Pseudocapacitive sodium storage of Fe_{1-x}S@N-doped carbon for low-temperature operation

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ABSTRACT Constructing potential anodes for sodium-ion batteries (SIBs) with a wide temperature property has captured enormous interests in recent years. Fe_{1-x}S, a zero-band gap material confirmed by density states calculation, is an ideal electrode for fast energy storage on account of its low cost and high theoretical capacity. Herein, Fe_{1-x}S nanosheet wrapped by nitrogen-doped carbon (Fe_{1-x}S@NC) is engineered through a post-sulfidation strategy using Fe-based metal-organic framework (Fe-MOF) as the precursor. The obtained Fe_{1-x}S@NC agaric-like structure can well shorten the charge diffusion pathway, and significantly enhance the ionic/electronic conductivities and the reaction kinetics. As expected, the Fe_{1-x}S@NC electrode, as a prospective SIB anode, delivers a desirable capacity up to 510.2 mA h g⁻¹ at a high rate of 8000 mA g⁻¹. Additionally, even operated at low temperatures of 0 and -25°C, high reversible capacities of 387.1 and 223.4 mA h g⁻¹ can still be obtained at 2000 mA g⁻¹, respectively, indicating its huge potential use at harsh temperatures. More noticeably, the full battery made by the Fe_{1-x}S@NC anode and Na₃V₂(PO₄)₂O₂F cathode achieves a remarkable rate capacity (186.8 mA h g⁻¹ at 2000 mA g⁻¹) and an impressive cycle performance (183.6 mA h g⁻¹ after 100 cycles at 700 mA g⁻¹) between 0.3 and 3.8 V. Such excellent electrochemical performance is mainly contributed by its pseudocapacitive-dominated behavior, which brings fast electrode kinetics and robust structural stability to the whole electrode.

Keywords: agaric-like structure, sodium ion batteries, Fe_{1-x}S, low-temperature performance, full cells

INTRODUCTION

Benefiting from the low cost and natural abundance of sodium resource, sodium-ion batteries (SIBs) have generally emerged as a promising renewable energy-storage

system relative to lithium-ion batteries (LIBs) [1–3]. However, the large ionic radius and high potential of Na ion lead to sluggish Na-ion diffusion kinetics and severe polarization, resulting in poor electrochemical performance [4,5]. Therefore, exploring the high-performance material is a challenge to promote the application of SIBs [6–8]. Nowadays, transition-metal sulfides have garnered tremendous attention as anode materials in SIBs due to their high reversible specific capacity, originating from stepwise intercalation-conversion reaction process [9,10]. Among them, the nonstoichiometric iron sulfides (Fe_{1-x}S) are of interest as active materials in SIBs due to their extraordinary properties of rich earth reserve, intrinsic safety, and narrow band gap [11–13]. Nevertheless, it has been noticed that the unsatisfactory electronic conductivity, sluggish Na⁺ diffusion kinetics, and obvious volume variation of Fe_{1-x}S undermine their effectiveness to present excellent performance, especially under low-temperature conditions [14–17]. Designing elegant nanostructures, constructing hybrid composites with conductive carbon, and heteroatom doping are effective strategies used to address these issues [18–20]. Liu *et al.* [21] achieved a satisfactory capacity of 573 mA h g⁻¹ at 0.1 A g⁻¹ for Fe_{1-x}S@PCNWS/rGO composite. Zhu *et al.* [22] reported a high capacity of 440 mA h g⁻¹ at 0.05 A g⁻¹ for wrapped N-doped carbon modified Fe_{1-x}S in graphene sheets. A remarkable capacity of 326.3 mA h g⁻¹ at 8 A g⁻¹ for carbon nanotube-encapsulated Fe_{1-x}S nanoparticles was obtained by Xiao *et al.* [11]. Recently, metal-organic frameworks (MOFs) have garnered increasing attention and been applied as a sacrificial template to synthesize heteroatom-doped nanostructures [23,24]. Specifically, MOFs have ample porosity, large surface area, and easily tailored structure,

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endowing the as-obtained derivatives with satisfactory chemical and physical properties that result in enhanced electrochemical properties [25–27]. Therefore, employing the MOFs as the template is a promising strategy to achieve special structural Fe_{1-x}S composite with excellent properties.

In this study, Fe_{1-x}S nanosheets wrapped in nitrogen-doped carbon layers ($\text{Fe}_{1-x}\text{S@NC}$) were synthesized through thermal annealing of the Fe-MOF, followed by a subsequent high-temperature sulfidation. The as-prepared agaric-like $\text{Fe}_{1-x}\text{S@NC}$ composite delivers a high performance, due to highly accessible active sites, short ion/electron transport pathways, and efficient contact with electrolyte ions. Additionally, the N-doped carbon layer not only enhances the conductivity but also serves as a robust buffer layer to aid structural stability. As expected, the $\text{Fe}_{1-x}\text{S@NC}$ composite displays excellent electrochemical performance in both half and full cells. The $\text{Fe}_{1-x}\text{S@NC}$ electrodes manifest a remarkable rate capability ($510.2 \text{ mA h g}^{-1}$ at a high rate of 8000 mA g^{-1}) and impressive long-term cycling stability. Notably, for the first time, the electrochemical properties of $\text{Fe}_{1-x}\text{S@NC}$ were evaluated at 0 and -25°C , representing specific capacity of 387.1 and $223.4 \text{ mA h g}^{-1}$ at 2000 mA g^{-1} , respectively, demonstrating the application at harsh temperatures. The sodium-ion full battery assembled by $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ (NVPOF) cathode and $\text{Fe}_{1-x}\text{S@NC}$ anode exhibits a superior capacity of $183.6 \text{ mA h g}^{-1}$ after 100 cycles at 700 mA g^{-1} in the voltage range of 0.3–3.8 V, highlighting its potential for practical applications. Further, the kinetics analysis clearly illustrates that the pseudocapacitive-dominated behavior was responsible for the excellent rate performance of $\text{Fe}_{1-x}\text{S@NC}$ electrode.

EXPERIMENTAL SECTION

Materials

Thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, 98%), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AR), *N,N*-dimethylformamide (DMF, 99.5%), dichloromethane (CH_2Cl_2 , 99.5%), *o*-vanillin ($\text{CH}_3\text{OC}_6\text{H}_3\text{-2-(OH)CHO}$, 99%), triethylamine ($\text{C}_6\text{H}_{15}\text{N}$, AR), and hydrazinium hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%) were purchased from Aladdin. All the raw materials were directly used without further treatment.

Synthesis of Fe-MOF

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.3 mmol) and *o*-vanillin (0.5 mmol) were dissolved in DMF/ CH_2Cl_2 (5 mL/25 mL), followed by the addition of triethylamine (1 mmol, 0.073 mL). Then hy-

drazinium hydrate (80%, 1 mmol, 0.061 mL) was added to the foregoing solution and stirred for $\sim 0.5 \text{ h}$. Dark brown block-shaped single crystals were obtained after several days.

Synthesis of $\text{Fe}_{1-x}\text{S@NC}$

The $\text{Fe}_{1-x}\text{S@NC}$ was prepared by a facile vacuum sulfidation process. The as-obtained Fe-MOF was annealed at 450°C for 1 h in an N_2 atmosphere with a temperature rise rate of 5°C min^{-1} . After that, the $\text{Fe}_2\text{O}_3\text{@NC}$ composite can be easily gained through low-temperature pyrolysis under an air atmosphere. Finally, the agaric-like $\text{Fe}_{1-x}\text{S@NC}$ was synthesized *via* vacuum sulfuring with thioacetamide as the sulfur source at 550°C for 6 h and the mass ratio between the $\text{Fe}_2\text{O}_3\text{@NC}$ composite and thioacetamide was about 1:1.

Material characterizations

The phase identification of the target samples was investigated by X-ray diffraction (XRD, Rigaku Smart Lab) using Cu K α radiation from 10° to 80° . X-ray photoelectron spectra (XPS, ESCALab220i-XL) with Al K α radiation were employed to analyze the surface electronic states. Scanning electron microscopy (SEM) analysis and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were performed using a JEOL-6700F equipment, while transmission electron microscopy (TEM) images were obtained on a JEOL-2100F equipment. Thermo-gravimetric analysis (TGA, Netzsch analyzer) was conducted with a fluid air of $10^\circ\text{C min}^{-1}$. Raman spectrum was measured on a JYHR-800 confocal Raman microscope with a laser source (488 nm). The pore size and the surface areas were characterized by nitrogen adsorption-desorption (Autosorb-iQ2) at 77 K. The data of the pore size and surface areas of $\text{Fe}_{1-x}\text{S@NC}$ composite were obtained from the Barrett-Joyner-Halenda method and Brunauer-Emmett-Teller (BET) model, respectively.

Electrochemical measurements

The working electrodes were prepared by coating the uniform slurry comprised of active materials, acetylene black, and carboxymethylcellulose (CMC) with mass ratio of 7:2:1 in distilled water (DW) on clean Cu/Al foils. The Cu/Al foils were dried in the vacuum oven at 60°C overnight. The 2032-type coin cells were built in a pure argon-filled glovebox using $\text{Fe}_{1-x}\text{S@NC}$ as the anode electrode, pure metallic sodium as a counter electrode, and NaClO_4 in propylene carbonate/ethylene carbonate (1:1) and 5 wt% fluoroethylene carbonate additive as an

electrolyte. A $\text{Fe}_{1-x}\text{S}@\text{NC}$ //NVPOF full cell was assembled with the NVPOF cathode and the $\text{Fe}_{1-x}\text{S}@\text{NC}$ anode. Cyclic voltammetry (CV) curves were recorded on a VersaSTAT 3 electrochemical workstation in the voltages of 0.01–3 V. Electrochemical impedance spectroscopy (EIS) spectra were collected using a PMC2000 electrochemical workstation with a frequency between 0.1 Hz and 100 kHz. Galvanostatic charge/discharge tests were taken using a LAND CT2001A testing system at different temperatures. For the low-temperature testing, the $\text{Fe}_{1-x}\text{S}@\text{NC}/\text{Na}$ system and the connecting wires were placed together in the refrigerator at different temperatures.

DFT calculations details

Our calculations in this work were performed in Vienna *ab-initio* Simulation Package (VASP) [28], a first-principle-based software package. We used the projector augmented wave (PAW) and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) to interpret the core-valence and the ion-electron interactions [29]. A 450 eV energy cut-off and a $3\times 3\times 1$ *k*-point grid were adopted.

RESULTS AND DISCUSSION

The detailed preparation process of the agaric-like $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite is illustrated in Scheme 1. The Fe-MOF was first synthesized by reacting $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ with DMF and CH_2Cl_2 at room temperature, followed with an annealing process. Finally, the as-obtained $\text{Fe}_2\text{O}_3@\text{NC}$ composite was annealed with thioacetamide as the S resource at 550°C under vacuum to obtain the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite. The detailed structural information of the as-obtained materials were investigated by SEM. Different-magnification SEM images of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite are shown in Fig. 1a–c, showing that the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite possesses a three-dimensional agaric-like structure consisting of interconnected nanosheets with the thickness of ~ 20 nm. The specific surface area and average pore size distribution of $\text{Fe}_{1-x}\text{S}@\text{NC}$ were obtained as about $54.625\text{ m}^2\text{ g}^{-1}$, and 3.7 nm, respectively, by the BET (Fig. S1a, b). Besides, nitrogen adsorption-desorption isotherms of $\text{Fe}_{1-x}\text{S}@\text{NC}$ displays a type IV isotherm with a hysteresis loop that is consistent with the property of the mesoporous materials. The high specific surface area and mesoporous structure provide sufficient active sites, desired electrical connection for electrolyte permeation and ion diffusion as well as accommodating the volume changes over repeated cycles. The structural features of the agaric-like $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite were

Scheme 1 Formation mechanism of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite with novel agaric-like structure (RT: room temperature).

further explored by TEM and high-resolution TEM (HRTEM). The overview of $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite in Fig. 1d verifies the agaric-like structure with different orientation nanosheets. It can be distinctly observed that the nanosheet is completely wrapped in ultrathin N-doped carbon layers with thickness around 2 nm, as shown in Fig. 1e. The enlarged HRTEM image shows clear lattice fringe with the *d*-spacing of ~ 0.29 nm, which is correlated with the (200) plane of Fe_{1-x}S (Fig. 1f). EDS elemental mapping patterns (Fig. 1g–k) reveal the well-distributed Fe, S, C, and N elements in the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite. In addition, the element contents of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite were investigated by EDS analysis, as displayed in Fig. S2. The result further confirms that the molar ratio of Fe and S is about 0.9:1, in agreement with the molecular formula.

To gain some clue to the structural evolution of the target product, we comprehensively analyzed the structure of the samples at different stages. It can be clearly observed that the pristine Fe-MOF exhibits ruffled morphology, as shown in Fig. S3a, d. After the annealing process, the conducted $\text{Fe}_2\text{O}_3@\text{NC}$ composites have a walnut kernel-like structure, which was attributed to the carbonization of organic ligands, as displayed in Fig. S3b, e. Such a structure is beneficial to constructing the sheet-like morphologies due to the sufficient clearance in the branches. Subsequently, the resulting specimen was collected by the chemical reaction between the $\text{Fe}_2\text{O}_3@\text{NC}$ and thioacetamide under vacuum. The precursor acts as an ideal frame to stabilize the structure to obtain the agaric-like $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite because of the preferred crystal growth orientation (Fig. S3c, f).

Preliminary component characteristic of the prepared samples was examined by XRD and XPS. As can be seen

Figure 1 (a–c) SEM images and (d, e) TEM images of the final product of $\text{Fe}_{1-x}\text{S}@\text{NC}$. The highlighted part of the frame in (e) is the nitrogen-doped carbon on the surface of the sample. (f) HRTEM image of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ sheets. (g–k) Elemental mapping images of the $\text{Fe}_{1-x}\text{S}@\text{NC}$, clearly revealing that the elements in the composite are evenly distributed.

in Fig. S4a, all the diffraction peaks match well with the $\alpha\text{-Fe}_2\text{O}_3$ (JCPDF 33-0664) and a broad peak at $\sim 24^\circ$ is attributed to the existence of carbon. The existence of Fe, O, C, and N elements in the $\text{Fe}_2\text{O}_3@\text{NC}$ composite once again was confirmed by XPS (Fig. S4b–f). Fig. 2a shows the crystal structure of the Fe_{1-x}S , in which Fe and S ions reside the octahedral site and the trigonal prismatic site, respectively [30]. It can be seen from Fig. 2b that the density of states (DOS) curve has no band gap near the Fermi level, indicating a good conductivity of the Fe_{1-x}S . In Fig. 2c, all the crystalline peaks of $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite correspond to the Fe_{1-x}S (JCPDS 29-0726), confirming the absolute transformation from $\text{Fe}_2\text{O}_3@\text{NC}$ to $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite. The XPS survey scan of $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite (Fig. 2d) clearly indicates the presence of Fe, S, C, and N elements in the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite. The high-resolution Fe 2p XPS spectrum (Fig. 2e) shows two strong peaks at 710.3 and 724.5 eV, which correspond to $\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$, respectively, implying the coexistence of Fe^{2+} and Fe^{3+} in the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite [31]. For the high-resolution S 2p XPS spectrum (Fig. 2f), three major peaks at 168.1, 163.8, and 161.1 eV are attributed to SO_x , S_n^{2-} , and S^{2-} [32,33], respectively. The

presence of SO_x suggests the partial surface oxidation of $\text{Fe}_{1-x}\text{S}@\text{NC}$ because of the inevitable contact with the air. In C 1s spectrum (Fig. S5a), the three peaks located at 287.1, 285.7, and 284.6 eV are assigned to C=O, C–N, and C–C, respectively [34]. The peaks of N 1s spectrum (Fig. S5b) centered at 400.4 and 398.4 eV are associated with C–N and C=N, suggesting the perfect N doping in the carbon frame [35]. The N-doping in the composite can result in more defects, thus increasing more active sites for Na storage, and meanwhile, this frame can improve the electronic conductivity of the composite [34,36]. In Fig. S6, the Raman spectrum of $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite displays two broad peaks at 1563.1 and 1384.7 cm^{-1} that are related to the G-band and D-band of the generated NC, respectively. The N doping in the carbon structure can lead to the overlapping and broadening of D/G bands [37,38]. The content of NC was about 20 wt% by TGA measurements, which was calculated according to the complete chemical conversion from $\text{Fe}_{1-x}\text{S}@\text{NC}$ to Fe_2O_3 under air atmosphere (Fig. S7) [33].

In order to explore the electrochemical properties of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ as the anode for SIBs, CV curves for the first five cycles were investigated at 0.1 mV s^{-1} , as shown

Figure 2 (a) The crystal structure, (b) calculated DOS curve, and (c) XRD pattern of the $\text{Fe}_{1-x}\text{S}@\text{NC}$. XPS spectra of the $\text{Fe}_{1-x}\text{S}@\text{NC}$: (d) survey spectrum, (e) Fe 2P spectrum, (f) S 2p spectrum.

in Fig. 3a. During the initial discharge, two cathodic peaks at 0.75 and 0.27 V are attributed to the multistep reaction of Fe_{1-x}S and Na as well as the formation of $\text{Fe}/\text{Na}_2\text{S}$ via intermediate phases. Moreover, the peak around 0.75 V is also assigned to the generation of solid electrolyte interphase (SEI). Meanwhile, two obvious anodic peaks around 1.43 and 1.81 V are concerned with the stepwise desodiation reactions [39]. During the subsequent cycles, the anodic and cathodic peaks appear with good reproducibility, indicating the high reversibility in the electrode. According to our results and previous reports of Fe_{1-x}S , the redox reactions upon cycling can be described as follows [12,21,22,30,40,41]:

The galvanostatic charge/discharge profiles of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ electrode at 200 mA g^{-1} are plotted in Fig. S8, which match well with the CV curves. The $\text{Fe}_{1-x}\text{S}@\text{NC}$ electrode displays the first discharge and charge capacities of 880.8 and $718.3 \text{ mA h g}^{-1}$, rendering an initial coulombic efficiency (CE) of 81.5%. The capacity loss is mainly ascribed to the formation of SEI layer. These

charge/discharge plots are well-overlapped over the subsequent cycles, implying the good reversibility of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ electrode [42]. Fig. S9 displays the cycling performance of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite at 200 mA g^{-1} remained a capacity of $737.6 \text{ mA h g}^{-1}$ after 100 cycles. Fig. 3b depicts the rate performance of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ electrode, the $\text{Fe}_{1-x}\text{S}@\text{NC}$ composite delivers the reversible capacities of 775.7, 670.1, 637.7, 598.7, 581.9, 562.6, 537.8 and $510.2 \text{ mA h g}^{-1}$ at 100, 500, 1000, 2000, 4000, 5000, 6000 and 8000 mA g^{-1} . More notably, the capacities of the electrode gradually return to the initial values as the current densities reduce back to 3000 mA g^{-1} step by step. Fig. 3c shows the corresponding charge/discharge plots at varying current densities. The typical electrode sodiation/desodiation plateaus are visible at all rates, manifesting that no critical polarization phenomenon has been noticed in the electrode. As shown in Fig. 3d, the performance of $\text{Fe}_{1-x}\text{S}@\text{NC}$ composites is comparable to the previously reported iron sulfides [11,12,21,22,39,40,43,44]. In order to assess the durability of the $\text{Fe}_{1-x}\text{S}@\text{NC}$ electrode, the cycling performance under a rate of 1000 mA g^{-1} was investigated (Fig. 3e). The $\text{Fe}_{1-x}\text{S}@\text{NC}$ electrode remains a reversible capacity of $647.9 \text{ mA h g}^{-1}$ with a high average CE of 99%. The slightly increased capacity is mainly attributed to two reasons: one is the activation effect, and the other is the formation of organic SEI film that can increase extra Na-

Figure 3 Na-storage properties of the $\text{Fe}_{1-x}\text{S}@NC$ electrode as an anode for SIBs. (a) CV curves for the initial five cycles at 0.1 mV s^{-1} . (b) The specific capacities of $\text{Fe}_{1-x}\text{S}@NC$ at different current densities. (c) Galvanostatic ($100\text{--}8000 \text{ mA g}^{-1}$) curves at different current densities. (d) Rate-capability comparisons of $\text{Fe}_{1-x}\text{S}@NC$ anode with some other reported metal sulfide anodes for SIBs. (e) The cycling performance of $\text{Fe}_{1-x}\text{S}@NC$.

storage sites *via* the alleged “pseudocapacitive behavior” [25,42,45]. In addition, the $\text{Fe}_{1-x}\text{S}@NC$ electrode also exhibits a high capacity of $\sim 533.6 \text{ mA h g}^{-1}$ at 3000 mA g^{-1} with stable capacity evolution (Fig. S10). We further characterized the morphology and structure of the sample after 100 cycles. As shown in Fig. S11, the preservation of the sheet-like shape confirms minimal volume change during the cycles, indicating the satisfactory structural stability upon cycles. In addition, the elemental mapping results show the even distribution of all elements. The results of the electrochemical characterization confirm the superior rate performance and impressive

cycling capability of $\text{Fe}_{1-x}\text{S}@NC$ electrode at room temperature, which mainly can be ascribed to the following reasons: the hierarchical structure of $\text{Fe}_{1-x}\text{S}@NC$ exposes more contact area to the electrolyte, which prompts all active surfaces to be electrochemically active. Meanwhile, the proper space between the sheets is beneficial for keeping structure integrity. In addition, the N-doped carbon layer wrapping Fe_{1-x}S nanosheets acts as an effective buffer layer to accommodate the volume change, guaranteeing the formation of stable SEI layer. Moreover, the carbon matrix can realize high ionic/electronic conductivities, which is favorable for ultrafast electron-

Figure 4 (a) The rate capability of $\text{Fe}_{1-x}\text{S@NC}$ at varied low temperatures (-25 and 0°C), and (b) rate-performance comparisons of $\text{Fe}_{1-x}\text{S@NC}$ at -25 and 0°C .

transfer kinetics.

Apart from the room-temperature performance of the electrode, the studies of low-temperature properties are also critical for the application of an anode [17]. A few studies so far have focused on the low-temperature properties of the electrode; however, because the rate properties of the electrode material are severely affected by the operation temperatures on account of the slowed kinetics [46]. The low-temperature performance of $\text{Fe}_{1-x}\text{S@NC/Na}$ half cells was investigated at -25 and 0°C , as shown in Fig. 4a, b. In the case of 0°C , the $\text{Fe}_{1-x}\text{S@NC/Na}$ exhibits a capacity of 499.2, 453.8, 429.0, 387.1, 362.9, and 338.3 mA h g^{-1} at a current density of 100, 500, 1000, 2000, 2500 and 3000 mA g^{-1} , respectively. Satisfactorily, even at -25°C , it shows a good capacity of 467.1, 369.3, 300.5, 223.4, 193.8, and 159.9 mA h g^{-1} at 100, 500, 1000, 2000, 2500 and 3000 mA g^{-1} , respectively. Such results magnify the infirm dependence on Na-storage of $\text{Fe}_{1-x}\text{S@NC}$ electrode under a low-temperature condition [46].

To unveil the Na-storage mechanism of $\text{Fe}_{1-x}\text{S@NC}$ composite, the kinetic analysis was further performed according to the CV measurements at different rates. As displayed in Fig. 5a, the CV curves ranging from 0.2 to 0.8 mV s^{-1} preserve similar shapes with specific anodic and cathodic peaks corresponding to the discharge and charge processes, suggesting the low polarization and outstanding electronic/ionic conductivity of the $\text{Fe}_{1-x}\text{S@NC}$ composite. The relation between the current (i) and scan rate (v) obeys the following equations [47,48]:

$$i = av^b, \quad (5)$$

or

$$\log i = b \log v + \log a, \quad (6)$$

where, a and b are adjustable parameters, and the b value

determines the type of Na^+ insertion/extraction. When b approaches 0.5, the process is mainly controlled by ion diffusion. While b is close to 1.0, the electrochemical reaction relies on the pseudocapacitance control [49]. Fig. 5b shows a good linear relationship between $\log i$ and $\log v$. The b values for redox peaks are 0.75, 0.93, 0.96, 0.89, and 0.84, respectively, implying coexistence of diffusion-controlled process and capacitance-controlled process. For more accurate analysis, we further quantitatively calculated the proportions of the surface capacitance contribution and Na-ion diffusion contribution during the processes based on the following equation [25,50,51]:

$$i = k_1 v + k_2 v^{1/2}, \quad (7)$$

where k_1 and k_2 can be determined by the fitting linear curve of $v^{1/2}$ versus $i/v^{1/2}$. Furthermore, $k_1 v$ represents the current contributions stemming from surface capacitance, whereas $k_2 v^{1/2}$ corresponds to the diffusion-controlled contributions. Fig. 5c depicts the calculated capacitance-controlled contributions of the $\text{Fe}_{1-x}\text{S@NC}$ electrode at 0.5 mV s^{-1} is about 84%, as shown in the prasinous region. As the scan rates gradually rise from 0.2 to 0.8 mV s^{-1} , the proportions of capacitance-controlled contributions increase from 82% to 90% (Fig. 5d), suggesting that the pseudocapacitive process is dominant in the whole charge storage process especially at high scan rates. The well-developed agaric-like structure of the electrode materials may be responsible for the overall surface capacitance, which plays an important role in achieving fast kinetics. In addition, *in-situ* EIS was further carried out to diagnose the kinetic process of the $\text{Fe}_{1-x}\text{S@NC/Na}$ system. As exhibited in Fig. S12, the $\text{Fe}_{1-x}\text{S@NC/Na}$ displays the characteristic Nyquist plots

Figure 5 Electrode kinetic analyses on the Fe_{1-x}S@NC electrode. (a) CV curves and (b) corresponding linear fitting of log*i* and log*v* at varied scan rates. (c) CV curve with the pseudocapacitive contribution displayed by the prasinous region at a scan rate of 0.5 mV s⁻¹. (d) Histogram showing the variation of pseudocapacitive fraction for Na-storage along with the scan rates.

over different cycles. The plots are composed of an inclined line and a semicircle, which describes the diffusion resistance and interfacial charge-transfer resistance (R_2), respectively [52–54]. The related equivalent circuit was investigated to analyze the EIS data more accurately. Obviously, the R_2 rapidly decreases from the 1st to 5th cycle on account of kinetic activation in the electrode and remains unchanged after 5 cycles (130.03 Ω), suggesting desirable sodium migration through the SEI layers and the electrode.

Furthermore, to evaluate the practicability of the Fe_{1-x}S@NC composite, the full cells were assembled by using Fe_{1-x}S@NC as an anode and NVPOF as a cathode. Fig. S13 shows that the as-obtained NVPOF has a nanorod structure [55]. Fig. 6a schematically illustrates the mechanism of the Fe_{1-x}S@NC//NVPOF full cell. Fig. 6b delivers the detailed galvanostatic charge/discharge voltage profiles of Fe_{1-x}S@NC//NVPOF full cell at a current density of 300 mA g⁻¹ in the voltage range of 0.3–3.8 V. It shows an initial discharge capacity of 306 mA h g⁻¹ with the initial CE of about 89%, which was calculated according to the mass of Fe_{1-x}S@NC electrode. As presented

in Fig. 6c, the Fe_{1-x}S@NC//NVPOF full cell shows capacities of 283.2, 211.9, 204.7, 186.8, 130.9 and 118.3 mA h g⁻¹ at current densities of 300, 700, 1500, 2000, 4000, and 5000 mA g⁻¹, respectively. Also, reversible capacity can stepwise return to 202.2 mA h g⁻¹ after 15 cycles as the current density reduces back to 700 mA g⁻¹. Furthermore, a reversible capacity of the Fe_{1-x}S@NC//NVPOF cell still remains at 183.6 mA h g⁻¹ after 100 cycles at 700 mA g⁻¹ with cycling retention of 95%, indicating that the Fe_{1-x}S@NC//NVPOF cell has a good cycle stability. As shown in Fig. 6d, a pig-like LED is successfully lighted by one full battery, further showing its practicability.

CONCLUSIONS

In summary, Fe_{1-x}S@NC was proposed to be an ideal electrode material for high-performance SIBs at a wide temperature range (–25 to 25°C) due to the intrinsically high conductivity. An agaric-like Fe_{1-x}S@NC composite has been synthesized, featuring well-defined Fe_{1-x}S nanosheets wrapped in conductive N-doped carbon layers with abundant channels. Kinetic analysis manifests that

Figure 6 The energy storage performances of $\text{Fe}_{1-x}\text{S@NC}/\text{NVPOF}$ full batteries. (a) The schematic diagram, (b) charge/discharge curves, and (c) rate capability of the $\text{Fe}_{1-x}\text{S@NC}/\text{NVPOF}$ full battery. (d) The photograph exhibits a pig-like LED lighted by one full battery.

dominant pseudocapacitive Na-storage mechanism makes a noteworthy contribution to the enhanced transport kinetics. The as-synthesized $\text{Fe}_{1-x}\text{S@NC}$ composite presents a high rate capability with $510.2 \text{ mA h g}^{-1}$ at 8000 mA g^{-1} and remains $647.9 \text{ mA h g}^{-1}$ at 1000 mA g^{-1} after 100 cycles. Even at 0 and -25°C , the $\text{Fe}_{1-x}\text{S@NC}$ electrode still exhibits a high capability of $387.1 \text{ mA h g}^{-1}$ and $223.4 \text{ mA h g}^{-1}$ at 2000 mA g^{-1} , respectively. Especially, the assembled full cell $\text{Fe}_{1-x}\text{S@NC}/\text{NVPOF}$ delivers a high capacity of $186.8 \text{ mA h g}^{-1}$ at a current density of 2000 mA g^{-1} and remains $183.6 \text{ mA h g}^{-1}$ at 700 mA g^{-1} after 100 cycles, further suggesting that the $\text{Fe}_{1-x}\text{S@NC}$ electrode can be a desirable anode for sodium storage.

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Author contributions Fan H and Qin B designed and prepared the materials; Wang Z finished the theoretical calculation; Li H supervised the revision of the paper; Guo J synthesized the cathode materials; Wu X and Zhang J supervised the analysis of the whole work. All authors took part in the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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赅电容氮掺杂碳包覆Fe_{1-x}S有效促进低温钠存储性能

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摘要 近年来, 构筑适用于宽温度范围的钠离子电池负极材料越来越引起人们的研究兴趣。Fe_{1-x}S作为一种典型的零带隙材料, 由于其低的成本和高的理论比容量, 被认为是钠离子电池理想的负极材料。本文以室温合成的Fe金属有机骨架(Fe-MOF)为前驱体, 借助硫化处理制备了木耳状氮掺杂碳包覆的Fe_{1-x}S化合物(Fe_{1-x}S@NC)。Fe_{1-x}S@NC独特的木耳状结构可以很好地缩短电荷扩散路径, 显著提高离子/电子电导率, 促进反应的动力学过程。该Fe_{1-x}S@NC电极在8000 mA g⁻¹的高电流密度下展示了高达510.2 mA h g⁻¹的理想比容量。即使在0和-25°C的工作环境中, 该电极在2000 mA g⁻¹的电流密度下仍能分别保持387.1和223.4 mA h g⁻¹的可逆比容量, 证实了该电极在严苛温度下的潜在应用。更值得注意的是, 由Fe_{1-x}S@NC负极和Na₃V₂(PO₄)₂O₂F正极组装的全电池在0.3和3.8 V之间同样呈现了出色的倍率容量(在2000 mA g⁻¹电流密度下的可逆容量为186.8 mA h g⁻¹)和优异的循环性能(在700 mA g⁻¹电流密度下、经过100个循环后可维持183.6 mA h g⁻¹可逆容量)。定量动力学分析进一步证实该电极是电容行为为主的电荷存储, 这种特质可加速电极电化学反应过程, 从而赋予Fe_{1-x}S@NC优异的电化学性能。