



The stabilization of sulfur species in coal-derived hard carbon by micropore confinement and chemical bonding to improve sodium storage

Zhu Hong^{1,2}, Cui Yu³, Han Qi^{1,2}, Li Cunhe³, Zhou Rui^{1,2}, Chi Xiaoyu³, Shen Yanfeng^{1,2,*}, Wang Meijun^{1,2}, Guo Chunli^{3,*}, Chang Liping^{1,2}

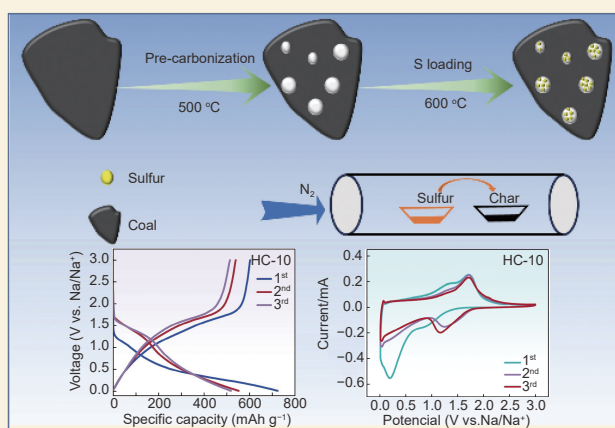
(1. College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China;

2. Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China;

3. College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China)

Abstract: To solve the problems of limited capacity, low initial coulombic efficiency, and poor long-term cycling stability in hard carbon anodes for sodium-ion batteries, a stabilization strategy is reported that uses both microporous confinement and chemical bonding to control the sulfur species. Hard carbon is derived from bituminous coal, taking advantage of its naturally condensed aromatic framework. Using a two-step thermal process, a microporous carbon framework was constructed, followed by gas-phase sulfidation to introduce sulfur species. The sulfur is confined in the micropores while forming stable covalent C-S bonds with the carbon matrix, which stabilizes the sulfur by both physical and chemical means and thus suppresses sulfur migration, which prevents interfacial side reactions and introduces additional redox-active sites. As a result, the sample delivers a high reversible capacity of 450 mAh/g after 800 cycles at a current density of 1 A/g, with excellent rate capability and cycling stability. Analysis of the storage mechanism shows that the stabilized sulfur species can reversibly participate in the sodium-ion storage and improve interfacial kinetics.

Key words: Sodium-ion batteries; Coal-derived hard carbon; Sulfur stabilization; Micropore confinement; Chemical bonding



1 Introduction

In recent years, the development of efficient, high-performance, and cost-effective energy storage technologies has become a critical research focus, driven by carbon neutrality goals, rising global energy demand, and increasing energy market volatility associated with geopolitical uncertainties^[1–3]. Compared with lithium-ion batteries, sodium-ion batteries (SIBs) have attracted increasing attention due to their abundant resources and low cost^[4–6]. Their similar rocking-chair operating mechanism further reinforces their potential as next-generation energy storage systems^[7–8]. However, their practical application is hindered by intrinsic limitations, including severe

volume expansion induced by the large Na^+ radius and sluggish solid-state diffusion kinetics, resulting in poor cycling stability and rate performance^[9–11]. Therefore, developing high-performance anode materials with fast kinetics remains a critical challenge.

Among various anode materials, coal-derived hard carbon is considered a promising candidate due to its low cost, abundant resources, and high carbon yield^[12–14]. Bituminous coal, featuring a highly con-

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densified aromatic structure, can generate robust carbon frameworks with disordered domains and short-range order during pyrolysis, providing favorable sites for sodium-ion storage^[15–16]. The coexistence of aromatic units, side chains, and oxygen-containing functional groups promotes the formation of defects and nanopores. However, its practical application is constrained by intrinsic drawbacks, including structural heterogeneity and compositional complexity, which results in unstable electrochemical performance compared with well-defined precursors^[17]. In addition, graphitization at elevated temperatures reduces defect density and active sites, hindering sodium storage^[18–20]. Therefore, precise structural regulation is crucial for improving performance.

To address these issues, extensive efforts have focused on microstructure engineering strategies, including heteroatom doping, activation, and template-assisted methods^[21–23]. Among them, sulfur incorporation is particularly attractive due to its ability to modulate electronic structure and introduce additional active sites^[24–25]. Existing approaches mainly involve substitutional sulfur doping and sulfur species introduction. The former modulates the electronic environment through limited sulfur incorporation, while the latter focuses on confining sulfur species within carbon matrices to enhance reversible capacity and suppress side reactions induced by sulfur migration. For instance, Wei et al.^[18] prepared sulfur-containing coal-based carbon via SO₂ activation, achieving a reversible capacity of 366.6 mAh/g. Li^[26] et al. reported sulfur-doped disordered carbon with a capacity of 516 mAh/g. However, these systems still suffer from low initial Coulombic efficiency (ICE < 60%), poor sulfur stability, and severe interfacial side reactions, leading to rapid performance degradation^[27].

2 Experiment

2.1 Preparation of samples

The bituminous coal came from Xinjiang, China, and sulfur powder was purchased from Aladdin (Shanghai, China). The coal was ground and sieved to <0.15 mm prior to use, followed by sequential acid

washing with hydrochloric acid and hydrofluoric acid to remove inorganic impurities. The sample was subsequently rinsed with deionized water until neutral pH and dried to obtain purified coal. Pre-carbonization was carried out in a tube furnace under a nitrogen atmosphere at 500 °C for 2 h with a heating rate of 5 °C/min, yielding the char sample. Subsequently, gas-phase sulfidation was performed using sublimed sulfur as the sulfur source. Sulfur and char were placed in separate porcelain boats at mass ratios of 5 : 1, 10 : 1 and 15 : 1, with the sulfur boat positioned upstream (~ 5 cm) to ensure sufficient vapor transport. The system was heated to 600 °C at a heating rate of 5 °C/min under nitrogen and maintained for 2 h, followed by natural cooling to room temperature. The obtained samples were denoted as HC-*X* (*X* = 5, 10, 15). A control sample without sulfidation treatment was prepared under identical conditions and labeled as HC.

2.2 Material characterizations

The morphology of the samples was characterized using field-emission scanning electron microscopy (SEM, JSM-7900F). Phase structures were analyzed by X-ray diffraction (XRD, Rigaku MiniFlex 600, Cu K α , λ = 0.154 nm). Raman spectroscopy (Renishaw inVia) was employed to evaluate structural defects and disorder degree. Specific surface area and pore size distribution were determined by nitrogen adsorption–desorption measurements (BET, Micromeritics ASAP 2460). Surface elemental composition and chemical states were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). Thermogravimetric analysis (TG, NETZSCH STA 409C) was conducted to investigate thermal behavior, and sulfur content was measured using an intelligent sulfur analyzer (ZK-SF300).

2.3 Electrochemical measurements

The working electrodes were prepared by mixing active material, Super P and sodium carboxymethyl cellulose (CMC) binder at a mass ratio of 8 : 1 : 1 in deionized water to form a uniform slurry. The slurry was coated onto copper foil using a doctor-blade method and dried at 80 °C under vacuum for

12 h. The dried electrodes were punched into discs with a diameter of 12 mm; Active substance loading is 1.2 mg/cm^2 . CR2032 coin cells were assembled in an argon-filled glove-box ($\varphi_{\text{H}_2\text{O}} < 0.1 \times 10^{-7}$, $\varphi_{\text{O}_2} < 0.1 \times 10^{-7}$), using sodium metal as the counter/reference electrode, glass fiber as the separator, and 1 mol/L NaPF_6 in DME (1,2-dimethoxyethane) as the electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on a CHI electrochemical workstation (Shanghai Chenhua). Galvanostatic charge-discharge (GCD) and Galvanostatic intermittent titration technique (GITT) measurements were conducted using a Land battery testing system (Wuhan). The voltage window was set to 0.01-3 V (vs. Na^+/Na).

3 Results and discussion

The synthesis process is illustrated in Fig. S1. Firstly, during the pre-carbonization of bituminous coal at 500°C , volatile matter is released and forms a rich microporous structure within the carbon framework, providing potential space for the subsequent adsorption and confinement of sulfur species. Subsequently, during the sulfidation stage at 600°C , sulfur fully contacts the carbon framework, preferentially enters the pores and defect regions of the coal-based carbon framework, and further forms a stable C—S bond.

The morphology of the samples was characterized by SEM. As shown in Fig. 1(a-d), both pristine

and sulfidized samples exhibited irregular blocky-like morphologies with no significant differences in particle surface, indicating that the sulfidation treatment does not disrupt the macroscopic framework of the carbon material. Notably, no obvious sulfur particles or agglomerates were observed on the surface of the sulfidized samples. Furthermore, EDS mapping (Fig. 1e) revealed a uniform distribution of sulfur throughout the carbon matrix, suggesting that sulfur species are highly dispersed rather than forming macroscopic phase-separated domains. This indicates that sulfur is preferentially confined within pore structures or defect regions instead of existing as bulk crystalline deposits.

To quantify sulfur incorporation, elemental analysis was performed (Table S1). The sulfur content increased from 0.32% in HC to 24.28% in HC-X samples, confirming the effective introduction of sulfur species into the carbon framework. TG analysis was further conducted to evaluate the stability and distribution of sulfur species. Generally, physically adsorbed sulfur located on external surfaces or in large pores volatilizes at relatively low temperatures ($\sim 220\text{--}330^\circ\text{C}$), whereas confined sulfur and chemically bonded C—S species exhibited significantly higher thermal stability^[28]. As shown in Fig. 2a, both samples exhibited minimal weight loss below 600°C , indicating a low content of volatile components and the C—S covalent bonds began to decompose above this temperature, leading to sulfur release. The primary weight loss occurred in the range of $620\text{--}800^\circ\text{C}$

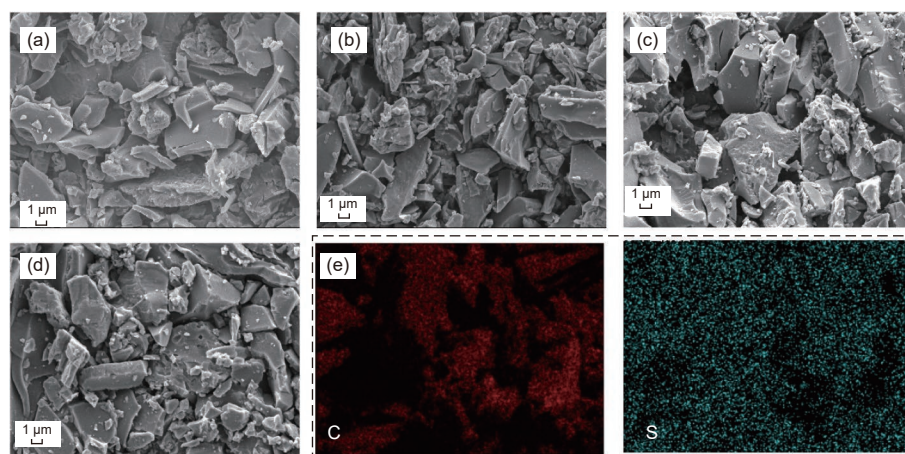


Fig. 1 SEM images of (a) HC, (b) HC-5, (c) HC-10 and (d) HC-15. (e) EDS mapping of HC-10

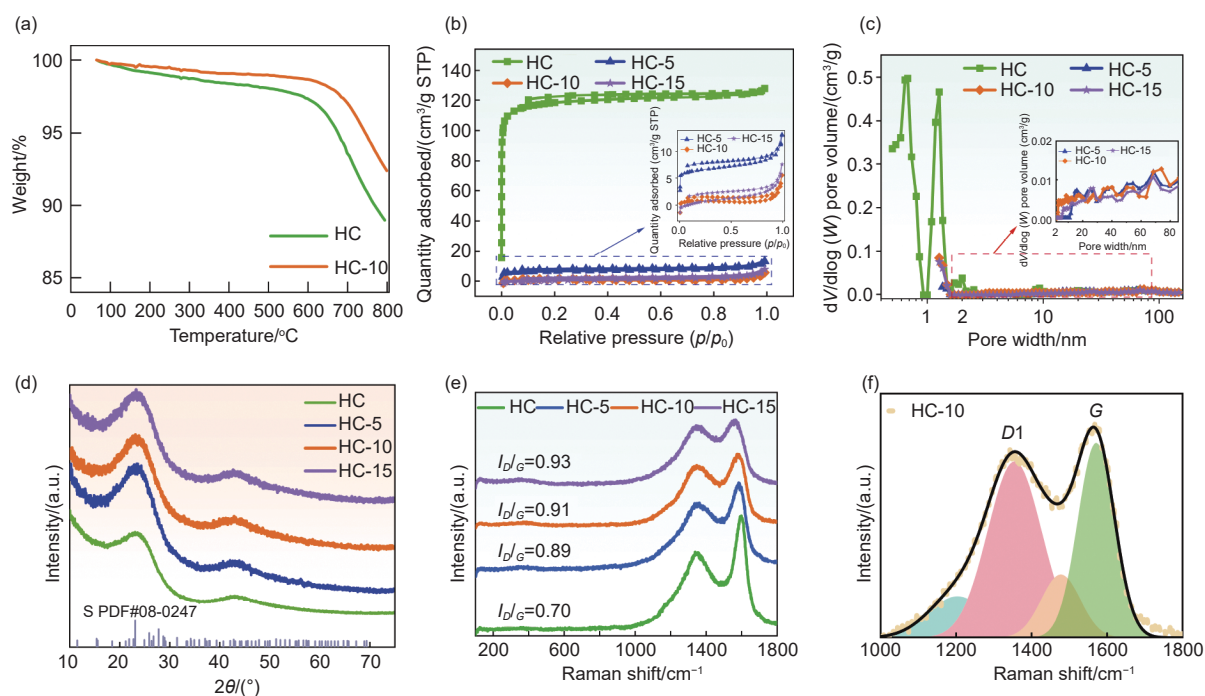


Fig. 2 (a) TG curves of HC and HC-10. (b) Nitrogen adsorption-desorption isotherms of HC and HC-X. (c) Pore size distribution of HC and HC-X. (d) XRD patterns of HC and HC-X. (e) Raman spectra of HC and HC-X. (f) Peak-fitted Raman spectrum of HC-10

°C. Notably, HC-10 showed a delayed onset of rapid weight loss and a higher residual mass compared with HC, indicating enhanced thermal stability. This suggests that sulfur species in HC-10 predominantly exist in thermally stable forms, such as micropore-confined sulfur and covalently bonded C—S species, while the proportion of physically adsorbed sulfur is significantly reduced.

The pore structure and specific surface area are key factors influencing the rate capability and cycling stability. N_2 adsorption-desorption tests were performed to characterize these properties. As shown in Fig. 2b, the pristine sample (HC) exhibited a typical Type I isotherm with a sharp uptake at low relative pressure ($p/p_0 < 0.1$), indicating a predominantly microporous structure^[29]. The corresponding pore size distribution (Fig. 2c) confirms that pores are mainly concentrated in the sub-nanometer range, with a dominant contribution around 1 nm. After sulfidation (HC-5, HC-10, HC-15), the adsorption capacity decreased significantly, and the isotherms evolve toward Type II behavior, accompanied by a diminished low-pressure uptake. This indicates a substantial reduction in the micropore volume and accessible surface area^[30].

Such changes suggest that sulfur species preferentially occupy micropores and defect sites, leading to pore blocking or filling effects. Consistently, the BET surface area decreased sharply from 449.15 m^2/g for HC to 24 m^2/g for HC-10 (Table S2), confirming effective sulfur incorporation within the porous structure.

XRD analysis was performed to further investigate the structural evolution and the existence of crystalline sulfur. As shown in Fig. 2d, all samples displayed 2 broad diffraction peaks at $\sim 23.5^\circ$ and 43° , corresponding to the (002) and (100) planes of carbon, respectively. The negligible shift of the (002) peak after sulfidation indicates that the average interlayer spacing remains largely unchanged. Moreover, no characteristic diffraction peaks of crystalline sulfur (PDF#08-0247) were detected, suggesting that sulfur does not exist as large crystalline domains but is instead highly dispersed or confined within the carbon matrix. Notably, the enhanced diffraction intensity in the 2θ range of 20° - 30° for sulfidized samples may be associated with sulfur ring-opening reactions under confinement, where the S_8 molecules transform into shorter-chain species (S_{2-4})^[31].

Raman spectroscopy was further employed to investigate structural disorder and defect evolution. As shown in Fig. 2e, all samples exhibited characteristic D ($\sim 1350\text{ cm}^{-1}$) and G ($\sim 1590\text{ cm}^{-1}$) bands, corresponding to disordered carbon and graphitic structures, respectively^[32]. Peak deconvolution of HC-10 (Fig. 2f) revealed multiple components ($D4$, $D1$, $D3$ and G), reflecting different defect types^[33]. The I_{D1}/I_G ratio increases from 0.70 (HC) to 0.89 (HC-5) and further to 0.93 with increasing sulfur content (Table S2), indicating a significant increase in defect density induced by sulfidation. Besides, when most of the limited active sites in carbon are occupied, the defect degree (I_{D1}/I_G) gradually tends to saturate. The gradual saturation of defect evolution suggests that sulfur preferentially occupies existing defect sites and pore walls at higher loading levels, rather than continuously disrupting the carbon framework. Furthermore, the absence of characteristic Raman peaks of crystalline sulfur (e.g., ~ 150 , ~ 217 and $\sim 471\text{ cm}^{-1}$)^[34] even at high sulfur content (HC-15) corroborates the XRD results, confirming that sulfur is predominantly present in an amorphous, highly dispersed, or confined state rather than as crystalline aggregates.

To elucidate the chemical states of sulfur species

and their interaction with the carbon framework, XPS analysis was conducted. As shown in Fig. 3a, the survey spectra exhibited characteristic peaks corresponding to C 1s, O 1s, S 2p and S 2s, respectively^[35]. While HC only shows C and O signals, clear sulfur signals appear in all sulfidized samples (HC- X), with intensities increasing with sulfur content, confirming successful sulfur incorporation. The high-resolution C 1s XPS spectrum (Fig. 3(b, e)) reveals an enhanced component at $\sim 285.5\text{ eV}$ in HC-10, which can be attributed to C—S/C—O bonding, indicating that sulfidation modifies the local chemical environment of the carbon framework. The S 2p XPS spectrum of HC-10 (Fig. 3d) showed characteristic spin-orbit doublets at ~ 163.5 – 164.2 eV (S 2p_{3/2}), corresponding to thiophene-like C—S—C bonds, confirming the formation of covalent interactions between sulfur species and the carbon skeleton^[36]. This indicates that a portion of sulfur is chemically anchored within the carbon framework. In addition, the peaks in the ~ 168 – 170 eV range are assigned to oxidized sulfur species ($-\text{SO}_x$), suggesting the presence of surface sulfur-oxygen functional groups. Consistently, the O 1s XPS spectrum (Fig. 3(c, f)) spectrum exhibited components in the ~ 531 – 533 eV region associated

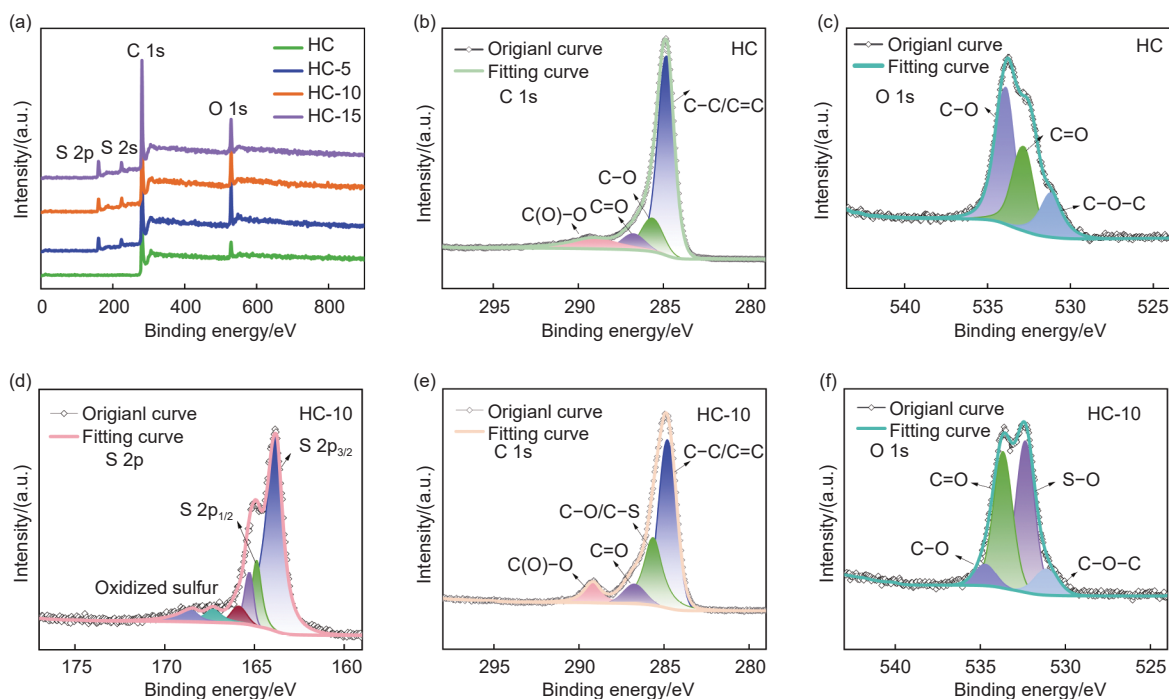


Fig. 3 (a) XPS survey spectra of HC and HC- X . (b, c) C 1s and O 1s spectra of HC. (d-f) C 1s, O 1s and S 2p spectra of HC-10

with S—O bonding, further supporting the existence of sulfur-oxygen species. These polar functional groups could enhance surface reactivity and contribute to improved electrochemical performance^[37]. Overall, the combined XPS results demonstrate that sulfur species are not only uniformly dispersed but also partially stabilized through covalent C—S bonding, providing strong chemical anchoring that underpins the enhanced stability and sodium storage behavior of the material.

4 Electrochemical properties

Fig. 4a, b presents the initial three CV curves of HC and HC-10. For HC, a pronounced irreversible cathodic peak appears in the first cycle at low potential, which is mainly attributed to electrolyte decomposition and the formation of solid electrolyte interphase (SEI)^[38]. In the subsequent cycles, the curves largely overlap, indicating gradual stabilization of the electrode-electrolyte interface. In contrast, HC-10 exhibited additional reversible redox peaks in the range of 0.8–2.0 V, which are absent in HC. These peaks intensify and stabilize upon subsequent cycling, indicating the activation of additional electrochemically active sites.

This behavior can be attributed to reversible conversion reactions between stabilized sulfur species and Na⁺ ($S \leftrightarrow Na_2S_x$)^[39], confirming the electrochemical activity of the confined and chemically bonded sulfur species.

Fig. 4c shows the rate performance of the samples. The sulfidized samples delivered significantly higher capacities than HC over the entire current density range (0.03–5 A/g), with HC-10 exhibiting the best performance. HC-10 delivered high capacities from 599.8 to 276.1 mAh/g as the current density increased from 0.03 to 5 A/g, demonstrating excellent rate capability. In contrast, HC exhibited much lower capacities with pronounced decay at high current densities, indicating sluggish sodium-ion diffusion and inferior interfacial kinetics. The enhanced rate performance of HC-10 suggests significantly improved reaction kinetics, which can be attributed to the synergistic effect of micropore confinement and covalent C—S bonding.

Fig. 4(d, e) present the GCD curves at 0.03 A/g. The pristine HC exhibited a low initial Coulombic efficiency (46.05%), mainly due to extensive SEI formation associated with its high surface area. However, the reduction in specific surface area of the sample

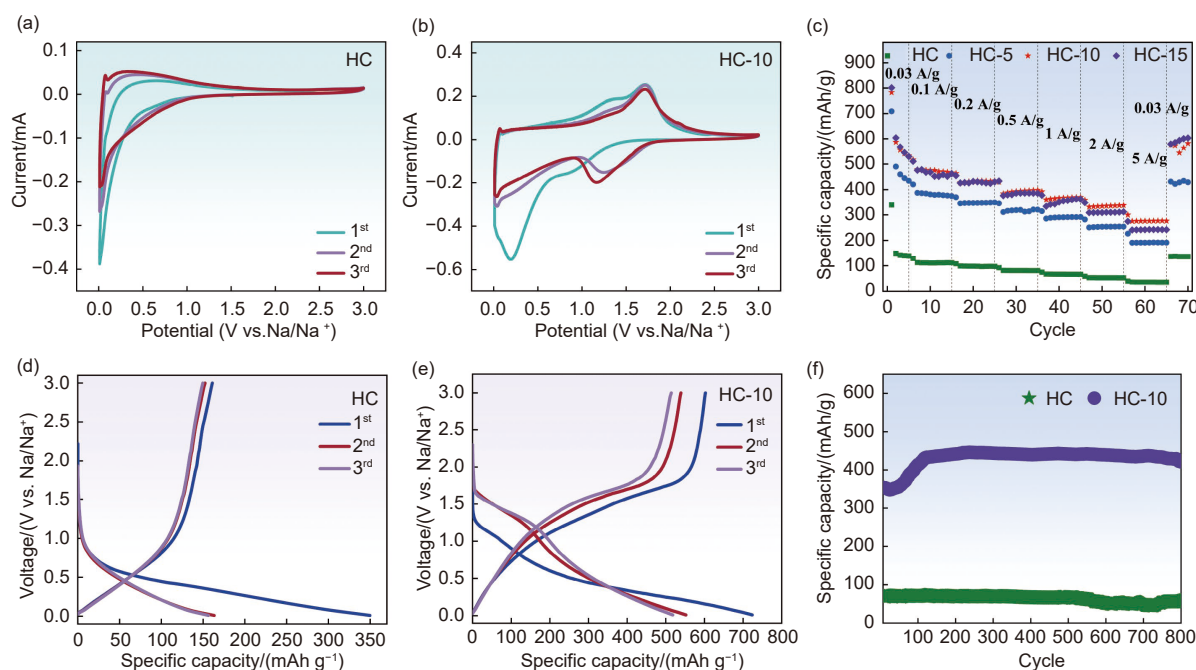


Fig. 4 (a, b) CV curves for HC and HC-10. (c) Rate performance plots of HC and HC-X. (d, e) GCD curves of HC and HC-10 at 0.03 A/g.

(f) Cycling performance plots of HC and HC-10 at 1 A/g

after sulfuration is not the decisive factor for its significant increase in ICE. This also explains why HC-15 had a lower specific surface area but its ICE is still lower than that of HC-10. In contrast, HC-10 delivers a significantly improved ICE of 83% and a higher capacity (602.4 mAh/g), indicating that sulfidation effectively suppresses side reactions while introducing additional reversible redox contributions.

The results of electrochemical performance comparison of HC with various carbon materials are shown in Table 1.

To further elucidate the sodium-ion storage kinetics of HC-10, CV tests were conducted at various scan rates (0.2–1.0 mV/s). The relationship between peak current (i) and scan rate (v) follows Eq. (1 and 2)^[50–51], where the b value reflects the charge storage mechanism.

$$i = av^b \quad (1)$$

$$\log(i) = b \log(v) + \log(a) \quad (2)$$

The calculated b value for peaks 1, 2 and 3 are 0.98, 0.57 and 0.61, respectively, indicating that peak 1 is dominated by a surface-controlled (capacitive) process, while peaks 2 and 3 involve mixed behavior with diffusion-controlled contributions. As shown in Fig. 5c, the capacitive contribution increases with scan rate, suggesting that fast surface-controlled reactions become more dominant at high rates. This behavior indicates that HC-10 possesses enhanced pseudo-capacitive characteristics, which facilitate rapid sodium-ion storage and contribute significantly to its superior rate performance.

EIS was further employed to investigate interfa-

cial kinetics. As shown in Fig. 5d, all samples exhibited a typical Nyquist profile consisting of a semicircle in the high-to-medium frequency region (charge-transfer resistance, R_{ct}) and a straight line in the low-frequency region (Warburg diffusion)^[52]. Compared with HC, the sulfidized samples (HC-5 and HC-10, Table S3) displayed significantly reduced semicircle diameters, indicating improved charge-transfer kinetics at the electrode-electrolyte interface. This suggests that sulfur incorporation effectively enhances electronic conductivity and facilitates interfacial charge transfer.

In contrast, HC-15 exhibited an enlarged semicircle, implying that excessive sulfur loading hinders charge transport. Notably, although the R_{ct} of HC-10 is slightly higher than that of HC-5, it still delivers superior overall electrochemical performance. This indicates that its superior behavior arises from a synergistic balance among interfacial kinetics, sulfur content, and pore structure.

The sodium-ion diffusion kinetics of HC-10 and HC were further evaluated using the galvanostatic intermittent titration technique (GITT). The diffusion coefficient (D_{Na^+}) was calculated according to Fick's second law (Eq. 3)^[53], where τ is the current pulse duration (0.5 h), and ΔE_s and ΔE_t are derived from the GITT profiles (Fig. 5e).

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (3)$$

As shown in Fig. 5f, HC-10 exhibits D_{Na^+} values approximately one order of magnitude higher than those of HC across most of the potential range. This result clearly demonstrates that sulfur incorporation

Table 1 Electrochemical performance comparison of various carbon materials

Sample	1 st cycle charge capacity/(mAh/g)	ICE/%	Current density/(A/g)	Refs.
HC-10	602.4	83.0	0.03	This work
SHC-3%	309.6	72.8	0.03	[40]
S/C-16%	480.0	83.0	0.10	[41]
SHC-900	281.4	80.7	0.03	[42]
SC-MC	417.0	86.7	0.05	[43]
SCNFs-2	227.8	67.0	0.10	[44]
NS-PHC-2	425.0	83.7	0.10	[45]
CCG-1400	320.7	83.34	0.03	[46]
HC-150	329.8	80.6	0.03	[47]
o-PDC-350-1400	276.8	86.7	0.03	[48]
PNHC-1	311.1	68.0	0.03	[49]

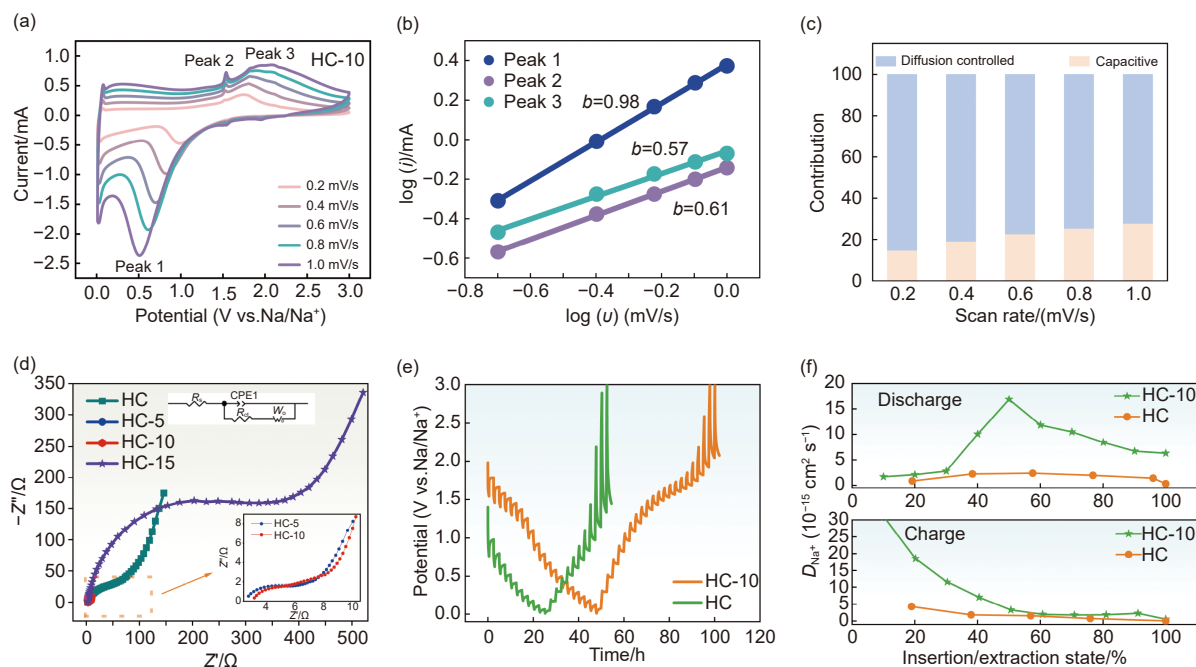


Fig. 5 (a) CV curves of HC-10 at different rates. (b) A linear relationship between $\log(i)$ and $\log(v)$. (c) Capacitance and diffusion contributions at different scan rates. (d) Nyquist plots of HC and HC-X. (e) GITT curves of HC and HC-10. (f) D_{Na^+} of HC and HC-10

significantly enhances Na^+ diffusion within the carbon matrix, providing direct evidence for the improved reaction kinetics observed in rate performance and CV analysis. The enhanced diffusion kinetics can be attributed to the synergistic effect of micropore confinement and covalent C—S bonding, which together facilitate ion transport and improve the accessibility of active sites.

In order to further analyze the changes of the state of S during the charge and discharge process, we performed ex situ XPS analysis on HC-10 electrodes at different states, including initial, discharged to 0.01 V, and recharged to 3.0 V. Compared with the initial electrode (Fig. 6a), the peaks representing C—S—C almost disappear after the terminal sodiation to 0.01 V (Fig. 6b). That result unequivocally shows that while

the C—S bonds are broken during discharge, they are not permanently lost. Instead, the sulfur species remain confined within the micropores. By contrast, the intensity of these characteristic peaks could be recovered after desodiation to 3.0 V, indicating that the covalent C—S—C bonds are reversible when reacted with sodium.

To further elucidate the sodium storage mechanism, in situ Raman spectroscopy was employed to monitor the evolution during cycling. As shown in Fig. 7a, the D-band intensity gradually decreases during discharge, indicating active involvement of defect sites in sodium-ion storage, likely associated with Na^+ adsorption and pore filling. Meanwhile, the G-band exhibited a redshift, suggesting electron transfer and weakening C—C bonds during Na^+ insertion^[54]. Upon

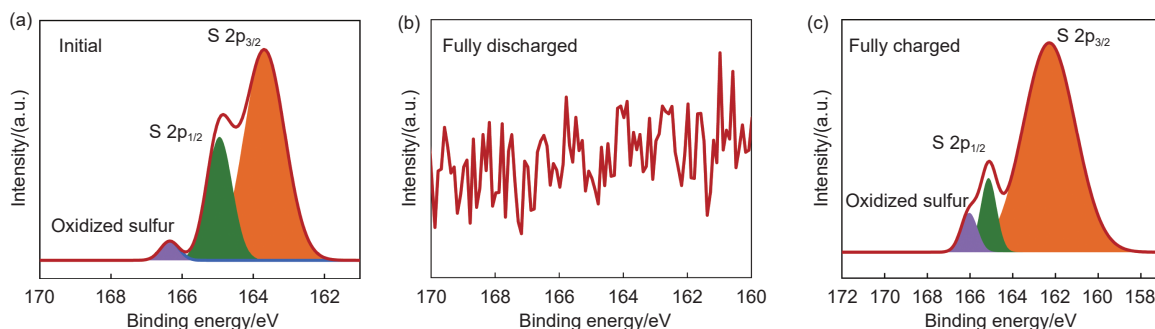


Fig. 6 (a-c) The ex situ XPS analysis of HC-10 at initial, fully discharged and fully charged states

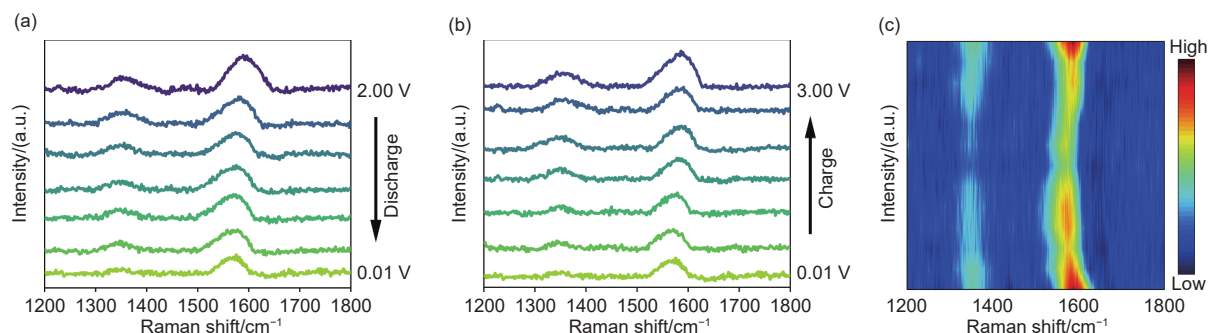


Fig. 7 In situ Raman spectra of HC-10 during the initial cycle (a) discharge and (b) charge process. (c) Contour plot of the initial charge-discharge process

charging to 3 V, the *D*-band intensity recovered and the *G*-band shifted back, demonstrating good structural reversibility. These results confirm that the sodium-ion storage process in HC-10 is highly reversible and primarily involves defect-mediated adsorption and pore-filling mechanisms.

5 Conclusions

A dual-stabilization strategy is proposed to stabilize sulfur species in coal-based hard carbon anodes. Through a two-step thermal process, sulfur species are effectively confined within micropores and chemically anchored via covalent C–S bonding, enabling synergistic physical–chemical stabilization. This design not only introduces additional redox-active sites but also enhances structural integrity and interfacial stability, leading to simultaneous improvements in capacity, rate capability, and cycling performance. The optimized HC-10 sample exhibited high initial Coulombic efficiency and excellent long-term cycling stability at high current densities. This work provides an effective strategy for stabilizing sulfur species in coal-derived carbon materials and offers new insights into the design of high-performance anodes for sodium-ion batteries.

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