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Establishing reaction networks in the 16-electron sulfur reduction reaction

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The sulfur reduction reaction (SRR) plays a central role in high-capacity lithium sulfur (Li-S) batteries. The SRR involves an intricate 16-electron conversion process, featuring multiple lithium polysulfide (LiPS) intermediates and reaction branches[1-3]. Deciphering the complex reaction network is essential for rationally tailoring the SRR for improved Li-S batteries, but represents a daunting challenge[4-6]. Herein we systematically investigate the electrocatalytic SRR to decipher its network, using the nitrogen, sulfur dual-doped holey graphene framework (N,S-HGF) as a model electrode to understand the role of electrocatalysts in accelerating the conversion kinetics. Combining cyclic voltammetry, *in situ* Raman spectroscopy and density functional theory calculations, we identify and directly profile the key intermediates (S_8, Li_2S_8, Li_2S_6, Li_2S_4, and Li_2S) at varying potentials and elucidate their conversion pathways. Li_2S_4 and Li_2S_6 are predominantly observed, in which Li_2S_4 represents the key electrochemical intermediate dictating the overall SRR kinetics. Li_2S_6, generated (consumed) through a comproportionation (disproportionation) reaction, doesn't directly participate in electrochemical reactions, but significantly contributes to the polysulfide shuttling process. We found that the N,S-HGF catalyst could help accelerate the polysulfide conversion kinetics, leading to a faster depletion of soluble LiPSs at higher

potential, hence mitigating the polysulfide shuttling effect and boosting the output potential. These results highlight the electrocatalytic approach as a promising strategy to tackle the fundamental challenges in Li-S batteries.

The lithium sulfur (Li-S) battery represents an attractive next generation energy storage device for its exceptional theoretical capacity of 1672 mAh g^{-1} and ultrahigh energy density of 2600 Wh kg^{-1} [7,8]. Despite extensive efforts devoted to improving the practical performance of Li-S batteries[3,9-11], the fundamental reaction mechanism, particularly for the sulfur reduction reaction (SRR) during discharge, remains a topic of considerable debate[4-6,12-15]. SRR involves a complex multistep 16-electron conversion from S_8 molecules to Li_2S solid, with multiple possible interwoven branches among a series of soluble lithium polysulfide (LiPS) intermediates. The soluble LiPS may readily shuttle across the cathode and anode, leading to rapid capacity fading. Recent investigations suggested that the conversion from high order polysulfides into insoluble Li_2S_2/Li_2S represents the most difficult step, leading to an accumulation of soluble LiPS in the electrolyte and exacerbating the shuttling issue[16]. An electrocatalytic process could help accelerate such conversion kinetics and reduce the LiPS accumulation, and diverse electrocatalysts have shown promise in improving the battery performance[17-25]. However, the exact role of such electrocatalysts in modifying the SRR mechanism remains elusive. A comprehensive elucidation of the SRR network and the electrocatalytic effect is essential for the rational design of electrocatalysts that can target specific steps to fundamentally solve the polysulfide shuttling problem.

Various approaches have been considered to elucidate the SRR mechanism, involving both experimental[4,5,12-14,26-28] and computational efforts[12,13,29-34]. Detailed mechanistic studies based on standalone electrochemistry are generally challenging, due to the complex convolution of multiple electrochemical reactions and nonelectrochemical side reactions (e.g., LiPS disproportionations[4,5,28]) at the same potential. Advanced *in situ* characterization to identify and track different PS species generated electrochemically or non-electrochemically, is essential for interpreting and corroborating electrochemical characteristics[5,13,14,27]. Computational efforts have focused on predicting the energetics of different species and furthermore the reaction network[12,34]. However, current studies do not treat the overall reaction network equilibrium and lack a

description of potential dependent properties such as the polysulfide concentrations along the SRR process. This hinders the direct comparison with experimental results. Therefore, it is highly desirable to determine the detailed mechanism based on *ab initio* energetics with validation from both electrochemical and *in situ* techniques.

Here we report a systematic investigation of the electrocatalytic SRR mechanism. We chose the previously developed nitrogen, sulfur dual-doped holey graphene framework (N,S-HGF) electrocatalysts and non-doped HGF as model systems to explore the impact of catalysts in modifying the reaction network and kinetics. Combining cyclic voltammetry (CV), *in situ* Raman spectroscopy and density functional theory (DFT) calculations, we establish a detailed reaction network, elucidate the dominant reaction pathway before and after the central Li_2S_4 intermediate, identify the key species as S_8, Li_2S_8, Li_2S_6, Li_2S_4, and Li_2S, and determine that the non-electrochemical comproportionation/disproportionation reaction between Li_2S_8 and Li_2S_4 is the main path for forming or consuming Li_2S_6. Comparison between N,S-HGF and HGF confirms the same key species in the reaction network, whilst the N,S-HGF catalyst accelerates LiPS conversion, leading to a faster depletion of LiPSs at higher potential to mitigate polysulfide shuttling effect and produce a larger output potential. These results emphasize electrocatalysis as a promising strategy to address fundamental Li-S battery challenges.

Reaction network in SRR and CV results

It has been previously shown that the N,S-HGF can considerably accelerate the SRR kinetics in comparison with non-doped HGF[16]. The CV curve for SRR with N,S-HGF (red curve in Fig. 1b) exhibits two main peaks during discharge: one appearing around 2.2-2.5 V and the second around 1.9-2.1 V. The charge number calculated from the integrated area in CV is converted to the formal electron transfer number in a full 16 e$^-$ process (Supplementary Fig. 1 and Supplementary Table 1). By separating the overall discharge process at the onset of the second peak, 2.11 V, a charge transfer ratio of 4.08:11.92 ($\approx$1:3) was obtained, which is also validated by galvanostatic charge discharge tests (Supplementary Fig. 2). This 1:3 charge transfer ratio suggests Li_2S_4 to be the primary intermediate separating these two reduction peaks, as the reaction $S_8+4Li^++4e^-\rightarrow2Li_2S_4$ involves 4 electrons out of the formally overall 16 electrons transferred, and the subsequent conversion $2Li_2S_4+12Li^++12e^-\rightarrow8Li_2S$ involves 12 electrons.

Interestingly, a non-zero plateau was observed in the voltage range of 2.11-2.25 V between the two peaks (inset, Fig. 1b). The charge integration results, as shown in Fig. 2a with colored regions, illustrate the non-negligible contribution of the plateau region between the two major redox peaks: ~1 out of 16 electrons per S_8 molecule in SRR. Comparing with a control group without sulfur (black baseline in Fig. 1b), the double layer capacity contribution to this plateau has been eliminated. Considering the instability and complexity of polysulfides[4,5,28], the voltage ranges of electrochemical reactions reflected on the CV can be affected by comproportionation/disproportionation reactions, although such non-electrochemical processes are not directly detectable *via* CV measurements.

To investigate the chemical origin of such a plateau, we have used first principles calculations to explore the fundamental energetics among different polysulfide intermediates. Computational modeling of the SRR network begins with the conversion from S_8 to Li_2S_8, yielding a calculated output potential of 2.41 V, the highest among all steps. The further conversion of the Li_2S_8 molecule involves multiple possible branches, while the calculated energetics shows that the pathway forming two Li_2S_4 is the most exergonic and hence the favored one, yielding an output potential of 2.24 V (Fig. 2d).

As the experimentally observed plateau might be originated from the delayed electrochemical conversion of comproportionation or disproportionation products, we checked the possibilities starting with one Li_2S_8 molecule and one Li_2S_4 molecule, or two Li_2S_4 molecules, and found that the reaction $Li_2S_8+Li_2S_4\rightarrow 2Li_2S_6$ is the only exergonic one, with a reaction Gibbs free energy of -0.16 eV, while the disproportionation reaction involving either Li_2S_8 and Li_2S_6 or Li_2S_4 and Li_2S_6 were found to be endergonic. These results suggest that Li_2S_6 formation by comproportionation of Li_2S_4 and Li_2S_8 is the only chemical elementary step that significantly competes with the electrochemical reaction network.

Combining the aforementioned DFT balances (Fig. 2d) with voltage effects, the potential dependent concentrations of different polysulfides were simulated, giving a sequence of dominant LiPS species as S_8, Li_2S_8, Li_2S_6, Li_2S_4, and Li_2S with reducing potential (Fig. 2c). The simulated CV curve was further derived from the concentrations, giving a charge ratio of 2.82:1.20:11.98, in the orange, yellow and green zones of Fig. 2b, respectively, which matches well with the experimental ratio in Fig. 2a.

Although Li_2S_6 appears right after Li_2S_8, it is not produced by electrochemical reduction of Li_2S_8. Instead, a fraction of Li_2S_8 (~1/3) is electrochemically transformed into Li_2S_4, providing a fractional amount of charge in the orange region of Fig. 2 a and b (~2/3 e), while the rest undergoes comproportionation with the produced Li_2S_4 to yield a large concentration of Li_2S_6 at ~2.25 V. Note that the exergonic nature of the $Li_2S_8 + Li_2S_4 \rightarrow 2Li_2S_6$ comproportionation provides additional driving force to initiate the electrochemical reduction of Li_2S_8 to Li_2S_4 at a potential higher (~2.35 V) than its equilibrium (2.24 V). At lower potential, when Li_2S_8 is largely consumed, the comproportionation reaction operates backwards to disproportionate Li_2S_6 into Li_2S_4 and Li_2S_8 ($2Li_2S_6 \rightarrow Li_2S_8 + Li_2S_4$), in which Li_2S_8 is electrochemically reduced to Li_2S_4, resulting in the discharge plateau seen in the yellow region. We found that the direct reduction of Li_2S_6 to Li_2S_4, Li_2S_3 or other lower order polysulfides cannot occur at a potential higher than 1.97 V, making the disproportionation reaction the only viable path in this potential regime (Supplementary Note 1). At even lower potential in the green zone, Li_2S_4 is eventually reduced to Li_2S, involving the extra 12 electrons of the electrochemical reduction reaction.

In situ Raman study on SRR

We used *in situ* Raman spectroscopy (Supplementary Fig. 3) to probe the specific reaction intermediates along a discharge CV scan (Fig. 3 a, b). At the beginning, the typical S_8 peak at 469 cm^{-1} confirmed the existence of elemental sulfur[30]. With reducing potential, the S_8 signal gradually decreases and mostly disappears at ~2.36 V, accompanied by the emergence of the Li_2S_8 signal at 508 cm^{-1} starting at ~2.44 V, along with the appearance of the Li_2S_6 peak at 399 cm^{-1}. As discussed in the computation section, this occurs by electrochemical transformation of Li_2S_8 to Li_2S_4 and the rapid comproportionation between the formed Li_2S_4 and the remaining Li_2S_8 to form Li_2S_6. The Li_2S_8 peak at 508 cm^{-1} reaches maximum at ~2.32 V, where a deconvoluted peak at 501 cm^{-1} for Li_2S_4 emerges. At 2.18 V, the 508 cm^{-1} Li_2S_8 peak largely disappears, while the Li_2S_4 peak at 501 cm^{-1} reaches its maximum. As the potential decreases, Li_2S_4 becomes the main polysulfides species, while Li_2S_6, formed through the comproportionation reaction ($Li_2S_8 + Li_2S_4 \rightleftarrows 2Li_2S_6$), is also significantly present. The Li_2S_6 peak at 399 cm^{-1} starts to decrease at ~2.30 V and almost disappears at 2.02 V. Similarly, most Li_2S_4 disappears at ca 2.00 V, indicating the conversion from Li_2S_4 to Li_2S_x (x=1, 2, 3) (see Fig. 5 for more details). A small amount of Li_2S_4 remains at the low voltage region below 1.90 V, likely due to incomplete conversion. Additionally, a minor Raman

peak at 531 cm^{-1} can be assigned to LiS$_3$·. Our calculations show that LiS$_3$· originates from an electrochemically passive branch (Li$_2$S$_6$ ⇌ 2LiS$_3$·) and is present as a minor species (< 3% of Li$_2$S$_6$, see Supplementary Fig. 4). LiS$_3$· has negligible impact on the equilibrium of other species or the overall reaction network, and is thus omitted in our subsequent analysis.

The voltage dependent concentration profile of each LiPS derived from the peak area (left panel in Fig. 3c) was further compared with the computational results (right panel in Fig. 3c). The comparison reveals a similar sequence of concentration evolution for S$_8$, Li$_2$S$_8$, Li$_2$S$_6$, Li$_2$S$_4$ with decreasing potential. Notably, Li$_2$S$_6$ appears at a similar potential as Li$_2$S$_8$ and is roughly depleted at a similar potential as Li$_2$S$_4$, suggesting the dynamic balance among these three species through the comproportionation/disproportionation reactions.

We also note that the experimental peak for Li$_2$S$_4$ appeared at a slightly higher potential value (by 0.09 V) than the theory prediction. Only thermodynamics was considered in the simulated voltage dependent equilibrium concentration, while the formation of Li$_2$S$_6$ could be slow due to kinetics and diffusion barriers, and thus Li$_2$S$_4$ accumulation may start at a slightly higher voltage. This further validates the origin of Li$_2$S$_6$ from the comproportionation reaction. Additionally, the low solubility of Li$_2$S$_4$ in the electrolyte (10 mM for Li$_2$S$_4$ vs. 1 M for Li$_2$S$_6$ and 0.5 M for Li$_2$S$_8$, see Supplementary Note 2) may also contribute to an apparent shift of the Li$_2$S$_4$ profile: taking the solubility limit into account shifts the onset of the simulated Li$_2$S$_4$ peak position from ~2.25 V to ~2.35 V with a better match with experimental results (Supplementary Fig. 5).

Together, these *in situ* Raman spectroscopy analyses provide a semi quantitative polysulfide tracking, in agreement with DFT computed values, thus robustly validating the SRR molecular pathway obtained by theory: S$_8$→Li$_2$S$_8$→2Li$_2$S$_4$ (Li$_2$S$_8$+Li$_2$S$_4$ ⇌ 2Li$_2$S$_6$)→8Li$_2$S. Base on Raman studies, we have also estimated the relative concentration ratio of 1.7 : 5.5 : 0.4 for the maximum concentration point of Li$_2$S$_8$: Li$_2$S$_6$: Li$_2$S$_4$ (Supplementary Table 2). Thus, both theoretical and experimental studies suggest that Li$_2$S$_6$ represents the dominant species during discharge and a major contributor to the shuttling effect.

The role of catalysis in the SRR network

To further understand the influence of electrocatalysts on the SRR network, the non-doped HGF was studied as a less active catalytic system to compare with the N,S-HGF (Supplementary

Fig. 6). Overall, our *in situ* Raman spectra studies (Supplementary Fig. 7) reveal that the HGF shows a similar polysulfide evolution sequence $Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4$, but with different voltage ranges for each species (Fig. 4).

The first step of discharge at high potential is weakly modified among the two different catalysts, the peak center (Supplementary Table 3) for Li_2S_8 being slightly delayed in HGF (2.29 V) compared to N,S-HGF (2.32 V). Transformation of Li_2S_6 is more sensitive and seriously delayed in HGF, with an average peak value at 2.19 V (compared to 2.27 V in N,S-HGF), and with about 20% (relative to the peak concentration of Li_2S_6) remaining at 1.80 V in HGF (compared to less than 3% remaining at 1.80 V in N,S-HGF). A similar delay is observed for Li_2S_4, from higher overpotential in the later steps, with an average peak value at 2.12 V (compared to 2.14 V in N,S-HGF), and with more than 30% remaining at 1.80 V in HGF (compared to 17% remaining in N,S-HGF). The delayed depletion of Li_2S_4 and Li_2S_6 until a much lower potential with non-doped HGF electrodes implies a more sluggish conversion kinetics to lower order polysulfide, potentially worsening the shuttling effect.

Our calculations described above indicate that direct electrochemical reduction of Li_2S_6 to lower order LiPSs above 1.97 V is unfavorable. Instead, elimination of Li_2S_6 relies on a thermodynamically unfavorable disproportionation reaction $(2Li_2S_6 \rightarrow Li_2S_8 + Li_2S_4)$ that requires rapid depletion of Li_2S_4 to proceed. In this case, a slower conversion kinetics of Li_2S_4 could seriously delay the consumption of Li_2S_6 until a much lower potential regime (<1.97 V), where a direct electrochemical reduction of Li_2S_6 may also start to occur. The conversion of Li_2S_4 thus dominates the electrocatalytic performance, especially at the start of the second stage of SRR, which is consistent with the previously reported critical role of Li_2S_4 on SRR overpotential[20].

Overall, slower conversion kinetics of Li_2S_6 results in its wider accumulation potential range, which exacerbates the PS shuttling problem. This is also reflected by the reduced charge number at high potential and within the overall SRR process: 2.36 and 9.24 electrons per S_8 molecule in HGF system, compared to 3.61 and 14.17 electrons in the N,S-HGF system (Supplementary Table 1). These CV and *in situ* Raman studies revealed distinct SRR kinetics between HGF and N,S-HGF, highlighting the fundamental benefits brought by efficient catalysts.

To understand the distinct potential ranges for these two electrocatalysts, we further investigated the reaction pathways of the second stage, i.e., the conversion from Li_2S_4 to Li_2S.

Considering all the possible 2e⁻, 4e⁻, and 6e⁻ steps starting from Li_2S_4 (Fig. 5), we examined a total of 12 different reaction pathways in the presence of various catalyst sites: armchair edge of graphene, zigzag edge and inner defects in the graphene plane with various doping situation (non-doped, S-doped, N-doped, and N,S-doped, see Supplementary Note 3). Two pathways were found to give the largest output potential: (1) one 4e⁻ step: $Li_2S_4+4Li^++4e^-\rightarrow Li_2S_2+2Li_2S$, followed by one 2e⁻ step: $Li_2S_2+2Li^++2e^-\rightarrow 2Li_2S$ (Fig. 5b); (2) a pathway consisting of one 6e⁻ step, i.e., at least one intermediate species is adsorbed on the surface during the reduction process: $Li_2S_4+6Li^++6e^-\rightarrow 4Li_2S$ (Fig. 5c). The results clearly show that in both pathways, N,S-codoped sites exhibited higher output potential, 2.11 V, compared to 2.03 V for non-doped sites, aligning with experimental results and showcasing N,S-HGF's superior performance[16].

Interestingly, the inner defect sites (see Supplementary Figs. 8 and 9) appear closer to the top of the output potential plot (circles in Fig. 5 b, c) compared to armchair and zigzag edge sites (triangles and squares, respectively), confirming the effectiveness of defect engineering, together with heteroatom doping, in holey graphene for electrocatalysis. It is worth mentioning that conversion from LiS to Li_2S solid is the potential limiting step for most of the sites with relatively large output potentials (~2.1 V), while one site has the adsorption of LiS as the potential limiting step. This indicates that the final conversion from Li_2S_2 to Li_2S is the potential limiting step, consistent with the experimental observation where the finals steps exhibited the largest overpotential[16]. Therefore, LiS adsorption energy can be used as a descriptor to classify site output potentials. Moreover, a smaller output potential in the second stage has far-reaching effects: the sluggish conversion of Li_2S_4 to lower order polysulfides could considerably retard the thermodynamically unfavorable disproportionation reaction ($2Li_2S_6\rightarrow Li_2S_8+Li_2S_4$), the essential path for consuming Li_2S_6.

Consistent with the experimental results, the simulated potential dependent concentrations for the HGF electrode show more sluggish conversion, i.e., lower depletion potentials for Li_2S_4 and Li_2S_6 species, 1.85 V and 2.00 V for HGF vs. 2.00 V and 2.05 V for N,S-HGF (Fig. 4). The simulation of HGF and N,S-HGF effective output potential only differs significantly in the second stage, largely comparable to the experimental results. Such a close correlation between the experiments and theory further validates the electrocatalytic strategy for improved Li-S batteries: an accelerated polysulfide conversion kinetics can not only produce a larger output potential, but

also narrow the potential range in which the LiPSs could appear and effectively mitigate the PS shuttling effect.

Conclusion

In conclusion, a combined experimental and theory investigation has allowed us to decipher and establish the complex reaction network for the 16-electron SRR, revealing two stages separated by the central Li_2S_4 intermediate. Our studies indicate that Li_2S_4 and Li_2S_6 represent the dominant intermediates, in which Li_2S_4 is the key electrochemical intermediate controlling the overall SRR kinetics, particularly in the more sluggish second reduction stage, while Li_2S_6 is generated by the comproportionation reaction between Li_2S_8 and Li_2S_4 and doesn't directly participate in electrochemical reactions, but is a major contributor to the shuttling effect due to its high solubility and energetically favorable accumulation in the electrolyte. It is found that the optimized N,S-HGF electrocatalytic electrode considerably accelerates the conversion of high order LiPSs, leading to a faster depletion of soluble LiPSs at higher potential regime, hence mitigating the PS shuttling effect and boosting the output potential. This study resolves the fundamental reaction network in SRR, and offers valuable insights into electrocatalyst design for improved Li-S batteries. For example, considering the origin of Li_2S_6 ($Li_2S_8+Li_2S_4\rightarrow2Li_2S_6$), designing electrocatalysts with enhanced Li_2S_8 or Li_2S_4 adsorption could restrain these species on the catalyst surface, thereby suppressing comproportionation reactions and limiting Li_2S_6 formation. Furthermore, this methodology can be applied to understand the sulfur evolution reaction (SER), to guide the design of bifunctional sulfur catalysts to accelerate both the SRR and SER processes, which is essential for developing robust Li-S batteries.

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Methods

Synthesis of graphene oxide and heteroatom-doped holey graphene framework.

The heteroatom-doped HGF can function as a conductive scaffold with flexible pore structure and exhibit tunable electrocatalytic properties in SRR[16,17], and hence serves as a good model system for investigating the fundamental reaction mechanism. Furthermore, compared with metal oxides or sulfides that are usually in the form of nanoparticles and require additional conductive additives and binders, the freestanding HGF electrode could offer a more robust and simplified binder-free model system for systematic investigation of the SRR process. The specific heteroatom-doped N,S-HGF was chosen for its superior SRR kinetics, considerably low activation energy, and excellent performance in Li-S batteries[16], and non-doped HGF as a control for comparison to evaluate the role of the catalyst in modifying the kinetics along the complex SRR network.

A typical hydrothermal process was used to construct the HGF structure with interconnected micro and nanopores. Graphene oxide was prepared using a modified Hummers' method[35]. Briefly, 6 g natural graphite (325 mesh, Sigma-Aldrich) was added into 140 ml concentrated sulfuric acid under vigorous stirring in an ice-water bath, followed by slowly adding 3 g sodium nitrate (Sigma-Aldrich) and 18 g potassium permanganate (Sigma-Aldrich). Due to the strong acidity of sulfuric acid and highly oxidative nature of the sodium nitrate and potassium permanganate, it is necessary to keep the temperature near 0 °C to slow down oxidation process and avoid possible safety concerns. After stirring for 30 min, the reaction system was transferred into a water bath at ~50 °C, under continued stirring till the mixture forming a thick paste. The system was next transferred back to the ice-water bath, followed by drop-wise addition of ~1 liter of iced deionized water. The mixture was then centrifuged and washed by 1:10 HCl aqueous solution for three times followed by repeated washing with deionized water. The final solution was dialyzed for one week to remove the extra H^+ ions absorbed on the graphene oxide surfaces.

The heteroatom-doped HGFs were synthesized by reacting the dopant sources and H_2O_2 with the graphene oxide (GO) aqueous dispersion through a typical hydrothermal method. N,S-HGF was synthesized by mixing 30 ml of 2 mg ml^{-1} GO aqueous dispersion solution, 45 μl of 30% H_2O_2 aqueous solution and 3.0 g NH$_4$SCN, followed by sonication and hydrothermal reaction at 180 °C for 6 h in an autoclave to produce a free-standing N,S-HGF hydrogel. The hydrogel was

then freeze-dried and annealed at 900 °C in Ar for 1 h to obtain the N,S-HGF aerogel. The control sample HGF was synthesized by substituting the dopant sources with ascorbic acid, following the same procedures.

Preparation of the electrolyte and Li$_2$S$_x$ solutions.

The electrolyte (denoted as blank electrolyte) was made of 1 M lithium bis(trifluoromethanesulfonyl)imide (Sigma-Aldrich) and 0.2 M lithium nitrate (Sigma-Aldrich) in the mixed 1,2-Dimethoxyethane (DME) (Sigma-Aldrich) and 1,3-Dioxolane (DOL) (Sigma-Aldrich) solution (1:1 by volume). The Li$_2$S$_6$ catholyte (0.1 M) was prepared by reacting the sublimed sulfur (Sigma-Aldrich) with Li$_2$S (Sigma-Aldrich) in stoichiometric proportion in the blank electrolyte. The mixture was vigorously stirred at 50 °C in an argon-filled glove box overnight to produce a brownish-red Li$_2$S$_6$ catholyte solution.

Electrochemical measurements.

The electrochemical performance of the catalyst was conducted in the CR2032 coin cells assembled in an argon-filled glovebox. The catalyst electrode was prepared by directly pressing the aerogel into a freestanding thin film. Afterwards, the catholyte (0.1 M Li$_2$S$_6$ in the blank electrolyte) was directly used as sulfur source to drop cast in the catalyst electrode. In our experiment, we specifically used a low mass ratio of the sulfur in the cathodes (33%) to ensure a complete conversion from S$_8$ to Li$_2$S for mechanistic understanding. The sulfur cathodes were then directly assembled into a CR2032 coin cell with lithium foil, Celgard 2500 separator and blank electrolyte.

To better probe the different stages in the SRR, we performed cyclic voltammetry (CV) measurements, followed by quantitative charge analysis by integrating the peak area in different potential regions. CV curves were recorded in the voltage range of 1.6 V-2.8 V at a scanning rate of 0.05 mV s^{-1}. The charge number transferred (Q) for the electrochemical steps in SRR can be calculated from CV curves. Q is calculated by integrating the area enclosed in CV:

$$Q = \int_{t_1}^{t_2} i(t)dt = \frac{1}{v}\int_{V_1}^{V_2} i(V)dV = \frac{A}{v}\int_{V_1}^{V_2} j(V)dV = \frac{AS}{v}$$

$$dt = \frac{dV}{v}$$

Where Q is Charge (C), i is current intensity (A), j is current density (A cm^{-2}), A is geometric area of the electrode (cm^2), v is scan rate (V s^{-1}), t is time (s), and S is integrated area.

In situ Raman spectroscopy.

With distinct Raman activity of elemental sulfur and polysulfides, *in situ* Raman spectroscopy offers an attractive technique for identifying and tracking polysulfides conversion process[30,36-41]. Raman spectroscopy measurements were collected by LN$_2$ cooled CCD array detector, using a Horiba Jobin Yvon T64000 open-frame confocal microscope using 10X objective follow by a triple monochromator leading to high spectral resolution (down to 0.15 cm^{-1}). The sample was subject to 514 nm laser for a 5 sec and averaged 70 times. The data were collected with a 1800 cm^{-1} grating, and 500 μm slit. For the *in situ* Raman, a regular coin cell is modified with a transparent window on the cathode side to allow the laser in. A same procedure as that in the electrochemical measurements was used to assemble the Raman cell. The laser was focused on the electrolyte near the boundary between HGF and electrolyte (see Supplementary Fig. 3). The Raman cell was running with a discharge CV scan at 0.05 mV s^{-1} when Raman data were collected.

The resulting Raman spectra (Supplementary Fig. 10) were carefully corrected and deconvolved. As the blank electrolyte shows multiple peaks in our interested spectral range, the *in situ* data were first corrected by "blank" subtraction. Specifically, a "blank" spectrum was collected using the same cell setup without active sulfur added and subtracted from the *in situ* data to eliminate the influence from electrolyte peaks. Subsequently, the *in situ* data were corrected by subtracting the baseline. The blank/baseline subtraction were conducted systematically using the Adaptive Iteratively Reweighted Penalized Least Squares[42] fitting implemented in the pybaseline package. The corrected Raman spectra were then loaded in *LabSpec* software to conduct the peak deconvolution and assignments for different polysulfides. We note the peak assignment for different polysulfides is complicated and divergent in different studies[30,36,39,43], due to the instability of various polysulfides and lack of pure polysulfide standard samples. Peaks used in our analysis are selected based on their behavior during SRR process, previous reports[30,36,39,43], and our DFT simulated results. We have deconvoluted all Raman peaks and analyzed multiple peaks for each given LiPS to confirm the validity of the assignments (Supplementary Figs. 11 and 12), and primarily used the peak at 501 cm^{-1}, 399 cm^{-1}, 508 cm^{-1} and 469 cm^{-1} for our quantification of Li$_2$S$_4$, Li$_2$S$_6$, Li$_2$S$_8$, and S$_8$.

DFT calculations.

Calculations were performed with DFT[44,45] using the Vienna ab initio simulation package[46]. The strongly constrained and appropriately normed (SCAN) functional[47] was used and other details are provided in Supplementary Note 4. Benchmark and comparison between different functionals are provided in Supplementary Note 5. Solvation effects were described using a micro-solvation model: the first solvation shell was described using explicit DOL molecules and the rest was described by an implicit dielectric model as implemented in the VaspSol[48] addon package (micro-solvated structures are given in Supplementary Fig. 13 and Supplementary Tables 4-5). We note the choice of the explicit solvent molecule is an approximation, and have also performed calculations with explicit DME solvation for Li_2S_4, which showed the same Li-O coordination number with very similar energies (Supplementary Note 6). The details of Gibbs free energies of the polysulfide species are provided in Supplementary Note 7. The reaction Gibbs free energies are provided in Supplementary Note 1. The details of potential dependent concentration calculations and simulated CV curves are provided in Supplementary Note 8. Possible effects of solubility on the simulated potential dependent concentration profile are discussed in Supplementary Note 2. Adsorption models (Supplementary Fig. 8, 9, and 14) are discussed in Supplementary Note 3. Volcano plot details (Supplementary Fig. 15) are discussed in Supplementary Note 9. The Raman intensity (Supplementary Fig. 16) was calculated within the double harmonic approximation and the details are provided in Supplementary Note 10. A sensitivity analysis is provided in Supplementary Note 11 and Supplementary Fig. 17 showing that conclusions from theory are unaffected by a reasonable change of calculated energies (up to 0.15 eV) arising from the considered approximations.

Data availability

The data that support the findings of this study are available in the main text, figures and Supplementary Information files. All relevant data are available from the corresponding authors upon request.

Code Availability

The code used for simulated voltage dependent concentrations and CV curves are available at https://github.com/lophocinalis/concentration_cv.

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Author contributions. X.D. conceived the research. X.D. and R.L. designed the experimental research; P.S. and Ziyang Wei designed and performed the DFT calculations; R.L. performed the experiments and conducted the data analysis with the contributions from Ziyang Wei, L.P., L.Z., P.W., C.W., D.Z., H.L., Zhaozong Wang, S.T., B.D., Y.H., P.S. and X.D.; A.Z. and R.S. contributed to Raman data collection; R.L. and Ziyang Wei wrote the original draft; X.D. and P.S. revised the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests. The authors declare no competing interests.

Fig. 1| Polysulfide conversion reactions involved in Li-S battery. a, A schematic illustration of the SRR network involved in the Li-S battery. Blue and yellow spheres represent lithium and sulfur, respectively. SRR encompasses a sophisticated 16-electron conversion process from S_8 molecules to Li_2S solid, involving multiple soluble lithium polysulfide intermediates. **b,** Cyclic voltammetry of the SRR in Li-S battery with N,S-HGF catalysts. The black baseline is obtained using the same N,S-HGF in the blank electrolyte without sulfur, indicating the negligible double layer capacity contribution to the overall capacity. The inset shows the plateau in the voltage range of ~2.11-2.25 V, which is originated from the delayed conversion of Li_2S_8 to Li_2S_4 due to $Li_2S_8 + Li_2S_4 \rightleftarrows Li_2S_6$ comproportionation/disproportionation reactions. **c,** A schematic illustration of *in situ* Raman technique used in this study.

Fig. 2| Charge analysis and reaction network for the sulfur reduction reaction. a, Experimental CV curve with the charge integration results, separated into three potential regions with a charge ratio as 2.98:1.10:11.92 from high potential to low potential. **b,** Simulated CV curve from first principles with the charge integration results, separated into the same three regions as in (a) with a charge ratio as 2.82:1.20:11.98. **c,** Simulated voltage dependent concentrations of the major species considered: S_8, Li_2S_8, Li_2S_6, Li_2S_4 and Li_2S. The concentrations are normalized according to the sulfur amount. **d,** The dominant reaction mechanism suggested by DFT energetics: $S_8 \rightarrow Li_2S_8 \rightarrow 2Li_2S_4 \rightarrow 8Li_2S$ ($Li_2S_8 + Li_2S_4 \rightleftarrows 2Li_2S_6$) where the chemical disproportionation part is in parentheses. Solid green and dotted red lines indicate major and minor electrochemical reactions, respectively. Blue lines indicate chemical reactions. Major products are labelled with green and blue boxes, corresponding to electrochemical and chemical origin. Thermodynamic output potentials are denoted for major electrochemical reactions. The catalytic site dependent output potentials for Li_2S_4 to Li_2S are detailed in Fig. 5.

Fig. 3| *In situ* Raman results during discharge with the N,S-HGF catalytic electrode. a, b, The CV profile (**a**) and the experimental *in situ* Raman spectra (**b**), where the same color indicates the same voltage. Characteristic peaks used to quantify the intermediates are marked with correspondingly colored shades. Small labels with darker color indicate the computed frequency values. **c,** The comparison between voltage dependent experimental concentrations (left panel) derived from *in situ* Raman spectra (**b**) and simulated concentrations from DFT (right panel). The normalized concentration of each species is calculated by dividing the concentration at each voltage by the highest concentration of that particular species over the whole discharge process.

Fig. 4| Comparison of different catalysts in SRR. a, d, Experimental CV curves for N,S-HGF (**a**) and HGF (**d**). **b, e,** Voltage dependent concentration for each polysulfide species in N,S-HGF (**b**) and HGF (**e**) derived from experimental *in situ* Raman spectra. **c, f,** Simulated voltage dependent concentration for each polysulfide species in N,S-HGF (**c**) and HGF (**f**). The normalized concentration of each species is calculated by dividing the concentration at each voltage by the highest concentration of that particular species over the whole discharge process. Colored bars in (**b**), (**c**), (**e**), and (**f**) represent the peak centers of the voltage

dependent concentration curves (Supplementary Table 3) for each specie: red for Li_2S_8, blue for Li_2S_6, and green for Li_2S_4.

Fig. 5| Simulated site-specific output potential of the Li_2S_4 to Li_2S conversion. a, Different possible combinations of 2e⁻, 4e⁻, and 6e⁻ steps considered for the second stage of SRR, the conversion of Li_2S_4 to Li_2S**.** Green, red, and blue lines indicate 2e⁻, 4e⁻, and 6e⁻ steps, respectively. **b, c,** Simulated multistep output potential from Li_2S_4 to Li_2S for the two pathways with largest output potentials considering various active sites on different catalytic electrode sites: armchair edge (A, triangles), zigzag edge (Z, squares), and inner defect sites (D, filled circles). Four types of dopants are considered: non-doped (black), S (green), N (blue) and N,S (red).