Enhancing sulfur oxidation reaction by overcoming redox barriers with FeSe$_2$@C for lithium–sulfur batteries†

Pengkun Zou,†‡ Yushuang Lin,†‡ Long Li,†‡ Jiaxin Wang,‡ Yu Chao,‡ Borong Li,‡ Hongyun Ma,§*‡‡ Zheyuan Liu,‡§ Yan Yu*‡ and Chengkai Yang*‡

The electrocatalytic sulfur oxidation reaction (SOR), marked by a multifaceted 16-electron transfer, stands as a pivotal advancement in lithium–sulfur battery technology. In this process, the initial conversion of Li$_2$S to Li$_2$S$_2$ during the charging phase is identified as the rate-determining step, characterized by a significant energy barrier. The integration of a nanoflower-shaped transition metal selenide catalyst on carbon (FeSe$_2$@C) catalyzes the SOR. The synergistic effect of d–p orbital hybridization in the Fe–S bond and the redox cycling between Fe$^{2+}$ and Fe$^{3+}$ facilitates electron transfer, thereby lowering the decomposition barrier of Li$_2$S. This has been confirmed through both density functional theory (DFT) calculations and experimental electrocatalysis. The oxidation of Li$_2$S is reliant on an efficient charge transfer mechanism, where electrons are progressively transferred to intermediate species, leading to direct interactions with Li$_2$S and the formation of Li$_2$S$_2$. This conversion is corroborated by in situ Raman spectroscopy. The FeSe$_2$@C catalyst significantly reduces the activation energy by enhancing charge transfer efficiency. At a current density of 1C, the battery exhibited an initial capacity of 581.3 mA h g$^{-1}$, with a remarkable capacity retention of 97.5% after 600 cycles and a minimal capacity decay rate of 0.004% per cycle, indicative of superior cyclability. This research propels the electrocatalysis of Li$_2$S in the charging phase of lithium–sulfur batteries, thereby accelerating the kinetics of the SOR and contributing to the field’s progress.

1 Introduction

In recent years, the electrocatalytic sulfur reduction reaction (SRR) has garnered significant research interest. In contrast, the kinetic aspects of the electrocatalytic sulfur oxidation reaction (SOR) in lithium–sulfur batteries have been comparatively overlooked. The SOR encompasses a multifaceted 16-electron transfer process, which is pivotal for the complete transformation of insoluble lithium sulfides (Li$_2$S/Li$_2$S) into a spectrum of soluble lithium polysulfides (LiPSs) with varying chain lengths, culminating in the formation of S$_8$-ring species. Despite the impressive theoretical energy density of lithium–sulfur batteries, reaching up to 1672 mA h g$^{-1}$, their practical chemical performance is impeded by the sluggish kinetics of sulfur redox processes and the detrimental polysulfide shuttle effect.1–4 These limitations are fundamentally rooted in the slow and intricate oxidation reaction of Li$_2$S. Furthermore, the unregulated deposition of Li$_2$S$_2$, along with its significant over-potential for oxidation, readily results in electrode passivation. Throughout repeated discharge cycles, a thick and dense Li$_2$S passivation layer forms on the surface of the electrocatalyst, leading to the deactivation of catalytic sites and irreversible capacity loss over extended cycling periods.5–14 Hence, it is imperative to expedite the decomposition of insoluble Li$_2$S$_2$, perpetually rejuvenate the surface of the electrocatalyst to expose and maintain more active sites, and guarantee swift electron/ion diffusion rates to attain efficient recovery of polysulfides.15,16 Nevertheless, a significant proportion of the catalysts investigated thus far, encompassing metal oxides,17 metal sulfides,18,19 metal nitrides,20,21 and metal phosphides,22 predominantly demonstrate their primary activity during discharge. The accumulation of insoluble products and their deposition on the catalyst surface remains an unaddressed challenge.

In this study, we utilize a nanoflower-shaped transition metal selenide on carbon (FeSe$_2$@C) catalyst to investigate the Li$_2$S to Li$_2$S$_2$ transformation pathway and elucidate its underlying catalytic reaction mechanism. By conducting a thorough analysis of the activation energies associated with the multi-
step sulfur oxidation reaction (SOR) process, we have delineated the distinctive conversion kinetics of each step. This investigation has also unveiled the inherent challenges linked to the initial oxidation of insoluble Li2S2/LiS to soluble PSSs, attributable to their elevated activation energy. The FeSe2@C catalyst effectively reduces the decomposition energy barrier of LiS, accelerating the breakdown and transformation of insoluble products, thereby exposing a greater number of active sites. This leads to a decelerated deactivation of the catalyst and demonstrates long-term stability.22–25 The FeSe2@C catalyst effectively lowers the activation energy barriers for both solid–solid and solid–liquid transformations in the SOR process via its redox couple of Fe2+/Fe3+. Simultaneously, it mitigates the PS shuttle effect. A robust chemical interaction between FeSe2 and polysulfides is evident, as substantiated by the outcomes of density functional theory (DFT) calculations and electrocatalytic experiments. The interaction between FeSe2 and polysulfides takes place through Se–Li and Fe–S bonds, inducing hybridization of Fe 3d orbitals with S 2p orbitals. The interaction through the Fe–S bond facilitates efficient electron transfer throughout the dynamic conversion process of Li2S, leading to a lower reaction activation energy barrier and promoting Li2S decomposition. By analyzing the pathway of Li2S catalyzed by FeSe2@C, this study has advanced the exploration of SOR and elucidated the catalytic mechanism of FeSe2@C. Capitalizing on its distinctive electrocatalytic performance in SOR, the FeSe2@C-based electrode demonstrates significantly enhanced rate capability and cycling stability.

2 Results and discussion

2.1 Mechanism of the SOR and FeSe2@C synthesis

The catalytic oxidation mechanism and pathway of Li2S in the presence of FeSe2@C are depicted in Fig. 1a. FeSe2 facilitates the adsorption and anchoring of polysulfides, proficiently constraining them to the cathode side. This strategic confinement mitigates the shuttle effect of polysulfides, thereby elevating the overall performance of the battery. The discharge product Li1S2 engages with the FeSe2 substrate, establishing Se–Li and Fe–S bonds. Hybridization of Fe 3d orbitals and S 2p orbitals takes place through d–p orbital overlap, efficiently diminishing the energy barrier for electron migration. This facilitates the electron transfer during the kinetic conversion process of Li1S2. Under applied voltage, Fe2+ undergoes preferential electron loss to form Fe3+, wherein the S2– ligands in Li2S donate electrons to Fe3+, subsequently regenerating Fe2+. This overall process aids in the decomposition of Li1S2. The conversion of Li1S2 to Li2S unfolds through a two-step electron transfer process. Initially, Li1S2 experiences electron loss, giving rise to the intermediate species LiS*. Subsequently, LiS* reacts directly with Li2S to yield Li2S2.

The synthesis of FeSe2 was accomplished through a hydrothermal method, as illustrated in Fig. 1b. During the reaction, ammonium ferrous sulfate served as the iron source, selenium powder as the selenium source, and hydrazine hydrate was employed to disperse and reduce selenium powder, thereby providing Se2–. The interaction between Fe2+ and Se2– led to the formation of Fe–Se bonds through chemical interactions. Under high-temperature and high-pressure conditions, crystalline grains gradually nucleated and grew, ultimately resulting in the formation of FeSe2. Under alkaline conditions, dopamine self-polymerizes to form a polydopamine coating, which is then enveloped onto the surface of FeSe2. Subsequently, through high-temperature carbonization under a nitrogen atmosphere, an efficient conductive network structure is established. This process concurrently aids in preventing the inherent agglomeration of FeSe2 at elevated temperatures. The ultimate product is denoted as FeSe2@C.

To characterize the microstructure, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM) were employed, as depicted in Fig. 1. As shown in Fig. 1c, the synthesized FeSe2@C exhibited a nanoflower-like structure consisting of nanorods, showcasing a relatively uniform distribution and growth sizes of the nanoflowers. In Fig. 1d and e, the nanorods exhibit close-packed growth, establishing a rapid pathway for electron and ion transportation. The nanorods have a diameter of approximately 40 nm, and a distinct carbon shell is evident, encapsulating FeSe2 and providing a site for high-loading of active sulfur. The lattice spacing was measured to be approximately 0.26 nm, corresponding to the (111) crystal plane of FeSe2. In Fig. 1f, energy-dispersive X-ray spectroscopy (EDS) revealed a uniform distribution of Fe, Se, and C elements on FeSe2@C. The X-ray diffraction (XRD) pattern of FeSe2@C is illustrated in Fig. S1† and the distinct diffraction peaks align well with the standard PDF#97-004-4751 of FeSe2. Thermogravimetric analysis (TGA) in Fig. S3† reveals that the weight percentage of active sulfur in the FeSe2@C/S composite material is approximately 80%. X-ray photoelectron spectroscopy (XPS) was employed for a more in-depth investigation into the surface chemical states of FeSe2@C. Fig. S2† presents the full-range XPS spectra of FeSe2@C, wherein the overall spectrum indicates the presence of Fe, Se, C, and O elements in FeSe2@C.

2.2 The adsorption of polysulfides and the reaction pathway of the SOR

The adsorption performance of FeSe2@C and conductive carbon black (C) was assessed through visual adsorption experiments. Equal weights of FeSe2@C and C were introduced into a Li2S6 solution and allowed to age for 6 hours, as depicted in Fig. 2a. Clearly, the Li2S6 solution containing FeSe2@C and C exhibits significantly improved adsorption capability for LiPSs compared to conductive carbon black. We employed theoretical density functional theory (DFT) to simulate the intrinsic interactions between FeSe2 and LiPSs at the atomic level, elucidating the adsorption mechanism. We selected representative models of LiPSs for demonstration. Fig. 2d, S4 and S6† illustrate the rendered optimized geometric configurations of typical soluble sulfur substances on the FeSe2 (111) surface and carbon surface. The adsorption energy of the corresponding sulfides with the materials is depicted in Fig. 2b. Our simulation results are
Fig. 1  Reaction mechanism and the morphology of FeSe₂@C. (a) Reaction pathway and mechanism. (b) Synthesis route of FeSe₂@C. (c) SEM image of FeSe₂@C. (d) Low-magnification TEM image. (e) High-magnification TEM images, (f) HAADF-STEM image along with corresponding EDS spectra.
consistent with the adsorption experimental outcomes, indicating that FeSe₂ has a stronger adsorption capacity for various LiPSs compared to carbon. This suggests a stronger anchoring effect. As depicted in Fig. 2c and S5, † illustrates that the Li₂S decomposition energy barrier on the FeSe₂ surface is significantly lower (0.16 eV) compared to the value of 2.18 eV on C. These results underscore the exceptional catalytic conversion ability of FeSe₂@C, effectively reducing the activation energy barrier of the rate-limiting step during the charging process. According to the Bader charge analysis in Fig. 2e, the differential charge of S atoms reaches as high as −1.07, while the two iron atoms bonded to sulfur have differential charges of 0.42 and 0.49, respectively. This electron transfer during the dynamic transformation of Li₂S reduces the reaction energy barrier, thereby promoting the nucleation and decomposition of Li₂S. Furthermore, we computed the density of states (DOS) for Li₂S adsorbed on the FeSe₂ surface. The d-band and p-band center theory can elucidate the underlying mechanisms of the catalytic process. From Fig. 2f, we can discern that there is a minimal band gap between the d-band center of Fe in FeSe₂ and the p-band center of S in Li₂S. The hybridization occurring between the d-band of Fe and the p-band of S suggests a low charge transfer energy, which promotes electron exchange between Fe and S, accelerates electron transfer, and consequently reduces the activation energy barrier for the decomposition of Li₂S, enhancing the oxidative kinetics of Li₂S decomposition.

Given that the initial sulfur oxidation reaction (2Li₂S → Li₂S₂ + 2Li⁺ + 2e⁻) exhibits a significantly higher rate than other conversion steps, our calculations primarily focus on the initial two-electron process. We hypothesize that the conversion of LiS to Li₂S involves a stepwise reaction, encompassing the formation of a LiS radical intermediate (LiS*), which interacts with catalytically active sites. Two potential reaction pathways have been considered, as outlined below:

Pathway 1: (efficient charge transfer pathway)

\[
\text{Li}_2\text{S} \rightarrow \text{LiS}^* + \text{Li}^+ + e^- \quad (1)
\]

\[
\text{LiS}^* + \text{Li}_2\text{S} \rightarrow \text{Li}_2\text{S}_2 + \text{Li}^+ + e^- \quad (2)
\]
Pathway 2: (charge transfer pathway)

\[ 2\text{Li}_2\text{S} \rightarrow 2\text{LiS}^* + 2\text{Li}^+ + 2\text{e}^- \quad (3) \]

\[ 2\text{LiS}^* \rightarrow \text{Li}_2\text{S}_2 \quad (4) \]

According to the calculations, it is evident that the highest reaction energy barriers for pathways 1 and 2 on the FeSe\textsubscript{2} surface are 1.86 and 3.28 eV, respectively. In this context, LiS\textsuperscript{*} represents the LiS radical intermediate adsorbed on the FeSe\textsubscript{2} substrate (Fig. 2g). These results signify that the conversion on the FeSe\textsubscript{2} surface through pathway 1 necessitates a lower reaction energy barrier compared to pathway 2. Therefore, pathway 1 is more favorable for the reaction on the FeSe\textsubscript{2} surface. This observation suggests that the reaction is more likely to occur on the FeSe\textsubscript{2} surface through the efficient charge transfer pathway.

2.3 Kinetics and electrochemical analysis of SOR

To further explore the adsorption mechanism, X-ray photoelectron spectroscopy (XPS) measurements were employed to study the surface states of FeSe\textsubscript{2}@C after adsorption of Li\textsubscript{2}S\textsubscript{6} and the pristine FeSe\textsubscript{2}@C (Fig. 3a and b). By analyzing the Fe 2p and Se 3d spectra before adsorption, we identified the Fe–Se bond, indicating successful bonding between iron and selenium. In the case of FeSe\textsubscript{2} prior to Li\textsubscript{2}S\textsubscript{6} adsorption, the pink peaks located near 55.6 and 54.8 eV are attributed to the 3d\textsubscript{3/2} and 3d\textsubscript{5/2} of Se–Se (the covalent bond of Se\textsubscript{2}\textsuperscript{2–} in the bulk phase), respectively. The blue peaks near 54.4 and 53.6 eV are assigned to the 3d\textsubscript{3/2} and 3d\textsubscript{5/2} of surface-Fe–Se (with Se atom termination), respectively. The purple peaks near 56.9 and 56.1 eV are ascribed to the 3d\textsubscript{3/2} and 3d\textsubscript{5/2} of surface-Se–Fe (with Fe atom termination), respectively.\textsuperscript{27} By comparing the XPS
spectra of the Fe 2p and Se 3d core levels before and after adsorption, a slight shift of the fitted peaks to lower binding energy can be observed after Li$_2$S$_6$ adsorption. This reveals the electron transfer between Li$_2$S$_6$ and FeSe$_2$, indicating good chemical affinity between Li$_2$S$_6$ and the polar FeSe$_2$. Moreover, we observed the emergence of Fe–S and Li–Se bonds after the adsorption of Li$_2$S$_6$, the synergistic effect of which enhances the adsorption of LiPSs and accelerates electron transfer in the catalytic process.\(^{28-30}\) Furthermore, through an examination of the valence states of Fe after charge–discharge cycles in Fig. 3c, the presence of Fe$^{2+}$ and Fe$^{3+}$ was observed. This observation suggests that the catalytic conversion of FeSe$_2$ with polysulfides is a dynamic process. The electron transfer between the discharge product and the catalyst facilitates the oxidation process.

In general, the decomposition of Li$_2$S during cycling encompasses solid–solid and solid–liquid transformations, with the highest reaction barrier acting as the rate-limiting step during the charging process. To investigate the decomposition of Li$_2$S during the charging process, kinetic tests of Li$_2$S decomposition were conducted using the constant potential charging method.\(^{31,32}\) As shown in Fig. 3d and e, the decomposition current of the FeSe$_2$@C electrode is higher, and the decomposition occurs earlier, indicating that FeSe$_2$@C has a significantly higher Li$_2$S dissolution capacity compared to C. This suggests that FeSe$_2$@C can effectively promote the dissolution of Li$_2$S during the charge process, accelerating the sulfur oxidation process.

To quantify the kinetics of the sulfur oxidation reaction (SOR), electrochemical impedance spectroscopy (EIS) at a given voltage was fitted to the Arrhenius equation (Fig. 3f), and the activation energy barriers of the SOR measured at different temperatures were determined. In the absence of a catalyst (C/S), the obtained activation energy ($E_a$) [Fig. 3g] for the activation energy barrier of the sulfur oxidation reaction (SOR) remained at a peak value (0.24–0.27 eV) during the initial and mid-oxidation stages (1.7–2.4 V). This suggests that the transition from insoluble products (Li$_2$S$_2$/Li$_2$S) to soluble polysulfides was relatively difficult and only gradually occurred at higher voltages. In the final oxidation stage (2.7–2.5 V), the $E_a$ value was relatively low, indicating that the liquid–liquid transition (Li$_2$S$_1$, Li$_2$S$_3$, and Li$_2$S$_6$) was relatively easy. In this scenario, the high reaction barrier of insoluble Li$_2$S$_2$/Li$_2$S leads to the gradual accumulation of insoluble discharge products, resulting in irreversible behavior of the active material and capacity decay of the battery. In contrast, for the FeSe$_2$@C/S cathode, the activation energy ($E_a$) value gradually decreases during the initial oxidation stage (1.7–1.9 V) [0.166–0.144 eV], remains constant during the mid-oxidation stage (2.0–2.4 V) (approximately 0.13 eV), and reaches the lowest $E_a$ value during the final oxidation stage (2.5–2.7 V). This indicates that the FeSe$_2$@C catalyst can effectively reduce the activation energy barriers for solid–solid and solid–liquid transformations, lower the high reaction barriers of rate-limiting steps, catalyze the sulfur oxidation reaction (SOR) process.

By utilizing in situ Raman spectroscopy, we further characterized the conversion process of LiPSs and the inhibitory effect on the shuttle effect during the discharge process.\(^{33}\) As shown in Fig. 3i, during the initial discharge, characteristic peaks of S$_{8}$, S$_{6}^–$, and S$_{4}$ appear. As the discharge reaction continues, these characteristic peaks gradually diminish, and peaks of Li$_2$S emerge. Subsequently, during the charging process, as the charging reaction progresses, the Li$_2$S characteristic peaks gradually vanish, and the Li$_2$S$_2$ and S$_{8}^2$ characteristic peak appears, accompanied by the dissolution of FeSe$_2$. In the initial charge–discharge processes of Li–S cells assembled with different cathodes, the in situ Raman contour maps are shown in Fig. 3h and S7.$^\dagger$ Clearly, during the charge–discharge process, the Raman signals of various polysulfides at the C cathode remain relatively constant, with S$_{2}^-$ being the most abundant species. This indicates that C cannot efficiently catalyze the conversion of polysulfides, leading to their substantial dissolution in the electrolyte without further conversion and causing a severe loss of active material. In contrast, it is evident that the Li$_2$S characteristic peak generated during the initial discharge stage at the FeSe$_2$@C cathode disappears after the first discharge plateau, indicating its complete conversion. The resulting polysulfides are also fully transformed during the charging process, further demonstrating that FeSe$_2$ can accelerate the decomposition of Li$_2$S and reduce the loss of active material.

The catalytic activity of FeSe$_2$@C was assessed through a series of electrochemical performance experiments. Cyclic voltammetry (CV) measurements were conducted in the voltage range of −0.8 V to 0.8 V at a scanning rate of 50 mV s$^{-1}$. As shown in Fig. 4a, the symmetric cell with the FeSe$_2$@C electrode exhibits a higher peak current compared to the C electrode, indicating faster kinetics of the redox reactions.\(^{34,35}\) As depicted in Fig. S8,$^\dagger$ the fitted EIS also indicates that FeSe$_2$@C possesses more rapid diffusion kinetics and a higher interfacial charge transfer conductivity.\(^{36}\) The charging and discharging processes of lithium–sulfur (Li–S) batteries involve a series of complex solid–liquid–solid phase conversions. The cyclic voltammetry (CV) curves at different scan rates were utilized to assess the diffusion of Li$^+\,$ during the redox processes Fig. 4b and c. The CV results exhibit two distinct reduction peaks and one oxidation peak, corresponding to the reactions of S$_{6}^–$ to S$_{4}^–$, S$_{4}^–$ to Li$_2$S$_2$/Li$_2$S, and Li$_2$S$_2$/Li$_2$S to S$_{8}$ respectively. The linear relationship between the current peaks and the square root of the scan rate indicates a diffusion-controlled process Fig. 4d–f. A larger slope suggests faster Li$^+$ diffusion, and the higher Li$^+$ diffusion coefficient of the FeSe$_2$@C/S cathode ensures the continuation of the reaction after Li$_2$S decomposition. The FeSe$_2$@C/S cathode also exhibits a higher peak current density, indicating that FeSe$_2$@C can significantly accelerate the kinetics of the redox reactions of polysulfides.\(^{37,38}\) Moreover, the FeSe$_2$@C cathode also exhibits a higher peak current density, indicating that FeSe$_2$@C can significantly accelerate the kinetics of the redox reactions of polysulfides.

To compare the electrochemical performance of FeSe$_2$@C and C as cathodes in the solid-state Li$_2$S conversion, the samples were mixed and assembled into lithium–sulfur batteries for Linear Sweep Voltammetry (LSV) tests using ground Li$_2$S as the solid-phase. As shown in Fig. 4g and h, the
Fig. 4  Electrochemical kinetic of sulfur species on FeSe₂@C and C host (a) CV curves of symmetric batteries at a scan rate of 50 mV s⁻¹. (b) CV curves of the FeSe₂@C/S cathode at scan rates ranging from 0.1 to 0.5 mV s⁻¹. (c) CV curves of the C/S cathode at scan rates ranging from 0.1 to 0.5 mV s⁻¹. (d–f) Peaks A, C₁, and C₂ currents of both FeSe₂@C/S and C/S cathodes are compared with the square root of the scan rate. LSV profiles of FeSe₂@C–Li₂S (g) and C–Li₂S (h) at different sweep speeds. (i) Peak currents versus square root of scan rates of FeSe₂@C–Li₂S and C–Li₂S. (j) GITT curves of the FeSe₂@C/S composite cathode. (k) GITT curves of the C/S composite cathode. (l) Ionic diffusion coefficients of the composite cathodes.
LSV curves of the batteries exhibited typical oxidation peaks, corresponding to the conversion of Li$_2$S into long-chain polysulfides and eventually the formation of sulfur. Compared to C, the LSV curves of FeSe$_2$@C exhibited distinct sharp oxidation peaks and the widest range of current response, indicating the oxidation decomposition of Li$_2$S at a lower potential. This suggests that FeSe$_2$@C acts as a catalyst for sulfur oxidation, promoting the charging process. Furthermore, the analysis of the relationship between different LSV scan rates and peak currents using the Randles–Sevick equation revealed that the slope of the fitted curve for FeSe$_2$@C was greater than that of C (Fig. 4i). This indicates that FeSe$_2$@C in the battery significantly enhances the diffusion of lithium ions and accelerates charge transfer. This factor is another important prerequisite for promoting the kinetic process of Li$_2$S oxidation with FeSe$_2$@C.

To analyze the ionic diffusion behavior during the charge-discharge process and the kinetics involved in the decomposition of Li$_2$S, we employed GITT to test the two composite cathodes as shown in Fig. 4j–l. We analyzed the potential difference and battery resistance during the Li$_2$S decomposition process. During the activation process of Li$_2$S, the FeSe$_2$@C cathode (76 mV) exhibits a smaller potential difference compared to the C cathode (147 mV) in the relaxation process. In this process, the calculated internal resistances of the batteries are 540 $\Omega$ and 1066 $\Omega$, respectively. The FeSe$_2$@C cathode demonstrates a smaller potential difference and lower resistance during the Li$_2$S decomposition process, indicating that FeSe$_2$@C provides superior reaction kinetics for the decomposition of Li$_2$S. Subsequently, the Li$^+$ diffusion coefficient during the discharge process of the composite cathode

---

**Fig. 5**  Electrochemical performance of Li–S batteries based on different cathodes. (a) Rate capabilities of FeSe$_2$@C/S and C/S. (b) Differential anode–cathode potentials in scans of FeSe$_2$@C and C at different scan rates. (c) Cycling performance of FeSe$_2$@C/S and C/S at 0.2C. (d) Corresponding galvanostatic charge–discharge curves at 0.2C. (e) Cycling performance of FeSe$_2$@C/S with sulfur loading of 3.0 and 4.2 mg cm$^{-2}$. (f) Charge–discharge curves at different cycles. (g) Long-cycle performance of FeSe$_2$@C/S at 1C.
was calculated, as shown in Fig. 4f. Throughout the entire charging process, Li⁺ consistently maintains a high diffusion coefficient, ensuring the continuation of the reaction after the decomposition of Li₂S. This indicates that FeSe₂@C possesses excellent sulfur oxidation–reduction (SOR) kinetics, which accelerates the decomposition and transformation of Li₂S.

2.4 Cell performances of Li–S batteries

To directly evaluate the impact of the electrocatalyst on battery performance, we conducted comprehensive comparative studies on the cycling and rate capabilities of lithium–sulfur batteries assembled with FeSe₂@C/S and C/S cathodes. The discharge specific capacities of FeSe₂@C/S at current densities of 0.2, 0.5, 1.0, 2.0, and 3.0C are found to be 1122.0, 901.9, 899.7, 695.8, and 495.3 mA h g⁻¹, respectively. Even after cycling, when the current density is reduced back to 0.1C, the capacity still maintains at 1017.0 mA h g⁻¹ (Fig. 5a). In contrast, C/S exhibits a significantly lower capacity, particularly at higher rates. Furthermore, at higher current densities, where more severe polarization and larger voltage gaps are typically observed, the FeSe₂@C catalyst demonstrates a remarkable reduction in polarization (Fig. 5b). The voltage gap only increases from 0.1C to 3C by 229 mV (from 170 mV to 399 mV). This value is notably lower than that observed with C (372 mV). As depicted in Fig. 5c, a comparative cycle performance study was conducted on the FeSe₂@C/S and C/S composite cathodes at a current density of 0.2C. Fig. 5f and S9† present the charge–discharge curves for the FeSe₂@C and C composite cathodes during the 1st, 50th, and 100th cycles at a current density of 0.2C. The results indicate that the FeSe₂@C/S composite cathode exhibits a significantly higher capacity retention rate. It demonstrates a higher initial capacity of 1223.4 mA h g⁻¹, and after 100 cycles, the capacity is still maintained at 1039.3 mA h g⁻¹, corresponding to a capacity retention rate of 84.9%. On the other hand, the C/S composite cathode only exhibited a discharge capacity of 912.4 mA h g⁻¹ at a current density of 0.2C, and after 100 cycles, the capacity decreased to 615.0 mA h g⁻¹, with a capacity retention rate of merely 67.4%. This clearly demonstrates the superior cycling performance of the FeSe₂@C/S composite cathode compared to the C/S. The accelerated conversion of solid Li₂S reduces the loss of active material, thereby enhancing the cycle stability.

As shown in Fig. 5d, the charge–discharge curves of FeSe₂@C/S and C/S were obtained under a current density of 0.2C. Moreover, the discharge capacity of FeSe₂@C/S was significantly higher than that of C/S. Additionally, in the figure, it can be observed that FeSe₂@C/S (ΔE = 0.221 V) exhibited lower electrochemical polarization compared to C/S (ΔE = 0.380 V), indicating that FeSe₂@C can significantly enhance the kinetic transformation of LiPSs compared to C. During the charging process, the intrinsic low electronic conductivity of Li₂S leads to a high activation energy barrier for the conversion process. Therefore, reducing the energy barrier for Li₂S oxidation during the charging process can effectively improve the conversion efficiency of lithium–sulfur batteries. Further analysis of the oxidation process of lithium sulfide during the charging curve revealed that the oxidation decomposition energy barrier of Li₂S on FeSe₂@C was 2.27 V, which is lower than that of C (2.34 V). The experimental results indicate that, compared to C, lithium sulfide is more easily oxidized and decomposed on the surface of FeSe₂@C, leading to a higher conversion into sulfur and exposing more active sites of the catalyst.

Fig. 5e presents the cycling performance of FeSe₂@C/S at higher sulfur loadings. As shown in the Fig. 5e, under the condition of 3.0 mg cm⁻² sulfur loading, FeSe₂@C/S shows an initial discharge capacity of 767.9 mA h g⁻¹ at 0.1C current density, and after 60 cycles, it still maintains a discharge specific capacity of 726.5 mA h g⁻¹. Under the condition of 4.2 mg cm⁻² sulfur loading, the initial capacity is 524.08 mA h g⁻¹, and after 60 cycles, it can still retain a discharge specific capacity of 445.5 mA h g⁻¹. These results demonstrate that FeSe₂@C/S electrodes exhibit remarkable cycling stability even at higher sulfur loadings. To investigate the enhancement effect of FeSe₂ active sites on the long-term cycling stability of lithium–sulfur batteries, the FeSe₂@C/S electrode was subjected to cycling tests at a high current density of 1C. Prior to the battery test, the cell was first cycled for 2 cycles at a low current density of 0.05C for activation. As shown in Fig. 5g, after 600 cycles at 1C, the FeSe₂@C/S electrode exhibits an outstanding capacity retention rate of 97.5%, showcasing a mere 0.004% decay per cycle, clearly highlighting the significant improvement in the cycling performance due to the catalytic activity of the sulfur oxidation reaction (SOR). The catalytic effect of FeSe₂ active sites plays a crucial role in enhancing the performance and stability of the battery during long-term cycling.

In summary, the superior rate capability and stable cycling performance observed in FeSe₂@C/S cathodes can be attributed to the strong adsorption of polysulfides and the efficient catalytic conversion of Li₂S facilitated by FeSe₂@C. The FeSe₂@C electrocatalyst exhibits excellent performance in terms of adsorbing polysulfide species, promoting their transformation into Li₂S and other soluble intermediates during the discharge and charge processes. These properties effectively suppress the shuttle effect and enhance the utilization of active sulfur, contributing to improved rate capability and prolonged cycling stability in lithium–sulfur batteries.

3 Conclusions

In this study, we successfully synthesized a nano-flower-like FeSe₂@C catalyst for application in lithium–sulfur batteries. The investigation into the conversion pathway and catalytic mechanism from Li₂S to Li₂S₂ revealed a two-step process facilitated by efficient electron transfer. Li₂S undergoes electron loss to form the intermediate LiS⁺, which then directly reacts with Li₂S to produce Li₂S₂. The d–p orbital hybridization of the Fe–S bond and the redox coupling of Fe⁺²/Fe⁺³ accelerated electron transfer, effectively reducing the energy barrier for the decomposition of Li₂S. Electrochemical tests, combined with in situ Raman spectroscopy and theoretical calculations, highlighted the enhanced anchoring capability of the catalyst for LiPSs and its role in accelerating the kinetics of the Li₂S to Li₂S₂.
transformation, achieving efficient charge catalysis. FeSe$_2$@C exhibits exceptional electrocatalytic activity towards the sulfur oxidation reaction (SOR), thereby significantly enhancing the rate capability and cycling stability of lithium–sulfur batteries. At a rate of 1C, the initial capacity is 581.3 mA h g$^{-1}$, and after 600 cycles, the discharge capacity remains at 560.8 mA h g$^{-1}$, with a capacity retention of 97.5% and a minimal decay of only 0.004% per cycle. This work highlights the promising potential of electrocatalytic SOR as a method for achieving high-performance lithium–sulfur batteries and expands the research on SOR, opening up possibilities for further studies in this field.

**Data availability**

The data supporting this article have been included as part of the ESI.†

**Author contributions**

C. K. Y. conceived and designed the experimental research and the DFT calculations, and exercises supervision. P. K. Z. performed the experiments and conducted the data analysis with contributions from Y. S. L. and L. L.. J. X. W., B. R. L., and Y. C. performed the DFT calculations. H. Y. M, Z. Y. L., Y. Y. exercises supervision. All authors discussed the results and commented on the manuscripts.

**Conflicts of interest**

The authors hereby declare that they have no known competing economic interests or personal relationships that could have influenced the work reported in this manuscript.

**Acknowledgements**

This work was supported primarily by National Natural Science Foundation of China (No. 22109025), National Key Research and Development Program of China (2020YFA0710303), Natural Science Foundation of Fujian Province, China (2021J05121), Major Scientific Research Projects and Key Research Projects of Shanxi Energy Internet Research Institute (SXEI 2023 A 004). P. K. Zou., Y. S. Lin., and L. Li contributed equally to this work.

**References**