

First-shell sulfur doping induced asymmetric FeN_3S_1 coordination for accelerating sulfur redox kinetics in Li-S batteries

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Cite this article: Nano Research, 2026, 19, 94908997. <https://doi.org/10.26599/NR.2026.94908997>

ABSTRACT: The asymmetric coordination engineering of single-atom catalysts emerges as a promising strategy to accelerate the sluggish redox kinetics of sulfur cathodes in Li-S batteries. Herein, an asymmetric coordination of Fe single-atom catalyst was exploited by simultaneously introducing sulfur atom and nitrogen atoms into the first coordination shell, where each Fe atom was connected with one sulfur and three nitrogen atoms (FeN_3S_1). This asymmetric coordination redistributed the electron density around the Fe center, which upshifted the d-band center and shortened the Fe-S(ads) bond length between the Fe site and lithium polysulfides (LiPSs), collectively strengthening LiPSs adsorption (where (ads) denotes the adsorbed atom). Moreover, these electronic modulations endowed the asymmetric FeN_3S_1 site, lowering the free energy barriers of the rate-determining steps (Li_2S_4 to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$), accelerating the sulfur redox kinetics. Consequently, the $\text{S@Fe}_2\text{S}_2\text{NC}^{15-1}$ (NC stands for nitrogen-doped carbon) cathode maintains a low capacity decay rate of only 0.05% per cycle over 500 cycles at 4.0 C. This work provides a rational asymmetric coordination engineering strategy toward high performance Li-S batteries.

KEYWORDS: asymmetric coordination, electron density, Fe single-atom catalyst, sulfur redox kinetics, lithium-sulfur batteries.

1 Introduction

Lithium-sulfur (Li-S) batteries are widely regarded as a leading candidate for next-generation energy storage and conversion technologies, owing to their high theoretical energy density ($2600 \text{ Wh}\cdot\text{kg}^{-1}$), large specific capacity ($1672 \text{ mAh}\cdot\text{g}^{-1}$), abundance of sulfur, and environmental compatibility [1–4]. Nevertheless, their practical application is severely hindered by inherent challenges, such as most notably sluggish redox kinetics and the severe shuttle effect of soluble lithium polysulfides (LiPSs) [5, 6]. In

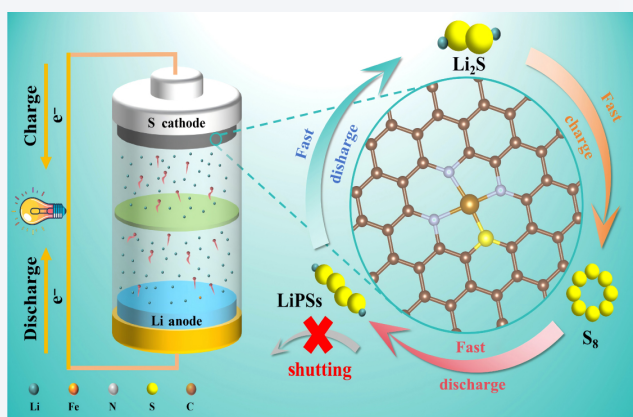
this context, metal single-atom catalysts (MSACs) have emerged as a promising solution [7]. Benefiting from maximal atomic utilization, high intrinsic catalytic activity, and tunable selectivity, MSACs can effectively accelerate the conversion of LiPSs, thereby addressing the fundamental limitations of Li-S batteries [8, 9]. Among various MSACs, iron SACs (FeSACs) stand out due to their natural abundance and excellent electrocatalytic performance [10].

The charge-discharge processes in Li-S batteries involve numerous liquid-phase intermediates (Li_2S_x , $4 \leq x \leq 8$) and solid-phase intermediates (Li_2S_2 and Li_2S) [11–13]. However, long-chain LiPSs are prone to dissolution, leading to irreversible loss of active materials [14]. Hence, precise modulation of LiPSs adsorption capacity for polysulfides is essential [15]. For FeSACs, the adsorption capacity is intimately linked to the local coordination environment of the Fe center [16–18]. For example, Cao et al. [19] precisely modulated the coordination environment of Fe by introducing B atoms into a B, N-co-doped carbon support,

Received: May 9, 2026; Revised: June 22, 2026

Accepted: July 3, 2026

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successfully synthesizing a Fe-N₂B₂/C catalyst featuring a symmetric N₂-Fe-B₂ active site. Experimental and theoretical results demonstrated that this modified catalyst exhibits enhanced affinity toward LiPSs, enabling their rapid capture via strong Lewis acid-base interactions. However, studies have revealed that the catalytic activity of FeSACs with symmetric coordination structures remains limited, underscoring the need to construct FeSACs with asymmetric configurations [20–22].

In recent years, the introduction of heteroatoms with distinct electronic properties (e.g., B, S, and P) into the coordination structure has proven to be an effective strategy for constructing asymmetric FeSACs [23, 24]. For instance, Song et al. [25] demonstrated that the local electronic structure of ferromagnetic BP monolayers doped with single atoms (Fe-BP) can be effectively modulated, leading to enhanced interactions with LiPSs species and significantly reduced energy barriers for both the sulfur reduction reaction (SRR) and Li₂S decomposition, thereby accelerating the overall sulfur conversion kinetics. Unfortunately, the promising strategy of introducing S atoms into FeSACs has not been fully explored for modulating their interactions with polysulfides [26]. Our team recently synthesized an FeSAC (FeN₂C₂-SO_x-nitrogen-doped carbon (NC)) featuring -SO_x functional groups in the second coordination and an FeN₂C₂ coordination geometry, which exhibits moderate adsorption toward LiPSs and further promotes its transformation [27]. In the field of oxygen reduction, previous studies have shown that introducing S into the first coordination shell is also effective for tuning the local coordination environment of Fe, thereby achieving higher catalytic activity [28–31]. Therefore, engineering the catalytic activity of FeSACs by incorporating S atoms into the first coordination shell to construct an asymmetric bonding configuration could open new avenues for Li-S batteries with high rate capability and long cycle life.

In this work, we leveraged the strong coupling between SCN⁻ and Fe ions to construct an asymmetric FeN₃S₁ coordination structure, wherein S atoms are directly incorporated into the first coordination shell of the Fe center. Through X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS), and density functional theory (DFT) calculations, we demonstrate that the lower electronegativity of S compared to N effectively modulates the electronic structure of the Fe center. This modulation increases the electron cloud density around Fe, shortens the Fe-S bond with lithium polysulfide intermediates, and upshifts the Fe d-band center toward the Fermi level, thereby enhancing the adsorption of LiPSs onto the FeSACs. Direct evidence for this enhanced adsorption for LiPSs is further provided by LiPS precursor adsorption tests. Furthermore, the asymmetric FeN₃S₁ configuration lowers the reaction energy barrier of the rate-determining step and accelerates the kinetics of the sulfur reduction reaction. Consequently, the FeSACs catalyst with the FeN₃S₁ asymmetric coordination structure effectively suppresses the shuttle effect in Li-S batteries and delivers excellent rate capability and cycling stability.

2 Experimental procedures

2.1 Preparation of NC

Zeolitic imidazolate framework-8 (ZIF-8) was synthesized by dissolving 10.52 g of 2-methylimidazole and 4.78 g of Zn(NO₃)₂·6H₂O in 100 mL of anhydrous methanol. After sonication for 5 min, the two solutions were mixed and stirred at

room temperature for 24 h. The resulting precipitate was collected by centrifugation, washed three times with anhydrous methanol, and dried under vacuum at 60 °C for 12 h. Subsequently, 0.2 g of ZIF-8 was dispersed in a 1:1 (v/v) mixture of anhydrous ethanol and deionized water (total volume of 100 mL). Separately, 45 mg of dopamine hydrochloride (PDA) was dissolved in 100 mL of deionized water. After the dispersion and solution were combined and dried, the resulting product was pyrolyzed at 900 °C for 1 h under an inert atmosphere to obtain NC.

2.2 Preparation of Fe-NC¹⁰⁻¹, Fe,S-NC¹⁰⁻¹, Fe,S-NC¹⁵⁻¹, and Fe,S-NC²⁰⁻¹

2.2.1 Synthesis of Fe,S-NC¹⁰⁻¹, Fe,S-NC¹⁵⁻¹, and Fe,S-NC²⁰⁻¹

A fixed amount of NC was added to separate solutions containing Fe(NO₃)₃·9H₂O, KSCN, and deionized water, where the mass ratios were 10:1. Subsequently, the resulting product was then pyrolyzed at 900 °C for 1 h to obtain the Fe,S-NC¹⁰⁻¹. For the synthesis of Fe,S-NC¹⁵⁻¹ and Fe,S-NC²⁰⁻¹, the procedures were the same as those of Fe,S-NC¹⁰⁻¹, except that the mass ratios are 15:1 and 20:1, respectively.

2.2.2 Synthesis of Fe-NC¹⁰⁻¹

A mixture of 100 mg of NC and a given amount of Fe(NO₃)₃·9H₂O (with Fe) was thoroughly ground and then calcined at high temperature (900 °C for 1 h).

2.3 Preparation of S@NC, S@Fe-NC¹⁰⁻¹, S@Fe,S-NC¹⁰⁻¹, S@Fe,S-NC¹⁵⁻¹, and S@Fe,S-NC²⁰⁻¹

The S@NC, S@Fe-NC¹⁰⁻¹, S@Fe,S-NC¹⁰⁻¹, S@Fe,S-NC¹⁵⁻¹, and S@Fe,S-NC²⁰⁻¹ cathodes were prepared via a straightforward fusion-diffusion method. The host materials and sulfur were mixed and then heated under an Ar atmosphere in a glass container.

3 Results and discussion

The synthetic procedure for Fe,S-NC¹⁵⁻¹ is illustrated schematically in Fig. 1(a). Briefly, PDA-coated ZIF-8 was calcined to form NC nanocages. Subsequently, Fe(NO₃)₃·9H₂O and SCN⁻ were introduced as the Fe and S sources, respectively, to construct an asymmetric FeN₃S₁ coordination structure. Unlike previously reported second-shell-modified Fe coordination structures, the strong binding affinity between Fe and SCN⁻ enables S modification to occur in the first coordination shell of the Fe single atoms. This approach enriches the strategies for tuning the coordination environment of Fe single atoms via S doping [32, 33]. All obtained catalysts exhibited a well-defined rhombic dodecahedral morphology (Fig. S1 in the Electronic Supplementary Material (ESM)). The microstructure of Fe,S-NC¹⁵⁻¹ was further investigated by transmission electron microscopy (TEM). As shown in Figs. 1(b) and 1(c), the Fe,S-NC¹⁵⁻¹ exhibits a carbon nanocage structure with a hollow core and thin-walled carbon layers, providing sufficient space to accommodate the volume expansion of sulfur species during cycling [34]. Notably, no visible metal clusters or aggregates are observed, indicating the absence of large-scale nanoparticle or alloy formation [35]. To further confirm the single-atom dispersion of Fe, the Fe,S-NC¹⁵⁻¹ was examined by spherical aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) (Figs. 1(d) and 1(e)). The images reveal that Fe atoms are atomically dispersed throughout the carbon matrix, confirming the successful construction of a single-atom catalyst [36]. Elemental

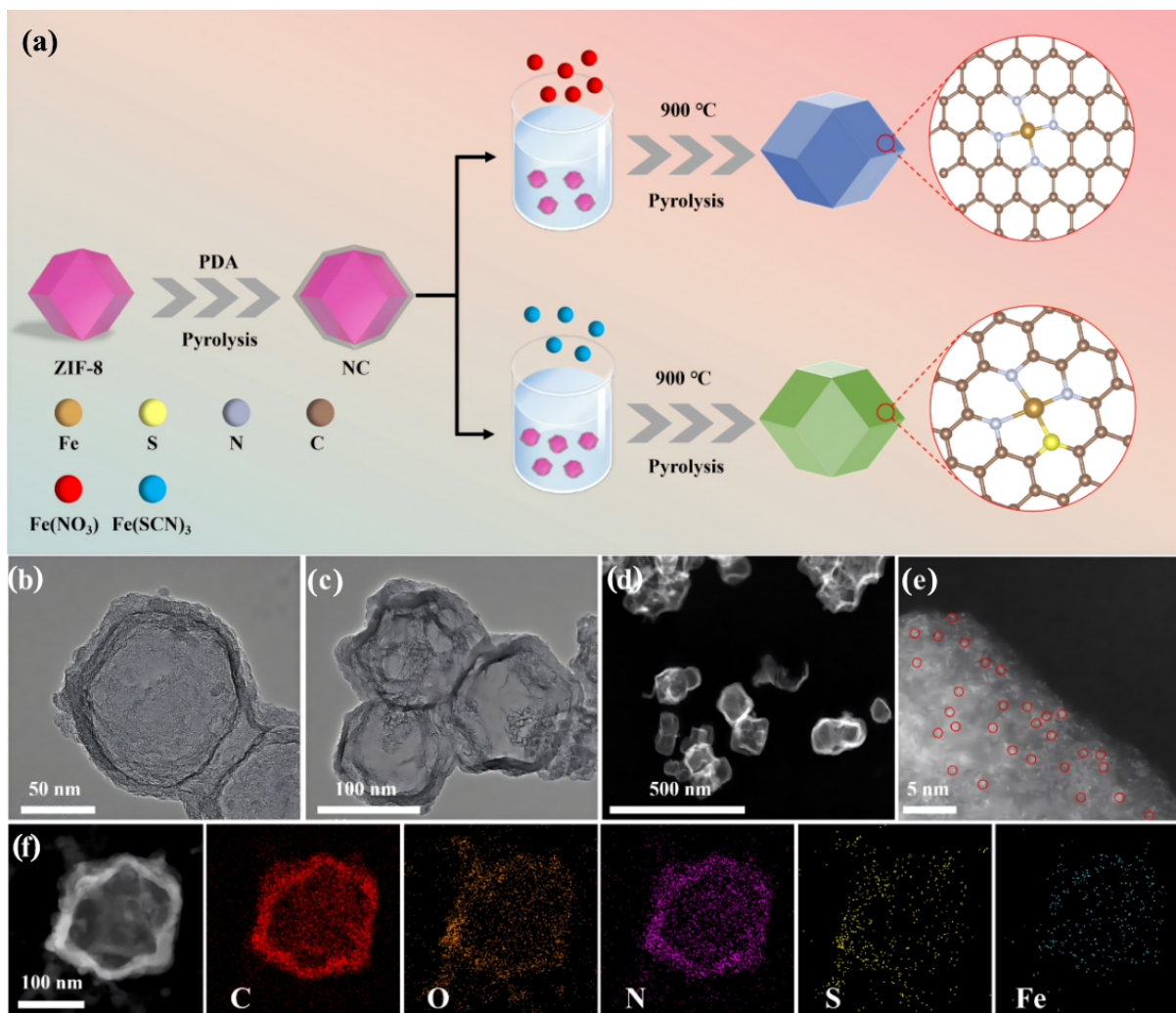


Figure 1 (a) Synthesis diagram, ((b) and (c)) TEM, ((d) and (e)) HAADF-STEM, and (f) STEM and energy dispersive X-ray spectroscopy (EDS) mapping images of Fe,S-NC¹⁵⁻¹.

mapping analysis (Fig. 1(f)) further demonstrates the homogeneous distribution of Fe, N, S, and C across the entire architecture [37].

X-ray diffraction (XRD) patterns further confirm that all samples exhibit only amorphous carbon peaks [38], with no characteristic peaks of any Fe species (Fig. 2(a)), which is consistent with the TEM analysis results. Raman spectroscopy of NC, Fe-NC¹⁰⁻¹, Fe,S-NC¹⁰⁻¹, and Fe,S-NC¹⁵⁻¹ displays two prominent peaks centered at approximately 1337 and 1576 cm⁻¹ (Fig. 2(b)), corresponding to the defect-induced D band and the graphitic G band, respectively. Notably, all samples show similar intensity ratio (I_D/I_G) values, a key indicator of the graphitization degree and defect density [39], indicating the S introduction has little effect on the structural defect density of the carbon substrate. Nevertheless, the strong binding affinity of S toward Fe can assist in anchoring Fe single atoms. Inductively coupled plasma optical emission spectrometry (ICP-OES) results show that Fe,S-NC¹⁰⁻¹ exhibits a higher Fe loading than that in Fe-NC¹⁰⁻¹ (Fig. 2(c)). In addition to the Fe content, the specific surface area, pore volume, and average pore size are also influenced by S introduction (Figs. S2 and S3 and Table S1 in the ESM). Although the specific surface area decreases significantly after S introduction, the reduction mainly occurs in the micropore area, whereas the mesopore ratio increases. This change is beneficial for subsequent sulfur loading and catalytic conversion. To

investigate the compositional characteristics, including elemental type, chemical states, and electronic configuration, XPS was employed. High-resolution Fe 2p spectra (Fig. 2(d)) reveal distinct peaks corresponding to Fe²⁺ and Fe³⁺ in the Fe-NC¹⁰⁻¹, Fe,S-NC¹⁰⁻¹, Fe,S-NC¹⁵⁻¹, and Fe,S-NC²⁰⁻¹. Notably, no characteristic peak attributable to Fe⁰ is detected at 706.7 eV, effectively ruling out the formation of metallic clusters. Furthermore, compared with Fe-NC¹⁰⁻¹, the Fe,S-NC exhibited a reduced Fe³⁺ content (37.90 at.%) alongside a correspondingly increased Fe²⁺ content (62.10 at.%) (Table S2 in the ESM). This is attributed to the lower electronegativity of S (2.58) compared to N (3.04). When S replaces N in the first coordination shell of the Fe center, it increases the electron cloud density around Fe, thereby enhancing its electron-donating ability and promoting the formation of Fe²⁺ species. The high-resolution N 1s spectra (Fig. 2(e)) of all samples reveal similar N species, including pyridinic N (398.5 eV), pyrrolic N (400.1 eV), graphitic N (401.05 eV), and oxidized N (402.9 eV). The high-resolution S 2p spectra (Fig. 2(g)) confirmed the presence of multiple S species in the Fe,S-NC¹⁰⁻¹, Fe,S-NC¹⁵⁻¹, and Fe,S-NC²⁰⁻¹, namely electron-donating C-S-C moieties, electronegative oxidized sulfur species (C-SO_x), and Fe-S bonds (161.7 eV). The distinct Fe-S bond further confirms that S is directly coordinated to the Fe center site in the first shell.

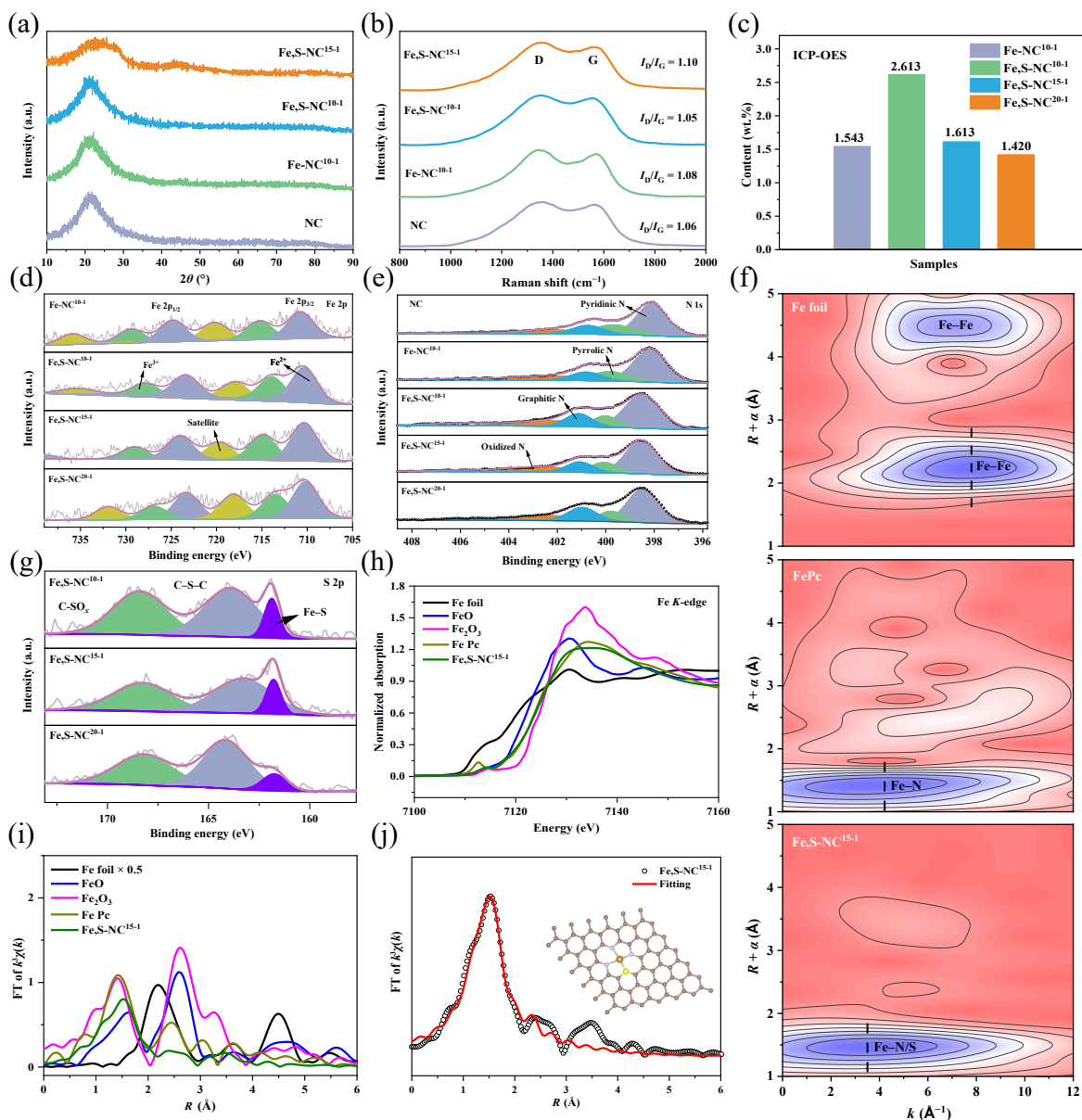


Figure 2 (a) XRD patterns. (b) Raman spectra and the corresponding I_D/I_G of NC, Fe-NC¹⁰⁻¹, FeS-NC¹⁰⁻¹, and FeS-NC¹⁵⁻¹. (c) ICP-OES results. (d) Fe 2p, (e) N 1s, and (g) S 2p spectra of NC, Fe-NC¹⁰⁻¹, FeS-NC¹⁰⁻¹, FeS-NC¹⁵⁻¹, and FeS-NC²⁰⁻¹. (f) Fe K-edge WT-EXAFS contour plots. (h) XANES and (i) FT-EXAFS spectra of Fe foil, FeO, Fe₂O₃, FePc, and FeS-NC¹⁵⁻¹ based on Fe K-edge. (j) R -space EXAFS fitting curves of FeS-NC¹⁵⁻¹.

X-ray absorption spectroscopy (XAS) was employed to precisely determine the coordination environment of the Fe centers. The X-ray absorption near-edge structure (XANES) spectra (Fig. 2(h)) show that the Fe K-edge absorption edge energy of FeS-NC¹⁵⁻¹, closely aligns with that of iron phthalocyanine (FePc), indicating a similar coordination structure of the central Fe atoms. Notably, the white line of FeS-NC¹⁵⁻¹ is slightly lower than that of FePc, suggesting a lower Fe valence state, which is attributed to the introduction of S into Fe coordination structure. The Fourier transform extended XAFS (FT-EXAFS) spectrum of FeS-NC¹⁵⁻¹ at the Fe K-edge (Fig. 2(i)) exhibits a prominent peak at 1.50 Å, corresponding to Fe-N coordination. In contrast, the Fe foil reference shows a peak at 2.21 Å, FeO and Fe₂O₃ display peaks at approximately 2.61 Å, both attributable to Fe-Fe scattering. Crucially, no Fe-Fe feature is observed in FeS-NC¹⁵⁻¹, further confirming the atomic dispersion of Fe. The R -space EXAFS fitting

results (Fig. 2(j)) reveal that the central Fe atom in FeS-NC¹⁵⁻¹ is coordinated by three N atoms and one S atom (FeN₃S₁), which is consistent with the XPS analysis results. The k^3 -weighted FT-EXAFS curves (Fig. S4 in the ESM), high-quality fitting of k -space curves (Fig. S5 in the ESM), and EXAFS fitting parameters at the Fe K-edge of various samples (Table S3 in the ESM) further confirm the FeN₃S₁ first-shell coordination configuration. Wavelet transform (WT) analysis provides high-resolution discrimination in both R -space and k -space. The WT contour plot of FeS-NC¹⁵⁻¹ (Fig. 2(f) and Fig. S6 in the ESM) displays a maximum scattering intensity at ~3.8 Å, analogous to that of FePc, whereas the Fe foil reference exhibits its intensity maximum at ~8.1 Å due to Fe-Fe contributions. These results collectively corroborate the atomic dispersion of Fe single atoms and their distinct FeN₃S₁ coordination environment.

To evaluate the adsorption and catalytic conversion for LiPSs by

the FeN_3S_1 active center, sulfur cathodes were prepared using single-atom materials as the host. The sulfur content was determined by thermogravimetric analysis (TGA) (Fig. S7 in the ESM), yielding values of 74.72 wt.% (S@NC), 67.56 wt.% (S@Fe-NC^{10-1}), 73.42 wt.% (S@Fe,S-NC^{10-1}), 73.14 wt.% (S@Fe,S-NC^{15-1}), and 71.68 wt.% (S@Fe,S-NC^{20-1}). The electrochemical performance of Li-S batteries assembled with these cathodes was evaluated by galvanostatic charge/discharge tests. At low current densities, the discharge profiles exhibit two characteristic cathodic plateaus, corresponding to the sequential reduction of sulfur to long-chain LiPSs and their further conversion to Li_2S , while the anodic plateau reflects the reverse oxidation of Li_2S to S_8 (Fig. 3(a)) [40]. Remarkably, the S@Fe,S-NC^{15-1} cathode maintains well-defined plateaus even at a high rate of 5.0 C (1.0 C = $1672 \text{ mA}\cdot\text{g}^{-1}$, equivalent to 9.455 mA), indicating superior reaction kinetics. Compared to S@NC , S@Fe-NC^{10-1} , S@Fe,S-NC^{10-1} , and S@Fe,S-NC^{20-1} , the S@Fe,S-NC^{15-1} cell exhibits a lower potential polarization across all current densities (Fig. S8 in the ESM), evidencing enhanced catalytic activity of the FeN_3S_1 sites toward both the SRR and the S evolution reaction (SER). Rate performance tests (Figs. 3(b) and 3(c)) revealed that S@Fe,S-NC^{15-1} not only delivers higher specific capacities at 4.0 and 5.0 C, but also shows superior rate retention relative to the control samples (Fig. S9 in the ESM). Electrochemical impedance spectroscopy (EIS) further manifests that S@Fe,S-NC^{15-1} cathode exhibits the lowest Ohmic resistance and charge-transfer resistance (Fig. 3(d) and Fig. S10 in the ESM). These enhancements are

attributed to the asymmetric FeN_3S_1 coordination structure, which facilitates charge transfer and efficient LiPSs redox conversion. The S@Fe,S-NC^{15-1} cathode delivers an initial discharge capacity of $674 \text{ mAh}\cdot\text{g}^{-1}$ and retains $478 \text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles at 1.0 C, substantially outperforming those of other cathodes (Fig. 3(e) and Fig. S11 in the ESM). Moreover, a 93% capacity retention of S@Fe,S-NC^{15-1} cathode is achieved after 100 cycles at 4.0 C (Fig. 3(f)), underscoring its effectiveness in suppressing LiPSs shuttling. The S@Fe,S-NC^{15-1} maintains an initial capacity of $470 \text{ mAh}\cdot\text{g}^{-1}$ with exceptional stability over 500 cycles at 4.0 C (7.564 mA), corresponding to an ultralow capacity decay rate of 0.05% per cycle (Fig. 3(g) and Fig. S12 in the ESM). After 500 cycles, the cell retained 73% of its initial capacity, far exceeding the retention rates of the control cathodes (Fig. 3(h) and Fig. S13 in the ESM). These results collectively demonstrate that the unique asymmetric coordination structure of FeN_3S_1 enhances LiPSs anchoring, accelerates redox kinetics, thereby enabling high-rate and long-life Li-S batteries.

Furthermore, as shown in Fig. 4(a), the cyclic voltammetry (CV) curves of asymmetric cells based on various cathodes at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$ exhibit two SRR peaks (Peaks I and II) and two SER peaks (Peaks III and IV) (Figs. S14 and S15 in the ESM). These peaks correspond to the reduction of S_8 to Li_2S , and the reverse oxidation of Li_2S back to S_8 via LiPSs, respectively. Among the cathodes tested, S@Fe,S-NC^{15-1} cathode displays higher reduction potentials (2.317 and 2.023 V) and a lower oxidation potential

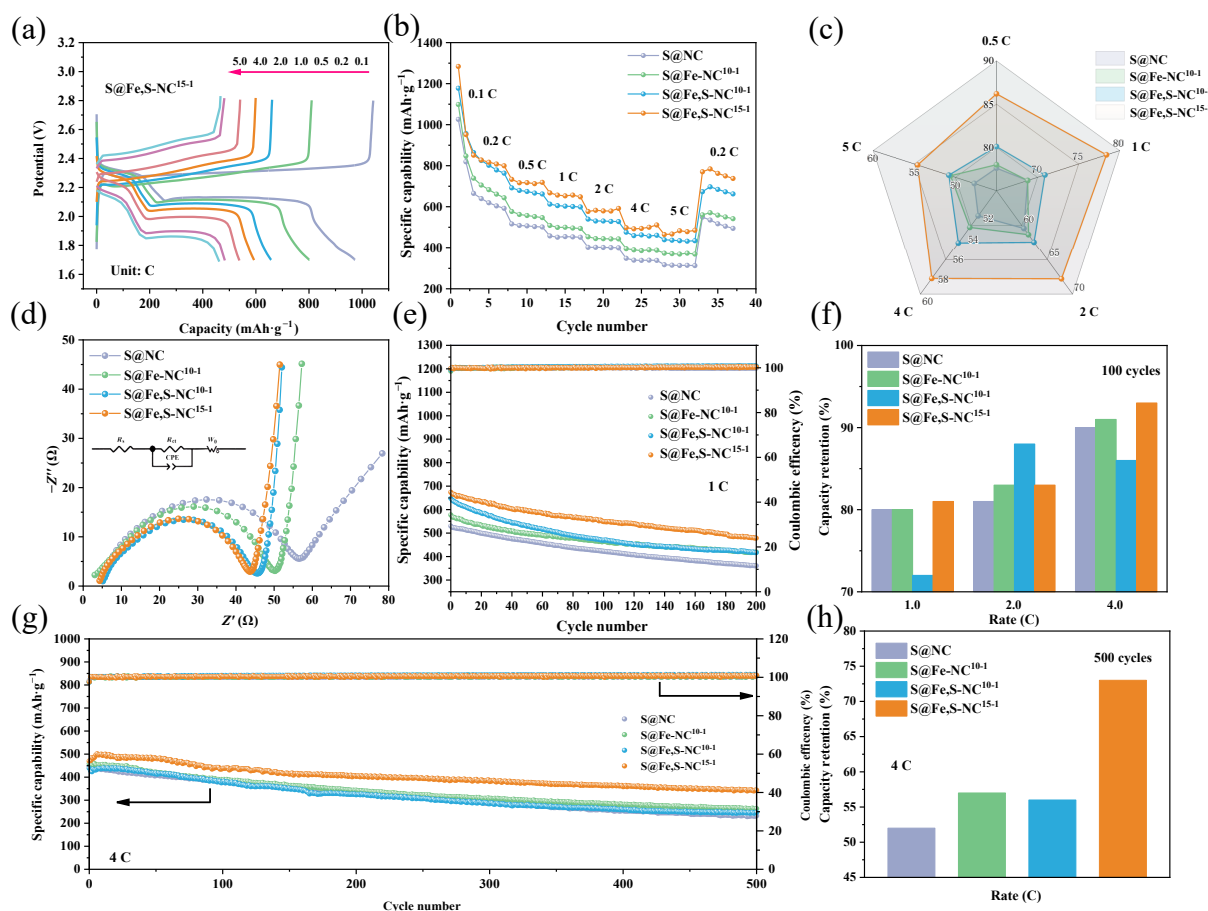


Figure 3 (a) Galvanostatic charge-discharge curves of the S@Fe,S-NC^{15-1} at 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, and 5.0 C. (b) Rate performances. (c) Rate performance retention rate. (d) EIS spectra of fresh batteries. Cyclic performance of S@NC , S@Fe-NC^{10-1} , S@Fe,S-NC^{10-1} , and S@Fe,S-NC^{15-1} at (e) 1.0 C and (g) 4.0 C. ((f) and (h)) Initial discharge capacity retention at different current densities of the S@NC , S@Fe-NC^{10-1} , S@Fe,S-NC^{10-1} , and S@Fe,S-NC^{15-1} based on the rate performances.

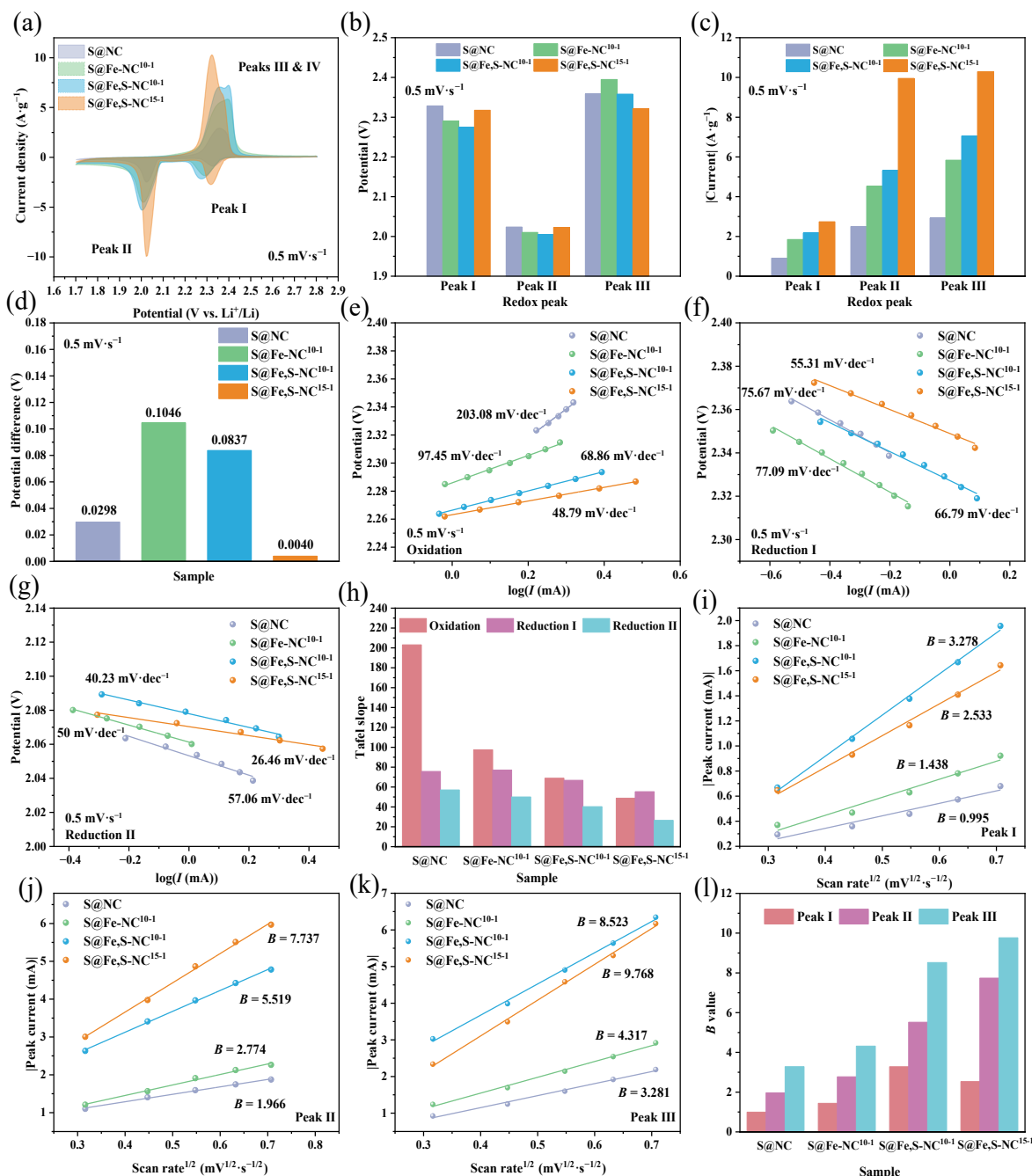


Figure 4 (a) CV curves of asymmetrical cells at $0.5 \text{ mV} \cdot \text{s}^{-1}$. (b) Potential and (c) current of Peaks I, II, and III in CV curves of S@NC, S@Fe-NC¹⁰⁻¹, S@Fe,S-NC¹⁰⁻¹, and S@Fe,S-NC¹⁵⁻¹ cathodes. (d) The potential differences between reduction Peak I and oxidation Peak III. Tafel plots of the S@NC, S@Fe-NC¹⁰⁻¹, S@Fe,S-NC¹⁰⁻¹, and S@Fe,S-NC¹⁵⁻¹ cathodes during (e) SER, (f) SRR I, and (g) SER II processes. (h) Tafel slope summary chart. The relationship between peak current density and square root of scan rates based on (i) Peak I, (j) Peak II, and (k) Peak III of S@NC, S@Fe-NC¹⁰⁻¹, S@Fe,S-NC¹⁰⁻¹, and S@Fe,S-NC¹⁵⁻¹ cathodes, and (l) the corresponding value of slopes.

(2.321 V) (Fig. 4(b)). Moreover, it delivers a higher response current densities of 2.738, 9.95, and $10.285 \text{ A} \cdot \text{g}^{-1}$, along with a smaller potential gap of 4 mV (Figs. 4(c) and 4(d)), indicating that the FeN₃S₁ coordination configuration possesses superior catalytic activity that accelerates the electrochemical conversion of sulfur species [23]. In addition, the S@Fe,S-NC¹⁵⁻¹ cathode achieves the lowest Tafel slopes for both the reduction process (55.31 and $26.46 \text{ mV} \cdot \text{dec}^{-1}$) and the oxidation process ($48.79 \text{ mV} \cdot \text{dec}^{-1}$) (Figs. 4(e)–4(h)), demonstrating that the asymmetric FeN₃S₁ structure accelerates the reaction kinetics of sulfur redox. Compared to the NC, Fe-NC¹⁰⁻¹, Fe,S-NC¹⁰⁻¹, and Fe,S-NC²⁰⁻¹, the

symmetric cell configured with the Fe,S-NC¹⁵⁻¹ exhibits a larger electrochemical active surface area and a higher current density (Fig. S16(a) in the ESM), confirming its pronounced catalytic activity toward sulfur conversion. Furthermore, the symmetric cell employing the Fe,S-NC¹⁵⁻¹ demonstrates a lower charge transfer resistance, indicating accelerated interfacial kinetics (Fig. S16(b) in the ESM).

To quantitatively evaluate the catalytic effect of the asymmetric FeN₃S₁ site on sulfur redox kinetics, we conducted Li₂S deposition and decomposition experiments (Figs. S17 and S18 in the ESM). As shown in Fig. S17 in the ESM, the Fe,S-NC¹⁵⁻¹ catalyst exhibits a Li₂S

deposition peak current of 0.248 mA with a peak time of 970 s, and achieves a deposition capacity of 274.1 mAh·g⁻¹, significantly outperforming the control samples. This result demonstrates that the incorporation of sulfur into the first coordination shell reduces the nucleation overpotential of Li₂S and accelerates the conversion from liquid polysulfides to solid Li₂S₂/Li₂S, consistent with the DFT-calculated reduction in the energy barrier for the Li₂S₄ → Li₂S₂/Li₂S step. Furthermore, the Li₂S decomposition curves (Fig. S18 in the ESM) show that Fe₃S-NC¹⁵⁻¹ delivers a decomposition capacity of 1367.3 mAh·g⁻¹, higher than those of the other samples. These findings confirm that the asymmetric FeN₃S₁ site promotes both Li₂S deposition and decomposition. Overall, the complementary experiments provide solid evidence for the synergistic catalytic effect of asymmetric coordination on sulfur species conversion, well corroborating the DFT calculations and electrochemical performance.

The Li-ion diffusion rate is another key parameter for evaluating the electrochemical activity of sulfur hosts, as it governs the kinetic behavior of Li⁺ within the host structure and directly affects redox reaction efficiency and overall cell performance. According to the Randles–Sevcik equation (Eqs. (1) and (2))

$$I_p = B\nu^{0.5} \quad (1)$$

$$B = 2.69 \times 10^5 n^{1.5} ADC^{Li+} \quad (2)$$

Here, n denotes the number of electrons transferred, A is the geometric electrode area, D is the diffusion coefficient of the electroactive species, and C^{Li+} represents the bulk concentration of lithium ions. The square root of the scan rate ($\nu^{0.5}$) is linearly related to the peak current density (I_p), and the slope (B) reflects the Li-ion diffusion capability [41]. As shown in Figs. 4(i)–4(l), the B values calculated for the reduction Peaks I and II, and the oxidation Peak III of the S@Fe₃S-NC¹⁵⁻¹ cathode are 2.533, 7.737, and 9.768, respectively. These values are consistently higher than those obtained for the other materials. Collectively, these results demonstrate that the modified local coordination structure of the FeN₄ site facilitates enhanced lithium-ion transport, thereby significantly improving the electrochemical performance of the sulfur cathode.

To elucidate how the tailored coordination configuration optimizes the electrochemical behavior of sulfur species, we first investigated the electronic characteristics of the central Fe atoms in FeN₄ and FeN₃S₁ after adsorbing Li₂S₄ as a representative LiPSs intermediate. As shown in Fig. 5(a), the Fe atom in the Li₂S₄-adsorbed FeN₃S₁ site exhibits a lower electron density than that in the FeN₄ site, indicating that the Fe atom in FeN₃S₁ possesses a higher initial electron density, which facilitates electron transfer during the sulfur redox reactions, consistent with the superior electrochemical performance observed. Furthermore, Figs. 5(b)–5(g) present the adsorption models of Li₂S, Li₂S₂, and Li₂S₄ on FeN₃S₁ and FeN₄, respectively. The corresponding bond lengths of the adsorbed LiPSs are compared in Table S4 in the ESM. Notably, the Fe–S(ads) bond length in FeN₃S₁ is shorter than that in FeN₄ (where (ads) denotes the adsorbed atom), demonstrating that FeN₃S₁ has a stronger chemical anchoring ability toward LiPSs. Direct experimental evidence of LiPSs adsorption efficacy is provided in Fig. S19 in the ESM. After adding Fe-NC¹⁰⁻¹ and Fe₃S-NC¹⁵⁻¹ to separate vials containing 0.2 M Li₂S₆ solution and allowing them to stand for 6 h, the solution containing Fe₃S-NC¹⁵⁻¹ with asymmetric FeN₃S₁ site became nearly transparent, whereas that

containing Fe-NC¹⁰⁻¹ endowed with FeN₄ remained almost unchanged. This visual evidence confirms the significantly enhanced LiPSs adsorption capability of Fe₃S-NC¹⁵⁻¹, attributed to the stronger binding sites provided by its optimized asymmetric coordination environment. The calculated adsorption energies of FeN₃S₁ and FeN₄ for Li₂S₄ are –1.87 and –1.04 eV, respectively (Fig. 5(h)), further demonstrating the enhanced adsorption capability and effective suppression of the shuttle effect. To gain insight into the electronic structure advantage, the projected density of states (PDOS) of the central Fe atoms in FeN₄ and FeN₃S₁ were analyzed (Figs. 5(i) and 5(j)). Compared with FeN₄, the d-band center of FeN₃S₁ shifts 0.153 eV toward the Fermi level. This indicates that S modification in the first coordination shell regulates the electronic structure of the Fe site, leading to stronger adsorption toward LiPSs intermediates, thereby directly lowering the thermodynamic barrier of the reaction [42–45]. The free energy change for the key step from Li₂S₄ to Li₂S was calculated. As shown in Fig. 5(k), the rate-determining step in this Li–S battery is the transition from *Li₂S₄ to *Li₂S₂. FeN₃S₁ not only reduces the free energy of this rate-limiting step but also lowers that of the subsequent *Li₂S₂ to *Li₂S conversion. This demonstrates that S doping effectively tunes the electronic structure of Fe and optimizes the thermodynamics of LiPSs conversion, thereby accelerating the reduction kinetics of LiPSs. To gain deeper insight into the suppression of LiPSs shuttling during sulfur redox reactions, *in situ* Raman spectroscopy was performed on the Fe₃S-NC¹⁵⁻¹ cathode. As depicted in Figs. 5(l) and 5(m), the characteristic peaks of the cell assembled with this cathode attenuated rapidly as the reaction proceeded, indicating that polysulfides were effectively converted rather than merely accumulated, thus significantly enhancing the suppression of the LiPSs shuttle effect.

4 Conclusions

In summary, we have successfully constructed an asymmetric FeN₃S₁ coordination structure in FeSACs by introducing S into the first coordination shell. S doping enriches the electron density around Fe, consequently upshifting the d-band center, strengthening the adsorption of LiPSs, and lowering the energy barriers of the rate-determining steps. As a result, the Fe₃S-NC¹⁵⁻¹ cathode with FeN₃S₁ exhibits outstanding electrochemical performance, achieving a high initial capacity of 485 mAh·g⁻¹ at 5.0 C and a low capacity decay rate of only 0.05% per cycle over 500 cycles at 4.0 C. Evidently, this asymmetric coordination environment effectively promotes sulfur conversion kinetics and suppresses the shuttle effect. This work provides a rational design strategy for tuning the coordination environment of SACs toward high-performance Li–S batteries.

Electronic Supplementary Material: Supplementary material (computational details, materials characterization and results, electrochemical testing and performance data, Figs. S1–S19 and Tables S1–S4) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908997>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

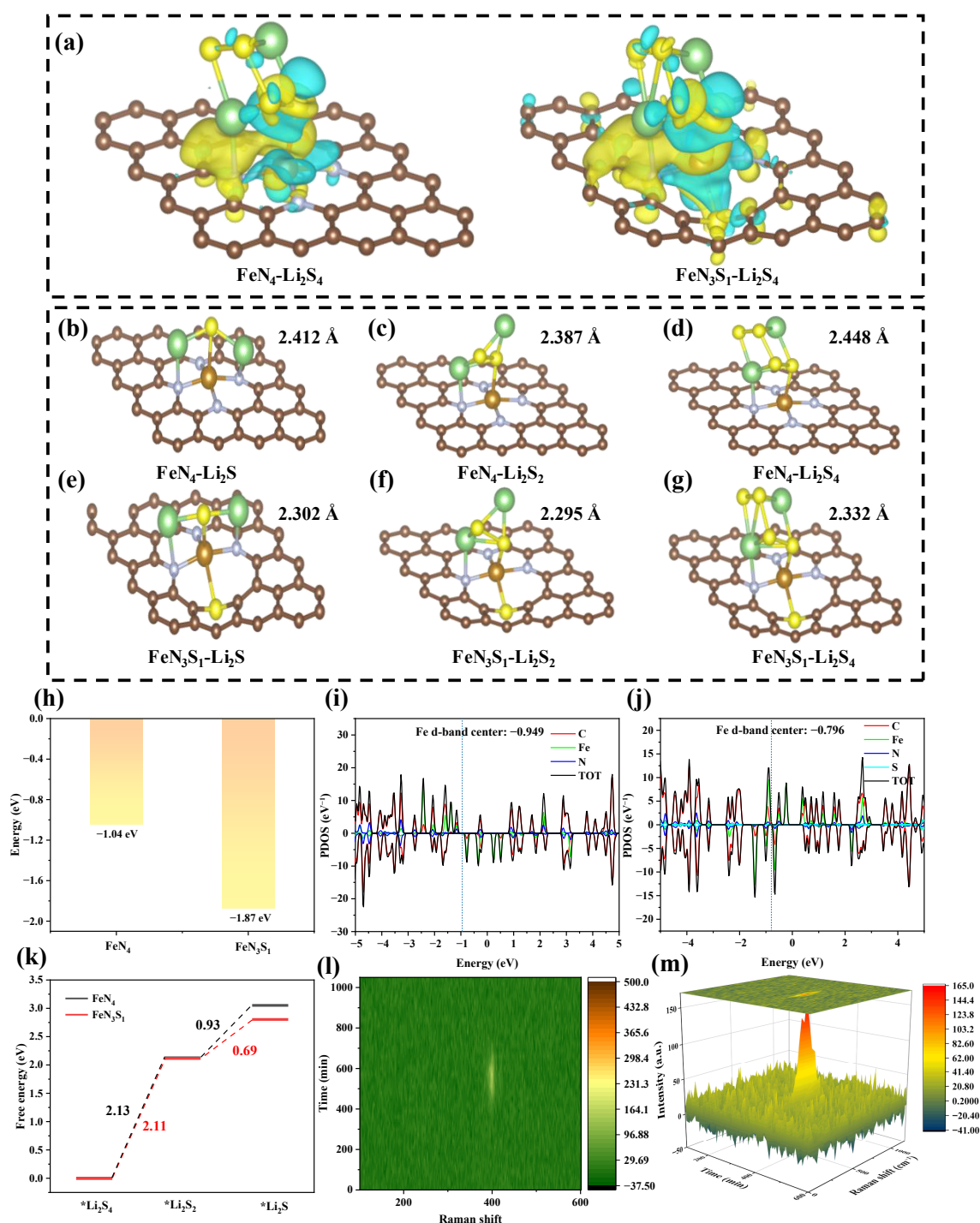


Figure 5 (a) Charge density differences of $\text{FeN}_4\text{-Li}_2\text{S}_4$ and $\text{FeN}_3\text{S}_1\text{-Li}_2\text{S}_4$, where blue and yellow represent electron consumption and agglomeration. The adsorption models of (b) and (e) Li_2S , (c) and (f) Li_2S_2 , and (d) and (g) Li_2S_4 on FeN_3S_1 and FeN_4 . (h) The adsorption energy of Li_2S_4 for FeN_4 and FeN_3S_1 . Fe PDOS of (i) FeN_4 and (j) FeN_3S_1 . (k) Energy barrier calculations for Li_2S , Li_2S_2 , and Li_2S_4 under the optimized models based on FeN_4 and FeN_3S_1 . (l) and (m) *In situ* Raman contour plots and corresponding Raman spectra based on $\text{Fe}_3\text{S-NC}^{151}$.

Acknowledgements

This work was supported by the Scientific Research Program Funded by Education Department of Shaanxi Provincial Government (Nos. 25JP129 and 24JP121), the Postdoctoral Fellowship Program of China Postdoctoral Science Foundation (No. GZC20250012), the Postdoctoral Science Foundation of China (No. 2025MD784072), Postdoctoral Research Project of Shaanxi

Province (No. 2025BSHSDZZ291), and the Doctoral Scientific Research Startup Foundation of Xi'an University of Technology (No. 101-256082410).

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. F. L.: Conceptualization, investigation, formal analysis, writing – original manuscript, experimental design. H. J. Y.: Formal analysis, writing – review & editing. G. Q. C.: Methodology, investigation. M. Y. L.: Writing – review & editing. C. Y. H.: Data analysis. R. X. D.: Data analysis. Y. T. Y.: Data analysis. R. J. B.: Writing – review & editing. X. T. L.: Writing – review & editing. G. H. L.: Supervision, funding acquisition. W. Y. J.: Supervision, funding acquisition. K. Q.: Supervision, funding acquisition. Q. Q. P.: Data analysis. X. F. L.: Validation, writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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