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# Boosted electrochemical performance of sodium-ion batteries via Sn-Fe binary metal sulfides as anode materials



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# ABSTRACT

The escalating demand for sustainable energy storage solutions has intensified the pursuit of advanced sodiumion batteries (SIBs) as a cost-effective alternative to lithium-ion batteries. Central to this endeavor is the development of high-performance anode materials. In this study, we synthesized Sn-Fe binary metal sulfides as a promising anode material for SIBs, focusing on enhancing electrochemical performance through the modulation of Sn/Fe ratios. We discovered that adjusting the Sn/Fe composition not only optimizes the electrochemical activity window in half-cells but also significantly boosts the energy density in full-cell configurations. The synthesized Sn-Fe sulfides demonstrated superior capacity of 117.8 mAh g<sup>-1</sup> at 0.1C after 100 cycles, attributes pivotal for the practical application of SIBs. Our findings underscore the potential of Sn-Fe binary metal sulfides as a viable anode material for next-generation SIBs, offering a pathway to improved energy storage technologies. This work provides insights into the design principles for advanced anode materials and paves the way for further material optimization and applications in sodium-ion battery systems.

# 1. Introduction

Driven by the increasing reliance on renewable energy sources and the demand of advanced power solutions for electric vehicles, the quest for sustainable and efficient energy storage systems increases rapidly [1]. Among the various battery technologies, sodium-ion batteries (SIBs) have emerged as a promising alternative to lithium-ion batteries, offering comparable energy densities and the significant advantage of sodium's abundant and widely distributed natural resources [2,3]. The performance of SIBs is heavily contingent upon the advancement of their constituent materials, particularly the anode, which must exhibit high specific capacity, excellent rate performance, and stable cyclability to meet the demanding requirements of modern energy applications [4–6].

In the realm of anode materials for SIBs, transition metal sulfides (TMSs) have garnered significant attention due to their ability to alloy with sodium ion, exhibit remarkable specific capacities and low discharge potentials [7]. The flexibility in composition and structure of sulfide materials allows for fine-tuning of their electrochemical properties to suit specific applications [8,9]. For instance, the incorporation of different metal elements can lead to the formation of multi-metal sulfides, which can further optimize the electrochemical performance by leveraging synergistic effects between the constituent metals [10–13]. For example, Yue et al. present a coherent heterostructures of FeS2/MnS nanoparticles, the confinement of FeS2/MnS nanoparticles showed a high energy capacity of 448 mAh g<sup>-1</sup> [14], Wu et al. synthesized a sodium -doped ferrous sulfide between Na<sub>2</sub>CO<sub>3</sub> and MIL-88A (Fe), which delivered 674mAh  $g^{-1}$  after 200 cycles at 0.5 A  $g^{-1}$  [15]. Besides, the selection of transition metals in sulfide anode materials is crucial for optimizing the electrochemical properties of SIBs. Herein, Tin (Sn) and iron (Fe) have emerged as promising candidates due to their distinct advantages [16]. Sn could alloy with sodium to form Na-Sn phases, which contribute to a large reversible capacity and a low

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potential plateau [17,18]. This property makes Sn an attractive material for achieving high energy densities in SIBs. Meanwhile, Fe has multiple oxidation states, which provides more active sites for sodium intercalation [19–21]. The combination of Sn and Fe in a single sulfide matrix offers a synergistic effect, where the high capacity of Sn is complemented by the stability and conductivity provided by Fe [22,23]. This dual-metal approach not only improves the overall electrochemical performance but also mitigates the issues of volume expansion and polarization, which are common challenges in alloy-type anode materials [24,25]. Therefore, the strategic incorporation of Sn and Fe in sulfide anode presents a compelling strategy for developing SIBs with enhanced energy storage capabilities and superior cycle life [26,27].

Inspired by this, we constructed a Sn-Fe binary metal sulfides (FSS) material as an advanced SIB's anode for sodium storge. Benefiting from the synergistic effect, the binary metal sulfides material delivered 596.4 mAh g<sup>-1</sup> after 1000 cycles at 1 A g<sup>-1</sup> and 98.7 % retention in terms of rate performance for half-cell. The excellent electrochemical performance in half-cell indicates the application in full-cell. We synthesized a series of FSS materials (FSS-1,2,3) and assembled them with commercial Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>(NVP) cathode material to form a full cell. It is shown that although their performances in the half-cell are comparable, the materials with different elemental ratios have very different performances in the full-cell. Therefore, finding a Sn/Fe ratio that is more compatible with the full-cell is important for constructing the FSS anode material.

Herein, we found the most suitable FSS material to form a full-cell with NVP cathode by adjusting the ratio between different Sn-Fe elements. The appropriate Sn-Fe ratio can make FSS materials have higher Coulomb efficiency, smaller side reactions, and thinner SEI. When the ratio of Fe-Sn is close to 2, the full cell performance could displaya high capacity of 117.4 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> after 100 cycles. Both half and full-cell digitals indicate that FSS is an excellent anode material for SIBs.

## 2. Experimental section

#### 2.1. Synthesis of Fe-MOF

In a typical procedure, 0.140 g of fumaric acid was dissolved in 50 mL of deionized water with magnetic stirring at 65 °C. After 0.340 g of Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O addition, the resulting mixture was then transferred into a 90 mL Teflon-lined stainless-steel autoclave and heated at 110 °C for 6 h. The obtained orange-yellow solution was filtered and washed with water and ethanol, alternately. Finally, the Fe-MOF precursor was achieved after air-dried at 60 °C.

# 2.2. Synthesis of FSS

0.110 g Fe-MOF precursor and 0.035 g Polyvinylpyrrolidone (PVP, K30) were firstly dispersed and dissolved in the mixture solution of deionized water (50 mL). Then, 0.200 g urea and 0.10 g SnCl<sub>4</sub>·5H<sub>2</sub>O were successively added to the above mixture solution. After magnetic stirring for 90 min, this solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and heated at 90 °C for 3 h. Subsequently, the precipitate was alternately washed by deionized water and ethanol, further dried at an oven (60 °C) for 12 h. Lastly, the dried precipitate was calcined with sulfur (the mass ratio of precursor and sulfur was 1:3) at 500 °C for 3 h under Ar atmosphere to obtain the final FeS<sub>2</sub>/SnS<sub>2</sub> heterostructure, denoted as FSS-1. The preparation process of SS-2 and FSS-3 were similar as the FSS-1 except the added mass of SnCl<sub>4</sub>·5H<sub>2</sub>O, which were 0.15 g and 0.06 g.

# 2.3. Synthesis of the counterparts

The preparation of FeS<sub>2</sub>. The preparation process of FeS<sub>2</sub> was similar as the FSS-1 except the addition of  $SnCl_4$ ·5H<sub>2</sub>O.

**The preparation of SnS**<sub>2</sub>. The preparation process of FeS<sub>2</sub> was similar as the FSS-1 except the addition of Fe-MOF and PVP.

## 3. Results and discussion

The microscopic morphology and synthesis steps were shown in Fig. 1. Pure FeS<sub>2</sub> exhibits a slender hexagonal shape, characterized by a smooth surface and good plasticity, making it an extremely stable precursor. SnS<sub>2</sub> nanoparticles are characterized by a dispersed flaky structure that encapsulates FeS<sub>2</sub>, forming a heterostructured FeS<sub>2</sub>/SnS<sub>2</sub> (FSS) system. The rough and compact texture surface of the synthesized FSS can be attributed to the growth of primary particles during the sulfidation process and the subsequent carbonization of organic ligands. This unique surface morphology is a result of the complex interplay between the crystallization of SnS<sub>2</sub>, which forms dispersed flaky structures around FeS<sub>2</sub>, and the carbonization process that contributes to the overall structural integrity and surface roughness of the material. This unique configuration not only enhances the electrochemical performance but also contributes to the stability of the material during the cycling process.

The phase composition and valence distribution of the prepared samples are determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The FSS-1 sample and the contrast sample FeS<sub>2</sub> and SnS<sub>2</sub> were shown in Fig. 2a and Fig. 2b All the diffraction peaks of FSS could correspond to the pyrite FeS<sub>2</sub> (PDF#71-2219) and SnS<sub>2</sub> (PDF#89-2358), the diffraction peaks of FSS located at 33.1,37.1, 40.8 and 56.3 ° corresponds to the FeS2 (200), (210), (211) and (311) crystal plane, 32.1, 41.9, 50.0, 52.5 and 54.9 °corresponds to the SnS<sub>2</sub> (011), (012), (110), (111) and (103) crystal plane, all the peaks are sharp and well-defined, indicating that the FSS sample has inherited the crystalline characteristics of its constituent phases [14,28-31]. The successful matching of all peaks to the respective standard cards for FeS<sub>2</sub> and SnS<sub>2</sub> confirms the successful synthesis of the FSS composite. Furthermore, the XPS provides a comprehensive understanding of the elemental composition and chemical states present on the surface. For C and S, the C 1 s spectrum (Fig. 2c) shows three peaks corresponding to C=C (284.8 eV), C-S (286.2 eV) and O-C=O (287.6 eV) covalent bonds, the S 2p spectrum (Fig. 2f) indicates three peaks 2p3/2, 2p2/1 and  $SO_4^{2-}$  which located at 162.2, 163.6 and 169.7 eV. The Sn 3d spectrum (Fig. 2e) is deconvoluted to identify the specific chemical states, with the Sn 3d5/2 peak observed at approximately 487 eV and the Sn 3d3/2 peak at around 495 eV. These binding energies are characteristic of Sn<sup>4+</sup> in the form of SnS<sub>2</sub>, which is consistent with the expected chemical states of tin in the FSS composite. The Fe 2p spectrum (Fig. 2d) shows two main peaks corresponding to Fe 2p3/2 (708.2 eV) and Fe 2p1/2 (721.4 eV), which are indicative of the Fe(II) state in FeS<sub>2</sub>, the prominent peaks at approximately 717 eV and 713 eV are identified as the characteristic Sn 3p3/2 and 3p5/2 peaks, indicative of tin's presence in the FSS sample [32-34]. The higher atomic sensitivity of tin leads to a more pronounced signal in the Fe 2p spectrum, where it appears significantly larger. This enhanced detectability is attributed to the atomic number effect, which influences the photoelectron emission intensity.

Fig. 3 presents the microstructural and morphological characteristics of the FSS composite and the comparison samples (FeS2 and SnS2) analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 5.3a, the  $SnS_2$  (Fig. 3a) sample exhibits a nanoflower-like morphology composed of petalshaped nanosheets with lateral dimensions of  $2\text{--}3\ \mu\text{m}$ . In contrast, the FeS<sub>2</sub> sample (Fig. 3b) displays a flower-like architecture formed by the aggregation of rhombic plates, demonstrating a smooth surface and stable structural integrity. Furthermore, the addition of polyvinylpyrrolidone (PVP) as a dispersing agent effectively suppressed the random stacking of nanosheets, ensuring morphological homogeneity of the composite. The imageclearly demonstrates the retention of the original rhombic shape of the FSS, which is a key feature of the material's structure. After the synthesis process involving the combination with Sn and subsequent sulfurization annealing, the FSS sample (Fig. 3c) maintains its fundamental morphological integrity [35,36]. These observations suggest that while the majority of the material has undergone



Fig. 1. Schematic illustration of the synthesis process for FSS composite.



Fig. 2. XRD patterns of final products (a) and precursors (contrast sample) (b). XPS core level spectra of FSS-(c) C 1 s (d) Sn 3d (e) Fe 2p and (f) S 2p.

the desired chemical transformation, there may be areas that require further optimization in the synthesis process to achieve full conversion to the desired sulfide phases.

The Transmission Electron Microscopy (TEM) image in Fig. 3d provides a complementary view to Fig. 3c, offering a deeper insight into the microstructure of the FSS sample [37]. The TEM image corresponds well with the SEM image, confirming the preservation of the rhombic shape of the Fe-MOF precursor after the synthesis process involving tin (Sn) complexation and sulfurization annealing. The image shows that while the majority of the material maintains its integrity, there are indeed regions where the sulfiding process may not be complete, as evidenced by the presence of a few scattered impurities. The HRTEM image (Fig. 4a) clearly shows the (102) crystal plane of  $SnS_2$ , the (200) crystal plane of  $FeS_2$  and the lattice interface layer between them, indicating the successful synthesis of the FSS heterojunction structured material. The TEM-EDS mapping Fig. 4b analysis confirms the uniform distribution of



Fig. 3. (a) SEM image of SnS<sub>2</sub>, (b) SEM image of FeS<sub>2</sub>, (c) SEM image of FSS and (d) TEM image of FSS.



Fig. 4. (a) HRTEM image of FSS and (b) elemental EDS mapping images of FSS.

C, O, S, Fe, and Sn within the FSS sample, which ensures that the active phases of  $FeS_2$  and  $SnS_2$  are evenly represented throughout the composite [38].

The electrochemical performance of FSS half-cell is shown in Fig. 5. The Galvanostatic Charge-Discharge (GCD) curves presented in Fig. 5a offer a detailed examination of the electrochemical properties of the FSS, SnS<sub>2</sub>, and FeS<sub>2</sub> samples within a potential window of 0.2 to 2.8 V. The FSS sample stands out with its pronounced discharge capacity, attributed to the synergistic contributions from both SnS2 and FeS2 phases within the triphasic heterostructure. This composite structure not only enhances the specific capacity but also stabilizes the cycling performance, as evidenced by the distinct charge and discharge plateaus in its GCD curve. Fig. 5b illustrates the cycling performance of the FSS, SnS<sub>2</sub>, and FeS<sub>2</sub> samples at a current density of 1 A  $g^{-1}$ . The FSS sample demonstrates a remarkable capacity retention, with a specific capacity of 596.4 mAh  $g^{-1}$  after 1000 cycles. In contrast, the SnS<sub>2</sub> and FeS<sub>2</sub> samples exhibit significantly lower capacities of 424.6 mAh g<sup>-1</sup> and 287.5 mAh  $g^{-1}$ . These results highlight the enhanced capacity of the FSS composite as an anode material for sodium-ion batteries, which can be attributed to the synergistic effects of the triphasic heterostructure that mitigates volume expansion and promotes stable cycling. Fig. 5c presents the rate capability of the FSS sample. It maintains 98.7 % of its initial capacity even after being subjected to different current densities, which indicative of the FSS sample's ability to accommodate rapid charge and discharge processes without significant loss in performance. Fig. 5d presents the cyclic voltammetry (CV) curves of the FSS sample at a scan rate of 0.1 mV  $s^{-1}$  for the initial five cycles. The peaks across the five cycles are pronounced and consistent, which indicates a high degree of electrochemical reversibility. The redox reactions including Fe conversion reaction and Sn conversion and alloying reaction corresponding to each peak are as follows [39-41]:

$$FeS_2 + xNa^+ + xe^- \rightarrow Na_xFeS_2 \tag{1}$$

 $Na_{x}FeS_{2}+(2-x)Na^{+}+(2-x)e^{-}\rightarrow Na_{2}S+Fe$ (2)

$SnS_2+yNa^++y$	$ye^{-} \rightarrow Na_ySnS_2$	(3)
	*	

$$Na_{v}SnS_{2} + (4-y)Na^{+} + (4-y)e^{-} \rightarrow 2Na_{2}S + Sn$$
(4)

$$Sn+2Na_2S \rightarrow SnS_2+4Na^++4e^-$$
(5)

$$Sn+yNa^++ye^- \rightarrow Na_ySn$$
 (6)

Fig. 5e presents the long-term cycling performance of the FSS sample under a high current density of 10 A g<sup>-1</sup>. It demonstrates exceptional performance, maintaining a substantial capacity of 412.7 mAh g<sup>-1</sup> after 5000 cycles. The FSS sample's ability to sustain such high capacities at elevated current densities is a clear indicator of its potential for applications requiring rapid charge and discharge capabilities.

The comparative analysis of the density of states (DOS) and structural models for the FSS composite,  $SnS_2$ , and  $FeS_2$  (Fig. 6) reveals distinct electronic characteristics and atomic arrangements that contribute to their electrochemical behavior. The FSS composite exhibits a higher total DOS at the Fermi surface, indicating its enhanced electronic conductivity and potential for improved electrochemical performance [42,43]. In essence, the DOS graphs illustrate the semiconducting nature of  $SnS_2$  and  $FeS_2$ , which contrasts with the metallic behavior suggested by the FSS composite's DOS. Structurally, the FSS composite model showcases a complex arrangement that integrates both  $FeS_2$  and  $SnS_2$  phases, contributing to its superior performance.

Fig. 7 presents the performance of full cells with three different Fe/ Sn ratios FSS materials. The Fe/Sn ratios are 3.5:1, 2:1, and 1.66:1, which named FSS-1, FSS-2, and FSS-3, respectively. The comprehensive evaluation of the full-cell performance for the FSS composites with varying Sn/Fe ratios underscores the pivotal role of the Sn/Fe ratio in dictating the electrochemical properties of the anode material. The schematic in Fig. 7a outlines the assembly of the full-cell. The FSS composites are paired with commercial Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NVP) as the cathode, maintaining an optimal N/P ratio of 1.2/1. The cycling performance of NVP cathode half-cell is presented in Fig. 7b, which could deliver 118 mAh g<sup>-1</sup> at 1C(1C=100 mA g<sup>-1</sup>) after 120 cycles. Based on the performance characteristics of NVP commercial cathode material



**Fig. 5.** (a) GCD curves of FSS, FeS<sub>2</sub> and SnS<sub>2</sub> (b) cycling performance of FSS, FeS<sub>2</sub> and SnS<sub>2</sub> at 1 A  $g^{-1}$  (c) rate performance of FSS (d) first five cycle CV curves of FSS, (e) long cycling performance of FSS at 10 A  $g^{-1}$ .



Fig. 6. Total density of states (TDOS) and projected density of states (PDOS) for each element of (a) the FSS composite, (b) SnS<sub>2</sub>, and (c) FeS<sub>2</sub>. Corresponding structural models are shown in (d-f).

and FSS anode electrode, the voltage test interval of the full-cell was controlled at 0.5–3.8V. The GCD curves of the FSS material is shown in Fig. 7d The trend of the platform curves of the three materials is more consistent with that of the cathode material NVP. Furthermore, the charging and discharging platform curves of FSS-1 around 3.4 V are more gentle, which indicates that the full-cell can release the performance of NVP material under the appropriate ratio of Sn-Fe. The cycling performance of the full-cells based on FSS-1, FSS-2, and FSS-3 is presented in Fig. 7e. The cycling performance reveals that FSS-1 sustains a superior capacity of 117.8 mAh  $\rm g^{-1}$  at 0.1C after 100 cycles, 273.25 Wh kg<sup>-1</sup> at 138. 70 W kg<sup>-1</sup>,outperforming FSS-2 and FSS-3, which have lower or higher Sn content. The rate performance is illustrated in Fig. 7f. The three materials were cycled at current densities ranging from 0.1 to 2 C. When subsequent current density returning to 0.1 C, FSS-1 exhibited a capacity of 113.2 mAh g<sup>-1</sup> with 93.1 % cycle retention, which is higher than the capacity and retention of FSS-2 and FSS-3, which presented 98.4 mAh g<sup>-1</sup> 87.7 % cycle retention and 97.6 mAh g<sup>-1</sup> 86.5 % cycle retention, respectively. The superior multiplicative performance of FSS-1 indicates that its chemical interface is more stable, and its cycling capacity is better maintained at different current densities. This enhanced capacity retention is complemented by the electrochemical impedance spectroscopy (EIS) results (Fig. 7c), where FSS-1 exhibits a lower Ohmic resistance, indicative of its superior conductivity [38]. The cyclic voltammetry (CV) curves for the half-cell of FSS composites demonstrate a consistent shape with a notable difference in the capacity contribution from the low-voltage region, where FSS-1 shows a higher proportion, suggesting increased reactivity and a broader voltage operation window. This translates to a higher energy density, longer cyclic life which is a critical factor for practical applications.

Fig. 8 delves into the reasons behind the performance differences among the three FSS composites. Fig. 7(a-c) present line scan images of the surface distribution of Cu and F elements on the electrode of fully charged (at 0.01 V) full-cells. Cu is the base material of the electrode and doesn't participate in the battery reaction, F is a component of the



**Fig. 7.** (a) Schematic diagram of the FSS||NVP full-cell. (b) cycling performance of NVP half-cell at 1C. (c) Nyquist plots of FSS-1,2,3. (d) GCD curves of FSS-1,2,3 full-cell (e) cycling performance of FSS-1,2,3 full-cell at 0.1C. (f) rate performance of FSS-1,2,3. (g-i) CV curves of FSS-1,2,3 half-cell at 0.6 mV s<sup>-1</sup>.

electrolyte that appears on the electrode's surface. The greater the distance between these two elements, the thicker the solid electrolyte interphase (SEI) film formed on the FSS electrode surface, leading to more "dead sodium" deposited on the electrode surface. which leads to lower coulombic efficiency and poorer cycling stability. It can be observed that FSS-1 has a smaller spacing between these two elements, corresponding to its better performance [41,44]. Fig. 8(d-F) illustrate the charging curves for the three materials, divided into three voltage ranges: 0.2-1 V, 1-2 V, and 2-2.8 V. It is evident that FSS-1 has a higher proportion in the low-voltage range. The pie charts in Fig. 8(g-i) corresponds to the CV curves represent the energy proportion of the three materials within the same voltage curve. These charts provide a visual representation of how the energy is distributed across different voltage intervals for each material, suggest that FSS-1 has higher reactivity in the low-voltage area, which is beneficial for enhancing the battery's energy density and efficiency [23,45,46].

Fig. 9 presents the XPS data of the electrode surfaces after 10 cycles for three distinct FSS materials, offering insights into the degradation profile of the electrolyte (1.0 mol NaPF<sub>6</sub> in DME). The C 1 s and F 1 s spectra reflect the electrolyte's interaction with the electrode material. The emergence of Na-F bonds post-decomposition of  $PF_6$ -suggests the formation of NaF, while the appearance of C-F bonds indicates reactions with organic components of the electrolyte. Additionally, the breakdown of DME contributes to the formation of C—O polymers and carbonate ( $CO_3^{2-}$ ) species bonds. Through comparative analysis of Figs. 8a (C 1 s) and 8d (F 1 s) between FSS-1 and FSS-2,FSS-3, it is observed that the intensities of the C—O, C-F,  $CO_3^{2-}$ , and Na-F peaks for FSS-1 are diminished. The reduction in peak intensity suggests a lower degree of electrolyte decomposition at the FSS-1 electrode surface [47, 48]. A lower level of electrolyte decomposition is beneficial for enhancing the battery's coulombic efficiency and cyclic stability. The findings align with the performance advantages observed for materials with optimized interfaces.

The DFT calculation are displayed in Fig. 10, which provide a comprehensive view of the electronic characteristics and atomic interaction. The DOS graphs illustrate the total atomic contributions and individual atomic contributions of Fe, S, and Sn, with a significant presence of states at the Fermi level across all materials, indicating metallic or semi-metallic behavior conducive to high charge carrier mobility rates. In particular, the electronic states derived from Fe species are more localized in the Fermi energy than those from S and Sn, indicating that the proportion of Fe in the system has a very large effect on the conductivity. Compared with FSS-2 and 3, FSS-1 with a higher concentration of Fe exhibits a relatively enhanced DOS near the fermi level (see the energy around -1 eV to 0 eV). The increased DOS near the Fermi energy demonstrates the higher electronic conductivity and is more conducive to charge diffusion kinetics. The differential charge density ( $\Delta \rho$ ) results presented in Fig. 10(d-F) reveal the intricate



**Fig. 8.** (a–c) Linear scanning distribution of Cu and F elements on the electrode surface after 10 cycles. (d–f) charging curves at 10th cycle of FSS-1(d), –2(e), –3(f). (g-i) Voltage-capacity ratio distribution of FSS-1(g), –2(h), –3(i).

interatomic charge redistribution induced by the heterojunction construction. The yellow regions represent charge accumulation (increased electron density), while the green regions indicate charge depletion (reduced electron density). This asymmetric charge redistribution directly reflects strong interatomic interactions at the interface. The non-uniform charge distribution induces a built-in electric field, which facilitates the directional migration of Na<sup>+</sup> ions by lowering ionic diffusion barriers. Concurrently, the electric field promotes the effective separation of electron-hole pairs and reduces parasitic reactions between the electrolyte and electrode surface, thereby suppressing the growth of a thick solid-electrolyte interphase (SEI) layer. Furthermore, the optimized charge transfer pathways enhance reactant adsorption and accelerate charge transport kinetics, leading to significantly improved reaction efficiency and electrochemical performance. This interfacial charge engineering effectively suppresses the decomposition of electrolytes and the formation of a thick solid-electrolyte interphase (SEI), ultimately contributing to improved electrochemical stability and cycling performance. Fig. 10(g-i) presents the calculated adsorption energies of Na<sup>+</sup>on heterojunction, the adsorption energy of FSS-1 (-2.144 eV) is lower than that of FSS-2 (-2.140 eV) and FSS-3 (-2.107 eV). Lower adsorption energy indicating a higher propensity for electrochemical reactions and a higher capability. The calculation results about the enhanced electronic structure near the Fermi level are consistent with the experimental results, which signifies the FSS-1 material's potential for improved electrochemical performance in sodiumion batteries.

# 4. Conclusion

In this study, we synthesized heterojunction structure FSS materials that exhibit a significant performance enhancement compared to individual  $SnS_2$  and  $FeS_2$  materials, which deliver a high specific capacity of 596.4 mAh g<sup>-1</sup> after 1000 cycles in half-cell. To further explore their potential in full-cell applications, we prepared three FSS composites with varying Fe/Sn ratios and conducted an in-depth investigation into their impact on full-cell performance. Our findings demonstrate that the FSS-1 composites offer superior electrochemical properties due to thinner SEI film formation and less electrolyte decomposition, which sustains a superior capacity of 117.8 mAh g<sup>-1</sup> at 0.1C after 100 cycles, making them promising candidates for next-generation sodium-ion batteries. The work underscores the critical role of the Sn/Fe ratio in optimizing the anode materials for enhanced energy storage applications.

# CRediT authorship contribution statement

Yilin Wang: Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. Xiaotian Yang: Methodology, Formal analysis, Conceptualization. Shengjun Yuan: Writing – review & editing, Writing – original draft, Conceptualization. Ting Hu: Conceptualization. Hao Xie: Conceptualization. Fan Yang: Validation. Qiaolin Ren: Conceptualization. Qiming Liu: Conceptualization.



Fig. 9. XPS patterns of FSS-1,2,3 after 10 cycles. (a,d) FSS-1 (b,e) FSS-2 (c,f) FSS-3.



Fig. 10. Total and partial density of states of (a) FSS-1, (b) FSS-2, and (c) FSS-3. (d-f) corresponding difference charge density results of the structures. (g-i) corresponding adsorption energies of Na<sup>+</sup>.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships to influence the work reported in this paper.

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# Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2025.146148.

## Data availability

No data was used for the research described in the article.

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