Wang *et al.*¹³⁵ realized a soft-carbon-coated hard carbon via a liquid-phase coating strategy combined with low-temperature carbonization. It was revealed that the soft carbon coating delivers multiple synergistic effects: it markedly reduces the specific surface area and surface defect density, increases the content of surface carbonyl groups, and simultaneously enriches the closed pores structure within the hard carbon matrix. As a consequence of these structural optimizations, both the ICE and the reversible capacity of hard carbon are substantially improved. Electrochemical evaluations demonstrate that, when employed as a SIBs anode, the soft-carbon-coated hard carbon achieves a high reversible capacity of $316.5 \text{ mAh}\cdot\text{g}^{-1}$ along with an excellent ICE of 85.3%. In addition, outstanding cycling stability is observed, with a capacity retention of 84.0% after 200 cycles at a current density of $150 \text{ mA}\cdot\text{g}^{-1}$. Similarly, Yin *et al.*¹³⁶ prepared a soft carbon/hard carbon composite by co-pyrolyzing asphalt with walnut shells. Their study shows that the introduction of the soft carbon component effectively seals most of the open pores on the hard carbon surface, leading to a pronounced decrease in specific surface area. This structural modification suppresses excessive growth of the SEI, thereby significantly enhancing the reversible capacity. Experimental results indicate that, compared with pristine hard carbon, the modified material exhibits an approximately 68.4% increase in specific capacity at $50 \text{ mA}\cdot\text{g}^{-1}$, while also demonstrating promising rate capability and long-term cycling stability.

Although metal-salt activation is effective in generating pores and enlarging the interlayer spacing to provide abundant sodium storage sites, it often results in a loosened surface structure that increases the susceptibility to parasitic reactions. In contrast, coal-tar pitch coatings exhibit limited intrinsic sodium storage capacity but are capable of passivating surface defects and constructing a robust physical barrier. To synergistically integrate high capacity with long cycling stability, Zhou *et al.*¹³⁷ proposed a combined strategy that couples potassium-salt activation with coal-tar pitch surface modification, using anthracite as the carbon precursor to induce the formation of abundant closed pores. Initially, activation with conventional potassium salts (e.g., KOH and $\text{KCl}/\text{K}_2\text{CO}_3$) generates a highly disordered carbon framework accompanied by rich oxygen-containing functional groups on the surface. During the subsequent high-temperature treatment, the coal-tar pitch coating undergoes crosslinking reactions with these oxygen functionalities, effectively converting the initially formed open nanopores into closed pores. Concurrently, the coating suppresses the graphitization of coal tar pitch, giving rise to a distinctive pseudo-graphitic overlayer on the carbon surface. Benefiting from

this tailored architecture, the resulting material achieves an ICE of 85.6% and an enhanced reversible specific capacity of 345.0 mAh·g⁻¹.

Although surface-coating strategies can effectively regulate the electrode–electrolyte contact interface, their contribution to enhancing bulk electronic conductivity is generally limited. In contrast, homojunction/heterojunction architectures exploit distinct structural features within the same chemical composition to generate a built-in electric field at the microscopic interface. To integrate surface protection with bulk-phase reinforcement, Yu *et al.*¹³⁸ engineered homo/heterojunctions on hard carbon surfaces, thereby successfully inducing the formation of a stable SEI film. This architecture effectively shields defect sites, substantially suppressing parasitic redox reactions at the electrode surface as well as continuous electrolyte decomposition. As evidenced by atomic force microscopy (AFM) (Figs. 17a and 17d) and mechanical property measurements (Figs. 17b and 17e), the Al₂O₃-based heterostructured sample (HC-Al₂O₃-5%) not only inhibits the

persistent decomposition of NaPF₆ and mitigates excessive NaF accumulation compared with pristine hard carbon, but also promotes the formation of a thinner and more compact SEI film, leading to a pronounced reduction in interfacial charge-transfer resistance (Figs. 17c and 17f). Fig. 17g further illustrates the mechanism by which the homotypic heterostructured HC-Al₂O₃ architecture improves the ICE. Benefiting from this interfacial engineering strategy, both the ICE and sodium storage capability are markedly enhanced, with the optimized anode delivering a reversible capacity of 321.5 mAh·g⁻¹ at a current density of 50 mA·g⁻¹. Moreover, even after 2,000 cycles at a high current density of 1 A·g⁻¹, a capacity retention of 86.9% is maintained, substantially outperforming the untreated counterpart (52.6%).

5 Conclusions and outlook

Hard carbon has emerged as one of the most promising anode materials for sodium-ion batteries due to its disordered structure,

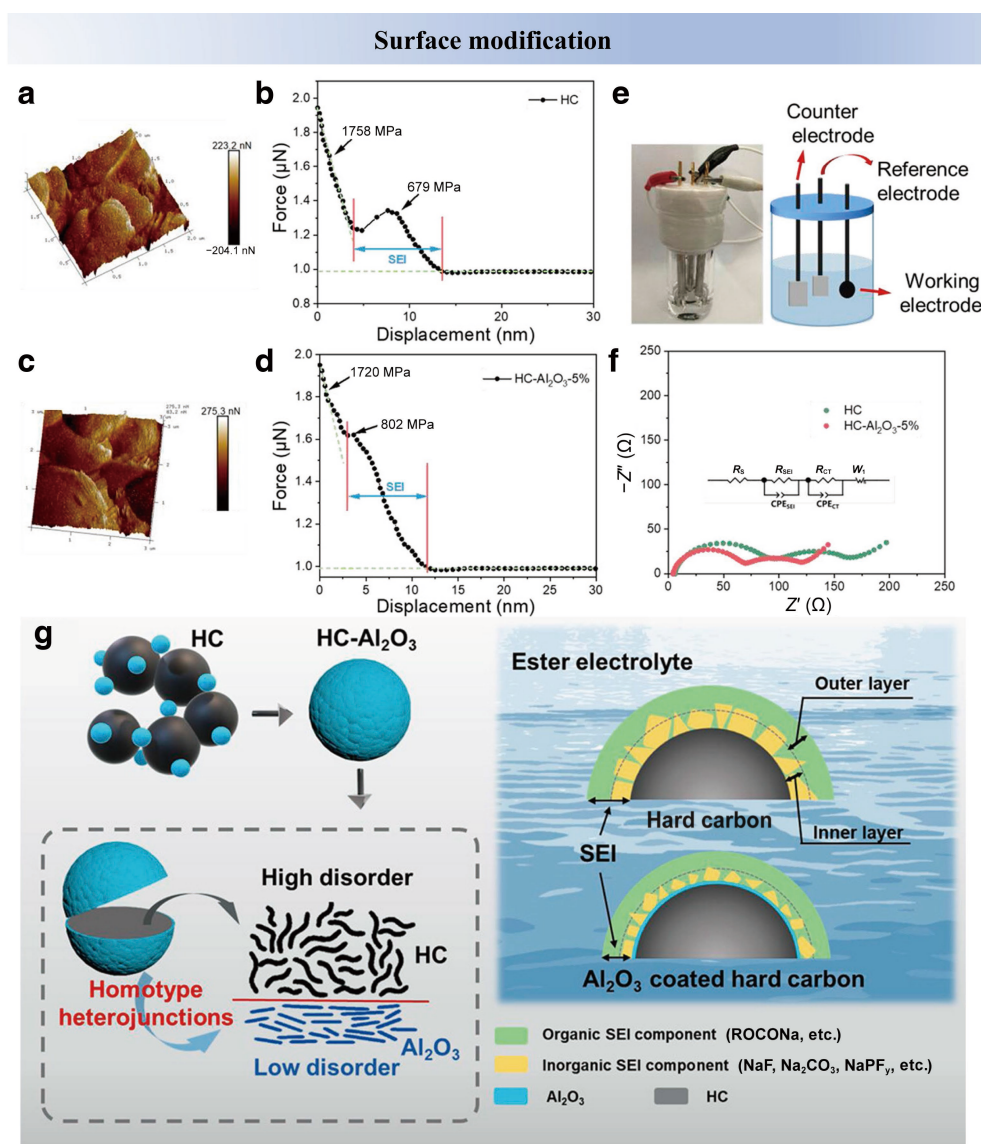


Fig. 17. Electrochemical performance and behavior of surface modification based hard carbon in Na-ion battery. a, d, AFM images and b, e mechanical properties of HC and HC-Al₂O₃-5% after 1 cycle; c, Digital photo and schematic diagram of the three-electrode system; f, EIS results of HC and HC-Al₂O₃-5% after 1 cycle; g, The schematic diagram of Al₂O₃ layers improving ICE of hard carbon electrode, Reproduced with permission from Ref.¹³⁸, © Yu, C. X. *et al.* 2023.

tunable pore architecture, and favorable sodium-storage properties, enabling high reversible capacity, stable cycling performance, and competitive rate capability. With the continuous advancement in the understanding of hard-carbon microstructures and sodium-storage mechanisms, increasingly precise regulation of the material's microstructural features and electrochemical properties has been achieved through strategies such as precursor engineering, pore structure engineering, heteroatom doping, and interfacial engineering. Despite substantial progress in microstructure regulation and mechanistic understanding, current research is still limited by insufficiently resolved structure-property relationships and a lack of unified interpretation of sodium-storage behavior.

These limitations are primarily associated with unresolved scientific inconsistencies in the field, including the coexistence of multiple sodium-storage mechanisms (surface adsorption, interlayer intercalation, and pore filling), the unclear dominance and coupling relationships among these mechanisms under different structural conditions, and the absence of a quantitative framework linking pore architecture with electrochemical performance. In addition, relatively low initial Coulombic efficiency and incomplete control of structural evolution further restrict practical optimization.

To address these challenges, future research should focus on the following key directions:

(1) Fundamental understanding and precise regulation of precursor effects. Hard-carbon precursors, including pitch, coal, resins, and biomass-derived materials, not only offer well-established processing routes and high structural tunability, but also provide critical design freedom through their molecular configurations, crosslinking degrees, and microscopic homogeneity. These intrinsic characteristics play a decisive role in regulating the disordered carbon framework, pore architecture, and defect distribution of the resulting hard carbon. Accordingly, systematic investigations of structure-evolution pathways enabled by precursor modification strategies, such as acid washing, alkali treatment, hydrothermal processing, and ball milling, are essential for elucidating the correlations among precursor composition, pyrolysis and carbonization kinetics, and the ultimate sodium-storage behavior. Establishing such relationships would facilitate the construction of a designable structure-property mapping linking precursor regulation, microstructural engineering, and electrochemical performance, thereby providing a mechanistic foundation for the rational development of high-performance hard-carbon anode materials.

(2) Quantitative elucidation of structure-property relationships and sodium-storage mechanisms. Although a broad consensus has been reached regarding the synergistic contributions of closed pores filling, interlayer adsorption, and surface adsorption to sodium storage in hard carbon, the relative contributions, governing conditions, and mutual interactions of these mechanisms remain insufficiently defined within a universal theoretical framework. In the future, the quantitative mapping between pore structure parameters (pore size distribution, closed pores ratio, layer spacing), graphitization degree and sodium storage behavior of hard carbon should be constructed by means of *in situ/ex situ* characterization technology, multi-scale computational simulation and machine learning, so as to realize the transition of sodium storage behavior from “empirical understanding” to “mechanism driven design”.

(3) Overcoming electrochemical performance bottlenecks. To address the insufficient ICE and the limitations in electron/ion transport, in depth investigations from both interfacial chemical

and physical perspectives are required. Through interface regulation, construction of conductive frameworks, and atomic doping (nitrogen, phosphorus, sulfur, and fluorine) induced electronic structure reconstruction, the intrinsic impacts on charge-transfer kinetics, interfacial stability, and Na⁺ adsorption energetics can be systematically elucidated.

(4) With the development of sodium-ion batteries toward practical applications, structural consistency, mechanistic stability, and electrochemical reproducibility of hard carbon under large-scale synthesis conditions are becoming increasingly important. Future efforts should focus on elucidating how synthesis parameters influence the long-term stability of microstructures and sodium-storage mechanisms, while also ensuring environmentally friendly and energy-efficient fabrication routes. In addition, systematic evaluation of the compatibility between hard carbon anodes and full-cell components, including cathodes and electrolytes, is essential to further improve electrochemical performance and accelerate practical implementation in sodium-ion battery systems.

Overall, the development of hard carbon anodes should advance toward a unified framework integrating precursor chemistry, microstructural evolution, and sodium-storage mechanisms. Establishing a closed-loop structure-property-performance relationship is expected to enable rational material design and accelerate the practical deployment of sodium-ion energy storage systems.

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Data availability

Not applicable.

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Competing interests

The authors declare no conflict of interest.

Use of AI statement

During the preparation of this paper, the authors used DeepSeek in order to improve the language of the manuscript. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.



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