S/N-doped carbon nanofibers affording Fe7S8 particles with superior sodium storage

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Abstract
2020 Iron sulfides draw much attention as electrode candidates for sodium-ion batteries (SIBs) due to the rich chemical stoichiometries and high capacity. However, they usually exhibit poor cycling performance due to the large volume change during sodiation/desodiation process. In this work, we embed Fe7S8 nanoparticles into sulfur, nitrogen-doped carbon (S/N-C) nanofibers through electrospinning/sulfurization processes. The heteroatom doped carbon matrixes could effectively protect the Fe7S8 from structural collapse, obtaining a stable cycling performance. Moreover, the conductive matrixes with 1D structure can facilitate the diffusion of electrons, leading to good rate capability. As results, the as-designed Fe7S8@S/N-C nanofibers present a discharge capacity of 347 m Ah g−1 after 150 cycles at 1 A g−1 and a high rate capacity of 220 m Ah g−1 at 5 A g−1 in virtue of unique structural characteristics.

Keywords
superior, particles, carbon, fe7s8, s/n-doped, affording, nanofibers, storage, sodium

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S/N-doped Carbon Nanofibers Affording Fe$_7$S$_8$ Particles with Superior Sodium Storage

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Abstract  Iron sulfides draw much attention as electrode candidates for sodium-ion batteries (SIBs) due to the rich chemical stoichiometries and high capacity. However, they usually exhibit poor cycling performance due to the large volume change during sodiation/desodiation process. In this work, we embed Fe$_7$S$_8$ nanoparticles into sulfur, nitrogen-doped carbon (S/N-C) nanofibers through electrospinning/sulfurization processes. The heteroatom doped carbon matrixes could effectively protect the Fe$_7$S$_8$ from structural collapse, obtaining a stable cycling performance. Moreover, the conductive matrixes with 1D structure can facilitate the diffusion of electrons, leading to good rate capability. As results, the as-designed Fe$_7$S$_8$@S/N-C nanofibers present a discharge capacity of 347 m Ah g$^{-1}$ after 150 cycles at 1 A g$^{-1}$ and a high rate capacity of 220 m Ah g$^{-1}$ at 5 A g$^{-1}$ in virtue of unique structural characteristics.

Keywords: Fe$_7$S$_8$; Carbon nanofibers; Anode; Sodium-ion batteries; S, N-co-doping
1. Introduction

Lithium ion batteries (LIBs) have been commercially applied into portable devices for several decades.\textsuperscript{1-2} With the merging of electric vehicles and large-scaled energy storage systems, however, the concerns of limited lithium resources and high prices forced researchers to explore alternative batteries systems with low-cost and high energy density. Considering these, sodium ion batteries (SIBs) have drawn great attention due to the nature abundance of sodium resources in earth and the similar electrochemical mechanism to LIBs.\textsuperscript{3-7} However, the real practical application of SIBs is hampered by the anode materials, which always showed low specific capacity and poor cycling stability.\textsuperscript{8-11} Therefore, exploring suitable anode materials for SIBs with advanced electrochemical performance is essential for further development of SIBs. Among the reported anode materials, iron sulfides have drawn much attention due to their relatively high specific capacity, abundant resources and low-cost.\textsuperscript{12-23} However, Nevertheless, iron sulfides usually suffer poor electrochemical performance due to the intrinsic sluggish kinetics, poor conductivity and severe volume change during sodiation process, which affect the rate capability and cycling stability and prevent their potential application as anode materials for SIBs.

To overcome these drawbacks, preparing nanostructured iron sulfides combined with conductive matrixes is a promising strategy.\textsuperscript{24-31} On the one hand, nano-sized materials usually could short the diffusion length of ions and electrons, resulting in fast reaction kinetics and good rate capability. In addition, nanostructured materials can alleviate
mechanical stress and maintain the integrity of materials without fractures, leading to good cycling stability. On the other hand, conductive matrixes can improve the conductivity of electrode materials, enhancing the utilization of iron sulfides and resulting in high capacity. Moreover, the conductive matrixes also could alleviate the volume changes of iron sulfides during cycling, obtaining long stable cycling performance. Therefore, preparing nanostructured iron sulfides combined with conductive matrixes materials as anode materials for SIBs could obtain good cycling stability and excellent rate capability.

Herein, we embedded Fe₇S₈ nanoparticles into sulfur and nitrogen doped carbon nanofibers (S/N-C) through electrospinning method. The whole experimental process was shown in Scheme 1. First, the α-Fe₂O₃ nanoparticles were synthesized via hydrothermal method, then the prepared α-Fe₂O₃ nanoparticles and polyacrylonitrile (PAN) was added into N,N-dimethylformamide (DMF) for electrospinning. The Fe₇S₈@S/N-C were obtained after annealing α-Fe₂O₃@PAN composites with sulfur at high temperature. The heteroatoms doped carbon nanofibers as conductive matrixes could alleviate the volume expansion Fe₇S₈ nanoparticles, avoid the agglomeration, and maintain the structure stability of electrode materials, resulting in stable cycling stability. In addition, the heteroatom could further improve the electronic conductivity of carbon nanofibers and provides more active sites for sodium storage. And the isolated Fe₇S₈ nanoparticles can display high specific capacity. Owing to unique structural characteristics, the Fe₇S₈@S/N-C electrodes exhibited stable cycling performance with a discharge capacity of 347 mA h g⁻¹ after 150 cycles at 1 A g⁻¹ and superior rate
capability showing a capacity of 220 mA h g\(^{-1}\) at 5 A g\(^{-1}\).

Scheme 1. Illustrative synthesis scheme of Fe\(_7\)S\(_8\)@S/N-C nanofibers.

2. Experimental section

2.1 Synthesis of Fe\(_7\)S\(_8\)@S/N-C

\(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles were prepared through a simple hydrothermal method according to the literature with minor modification.\(^{32}\) In a typical synthesis, 0.54 g FeCl\(_3\)·6H\(_2\)O was firstly dissolved into 20 mL deionized water. Then, 10 mL aqueous ammonia was added drop by drop. After that, this mixture was transferred into an autoclave and maintained at 180 °C for 12 h. The resulting product was collected by centrifugation and washed with DI water and ethanol several times.

The Fe\(_7\)S\(_8\)@S/N-C composites were synthesized through the electrospinning/sulfdation processes. Typically, 0.5 g as-prepared \(\alpha\)-Fe\(_2\)O\(_3\)
nanoparticles and 1 g polyacrylonitrile (PAN) were added into 10 mL N,N-dimethylformamide (DMF), which were stirred at 60 °C for overnight to form a stable suspension. Then, the obtained suspension was transferred into a syringe. A stainless-steel plate was placed to collect the nanofibers with 15 cm away from the syringe. The flow rate was about 0.4 mL h\(^{-1}\) and the voltage was applied to 15 kV. The collected nanofibers were pre-oxidized at 230 °C for 2 h in air. At last, the pre-treated nanofibers were sulfureted with sulfur at 600 °C for 2 in argon atmosphere to obtain Fe\(_7\)S\(_8\)@S/N-C. For comparison, 0.5 g \(\alpha\)-Fe\(_2\)O\(_3\) nanoparticles and 0.5 g sulfur power were heated under the same condition to transfer \(\alpha\)-Fe\(_2\)O\(_3\) to Fe\(_7\)S\(_8\). The pure S/N-C nanofibers were synthesized by the same electrospinning method without adding \(\alpha\)-Fe\(_2\)O\(_3\) precursor.

2.2 Materials characterization

The morphologies information of the prepared samples were characterized by the scanning electron microscope (SEM, Hitachi S4800) with Energy Dispersive Spectrometer (EDS) and field-emission transmission electron microscope (TEM, Tecnai G2 20). The X-ray diffractions (XRD, Rigaku D/max-2500 X-ray diffractometer, Cu K\(\alpha\), \(\lambda = 0.154056\) nm) were carried out with a scan rate of 8° min\(^{-1}\). The thermogravimetric analysis (TGA) was conducted in air using the STD Q600 thermogravimetric analyzer. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were obtained by a Nova 2000e volumetric adsorption analyzer. Raman spectra were carried out using a HORIBA LabRAM HR Evolution Raman spectrometer. The X-ray photoelectron spectroscopies (XPS) was characterized to
evaluate the elemental composition of the samples on a Thermo scientific $K_a$ spectrometer.

2.3 Electrochemical measurements

For the electrochemical evaluations, the working electrodes were prepared by combining 80 wt% active materials, 10 wt% acetylene black and 10 wt% carboxymethyl cellulose (CMC), which were dissolved into water and stirred for overnight to form a slurry. Then, the slurry was pasted on the Cu foil to get the electrodes. The specific capacity was calculated based on the whole mass of the electrode. A sodium foil was used as the counter electrode. The used electrolyte was 1 M NaClO$_4$ in the propylene carbonate and ethylene carbonate (EC-PC, 1:1, v:v), and glass fiber (Whatman, Grade GF/A) was utilized as the separator. The CR2025-type coin cells were assembled in the Ar-filled glove box. Galvanostatic charge-discharge test were measured at room temperature with the voltage range of 0.01 - 2.5 V.

3. Results and Discussion
Figure 1 (a) SEM image of Fe$_7$S$_8$@S/N-C nanofibers; (b) Low-resolution and (c) high-resolution TEM images of Fe$_7$S$_8$@S/N-C nanofibers; (d) TGA curves of prepared Fe$_7$S$_8$ nanoparticles and Fe$_7$S$_8$@S/N-C nanofibers in air atmosphere; (e) Element mapping of Fe$_7$S$_8$@S/N-C nanofibers.

The morphologies and structures of prepared α-Fe$_2$O$_3$, Fe$_7$S$_8$, Fe$_7$S$_8$@S/N-C and S/N-C samples were characterized by SEM and TEM techniques, which were shown in Figure 1 and Figure S1. As shown in Figure S1 a, the prepared α-Fe$_2$O$_3$ particles with size about 150 nm show a uniform morphology, which make it possible to be electrospun into PAN polymer fibers. After sulfureted process, α-Fe$_2$O$_3$ particles were successfully transferred into Fe$_7$S$_8$ particles (Figure S1 b), which exhibited irregular particle morphology with agglomeration and had a diameter of 100 - 400 nm. The HR-TEM
image of Fe$_7$S$_8$ particles show clear lattice fringes, indicating the crystal structure of obtained Fe$_7$S$_8$ materials (Figure S1 c). The designed Fe$_7$S$_8$@S/N-C samples show fiber-like structure and there are no particles on the surface, as shown in Figure 1a, which confirms that the Fe$_7$S$_8$ particles were embedded into carbon nanofibers. The TEM images further show the Fe$_7$S$_8$ particles were isolated distributed in the carbon matrixes (Figure 1b). The HR-TEM image of Fe$_7$S$_8$@S/N-C in Figure 1c indicates that two lattice fringes with 0.263 nm and 0.172 nm can be observed, which are assigned to the (203) and (220) planes, respectively. The morphology of S/N-C nanofibers without Fe$_7$S$_8$ was also characterized by SEM and HR-TEM images (Figure S1 d), which indicated the uniform size distribution and amorphous structure of S/N-C nanofibers.

The content Fe$_7$S$_8$ in the Fe$_7$S$_8$@S/N-C composites was measured using the thermogravimetric analysis (TGA), which was carried out in air atmosphere, as shown in Figure 1d. For Fe$_7$S$_8$, there is an obvious mass increasing below 400 °C due to the oxidation of Fe$^{2+}$ to Fe$^{3+}$. In the range of 400 - 600 °C, the Fe$_7$S$_8$ particles was completely transferred into Fe$_2$O$_3$, causing the weight loss of 15.5%. For the Fe$_7$S$_8$@S/N-C composite, there are two stage weight loss: the first one between 380 - 480 °C is related to the consumption of carbon; the second one between 480 - 600 °C was ascribed to the transformation of Fe$_7$S$_8$ into Fe$_2$O$_3$. It can be calculated that the content of Fe$_7$S$_8$ in Fe$_7$S$_8$@S/N-C composite was ~ 39.8 %. The energy dispersive X-ray (EDX) element mapping images indicated that the S, C, and N elements are uniformly distributed throughout the Fe$_7$S$_8$@S/N-C nanofiber (Figure 1e), while Fe element is isolated distributed due to the distribution of isolated Fe$_7$S$_8$ nanoparticles in
the nanofibers, which is consistent with the results of TEM images.

Figure 2 (a) XRD patterns of as-prepared $\alpha$-Fe$_2$O$_3$, Fe$_7$S$_8$, S/N-C and Fe$_7$S$_8$@S/N-C samples; (b) Raman spectra of as-prepared Fe$_7$S$_8$, S/N-C and Fe$_7$S$_8$@S/N-C samples; High-resolution XPS spectra of Fe$_7$S$_8$@S/N-C: (c) Fe 2p; (d) S 2p; (e) C 1s; (f) N 1s.

XRD measurement was carried out to characterize the crystal phase of as-prepared $\alpha$-Fe$_2$O$_3$, Fe$_7$S$_8$, Fe$_7$S$_8$@S/N-C and S/N-C samples, as shown in Figure 2a. The all diffraction patterns of Fe$_7$S$_8$, Fe$_7$S$_8$@S/N-C can be well indexed to pyrrhotite Fe$_7$S$_8$ (JCPDS No. 24-0220), indicating that the $\alpha$-Fe$_2$O$_3$ particles were completely
transformed into Fe₇S₈ materials. Moreover, there are no other impurity peaks, suggesting the good crystallinity and high purity. The XRD pattern of S/N-C is ascribed to the typical carbon. As displayed in Raman spectra (Figure 1b), Fe₇S₈@S/N-C and S/N-C samples show D peak (1320 cm⁻¹) and G peak (1590 cm⁻¹). The intensity ratio of the D peak to G peak for Fe₇S₈@S/N-C (I_D : I_G, 1.5) and S/N-C samples (I_D : I_G, 1.4) indicates that there are more defect sites in Fe₇S₈@S/N-C, which might be caused by the N and S more doping.³³ The Raman spectrum of pure Fe₇S₈ only shows some small peaks located at ~ 1390 cm⁻¹, which are attribute to the small defect site in Fe₇S₈.³⁴

To understand the chemical status of Fe₇S₈@S/N-C, XPS measurement was conducted. The Fe 2p spectrum in Figure 2c shows two valences of Fe existed in the sample. The peaks of Fe 2p3/2 located at 711 eV and 715.7 eV (satellite peak) indicate the existence of Fe²⁺, while the Fe 2p1/2 peaks at 725 eV and 732.5 eV (satellite peak) can be assigned to Fe³⁺.³⁵ In the S 2p spectrum (Figure 2d), the peaks at 163.6 eV and 164.8 eV can be attributed to the S²⁻ and Sn²⁻.³⁶ The small peak at 161.7 eV suggests that some C-S bonds formed during sulfidation process. Besides, another peak located at 168.6 eV can be indexed to the S-O bond caused by the adsorbed oxygen on the active surface of Fe₇S₈ particles in the sample.³⁷ In C 1s spectrum (Figure 2e), the peaks at 289.0, 286 and 284.6 eV are attributed to C=O, C-N/C-S and C-C bonding, respectively. In addition, N 1s spectrum in Figure 2f reveals the existing of pyridine, pyrrolic and graphitic N.³⁸ In this work, the S/N-C matrixes could provides many advantages for improving the electrochemical performance of Fe₇S₈@S/N-C composites. First, the N and S atoms can enhance the electronic conductivity of the composites. Second, the defect sites
brought by N and S could offer much more absorption site for Na ions to improve its capacitive capability. Third, the 1D disorder honeycomb carbon could offer short diffusion length for Na\(^+\), resulting in good rate performance. The N\(_2\) adsorption-desorption isotherms of Fe\(_7\)S\(_8\)@S/N-C, S/N-C and Fe\(_7\)S\(_8\) samples was also shown in Figure S2. The Brunauer-Emmett-Teller (BET) of the Fe\(_7\)S\(_8\)@S/N-C composites (21.41 g m\(^{-2}\)) show higher specific surface area than that of S/N-C (14.47 g m\(^{-2}\)) and Fe\(_7\)S\(_8\) (14.47 g m\(^{-2}\)), which provides more active site for Na\(^+\) adsorption.

**Figure 3** (a) CV curves at 0.2 mV s\(^{-1}\) and (b) charge-discharge profiles at 0.1 A g\(^{-1}\) of the Fe\(_7\)S\(_8\)@S/N-C electrode. (c) Rate capability of Fe\(_7\)S\(_8\)@S/N-C, Fe\(_7\)S\(_8\) and S/N-C electrodes at various current densities. (d) Cycling performance of Fe\(_7\)S\(_8\)@S/N-C, Fe\(_7\)S\(_8\) and S/N-C electrodes at 1 A g\(^{-1}\).

The Na storage performance of the Fe\(_7\)S\(_8\)@S/N-C, Fe\(_7\)S\(_8\) and S/N-C electrodes was evaluated, which are shown in Figure 3. **Figure 3a** exhibits the initial three CV scans.
of Fe$_7$S$_8$@S/N-C electrode. During the first scan process, there exists a sharp cathodic peak at ~0.6 V, presenting the intercalation reaction (Eqn. 1) and the formation of electrolyte interphase (SEI) film. In the low potential range, the small cathodic peak is ascribed to the conversion reaction to form Fe and Na$_2$S (Eqn. 2).\textsuperscript{21} In the first anodic scan, the sharp peak at 1.4 V and broad peak at about 1.6-2.0 V indicate the counter reaction of conversion reaction (Eqn. 3) and the deintercalation reaction (Eqn. 4), respectively.\textsuperscript{18} According previous work, only part of Na ions can be deintercalated out of the Fe$_7$S$_8$-based electrode, leading to the irreversible capacity of the initial cycle.

Sodiation: \[ \text{Fe}_7\text{S}_8 + 8\text{Na}^+ + 8\text{e}^- \rightarrow 4\text{Na}_2\text{FeS}_2 + 3\text{Fe} \] (1)

\[ \text{Na}_2\text{FeS}_2 + 2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}_2\text{S} + \text{Fe} \] (2)

Desodiation: \[ 2\text{Na}_2\text{S} + \text{Fe} \rightarrow \text{Na}_2\text{FeS}_2 + 2\text{Na}^+ + 2\text{e}^- \] (3)

\[ \text{Na}_2\text{FeS}_2 \rightarrow \text{Na}_{2-x}\text{FeS}_2 + x\text{Na}^+ + xe^- \] (4)

In the subsequent cathodic scans, the sharp peak at 0.6 V became broader and shifted to 0.95 V because of the formation of SEI film. Besides, the CV profiles of the 2nd and 3rd cycles did not change obviously, demonstrating a good structural stability. For Fe$_7$S$_8$ electrode, as shown in Figure S3 a, it suffered a worse reversibility. During the second and third cycles, the intercalation reaction of Na$^+$ ion could hardly take place, indicating the S,N-doped carbon nanofibers could effectively protect the Fe$_7$S$_8$ from structure collapse and improving its cycling reversibility. In Figure S3 b, the CV profiles of S/N-C electrode shows a reduction peak around at 0.5 V in the first cycle, which is ascribed
to the formation of an irreversible solid electrolyte interphase (SEI) film. In the following cycles, the curves are well overlapped, demonstrating good reversibility.

The charge-discharge profiles of the first three cycles for the Fe$_7$S$_8$@S/N-C was displayed in Figure 3b. During the first discharge process, a remarkable plateau located at 0.9 - 0.6 V was attributed to the irreversible intercalation reaction and formation of SEI film. In the subsequent cycles, two plateaus can be observed, caused by the reversible intercalation and conversion reactions. In contrast, for Fe$_7$S$_8$ and S/N-C electrodes (Figure S3 c and d), there was no remarkable plateau on the discharge profiles during the 2nd and 3rd cycles. Moreover, the coincidence of subsequent discharge/charge curves for Fe$_7$S$_8$@S/N-C and S/N-C electrodes indicates that S/N-C could afford Fe$_7$S$_8$ with a reversible and stable Na storage performance. Benefited from the defect-decorated carbon nanofibers as conductive matrix with high ion diffusion rate, the Fe$_7$S$_8$@S/N-C electrode showed the best rate capability among three electrodes, as shown in Figure 3c. With the current density increasing, the Fe$_7$S$_8$@S/N-C electrode delivered capacities of 470, 445, 415, 365, 280 and 220 mA h g$^{-1}$, at 0.1, 0.2, 0.5, 1, 2, 5 A g$^{-1}$, respectively. When the current density was adjusted back to 0.1 A g$^{-1}$, a capacity of 475 mA h g$^{-1}$ could still be obtained. The Fe$_7$S$_8$ electrode only showed the limited capacities of 272, 208, 137, 86, 53 and 26 mA h g$^{-1}$, at current densities of 0.1, 0.2, 0.5, 1, 2, 5 A g$^{-1}$, respectively. Besides, when current density was back to 0.1 A g$^{-1}$, Fe$_7$S$_8$ electrode only offered a capacity of 147 mA h g$^{-1}$. This suggests that S/N-C nanofibers could improve the performance of Fe$_7$S$_8$ in the stability and conductivity. Moreover, although S/N-C also exhibited good stability and rate capability, it sustained relatively
lower capacities than Fe$_7$S$_8$@S/N-C at all current densities. As shown in Figure 3d, Fe$_7$S$_8$@S/N-C still showed a high capacity of 347 mA h g$^{-1}$ after 150 cycles at 1 A g$^{-1}$, with the retention rate of about 94% (compared with the 2nd cycle). However, the Fe$_7$S$_8$ and S/N-C displayed a capacity of 41 and 274 mA h g$^{-1}$ at the same current density after 150 cycles, respectively. The better rate and cycling performance of Fe$_7$S$_8$@S/N-C composites could be ascribed to the following reasons: first, the carbon matrixes can alleviate the volume change of Fe$_7$S$_8$ particles during sodiation/desodiation process, maintaining the structure stability. Moreover, the 1D matrixes offer short Na$^+$ diffusion length, leading to good rate capability. Second, the heteroatom could further improve the conductivity of the prepared sample, benefitting the transportation of electrons, which can be proved by the EIS profiles. The EIS profiles of the Fe$_7$S$_8$@S/N-C and Fe$_7$S$_8$ electrodes are show in Figure S4. Before and after galvanostatic tests, the charge transfer resistances of Fe$_7$S$_8$@S/N-C were both smaller than those of Fe$_7$S$_8$, indicating the higher electronic conductivity of Fe$_7$S$_8$@S/N-C.

To explore the sodium storage kinetics of Fe$_7$S$_8$@S/N-C electrode, CV measurements were carried out at various scan rate from 0.2 to 5 mV s$^{-1}$. As shown in Figure 4a, both the anodic and cathodic peaks became broader with the increasing of scan rate. The curves at low and high scan rates show the similar shapes, indicating a small polarization voltage. It is reported that the electrochemical energy storage for metal sulfides is generally consisted of two parts: diffusion-controlled process and capacitance-controlled behavior. The relationship between the peak current ($i$) and sweep rate ($v$) obey the law, as following.$^{39}$
\[ i = a v^b \]  

(5)

where \( a \) and \( b \) are adjustable parameters. When the \( b \)-value closes to 0.5, it indicates the diffusion-controlled process. While the \( b \)-value closes to 1, it indicates the capacitance-controlled behavior. The \( b \)-value can be calculated by fitting the \( \log(v) \) to \( \log(i) \). Surprisingly, depending on the calculation result, the \( b \)-values are 0.88, and 0.68 for anodic and cathodic peaks, respectively, as shown in Figure 4b.

**Figure 4** (a) CV curves at various sweep rates from 0.2 to 5 mV s\(^{-1}\); (b) relationship between the peak currents and scan rates in logarithmic format; (c) capacitive contribution at a scan rate of 0.5 mV s\(^{-1}\) and (d) contribution ratio of the capacitive and diffusion-controlled capacity of Fe\(_7\)S\(_8\)@S/N-C electrode.

The total capacitive contribution to the total capacity can be calculated by the following equations:\(^{40}\)}
\[ i = k_1 v + k_2 v^{1/2} \]  \hspace{1cm} (6)

where \( k_1 v \) reveals the capacitive contribution and \( k_2 v \) represents the diffusion-controlled contribution. As shown in Figure 4c, 49.0% of the total capacity at the scan rate of 0.5 mV s\(^{-1}\) was contributed from capacitive controlled processes for Fe\(_7\)S\(_8\)@S/N-C electrode. From Figure 4d, the contribution ratio of capacitance-controlled process gradually increased with the increasing of the scan rates and finally a maximum value of 80.2% achieved at 5 mV s\(^{-1}\). For pure Fe\(_7\)S\(_8\) electrode, based on the calculation of CV curves (Figure S5 a), a high ratio of capacitive contribution at various scan rate was also obtained, as shown in Figure S5 b. It indicates that the fast charge-discharge process not only occurs on the defect-site of S, N-doped carbon nanofibers, but also takes place on the surface of Fe\(_7\)S\(_8\).

4. Conclusions

In summary, we have successfully synthesized the Fe\(_7\)S\(_8\)@S/N-C nanofibers by electrospinning/sulfidation methods. The S/N-C nanofibers matrixes could offer this composite good structure stability by preventing the collapse of Fe\(_7\)S\(_8\) during charge/discharge process. Moreover, the stable 1D structure facilitate the transportation of ions and electrons, leading to good rate capability. And Fe\(_7\)S\(_8\) nanoparticles grante a high specific capacity. As results, the Fe\(_7\)S\(_8\)@S/N-C demonstrated superior rate capability (a specific capacity of 220 mA h g\(^{-1}\) at 5 A g\(^{-1}\)) and stable cycling performance (a specific capacity of 347 mA h g\(^{-1}\) at 1 A g\(^{-1}\) after 150 cycles). This work will give useful guidance to design other metal sulfide anodes with the adjustment of structure.
and compositions.

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