



High-performance carbon cathode materials for sodium ion capacitors

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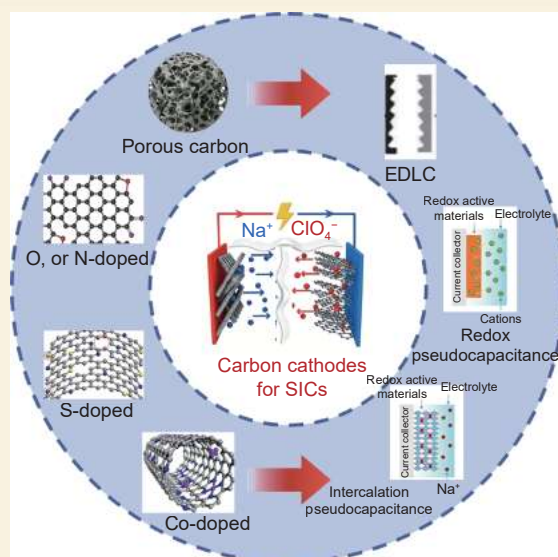
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Abstract: Sodium-ion capacitors (SICs), integrating battery-type anodes and capacitive cathodes, are an excellent bridge between the high energy density of sodium-ion batteries and the high power density of supercapacitors. Among their various components, carbon-based cathode materials play a pivotal role in dictating the overall energy/power output and cycling stability of SICs, yet their development remains a critical problem. Recent advances in high-performance carbon cathode materials for SICs are summarized, with a particular focus on porous carbon structures and heteroatom (O, N, S) doped carbons. Furthermore, the underlying energy storage mechanisms, including the adsorption/desorption of dual ions (Na^+ and anions) and surface redox pseudocapacitance, are thoroughly discussed. Finally, rational design strategies and promising prospects for the scalable production of SICs are proposed. This work aims to provide deep insights and practical guidelines for the future development of advanced carbon cathodes to meet the ever-growing demands of electrochemical energy storage.

Key words: Carbon materials; Cathodes; Sodium ion capacitors; Supercapacitor



1 Introduction

With the rapid expansion of renewable energy and the pressing demands of smart grids, developing next-generation electrochemical energy storage devices that simultaneously feature high energy density, high power density, and long cycle life has become an urgent priority^[1–10]. Sodium-ion capacitors (SICs), as a highly promising hybrid system, ingeniously integrate battery-type anodes (providing high capacity) with capacitive-type cathodes (delivering high power) to bridge the gap between conventional supercapacitors and sodium-ion batteries^[1,4–5,10–22]. However, the overall performance of SICs is often hindered by the kinetic and capacity mismatches between the two electrodes^[23]. Notably, the carbonaceous cathode plays a decisive role in determining

the energy/power output and cycling stability of the full device, a status rooted in its irreplaceable advantages: abundant raw material sources (e.g., coal-based humic acid, biomass), low fabrication cost, exceptional electrical conductivity, and tunable pore/chemical structures that enable ultrafast ion adsorption/desorption kinetics^[24–26]. Consequently, a profound understanding of the energy storage mechanisms in carbon cathodes and the rational design of their architecture are of paramount importance for the practical application of SICs.

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cathodes is highly intricate, primarily encompassing electrical double-layer capacitance (EDLC), pseudocapacitance, and intercalation/adsorption mechanisms^[16,26]. It is worth noting that within the operating voltage window of SICs, the carbon cathode is involved not only in the physical/chemical adsorption/desorption of anions but also in the surface redox reactions or intercalation of sodium cations (Na^+). Based on the charge compensation mechanism, the energy storage process can be further classified into anion-dominated electrolyte-consuming and cation-dominated metal-ion exchanging types^[5,27–28]. The former, relying heavily on anion adsorption/desorption, often leads to electrolyte concentration imbalances and irreversible ion trapping. In contrast, the latter effectively maintains electrolyte concentration by utilizing the reversible insertion/extraction of Na^+ , demonstrating superior cycling retention. Therefore, the precise manipulation of surface chemistry and microstructure to achieve efficient and stable dual-ion cooperative storage is currently a research focal point.

In recent years, significant advancements have been made in enhancing the energy storage performance of carbon cathodes through strategies such as constructing multidimensional porous structures and introducing heteroatom dopants^[6,24,26,29–30]. On one hand, porous carbon, with its interconnected pore networks, high specific surface area, and tunable pore size distributions (especially the synergy between micro- and mesopores), provides abundant active sites and facilitates rapid ion transport^[31]. On the other hand, heteroatom doping (e.g., O, N, S, B) can effectively modulate the electron cloud density of the carbon skeleton, introduce additional Faradaic pseudocapacitance, and enhance the adsorption energy for specific ions^[32–36]. For instance, oxygen doping introduces functional groups like carbonyls ($\text{C}=\text{O}$) that promote Na^+ adsorption, while nitrogen doping alters the spin density and electron-donating properties of the carbon layers, significantly boosting anion adsorption. Furthermore, sulfur doping, owing to its larger atomic radius, induces more structural defects and optimizes ion diffusion kinetics. Despite these pro-

gresses, a systematic summary and deep mechanistic analysis regarding the synergistic modulation of porosity and surface chemistry to maximize dual-ion storage efficacy are still lacking.

This review focuses on the latest developments in carbon-based cathode materials for sodium-ion capacitors. Moving beyond traditional narratives, we emphasize the relationships between materials structure property and storage performances, providing a deep dive into the design principles and electrochemical behaviors of porous carbon and heteroatom (O, N, S)-doped carbons (Fig. 1). By integrating advanced in/ex-situ characterization techniques with theoretical calculations, this work elucidates the adsorption/desorption kinetics and redox mechanisms of Na^+ and anions on the carbon cathode interface. Finally, we outline the existing challenges and future opportunities in this field. This review aims to offer novel design philosophies and theoretical guidance for the development of high-performance, cost-effective sodium-ion capacitors.

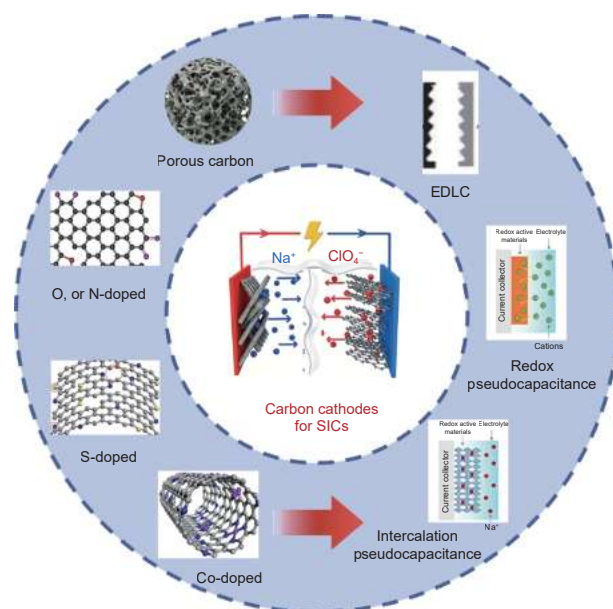


Fig. 1 Carbon cathodes for sodium-ion capacitors

2 Carbon cathodes for SICs

Despite the significant progress in developing advanced cathode materials, carbon-based cathodes remain the dominant and most pragmatic choice for

commercial SICs. Their overwhelming advantages, including exceptional electrical conductivity, earth-abundance, environmental benignity, and a wide electrochemical stability window, perfectly cater to the demands of high-power and long-cycle-life applications. Furthermore, the charge storage mechanism in carbon cathodes is primarily based on the rapid adsorption/desorption of ions, which inherently bypasses the severe lattice strain and structural degradation commonly encountered in inorganic insertion compounds. However, the energy density of SICs is still fundamentally limited by the relatively low specific capacity of carbon cathodes and the sluggish kinetics of conventional microporous structures. Therefore, future research must pivot towards the rational design of multi-level porous architectures and the strategic introduction of heteroatom dopants. Such modifications are essential to optimize the ion transport pathways, enhance the surface wettability, and ultimately unlock the full potential of carbon cathodes in next-generation sodium-ion capacitors.

2.1 Porous carbon cathodes

Porous carbon stands as the predominant cathode material for sodium-ion capacitors due to its exceptional electrical conductivity, earth-abundant precursors, and highly tunable textural properties. Its rationally designed hierarchical pore structure, featuring abundant micropores (< 2 nm) synergistically combined with small mesopores, maximizes ion-accessible surface area while significantly shortening electrolyte transport pathways. This unique architecture enables rapid charge storage kinetics and robust structural stability, laying a solid foundation for high-performance dual-ion storage.

As exhibited in Fig. 2a, Zhu and colleagues devised a scalable synthesis route to fabricate spherical porous carbons (SPCs) derived from coal-based humic acid (CHA) via spray drying followed by KOH activation^[37]. Morphological characterization revealed that the resulting carbonaceous spheres possessed uniform diameters ranging from 2 to 4 μm (Fig. 2b). After carbonization and activation, the TEM images indicated a dense architecture devoid of macroscopic

pores, confirming a narrow pore size distribution (Fig. 2c). As listed in Fig. 2d, complementary nitrogen sorption analysis further verified that the pore sizes were predominantly concentrated in the micropore (< 2 nm) and small mesopore (2–4 nm) regions, which benefited the adsorption of electrolyte ion.

Electrochemical evaluations were conducted using SPCs-3 as the cathode paired with a hard carbon anode (HASH-1300) at varying mass ratios of 1 : 1, 1 : 2 and 1 : 3, designated as SICs-1, SICs-2 and SICs-3, respectively. Galvanostatic charge-discharge (GCD) profiles conducted at 0.1 A g^{-1} demonstrated quasi-rectangular shapes across all configurations, signifying ideal capacitive behavior (Fig. 2e). The device with a 1 : 2 mass ratio (SICs-2) exhibited the longest discharge duration, delivering a high energy density of 179.8 Wh kg^{-1} at a power density of 155 W kg^{-1} . Furthermore, SICs-2 maintained 89.4% of its initial capacitance after 10 000 cycles at 0.1 A g^{-1} (Fig. 2f), highlighting the structural robustness and favorable longevity of the SPCs cathode. This work establishes a viable pathway for constructing high-performance hybrid capacitors using spherical porous carbon architectures.

Biomass-derived porous carbons have emerged as a cornerstone for porous carbon cathodes, not only due to their low cost and sustainability but also because of their highly tunable textural properties. A landmark study by Liu and co-workers demonstrated this potential by utilizing garlic, a globally abundant crop, to fabricate both electrodes via differentiated thermal treatments^[38]. The resulting garlic-derived porous carbon (GDPC) cathode exhibited a remarkable specific surface area of $1682 \text{ m}^2 \text{ g}^{-1}$ and a hierarchical pore structure, which facilitated rapid ion transport and delivered a high specific capacity of 152 mAh g^{-1} at 0.05 A g^{-1} . Crucially, the success of this full cell relied on balancing the GDPC cathode with a hard carbon anode (GDHC-1300) derived from the same precursor. The anode possessed an expanded interlayer spacing of 0.371 nm and an exceptional initial coulombic efficiency of 50.7%. By precisely tuning the electrode potentials rather than merely ad-

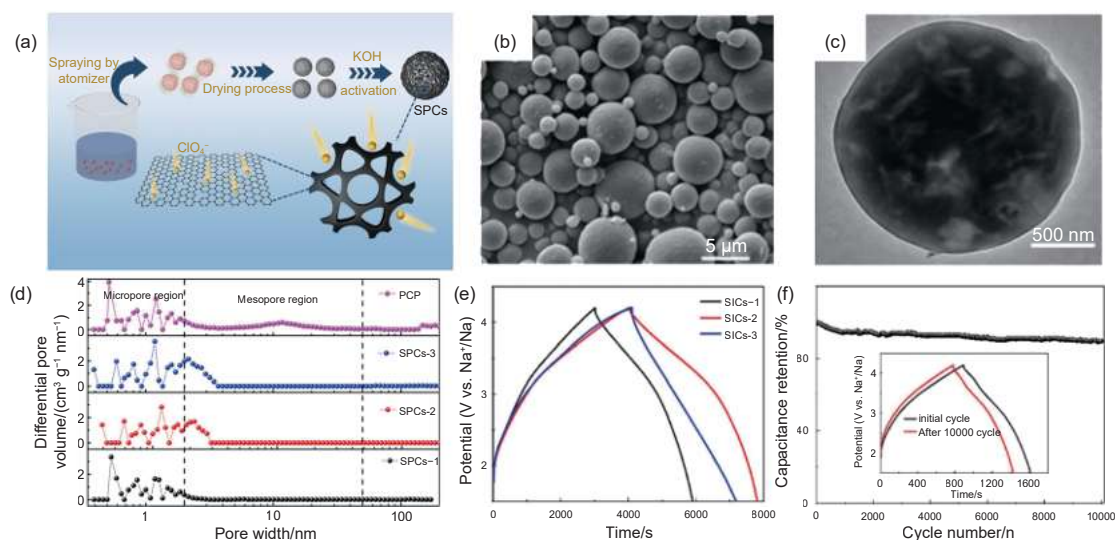


Fig. 2 Schematic illustration, structural characterization, and electrochemical performance of spherical porous carbons (SPCs)^[37]. (a) Schematic diagram illustrating the scalable synthesis of SPCs from coal-based humic acid. (b) SEM image. (c) TEM image. (d) Pore size distribution curves. (e) GCD profiles of SICs with different cathode/anode mass ratios (1 : 1, 1 : 2, 1 : 3) at 0.1 A g⁻¹. (f) Long-term cycling stability of the optimized SICs-2 device at 0.1 A g⁻¹.

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justing mass ratios, the assembled symmetric-origin SICs achieved an impressive energy density of 156 Wh kg⁻¹ at a power density of 355 W kg⁻¹, alongside outstanding cycling stability with 73% capacity retention after 10 000 cycles. This work exemplifies how leveraging the intrinsic heteroatoms and structures of biomass can yield well-matched electrodes, effectively bridging the kinetic gap between battery-type anodes and capacitor-type cathodes.

Transitioning from powdered materials to free-standing fabrics, Wang and co-workers recently demonstrated a cost-effective and scalable strategy to fabricate high-performance carbon cloth electrodes for flexible sodium-ion capacitors (SICs)^[39]. By employing renewable cotton cloth as the sole precursor and applying differentiated thermal treatments, they successfully obtained a porous carbon cloth (PCC) cathode and a hard carbon cloth (HCC) anode, effectively replacing expensive commercial carbon cloths. The PCC cathode was engineered with a full microporous structure (pore size centered at ~ 1 nm) and a remarkably high specific surface area of 1995.2 m² g⁻¹. This unique architecture enabled pure surface-controlled capacitive energy storage based on adsorption, delivering an exceptional rate capability (119 mAh g⁻¹ at 0.1 A g⁻¹ and retaining 85 mAh g⁻¹ even at an ul-

trahigh current density of 50 A g⁻¹) and outstanding cycling stability (99% capacity retention over 3000 cycles). Benefiting from the synergistic matching of the PCC cathode and HCC anode, a novel all-cloth SIC (ACSIC) was assembled. The device not only achieved a high energy density of 123 Wh kg⁻¹ and a peak power density of 12 152 W kg⁻¹ but also exhibited incredible mechanical stability, maintaining stable power output even under extreme bending and cutting conditions.

Based on the preceding discussion, while porous carbon offers high surface area, its low tap density often limits the volumetric energy density of SICs, and the over-reliance on purely physical adsorption restricts the overall specific capacity. Future research should prioritize the construction of hierarchical pore architectures that balance ion accessibility with packing density to overcome these inherent trade-offs. Furthermore, integrating precise heteroatom doping into these tailored frameworks is essential to introduce pseudocapacitance and enhance the adsorption energy for sodium ions.

2.2 O-doped carbon cathodes

Oxygen doping serves as a powerful strategy to transcend the limitations of pure porous carbon by introducing surface redox activity. The incorporation of

specific functional groups, particularly carbonyls ($\text{C}=\text{O}$), significantly enhances the electropositivity of the carbon framework, enabling strong synergistic adsorption of both Na^+ and anions. Consequently, this surface modification effectively boosts the specific capacity and improves the overall energy density of the sodium-ion capacitor.

Inspired by the ancient alchemical practice of purifying substances through thermal refinement, researchers have pioneered a localized oxygen reconstruction strategy to precisely manipulate the surface chemistry of carbon materials^[40]. Li and colleagues demonstrated that by carefully controlling the oxidation temperature, the population of specific oxygen-containing functional groups, particularly carbonyl groups ($\text{C}=\text{O}$), could be selectively increased from 27.9% to 43.3% (atom fraction). Theoretical calculations, which accounted for surface defects by passivating edge sites with hydrogen atoms, revealed that the introduction of carbonyl groups significantly enhanced the electropositivity of the carbon framework. This modification facilitated the synergistic adsorption of both Na^+ and ClO_4^- . Charge density difference analyses (Fig. 3a-b) confirmed that the carbonyl configuration (O_{c1}) and ether bonds (O_{e}) exhibited the strongest interactions with ClO_4^- , while O_{c1} and carboxyl groups (O_{c2}) showed superior charge accumulation for Na^+ adsorption. As presented in Fig. 3c-d, experimental validation was conducted using carbon materials oxidized at varying temperatures (CRPCx series). X-ray photoelectron spectroscopy (XPS) analysis of the O 1s orbital illustrated the thermal evolution of functional groups: the content of $\text{C}=\text{O}$ reached its maximum at an oxidation temperature of 450 °C (CRPC450), whereas $\text{C}-\text{OH}$ and COOH groups diminished due to dehydration and thermal instability, respectively. Correspondingly, electrochemical assessments (Fig. 3e-f) showed that CRPC450 delivered a high specific capacity of 145 mAh g^{-1} at 0.1 A g^{-1} , significantly outperforming the pristine sample. Even at a high current density of 10 A g^{-1} , it retained 79 mAh g^{-1} , alongside excellent capacity recovery, confirming the structural stability

imparted by the optimized oxygen configuration.

As shown in Fig. 3g, they used the ex-situ XPS and in-situ Raman characterizations to elucidate the dual-ion storage mechanism. The results indicated that while $\text{C}-\text{O}$ content varied inversely with $\text{C}=\text{O}$, the charging process involved the desorption of Na^+ and the adsorption of ClO_4^- . Specifically, they found that the carbon atoms in $\text{C}=\text{O}$ groups participated in redox reactions with ClO_4^- when the voltage exceeded 2 V, contributing to pseudocapacitance capacity, whereas oxygen atoms in $\text{C}=\text{O}$ groups primarily interacted with Na^+ when the voltage is below 2 V. They found that within the discharge voltage window of 4.2-3.0 V, ClO_4^- desorbs from the surface of the carbon cathode, while $\text{C}-\text{O}-\text{C}$ undergoes electron gain and transforms into $\text{C}=\text{O}$. In the subsequent 3-2 V range, ClO_4^- desorption and Na^+ adsorption occur concurrently, meaning that the conversion of $\text{C}-\text{O}-\text{C}$ to $\text{C}=\text{O}$ happens alongside the conversion of $\text{C}=\text{O}$ to $\text{C}-\text{O}^-$. Finally, across the 2-1.5 V discharge region, $\text{C}=\text{O}$ continues to adsorb Na^+ from the electrolyte. When assembled into full sodium-ion capacitors, an optimal cathode/anode mass ratio of 1 : 1.5 was identified to balance cell capacity (PHC//CRPC450-1.5, Fig. 3h-i). The deviation from ideal rectangular CV curves and non-linear GCD profiles indicated a combined Faradaic and non-Faradaic storage mechanism. At 250 W kg^{-1} , devices with 1 : 1, 1 : 1.5 and 1 : 2 ratios delivered energy densities of 154, 162 and 148 Wh kg^{-1} , respectively. Notably, the device with 1 : 1.5 maintained a high energy density of 76.7 Wh kg^{-1} even at an ultra-high power density of 10 kW kg^{-1} . This work underscores the efficacy of targeted oxygen functionalization in balancing dual-ion storage and advancing the energy density of hybrid capacitors.

Despite these improvements, the thermal instability of certain oxygen groups, such as carboxyls, poses a challenge to the long-term stability of the cathode. Future research should focus on precise thermal control to maximize stable carbonyl content while minimizing detrimental groups. Furthermore, integrating oxygen doping with other heteroatoms could unlock

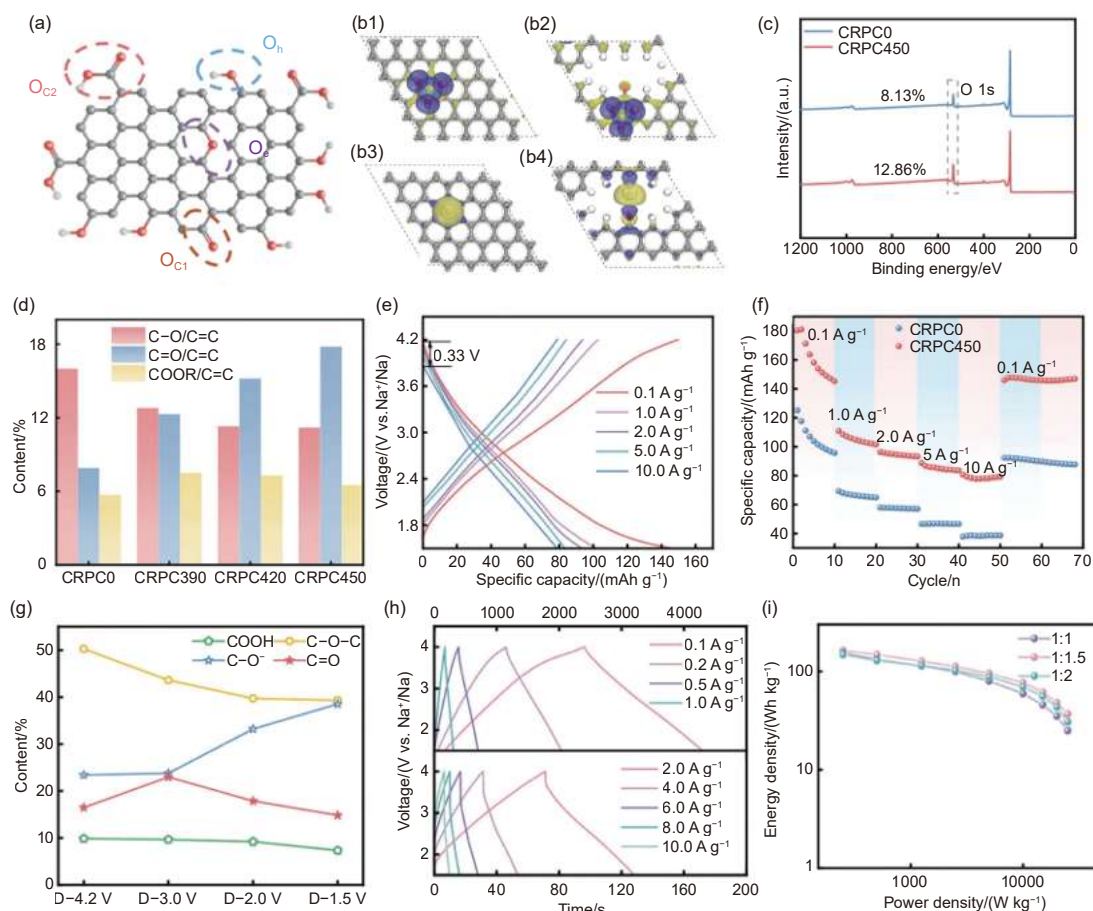


Fig. 3 Localized oxygen reconstruction strategy and dual-ion storage mechanism in CRPCx^[40]. (a–b) Charge density difference plots illustrating the interaction strength between functional groups and $\text{ClO}_4^-/\text{Na}^+$. (c–d) XPS spectra and quantitative analysis of oxygen-containing functional groups showing the evolution of C=O content with oxidation temperature. (e–f) Galvanostatic charge-discharge profiles and rate performance of CRPCx electrodes. (g) Ex situ XPS analysis tracking the transformation of oxygen functional groups during the discharge process. (h–i) Electrochemical performance of the PHC//CRPC450-1.5 full cells, including GCD curves and the Ragone plot demonstrating high energy/power density. Copyright 2025, Wiley-VCH GmbH

new synergistic effects to further refine the dual-ion storage mechanism.

2.3 N-doped carbon cathodes

Nitrogen doping effectively modulates the electronic structure and defect density of carbon frameworks, enhancing their affinity for anion adsorption. It expands the interlayer spacing to facilitate rapid ion transport and improves electrolyte wettability, boosting both rate capability and specific capacity. These advantages position N-doped carbons as promising candidates for high-performance SIC cathodes.

Cai and colleagues explored the pseudocapacitive storage mechanisms of ClO_4^- and Na^+ ions within carbon electrodes through a novel room-temperature NH_3 plasma strategy^[41]. Utilizing bamboo as a sustainable carbon precursor, the team fabricated nitrogen-doped porous carbon (NPC) composites via cal-

cination followed by controlled NH_3 plasma treatments. Structural characterizations revealed that the plasma etching process effectively modulated the carbon architecture. XRD patterns indicated that the (002) diffraction peak shifted to lower angles with increasing treatment time from 15 to 60 min, signifying an expansion of the interlayer spacing (Fig. 4a). Concurrently, Raman spectroscopy showed a progressive increase in the I_D/I_G ratio, confirming that prolonged plasma exposure introduced a higher degree of defects, although excessive treatment (75 min) led to structural collapse and a reduction in defect density (Fig. 4b). The etching effect was further corroborated by pore structure analysis, which demonstrated that optimized treatment times increased the volume of meso/macropores and reduced the contact angle from 15° to 7° , thereby enhancing electrolyte infiltration

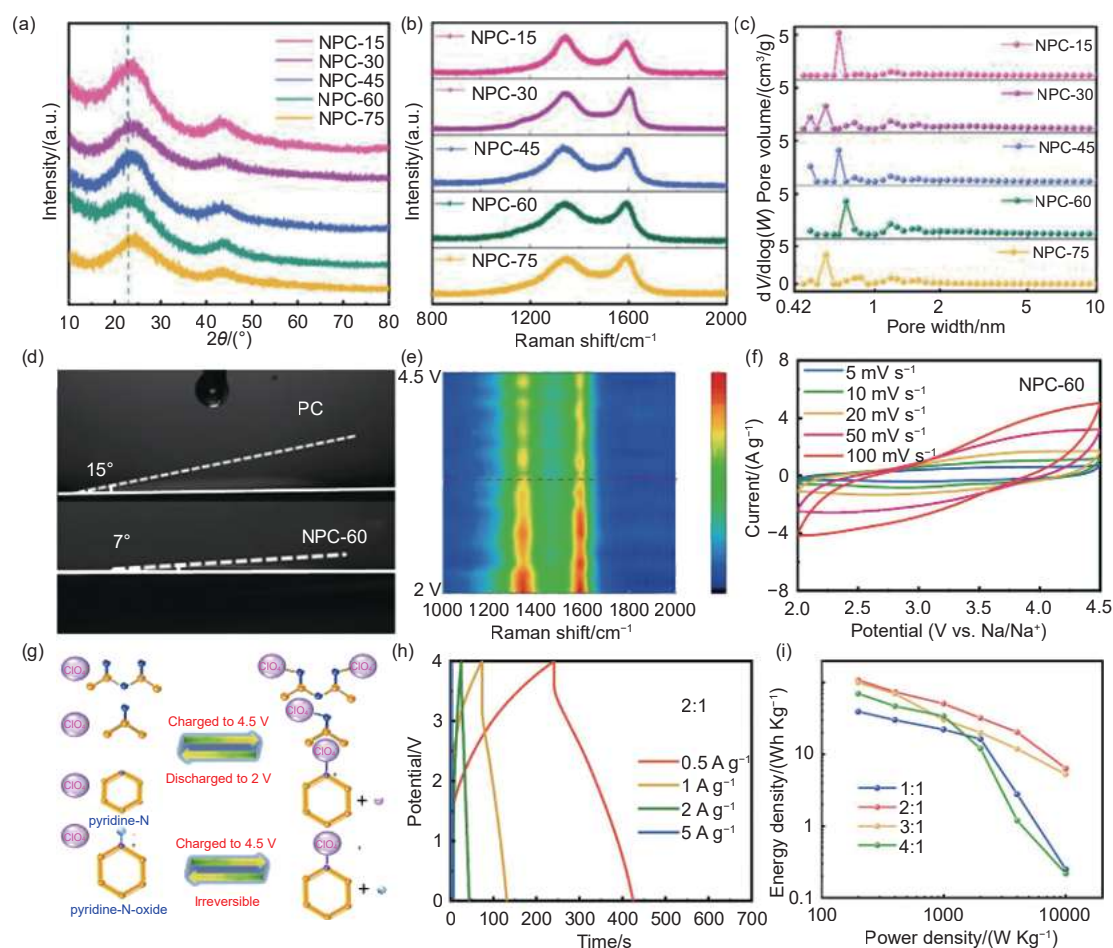


Fig. 4 Structural evolution and electrochemical performance of N-doped porous carbons (NPCs) via NH_3 plasma engineering^[41]. (a) XRD patterns, (b) Raman spectra, (c) Pore size distribution, and (d) Contact angle measurements of related samples. (e) Ex situ Raman spectra delineating the dual-ion storage regimes during charging. (f) Galvanostatic charge-discharge profiles and rate performance of NPC electrodes. (g) Proposed mechanism of anion adsorption on pyridinic-N and C=O sites. (h) GCD profiles and (i) Ragone plot of the optimized NPC-based SICs. Copyright 2021, Elsevier Ltd

(Fig. 4c-d). Ex-situ Raman analysis during the initial charge cycle delineated 2 distinct processes: a low-voltage region (2-3.75 V) governed by physical ion adsorption without altering the carbon structure, and a high-voltage region (3.75-4.5 V) where pseudocapacitive reactions induced changes in the *D/G* band intensity (Fig. 4e). Electrochemical evaluations identified the NPC-60 sample as the optimal performer, delivering a specific capacity of 101 mAh g^{-1} at 0.1 A g^{-1} , significantly outperforming other variants (Fig. 4f). Electrochemical analysis revealed that pyridinic-N lost electrons upon charging, acquiring a positive charge that facilitated anion adsorption. However, due to the stable structure of pyridine-N-oxide, this process proved largely irreversible. Conversely, the reversible charge transfer involving C=O groups demonstrated their suitability for effective an-

ion adsorption (Fig. 4g). The enhanced performance was attributed to the formation of specific nitrogen functionalities and defects that facilitated anion adsorption. When assembled into full cells with an optimized cathode/anode mass ratio of 2 : 1, the devices operated stably up to 4.5 V (Fig. 4h). The resulting sodium-ion capacitors exhibited excellent rate capability and achieved energy densities of 107, 73, 50, 31 and 20 Wh kg^{-1} at corresponding power densities of 200, 400, 1000, 2000 and 4000 W kg^{-1} , respectively (Fig. 4i). This work highlights the efficacy of room-temperature plasma engineering in tailoring carbon surface chemistry for high-performance dual-ion storage.

While nitrogen doping effectively enhances the electrochemical performance of carbon cathodes, it still faces persistent challenges. The difficulty in dir-

ectionally regulating nitrogen-containing functional groups and the typically low nitrogen content limit the precise optimization of dual-ion storage capabilities. Future work should focus on developing more controllable doping strategies to balance defect density and functional group stability for long-term cycling applications.

2.4 S-doped carbon cathodes

Sulfur doping leverages its larger atomic radius to introduce abundant structural defects, significantly enhancing ion diffusion kinetics. The synergistic effect of sulfur and oxygen co-doping optimizes surface wettability and creates additional active sites for dual-ion storage.

Liu and colleagues engineered sulfur and oxygen co-doped porous carbons (SOPCs) through a sophisticated synthesis involving directional freezing and multi-step activation^[29]. The process began with the mixing of methyl cellulose, β -cyclodextrin, and NaCl, followed by directional freezing to induce NaCl crystallization, which acted as a template for macro/mesopore formation (Fig. 5a). Subsequent carbonization at 400 °C and KOH activation at 700 °C yielded an oxygen-rich porous carbon (OPC). Sulfur was then incorporated by co-calcination at 550 °C; due to its larger atomic radius, sulfur preferentially occupied edge and defect sites, inducing additional lattice strain and generating more defects (Fig. 5b-c). XPS analysis confirmed the successful integration of thiophene-like and oxidized sulfur species (Fig. 5d). Structural characterization revealed that increasing sulfur content correlated with a higher proportion of micropores (< 2 nm) and a decrease in average pore size, as larger sulfur atoms tended to block mesopores (Fig. 5e). Electrochemical evaluations identified SOPC-20 as the optimal formulation, delivering a high specific capacity of 178.9 mAh g⁻¹ at 0.05 A g⁻¹ (Fig. 5f). This sample also exhibited superior rate capability, retaining 63.8 mAh g⁻¹ even at 10 A g⁻¹, with excellent capacity recovery (Fig. 5g). Ex situ XPS analysis elucidated the dual-ion storage mechanism (Fig. 5h). During charging, Na₂S_x lost electrons to form S species and Na⁺, while PF₆⁻ adsorbed onto the

cathode surface. Conversely, during discharging, PF₆⁻ desorbed and Na⁺ re-intercalated, forming C—O—Na bonds and regenerating Na₂S_x. When assembled into a full cell (graphite//SOPC-20), the device exhibited ideal capacitive behavior with a quasi-rectangular CV curve and triangular GCD profiles (Fig. 5i). The SIC achieved a remarkable energy density of 105.6 Wh kg⁻¹ at 714 W kg⁻¹, maintaining 39.7 Wh kg⁻¹ even at an ultra-high power density of 14 286 W kg⁻¹, highlighting the potential of S, O co-doping for high-power applications.

However, the irreversible formation of residual sulfide species during cycling remains a challenge to long-term stability. Future research should focus on stabilizing sulfur-containing functional groups and mitigating side reactions. Integrating sulfur doping with hierarchical pore designs could further unlock the potential of these materials for practical SIC applications.

2.5 Co-doped carbon cathodes

While single heteroatom doping (e.g., N or S alone) effectively modulates the electronic structure and introduces active sites, co-doping strategies synergistically integrate the merits of multiple heteroatoms, thereby overcoming the inherent limitations of single-doping approaches. By incorporating two different heteroatoms (such as N/S, N/O or N/P), the charge distribution, spin density, and chemical reactivity of the carbon matrix can be finely tuned. This multi-heteroatom synergy not only creates a greater number of defective active sites for ion adsorption but also optimizes the surface wettability and electronic conductivity, leading to a significant enhancement in both gravimetric and volumetric capacitive performance.

A prime example of advanced architectural control via heteroatom doping is the development of nitrogen-modulated densified carbon architectures^[42]. Li and co-workers demonstrated that by introducing nitrogen species during the carbonization of organic sodium salts, the reaction pathways of the intermediates could be precisely regulated. The nitrogen functionalities suppressed the formation of active pore-forming agents (e.g., Na₂C₂O₄ decomposing into Na₂CO₃) and

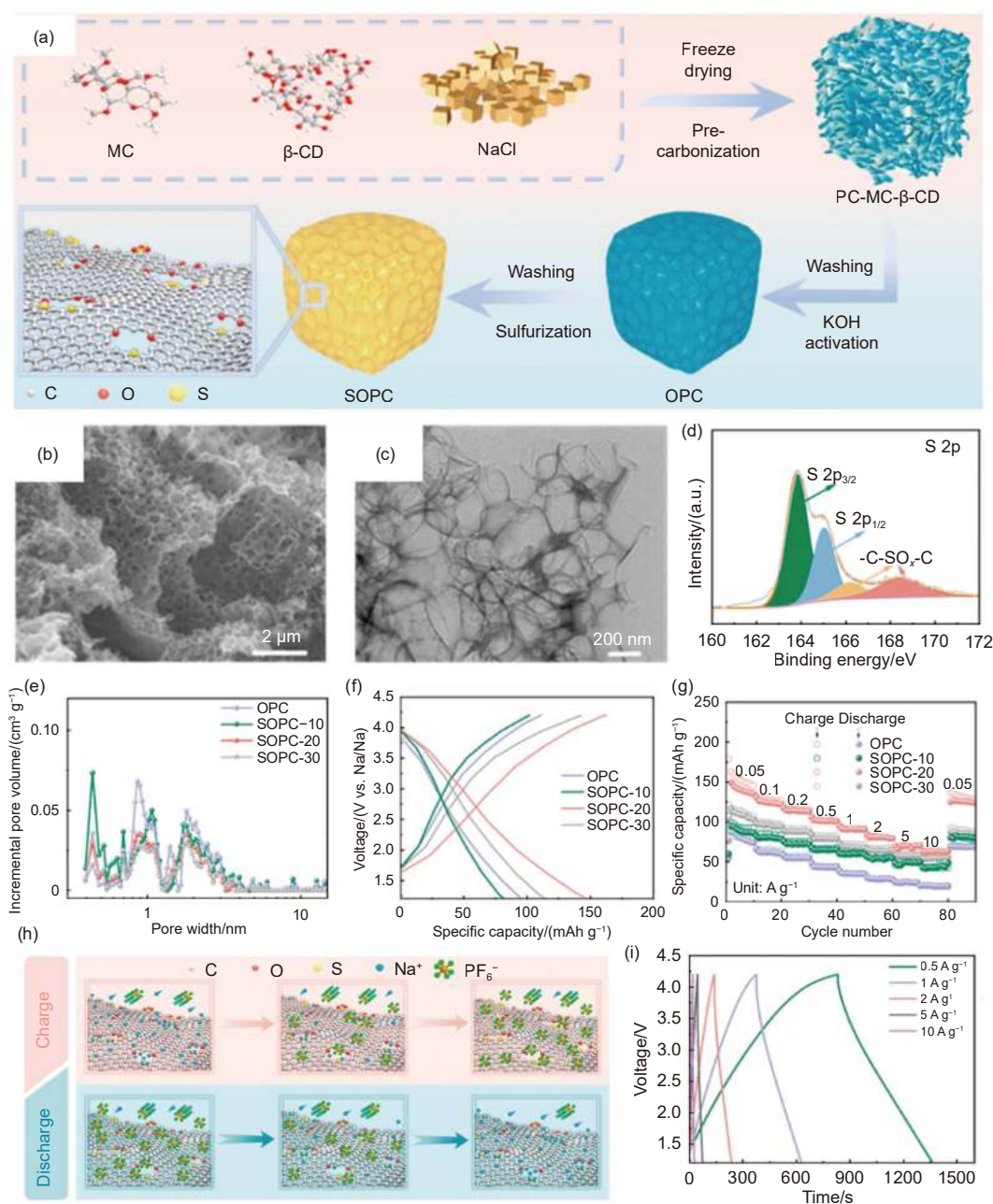


Fig. 5 Synthesis, structural characterization, and dual-ion storage mechanism of S, O co-doped porous carbons (SOPCs)^[29]. (a) Schematic illustration of the synthesis process involving directional freezing, salt templating, and sulfur doping. (b-c) SEM and TEM images. (d) High-resolution S 2p XPS spectrum. (e) Pore size distribution. (f-g) Electrochemical performance of SOPC-x cathodes in half-cells, including charge-discharge profiles and rate capability. (h) Proposed dual-ion storage mechanism involving the reversible transformation between Na_2S_x and $\text{C}=\text{O}/\text{PF}_6^-$. (i) GCD profiles of the graphite//SOPC-20 full cell. Copyright 2025, Elsevier Ltd

instead promoted the generation of inert molten salts (e.g., NaCN). This innovative approach effectively inhibited excessive pore expansion, thereby dramatically increasing the tap density of the carbon material from 0.22 to 0.55 g cm⁻³. Consequently, the optimized nitrogen-doped carbon delivered an exceptionally high volumetric capacity of 68 mAh cm⁻³ and an

impressive areal capacity of 1.58 mAh m⁻², far surpassing conventional high-surface-area porous carbons. Furthermore, the compact structure and enriched active groups (e.g., pyridinic-N and carbonyls) facilitated a substantial pseudocapacitance contribution, while simultaneously reducing the consumption of toxic solvents (like NMP) and electrolytes by over

30% during electrode fabrication and electrochemical testing. This highlights a highly cost-effective and environmentally friendly route for practical, high-volumetric-energy-density SICs.

Beyond bulk density optimization, co-doping plays a pivotal role in addressing the kinetic mismatches in full-cell configurations^[43]. Zou et al. utilized nitrogen-doped 3D hierarchical porous carbons (NHPCs) as a platform to achieve kinetic matching in a full-carbon sodium-ion capacitor. The incorporation of nitrogen into the carbon framework provided abundant active sites and improved electrical conductivity, endowing the NHPC anode with a remarkable pseudocapacitive contribution (dominating its storage mechanism) and a high reversible capacity of 197 mAh g^{-1} at 2 A g^{-1} . When paired with a KOH-activated counterpart (NHPAC) serving as the cathode which possessed a large specific surface area ($1478 \text{ m}^2 \text{ g}^{-1}$) and abundant meso/macropores for rapid anion adsorption—the resulting full-carbon SIC benefited immensely from their similar material chemistries. This strategic design bridged the kinetic gap between the battery-type anode and the capacitor-type cathode, enabling the device to achieve a high energy density of 115 Wh kg^{-1} at a power density of 200 W kg^{-1} , along with exceptional long-term cyclability.

In summary, co-doping strategies offer a powerful and versatile toolkit for transcending the trade-offs between gravimetric capacity, volumetric energy density, and rate capability. However, precisely controlling the doping sites, understanding the complex interplay between different dopants, and scaling up the synthesis of such tailored co-doped carbons remain formidable challenges. Future research should therefore focus on leveraging advanced in situ characterization techniques and theoretical simulations to unravel the synergistic mechanisms of co-doping at the atomic level. Such insights will be crucial for guiding the rational design of next-generation carbon cathodes that seamlessly integrate high density, rich active sites, and rapid ion kinetics for cutting-edge energy storage applications.

3 Conclusions and prospects

This mini-review has systematically summarized the recent advancements in carbon-based cathode materials for sodium-ion capacitors (SICs), emphasizing the critical relationships between structure property and electrochemical performance that govern dual-ion storage mechanisms. By moving beyond conventional electric double-layer capacitance, significant breakthroughs have been achieved through rational architectural design and precise heteroatom doping strategies. Biomass-derived porous carbons, such as garlic-based and cotton cloth electrodes, demonstrate that sustainable precursors can yield hierarchical pore structures capable of delivering high energy densities and exceptional cycling stability. However, the inherent limitations of pure porous carbon, particularly low specific capacity and insufficient volumetric energy density due to low tap density, necessitate further modification.

Heteroatom doping has proven to be a powerful tool to transcend these bottlenecks. Oxygen doping, specifically the selective introduction of carbonyl groups ($\text{C}=\text{O}$), effectively modulates the electropositivity of carbon frameworks, enabling synergistic adsorption of both cations and anions and boosting energy density. Similarly, nitrogen doping via plasma engineering expands interlayer spacing and introduces defects, facilitating rapid ion transport, while sulfur doping leverages its larger atomic radius to create abundant active sites for high-power applications. The integration of these strategies, as seen in co-doped systems, offers a synergistic effect that balances gravimetric capacity with volumetric energy density and achieves kinetic matching in full cells.

Despite these progress, several challenges remain for the commercial viability of SICs. First, the precise control over doping sites and the thermal stability of functional groups (e.g., the irreversibility of pyridine-N-oxide or the volatility of sulfur species) require deeper investigation to ensure long-term cyclic stability. Second, while high specific surface areas are beneficial for capacity, they often lead to low tap

density and high electrolyte consumption, undermining the practical volumetric energy density and increasing costs. Third, the complex interplay between Na^+ and anion storage in co-doped systems is still not fully understood at the atomic level.

Future research should pivot towards the following directions: (1) Deepening mechanistic insights into ion kinetics. Beyond standard in situ characterization and theoretical calculations, future studies must focus on quantifying desolvation energy barriers in micropores, as the energy penalty for stripping solvent molecules often dictates the rate capability of SICs. Crucially, establishing the matching relationship between anion solvation structures and pore sizes is essential; designing pores that fit the desolvated ion or the solvated cluster can drastically reduce kinetic hindrance and enhance capacitance. (2) Integrating machine learning with rational design. To move beyond trial-and-error experimentation, machine learning (ML) algorithms should be employed to decode complex structure-property relationships. ML models can assist in predicting optimal heteroatom configurations, simulating ion diffusion pathways, and guiding the synthesis of compact, hierarchically porous carbons that minimize dead volume while maximizing ion-accessible surfaces, thereby resolving the long-standing trade-off between gravimetric and volumetric performance. (3) Advancing scalable synthesis and sustainability metrics. While exploring novel, low-cost synthesis routes for heteroatom-doped carbons that maintain structural integrity under high-voltage operation, the field must adopt a holistic view by conducting comprehensive life cycle assessments. Evaluating the environmental footprint and economic viability, from precursor sourcing to electrode fabrication and end-of-life recycling, is imperative to validate the practical viability and ensure the sustainable scalability of SICs technologies. Addressing these intertwined physicochemical and techno-economic challenges will undoubtedly accelerate the transition of SICs from laboratory curiosities to commercially competitive energy storage solutions.

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