

**Towards Robust Lithium–Sulfur Batteries:
Enhancing Polysulfide Conversion through Catalyst Engineering**

Jing Yu

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Doctorate Program in Material Science

PhD Thesis

**Towards Robust Lithium-Sulfur Batteries:
Enhancing Polysulfide Conversion through
Catalyst Engineering**

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Jing Yu 于静

Abstract-English

Sulfur cathodes offer a highly promising route to high-energy-density, cost-effective, and sustainable energy storage. However, their practical implementation is limited by the sluggish and complex multistep sulfur redox reactions (SRRs), which involve coupled electrochemical and chemical processes. Catalytic additives that can accelerate these lithium–sulfur redox reactions are therefore crucial components of advanced sulfur cathodes in lithium sulfur batteries (LSBs). Rational catalyst design and separator engineering provide effective strategies to overcome these challenges. Chapter 1 offers a comprehensive overview of the current state of LSBs, the challenges they face, and the key performance requirements. Parts of this chapter are adapted from review articles published in *Communication Materials* in 2025 and *ACS Energy Letters* in 2024.

Chapter 2 outlines the dissertation’s objectives, focusing on improving LSBs performance through advanced materials design and catalyst engineering. It highlights the research goals of synthesizing and characterizing novel materials to address key challenges in energy storage, setting the foundation for the later chapters.

Chapter 3 outlines the experimental methods and materials used in this study. It details the chemical reagents and characterization techniques to analyze the structural and chemical properties of the catalyst materials. Electrochemical methods are described for evaluating the performance of LSBs. Additionally, operando techniques are employed to study real-time material changes during cycling. The chapter also includes theoretical simulations to support the experimental findings.

Chapter 4 reports the synthesis of NiSe₂ and Fe-doped NiSe₂ particles and investigate the impact of Fe doping on the electronic structure, catalytic activity, and performance of NiSe₂ introduced as a coating on the cathode side of the LSBs separator. Experimental analyses and first principles calculations reveal that Fe-rich cores and surface doping in NiSe₂ enhance the density of states at the Fermi level and introduce unpaired electrons, boosting LiPS adsorption and catalytic conversion. These synergistic effects significantly improve the catalytic performance, cycling stability, and overall performance of LSBs. Specifically, LSBs based on Fe-doped NiSe₂-based separators achieve specific capacities of 1483 mAh g⁻¹ at 0.1C and 1085 mAh g⁻¹ at 1C, along with remarkable cycling stability, retaining 84.4% capacity after 800 cycles. High sulfur-loading tests further validate the multifunctional membrane’s effectiveness, showing significant

capacity retention and reduced polysulfide loss. This work was published in *Advanced Functional Materials* in 2025.

In chapter 5, we explore the role of the electronic spin configuration on the polysulfide adsorption properties and catalytic activity of the additive. We showcase the importance of this electronic parameter by generating spin polarization through a defect engineering approach based on the introduction of Co vacancies on the surface of CoSe nanosheets. We show vacancies change the electron spin state distribution, increasing the number of unpaired electrons with aligned spins. This local electronic rearrangement enhances the polysulfide adsorption, reducing the activation energy of the Li-S redox reactions. As a result, more uniform nucleation and growth of Li₂S and an accelerated liquid-solid conversion in LSB cathodes are obtained. These translate into LSB cathodes exhibiting capacities up to 1089 mAh g⁻¹ at 1C with 0.017% average capacity loss after 1500 cycles, and up to 5.2 mAh cm⁻², with 0.16% decay per cycle after 200 cycles in high sulfur loading cells. This work was published in *ACS Nano* in 2024.

In chapter 6, we demonstrate that accelerating electrochemical processes, particularly Li₂S nucleation, over competing chemical pathways is fundamental to minimizing sulfur loss and achieving high-rate performance. To this end, we present a scalable and cost-effective strategy for synthesizing a series of 3d transition metal–bismuth (TM–Bi) atomic pairs anchored on carbon nitride (CN) and investigate their potential to activate SRRs in LSBs. An initial screening identifies Ni-Bi/CN and Co-Bi/CN as highly effective in improving rate performance. Detailed analysis shows these catalysts promote direct electrochemical transitions and rapid Li₂S nucleation over competing chemical reactions, enabling high charge-discharge rates while preventing active material loss and enhancing stability. Electrochemical analysis, density functional theory, and operando spectroscopy reveal that TM-Bi pairing shifts d-band states closer to the Fermi level and modulates HOMO-LUMO levels, promoting LiPS interaction and facilitating efficient charge transfer. These findings offer valuable insights for designing advanced catalysts for LSBs and broader electrocatalytic applications. This work was published in *Advanced Materials* in 2025.

Finally, Chapter 7 presents the general conclusions drawn from the research conducted throughout this dissertation. It synthesizes the key findings, reflects on their implications, and outlines potential directions for future work, offering a brief but thoughtful outlook on how this dissertation could inform and inspire subsequent research in the field.

Resum-Català

Els càtodes de sofre ofereixen una via molt prometedora cap a l'emmagatzematge d'energia d'alta densitat energètica, rendible i sostenible. Tanmateix, la seva implementació pràctica està limitada per les reaccions redox del sofre (SRR) de múltiples passos, lentes i complexes, que impliquen processos electroquímics i químics acoblats. Per tant, els additius catalítics que poden accelerar aquestes reaccions redox de liti-sofre són components crucials dels càtodes de sofre avançats en bateries de liti-sofre (LSB). El disseny racional de catalitzadors i l'enginyeria de separadors proporcionen estratègies efectives per superar aquests reptes. El capítol 1 ofereix una visió general completa de l'estat actual dels LSB, els reptes als quals s'enfronten i els requisits clau de rendiment. Parts d'aquest capítol estan adaptades d'articles de revisió publicats a **Communication Materials** el 2025 i **ACS Energy Letters** el 2024.

El capítol 2 descriu els objectius de la dissertació, centrant-se en la millora del rendiment de les bateries de liti-sofre mitjançant el disseny de materials avançats i l'enginyeria de catalitzadors. Destaca els objectius de recerca de sintetitzar i caracteritzar nous materials per abordar els reptes clau en l'emmagatzematge d'energia, establint les bases per al treball experimental i teòric en capítols posteriors.

El capítol 3 descriu els mètodes i materials experimentals utilitzats en aquest estudi. Detalla els reactius químics i les tècniques de caracterització per analitzar les propietats estructurals i químiques dels materials catalitzadors. Es descriuen mètodes electroquímics per avaluar el rendiment dels LSB. A més, s'utilitzen tècniques operando per estudiar els canvis de material en temps real durant el ciclatge. El capítol també inclou simulacions teòriques per donar suport a les troballes experimentals.

Al capítol 4, informem de la síntesi de partícules de NiSe₂ i de NiSe₂ dopades amb Fe i investiguem l'impacte del dopatge amb Fe en l'estructura electrònica, l'activitat catalítica i el rendiment del NiSe₂ introduït com a recobriment al costat del càtode del separador de LSB. Les anàlisis experimentals i els càlculs de primers principis revelen que els nuclis rics en Fe i el dopatge superficial en NiSe₂ augmenten la densitat d'estats al nivell de Fermi i introdueixen electrons no aparellats, augmentant l'adsorció de LiPS i la conversió catalítica. Aquests efectes sinèrgics milloren significativament el rendiment catalític, l'estabilitat del ciclatge i el rendiment general dels LSB. Concretament, els LSB basats en separadors de NiSe₂ dopats amb Fe aconsegueixen capacitats específiques de 1483 mAh g⁻¹ a 0,1 °C i 1085 mAh g⁻¹ a 1 °C, juntament amb una

estabilitat cíclica notable, mantenint un 84,4% de capacitat després de 800 cicles. Les proves d'alta càrrega de sofre validen encara més l'eficàcia de la membrana multifuncional, mostrant una retenció de capacitat significativa i una pèrdua reduïda de polisulfur. Aquest treball es va publicar a **Advanced Functional Materials** el 2025.

Al capítol 5, explorem el paper de la configuració de l'espín electrònic en les propietats d'adsorció de polisulfurs i l'activitat catalítica de l'additiu. Mostrem la importància d'aquest paràmetre electrònic generant polarització d'espín mitjançant un enfocament d'enginyeria de defectes basat en la introducció de vacants de Co a la superfície de nanocapes de CoSe. Mostrem que les vacants canvien la distribució de l'estat d'espín electrònic, augmentant el nombre d'electrons no aparellats amb espins alineats. Aquest reordenament electrònic local millora l'adsorció de polisulfurs, reduint l'energia d'activació de les reaccions redox de Li-S. Com a resultat, s'obté una nucleació i un creixement més uniformes de Li₂S i una conversió líquid-sòlid accelerada en càtodes LSB. Això es tradueix en càtodes LSB que presenten capacitats de fins a 1089 mAh g⁻¹ a 1C amb una pèrdua de capacitat mitjana del 0,017% després de 1500 cicles, i fins a 5,2 mAh cm⁻², amb un decaïment del 0,16% per cicle després de 200 cicles en cel·les amb alta càrrega de sofre. Aquest treball es va publicar a **ACS Nano** el 2024.

Al capítol 6, demostrem que accelerar els processos electroquímics, en particular la nucleació de Li₂S, sobre vies químiques competidores és fonamental per minimitzar la pèrdua de sofre i aconseguir un rendiment d'alta velocitat. Amb aquesta finalitat, presentem una estratègia escalable i rendible per sintetitzar una sèrie de parells atòmics de metall de transició-bismut tridimensionals (TM-Bi) ancorats en nitrur de carboni (CN) i investiguem el seu potencial per activar SRR en bateries de liti-sofre (LSB). Una selecció inicial identifica el Ni-Bi/CN i el Co-Bi/CN com a altament eficaços per millorar el rendiment de la velocitat. Una anàlisi detallada mostra que aquests catalitzadors promouen transicions electroquímiques directes i una nucleació ràpida de Li₂S sobre reaccions químiques competidores, permetent altes taxes de càrrega-descàrrega alhora que evita la pèrdua de material actiu i millora l'estabilitat. L'anàlisi electroquímica, la teoria funcional de la densitat i l'espectroscòpia operando revelen que l'aparellament TM-Bi desplaça els estats de banda d més a prop del nivell de Fermi i modula els nivells HOMO-LUMO, promovent la interacció de LiPS i facilitant una transferència de càrrega eficient. Aquestes troballes ofereixen informació valuosa per al disseny de catalitzadors avançats

per a LSB i aplicacions electrocatalítiques més àmplies. Aquest treball es va publicar a **Advanced Materials** el 2025.

Finalment, el capítol 7 presenta les conclusions generals extretes de la investigació duta a terme al llarg d'aquesta tesi. Sintetitza les principals troballes, reflexiona sobre les seves implicacions i descriu possibles direccions per a treballs futurs, oferint una breu però reflexiva perspectiva sobre com aquesta tesi podria informar i inspirar investigacions posteriors en el camp.

Resumen-Castellano

Los cátodos de azufre ofrecen una vía muy prometedora para el almacenamiento de energía de alta densidad energética, rentable y sostenible. Sin embargo, su implementación práctica se ve limitada por las lentas y complejas reacciones redox de azufre (SRR) de múltiples etapas, que implican procesos electroquímicos y químicos acoplados. Por lo tanto, los aditivos catalíticos que pueden acelerar estas reacciones redox de litio-azufre son componentes cruciales de los cátodos de azufre avanzados en baterías de litio-azufre (LSB). El diseño racional de catalizadores y la ingeniería de separadores proporcionan estrategias eficaces para superar estos desafíos. El capítulo 1 ofrece una visión general completa del estado actual de las LSB, los desafíos que enfrentan y los requisitos clave de rendimiento. Partes de este capítulo son adaptaciones de artículos de revisión publicados en **Communication Materials** en 2025 y **ACS Energy Letters** en 2024.

El capítulo 2 describe los objetivos de la tesis, centrándose en mejorar el rendimiento de las baterías de litio-azufre mediante el diseño avanzado de materiales y la ingeniería de catalizadores. Se destacan los objetivos de investigación de sintetizar y caracterizar nuevos materiales para abordar los desafíos clave del almacenamiento de energía, sentando las bases para el trabajo experimental y teórico en capítulos posteriores.

El capítulo 3 describe los métodos y materiales experimentales utilizados en este estudio. Detalla los reactivos químicos y las técnicas de caracterización para analizar las propiedades estructurales y químicas de los materiales catalizadores. Se describen métodos electroquímicos para evaluar el rendimiento de los separadores de baja frecuencia (LSB). Además, se emplean técnicas operando para estudiar los cambios del material en tiempo real durante el ciclado. El capítulo también incluye simulaciones teóricas que respaldan los hallazgos experimentales.

En el capítulo 4, se informa sobre la síntesis de partículas de NiSe_2 y NiSe_2 dopadas con Fe e investigamos el impacto del dopaje con Fe en la estructura electrónica, la actividad catalítica y el rendimiento del NiSe_2 introducido como recubrimiento en el lado catódico del separador de LSB. Los análisis experimentales y los cálculos de primeros principios revelan que los núcleos ricos en Fe y el dopaje superficial en NiSe_2 mejoran la densidad de estados a nivel de Fermi e introducen electrones desapareados, lo que potencia la adsorción de LiPS y la conversión catalítica. Estos efectos sinérgicos mejoran significativamente el rendimiento catalítico, la estabilidad de ciclado y el rendimiento general de las membranas LSB. En concreto, las membranas LSB basadas en separadores de NiSe_2 dopados con Fe alcanzan capacidades específicas de 1483 mAh g^{-1} a

0,1 °C y 1085 mAh g⁻¹ a 1 °C, junto con una notable estabilidad de ciclado, manteniendo el 84,4 % de su capacidad después de 800 ciclos. Las pruebas con alta carga de azufre validan aún más la eficacia de la membrana multifuncional, mostrando una significativa retención de capacidad y una menor pérdida de polisulfuro. Este trabajo se publicó en **Advanced Functional Materials** en 2025.

En el capítulo 5, exploramos el papel de la configuración electrónica del espín en las propiedades de adsorción de polisulfuro y la actividad catalítica del aditivo. Demostramos la importancia de este parámetro electrónico generando polarización de espín mediante un enfoque de ingeniería de defectos basado en la introducción de vacantes de Co en la superficie de nanoláminas de CoSe. Demostramos que las vacantes modifican la distribución del estado de espín electrónico, aumentando el número de electrones desapareados con espines alineados. Este reordenamiento electrónico local mejora la adsorción de polisulfuro, reduciendo la energía de activación de las reacciones redox Li-S. Como resultado, se obtiene una nucleación y un crecimiento más uniformes de Li₂S y una conversión líquido-sólido acelerada en cátodos LSB. Esto se traduce en cátodos LSB con capacidades de hasta 1089 mAh g⁻¹ a 1 °C con una pérdida de capacidad promedio del 0,017 % después de 1500 ciclos, y hasta 5,2 mAh cm⁻², con un decaimiento del 0,16 % por ciclo después de 200 ciclos en celdas con alta carga de azufre. Este trabajo se publicó en **ACS Nano** en 2024.

En el capítulo 6, demostramos que acelerar los procesos electroquímicos, en particular la nucleación de Li₂S, frente a las vías químicas competidoras es fundamental para minimizar la pérdida de azufre y lograr un alto rendimiento. Para ello, presentamos una estrategia escalable y rentable para sintetizar una serie de pares atómicos tridimensionales de metal de transición-bismuto (TM-Bi) anclados en nitruro de carbono (CN) e investigamos su potencial para activar los SRR en baterías de litio-azufre (LSB). Un análisis inicial identifica a Ni-Bi/CN y Co-Bi/CN como altamente eficaces para mejorar el rendimiento. Un análisis detallado muestra que estos catalizadores promueven transiciones electroquímicas directas y una rápida nucleación de Li₂S frente a las reacciones químicas competidoras, lo que permite altas tasas de carga-descarga, a la vez que previene la pérdida de material activo y mejora la estabilidad. El análisis electroquímico, la teoría del funcional de la densidad y la espectroscopia operando revelan que el emparejamiento TM-Bi desplaza los estados de la banda d hacia niveles más cercanos al nivel de Fermi y modula los niveles de HOMO-LUMO, lo que promueve la interacción LiPS y facilita una transferencia de carga eficiente. Estos hallazgos ofrecen información valiosa para el diseño de catalizadores

avanzados para LSB y aplicaciones electrocatalíticas más amplias. Este trabajo se publicó en **Advanced Materials** en 2025.

Finalmente, el Capítulo 7 presenta las conclusiones generales extraídas de la investigación realizada a lo largo de esta tesis. Sintetiza los hallazgos clave, reflexiona sobre sus implicaciones y describe posibles líneas de trabajo futuro, ofreciendo una perspectiva breve pero reflexiva sobre cómo esta tesis podría informar e inspirar la investigación posterior en este campo.

Abbreviations

Abbreviation	Full Form
AC-HAADF-STEM	Aberration-Corrected High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy
AFM	Atomic Force Microscopy
BET	Brunauer–Emmett–Teller
CNT	Carbon Nanotube
CV	Cyclic Voltammetry
DAC	Dual-Atom Catalyst
DFT	Density Functional Theory
DME	1,2-Dimethoxyethane
DOL	1,3-Dioxolane
DOS	Density of States
EDS	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
ELNES	Energy Loss Near-Edge Structure
EIS	Electrochemical Impedance Spectroscopy
E/S	Electrolyte-to-Sulfur
EPR	Electron Paramagnetic Resonance
EXAFS	Extended X-ray Absorption Fine Structure
FFT	Fast Fourier Transform
FWHM	Full Width at Half Maximum
GCD	Galvanostatic Charge–Discharge
GPA	Geometric Phase Analysis

HOMO	Highest Occupied Molecular Orbital
ICP-OES	Inductively Coupled Plasma–Optical Emission Spectroscopy
LSB	Lithium–Sulfur Battery
LSV	Linear Sweep Voltammetry
LiPS	Lithium Polysulfide
LiTFSI	Lithium Bis(trifluoromethanesulfonyl)imide
LUMO	Lowest Unoccupied Molecular Orbital
MCR	Multicurve Resolution
MD	Molecular Dynamics
MOF	Metal–Organic Framework
NI	Neutron Imaging
NMR	Nuclear Magnetic Resonance
NMP	N-Methylpyrrolidone
OM	Optical Microscopy
PAW	Projector Augmented Wave
PBEs	Perdew–Burke–Ernzerhof
PE	Polyethylene
PEO	Polyethylene Oxide
PDOS	Partial Density of States
PP	Polypropylene
PVDF	Polyvinylidene Fluoride
RKKY	Ruderman–Kittel–Kasuya–Yosida
SACc	Single-Atom Catalyst

SAXS	Small-Angle X-ray Scattering
SANS	Small-Angle Neutron Scattering
SEM	Scanning Electron Microscopy
SEI	Solid Electrolyte Interphase
SP	Super P Carbon
SQUID	Superconducting Quantum Interference Device
SRR	Sulfur Redox Reaction
TDOS	Total Density of States
TM	Transition Metal
TXM	Transmission X-ray Microscopy
UV–Vis	Ultraviolet–Visible
VASP	Vienna Ab-initio Simulation Package
VBC	Valence Band Center
XMCD	X-ray Magnetic Circular Dichroism
XANES	X-ray Absorption Near-Edge Structure
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XTM	X-ray Tomography

Chapter 1 Introduction

.1 Lithium sulfur batteries (LSBs)

The replacement of fossil fuels with renewable energy sources has emerged as a critical challenge in the pursuit of a sustainable energy future. One of the central obstacles in this transition is the development of clean, cost-effective, and scalable energy storage systems, which are essential not only for integrating intermittent renewable sources such as solar and wind into the power grid, but also for the widespread electrification of transportation. In this context, electrochemical energy storage, particularly in the form of batteries, plays a pivotal role due to its ability to store and deliver electricity efficiently and on demand.^[1]

However, current electrochemical energy storage technologies still face limitations in terms of cost, performance, and long-term stability. Among them, lithium-ion batteries (LIBs), which dominate the market, rely on intercalation-type electrodes such as graphite anodes and transition metal (TM) oxide or phosphate cathodes. While these systems offer good reversibility and cycle life, they are fundamentally constrained by their limited gravimetric energy density, which typically does not exceed 400 Wh kg^{-1} .^[2]

To overcome this bottleneck, the development of novel electrode materials is urgently required. In particular, conversion-type cathodes, such as those based on oxygen, sulfur, and halide chemistries, offer significantly higher theoretical energy densities. These electrodes operate via a chemical transformation reaction between the migrating ions (e.g., Li^+) and the active cathode material, forming new compounds during charge and discharge. Despite their potential, such conversion reactions are often associated with sluggish kinetics, leading to limited rate capability and reduced energy efficiency in secondary battery systems.^[3]

As in the case of fuel cells, where catalytic enhancement is essential, electrocatalysts are increasingly recognized as crucial for activating and accelerating these chemical reactions in conversion-type batteries. Their incorporation holds promise for overcoming the inherent kinetic barriers, improving both the reaction reversibility and the overall performance of high-energy battery chemistries.^[4]

Sulfur cathodes, which operate based on the reaction of metal ions (e.g., Li^+) with sulfur to form metal sulfides (e.g., Li_2S), have attracted particular attention due to their exceptionally high

theoretical energy density ($\sim 2600 \text{ Wh kg}^{-1}$) and specific capacity (1675 mAh g^{-1}), as well as the abundance and low cost of sulfur, see scheme in Figure 1.1a.

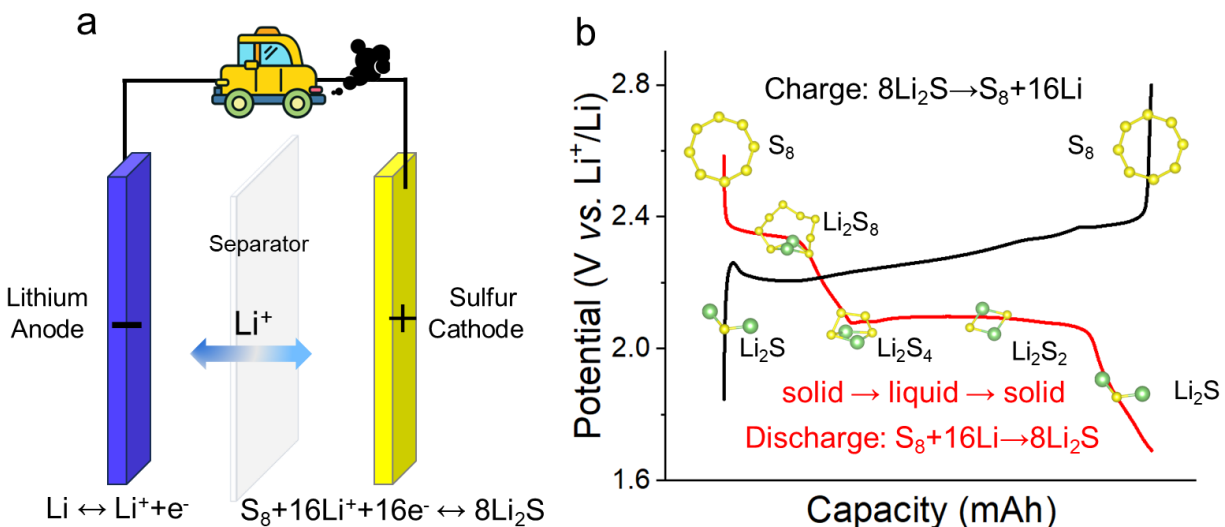


Figure 1.1. (a) Schematic illustration of an LSB. (b) Typical charge-discharge voltage curves of an LSB in an ether-based electrolyte.

1.2 Challenges of lithium sulfur batteries

Despite these appealing advantages, secondary sulfur-based batteries have yet to achieve widespread commercial deployment. This is primarily due to a number of performance limitations, including moderate rate capability, high self-discharge rates, low round-trip energy efficiency, and rapid capacity fading over repeated cycles. These issues become particularly severe under the lean-electrolyte and high-sulfur-loading conditions required to realize the high energy densities that sulfur batteries promise.^[5,6] In this section, we will address the key technical challenges currently facing LSBs.

1.2.1 Polysulfide dissolution and shuttle effect

The main challenge is the sluggish sulfur redox reaction (SRR) that involves the generation of several metal polysulfide intermediates during the conversion between sulfur and the metal sulfide as shown in Figure 1.1b and equation (1) for the case of LSBs:^[5]



However, this process will be more complicated, as shown in Figure 1.2: two S_4^{2-} anions can combine and dissociate into S_n^{2-} and $S_{(8-n)}^{2-}$, $n = 1, 2, 3, 4$ (Reaction 4-1~4-4). Then combine S_n^{2-} and $S_{(9-n)}^{2-}$, $n = 2, 3, 4$ to give S_1^{2-} and S_8^{2-} (reactions 4-5~4-7). This situation corresponds to the formation of $(\frac{8}{7}S_1^{2-} + \frac{6}{7}S_8^{2-})$ from $2S_4^{2-}$ (reaction 4) Further electrochemical reduction of $\frac{6}{7}S_8^{2-}$ via the same pathway (i.e., reaction $2 \rightarrow 3 \rightarrow 4$) will result in a total of $14 e^-/S_8$ processes.

The intermediate polysulfide species generated during cycling are highly soluble in the electrolyte and can diffuse away from the cathode, where they undergo parasitic reactions at the metal anode. This process, known as the polysulfide shuttle effect, arises because reduced polysulfides at the anode migrate back to the cathode and are reoxidized at inappropriate stages of the charge–discharge cycle. Such shuttling, and more broadly the uncontrolled migration of polysulfides through the separator, results in irreversible sulfur loss, metal anode degradation, and a marked decline in charge–discharge capacity. Collectively, these effects compromise the energy efficiency, cycling stability, and self-discharge characteristics of metal–sulfur batteries.

Within LSBs based on conventional ether-based liquid electrolytes, during the discharge process, sulfur is converted into soluble LiPSs, (Li_2S_X , $4 \leq X \leq 8$) that dissolve in the electrolyte, resulting in the loss of active cathode material and reduced ionic conductivity.^[7] This leads to capacity fading, shortened cycle life, and lower charge/discharge rates. These dissolved polysulfides can migrate to the lithium anode, where they are reduced to insoluble Li_2S_2/Li_2S . While charging, these species are re-oxidized into soluble polysulfides that return to the cathode, creating a continuous shuttling effect. This shuttling is akin to an internal short circuit, contributing to self-discharge and reduced coulombic efficiency. The ongoing cycle of dissolution and precipitation ultimately causes active material loss and the formation of insulating layers on the electrodes, further degrading battery performance.

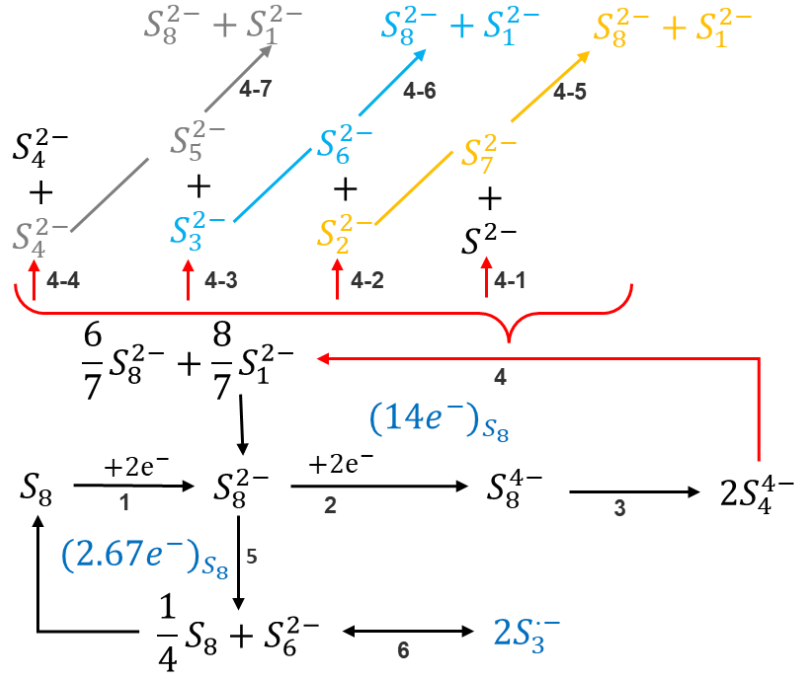


Figure 1.2. The mechanism of polysulfide conversion during the discharge process of LSBs.

1.2.2 Low electrical conductivity

Low electrical conductivity of sulfur (5×10^{-30} S/cm) and its discharge products Li_2S and Li_2S_2 (3.4×10^{-7} S/cm). The insulating sulfur and lithium sulfide formed during charging and discharging passivates the cathode surface, hindering the complete reaction of the active material. This reduces the utilization rate of the active material, thereby limiting the achievable discharge capacity. This effect is further exacerbated by the highly inhomogeneous nucleation and growth of S and Li_2S , leading to the formation of large precipitates that are never fully re-oxidized or re-reduced, resulting in additional capacity loss.^[8]

1.2.3 The substantial volume changes

The substantial volume changes of sulfur during lithiation and delithiation cycles (ca. 80%) associated with the differences in density between sulfur (2.03 g/cm^3) and lithium sulfide (1.66 g/cm^3). When sulfur is fully lithiated to lithium sulfide, it undergoes a substantial volume expansion that induces mechanical stress. This large expansion rate can lead to mechanical stress and structural degradation of the electrode, further compromising the battery's stability and performance. At the same time, during delithiation, the decrease in volume may disconnect part of

the active material from the electronic transport framework. This detachment prevents those regions from participating further in the reaction, effectively reducing the overall capacity of the battery.

1.2.4 Solid electrolyte interphase (SEI)

Lithium metal readily reacts with the electrolyte at the solid electrolyte interface to form an ionically conductive but electronically insulating solid electrolyte interphase (SEI) film. This film consumes lithium and electrolyte that no longer participate in electrochemical reactions, and charge thus decreasing Coulombic efficiency. During cycling, the significant volume changes in the Li can fracture the SEI film, exposing fresh lithium metal. This unpassivated lithium continues to react with the electrolyte, further depleting lithium and electrolyte reserves, leading to reduced battery reversibility and efficiency over multiple charging cycles. Additionally, as the SEI layer thickens, battery impedance increases, reducing energy efficiency. The excessive consumption of electrolyte eventually leads to electrolyte depletion, which can result in irreversible damage to the battery.

1.2.5 Dendrite growth

Dendrite growth on lithium metal surfaces significantly undermines battery performance and safety. These dendrites disrupt the passivation layer, continuously consuming lithium and electrolyte. In severe cases, dendrites can puncture the separator and reach the cathode, leading to short circuits. This not only renders the battery inoperative but also poses a significant fire hazard. Figure 1.3 provides a summary of the key aspects of the electrochemical processes in LSBs.

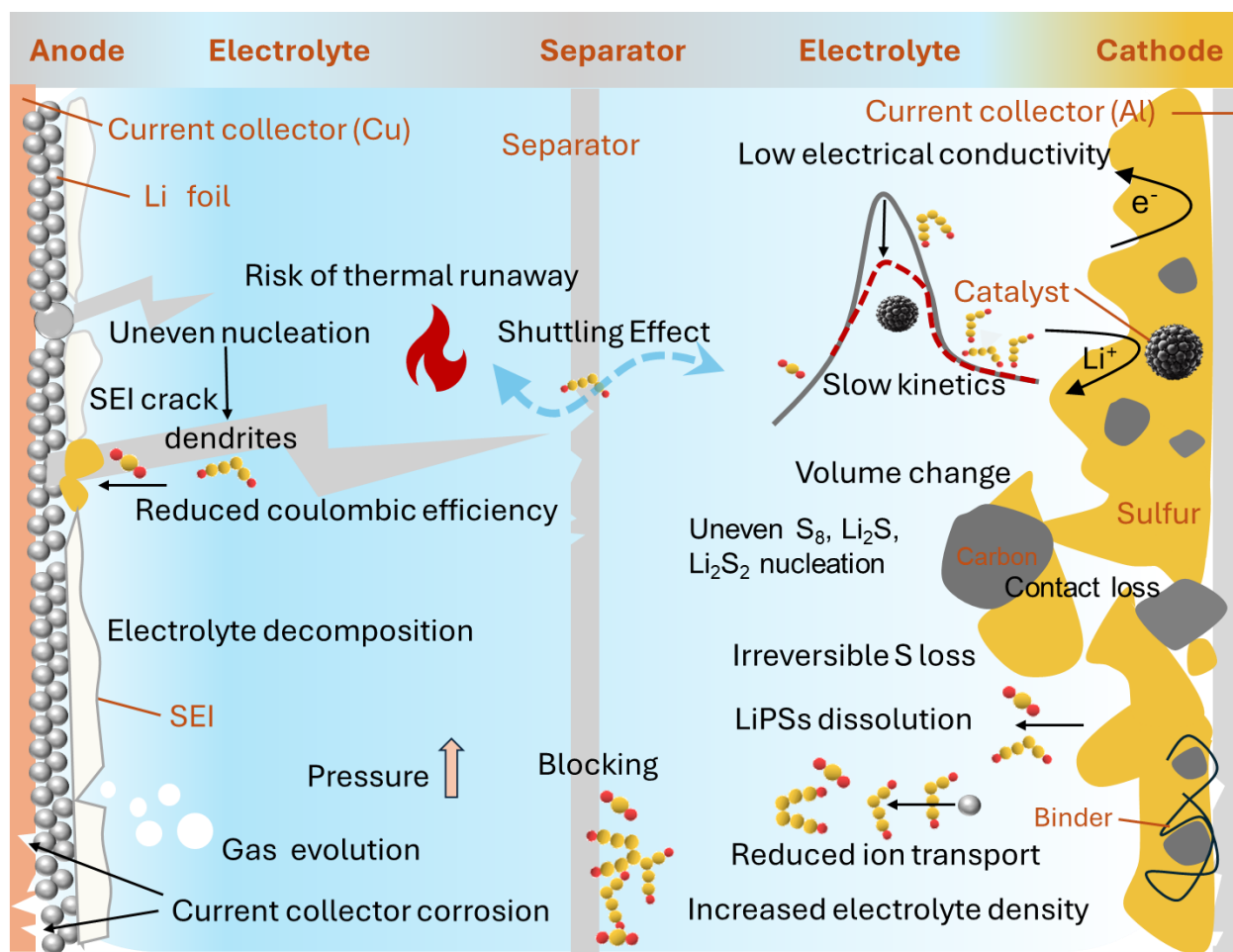


Figure 1.3. The figure illustrates various complex electrochemical processes, degradation mechanisms and structural and chemical transformations in sulfur-based batteries, using the example of the LSB.

1.3 Solutions

To suppress polysulfide migration, minimize self-discharge, enhance sulfur utilization, and support high-rate operation, particularly under the high sulfur loadings required for practical applications, highly active catalytic additives in the cathode or modification and optimization of the separator can be used to accelerate the SRR. This section discusses the principal strategies of separator modification and cathode catalyst additives investigated in this dissertation.

1.3.1 Separator modification

Traditional polyethylene (PE) or polypropylene (PP) separators are widely used in lithium-ion batteries but face limitations when applied to LSBs.^[9] These separators often suffer from poor compatibility with LiPSs, which are formed during the discharge process in LSBs. The dissolution and migration of LiPSs into the electrolyte leads to the "shuttle effect," a phenomenon that results in capacity loss, reduced cycling stability, and poor rate performance. This issue is exacerbated by the insulating nature of sulfur and its reaction products, which also hinder efficient electron and ion transport. Additionally, the high volumetric expansion of sulfur during cycling can lead to mechanical deformation of the separator, further compromising the battery's performance. As a result, modifying the separator to mitigate these issues is a critical area of research.^[10]

Several strategies have been explored to modify separators and improve the performance of LSBs. These modifications aim to enhance the ionic conductivity, suppress polysulfide dissolution, and ensure structural integrity during cycling.

One of the most common approaches to separator modification is coating or functionalizing the separator with materials that interact with LiPSs. Coatings such as carbon-based materials (e.g., graphene, CNTs) and metal oxides (e.g., TiO_2 , Al_2O_3) are particularly effective. These materials can adsorb or anchor LiPSs, preventing them from migrating to the anode and reducing the shuttle effect.^[11]

Graphene oxide, for example, has shown the ability to trap LiPSs through van der Waals interactions and chemical bonding, which helps retain sulfur within the cathode and improves the overall cycle stability. Additionally, the conductive nature of graphene enhances the overall ionic and electronic conductivity of the separator.^[12]

Another modification strategy involves the incorporation of functional polymers or ionic liquids into the separator. Polymers such as polyethylene oxide (PEO) or polyvinylidene fluoride (PVDF) have been used to form a composite layer that increases the wettability of the separator and enhances the ionic conductivity. These polymers can also act as a barrier to LiPS migration by forming a stable interface between the electrolyte and the separator.^[13]

Ionic liquids, with their high ionic conductivity and low volatility, have also been integrated into separator designs. Their ability to suppress polysulfide dissolution and enhance the stability of the electrolyte makes them attractive for improving the overall performance of LSBs.

The development of 3D structured separators has attracted significant attention due to their ability to provide high surface area, excellent mechanical strength, and enhanced ionic

conductivity. These separators can be fabricated by incorporating materials such as carbon nanotubes (CNTs), metal-organic frameworks (MOFs), or porous silica into the separator matrix. The 3D structures allow for better confinement of LiPSs and enhanced electrolyte retention, which improves the stability of the battery during cycling.^[14]

Composite separators, made by combining different materials with complementary properties, are also being investigated. For instance, combining a polymer matrix with carbon nanomaterials or metal oxides can create a separator that provides both structural integrity and effective interaction with LiPSs. This dual functionality enhances both the ionic conductivity and the suppression of the shuttle effect.

Separator modification has shown significant improvements in the performance of LSBs. By minimizing the shuttle effect, these modified separators help to stabilize the discharge/charge cycles, resulting in improved capacity retention and higher cycling stability. For example, separators with carbon-based coatings or polymeric layers can trap LiPSs more effectively, reducing their migration to the anode and leading to more stable long-term performance.

The incorporation of materials that enhance the conductivity of the separator also contributes to better rate performance, allowing LSBs to deliver higher power output while maintaining their efficiency over multiple cycles. Additionally, the use of separators with improved mechanical properties helps mitigate issues arising from sulfur's volumetric expansion, maintaining the structural integrity of the battery during cycling and extending the lifespan of the device.

While significant progress has been made in separator modification, further research is needed to develop more efficient and cost-effective solutions for LSBs. Some areas that warrant attention include scalability; optimization of interaction with LiPSs; and long-term durability.

Separator modification plays a pivotal role in overcoming some of the key limitations of lithium-sulfur batteries, particularly those related to the shuttle effect and cycling stability. By enhancing the interaction between the separator and the polysulfide intermediates, improving ionic conductivity, and ensuring mechanical integrity, modified separators contribute significantly to the performance of LSBs. Continued research in this area will be vital for the commercialization and widespread adoption of LSBs in energy storage technologies.

1.3.2 Cathode catalyst additives

The electrocatalytic activity of an electrode is governed by several key factors, including its charge and mass transport properties, the density of active sites, and its ability to facilitate electron transfer and effectively interact with the reactant species.⁵ Achieving efficient charge and mass transport requires the rational design and engineering of the electrode architecture, ensuring the presence of both continuous pathways for electron and ion transport and a large electrochemically active surface area. This typically involves creating structures with high porosity and extensive surface exposure. In metal–sulfur batteries, the incorporation of porous host materials, such as hollow nanospheres, nanowires, nanotubes, nanosheets, sandwich structures, monoatomic or diatomic catalyst materials,^[15] and metal-organic frameworks,^[16] has proven particularly effective. These structures not only enhance ion transport and active site accessibility but also offer physical confinement for the active material, improving sulfur utilization and stability. Furthermore, efficient charge transport also depends on the intrinsic structural and morphological properties of the electrode material. This can be further optimized through strategies such as lattice distortion, the introduction of structural defects, heteroatom doping,^[17] and the construction of heterostructures.^[18]

The ability of a catalyst to interact with reactants and facilitate electron transfer is a fundamental determinant of its intrinsic activity and overall efficiency. This capability is governed by the position and occupancy of the catalyst's electronic energy levels, which in turn influence the binding energies of reaction precursors, intermediates, and products.^[19] In a simplified framework, the most effective catalysts are those that exhibit intermediate adsorption strengths, strong enough to activate reactants but weak enough to allow facile desorption of products.^[20,21] To accelerate the identification of promising catalytic materials, this concept can be further reduced to a single electronic descriptor: the position of the d-band center relative to the Fermi level. This parameter has been widely adopted as a reliable predictor of catalytic activity, enabling the rapid screening of candidate materials.^[22,23]

Within this framework, efforts to optimize electrocatalytic reaction sites have focused primarily on modulating composition, atomic coordination, and local chemical environment to modulate the electronic energy levels and improve catalytic performance.^[24] In this context, the interactions between various TM-based compounds and polysulfides have been extensively studied, including systems based on carbides,^[25] phosphides,^[26] sulfides,^[27] nitrides,^[28] selenides,^[29] and tellurides.^[30]

Among the various catalyst design strategies, this dissertation focuses on two key approaches: vacancy induced spin modulation and single-atom engineering. The following sections provide a detailed discussion of each strategy.

1.3.2.1 Spin-modulated catalysts

In optimizing electrocatalytic reaction sites, significant efforts have been made to fine-tune composition, coordination, and chemical environment, aiming to achieve appropriate electronic energy levels. Despite its pivotal role in these processes, electron spin remains largely underexplored in the field of electrocatalysis.

Quantum mechanics has long established the profound impact of electron spin on molecular structures and the electronic and magnetic properties of materials.^[31] The Pauli exclusion principle dictates that two electrons occupying the same spatial eigenstate must have opposite spins, a rule that is fundamental to the formation of chemical bonds. Additionally, the interaction of electrons with nuclei, influenced by the electrons' intrinsic charge and angular momentum, is key in defining a material's electronic structure.^[32] The interaction between the electron spin and its orbital angular momentum also affects charge transport.^[33]

Electrochemical reactions are governed by three fundamental parameters, namely energy and occupation of the electronic energy levels and the angular momentum or spin.^[31] Following the Pauli exclusion principle, chemical reactions proceed through electron transfer between aligned energy levels only if reactants and products have the same spin state.^[34] Besides microwave irradiation, there are three main practical methods to modify the electron spin within a catalytic system (Figure 1.4): (i) through an external magnetic field; (ii) using chiral elements; and (iii) through modifying the coordination state of catalytic sites.^[35–37] Additionally, external or internal magnetic fields can affect charge transport within the electrode, and the charge and mass transport and ion concentrations within the electrolyte. Alternating magnetic fields can also increase the system temperature. Thus, the strategies used to optimize the electrochemical performance of batteries can be divided into three main groups: (1) those relying on the application of an external magnetic field to modify the catalyst or the electrolyte; (2) those based on the spin-engineering of the catalyst itself; and (3) the incorporation of spin filters such as chiral elements at the catalyst surface. As shown in the Figure 1.4.

In the field of LSBs, various innovative approaches have been recently proposed to tune the electronic structure and manipulate the spin of transition metal-based materials to improve the reactivity of polysulfides in SRR catalytic conversion, including tuning the catalyst coordination environment or applying an external magnetic field to the material.^[37,38] The electron spin can influence the catalyst surface electronic structure and charge distribution, which can alter the ion transfer ability, energy barrier, adsorption capacity, and stability of reaction intermediates, ultimately controlling the reaction rate and selectivity.

The use of external magnetic fields is a convenient strategy to fundamentally investigate the effect of spin state on electrochemical performance. However, the application of external magnetic fields to enhance the performance of batteries during operation is impractical owing to the additional cost, mass, and volume associated with the material or system used to generate the field. The integration of multifunctional/structural materials exhibiting hard ferromagnetic properties within the electrode or battery encapsulation could be a way around solving this limitation. Another potentially more practical solution to optimize the battery performance is through a proper design and engineering of the spin states within the electrode materials. This can be accomplished through a proper exchange coupling or spin pinning design. In this dissertation, we applied spin-engineering of the catalyst.

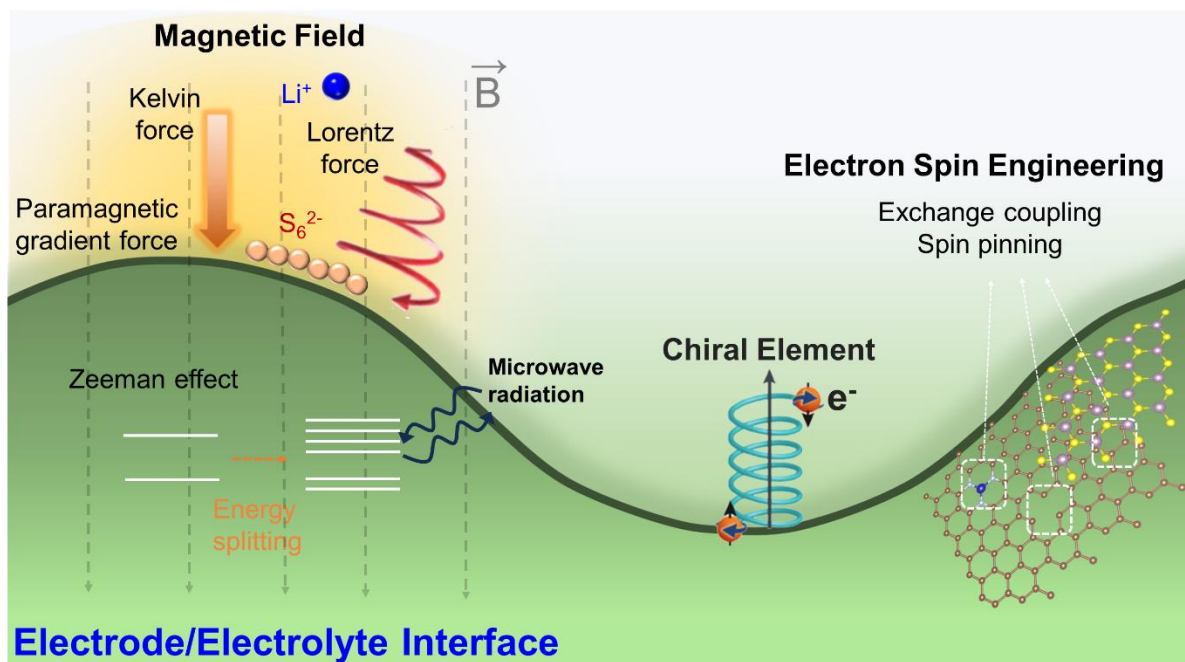


Figure 1.4. General scheme shows the influence of magnetic field on catalysis and additional strategies to modify electronic spins within the system. The scheme includes microwave irradiation, magnetic field effects at the electrolyte and electrode level, chiral elements for spin-selective charge transfer at the interface, and coordination design and engineering to tune electronic spin within the catalyst through exchange coupling and spin pinning.

1.3.2.2 Single-atom catalysts (SACs) and dual-atom catalysts (DACs)

Single-atom catalysts (SACs) have emerged as a revolutionary class of materials, offering remarkable opportunities to enhance the efficiency of electrochemical reactions, particularly in energy conversion and storage applications.^[39] By isolating individual metal atoms on a suitable support, SACs maximize the utilization of active metal centers, resulting in a theoretical catalytic site density of 100% active sites. This is in stark contrast to traditional nanoparticle catalysts, which often contain significant portions of inactive material that limit their catalytic efficiency.

The unique electronic structure of SACs—where the metal atoms are isolated and coordinated in a well-defined environment—imparts distinct chemical properties not found in bulk or nanoparticulate materials. These properties include high catalytic activity, selective reactivity, and enhanced stability, making SACs ideal for complex electrochemical processes. One such process is the SRR in LSBs, which is critical for efficient battery operation. The SRR faces high thermodynamic barriers and slow reaction kinetics, making SACs an attractive choice to improve the catalytic efficiency of this reaction.

Among SACs, TM-based catalysts, particularly those derived from 3d transition metals such as Mn, Fe, Co, Ni, Cu, and Zn, have garnered significant attention.^[40–42] These metals are not only abundant and cost-effective but also offer relatively low atomic weight, contributing to reduced material costs for large-scale applications. Additionally, their catalytic properties can be fine-tuned by modifying their electronic structure and coordination environment through the careful selection and engineering of support materials.

While SACs provide high catalytic efficiency, they are sometimes limited by the uniformity of their electronic structure and the inability to synergistically activate multiple reactants simultaneously. To address these limitations, dual-atom catalysts (DACs) have been developed as

a next-generation strategy. DACs consist of two adjacent metal atoms, either of the same or different elements, anchored on a suitable support. The interaction between the two metal centers introduces cooperative effects that can significantly modify the electronic structure, optimize adsorption energies, and facilitate multi-electron transfer reactions. These features allow DACs to surpass the activity of conventional SACs, particularly for complex reactions such as the SRR in LSBs, where multiple intermediate species are involved.^[43–46]

The exceptional catalytic activity of 3d TM SACs and DACs is attributed to their increased surface area and the enhanced electron density around the metal centers. These characteristics promote the activation of reactants and enable faster electron transfer, resulting in improved reaction rates and higher efficiency compared to traditional nanoparticle catalysts. Moreover, both SACs and DACs offer distinct advantages in terms of sustainability. By utilizing atomic-scale precision, they reduce the need for precious or rare metals, making them more economical and environmentally friendly. This is particularly crucial for large-scale electrochemical processes, where minimizing material usage is vital for both cost-effectiveness and environmental sustainability.

The application of SACs and DACs has already shown significant promise in various energy storage systems. For example, iron-based single-atom catalysts (Fe-SACs) and Fe-based dual-atom catalysts have been successfully applied in lithium-sulfur batteries, demonstrating improved catalytic activity and cycling stability.

While challenges remain in the precise synthesis and stabilization of SACs and DACs, significant progress has been made through the development of advanced support materials—such as carbon-based structures and metal-organic frameworks—and atomic-resolution characterization techniques. These advances enable more effective design and application of atomically precise catalysts in energy-related catalysis.

In summary, SACs and DACs offer a compelling strategy for enhancing the performance of LSBs. Their high atomic utilization, tunable electronic properties, and strong interfacial interactions make them ideal candidates for improving the efficiency and sustainability of energy storage technologies. With ongoing advancements in synthesis and characterization, these materials are poised to play a crucial role in the future of advanced energy storage and electrochemical catalysis.

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Chapter 2 Objectives

The overarching objective of this dissertation is to establish fundamental design principles for catalytic materials that enhance the electrochemical performance of LSBs through atomic-level engineering.

Overcoming sluggish kinetics of SRRs and the shuttle effect of soluble LiPSs requires a deep understanding of the catalytic mechanisms governing SRRs and the rational design of catalysts capable of accelerating the conversion reactions and stabilizing intermediate species. To address these challenges, this dissertation focuses on two main representatives (separator modification and cathode catalyst additives), covering three complementary material design strategies: heteroatom doping, vacancy engineering, and DACs design. Each approach aims to regulate the local electronic structure, spin configuration, and adsorption behavior of the catalytic active sites, thereby optimizing their interaction with sulfur species and improving the overall redox kinetics.

These strategies are selected to represent distinct yet complementary approaches to tuning the physicochemical and electronic structures of active sites at the atomic scale. The key objectives are as follows:

(1) To design and fabricate high-performance catalytic materials with controlled defect structures and atomic dispersion, enabling enhanced SRR kinetics, suppressed shuttle effect, and improved long-term cycling stability in LSBs.

(2) To investigate the catalytic mechanisms that govern sulfur redox reactions, including the adsorption, conversion, and stabilization of lithium polysulfides, using a combination of advanced characterization techniques (e.g., atomic-resolution (S)TEM, EELS, and *in situ/operando* analyses), advanced data analysis to obtain statistically meaningful characterization results and experimental atomic models of the element distribution and overall material structure down to the atomic scale, and finally theoretical simulations to further understand the catalytic redox mechanisms during the charge and discharge cycles.

(3) To elucidate the fundamental relationship between atomic structure and catalytic activity in sulfur cathodes by examining how engineered vacancies, dopants, and isolated metal atoms modify the electronic configuration, spin state, and local coordination environment of the active sites.

(4) To establish structure–property–performance correlations that provide scientific guidance for the rational design of next-generation sulfur cathode catalysts and extendable principles applicable to other electrochemical systems.

Through these objectives, this work seeks to bridge the gap between atomic scale understanding and macroscopic electrochemical performance. The insights obtained not only contribute to advancing lithium–sulfur battery technology but also offer broader implications for the design of catalytic materials in other redox-based energy conversion and storage systems, such as metal–air batteries and electrocatalysis. Ultimately, this dissertation aims to demonstrate how precise control over atomic structure can be leveraged to achieve sustainable, high-efficiency energy storage solutions.

Chapter 3 Experimental section

The experimental methods employed in this study are presented in detail within the corresponding chapters. This chapter primarily focuses on the synthesis methodology, characterization techniques used for the investigated synthesized materials, encompassing the analysis of their fundamental physical and chemical properties, electrochemical performance, *in situ/operando* electrochemical characterization of physicochemical processes, and theoretical simulation methods.

3.1 Chemicals and raw materials used in experiments.

Table 3.1. List of chemicals used in experiments (all acquired at Sigma Aldrich).

Chemical name	Chemical formula / abbreviation
Polyvinylidene fluoride	PVDF
N-methylpyrrolidone	NMP
Lithium bis(trifluoromethanesulfonyl)imide	LiTFSI
Lithium nitrate	LiNO ₃
Lithium sulfide	Li ₂ S
Cobalt(II) acetate monohydrate	Co(CH ₃ COO) ₂ ·H ₂ O/Co(AC) ₂ ·H ₂ O
Sodium selenite	Na ₂ SeO ₃
Ethylenediaminetetraacetic acid	EDTA
1,2-dimethoxyethane	DME
1,3-dioxolane	DOL
Chloroanilic acid	C ₆ Cl ₂ O ₂ (OH) ₂
Cobalt(II) chloride	CoCl ₂
Nickel(II) chloride	NiCl ₂
Hydrazine hydrate	N ₂ H ₄ ·H ₂ O
Selenium powder	Se

Iron(III) nitrate nonahydrate	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Manganese(II) nitrate tetrahydrate	$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
Cobalt(II) nitrate hexahydrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Bismuth(III) nitrate pentahydrate	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$
Nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Sulfuric acid	H_2SO_4

3.2 Materials characterization

3.2.1 Scanning electron microscopy (SEM)

SEM generates nanometer scale resolution images by scanning a sample with a focused electron beam, where the image is formed by correlating the beam's position with the intensity of the detected signals. The interaction between electrons and the sample produces various signals, including secondary electrons and backscattered electrons, which provide valuable insights into the sample's composition, morphology, and topography.

In this dissertation, SEM was primarily used to examine the size and morphology of the sample. The sample was dispersed in ethanol, followed by ultrasonic treatment to achieve uniform distribution. It was then placed onto a copper grid and metallized to enhance conductivity. Measurements were performed using a FEI Quanta 650F Environmental Scanning Electron Microscope (ESEM) and a FEI Magellan 400L XRSEM field-emission scanning electron microscope (FE-SEM).

3.2.2 (Scanning) Transmission electron microscopy ((S)TEM)

(S)TEM provides detailed insights into the morphology, structure, and chemical composition of materials and interfaces at atomic resolution, enabling both direct imaging and complementary spectroscopic analyses. In these techniques, a highly focused electron beam is accelerated to penetrate ultrathin specimens. As the electrons interact with the sample atoms, they scatter, producing deflections in their trajectory and giving rise to a solid-angle scattering

phenomenon. The scattering intensity is influenced by material parameters such as density, thickness, and atomic number, which in turn generate the bright and dark contrasts observed in the resulting images. After magnification and digital processing to enhance clarity, these images are displayed on an imaging system, allowing for high-resolution visualization of internal structural features. Maintaining sample integrity is critical, as the high vacuum, intense electron beam, strong electric fields, and other extreme conditions within the microscope can induce structural modifications or damage. These imaging capabilities provide the foundation for the application of advanced analytical techniques such as geometric phase analysis (GPA), energy-dispersive x-ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS), enabling comprehensive characterization of structural and chemical information from the nanoscale to the atomic scale.

GPA is a quantitative analytic algorithm that can be applied to high-resolution (S)TEM images showing atomic columns. The algorithm evaluates phase variations corresponding to specific spatial frequencies in Fourier space. By analyzing these phase shifts, GPA enables the mapping of local lattice distortions, strain fields, and rotational variations at the nanoscale. Unlike conventional imaging, which provides primarily qualitative information, GPA translates subtle differences in atomic arrangements into precise, measurable quantities, facilitating a detailed understanding of material deformation, defects, and interfacial phenomena. Practically, GPA involves selecting one or more Bragg reflections in the Fourier transform of a high-resolution image and tracking the spatially resolved phase variations associated with these reflections. These variations can be directly related to lattice strain, allowing the construction of high-resolution strain maps that reveal local heterogeneities, dislocations, and other crystallographic imperfections. GPA is non-destructive and highly precise, making it indispensable for studying advanced materials under operational or in-situ conditions and providing insight into how atomic-scale structural features influence macroscopic properties.

EDS is commonly integrated into (S)TEM for elemental identification and quantification. Its working principle can be described using the Bohr atomic model: incident high-energy electrons can excite inner-shell electrons, causing them to be ejected from the atom and creating vacancies. Electrons from higher energy levels then fill these vacancies, releasing energy either as X-ray photons or Auger electrons. The emitted X-ray photons are detected and analyzed; their energies correspond to the difference between the binding energies of the electron shells involved ($E_{\text{x-ray}} = E_{\text{inner}} - E_{\text{outer}}$). Because these energies are element-specific, EDS enables

straightforward qualitative elemental identification. Quantitative analysis is achieved by comparing the intensities of characteristic peaks, though low-Z elements are less efficiently detected due to the predominance of Auger emission.

EELS is another complementary technique that probes the inelastic scattering of electrons in (S)TEM, providing detailed chemical and electronic information. By measuring the energy lost by electrons as they interact with the sample, EELS can reveal elemental composition, bonding states, and electronic structures. Its sensitivity to subtle electronic transitions makes it particularly effective for analyzing light elements that are challenging to detect using X-ray-based methods. Moreover, features such as energy loss near-edge structure (ELNES) provide information on oxidation states and local electronic configurations, enabling atomic-scale investigation of chemical bonding and electronic properties, especially in complex oxides.

Atomic-resolution imaging in this study was performed using a Thermo Fisher Spectra 300 STEM, equipped with double aberration corrector system, a monochromator and usually operated at 300 kV within the present work. The instrument was also outfitted with a Super-X EDS detector for elemental analysis. For EELS analyses there is a GATAN Continuum K3 detector with direct electron detection capabilities. Data processing and analysis were conducted using VELOX and Digital Micrograph software, enabling quantitative evaluation of structural and compositional features at the atomic scale.

3.2.3 X-ray diffraction (XRD)

XRD was employed to provide valuable information on the material crystal structure, phase composition, and crystallinity of materials. When X-rays interact with a crystalline sample, they are diffracted according to Bragg's law:

$$2d \sin \theta = k\lambda$$

where d is the interplanar spacing, θ is the diffraction angle, k is a constant, and λ is the X-ray wavelength.

In this dissertation, XRD was performed using a Bruker D8 Advance XRD system. The procedure involves placing the powder sample on a tray, which is then loaded into the instrument for testing. The test parameters are set with a scan range from 5° to 90° , a wavelength of $\lambda=0.154$ nm, and a scan speed of 5° per minute. The resulting diffraction pattern is compared with a standard

PDF (Powder Diffraction File) card to verify accurate sample preparation and proper phase identification using JADE and HighScore Plus software.

3.2.4 X-ray photoelectron spectroscopy (XPS)

XPS is a surface-sensitive analytical technique used to probe the elemental composition, chemical states, and electronic structure of materials. In this method, X-rays irradiate the sample, inducing the emission of photoelectrons from its surface. By measuring the kinetic energy of these emitted electrons, their binding energies can be determined, allowing for the identification of elements and the analysis of their chemical states.

In this study, measurements were performed using a state-of-the-art XPS and Ultraviolet Photoelectron Spectroscopy (UPS) system (SPECS PHOIBOS 150 hemispherical energy analyzer), which enables detailed chemical and electronic characterization of material surfaces. During testing, the vacuum was maintained below 5×10^{-9} Torr. Measurements were conducted with a Phi Genesis system equipped with a monochromated Al K α X-ray source. Fine analysis of the photoelectron peaks was carried out using XPS Casa software, with binding energies calibrated against the C 1s peak of adventitious carbon, set at 284.8 eV, to ensure accurate energy referencing.

3.2.5 X-ray adsorption spectroscopy (XAS)

XAS is used to probe the local atomic structure, oxidation state, and electronic environment of specific elements in a material. In XAS, a sample is irradiated with tunable X-rays, and the absorption of X-ray photons is measured as a function of energy. The resulting absorption spectrum is typically divided into two regions: the X-ray Absorption Near Edge Structure (XANES), which provides information on the oxidation state and electronic structure, and the Extended X-ray Absorption Fine Structure (EXAFS), which reveals local atomic coordination, bond lengths, and structural disorder.

All the XAS data were acquired at the CLAEISS beamline of CELLS-ALBA synchrotron light source.

In chapter 5, the XAFS data was processed according to the standard procedures using the Athena module implemented in the IFEFFIT software package. The EXAFS spectra were obtained

by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, the $\chi(k)$ data were Fourier transformed to real (R) space using Hanning windows ($dk = 1.0 \text{ \AA}^{-1}$) to separate the EXAFS contributions from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of the IFEFFIT software packages.

In chapter 6, Data processing for *ex situ* measured spectra of electrodes, including energy calibration and normalization, was performed Athena module DEMETER software package. Operando data of Co-edge and S K-edge were analyzed using original Python scripts utilizing the xtalarch library. EXAFS. Spectra were obtained by subtracting the background function from the overall absorption, normalizing the data with respect to the edge-jump step, and Fourier transforming the $\chi(k)$ data into real (R) space using Hanning windows ($dk = 1.0 \text{ \AA}^{-1}$). This process separated the contributions from different coordination shells. Standard 1st shell Fourier analysis. The fit of EXAFS data was performed with the ARTEMIS module of the DEMETER software package. To extract quantitative structural parameters such as interatomic distances, theoretical models were used to simulate the EXAFS signal was calculated using FEFF software implemented in the same package. Principal components analysis (PCA) for Co/CN and Co-Bi/CN operando datasets was performed within PyFitit software.^[1] The minimal number of principal components was selected to 2. The decision was made based on using scree plot, factor indicator function (IND), the embedded error function (IE), and the Vogt–Mizaikoff F-test. The multivariate curve resolution (MCR) approach was used to decompose the dataset described above into pure MCR components with the original Python script utilizing the pymcr library.

3.2.6 Raman spectroscopy

Raman Spectroscopy is a non-destructive technique used to investigate the vibrational, rotational, and other low-frequency modes of molecules, providing insights into a material's structural properties, chemical composition, and crystallinity. In Raman spectroscopy, a monochromatic laser irradiates the sample, and the inelastically scattered light is collected. The energy shift between the incident and scattered light corresponds to specific vibrational modes,

which can be analyzed to identify molecular structures, bonding characteristics, and material defects.

In this study, Raman measurements were performed using a Horiba LabRAM HR Evolution Raman microscope equipped with a 500 nm laser. Multiple scans were conducted to improve signal-to-noise ratio, and the resulting spectra were analyzed to evaluate the structural features and defects of the samples.

3.2.7 Ultraviolet–visible spectroscopy (UV–Vis)

UV–Vis is a widely used analytical technique for investigating the electronic structure and optical properties of materials. It measures the absorption of ultraviolet and visible light by a sample, providing information on electronic transitions, the concentration of absorbing species, and chemical interactions.

In this study, UV–Vis measurements were performed using a Lambda 950 UV–Vis–NIR spectrophotometer (Perkin Elmer). Samples were prepared in DOL/DME and measured over a wavelength range of 200–800 nm. The absorption spectra were recorded and analyzed to investigate the presence of polysulfides, catalyst–sulfur interactions, and adsorption performance of electrode materials toward polysulfides.

3.2.8 Specific surface area and pore size analysis

Brunauer–Emmett–Teller (BET) analysis is a widely used technique to determine the specific surface area and porosity of materials. It is based on the physical adsorption of gas molecules (commonly nitrogen) on the surface of a material and the analysis of adsorption–desorption isotherms. BET provides quantitative information on surface area, while pore size distribution and pore volume can be further analyzed using methods such as the Barrett–Joyner–Halenda (BJH) model.

To investigate the microstructure and performance of the composite materials, this study employed specific surface area measurements to accurately determine the materials' surface area and pore size distribution. This analysis is critical for understanding properties such as adsorption capacity, catalytic activity, and other related characteristics. N₂-physisorption measurements were

performed at liquid nitrogen temperature using a TriStar II 3020-Micromeritics instrument. 100 mg of sample were used for each measurement. Before the measurements, the samples were degassed under N₂ flow at 90 °C for 1 h and then at 250 °C for 5h in a FlowPrep 060-Micromeritics instrument. The Brunauer-Emmett-Teller (BET) method was used to calculate the BET surface area within a relative pressure (P/P₀) range of 0.05–0.3. The average pore size was calculated using the Barrett-Joyner-Halenda (BJH) method applied to the isotherm desorption branch. The total pore volume was obtained from the maximum adsorption value at P/P₀ = 0.997.

3.2.9 X-ray magnetic circular dichroism (XMCD)

XMCD is an element-specific technique that measures the difference in X-ray absorption between left- and right-circularly polarized X-rays under an applied magnetic field, providing quantitative information on spin and orbital magnetic moments, as well as the electronic states of specific elements. When a circularly polarized X-ray beam interacts with a magnetic material, the absorption depends on the relative orientation between the photon helicity and the sample magnetization.

The difference in absorption between left- (σ^-) and right- (σ^+) circularly polarized X-rays gives the XMCD signal:

$$\text{XMCD} = \mu^+ - \mu^-$$

where μ^+ and μ^- are the X-ray absorption coefficients for opposite helicities.

To investigate the magnetic properties of CoSe, XMCD measurements were performed at Beamline 29 BOREAS of the ALBA Synchrotron. In this study, the XMCD spectra at the Co L_{2,3} edges were collected under controlled magnetic field and temperature conditions. Analysis of these spectra allowed for a detailed understanding of the electronic and magnetic states of cobalt in CoSe, revealing insights into its magnetic behavior at the atomic scale.

3.2.10 Temperature-dependent magnetization measurement

Magnetization measurements were carried out to investigate the magnetic behavior of the samples as a function of temperature. These measurements provide insights into magnetic transitions, thermal evolution of magnetization, and magnetic ordering. All measurements were

performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS, from Institute of Materials Science of Barcelona, ICMA B's Scientific and Technical Services) under an applied magnetic field of 50 Oe for all samples.

3.2.11 Electron paramagnetic resonance (EPR) spectroscopy

EPR spectroscopy is a sensitive technique that detects and analyzes unpaired electrons in paramagnetic materials. It provides valuable information about the electronic structure, local environment, and interactions of unpaired spins, making it especially useful for studying transition-metal ions, radicals, and defects in materials.

In this study, EPR spectroscopy was employed to investigate unpaired electrons and paramagnetic centers in the samples. The EPR spectra were recorded using a Bruker EMX-plus 10/12 spectrometer at X-band, with a microwave frequency of approximately 9.8 GHz and microwave power of 2 mW. The center magnetic field was set to 3500 G, with a sweep width of 100 G, and the magnetic field was modulated at a frequency of 100 kHz with an amplitude of 1 G. The resulting spectra were analyzed to extract g-values, spin concentration, and details on the local electronic environment and coordination of paramagnetic centers in the material.

3.2.12 Inductively coupled plasma -optical emission spectroscopy (ICP-OES)

ICP-OES is a powerful and widely used technique for determining the elemental composition of materials. It involves the ionization of a sample in an argon plasma, followed by the measurement of emitted light from the resulting ions or atoms. This technique is highly sensitive, capable of analyzing a broad range of elements at trace concentrations.

In this dissertation, ICP-OES was employed to quantify the elemental composition of the samples. Measurements were conducted using an Agilent 5100 ICP-OES. The solid catalyst samples underwent a systematic digestion and dilution process. First, they were digested in aqua regia, producing a stock solution. A 0.2 mL aliquot of this solution was filtered and diluted with 9.8 mL of 2% HNO₃, achieving a 100-fold dilution relative to the original digest. The resulting solution was then introduced into the plasma, and the emitted light was analyzed to determine the

concentrations of various elements. Calibration standards were used to ensure the accuracy and precision of the results.

3.3 Electrochemical and catalytic characterization

3.3.1 LSBs assembly

The cathode was prepared by mixing the electrode material, Super P, and PVDF binder in a weight ratio of 8:1:1. The components were ground together, and NMP was added during the grinding process to form a slurry. This slurry was then evenly cast onto an aluminum foil current collector, followed by drying at 60°C for 12 hours. The dried electrode was subsequently punched into 12 mm circular pieces to obtain the working electrode, with a sulfur loading content of approximately 1-1.2 mg cm⁻². To explore higher sulfur loadings, a high-loading cathode was prepared using the same procedure.

For electrochemical testing, the sulfur electrode was used as the cathode, lithium foil as the anode, and Celgard 2400 as the separator. The electrolyte consisted of 1.0 M LiTFSI and 0.1 M LiNO₃ dissolved in a 1:1 mixture of DOL/DME. A 2032-coin cell was assembled in an argon-filled glove box, with the electrolyte volume adjusted according to the test requirements.

The prepared battery was then subjected to a series of electrochemical tests.

3.3.2 Cyclic voltammetry (CV)

CV is a widely utilized electrochemical technique for probing the redox behavior of materials, offering valuable insights into their electrochemical properties, such as oxidation/reduction processes, stability, and reversibility. In this technique, a linear potential sweep is applied to the working electrode, and the resulting current is measured. The current-voltage (I-V) curve, or voltammogram, provides detailed information about the electrochemical processes occurring at the electrode surface.

In this dissertation, CV was employed to investigate the electrochemical behavior of LSBs within a voltage window of 1.7 to 2.8 V. This range was specifically chosen to encompass the critical redox reactions of sulfur, including the reduction of sulfur to lithium polysulfides (Li₂S_x) during discharge and the oxidation of polysulfides back to sulfur during charge. The CV

measurements were conducted to evaluate key electrochemical parameters, such as the reversibility, kinetics, and stability of the cathode material. The resulting data provide insights into the charge-discharge mechanisms and the overall electrochemical performance of the LSBs.

3.3.3. Galvanostatic charge–discharge (GCD)

GCD is a widely used electrochemical technique for evaluating the performance and efficiency of energy storage devices, including batteries and supercapacitors. In this method, a constant current is applied to the working electrode during both the charge and discharge processes, while the resulting voltage changes are monitored over time. The obtained charge–discharge profiles provide critical information on capacity, rate capability, energy efficiency, and cycling stability of the material or device.

In this dissertation, the fabricated lithium-sulfur batteries were rested for 3 hours prior to testing to ensure equilibrium. The rate capability and long-term cycling performance were evaluated using a NEWARE battery tester at a constant temperature of 25 °C. The tests were conducted within a voltage window of 1.7–2.8 V, capturing the key redox processes of sulfur and lithium polysulfides. The resulting data provide detailed insights into the discharge behavior, cycling stability at various current densities, and overall electrochemical performance of the LSBs.

3.3.4. Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a powerful technique used to probe the charge transport, interfacial properties, and kinetic processes in electrochemical systems. In EIS, a small-amplitude alternating current (AC) voltage is applied over a range of frequencies, and the resulting current response is measured. The frequency-dependent impedance provides detailed information on charge-transfer resistance, ion diffusion, double-layer capacitance, and other key electrochemical parameters. EIS is particularly useful for evaluating the conductivity, reaction kinetics, and interfacial behavior of electrodes and electrolytes in batteries and supercapacitors.

In this dissertation, EIS measurements were performed on the lithium-sulfur batteries using a CORRTTEST multichannel potentiostat/galvanostat over a frequency range of 100 kHz to 0.01 Hz with an AC amplitude of 5 mV. The resulting impedance spectra were fitted using an equivalent

circuit model to extract parameters such as solution resistance (R_s), charge-transfer resistance (R_{ct}), and Warburg impedance, providing insights into the charge transport and electrochemical kinetics of the cathode materials.

3.3.5 Synthesis of Li_2S_6 solution and adsorption test

A Li_2S_6 solution was prepared by dissolving S and Li_2S in a 5:1 molar ratio into a mixed solvent of 1,2-dimethoxyethane (DME) and 3-dioxolane (DOL) in a 1:1 v/v ratio. The mixture was then heated at 80°C overnight to obtain the Li_2S_6 solution. For the adsorption tests, 15 mg of each sulfur cathode host material was immersed in the Li_2S_6 solution and allowed to stand for 10 hours for the chapter 4, and 1.5 hours for chapter 5. During this period, color changes in the solution were observed, and UV-vis absorption spectra were measured to assess the interaction between the host materials and Li_2S_6 .

3.3.6 Symmetrical cells assembly and measurements

Symmetrical cells were fabricated using a similar method as for LSBs. Two identical electrodes were prepared by combining catalysts, SP, and PVDF in a weight ratio of 8:1:1, serving as the working and counter electrodes, respectively. $40\ \mu\text{L}$ of 0.5 M Li_2S_6 and 1 M lithium LiTFSI were dissolved in a 1:1 (v/v) mixture of DOL and DME as the electrolyte. The loading mass of the electrode was about $0.5\ \text{mg cm}^{-2}$. The fabricated symmetric cells underwent testing using CV at various scan rates and within a confined testing voltage window.

3.3.7 Nucleation experimental test of Li_2S

The prepared sulfur cathode host material was initially dissolved in an ethanol solution. Subsequently, it was coated onto carbon paper, serving as the working electrode, while lithium disk acted as the counter electrode, a Celgard 2400 membrane as the separator. For the electrolyte, a solution consisting of 0.25 M Li_2S_8 with 1.0 M LiTFSI in tetraethylene glycol dimethyl ether solution was utilized as the catholyte, while a 1.0 M LiTFSI solution devoid of

Li₂S₈ served as the anolyte in chapter 5, while a 0.5 mM Li₂S₆ solution as the electrolyte in chapter 6.

The assembled coin cells were first discharged to 2.06 V at a constant current and then subjected to potentiostatic deposition at a voltage of 2.05 V.

3.3.8 Assembly of single-layer Li-S pouch cells

In chapter 5, the cathode and lithium anode were cut into 4×3 cm pieces. The sulfur loading of the cathode in the pouch cell was 1.8 mg cm⁻². The E/S ratio was about 20 μL mg⁻¹, and the thickness of the lithium belt anode was 0.4 mm. The separator and electrolyte were sandwiched between the tailored v-CoSe /S and lithium belt.

In the chapter 6, single-sided lithium metal coated on copper foil (50 μm, from China Energy Lithium Co., Ltd) was punched into pieces with 58 mm × 45 mm to serve as the Li metal anodes. Each pouch cell was assembled by stacking one single-sided sulfur cathode (with a sulfur loading of ~1.85 mg cm⁻²), one layer of Celgard 2400 separator, and one lithium metal anode. The stack was welded with a tab and placed into an aluminum-laminated pouch cell case. Electrolyte was injected through the top opening of the pouch cell, with the amount adjusted to achieve an electrolyte-to-sulfur (E/S) ratio of 10 μL mg⁻¹. The pouch cell was then sealed under vacuum (-25 kPa) using a hot sealer (180 °C, MSK-115-III, MTI Corp.). All cell assembly and electrolyte injection steps were carried out inside an argon-filled glove box, with oxygen and moisture levels maintained below 0.1 ppm. The assembled Li-S pouch cells were initially cycled at 0.05 C, followed by cycling at 0.2 C using an Arbin battery testing system.

3.4 Operando characterization

Ex situ and post-mortem characterization methods, which analyze battery components outside their operational environment, offer detailed useful snapshots of battery components but fall short in capturing real-time dynamics and material/component interaction in real operation conditions. This limitation reduces not only the comprehensiveness but also potentially the accuracy of the results as side reactions during sample preparation can distort the structure-to-performance relationships, potentially leading to misleading conclusions. In this direction, sample

handling and specific instrument conditions may compromise sample integrity and introduce artifacts. *Ex situ* and *post-mortem* analyses require treating the sample to adapt it to the characterization technique. This preparation often involves exposure to atmospheres different from the battery's internal environment and processing steps such as washing or drying within an inert gas environment to remove residual surface electrolytes that could interfere with the analysis. Moreover, the operational environment of the characterization, often involving vacuum or specific conditions, can for instance alter or remove surface polysulfides through dissolution, further contributing to artifacts in the results.

To overcome these limitations, *in situ*, *quasi-operando* and *operando* techniques have emerged as powerful tools for real-time probing of dynamic processes. These techniques enable direct observation of electrochemical reactions and structural changes during battery operation with all interacting components, providing critical insights into the mechanisms driving the performance and degradation of sulfur-based batteries, insights that are essential for the rational development of next-generation battery technologies.^[2]

Operando specifically refers to real-time analysis of battery components during active operation, such as during charging and discharging cycles, providing direct observation of system behavior under actual working conditions. In contrast, *in situ* is a broader term that involves the analysis of components within their original operational environment, even when the system is not actively operating, allowing for pauses in the process of acquiring data.^[3]

Several *in situ* and *operando* characterization techniques have been employed to study the components and processes of sulfur-based batteries. Each *in situ/operando* technique has specific analytical requirements, along with distinct strengths and limitations. Therefore, selecting the most appropriate technique or a combination of techniques according to the research objectives is crucial for advancing the study of sulfur-based batteries, elucidating underlying mechanisms, and addressing technical challenges. In this dissertation, we mainly introduce two typical *operando* techniques: *operando* XRD and *operando* XAS.

3.4.1 Operando XRD

Operando XRD enables the real-time probing of crystalline solid phases in batteries, allowing for the monitoring of structural modifications that occur during battery operation under

conditions that closely mimic real-world functioning.^[4,5] This technique is sensitive to the formation of metastable intermediates and avoids the risks of sample alteration associated with *ex situ* measurements, making it widely used to study reaction mechanisms, as well as aging and failure processes in batteries.

The first reports on *operando* XRD on sulfur batteries helped establish a consensus on the main structural transformations occurring in LSBs. Nelson et al. reported the gradual dissolution of α -S₈, with the complete disappearance of crystalline sulfur at the end of the first discharge plateau, followed by its reappearance towards the end of charge.^[6] However, the observation of Li₂S remained elusive in these initial studies. Later *operando* studies by Cañas et al. and Walus et al. confirmed the formation of nanocrystalline Li₂S through the lower voltage plateau.^[4,7] The duration of the charge and discharge process during which crystalline S₈ and Li₂S can be observed varies across studies due to differences in experimental conditions and analytical techniques, as summarized by Zhang et al.^[8] Despite this, there is consensus that during charging, sulfur recrystallizes into the high-temperature monoclinic β -S₈ allotrope, which is kinetically favored over the thermodynamically stable α phase.^[9] In the subsequent cycles, sulfur continues to recrystallize in the β -S₈ form.

While XRD is *a priori* unsuitable for probing the formation of LiPSs due to their solubility, Conder et al. reported observing the evolution of two broad peaks related to high-order LiPSs, such as Li₂S₈ and Li₂S₆, when using glass fiber separator in which the fumed SiO₂ acts as a polysulfide scavenger.^[10] Additionally, Paoletta et al. identified crystalline Li₂S₂ as a transient species formed not as a reaction intermediate but through a disproportionation reaction from higher-order polysulfides under specific conditions, such as highly concentrated “solvent-in-salt” electrolytes.^[11] However, it has been experimentally proved, by synthetically making different Li₂S_n polysulfides, that α -S₈ and Li₂S are the only stable crystalline phases. *In situ* and *operando* XRD have also been employed to investigate the formation of crystalline deposits on the Li metal anode resulting from the shuttling of Li₂S_n species and electrolyte decomposition, and to study the benefits of strategies such as the use of polymer interfacial layers to prevent the electrolyte decomposition at the Li electrode.^[12]

In addition, catalysts are widely used in advanced cathodes to accelerate the redox reactions of sulfur. The evolution of the catalyst structure and the underlying catalysis mechanisms are critical aspects that can also be effectively monitored using *operando* XRD, providing valuable

insights into their role in enhancing battery performance. Both laboratory and synchrotron-based *operando* XRD have become widespread characterization techniques to investigate reaction mechanisms in catalytic cathodes. *Operando* XRD has also been employed to study various catalysts as well as catalyst optimization strategies like surface engineering and defect engineering,^[13] all aimed at promoting polysulfide conversion. Additionally, different nucleation behaviors were observed on open-hollow S decorated with MnO₂ nanosheets, leading to faster Li₂S and β -S₈ nucleation during discharge and charge processes.^[14]

In chapter 5, *operando* XRD patterns were acquired on a Bruker D8 Advance A25 diffractometer in a Debye-Scherrer configuration equipped with a Mo K α 1 radiation source ($\lambda = 0.7093$ Å) using a custom holed-designed 2032 coin cells with a 5 mm diameter hole drilled and equipped with a 75 μ m Kapton window. Diffraction patterns were measured upon continuous operation of the electrochemical cells between 8.5 and 13.5° with a step size of 0.02° and acquisition time of 60 min per pattern. The cells were cycled at C/25 rate with a Biologic SP-50 potentiostat in galvanostatic mode with potential limitation.

In chapter 6, *operando* XRD patterns were conducted at the MSPD beamline of CELLS-ALBA synchrotron light source to investigate the polysulfide conversion process under operating conditions. The experiments were performed under 29 keV using a CR2032 coin cell, which featured a 4 mm hole, purchased from KIT. Kapton film was applied to seal the holes in the negative and positive caps, preventing electrolyte evaporation and ensuring stable electrochemical operation throughout the measurement.

3.4.2 Operando XAS

Operando XAS allows for real-time monitoring of the geometric and electronic structures of materials during battery operation, providing crucial insight into chemical bonding, oxidation states, band structures, and local symmetries. This technique offers a detailed picture of the evolving state of materials under working conditions.^[15] As an element-specific technique, XAS is sensitive to the speciation of sulfur in both liquid and solid phases. One of XAS's key advantages lies in its particular sensitivity to sulfur oxidation states, as sulfur K-edge exhibits a substantial shift of around 6 eV between elemental sulfur and sulfate, allowing for clear discrimination between sulfur species at different stages of oxidation.^[16] Additionally, the shape of the sulfur edge

and pre-edge resonances is strongly influenced by the local symmetry of sulfur atoms in the compound, serving as a distinctive fingerprint for identifying individual sulfur compounds in complex mixtures. These capabilities make *operando* XAS an essential tool for elucidating the complex reaction mechanisms, failure pathways, and degradation processes in sulfur-based batteries, especially in tracking polyanionic intermediates during the solid-liquid and liquid-liquid conversion steps.

The sulfur K-edge falls in the tender X-ray energy range (2–5 keV), which does not strictly require vacuum conditions but does pose some challenges for *operando* cell design due to the limited penetration depth of X-rays at these energies. Thin windows made of lightweight elements are required, typically less than 8 μm thick for Be or Si_3N_4 , and less than 25 μm for Kapton. These windows are mounted either on modified coin cells (Figure 3.1a),^[17,18] pouch cells,^[19] or specially designed *operando* cells.^[20] At these tender X-ray energies, it is crucial to minimize absorption by other cell components, namely the contributions from the electrolyte can severely mask those from the sulfur on the electrode. Moreover, due to the low attenuation length, detection is generally limited to total fluorescence yield or total electron yield. An important obstacle in measurements done in fluorescence mode is that they can be heavily distorted by self-absorption effects, generally requiring diluted samples to avoid spectral distortions.^[5,10,19,21] On the other hand, by combining both total fluorescence yield and total electron yield detection modes a chemical depth profile of the electrode can be obtained, ranging from a few nanometers up to several microns, giving a surface and bulk information of the electrode speciation. Another challenge in sulfur K-edge XAS is radiation damage. Prolonged exposure to synchrotron X-rays can induce morphological changes in the sulfur particles, affecting the accuracy of the measurements.^[22] Therefore, experimental conditions must be carefully controlled to minimize such effects.

The first *in situ* XAS experiments on LSBs reported by Gao et al. took advantage of the low penetration depth of S K-edge X-ray radiation to probe the electrolyte phase and track variations in sulfur species across different electrolyte compositions.^[18] Later *operando* XAS studies performed in real-time upon battery operation on Li-S system reported by Cuisinier et al. employed sulfur K-edge XANES to follow semi-quantitatively the evolution of different sulfur species during the charge and discharge process (Figure 3.1b). By performing a linear combination fit of the XANES data and comparing it with reference spectra of elemental S_8 (2472 eV), Li_2S (2479 eV) and various linear polysulfides (S_x^{2-} with $2 < x < 6$) (2470 eV), they proposed a reaction

mechanism where elemental sulfur is rapidly formed and consumed at expenses of the transient species (S_6^{2-} and S_4^{2-}) at final and initial stages of charge and discharge, respectively. In contrast, Li_2S forms rapidly at the end of discharge but is slowly consumed during most of the charging process, revealing a hysteresis related to the different kinetics of dissolution and deposition in carbon-sulfur composite electrodes.^[23]

Highly time-resolved *operando* XAS studies conducted at various C-rates provided evidence for the multi-step, kinetic-determining conversion reactions, especially the transition from α - S_8 to long-chain soluble polysulfides.^[24] *Operando* XAS has also been used amongst other techniques to understand the differences in the reaction mechanism of Li_2S electrodes compared to S_8 electrodes.^[25] Moreover, it was used to understand self-discharge phenomena related to the spatial distribution of soluble species^[26] and to assess the various strategies aimed to overcome the current limitation of Li-S technology. These strategies include the selection of optimal electrolytes that minimize the dissolution of polysulfides,^[27,28] methods to reduce the shuttle effect by confining polysulfides using supporting matrices that covalently bond to sulfur,^[29] and the development of multifunctional polymer binders that mitigate shuttling.^[30,31] Further innovations explored using *operando* XAS involve modified separators designed to anchor the polysulfides^[32] and the use of electrocatalysts to reduce shuttling and facilitate the otherwise sluggish polysulfide conversion kinetics.

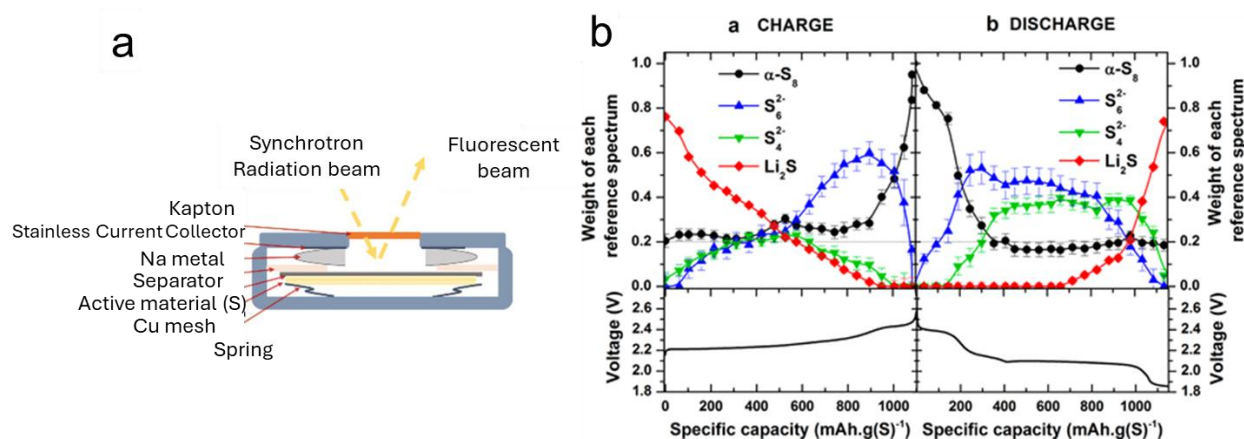


Figure 3.1. (a) Schematic illustration of an *operando* XAS coin cell used to measure S K-edge in fluorescence mode.^[33] (b) Evolution of *operando* sulfur K-edge XANES upon electrochemical cycling based on linear combination analysis.^[34]

In chapter 6, *operando* Co-K edge XAS measurements were conducted at the CLAEISS beamline of CELLS-ALBA synchrotron light source to investigate the electronic structure of Co under operating conditions. The experiments were performed in fluorescence mode using a CR2032 coin cell, which featured a 4 mm hole, purchased from KIT. To ensure full penetration of the X-ray beam and enable real-time monitoring of electrochemical reactions, three 4-mm diameter holes were precisely punched into the negative and positive caps, as well as the spacer. Additionally, Kapton film was applied to seal the holes in the negative and positive caps, preventing electrolyte evaporation and ensuring stable electrochemical operation throughout the measurement.

3.5 Theoretical simulations

Beyond the experimental findings obtained in the laboratory, a theoretical perspective is crucial for steering battery design strategies more effectively and unraveling the underlying mechanisms. All density functional theory (DFT) calculations were performed using the Vienna ab-initio simulation package (VASP). The Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correlation term was used with the projector augmented wave (PAW) potentials and a cutoff energy of 500 eV. The convergence of energy and forces were set to 1×10^{-5} eV and 0.05 eV/Å, respectively. The adsorption energy E_{ad} was calculated as:

$$E_{ad} = E_{(surf+ad)} - E_{surf} - E_{ad}$$

where $E_{(surf+ad)}$ is the energy of the LiPS adsorbed on the surface, E_{surf} is the energy of the clean surface, and E_{ad} is the energy of the free LiPS.

The formula for calculating the Gibbs free as follow:

$$\begin{aligned}\Delta G(S_8-Li_2S_8) &= E_{Li_2S_8} - E_{S_8} - 2E_{Li^+} \\ \Delta G(Li_2S_8-Li_2S_6) &= E_{Li_2S_6} - E_{Li_2S_8} + 0.25E_{S_8} \\ \Delta G(Li_2S_6-Li_2S_4) &= E_{Li_2S_4} - E_{Li_2S_6} + 0.25E_{S_8} \\ \Delta G(Li_2S_4-Li_2S_2) &= E_{Li_2S_2} - E_{Li_2S_4} + 0.25E_{S_8} \\ \Delta G(Li_2S_2-Li_2S) &= E_{Li_2S} - E_{Li_2S_2} + 0.125E_{S_8}\end{aligned}$$

3.6 References

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Chapter 4 Boosting polysulfide conversion on Fe-doped nickel diselenide towards robust lithium-sulfur batteries

4.1 Introduction

LSBs are widely regarded as one of the most promising next-generation energy storage technologies due to the abundance and low cost of sulfur as a cathode material, combined with its high theoretical specific capacity and energy density.^[1–6] Despite these advantages, the commercialization of LSBs is hindered by several challenges, including the insulating nature of both the charged (S_8) and discharged (Li_2S) cathode materials and sluggish Li-S reaction kinetics.^[7–9] These issues limit charge/discharge rates, reduce the utilization of active material, and impair cycling stability. These challenges are further compounded by active material loss due to LiPSs dissolution and inhomogeneous nucleation of solid phases.^[10–12] Furthermore, the migration of LiPSs to the anode causes corrosion and eventual battery failure.

To address the issue of poor electrical conductivity, carbon-based materials are commonly employed as sulfur hosts.^[13] Additionally, the incorporation of additives able to trap LiPSs while simultaneously accelerating their conversion is critical for mitigating their migration and enhancing LSB stability.^[14] These additives can be incorporated either into the cathode composite material or applied to the cathode side of the separator. The latter approach simplifies cell manufacturing while delivering comparable or even superior performance.^[8,9]

Extensive research has focused on developing efficient catalytic additives for LSBs, particularly those based on 3d transition metal oxides,^[2,15–17] nitrides,^[18–21] phosphides,^[22–24] and chalcogenides.^[25–29] Beyond compositional tuning, the performance of these materials can be significantly enhanced through approaches such as doping, heterostructure design, defect engineering, and morphology control to optimize electronic states and promote SRRs.^[30–32]

We, along with others, have demonstrated that generating unpaired spin electrons within Li-S catalysts is an effective strategy to enhance their performance.^[33–38] This phenomenon has been investigated using diverse approaches, such as the application of external magnetic fields,^[33] the design of heterostructures,^[35] and the introduction of atomic vacancies,^[34] particularly in Co-based catalysts. The enhanced catalytic activity arises from the increased adsorption of LiPSs, facilitated by the higher density of unpaired electrons generated at the 3d bands of Co.^[34] These unpaired

electrons not only strengthen the interaction with LiPS but also weaken the S–S bonds, thereby promoting their cleavage during the sulfur reduction reaction.^[33]

In this work, we present a significant advancement in this direction by extending the strategy to cost-effective Fe-Ni-based catalysts synthesized via a simple one-step solution process. Specifically, we report the synthesis of NiSe₂ and Fe-doped NiSe₂ particles, and their introduction as a coated layer on the cathode side of the LSB cell separator. Comprehensive experimental analyses, supported by DFT calculations, are used to explore the effects of Fe doping on the electronic structure, polysulfide affinity, and catalytic activity of NiSe₂, as well as their influence on the cycling stability and overall performance of LSB cells equipped with the modified separators.

4.2 Experimental methodology

4.2.1 Synthesis of NiSe₂

10 mL of hydrazine hydrate (N₂H₄·H₂O, 50-60%) was mixed with 4.4 mmol of selenium powder (Se, 99.5%, 100 mesh) in a beaker. This mixture was then ultrasonicated for 10 minutes, producing a homogeneous black solution. In a separate procedure, 2.2 mmol of nickel nitrate (Ni(NO₃)₂·6H₂O, 98%) was dissolved in 5 mL of deionized water (18.2 MΩ·cm). These two solutions were then combined and ultrasonicated for 30 minutes, resulting in a black suspension that was transferred to a Teflon-lined reaction vessel for hydrothermal treatment at 180°C for 24 hours. Then, the product was collected by centrifugation at 7000 rpm, washed four times with deionized water, and dried in a vacuum oven at 60°C for 12 hours, yielding black powder.

4.2.2 Synthesis of FeSe₂@NiSe₂

For the synthesis of FeSe₂@NiSe₂ particles, the same methodology was applied but included a combination of iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, ≥98%) and nickel nitrate in an atomic Fe/Ni ratio of 1/19. The remaining synthesis steps and conditions were kept identical.

4.2.3 Synthesis of S@Super P cathode

For the synthesis of S@Super P cathode, Super P was mixed with sulfur power with a weight ratio of 2:8. The mixture was then heated to 155°C overnight in a sealed glass bottle under argon. The redundant sulfur was removed by a 3 mL CS₂ and ethanol solution (1:4, volume ratio).

4.3 Results and discussion

4.3.1. FeSe₂@NiSe₂ characterization

NiSe₂ and Fe-modified NiSe₂ particles were synthesized using a one-step hydrothermal method, as illustrated in Figure 4.1a. Briefly, aqueous solutions of selenium, nickel, and eventually 5 at% of iron in hydrazine were mixed and hydrothermally processed at 180 °C for 16 hours in a sealed autoclave (details provided in the Experimental Section). The resulting particles exhibited a quasi-cubic morphology with an average size of 100±30 nm, as observed by SEM analysis (Figure 4.1a). The incorporation of iron did not significantly alter the particle morphology. XRD analysis confirmed the crystallographic phase of the powders as cubic NiSe₂ (JCPDS No. 96-153-7618, Figure 4.1b).^[39] A slight peak shift to higher diffraction angles, indicating lattice contraction, was observed upon the addition of iron.^[40–42] No additional peaks were obtained on the Fe-doped sample. EDS analysis showed the overall composition of the final material to match the nominal amounts of Fe and Ni introduced (Figure 4.2a).

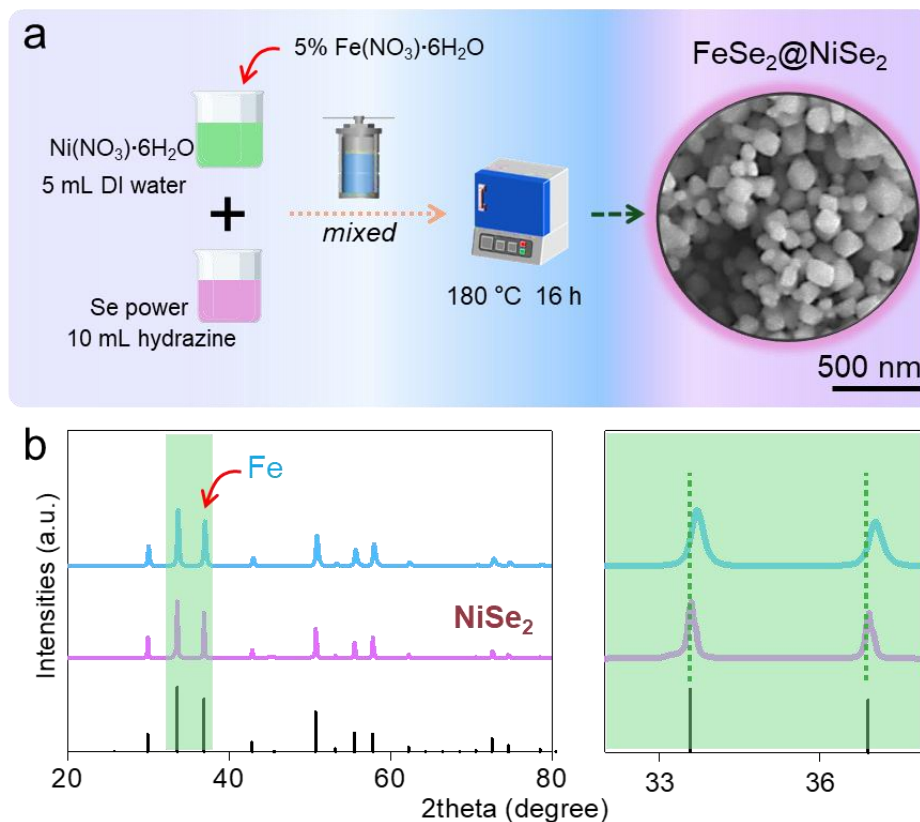


Figure 4.1. (a) Schematic representation of the FeSe₂@NiSe₂ synthetic procedure and SEM image of the obtained material. (b) XRD patterns of NiSe₂ and FeSe₂@NiSe₂ samples.

XPS provided further insights into the chemical environments of the elements (Figure 4.2b). The Ni 2p_{3/2} XPS spectrum displays main peaks at 852.7 eV and 855.1 eV, corresponding to Ni in Ni-Se and Ni-O environments, respectively.^[43–45] An additional satellite peak at 860.2 eV is also observed. The Se 3d spectra reveal two doublets, indicative of Se²⁻ in the Ni-Se lattice alongside a Se-O chemical environment. A small amount of Fe was detected at the surface of the particles. The Fe 2p_{3/2} spectrum exhibits peaks at 705.9 eV and 712.1 eV, associated with Fe-Se and Fe-O chemical states, respectively.^[42] The introduction of iron caused shifts to lower binding energies in both Ni 2p and Se 3d spectra, suggesting changes in the electronic environment of these elements. The oxygen-based chemical states of Ni, Fe, and Se are likely due to surface oxidation from air exposure during sample preparation for XPS analysis.^[46–48] These findings collectively confirm the successful incorporation of iron into the NiSe₂ lattice and highlight its influence on the material's structural and electronic properties.

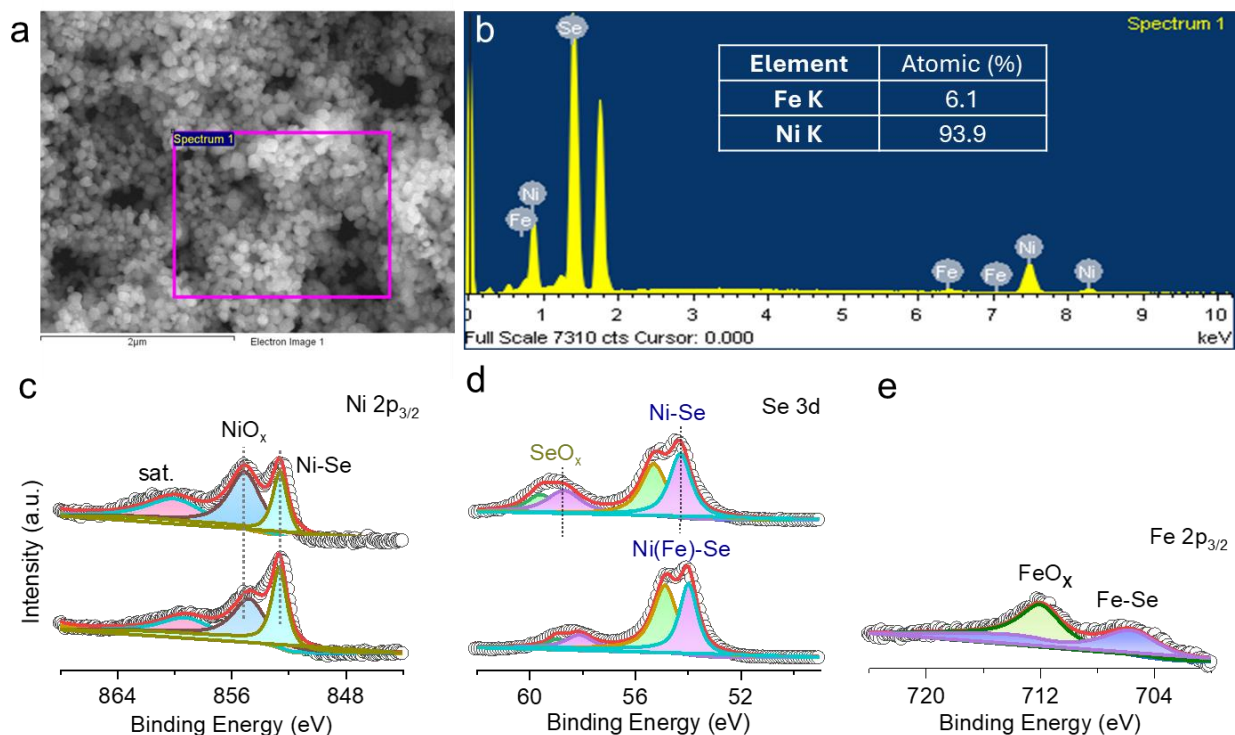


Figure 4.2. (a,b) SEM-EDS data of the FeSe₂@NiSe₂ particles. (c) Ni 2p_{3/2}; (d) Se 3d; and (e) Fe 2p_{3/2} XPS spectra of NiSe₂ and FeSe₂@NiSe₂.

Atomic resolution aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) analysis confirmed the quasi-cubic morphology and size of the particles (Figure 4.3a). EELS elemental mapping revealed a distinct core-shell architecture, with a Fe-rich core surrounded by a NiSe₂ shell (Figure 4.3b left and middle panels). Line scans illustrate the variation in metal ratios across two particles shown in Figure 4.3b right panel, while a more intuitive 2D elemental distribution is presented in Figure 4.3c. The core size and shell thickness are estimated at approximately 40 nm and 30 nm, respectively. Near the particle surface, the Ni ratio is close to 1, indicating a minor Fe concentration in the shell, and decreases to ~0.68 towards the core. Assuming all the Fe is concentrated within the particle core, the introduced Fe atomic ratio (Ni/Fe = 19) corresponds to a pure FeSe₂ core with an estimated size of approximately 37 nm within a 100 nm particle. This configuration would result in a calculated Ni concentration of approximately 0.63. These estimations are consistent with the

dimensions and Ni concentration observed in the electron microscopy analysis, suggesting that the core predominantly consists of FeSe₂ with minor Ni incorporation.

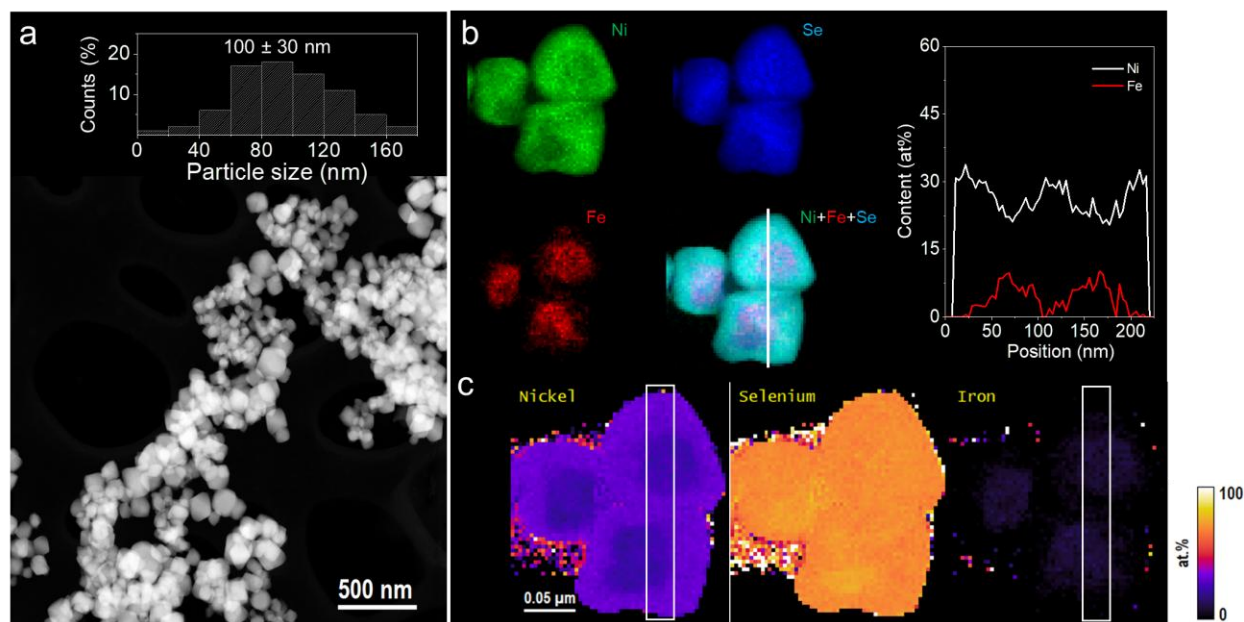


Figure 4.3. (a) AC-HAADF-STEM image of the FeSe₂@NiSe₂ core-shell nanoparticles and the corresponding particle size histogram. (b) EELS-STEM compositional maps (left and middle panel) and the corresponding line scan (right panel). (c) Element distribution in 2D form for the FeSe₂@NiSe₂ particles. Using the scale bar analysis marked on the right, the percentage of Se is depicted in orange, indicating the highest content. In contrast, the percentage of Ni is shown in purple, representing a lower content, particularly lower in the center of the particle. The Fe content is the lowest among the elements and is primarily concentrated in the center of the particle.

Detailed structural analysis of the cubic NiSe₂ phase, viewed along the [011] crystallographic axis (Figures 4.4a-c), revealed a BBABB (A = Ni, B = Se) atomic arrangement. Although selenium has a slightly higher atomic number, the Ni atomic columns appear brighter in HAADF images due to their higher density along the visualized atomic column. To investigate the influence of Fe doping on the crystal structure, geometric phase analysis (GPA) was performed on HAADF images viewed along the [100] crystallographic axis (Figures 4.4d-f). This analysis highlighted the presence of stacking faults, likely introduced by structural defects during crystal growth.

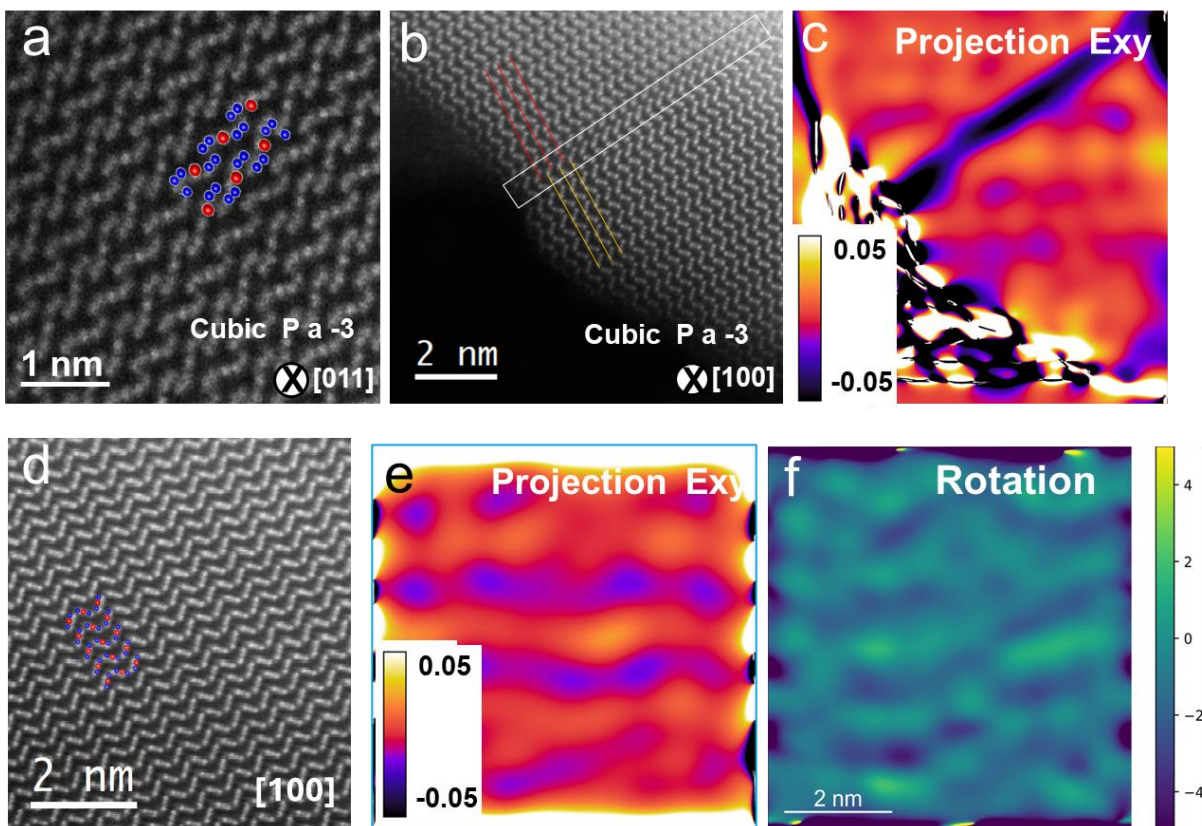


Figure 4.4. (a) AC-HAADF-STEM image along the [011] crystallographic axis showing the BBABB (A = Ni = red, B = Se = blue) atomic arrangement of the NiSe₂ shell crystal structure. (b) AC-HAADF-STEM image along the [100] crystallographic axis displaying a stacking fault, and (c) its corresponding GPA analysis. (d-f) AC-HAADF-STEM image and corresponding GPA analysis.

4.3.2 Adsorption and catalytic performance

Li₂S₄ adsorption experiments were conducted to assess the LiPS trapping capabilities of the NiSe₂ and FeSe₂@NiSe₂ particles. Equal amounts of each material were introduced into 5 mM Li₂S₆ solutions and left undisturbed overnight. A high-conductivity carbon material, Super P, was also tested as a reference. After the adsorption period, optical images (Figure 4.5a) revealed that the Li₂S₄ solution retained a deep orange color, while the solutions containing NiSe₂ and Super P exhibited a lighter yellowish color, and the solution containing FeSe₂@NiSe₂ was nearly transparent. Further evidence of the reduced LiPS concentration in solution was provided by UV-vis spectroscopy (Figure 4.5b). The characteristic absorption band of Li₂S₄, observed between 350

nm and 400 nm, was notably diminished in the presence of the adsorbent materials. Most prominently, the solution containing $\text{FeSe}_2@\text{NiSe}_2$ exhibited minimal UV-vis absorption peaks, indicating a strong adsorption capacity that effectively removed Li_2S_4 from the solution. These findings highlight the superior performance of $\text{FeSe}_2@\text{NiSe}_2$ in polysulfide adsorption, suggesting that the FeSe_2 core and Fe doping enhance the interaction of the NiSe_2 surface with polysulfides.^[49]

Figure 4.5c-e presents the Ni 2p, Se 3d, and Fe 2p XPS spectra of NiSe_2 and $\text{FeSe}_2@\text{NiSe}_2$ after the LiPS adsorption tests. The spectra for each element exhibit two distinct contributions: one corresponding to the lattice environment and another to a surface oxidized state. Notably, all the spectra show a slight shift following LiPS adsorption, as compared to the data in Figures 4.2c-e. This shift is attributed to the interaction between the catalyst's surface sites and Li_2S_4 , reorganizing electronic density.^[50]

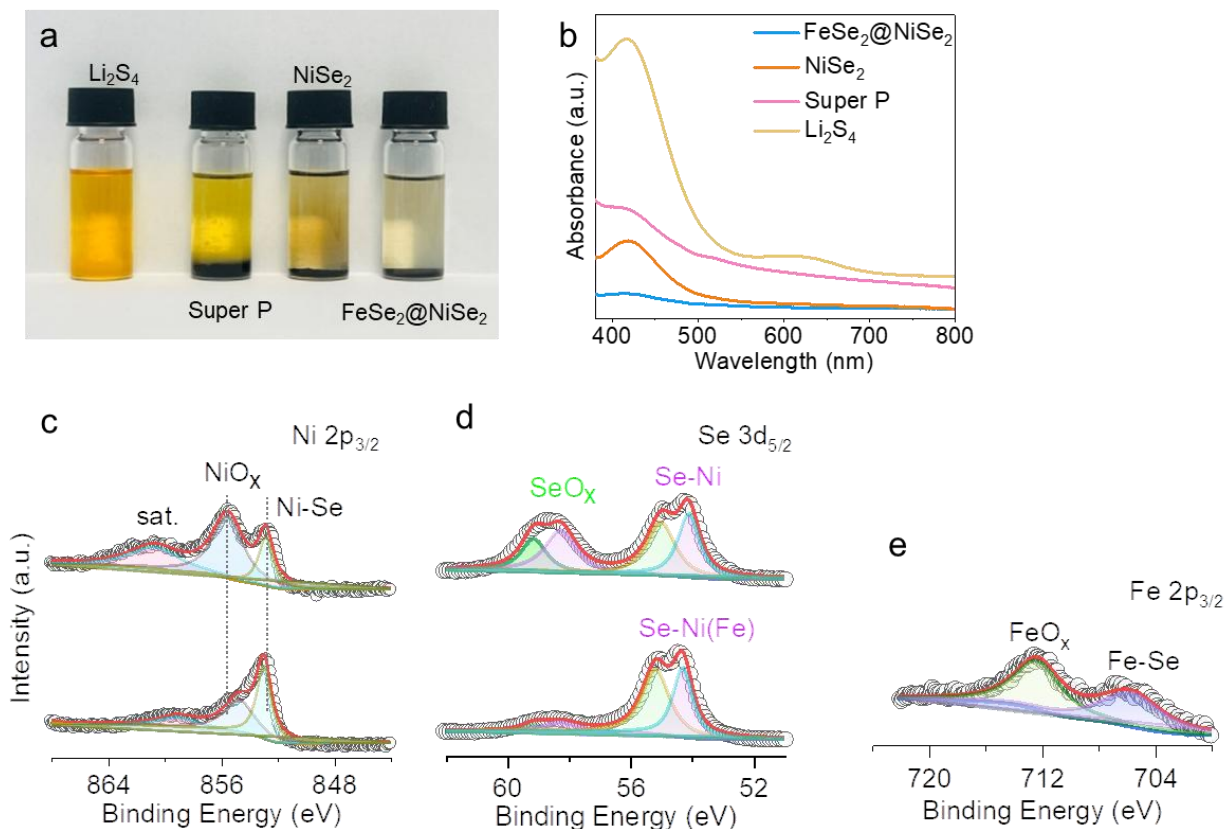


Figure 4.5. (a) Optical images of the polysulfide solutions after overnight interaction with different adsorbents. (b) UV-vis spectra of the polysulfide solutions after overnight interaction with

different adsorbents. (c-e) Ni 2p_{3/2}, Se 3d, and Fe 2p_{3/2} XPS spectra of NiSe₂ and FeSe₂@NiSe₂ after the LiPSs adsorption tests.

DFT calculations were used to analyze the electronic structure of the material and its influence on the interaction between the host materials and LiPSs.^[51–53] The presence of Fe introduces a large density of states (DOS) at the Fermi level (Figures 4.6a,b). Quantitatively, the d-band center of the FeSe₂@NiSe₂ is calculated to be at -0.556 eV, closer to the Fermi level compared to NiSe₂ (-1.035 eV). This shift increases the probability of electrons filling the antibonding orbital, thereby enhancing the adsorption of LiPSs and promoting the deposition of Li₂S.^[15,54] In parallel, the presence of Fe introduces a significant asymmetry in the electron spin configuration, as seen in Figures 4.6c,d, resulting in up to 24% increase in spin polarization at surface metal sites. Figures 4.7a,b further illustrates the enhanced density of unpaired electrons due to Fe incorporation and their localization. This result is corroborated by magnetization measurements at room temperature, which reveal that Fe addition significantly increases the material's magnetization (Figures 4.7c). This result is consistent with the weaker Ni satellite peaks observed in the XPS spectra of FeSe₂@NiSe₂ compared to NiSe₂ that also suggests higher magnetic susceptibility in the FeSe₂@NiSe₂ system (Figures 4.2c-e).

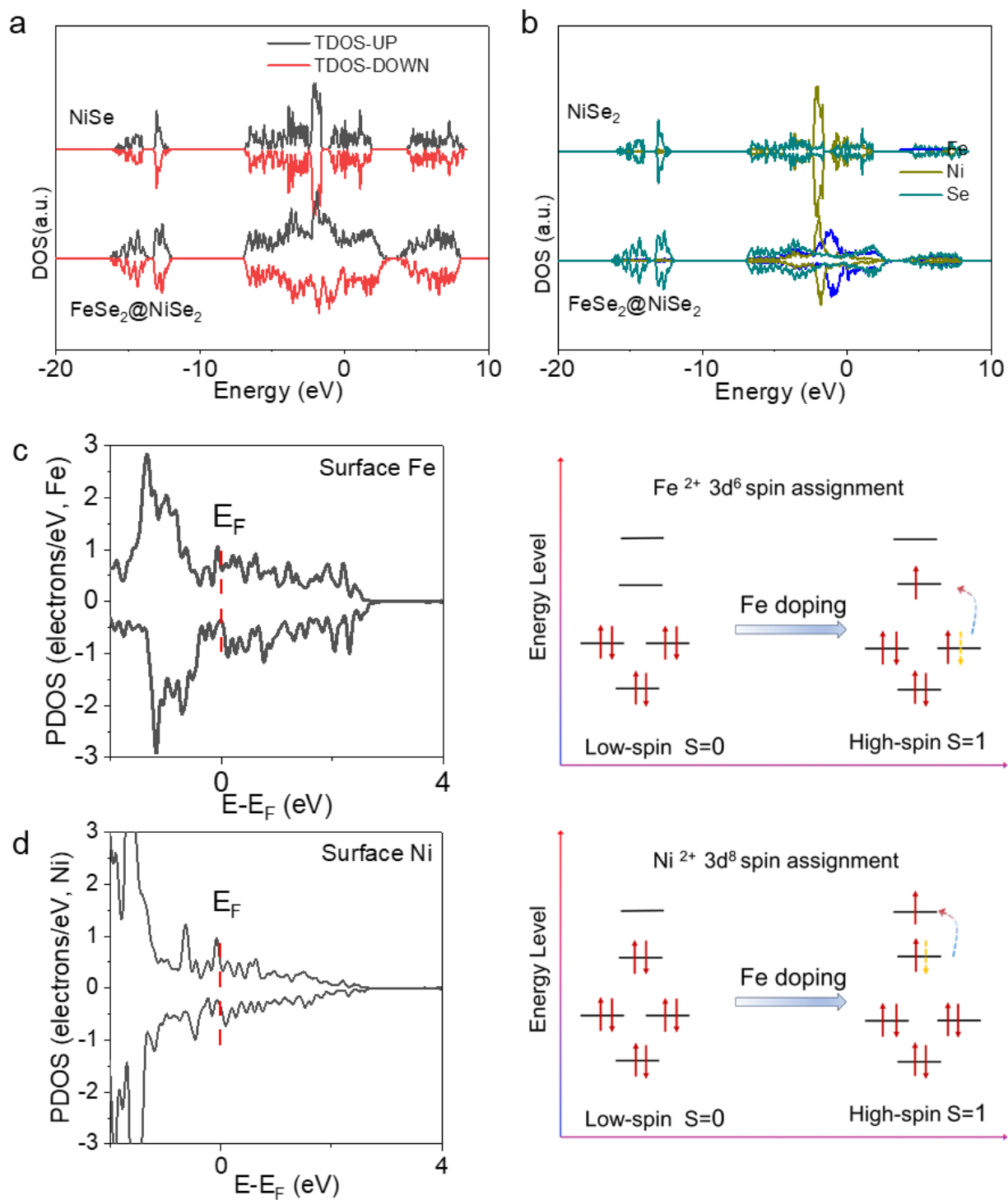


Figure 4.6. (a,b) DOS and PDOS of NiSe₂ and FeSe₂@NiSe₂. (c,d) Spin polarization for surface Fe and Ni.

Figures 4.7d,e shows the Li_2S_6 adsorption configuration on a pure NiSe_2 surface and a Fe-doped NiSe_2 surface grown over FeSe_2 . The DFT results revealed that the Li_2S , Li_2S_2 , Li_2S_4 , Li_2S_6 and Li_2S_8 binding energy on the $\text{FeSe}_2@\text{NiSe}_2$ is higher than that of NiSe_2 (Figures 4.7d-f). Specifically, the adsorption energies of Li_2S , Li_2S_2 , Li_2S_4 , Li_2S_6 and Li_2S_8 on $\text{FeSe}_2@\text{NiSe}_2$ were calculated at -0.393 eV, -0.859 eV, -1.344 eV, -0.279 eV, and -0.821 eV, which are significantly larger than the values obtained on the NiSe_2 surface (-0.119 eV, -0.686 eV, -0.871 eV, -0.252 eV, and -0.252 eV).

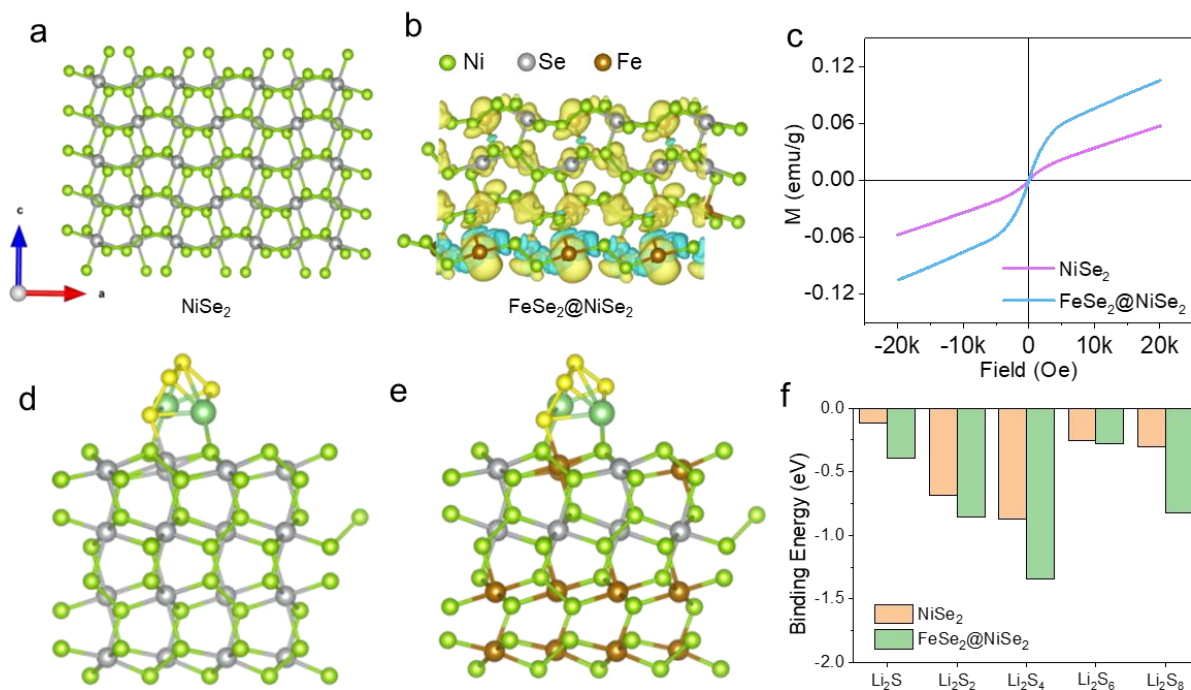


Figure 4.7. (a,b) Spin density of NiSe_2 and $\text{FeSe}_2@\text{NiSe}_2$. Yellow = spin-up and blue = spin-down. The isosurface level of spin density is 0.001 e/a_0^3 . (c) M-H curve of NiSe_2 and $\text{FeSe}_2@\text{NiSe}_2$ particles at room temperature. (d,f) Relaxed Li_2S_6 -adsorbed structures on the surface of NiSe_2 and $\text{FeSe}_2@\text{NiSe}_2$. Brown = Fe; Grey = Ni; Green = Se.

4.3.3. Electrocatalytic performance

To assess the electrocatalytic activity towards the conversion of polysulfides, symmetric cells containing 0.5 M Li_2S_6 electrolyte were assembled and tested using CV in the voltage range

of -1 to 1 V. As can be seen in Figure 4.8a, the symmetric cell based on FeSe₂@NiSe₂ electrodes exhibited larger current densities, indicating a higher electrochemical activity for the conversion of polysulfides.

Subsequently, coin-type cells based on a S@Super P cathode, a Li anode, and a polypropylene (PP) membrane coated with the NiSe₂ or FeSe₂@NiSe₂ catalyst at the cathode side as the separator were assembled and tested. Figure 4.8b shows the GCD profiles under a constant current of the NiSe₂/PP and FeSe₂@NiSe₂/PP cells and a reference cell with an uncoated PP separator, thus containing no catalyst. GCD profiles display one charge plateau and two distinct discharge plateaus. The first discharge plateau, from 2.4 to 2.1 V, yields a capacity Q₁, which corresponds to the reduction of S₈ to Li₂S₄ ($S_8 + 4Li^+ + 4e^- \rightarrow 2Li_2S_4$). The second discharge plateau, occurring between 2.1 and 1.7 V, yields capacity Q₂ and is associated with the reduction of Li₂S₄ to insoluble lithium sulfide ($2Li_2S_4 + 12Li^+ + 12e^- \rightarrow 8Li_2S$). As displayed in Figure 4.8b, the FeSe₂@NiSe₂/PP cell exhibited a discharge capacity of 1484 mAh g⁻¹, which is well above the capacities of the NiSe₂/PP cell at 1186 mAh g⁻¹ and that of the catalyst-free cell at 885 mAh g⁻¹.

The potential difference, ΔE, between the charge and discharge curves at 50% of the discharge capacity is commonly defined as the polarization potential of the LSBs.^[55–57] This metric provides a quantitative assessment of the LiPS conversion kinetics. The cell with the FeSe₂@NiSe₂/PP separator exhibited a reduced polarization voltage of ΔE = 150 mV, which is lower than that observed for cells with the NiSe₂/PP (ΔE = 160 mV) and PP (ΔE = 168 mV) separators (Figure 4.8c).

The electrocatalytic performance of the catalysts was further evaluated by analyzing the capacity ratio between the two reduction plateaus, Q₂/Q₁. Ideally, this ratio should approach 3, as Q₁ corresponds to a 4-electron reduction reaction and Q₂ to a 12-electron reduction reaction.^[58–60] However, in practical applications, lower Q₂/Q₁ ratios are commonly observed due to the incomplete reduction of Li₂S, often resulting in the formation of partially discharged Li₂S₂ products and the migration of LiPSs to the negative electrode. This reduces the active material available at the cathode. As shown in Figure 4.8c, cells with FeSe₂@NiSe₂/PP separators achieved an exceptionally high Q₂/Q₁ ratio of 2.6, surpassing those with NiSe₂/PP separators (2.4) and catalyst-free PP separators (2.1). These findings demonstrate that the presence of Fe significantly enhances the redox kinetics of the Li-S reaction.

To gain deeper insight into the electrochemical processes during battery cycling, the CV curves of the assembled cells are presented in Figure 4.8d. Each curve features a single oxidation peak (Peak III) and two reduction peaks (Peaks I and II), corresponding to the S to Li₂S conversion reactions, consistent with the charge-discharge profiles.^[61] A comparison of the two cells reveals that the one utilizing the FeSe₂@NiSe/PP separator exhibits the highest peak current density and the most pronounced onset potentials for both reduction and oxidation (Figures 4.8d–e). These observations align with the polarization voltage results, highlighting the superior electrocatalytic performance of the FeSe₂@NiSe₂/PP separator.

As the scan rate increases from 0.1 to 0.4 mV s⁻¹ (Figures 4.8f,g), the reduction peaks shift to more negative potentials, while the oxidation peak shifts to more positive potentials, reflecting an increase in polarization voltage. Notably, cells equipped with FeSe₂@NiSe₂/PP separators exhibit significantly higher current densities and reduced polarization voltage compared to their counterparts in the entire scan rate range. The linear relationship observed between the peak current and the square root of the scan rate indicates that the reactions are diffusion-controlled. This behavior allows the estimation of the lithium-ion (Li⁺) diffusion coefficient using the Randles–Ševčík equation:^[62]

$$I_p = (2.69 \times 10^5) n^{1.5} A D_{Li^+}^{0.5} C_{Li^+} v^{0.5}$$

where I_p is the peak current, n is the number of electrons transferred, A is the electrode's area, D_{Li^+} is the Li⁺ diffusion coefficient, C_{Li^+} is the Li⁺ concentration in the electrolyte, and v is the scan rate.

Figure 4.8f shows that cells with FeSe₂@NiSe₂/PP membranes have the steepest slopes across all three reaction peaks, indicating the highest Li⁺ diffusion rate. As shown in Figures 4.8h,i, for Peaks I, II, and III, the Li⁺ diffusion coefficients in FeSe₂@NiSe₂/PP cells are 7.2×10^{-7} , 2.5×10^{-7} , and 4.5×10^{-7} cm² s⁻¹, substantially higher than those for NiSe₂/PP cells (5.7×10^{-7} , 2.2×10^{-7} , and 4.0×10^{-7} cm² s⁻¹). These are related to the electrolyte viscosity, which increases with LiPS accumulation, and the formation of insulating Li₂S/Li₂S₂ layers on electrodes, both strongly affecting Li⁺ diffusivity.^[63] The higher diffusion coefficients observed in FeSe₂@NiSe₂/PP cells further confirm that iron presence enhances the Li-S reaction and effectively traps LiPS.

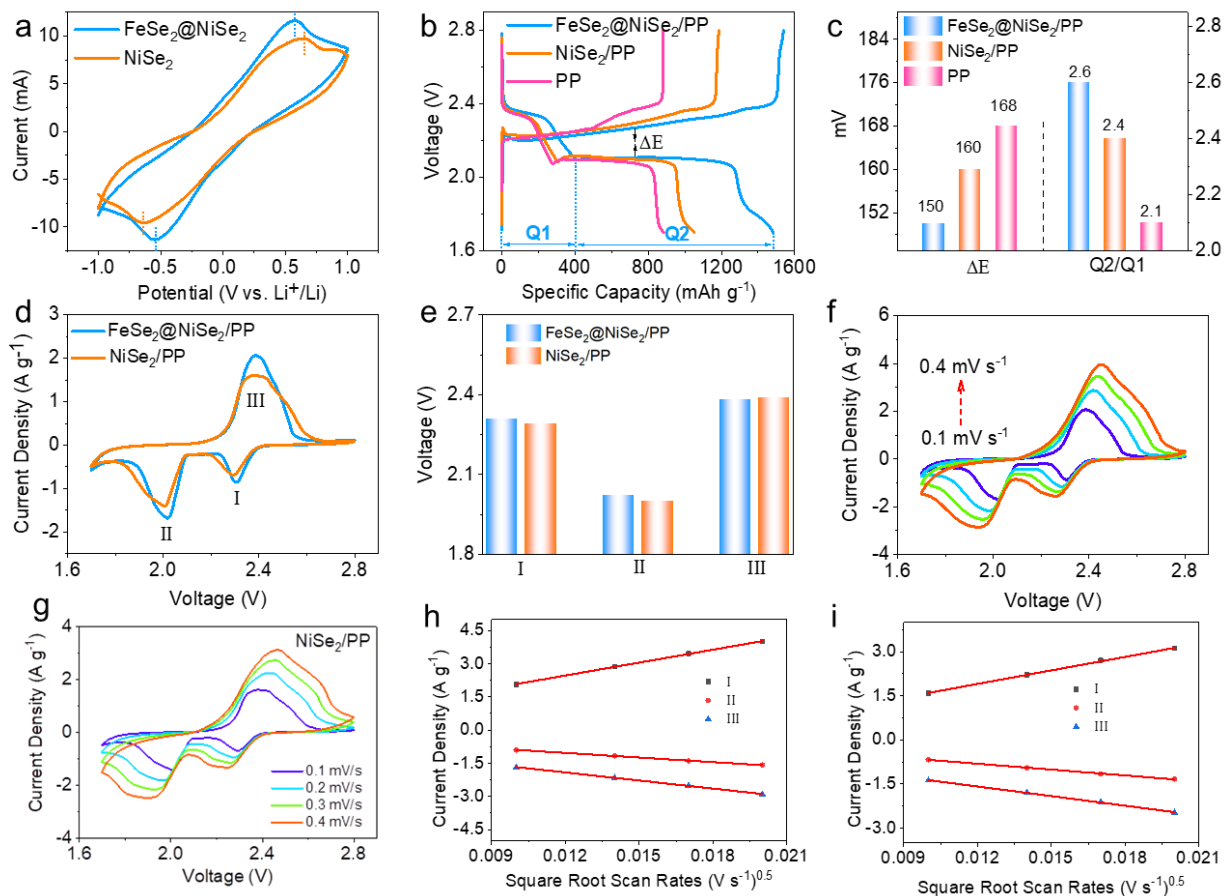


Figure 4.8. (a) CV profiles of symmetrical cells with NiSe₂ and FeSe₂@NiSe₂ electrodes using an electrolyte containing 0.5 M Li₂S₆ and 1 M LiTFSI dissolved in DOL/DME (v/v = 1/1). (b) GCD profiles of cells based on NiSe₂/PP or FeSe₂@NiSe₂/PP separators at the current rate of 0.1 C. (c) ΔE and Q₂/Q₁ values derived from GCD profiles. (d) CV profiles of Li-S coin cells with different separators. (e) Peak voltages obtained from CV curves with different separators. (f) CV curves of FeSe₂@NiSe₂/PP cells at various scan rates from 0.1 to 0.4 mV s⁻¹. (g) CV curves of NiSe₂-based battery at various scan rates from 0.1 to 0.4 mV s⁻¹. Linear fitting for the (h) FeSe₂@NiSe₂ and (i) NiSe₂-based battery between the current density and the square root of scan rates.

Li₂S deposition experiments were used as an additional quantitative measure of the catalytic activity of different active materials.^[57] In this case, FeSe₂@NiSe₂ and NiSe₂ were tested as electrode materials (see details in the SI). The FeSe₂@NiSe₂-based electrode exhibits a higher current response during constant potential polarization at 2.05 V, as shown in Figure 4.9g. According to Faraday's law ($Q = It$, where Q , I , and t represent capacity, discharge current, and

time, respectively),^[64] the deposition capacity of FeSe₂@NiSe₂ (165 mAh g⁻¹) is significantly larger than that of NiSe₂ (126 mAh g⁻¹). Thus, nucleation experiments also indicate that the Fe presence effectively reduces the reaction barrier for Li₂S nucleation, thereby promoting the complete conversion of LiPS.

DFT calculations were further used to compare the Gibbs free energy evolution of the sulfur reduction reaction on the surface of FeSe₂@NiSe₂ and NiSe₂. The optimized model and free energy distribution of polysulfide intermediates are shown in Figure 4.9h. The first step of the sulfur lithiation pathway is the reaction of two Li⁺ with S₈ to form Li₂S₈, followed by a subsequent reduction to Li₂S₆, Li₂S₄, Li₂S₂, and finally Li₂S. As can be seen from the first step, the formation of Li₂S₈ was enhanced with the presence of Fe. Besides, the energy barrier for the rate-limiting step, the conversion of Li₂S₂ to Li₂S was lower for FeSe₂@NiSe₂, at 1.66 eV, than for NiSe₂, at 1.76 eV.

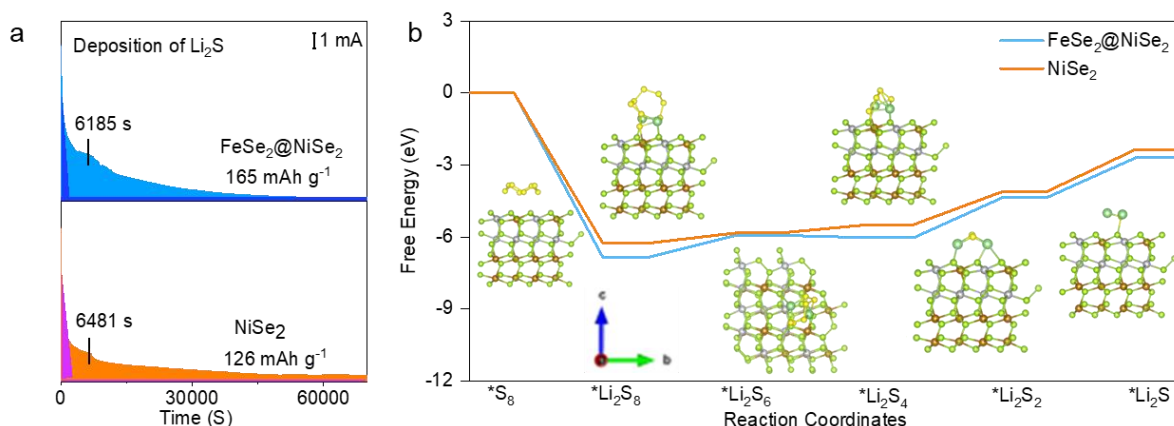


Figure 4.9. (a) Potentiostatic discharge profile of Li₂S nucleation at 2.05 V on different materials with Li₂S₈ catholyte. (b) Relative energy distribution of various reacting species along the reaction pathway on the NiSe₂ and FeSe₂@NiSe₂ surface.

Figure 4.10a displays the rate performance of cells based on FeSe₂@NiSe₂/PP and NiSe₂/PP separators in the current density range of 0.1C to 5C. FeSe₂@NiSe₂/PP cells consistently exhibit the highest discharge specific capacities. Notably, FeSe₂@NiSe₂/PP cells display a remarkable capacity of 1483 mAh g⁻¹ in the initial discharge at 0.1C and maintain a high specific capacity up 1154, 963, 880, 810, 754, and 624 mAh g⁻¹ at 0.2C, 0.5C, 1.0C, 2.0C, 3.0C, and 5.0C (Figure 4.10b), higher than that obtained from the NiSe₂ and catalyst-free cells (Figures 4.10c,d).

When the current rate is set to 0.2C again, the cell still delivers a substantial specific capacity of 1000 mAh g⁻¹, demonstrating excellent stability.

Figure 4.10e displays the cycling performance of different electrodes at a 1C current rate. The FeSe₂@NiSe₂/PP cell exhibits the highest capacity over continuous 800 cycles. Specifically, it has an initial discharge capacity of approximately 1085 mAh g⁻¹ at 1C, and it retains 84.4% of its initial capacity after 800 cycles. The decay in cycling performance is similar to the NiSe₂-based cell. Thus, we selected the FeSe₂@NiSe₂/PP multifunctional separator to assess its cycling performance at 3C. As shown in Figure 4.10g, after a few initial activation cycles at 0.1C, the FeSe₂@NiSe₂/PP cell delivers a discharge specific capacity of 1613 mAh g⁻¹, and even after 800 cycles, the specific capacity was found to be 495 mAh g⁻¹, corresponding to an average decay rate of 0.55% per cycle.

To achieve the high energy density needed for practical applications, increasing the sulfur loading is essential. Consequently, a series of electrochemical tests were performed on cells equipped with a FeSe₂@NiSe₂/PP membrane under high sulfur loading conditions (3.34 mg g⁻¹). Figure 4.10f displays the cycling performance, which demonstrates an initial discharge capacity of 940 mAh g⁻¹ at 0.1C, stabilizing after over 100 continuous cycles at 564 mAh g⁻¹.

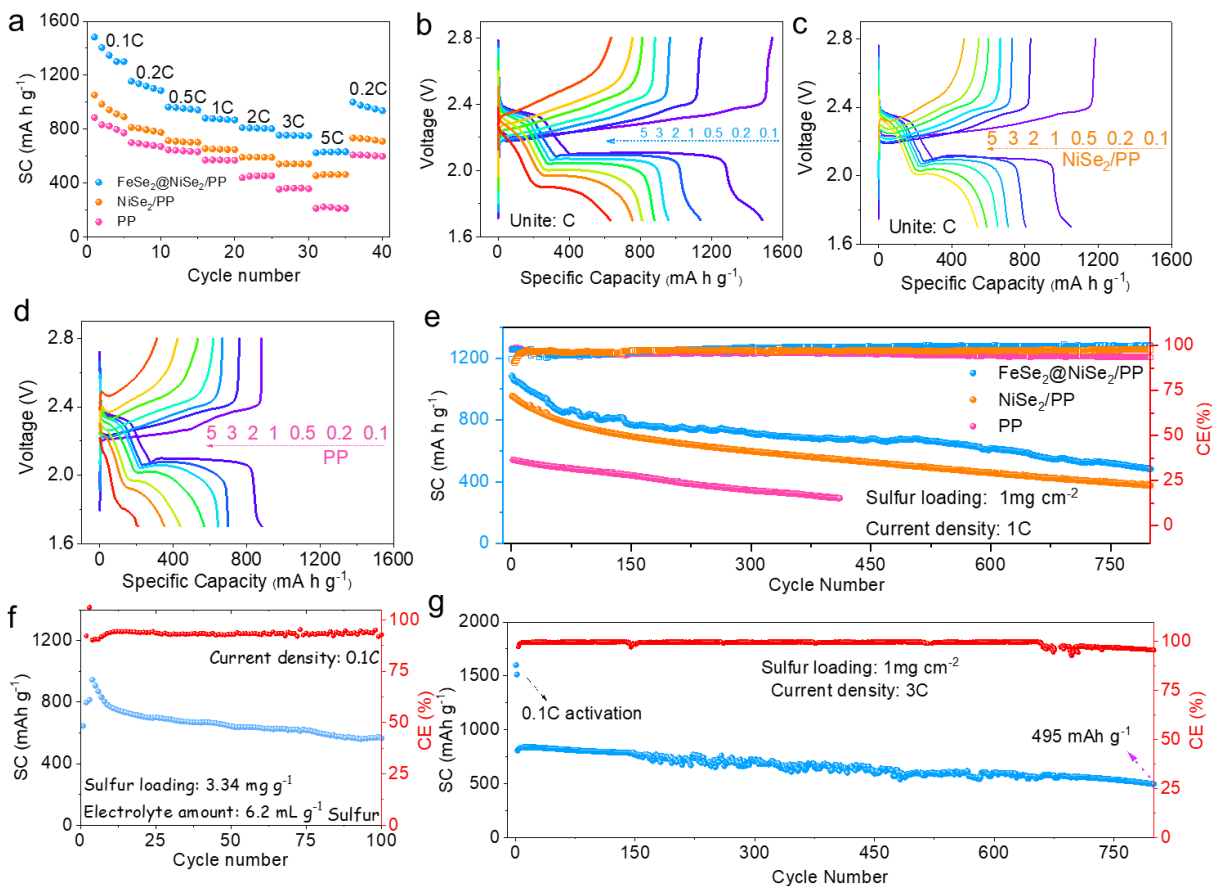


Figure 4.10. (a) Rate performances of PP, NiSe₂/PP, and FeSe₂@NiSe₂/PP cells. (b-d) GCD curves of (b) FeSe₂@NiSe₂/PP; (c) NiSe₂; (d) SP-based cells at current rates from 0.1 to 5C (e) Capacity retention of PP, NiSe₂/PP, and FeSe₂@NiSe₂/PP cells at 1C over 800 cycles. (f) Cycling stability of a FeSe₂@NiSe₂/PP cell with high sulfur loading and lean electrolyte conditions. (g) Cycling stability of FeSe₂@NiSe₂/PP cell at 3C over 800 cycles.

4.4 Conclusions

In summary, we successfully synthesized Fe-doped NiSe₂ particles containing a Fe-rich core via a one-step hydrothermal method and investigated their application as electrocatalysts on the cathode side of a PP separator in LSBs. Electrochemical performance tests demonstrated that FeSe₂@NiSe₂/PP cells achieved outstanding rate capabilities and cycling stability, with specific capacities of 1483 mAh g^{-1} at 0.1C and 1085 mAh g^{-1} at 1C. Remarkably, the cells retained 84.4%

of their capacity after 800 cycles, highlighting their long-term durability. Even under high sulfur loading, the electrode exhibited excellent capacities and stable cycling performance. DFT calculations revealed that the substantial DOS at the Fermi level, coupled with the additional unpaired electrons generated by the Fe-rich core and Fe doping on the NiSe₂ surface, significantly enhanced the binding affinity for LiPSs. This, in turn, facilitated efficient sulfur redox reactions, accelerating the Li-S reaction kinetics. The increased binding energies for LiPSs due to Fe doping were also confirmed, further validating its role in improving catalytic activity. This study highlights the potential of Fe-activated NiSe₂ particles as robust electrocatalysts for LSBs, offering a promising pathway toward the development of next-generation energy storage technologies.

4.5 References

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Chapter 5 Promoting polysulfide redox reactions through electronic spin manipulation

5.1 Introduction

LSBs are promising energy storage devices due to their high theoretical energy density, large specific capacity, potential cost-effectiveness, and environmental friendliness.^[1] However, the commercialization of LSBs is limited by factors such as polysulfide migration, sluggish kinetics of the SRRs, and poor electronic and ionic cathode conductivities.^[2]

While the introduction of porous carbon is crucial to promote mass and charge transport within the cathode, the use of catalytic additives is becoming essential to accelerate the SRR and thereby prevent sulfur loss through polysulfide migration. Notable research efforts have been devoted to developing catalysts able to promote the SRR kinetics.^[3] These catalytic materials have been tailored through the design and engineering of most of their parameters,^[4] including their composition,^[5] surface chemistry,^[6,7] architecture,^[8] interface,^[9] strain,^[10] and defects.^[11] Defect engineering, although not widely used in LSBs, is particularly straightforward and effective for adjusting the surface electronic structure of the catalyst. This adjustment allows for better control over the catalyst's activity and selectivity, as shown in many other relevant electrochemical reactions.^[12,13] In particular, vacancies can expose unsaturated coordination bonds as active sites to enhance the adsorption of relevant species and activate their reaction.^[14–16] At the same time, atomic vacancies can introduce additional free charges and may even facilitate ionic transport.^[17,18] While numerous examples of the potential of defect engineering to promote the performance of several catalytic reactions have been reported, the precise manipulation of the defect type, location, electronic state, and concentration still poses a formidable challenge. Besides, the mechanisms behind the defect-related performance improvement are not well understood, which limits the rational design of defect-engineered catalysts, particularly in the field of LSBs where this strategy is relatively novel.

Most previous work on defect engineering has focused on demonstrating that defects modify the electronic energy level position and occupancy, considering the carrier charge as the unique relevant parameter. Recently, the often overlooked electronic spin configuration of catalysts has emerged as a critical factor influencing their activity in electrocatalytic processes such as oxygen evolution.^[19,20] In the oxygen evolution reaction, the spin state strongly influences

the catalyst's electron transfer kinetics, the adsorption of intermediate species, and thus the overall activity.^[21] Various methodologies exist for manipulating the spin state of the catalyst. The simplest and most common one is the use of external magnetic fields to polarize the spins of ferromagnetic materials, which we have shown to strongly impact the performance of Li-S and Na-S batteries.^[22,23] Besides, external magnetic fields can also promote battery performance through magnetohydrodynamic effects.^[24] Despite the notable improvement in battery performance demonstrated in the lab, the application of external magnetic fields during battery operation is impractical in real-world applications. A more realistic solution to tune the electron spin state to promote the battery performance is the modification of the surface atomic coordination. Exchange interaction and spin states are closely intertwined with the atomic chemical environment which is determined by the crystal structure, atomic arrangement, and defects of the material. For instance, depending on the arrangement and coordination of d-orbital electrons, the spin state of transition metal cations, which is defined by the d-orbital electron spin configuration of the metal and its occupation, can vary between low-spin, intermediate-spin, and high-spin states. This spin state in turn determines the orbital interaction between the transition metal cation and the reactant.^[25]

The coordination environment of surface active sites can be modified through atomic doping,^[26,27] the formation of heterojunctions,^[28] changing the geometric configuration,^[29] topographically disordered design,^[30] or adjusting the stoichiometry.^[31,32] In particular, beyond affecting the charge carrier density and thus the charge transport properties of the material, the introduction of vacancies modifies the spin coupling within the catalyst, thus the number of unpaired electrons. This is reflected by a change in magnetic properties related to the exchange interaction and crystal field effects, which determines the splitting of the d orbital energy level that can impact the catalyst activity and selectivity.^[33–36]

Among the numerous SRR catalyst candidates, compared with other 3d transition metals, cobalt-based materials have generated particular interest due to their high electron density and large angular momentum of 3d electron orbit, enhancing its participation in electron transfer and the formation and breaking of chemical bonds.^[36,37] Thus, we selected CoSe as a catalytic material to showcase the effect of cation vacancies on the SRR activity. We analyze here how CoSe with cobalt vacancies undergoes spatial spin polarization while readjusting the surface electronic energy levels. This local spin rearrangement can activate the vacancy sites for effective chemical

adsorption and conversion, which results in faster and more uniform nucleation and growth of the SRR solid products. As a consequence, the introduction of cation vacancies can significantly improve the electrochemical performance of LSBs. Ultimately, we evaluate here the electron spin state as a fundamental parameter to take into account when designing advanced SRR catalysts and how this spin state can be effectively controlled through defect engineering.

5.2 Experimental methodology

5.2.1 Synthesis of CoSe

A facile hydrothermal synthesis approach was employed to produce CoSe nanosheets. Specifically, a solution containing 1 mmol of $\text{Co}(\text{AC})_2 \cdot \text{H}_2\text{O}$ and 1 mmol of Na_2SeO_3 in a mixed solvent (40 mL) with a volumetric ratio of ethylenediaminetetraacetic acid (EDTA) /deionized water set at 2:1 was prepared. Following 30 minutes of stirring, the resulting solution was transferred into a Teflon-lined autoclave, possessing a filling volume ratio of 80%. The autoclave was subsequently sealed and subjected to a thermal treatment at 180 °C for 16 hours, followed by natural cooling to room temperature. The resultant black floccules were collected, subjected to washing procedures involving distilled water and absolute ethanol to eliminate residual ions and impurities, and subsequently dried under vacuum at 60 °C overnight.

5.2.2 Synthesis of v-CoSe

Post-drying, plasma (radio frequency) etching was conducted on the synthesized material for a brief duration of irradiation time 1 minute (v1-CoSe), power (400 W, 50 kHz continuously variable power supply) and pressure (60 Pa) with plasma rotating vacuum plasma instrument (TS-VPR10). Additional samples were obtained extending the plasma etching time to durations of 2 minutes, and 3 minutes, denoted as v2-CoSe, and v3-CoSe, respectively.

5.2.3 Synthesis of v-CoSe/S

The synthesis process of v-CoSe/S involves three sequential steps. Firstly, the cathode host material, which comprises CoSe (or v-CoSe), is mixed with sulfur powder in a ratio of 1:3. Secondly, the mixture undergoes thorough grinding in a mortar and is subsequently subjected to

155°C for 12 hours. The resulting products, CoSe/S and v-CoSe/S, are then collected for further analysis.

5.2.4 Calculation of spin-state

We name the low spin ratio of Co^{2+} in CoSe as R^{2+}_{low} , and the high spin ratio of Co^{2+} in CoSe as R^{2+}_{high} , so we could propose the formula (1-2) below.

$$\text{In CoSe: } 1 \text{ muB} * R^{2+}_{\text{low}} + 3 \text{ muB} * R^{2+}_{\text{high}} = 1.7 \text{ muB} \quad (1)$$

$$\text{In v-CoSe: } 1 \text{ muB} * R^{2+}_{\text{low}} + 3 \text{ muB} * R^{2+}_{\text{high}} = 2.8 \text{ muB} \quad (2)$$

Thus, the $R^{2+}_{\text{low}} = 65\%$, $R^{2+}_{\text{high}} = 35\%$ in CoSe from formula (1), while $R^{2+}_{\text{low}} = 10\%$, $R^{2+}_{\text{high}} = 90\%$ in v-CoSe from formula (2).

To be more specific, in the case of v-CoSe, it is supposed to take into account the presence of 20% of Co^{3+} ions, which have the three potential spin configurations, low spin (0 muB), medium spin (2 muB), and high spin 4 (muB), then the calculation formula should apply the following formula (3):

$$80\% * (1 \text{ muB} * R^{2+}_{\text{low}} + 3 \text{ muB} * R^{2+}_{\text{high}}) + 20\% * (0 \text{ muB} * R^{3+}_{\text{low}} + 2 \text{ muB} * R^{3+}_{\text{med}} + 4 \text{ muB} * R^{3+}_{\text{high}}) = 2.8 \text{ muB} \quad (3)$$

In this scenario, since there are too many uncertain values, we assume two extreme cases which is if all Co^{3+} are with low spin ($R^{3+}_{\text{low}}=1$, $R^{3+}_{\text{med}}=0$, $R^{3+}_{\text{high}}=0$), then $R^{2+}_{\text{high}}=100\%$; Or all Co^{3+} are with high spin, ($R^{3+}_{\text{low}}=0$, $R^{3+}_{\text{med}}=0$, $R^{3+}_{\text{high}}=1$), then $R^{2+}_{\text{high}}=75\%$.

5.2.5 Thickness calculation

To calculate the thickness of the nanosheets composing our sample, we utilize low-loss EELS spectra. The thickness (t) is computed using the logarithmic-ratio formula (4).

$$t = \lambda \ln\left(\frac{I_t}{I_0}\right) \quad (4)$$

Where λ represents the inelastic mean free path, I_t denotes the total area under the low-loss EELS spectrum and I_0 is the area under the zero-loss peak. The logarithmic term is computed using DigitalMicrograph 3.0 software. We designate a specific region of the image and determine a value of 0.09 for this term.

To calculate the λ , we employ Equation (5) as proposed by T. Malis et al.^[38].

$$\lambda = \frac{106 F E_0}{E_m \ln\left(\frac{2\beta E_0}{E_m}\right)} \quad (5)$$

Where E_0 is the incident energy in keV, β is the collection semiangle mrad, Z is the effective atomic mass of our material and:

$$F = \frac{1 + \frac{E_0}{1022}}{\left(1 + \frac{E_0}{511}\right)^2} \quad (6)$$

$$E_m = 7.6 Z^{0.36} \quad (7)$$

The parameter values for our sample are presented in Table 5.1. Substituting these values into the equations yields $\lambda = 92$. Thus, utilizing Equation (4) and considering a 20% error in this calculation, we determine a thickness of 8.3 ± 1.6 nm.

Table 5.1. Values used for λ calculation.

E_0	β	Z
200 keV	15.1 mrad	30.5

5.3 Results and discussion

5.3.1 Vacancy characterization.

CoSe nanosheets extending several hundred nanometers and with a calculated thickness of 8.3 ± 1.6 nm (Figure 5.1) were produced by a facile hydrothermal synthesis approach (see details in the Experimental section). Cobalt vacancies were generated using plasma etching. The amount was tuned by adjusting the etching time (see details in the SI). The plasma etched samples were generally named as v-CoSe, and more specifically as v1-CoSe, v2-CoSe, v3-CoSe, and v10-CoSe, according to the plasma etching time used (1, 2, 3 minutes, respectively). XRD patterns of all the samples (Figure 5.2a) display the fingerprint of the hexagonal CoSe phase.^[39] v-CoSe samples that underwent a plasma etching time of 3 minutes or less do not show any additional peaks in the XRD pattern. Figure 5.2b displays the enlarged view of the main CoSe XRD peaks, showing a significant shift to higher 2θ values with the increase of etching time, corresponding to a reduction of the interplanar spacing. This reduction in the lattice parameters reflects the contraction of the

hexagonal CoSe lattice with the introduction of Co vacancies, which favors a partial transition to $\text{Co}_{0.875}\text{Se}$, and eventually to the cubic CoSe_2 lattice. Besides, as the density of vacancies increased, a more disordered crystal was generated, as observed in the increase of the full width at half-maximum (FWHM) of the XRD peaks.^[40] While we aimed at introducing a controlled density of vacancies to study their effect as potential active reaction sites,^[41] because excessive plasma etching resulted in a rearrangement of the remaining cations and anions to form a different phase, the cubic CoSe_2 phase, the v10-CoSe was not further considered in this study.

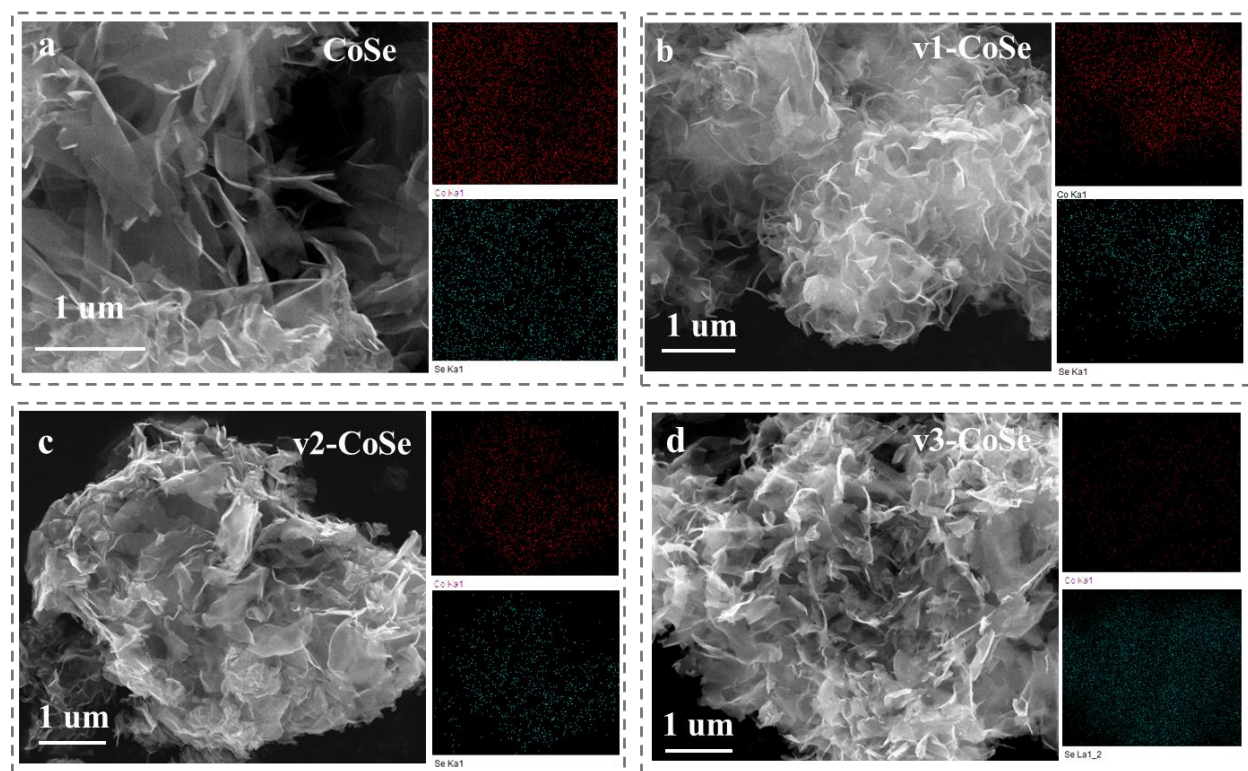


Figure 5.1. SEM images and EDS composition maps of (a) CoSe, (b) v1-CoSe, (c) v2-CoSe, (d) v3-CoSe. Red = Co; Blue = Se.

The characterization of the molecular bond vibrations by Raman spectroscopy was used to gain additional insight from the CoSe vacancies (Figure 5.2c). The sharp Raman peak at 187 cm^{-1} is related to the Se-Se bond vibration within CoSe.^[42] Besides, the signals at 167 cm^{-1} , 463 cm^{-1} , 510 cm^{-1} , 604 cm^{-1} , and 661 cm^{-1} are attributed to the CoSe $\text{F}_{2g}(1)$, E_g , $\text{F}_{2g}(2)$, $\text{F}_{2g}(3)$, and A_{1g} modes, respectively.^[43] The intensity of the CoSe A_{1g} at 661 cm^{-1} decreases with the plasma treatment time, which is associated with an increase in the cation disorder. Besides, the intensity

of the $F_{2g}(1)$ peak at 167 cm^{-1} decreased significantly to quasi-disappear, confirming the severe disorder of the Co ions within the v-CoSe lattice due to the large vacancy concentrations.

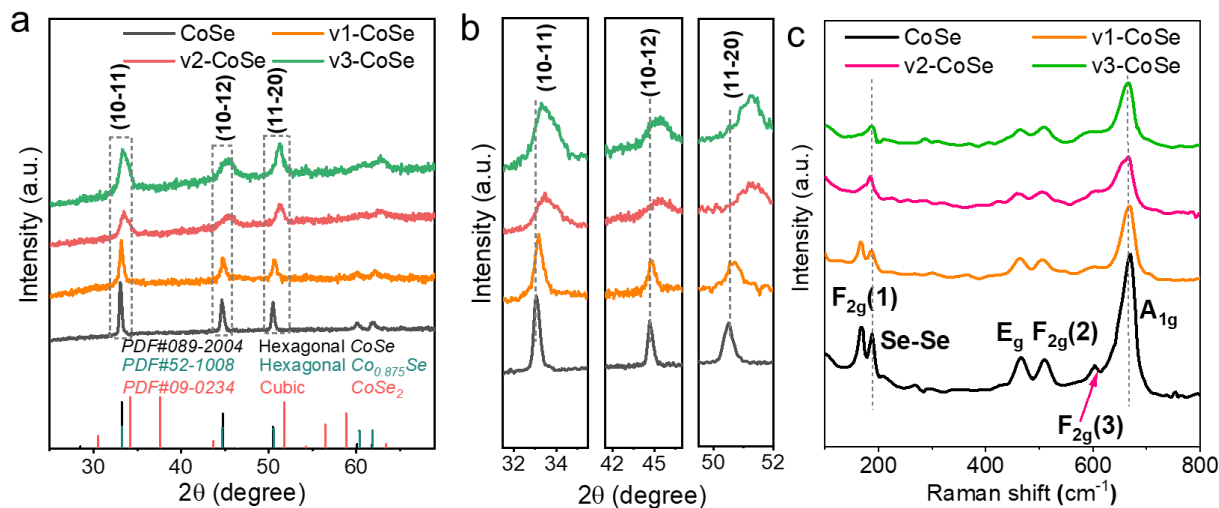


Figure 5.2. (a, b) XRD patterns. (c) Raman spectra of CoSe, v1-CoSe, v2-CoSe and v3-CoSe samples.

AC-HAADF-STEM was used to gain in-depth insights into the spatial distribution of Co vacancies. The AC-HAADF-STEM images together with their corresponding fast Fourier transform (FFT) patterns obtained from the nanostructures in Figure 5.3 reveal the CoSe and v-CoSe nanosheets to have the hexagonal crystal structure (space group = $P6_3\text{mmc}$) with $a=b=3.62(0)\text{ Å}$, $c=5.20(0)\text{ Å}$, which is consistent with XRD results. FFTs clearly show the (11-20), (2-1-10), and (1-210) lattice planes along the $[0001]$ zone axis, which defines the nanosheet basal plane. The (11-20) lattice plane spacing of v-CoSe was measured at 0.179 nm , slightly shorter than the 0.181 nm obtained for pristine CoSe, in good agreement with XRD patterns.

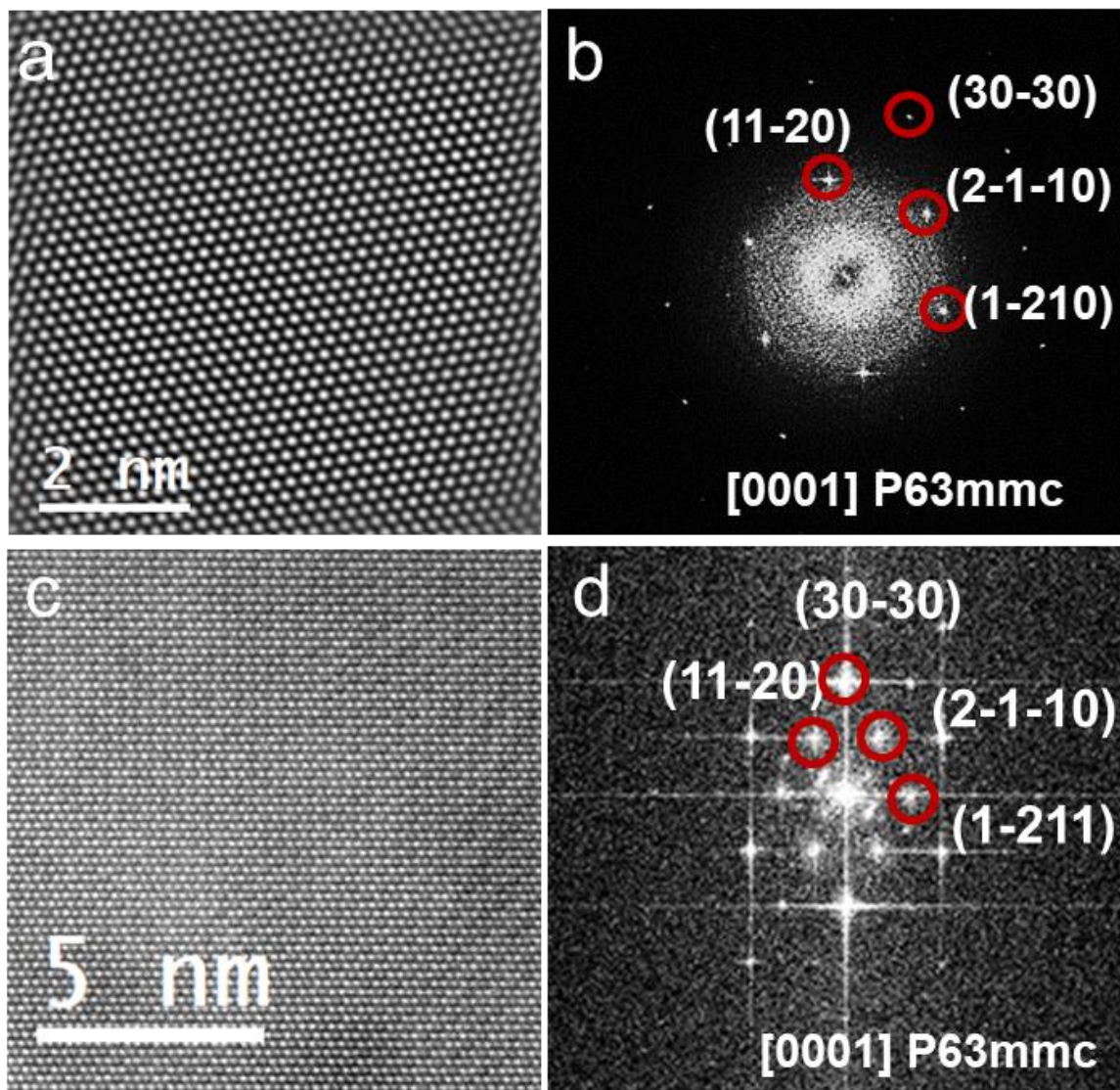


Figure 5.3. AC-HAADF-STEM image (a,c) and the corresponding FFT (b,d) of CoSe (top) and v-CoSe (below) nanosheets.

Co vacancies are visible as relatively low-intensity white spots in the atomic resolution AC-HAADF-STEM images of the v-CoSe nanosheets, as shown in Figure 5.4 and represented models Figures 5.4e-f. The intensity profiles along the selected rectangular regions in Figures 5.4a-d show the atomic columns of Co and Se to have some weaker Co signals pointing at a lower amount of cobalt atoms within the column, i.e. to the presence of Co vacancies. Besides the observable vacancies, additional line and plane defects can be found in the v-CoSe samples, particularly in the v3-CoSe sample (Figures 5.4b-d). Atomic models for the CoSe and v-CoSe

nanostructures and the corresponding linear-STEM image simulations are displayed in Figure 5.5. The simulation results fit well with the experimental data, further demonstrating the relatively low-intensity peaks to be associated with Co vacancies.

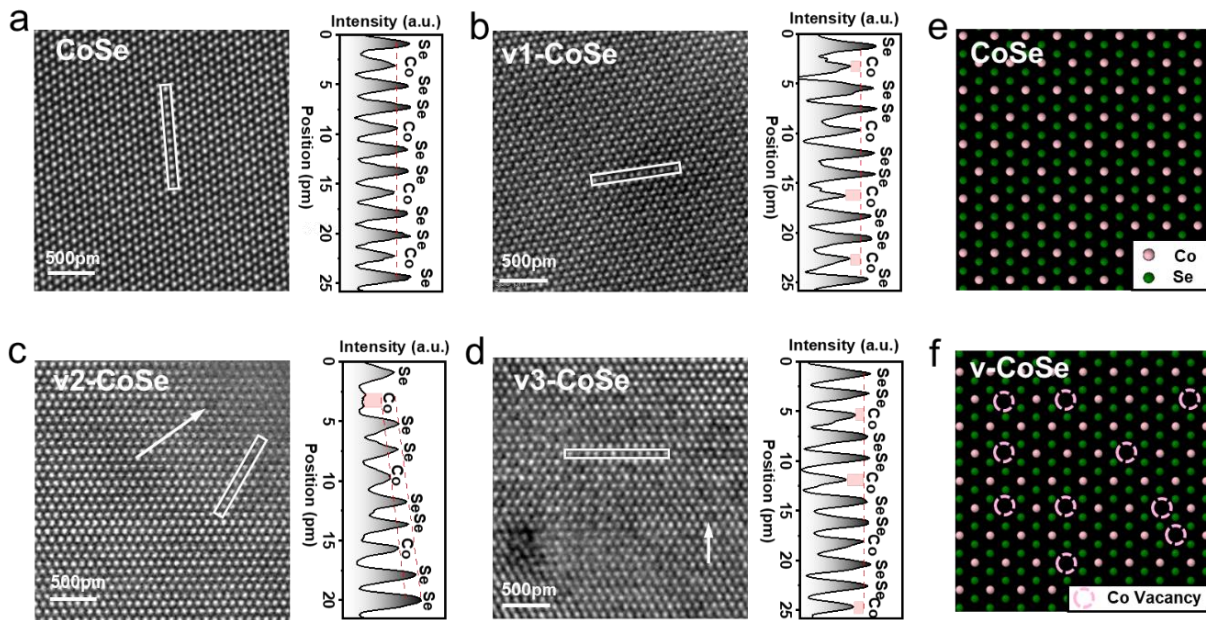


Figure 5.4. (a-d) Atomic resolution AC-HAADF-STEM images with the intensity profiles along the selected rectangular regions suggesting missing Co atoms in (a) CoSe, (b) v1-CoSe, (c) v2-CoSe, and (d) v3-CoSe, respectively. (e, f) Atomic model schemes of the vacancies for (e) CoSe and (f) v-CoSe samples.

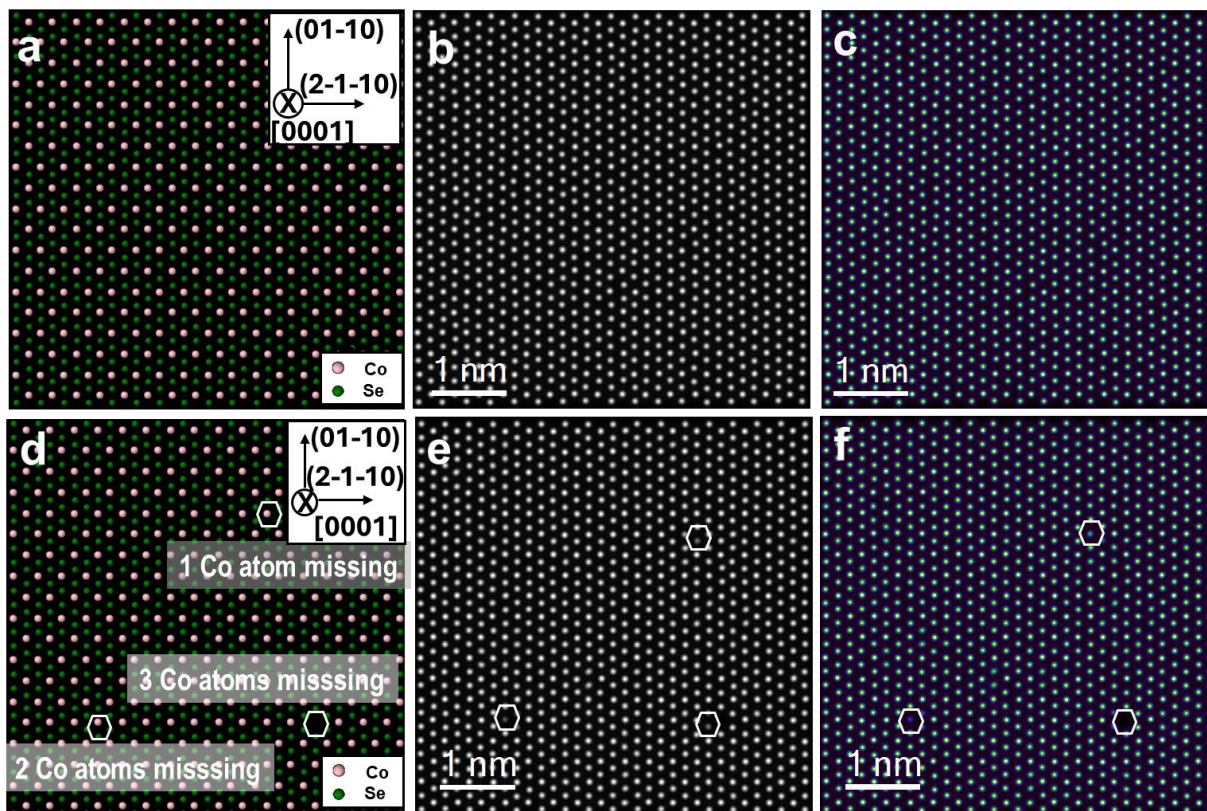


Figure 5.5. Atomic models and the corresponding simulated AC-HAADF-STEM images for (a-c) CoSe, and (e-f) v-CoSe along its [0001] zone axis, evidencing the different image contrast dependence on the number of Co atoms vacancy within the same atomic column.

SEM images combined with EDS elemental maps show the Co and Se atoms to be homogeneously distributed throughout the nanosheet (Figure 5.1). The EDS-AC-HAADF-STEM maps of individual nanosheets (Figure 5.6a) further verify the homogeneous Co and Se compositional distribution at the nanometer scale. With the increase of the plasma etching time, the atomic ratio of Co decreases from 52% in the pristine CoSe sample to 45% (v1-CoSe), 44% (v2-CoSe), and 43% (v3-CoSe), as shown in Figure 5.6b. The non-linear decrease in Co concentration may be related to the increasingly higher amount of energy required to remove additional Co from the structure.^[44]

XPS analysis was used to study the surface chemistry of CoSe with different cation vacancy structures. As shown in Figure 5.6c, the high-resolution Co 2p XPS spectrum of CoSe shows the characteristic asymmetric main peaks of Co at 778.20 eV ($3p_{3/2}$) together with a satellite peak at 785.21 eV, matching well the reported values for CoSe.^[45] The Co 2p XPS spectrum of v-

CoSe shows a significant binding energy blueshift with respect to the CoSe, with the Co 3p_{3/2} position at 778.49 eV (v3-CoSe). This shift is attributed to the increased electronegativity of the chemical environment of the Co atoms that remain in the v-CoSe. This leads to an increased sharing of electrons between the Co atoms and the adjacent Se ions, i.e. an increase of the Co oxidation state, which involves a higher energy cost to extract additional electrons. We also noticed that the Co satellite peak intensity increased gradually with the etching time, i.e. with the density of vacancies, which is related to the spatial spin polarization arrangement of 3d electrons, as discussed below.^[46]

The vacancy-tuned electronic structure was analyzed using electron energy-loss spectroscopy (EELS). The Co L-edge EELS spectra show two strong L₃ and L₂ white lines for Co, ascribed to the electronic transition from the spin-orbit split levels 2p_{3/2} and 2p_{1/2} to the unoccupied 3d states. The charge transfer occurring during the vacancy creation processes is reflected in the change in energy position and intensity ratio of the L₃ and L₂ white lines.^[47] Compared with pristine CoSe, the L₃-line energy in v-CoSe increased from 778.35 eV to 779.95 eV (Figure 5.6d), while the peak position of the Se L-edge remained constant (Figure 5.6e), indicating a change in the electronic environment around Co vacancies. Moreover, we observed a shift in the relative peak intensity of Co L₃/L₂ from 2.56 (CoSe) to 1.16 (v-CoSe), which points to a higher occupation of Co 3d states in v-CoSe as the white-line ratio decreases with d occupancy (n_d) when $n_d > 5$.^[48]

Nitrogen adsorption/desorption isotherms show the surface area of the samples to slightly increase with the plasma etching process. As displayed in Figure 5.6f, the BET surface area was 224 cm²g⁻¹ for CoSe and 242 cm²g⁻¹ after plasma etching (v2-CoSe). This slight increase in surface area can be associated with the generation of some microporosity in the nanosheets or the dispersion of some stacked CoSe nanosheets aided by the plasma etching process.

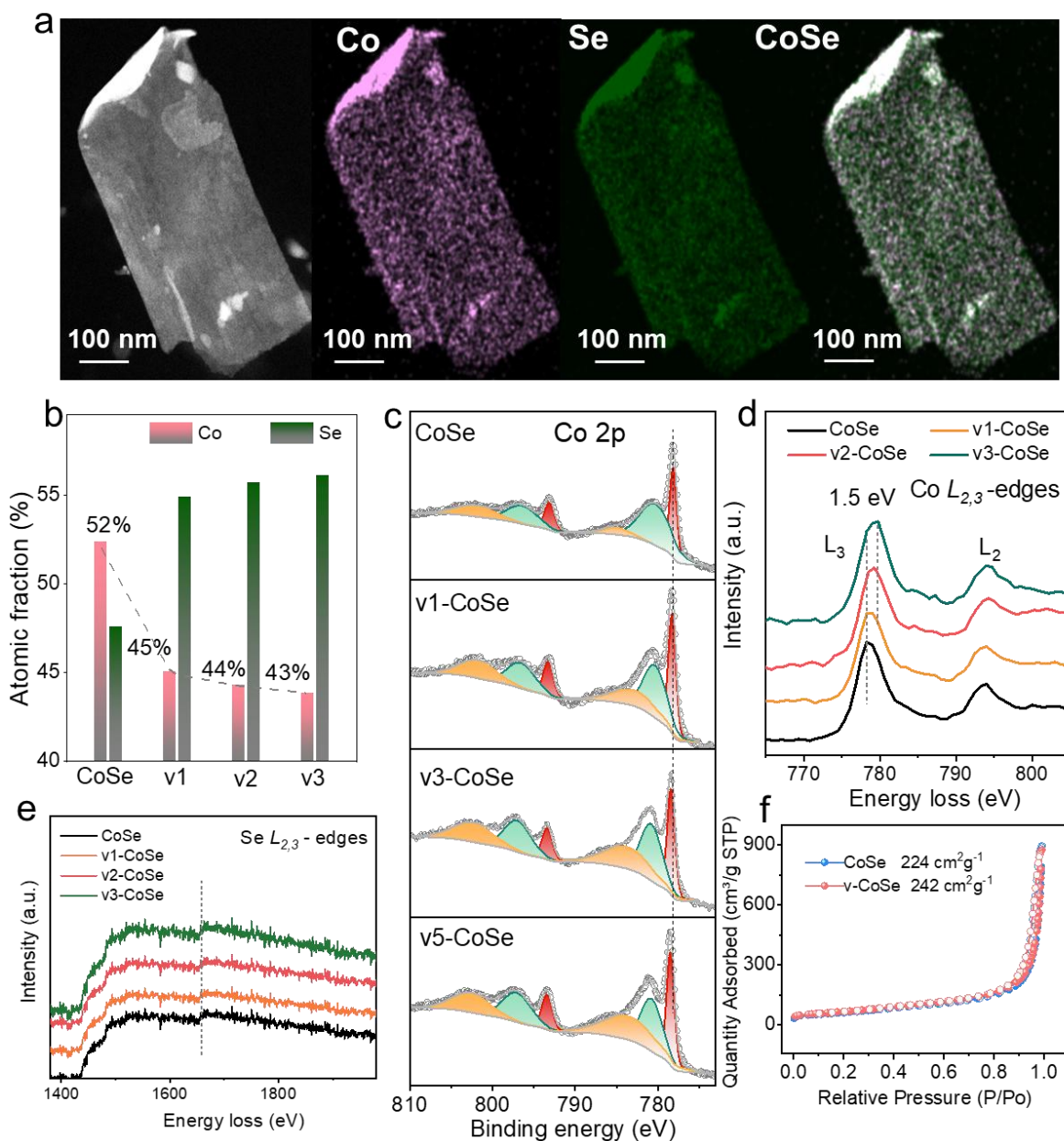


Figure 5.6. (a) STEM-EDS elemental maps of v2-CoSe. (b) Co and Se atomic fraction obtained from STEM-EDS maps. (c) High-resolution Co 2p XPS spectra. (d) Co L-edge EELS spectra. (e) Se $L_{2,3}$ -edges EELS spectra of CoSe and v-CoSe. (f) Nitrogen adsorption/desorption isotherms of CoSe and v-CoSe.

A preliminary assessment of the influence of vacancies on the catalytic ability of the materials towards the conversion of lithium polysulfides was obtained using symmetrical cells, i.e. using CoSe, v1-CoSe, v2-CoSe, or v3-CoSe catalysts in both electrodes (see the Experimental

Section for details).^[49] CV tests were performed in the voltage range from -1.5 V to 1.5 V, using 0.5 M Li_2S_6 and 1M LiTFSI in a 1:1 volumetric mixture of DOL and DME as electrolyte. As shown in Figure 5.7 and Table 5.2, the v2-CoSe electrode shows the largest charge and the smallest overpotential, i.e. the lowest redox reaction barrier for lithium polysulfide conversion. Thus, v2-CoSe was the v-CoSe material considered for additional studies, and in the following, it is referred to as just v-CoSe.

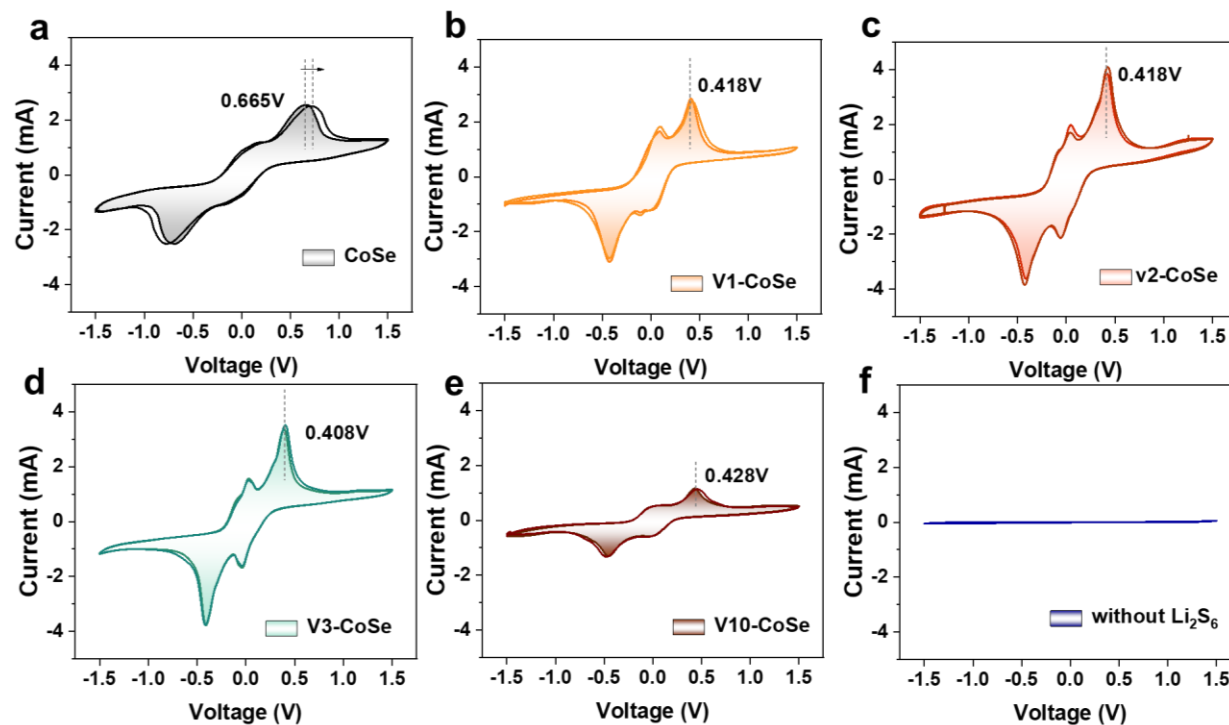


Figure 5.7. CV curves of symmetric cells for (a) CoSe, (b) v1-CoSe (c) v2-CoSe, (d) v3-CoSe, (e) v10-CoSe, and (f) without Li_2S_6 at a scan speed of 3 mV/s.

Table 5.2. Overpotential and square area of symmetrical cells CV curves of different catalysts.

Catalyst	Charge (Coulomb)	Overpotential
CoSe	3.11	0.665 V
v1-CoSe	2.45	0.418 V
v2-CoSe	3.53	0.418 V
v3-CoSe	2.78	0.408 V

v10- CoSe	1.44	0.428 V
Without	0.05	—

5.3.2 Spin state structure.

The 3d orbital of Co^{2+} in CoSe splits in an octahedral field and it is very sensitive to the coordination environments. EXAFS and XANES were used to analyze the electronic structures of Se and Co within CoSe and v-CoSe. In the Co K-edge spectrum, the $1s \rightarrow 3d$ transition in the pre-edge region is particularly influenced by the spin state, oxidation state, and coordination geometry.^[50] As shown in Figure 5.8a, the Co pre-edge of both samples shows the conventional octahedral electron structure. A similar pre-edge peak was measured for CoSe and v-CoSe, involving no difference in the octahedron structure. The sharper peak at 7710.2 eV in v-CoSe (Figure 5.8b) is assigned to local electron transitions into unoccupied e_g states of the high-spin Co ion in an octahedral environment,^[51,52] which matches well with the satellite peaks observed in the Co 2p XPS spectra (Figure 5.6c). In terms of spin states, high-spin Co^{2+} usually has strong Co 2p satellite structures, about 5 eV higher in binding energy than the main Co 2p peak in the XPS spectra. On the other hand, low-spin Co^{2+} has associated a Co 2p XPS spectrum with less intense and poorly resolved satellite structures.^[53,54] The slight blueshift of the K-edge in XANES spectra of v-CoSe, as compared to CoSe, is related to a 20% increase in the average oxidation state of cobalt.^[52] At the same time, the different intensity of the peak shown in Figure 5.8a inset is related to the higher local disorder caused by vacancies. In addition, the EXAFS oscillations obtained from the K-edge spectra show a lower amplitude in v-CoSe than in CoSe (Figure 5.8c), which is also related to the higher degree of disorder associated with the structural alteration in the Se coordination environment after extensive Co vacancy introduction.

X-ray magnetic circular dichroism (XMCD) was used to gain information on the spin and orbital magnetic moment of Co and Se within CoSe and v-CoSe.^[55] Co $L_{2,3}$ edges and Se L_I edge measurements were conducted at 50 K and 6 T. The XMCD spectra were obtained by subtracting the XAS spectra acquired with photon helicity polarization antiparallel (σ^-) and parallel (σ^+) to the applied magnetic field, while the average XAS spectra were calculated as $(\sigma^+ + \sigma^-)/2$. As illustrated in Figures 5.8d-f, v-CoSe exhibits a strong Co dichroic signal with a spin magnetic moment significantly larger than that of CoSe according to the spin sum rule.^[56] This result probes the

strong spatial spin polarization generated by the presence of Co vacancies on Co sites. On the other hand, no obvious changes were detected in Se L_1 edge signals.

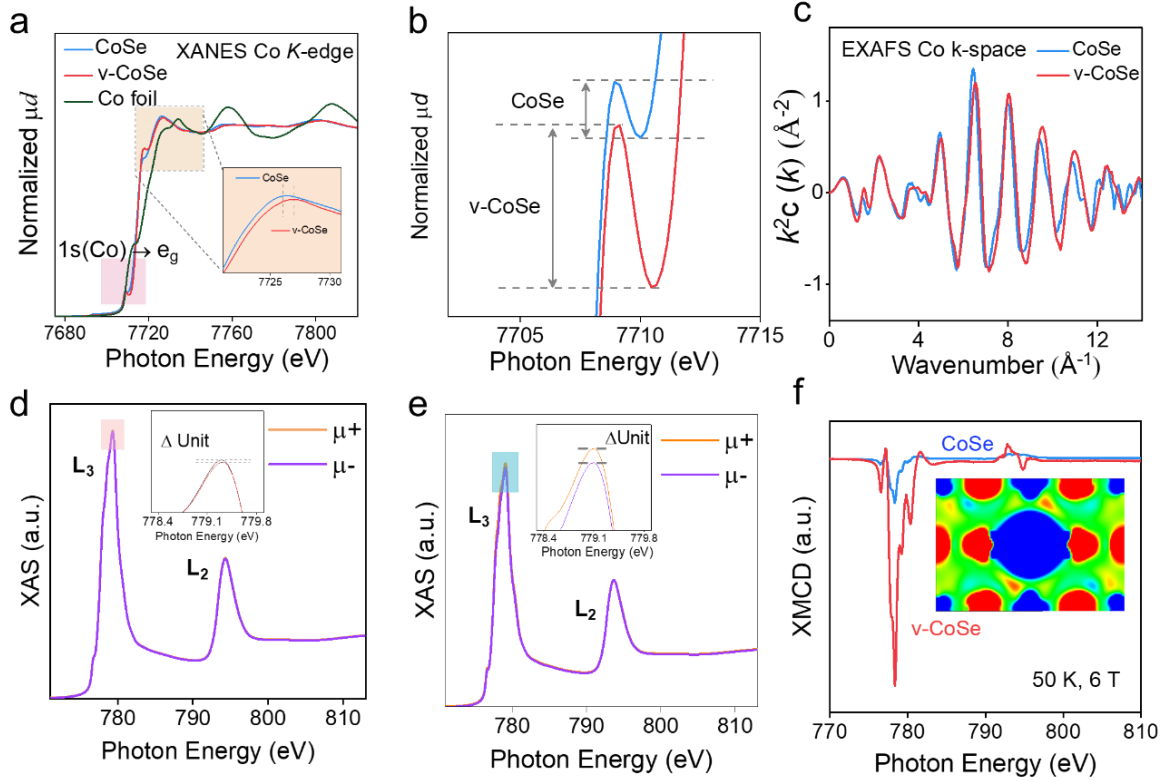


Figure 5.8. (a, b) Co K-edge XANES spectra. (c) EXAFS oscillation extracted from K-edge spectra of the composites in k space. (d, e) Co $L_{2,3}$ XAS (average of μ^+ and μ^-) of (d) CoSe and (e) v-CoSe at 50 K under an applied field $B = 6$ T. (f) XMCD ($\mu^+ - \mu^-$)/2 spectra. The inset shows the differential spin density between CoSe and v-CoSe.

Both CoSe and v-CoSe exhibit paramagnetic behavior with antiferromagnetic correlations at low temperatures, Figure 5.9a shows the temperature dependence of the inverse magnetic susceptibility for v-CoSe at 50 Oe. The inverse susceptibility was fit in the paramagnetic range from 50 to 300 K to the Curie-Weiss law with some parasitic diamagnetic contribution. Figure 5.9b shows the magnetization curves at 2 K for CoSe and v-CoSe. The CoSe and v-CoSe curves were fitted with a linear susceptibility term that is probably related to antiferromagnetic interactions, and a Brillouin term that gives a moment per Co ion of approximately 1.7 μ_B and 2.8 μ_B , respectively. The increase in the effective moment for sample v-CoSe confirms the significant increase in the ratio of ions in the high spin state. The 7 electrons in the 3d orbit of Co^{2+}

are preferentially distributed in those orbitals with lower energy according to the Hunter rule and the Pauli exclusion principle.^[57] Considering that each Co^{2+} ion can contribute either with 1 μB (low spin state) or 3 μB (high spin state), depending on their electronic configuration (Figure 5.9c), we estimate CoSe to have 35% of Co^{2+} ions in high spin state. This value increases to up to 90% in the $\nu\text{-CoSe}$ sample. When considering the presence of 20% of Co^{3+} ions within $\nu\text{-CoSe}$ and taking into account the three potential spin configurations, low spin (0 μB), medium spin (2 μB), and high spin (4 μB), we still estimate a percentage between 75% and 100% of Co^{2+} ions in the high spin state. The detailed calculation can be found in the Experimental section. Overall, despite the uncertainty regarding the electronic arrangement of Co^{3+} , $\nu\text{-CoSe}$ demonstrates much higher spin polarization than CoSe.

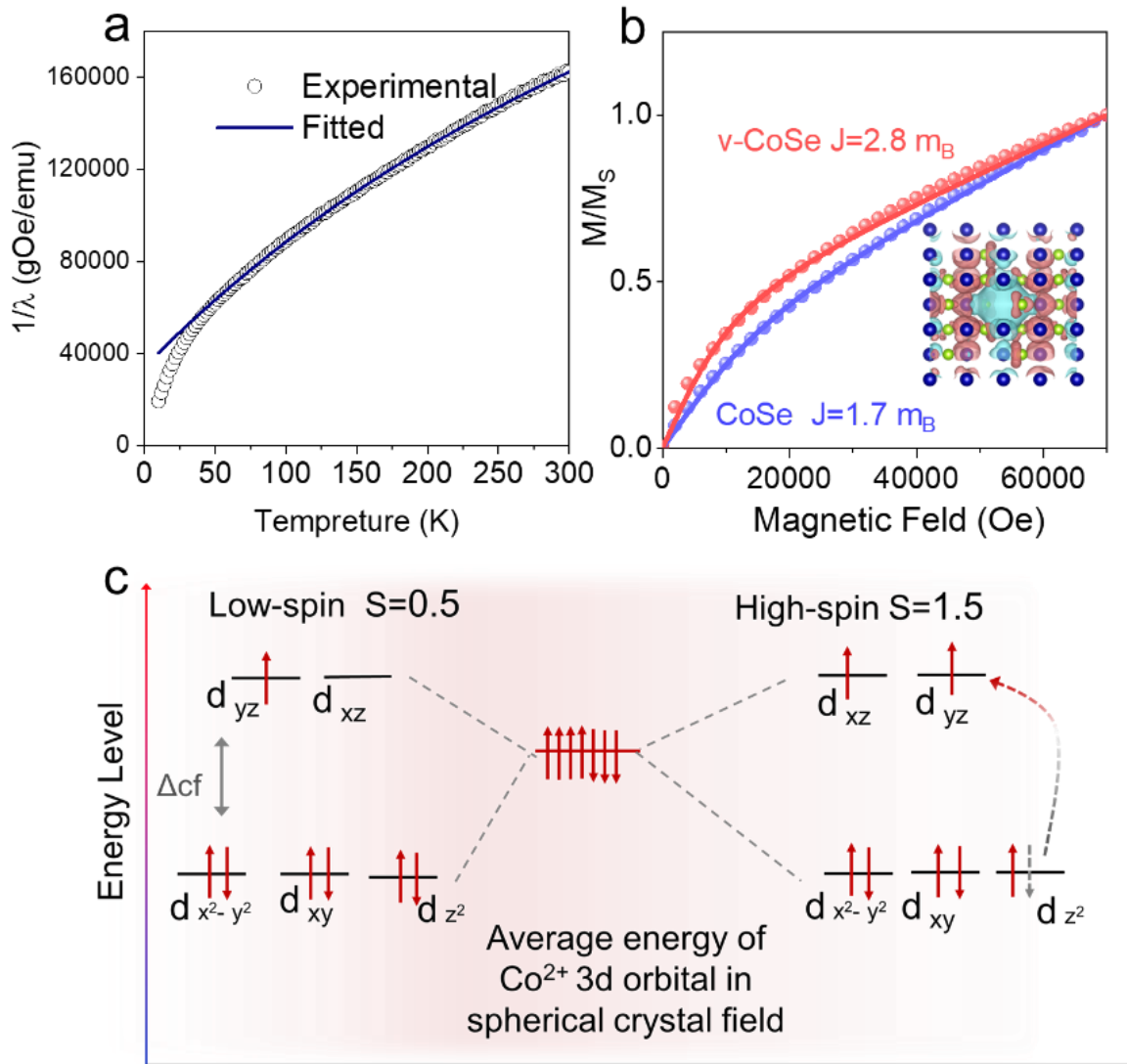


Figure 5.9 (a) Temperature dependence of inverse magnetic susceptibility for v-CoSe at 50 Oe. Normalized magnetization curves at 2 K. (b) The inset shows the differential spin density model between CoSe and v-CoSe. (c) Schematic diagram of electron spin-orbit configuration in Co^{2+} .

The electron paramagnetic resonance (EPR) spectra of v-CoSe and CoSe are displayed in Figure 5.10a. The EPR spectrum of v-CoSe shows a strong signal at $g=2.004$ not present in the CoSe sample, which further confirms the generation of additional electrons with unpaired spins by the introduction of Co vacancies (Figure 5.8b).^[58]

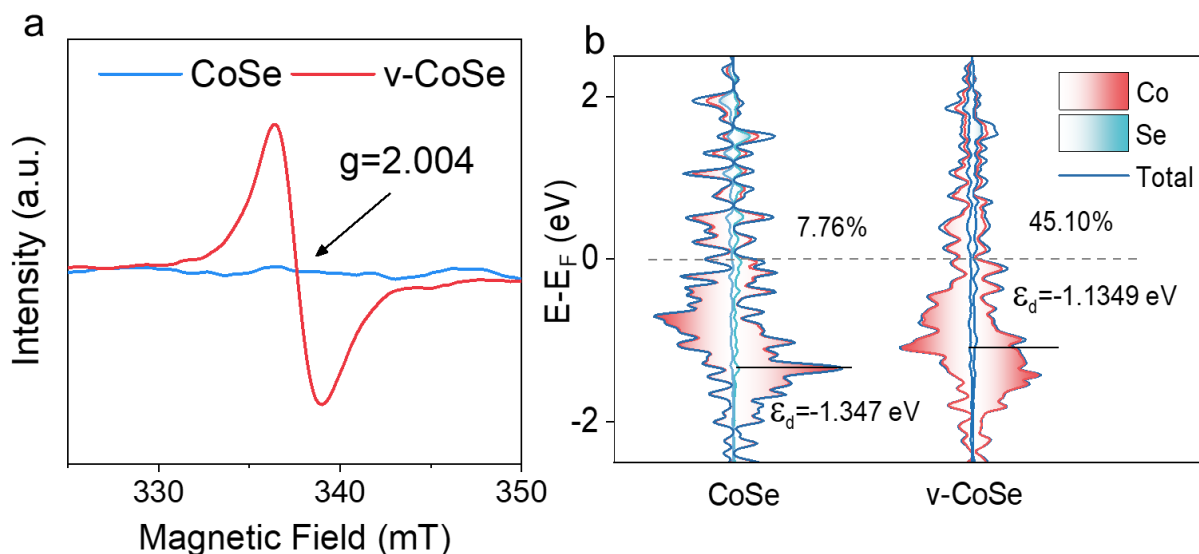


Figure 5.10. (a) EPR spectra. (b) Total density of states (TDOS) and partial density of states (PDOS) of CoSe and v-CoSe.

To study the influence of cation vacancies on the electronic structure, the DOS of the material was calculated by DFT (Figure 5.11). Despite the slight reduction in electron density resulting from the decrease in Co atoms, DFT calculation results show that the d band center of v-CoSe (-1.135 eV) is slightly closer to the Fermi level than that of CoSe (-1.347 eV). This shift involves an increase in orbital energy, thus electrons are more prone to disperse in the high-spin configuration. This result also indicates that the presence of vacancies in v-CoSe should enhance the material's ability to adsorb relevant species during the catalytic process.^[59] We further differentiated between DOS with up and down electron spin states and determined the spatial spin polarization defined as:^[60]

$$P = \frac{DOS \uparrow_{E_F} - DOS \downarrow_{E_F}}{DOS \uparrow_{E_F} + DOS \downarrow_{E_F}} \quad (1)$$

where $DOS \uparrow_{E_F}$ (or $DOS \downarrow_{E_F}$) are the spin-up (spin-down) charge density calculated in the vacuum for an energy interval extending up to the Fermi level.^[61] According to this equation, the spatial spin polarization of CoSe and v-CoSe is 7.6% and 45.1%, respectively (Figure 5.10b).

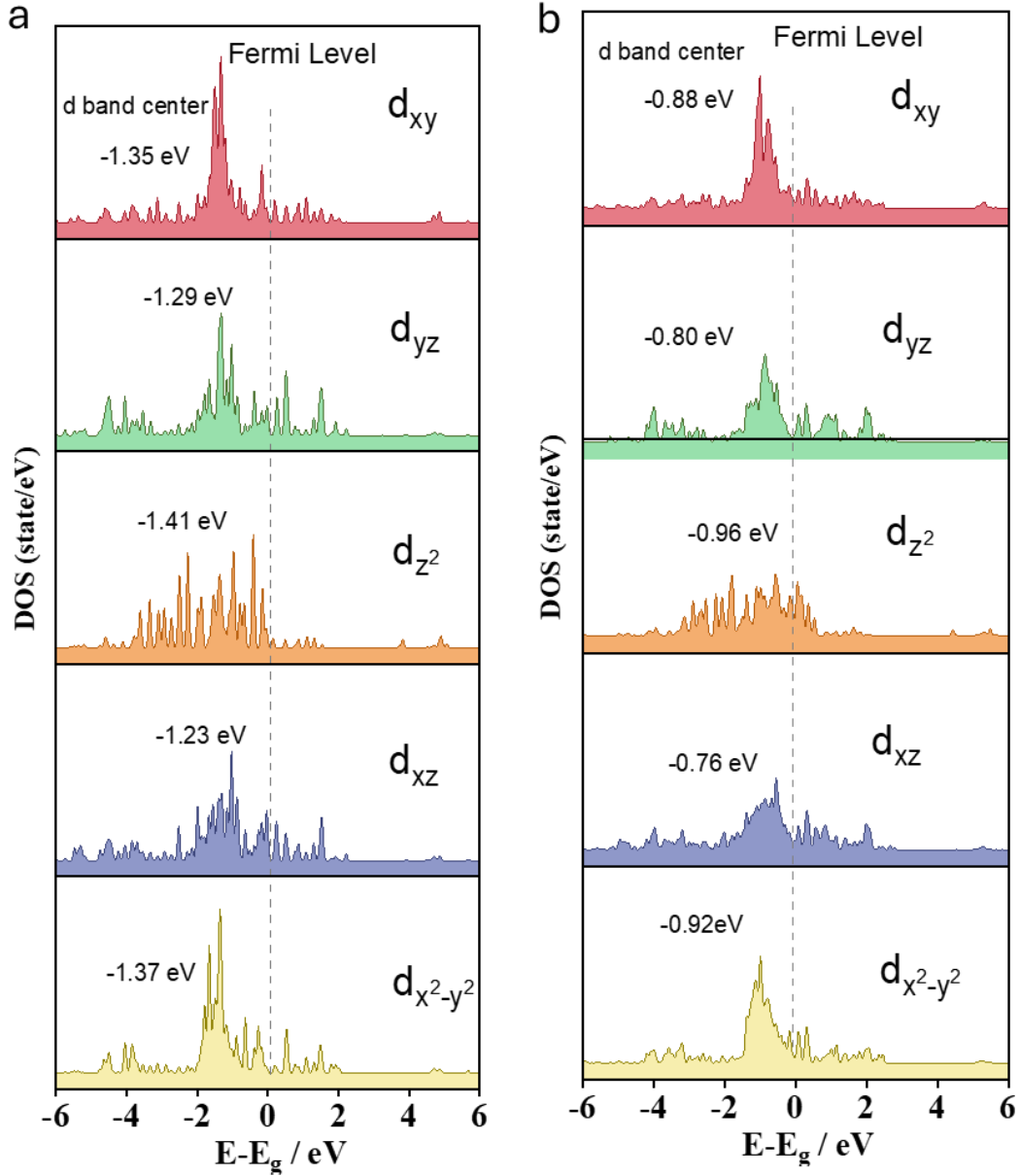


Figure 5.11. Partial density of states (PDOS) of Co at d-orbital for (a) CoSe and (b) v-CoSe.

The calculated charge and spin distribution in the surroundings of a Co vacancy and the differential maps between v-CoSe and CoSe in the surroundings are displayed in Figure 5.12 and

Figures 2g,i insets. We observe that the Co sites neighboring a Co vacancy show a redistribution of the charge density with higher electron densities in the vicinity of the vacancy site. Additionally, highly asymmetric spin distributions are generated in the vicinity of a Co vacancy. Such asymmetry and the higher charge density may facilitate electron transfer between v-CoSe and polysulfides and thus be helpful to the adsorption of polysulfides, as discussed below.

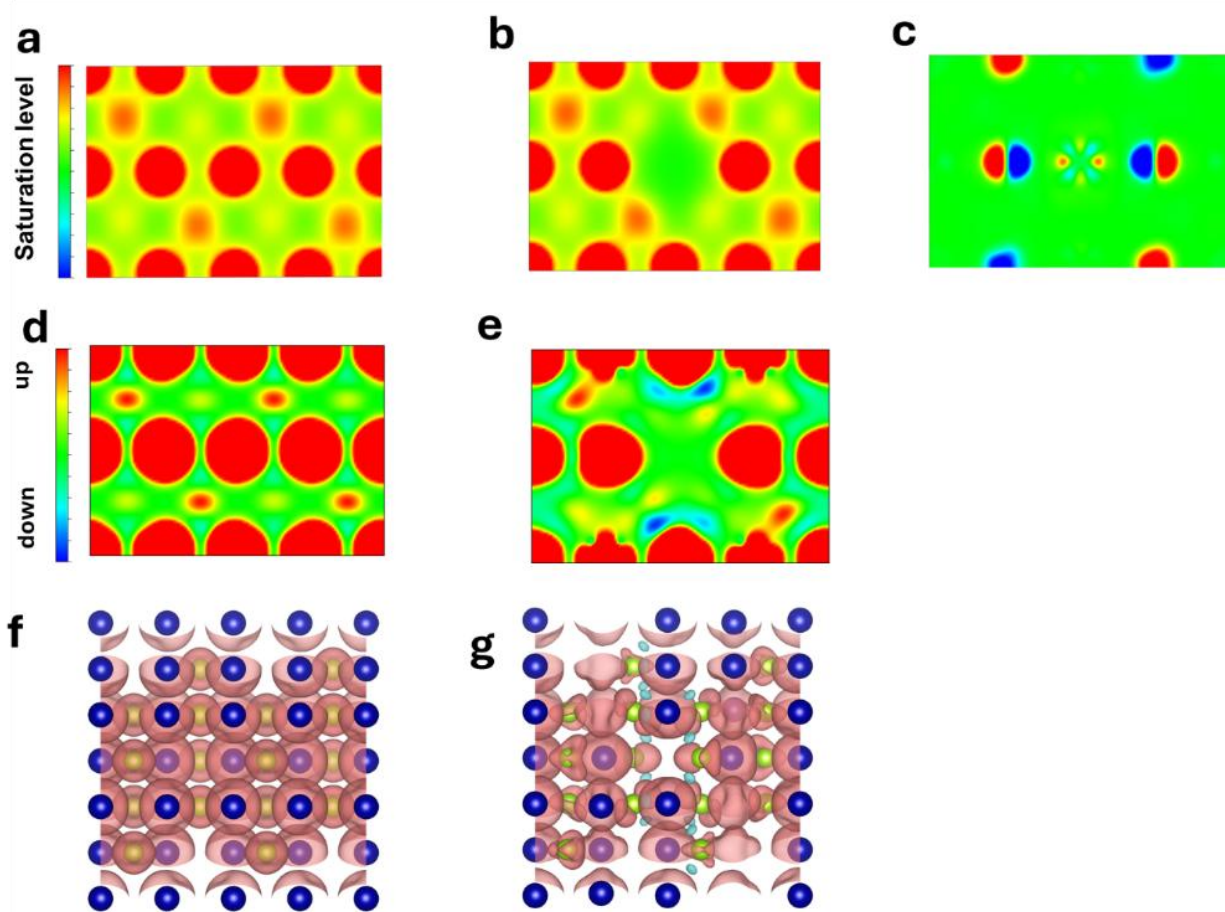


Figure 5.12. (a) Charge density distribution of CoSe. (b) Charge density distribution of v-CoSe. (c) Differential charge density map, between CoSe and v-CoSe. To obtain the differential map, a Co atom and its associated charge density were removed from the CoSe charge density distribution. (d) 2D spin density map of CoSe. (e) 2D spin density map of v-CoSe. (f) 3D spin density model of CoSe. (g) 3D spin density model of v-CoSe.

5.3.3 Chemical adsorption and catalytic mechanism.

To assess the difference in polysulfide adsorption capacity, DFT calculations were conducted. Figure 5.13a shows the model of the Li_2S_4 adsorbed on the catalyst surface and Figures 5.13b-c shows the spin state difference. A redistribution of the electron spins is observed, which illustrates the formation of a more stable adsorption bond. Experimentally, CoSe and v-CoSe were introduced in a Li_2S_6 solution (Figure 5.13d). After 10 hours, the characteristic brown color of the dissolved Li_2S_6 molecules strongly decreased for the v-CoSe-containing solution, denoting major adsorption of the lithium polysulfide on the v-CoSe surface. On the other hand, the color of the solution containing CoSe showed a more moderate change, thus lower adsorption, as displayed in the optical photographs in the inset of Figure 5.13a. UV-Vis spectra further confirmed this differential absorption in the visible and UV region of the spectra where Li_2S_6 shows a strong absorption band (Figure 5.13d).

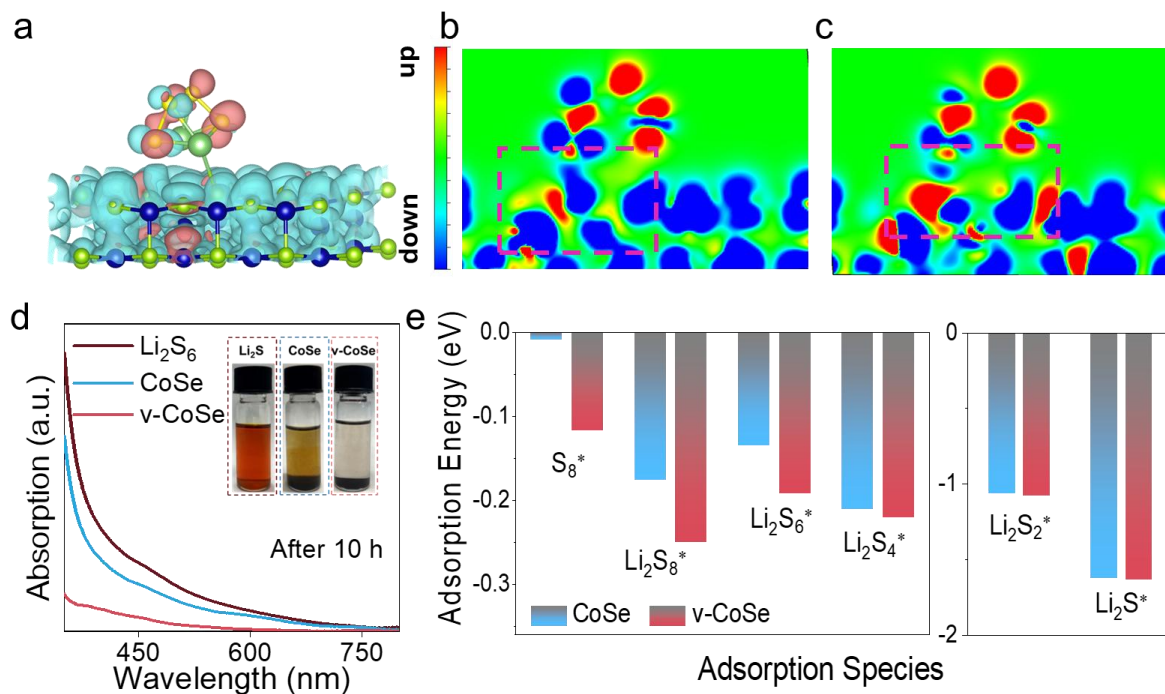


Figure 5.13. (a) 3D spin density model of CoSe in conjunction with Li_2S_4 , (b) 2D spin density map of CoSe and (c) v-CoSe with Li_2S_4 . (d) UV-visible spectrum showing Li_2S_6 adsorption experiments, with optical photos inserted. (e) Adsorption energy of the surface for different sulfur species.

DFT calculations were used to further investigate the interaction between CoSe and polysulfides. Figure 5.13e shows the adsorption energies of Li_2S , the different polysulfides (Li_2S_2 , Li_2S_4 , Li_2S_6 , Li_2S_8), and S_8 on the surface of hexagonal CoSe, with and without Co vacancies. The surface adsorption configurations are shown in Figures 5.14 and 5.15. Compared with CoSe, v-CoSe has significantly higher adsorption energies, thus improved adsorption ability, especially for soluble polysulfides (Li_2S_4 , Li_2S_6 , Li_2S_8) which are favor to the improvement of shuttle effect.^[62] This is related to the charge and spin redistribution near Co vacancies shown in Figures 5.11a-g.

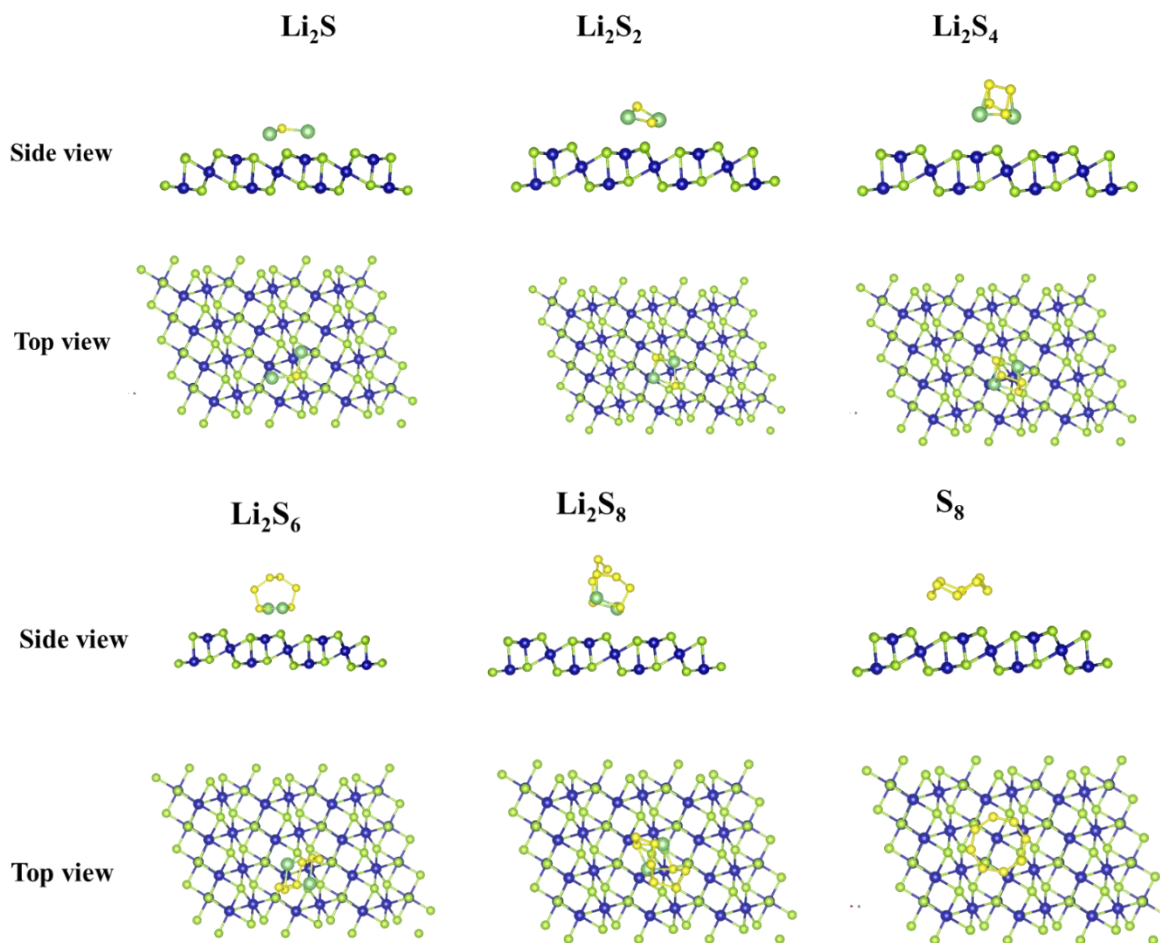


Figure 5.14. DFT optimized geometrical configuration of CoSe with LiPSs.

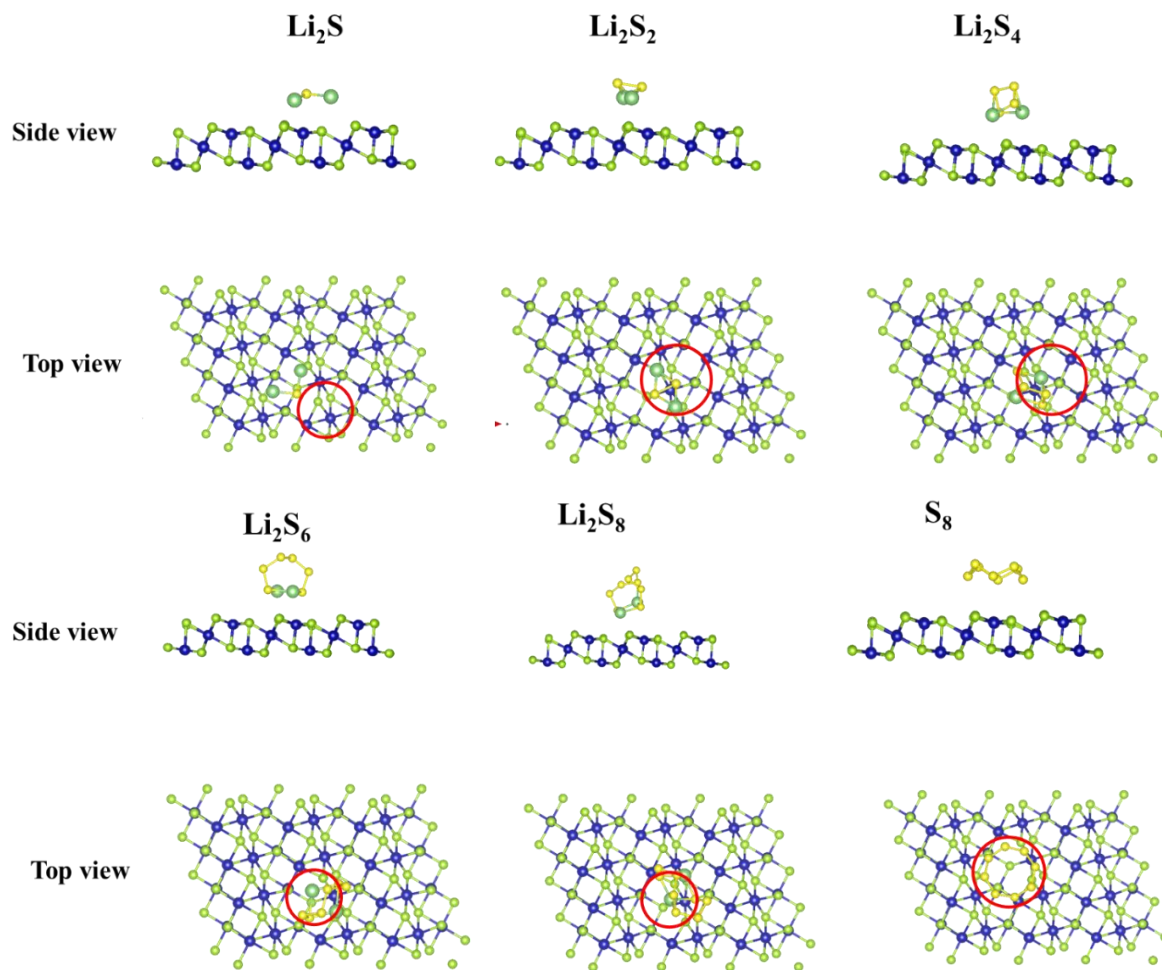


Figure 5.15. DFT optimized geometrical configuration of v-CoSe with LiPSs.

Experimentally, the Co 2p XPS spectrum of v-CoSe after the Li_2S_6 adsorption (Figure 5.16a) shows a 0.4 eV redshift. Additionally, upon adsorbing Li_2S_6 , a significant decrease in the satellite peak of v-CoSe is observed, which indicates a decrease in the high spin electronic density related to the transference of electrons to the polysulfide.^[63] Both experimental results are in good agreement with DFT calculation outcomes.

LSB cathodes were prepared by loading S (69%) into the catalytic additive, CoSe or v-CoSe, and combining the mixture with super P and PVDF binder in a ratio of 8:1:1. The material was coated on aluminum foil as the current collector, cut into circular pieces with a diameter of 12 mm. For operando XRD experiments, coin cells with a 5 mm diameter window sealed with a Kapton were assembled using the CoSe/S or v-CoSe/S cathode, a Li anode, and a polypropylene separator. The electrolyte contained 1.0 M LiTFSI and 0.2 M LiNO_3 in a DOL/DME (V:V=1:1)

mixture (see details in the Experimental Section). The operando X-ray powder diffraction patterns of the electrode materials during the first discharge and charge processes are illustrated in Figure 5.16b. In their pristine state, both CoSe/S and v-CoSe/S exhibit characteristic diffraction peaks corresponding to an orthorhombic α -S₈ phase. Upon discharge, the sulfur signal diminishes rapidly, with no major diffraction peaks apparent until the end of discharge, where a weak signal corresponding to Li₂S emerges, with the main peak at 12.5°. During the charging process, the Li₂S signal decreases, and only at the final stage of charging the diffraction peaks corresponding to monoclinic β -S₈ appear in both CoSe/S and v-CoSe/S. Additionally, subtle deformations in the background within the 8-10° region could be attributed to the formation of soluble polysulfides.^[64] This effect is particularly notable for v-CoSe/S, where the signal intensity increases notably at the end of discharge and the beginning of the charging process, reducing considerably by the end of charging, thus demonstrating high lithium polysulfide redox activity.

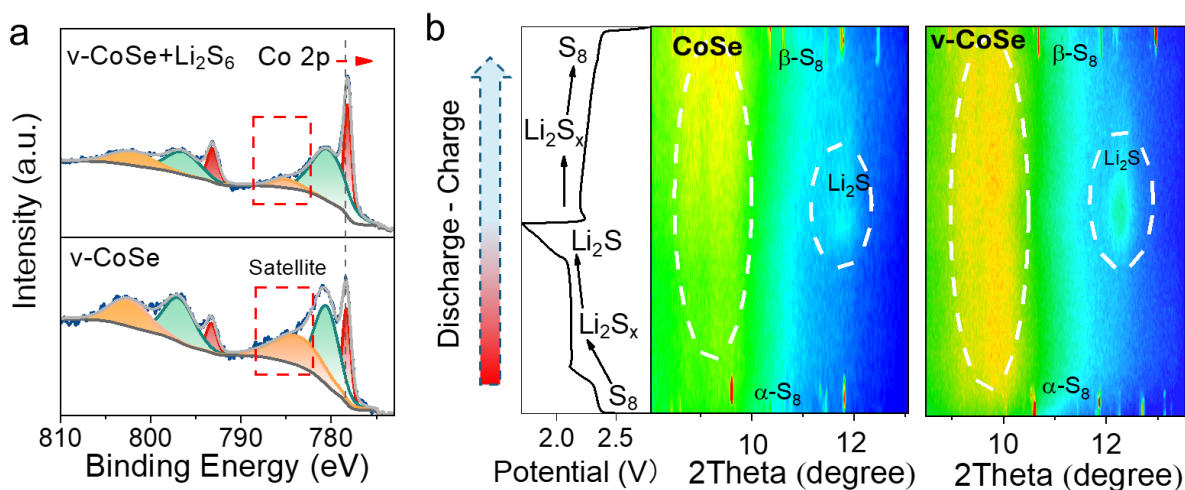


Figure 5.16. (a) Co 2p XPS spectra obtained for v-CoSe before and after Li₂S₆ adsorption. (b) *Operando* XRD patterns during charging and discharging of batteries based on CoSe /S and v-CoSe /S.

The polysulfide conversion energy barrier during the discharging process was estimated using EIS measurements. In the discharge potential range between 2.4 V and 2.0 V, the Nyquist plots of the EIS spectra show two semicircles. Considering the circuit model shown in the inset of Figure 5.19a, the intersection of the EIS spectra with the x-axis at high frequencies provides the internal resistance (R_s) of the battery associated mainly with the electrolyte and electrical connection resistances. The higher frequency semicircle (C_{Li} , R_{Li}) is mainly related to the

capacitance and charge transfer resistance of the Li/electrolyte interphase and includes also the contribution of the cathode porous structure.^[65] The lower frequency semicircle (C_{CT} , R_{CT}) is related to the charge transfer process at the cathode/electrolyte interphase that is associated with the polysulfide conversion process. The *tail* in the low-frequency range is related to the ion transfer resistance inherent to the cell, which is accommodated through a Warburg impedance term (Z_{wo}).^[66] The activation energy (E_a) of the charge transfer process linked to the polysulfide conversion was determined by fitting the temperature-dependence of the obtained charge transfer resistance (R_{ct}) values using the Arrhenius equation (Figures 5.17 and 5.18):^[67,68]

$$k = A \times \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

$$\ln\left(\frac{1}{R_{ct}}\right) \sim \ln A + \frac{-E_a}{RT} \quad (3)$$

where the reaction rate constant (k) is assimilated to the inverse of the charge transfer resistance (R_{ct}), the pre-exponential factor (A) represents the collision frequency before reactants attain an excited state, and T is the absolute temperature.

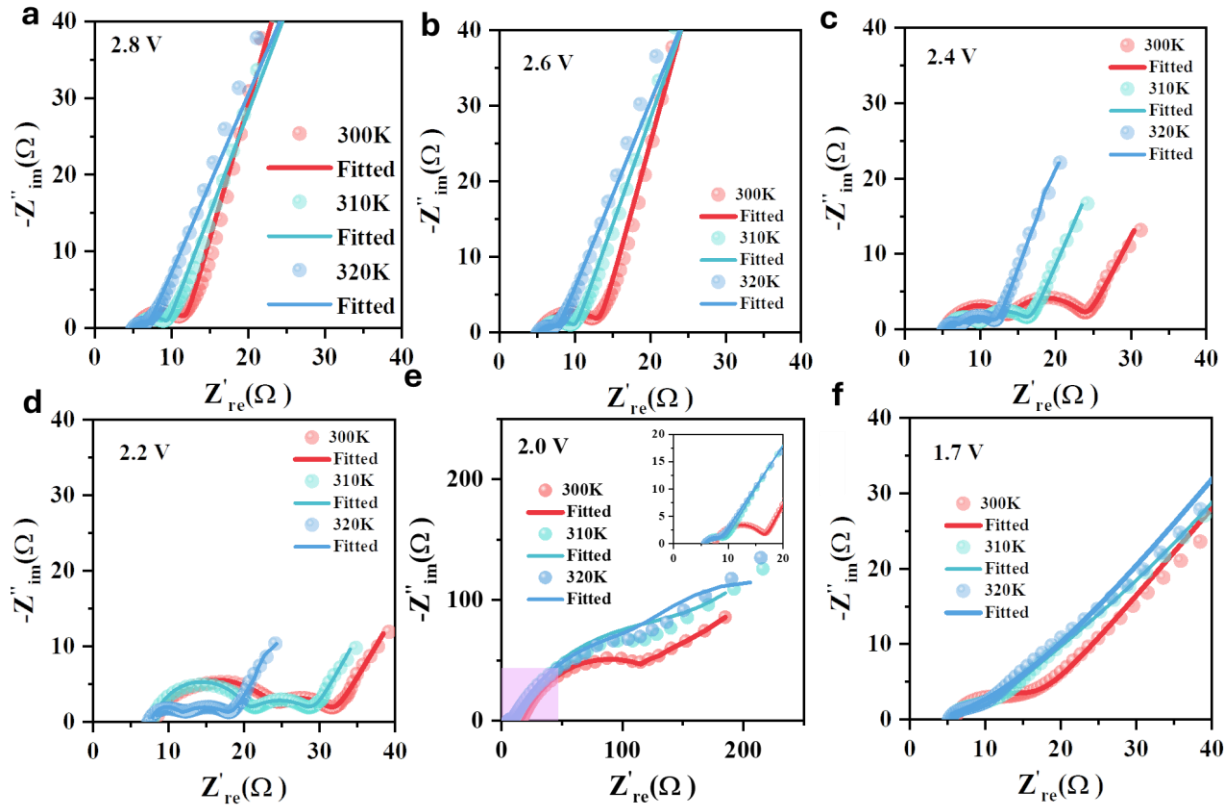


Figure 5.17. Nyquist plots of the EIS spectra of the CoSe/S electrodes at (a) 2.8 V, (b) 2.6 V, (c) 2.4 V, (d) 2.2 V, (e) 2.0 V with the enlarged figure inserted, and (f) 1.7 V during discharging at

different temperatures (300 K, 310 K, and 320 K). The raw impedance data and the fitted data are shown as symbols and lines, respectively.

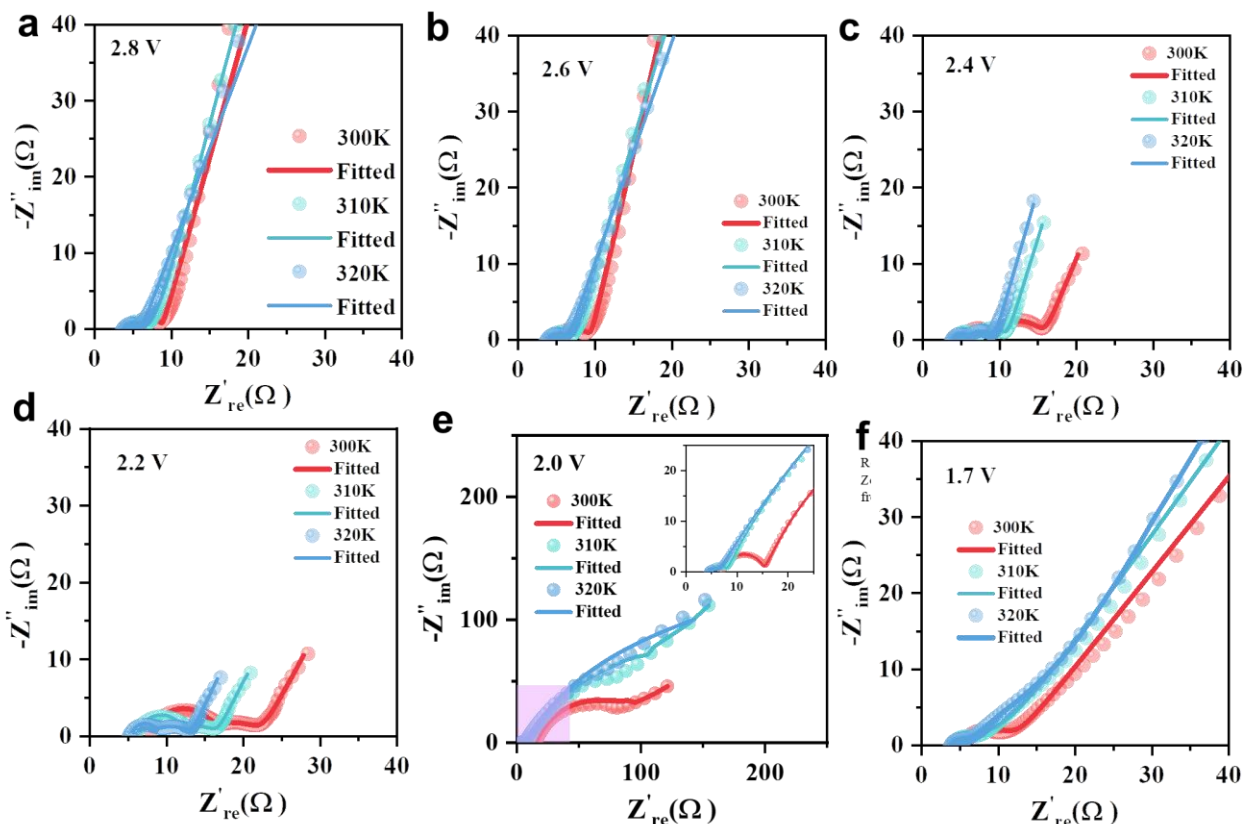


Figure 5.18. Nyquist plots of the EIS spectra of the v-CoSe/S electrodes at (a) 2.8 V, (b) 2.6 V, (c) 2.4 V, (d) 2.2 V, (e) 2.0 V with the enlarged figure inserted, and (f) 1.7 V during discharging at different temperatures (300 K, 310 K, and 320 K). The raw impedance data and the fitted data are shown as symbols and lines, respectively.

As shown in Figures 5.19b-d, throughout the voltage interval of 2.4 – 2.0 V, the SRR E_a of v-CoSe is significantly smaller than the values obtained from CoSe. In particular, the phase transition from liquid and soluble Li_2S_x to solid and unsoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ plays an important role in the whole SRR process due to the substantial energy barrier associated with the nucleation and growth of the solid phase.^[69] Notably, at 2.4 and 2.2 V, corresponding to this liquid-solid conversion stage, there is a substantial reduction in activation energy with the introduction of the Co vacancies.

DFT calculation results (Figure 5.19e) considering the different spin states were consistent with the more favorable thermodynamic reduction process in v-CoSe compared with CoSe, especially during the liquid state (Li_2S_4) to solid-state Li_2S_2 transition, with a much lower energy barrier for v-CoSe (0.34 eV) than for CoSe (0.63 eV). The different energy is related to the spin-polarized electrons exhibiting enhanced transfer rates from the catalyst surface to the surface of liquid polysulfides (Li_2S_6 and Li_2S_4). This facilitates expedited liquid-solid conversion from Li_2S_4 to Li_2S_2 , consequently optimizing solid-phase nucleation reaction kinetics for greater efficiency.

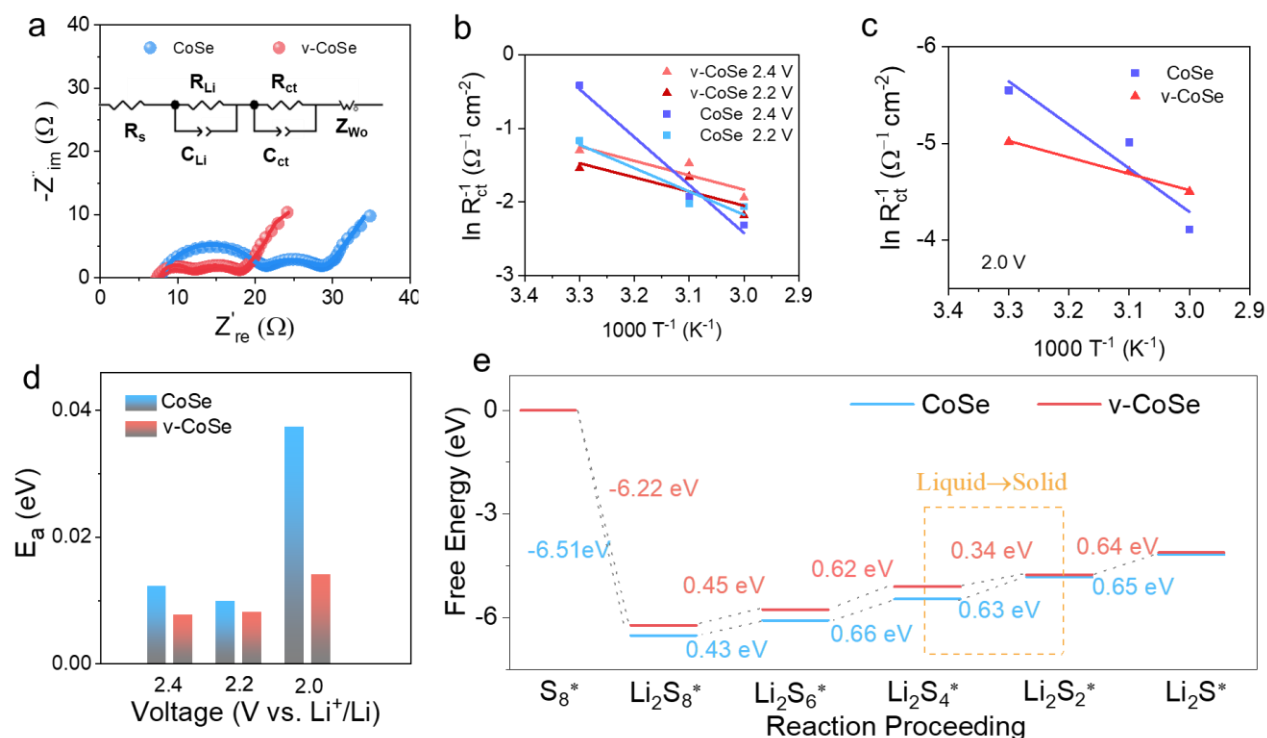


Figure 5. 19. (a) Fitted EIS spectra at 2.2 V and model circuit. (b,c) Arrhenius plot of R_{ct} calculated from CoSe (b) and v-CoSe (c). (d) Calculated activation energies at different voltages. (e) Gibbs free energy profiles and adsorption conformation of polysulfide species.

Symmetric cells were used to experimentally verify the above activation energy values and theoretical calculation results. CV curves acquired in the absence of Li_2S_6 in the electrolyte show very low currents (Figures 5.20a and 5.7), implying that the current response in the symmetric cell primarily arises from the conversion of the polysulfides within the electrolyte. In the presence of Li_2S_6 , the freshly assembled symmetric cell shows an initial 0 V open-circuit voltage due to its electrode symmetry. However, as the negative scanning process progresses, Li_2S_6 gradually

transforms into Li_2S_4 in one of the electrodes, as evidenced by peak I. Further reduction results in the conversion of Li_2S_4 to $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ (peak II). Both oxidation and reduction processes show cycling reversibility. Compared with the symmetric cell based on CoSe electrodes, the v-CoSe-based cell displays a lower polarization voltage and a sharper and higher current density at each oxidation-reduction peak. Specifically in peak II, v-CoSe shows a potential of -0.39 V, well below (in absolute value) that of CoSe, at -0.83 V. These experimental results underscore the outstanding catalytic efficacy of v-CoSe in facilitating the conversion of long-chain polysulfides, and are consistent with EIS spectra and DFT calculation results.

To gain deeper insight into the influence of vacancies on the nucleation and growth process, Li_2S deposition experiments were conducted. In this experiment, the assembled coin cells were firstly galvanostatic discharged to 2.06 V, and then subjected to potentiostatic deposition at 2.05 V for 4 hours. The shorter deposition time (575 s) observed from v-CoSe compared with CoSe (1076 s) indicates a much faster nucleation rate (Figures 5.20b-c). Applying Faraday's law, the calculated Li_2S deposition capacity for v-CoSe is 442.7 mAh g^{-1} , well above that of CoSe at 385.4 mAh g^{-1} , demonstrating an effective promotion of the Li_2S nucleation process in v-CoSe.

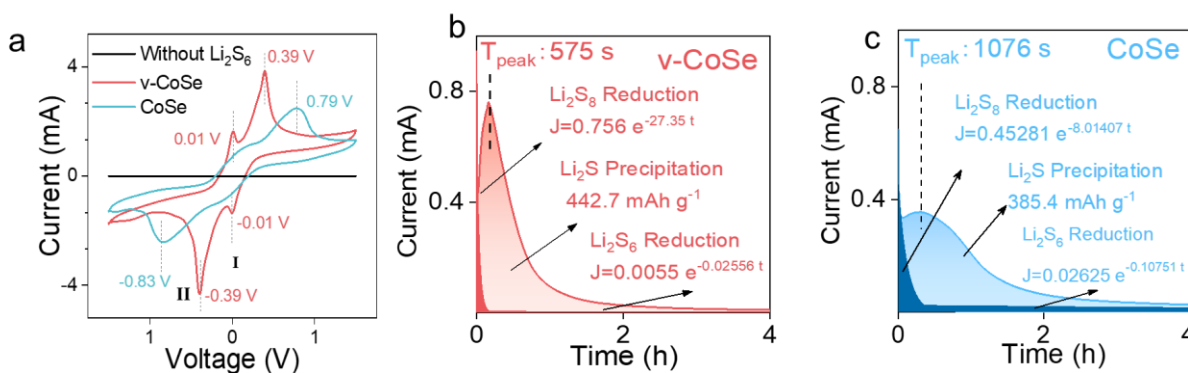


Figure 5.20. (a) CV curves obtained from symmetric cells at a scan speed of 1 mV/s. (b, c) Potentiostatic discharge curves on CoSe (b) and v-CoSe (c) to study the Li_2S nucleation kinetics.

SEM images after deposition further supported these results, showing a larger amount of Li_2S nucleated on the surface of v-CoSe than on the CoSe surface (Figure 5.21). This experimental result is consistent with the above calculation results showing that when the catalyst is combined with polysulfide, the active spin-polarized single electrons from v-CoSe are easier to transfer to the polysulfide to form bonds, achieving a rapid solid-liquid conversion process. This promoted

charge transfer lowers the free energy required for nucleation, enhances polysulfide binding energy, and expedites surface electron exchange, thereby facilitating swift redox reactions.

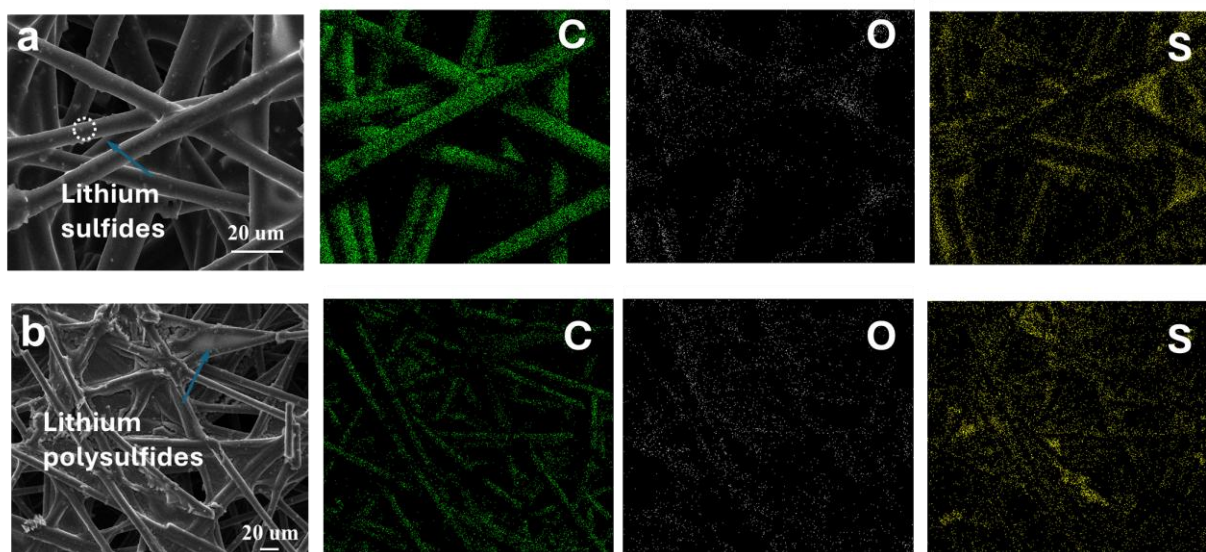


Figure 5.21. SEM images and EDX elemental maps of lithium sulfide particles deposited on a carbon paper electrode of (a) CoSe/S and (b) v-CoSe/S.

DFT calculations were conducted to elucidate the electronic orbital occupation information of polysulfides after catalyst adsorption. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) changes upon adsorption are shown in Figure 5.22a. The polysulfide adsorption on CoSe only marginally reduces its HOMO-LUMO band gap from 2.6911 eV to 2.6875 eV. On the other hand, the alteration in the spin configuration of Co in proximity to a Co vacancy results in additional unpaired electrons with a swift transferability from the catalyst surface to the polysulfide. This significantly diminishes the polysulfide LUMO upon adsorption and thus its HOMO-LUMO band gap is down to 1.5869 eV. This reduction in the band gap reflects the decrease of the polysulfide stability upon adsorption in the v-CoSe surface, thus enhancing the polysulfide conversion activity.

Figure 5.22b shows the energy level diagram of the orbital hybridization between Li_2S_4 and CoSe and v-CoSe surfaces. The calculated polysulfide DOS on the catalyst surface, especially at Co and vacancy sites, indicate that the polysulfide bonding on CoSe and v-CoSe has a different impact on the bonding states around the Fermi level of the sulfur atom^[29,70] (Figure 5.22b), having the v-CoSe a higher density of electrons close to the E_F . In brief, the adsorption of the polysulfide results in a notable shift of the bonding state towards the Fermi level, especially for v-CoSe.

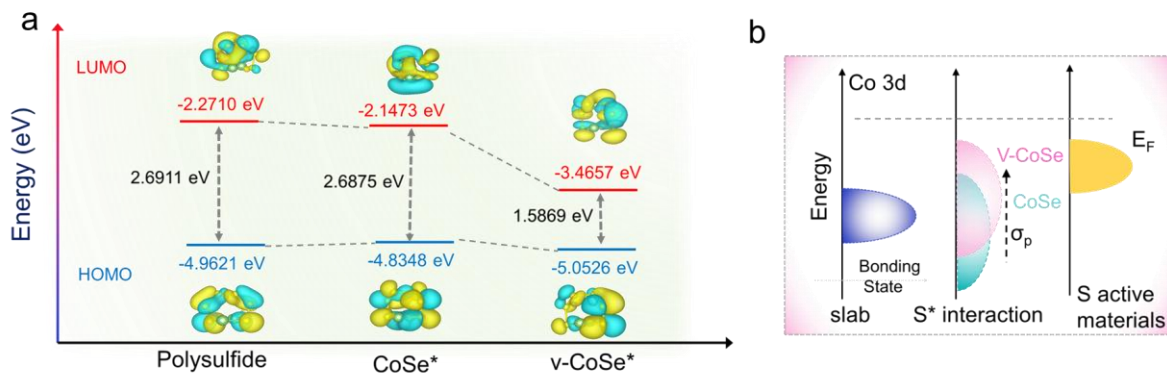


Figure 5.22. (a) Energy level scheme for pristine polysulfide and after adsorption. (b) Energy level diagram showing orbital hybridization for Li₂S₄ according to DOS results. E_F represents the Fermi level of the substrate; σ_p indicates bonding states.

5.3.4 Electrochemical performance.

To evaluate the electrochemical performance of CoSe- and v-CoSe-based sulfur cathodes, CR2032 coin-type cells were assembled and cycled within the voltage range of 1.7 V - 2.8 V, as detailed above and in the Experimental section. Figure 5.23a displays the CV curve of a coin cell at a scan rate of 0.2 mV s⁻¹, revealing several clear redox peaks. Notably, the v-CoSe electrode exhibited a stronger current response and sharper redox peaks. The reduction peak at 2.31 V accounts for the transformation from solid sulfur to long-chain polysulfide (Li₂S_x (x ≥ 4)). The subsequent reduction peak at 2.02 V denotes the liquid-to-solid conversion of long-chain polysulfides to Li₂S₂/Li₂S. The oxidation peak represents the process of converting Li₂S₂/Li₂S into long-chain polysulfides and ultimately into S₈. The reduction peaks of v-CoSe/S exhibit a noticeable right shift when compared with those of CoSe/S, indicating a decrease in the polarization voltage during polysulfide conversion.

Figure 5.23b shows the linear sweep voltammetry (LSV) curve from the pink areas in Figure 5.23a, and Figure 5.23c shows the Tafel plots obtained from the reduction process in the LSV curves. The Tafel slope was calculated from a narrow voltage interval around the zero current voltage to prevent mass transfer limitation. The Tafel slope of the v-CoSe/S cathodic reduction process I was estimated at 59 mV dec⁻¹, significantly below that of CoSe/S (72 mV dec⁻¹). Notably, at the second reduction peak, v-CoSe/S displays a higher onset voltage and faster reduction current response signal compared to CoSe/S, yielding a Tafel slope of 78 mV dec⁻¹ for v-CoSe/S, in

contrast to CoSe/S with a Tafel slope of 158 mV dec⁻¹. This result further demonstrates the superior catalytic effect of v-CoSe/S on the polysulfide conversion process, particularly in the solid-liquid conversion of the second reduction process.

To compare catalytic reaction kinetics, CV curves of CoSe/S and v-CoSe/S at different rates (0.2 mV s⁻¹ to 0.5 mV s⁻¹) were measured (Figures 5.23d-e). Each cathode exhibited a linear correlation between the peak current (I_p) and the square root of the scan rate (v), indicating a diffusion-limited response (Figure 5.23f). According to the Randles-Sevcik equation, the Li⁺ diffusion coefficient (D_{Li^+}) can be calculated from the dependence of the peak current density versus the square root of the scan rate:

$$I_p = 2.69 \times 10^5 n^{1.5} A D_{Li^+}^{0.5} C_{Li^+} v^{0.5} \quad (4)$$

In this equation, n , A , and C_{Li^+} represent the number of charges involved in the reaction, the electrode area, and the concentration of Li⁺, respectively. For CoSe/S and v-CoSe/S, the D_{Li^+} estimated from the cathodic peaks are $3.78 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $4.96 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively (Figure 5.23f).

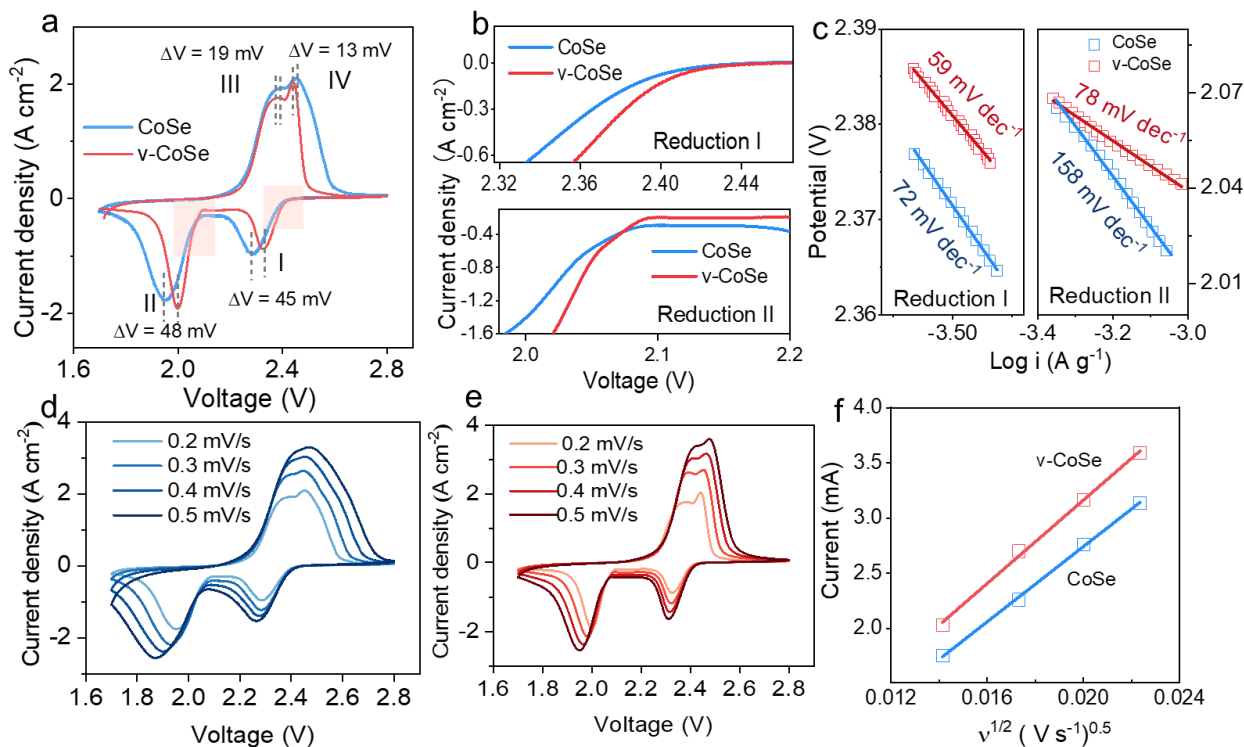


Figure 5.23. (a) CV curves. (b) LSV curves of reduction I and reduction II processes from the Figure (a) pink regions. (c) Tafel plots calculated from the reduction peaks I and II, respectively.

CV curves of (d) CoS/S and (e) v-CoSe/S at different scanning rates. (f) Peak current vs. square root of scan rate in oxidation process.

The GCD curves of the two different cells at a current density of 0.1C ($1C=1675 \text{ mAh g}^{-1}$) are shown in Figure 5.24a. The usual pair of discharge plateaus (Q1 and Q2) were measured for the two cells. v-CoSe/S shows a larger specific capacity, especially in the second discharge plateau (Q2). Besides, a smaller polarization voltage (ΔE), defined as the potential difference between the charge and discharge plateaus at 50% of the charge/discharge capacity, was measured for v-CoSe/S (38 mV) when compared with CoSe/S (52 mV). This result is consistent with the lower activation energy discussed above that was related to the fast liquid-solid conversion caused by the spin-polarized unpaired electrons transfer.

The rate performance of electrodes and the corresponding GCD at different currents are depicted in Figure 5.24b. The clear discharge plateaus at rates up to 4C indicate effective catalysis of the polysulfide conversion in the v-CoSe. With increasing current density, v-CoSe-based cells exhibit consistently higher initial specific capacities at all current densities compared with CoSe. In addition, upon returning to a current density of 0.1C, v-CoSe/S demonstrates a substantial recovery of high specific capacity. Moreover, a lower ΔE is also observed at every current density, which further confirms the effective role of vacancy manipulation in promoting the Li-S reaction kinetics. As an example, at 0.1C, v-CoSe/S exhibits a smaller polarization voltage of 103 mV compared to the 142 mV of CoSe/S (Figure 5.24c). Besides, the v-CoSe/S demonstrates higher Q_2/Q_1 values than CoSe/S consistently across all current densities presented in Figure 5.24c. As an example, the Q_2/Q_1 at 0.1C was 2.88 for v-CoSe and just 2.30 for CoSe. Q_1 accounts for the capacity contribution associated with the reaction of sulfur with Li^+ to form soluble polysulfide.^[71] Q_2 accounts for the capacity contribution associated with the conversion of soluble polysulfide into solid $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$. Hence, the ratio Q_2/Q_1 is an indicator of the polysulfide conversion efficiency. The higher Q_2/Q_1 value in v-CoSe/S than CoSe/S demonstrates a higher catalyst activity in the soluble polysulfide to solid $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ phase transformation.

The long-term cycling performance at a current density of 1C is shown in Figure 5.24d. Both CoSe/S and v-CoSe/S electrodes have close initial specific capacities, 1089 mAh g^{-1} (v-CoSe) and 1047 mAh g^{-1} (CoSe), respectively. However, the capacity retention of v-CoSe/S is much higher, maintaining 805 mAh g^{-1} after 1500 cycles for just 161 mAh g^{-1} after 723 cycles in the

CoSe/S electrode. The outstanding stability of v-CoSe/S is the result of the improved lithium polysulfide redox activity and low SRR activation energy, particularly for the liquid-solid conversion stage that promotes Li_2S nucleation, and it is also manifested in the reduced polarization voltages and higher Q_2/Q_1 ratios. Besides, the v-CoSe/S electrode shows outstanding specific capacity retention compared with previously reported sulfur cathodes (Figure 5.24e).

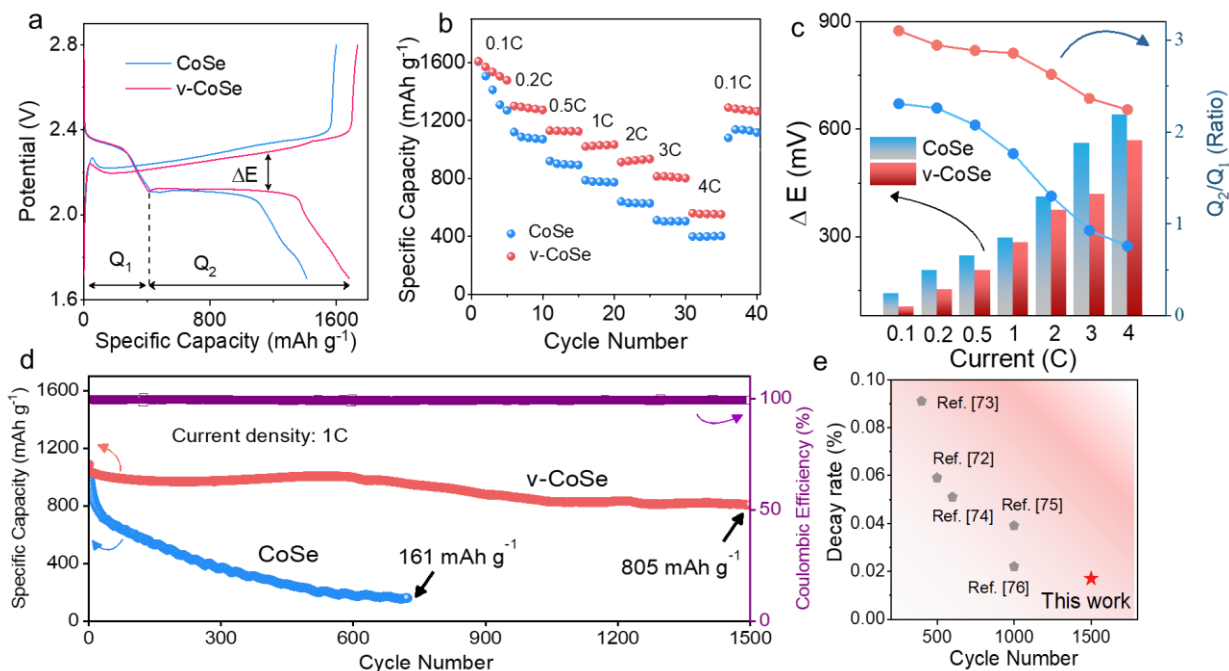


Figure 5.24. (a) GCD curves at 0.1C. (b) Rate performance. (c) ΔE and Q_2/Q_1 values. (d) Long cycling performance at 1C over 1500 cycles. (e) Comparison of the capacity obtained with the v-CoSe/S cathode with specific capacities of previously reported S catalysts electrodes.

5.3.4 High sulfur loading LSBs.

To assess the practical application potential of LSBs based on v-CoSe/S electrodes, cells were assembled using larger sulfur loadings. Long-term cycling was conducted at a sulfur loading of 4.2 mg cm^{-2} and a current density of 0.1 C, as shown in Figure 5.25a. In these conditions, initial capacities up to 5.2 mAh cm^{-2} , with only a 0.16% decay per cycle after 200 cycles, were measured. Additionally, the corresponding GCD curves reveal clearly defined plateaus, consistent with the excellent catalytic performance of v-CoSe (Figure 5.25b). Besides, as shown in the rate performance measurement (Figure 5.25c), v-CoSe demonstrates notable discharge-specific

capacities at current densities up to 4C. Moreover, the low R_{ct} (119 Ω) obtained from the EIS spectra (Figure 5.25d) indicates fast electron transfer even at this high sulfur loadings. Finally, Figure 5.25e showcases the capability of v-CoSe-based pouch cells to power our temperature and humidity monitoring clock, highlighting the practical utility of the fabricated electrodes.

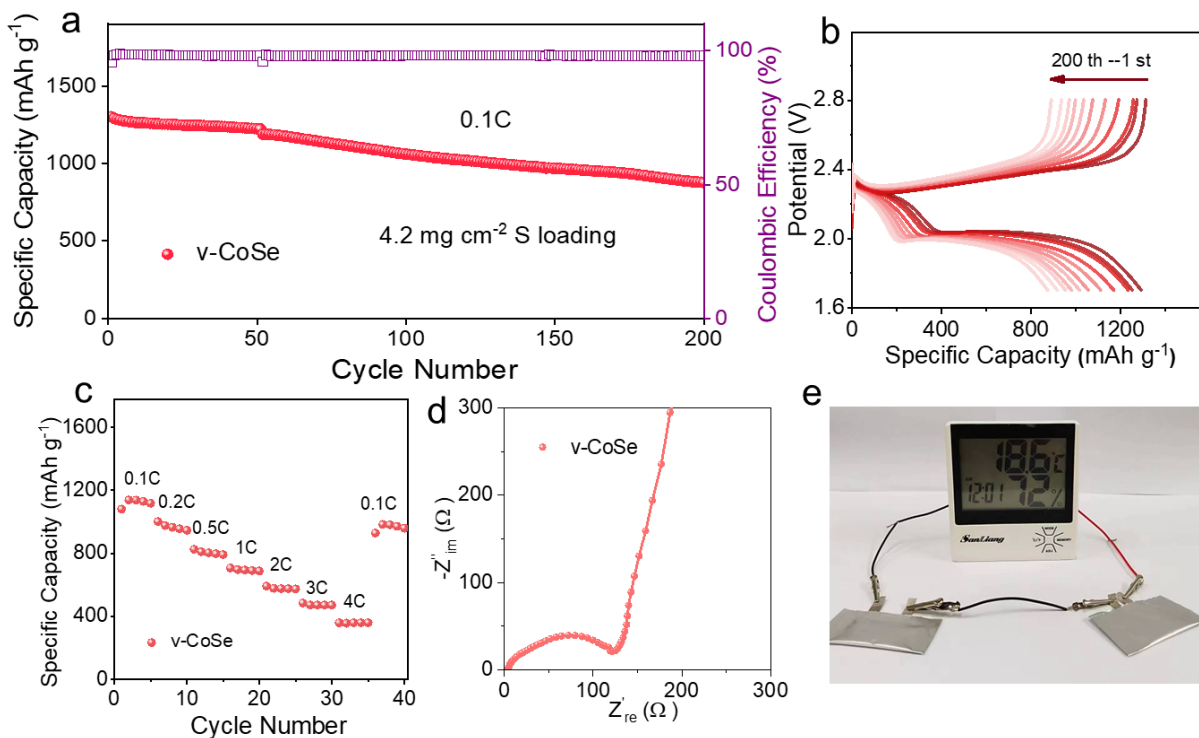


Figure 5.25. (a) Long-term cycling performance at 0.1 C. (b) GCD curves at 0.1 C from the 1st to the 200th cycles. (c) Rate performance from 0.1 C to 4 C. (d) EIS before cycling. (f) Pouch cells powering a temperature and humidity monitoring clock.

5.4 Conclusions

In this study, a defect engineering strategy was used to tune the electron spin state of an SRR electrocatalyst. This strategy was showcased by introducing controlled amounts of cation vacancies within ultrathin CoSe nanosheets. Theoretical calculations combined with experimental measurements showed the altered spin configuration results in enhancing both polysulfide adsorption and conversion activity and a more favorable thermodynamic reduction process, particularly for the transition from soluble polysulfide to solid Li₂S that showed a lower nucleation energy barrier. v-CoSe cathodes not only demonstrated excellent electrocatalytic properties but

also outstanding LSB electrochemical performance in terms of specific capacity, rate performance, and cycling stability, even at high sulfur loadings. Overall, this study demonstrates the need for considering the electronic spin configuration in the design of electrocatalysts, particularly for developing robust LSBs. Thus, the spin engineering approach showcased here paves the way to the rational design of new generations of LSB cathodes based on defect-engineered SRR electrocatalysts, toward the development of a cost-effective LSB technology with market-ready potential.

5.5 References

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Chapter 6 Promoting electrochemical reactions with dual-atom catalysts for high-rate lithium–sulfur batteries

6.1. Introduction

Conversion-type cathodes, including those based on oxygen, chalcogens, and halogens, hold great promise for next-generation high-energy-density rechargeable batteries. However, despite significant progress in recent years, their practical implementation still faces critical challenges.^[1] Among these, the activation of the conversion reaction stands out as a major hurdle, requiring catalysts that are both highly active and stable while contributing minimal additional weight to the system.^[2,3] Sulfur cathodes represent a paradigmatic example of high-energy-density, conversion-type cathodes, offering an impressive theoretical energy density of 2600 Wh kg⁻¹ while relying on a low-cost, abundant, and environmentally benign resource.^[4] However, the sluggish sulfur redox kinetics, which leads to low charge/discharge rates and limited cycling stability, remain a major challenge to their commercial viability. Addressing this limitation necessitates the development of catalysts that efficiently accelerate the SRRs, prevent the loss of active material,^[5] and thereby enhance overall battery performance.^[6–8]

The development of optimized catalysts for the SRRs remains a significant challenge due to their intrinsic complexity, involving multiple electrochemical steps alongside coupled chemical processes such as dissociation, disproportionation, and comproportionation.^[9–15] Additionally, the reaction pathway is likely influenced by various factors, including charge/discharge rate, cycling history, and cell architecture, particularly solvent composition and cathode additives. While numerous mechanisms have been proposed to describe this conversion process, the specific sulfur species involved and the liquid-solid transition mechanisms remain a topic of ongoing debate. A critical gap in current understanding lies in the formation and transformation of solid phases and the role of catalysts in facilitating these processes. For instance, C. Prehal et al. reported evidence of Li₂S formation from Li₂S₂ in a catalyst-free solid-state conversion process, showing that at relatively low current densities, preformed Li₂S₂ particles transform into aggregates of Li₂S grains with small crystallite sizes.^[16] Z. Wu et al. demonstrated that a catalyst can promote epitaxial growth of Li₂S from LiPS dissociation into Li₂S₂ and short-chain LiPS on the Li₂S (100) plane, followed by lithiation of Li₂S₂ into crystalline Li₂S.^[17] S. Zhou et al., using in situ TEM measurements, revealed that catalysts can act as a LiPS attraction pole, drawing a dense liquid

phase of LiPS that instantaneously deposits as crystalline Li₂S particles.^[6] These findings highlight the complexity of the Li₂S formation pathway and the pivotal role of catalysts in this process, emphasizing the need for a deeper understanding of catalytic mechanisms to advance technologies based on sulfur cathodes and optimize catalyst performance.

Single-atom catalysts (SACs) have emerged as promising candidates for accelerating cathodic conversion reactions, particularly SRRs.^[18,19] SACs offer maximized atomic utilization efficiency, unique electronic structures, and often superior catalytic activity, all achieved with minimal metal usage and added weight. Among them, 3d TM SACs, such as those based on manganese, cobalt, and nickel, have drawn particular attention due to their abundance, low cost, relatively low weight, and remarkable ability to catalytically enhance various electrochemical reactions, including the SRRs.^[20–22]

Unlike 3d TM, p-block metals have fully occupied 3d orbitals, leaving them with relatively inactive d electrons for bonding or electronic interactions.^[23] However, their unfilled p orbitals can interact with the 2p electrons of elements such as oxygen, chalcogens, or halogens, enabling the formation of π -electron conjugation.^[24] This interaction transforms the localized p orbitals into a delocalized state, effectively mimicking the electronic characteristics commonly associated with the d orbitals of TMs. As a result, p-block elements can also create tunable and multifunctional electronic structures, contributing to catalytically accelerating conversion reactions.^[25] These unique properties make p-block elements increasingly attractive metal electrocatalysts, offering a cost-effective and versatile alternative to traditional noble metal catalysts.^[26]

Among the p-block metals, bismuth stands out for its relatively high abundance, stability, low cost, and moderate environmental and health impact. Despite these advantages, its potential in catalysis remains largely unexplored. With an electronic configuration of [Xe] 4f¹⁴5d¹⁰6s²6p³, Bi benefits from the weak shielding effect of 4f electrons, a phenomenon commonly referred to as lanthanide contraction.^[24] This effect imparts Bi(III) with soft Lewis acidity, making it particularly effective in activating polysulfides. In sulfur cathodes, the 6p orbitals of Bi readily hybridize with the 2p orbitals of sulfur, enhancing charge transfer and lowering the energy barrier for polysulfide conversion.^[26] While these interactions enhance Bi's ability to bind polysulfides and catalyze the SRRs, they also introduce a limitation. The strong interaction between Bi and S–S multiple bonds hampers the cleavage of S–Bi bonds after the sulfur reduction process, thereby reducing the efficiency of subsequent reaction cycles.^[9]

To address these issues, we propose harnessing the robust π -activation properties of 6p main-group elements in synergy with the versatile and multifunctional nature of 3d TMs to activate the SRRs. To maximize catalytic activity with minimal weight addition, we suggest integrating these components into asymmetric diatomic catalysts (DACs).^[27] DACs are particularly advantageous for complex reactions requiring intricate electronic interactions, as their dual metal sites provide unique electronic structures and coordination environments that often surpass the performance of SACs. DACs also offer greater tunability compared to SACs, thanks to their inherent asymmetry, broader compositional flexibility, and the potential synergistic effects between the two distinct atomic centers. These features enhance catalytic activity, selectivity, and stability across various reactions.^[28] In DACs, the local charge symmetry is disrupted, leading to a dynamic redistribution of the electron cloud density at the active center during the reaction.^[18,29] This redistribution significantly influences the catalytic properties but adds complexity to the system, which has been seldom investigated. Understanding this interaction between the paired elements is crucial for optimizing DAC performance and unlocking their full potential in catalytic applications.

This study introduces 3d-6p DACs to accelerate SRR kinetics in LSBs and investigates the $S_8 \rightleftharpoons Li_2S$ conversion pathway behind their enhanced rate performance and stability. We first present a general, straightforward, low-cost, and scalable liquid-phase method for synthesizing DACs, in which TM-Bi atomic pairs are uniformly dispersed in a carbon nitride (CN) matrix. Three TMs are considered: Co and Ni with partially filled 3d orbitals, and Mn with a half-filled 3d shell. LSBs incorporating these catalysts as cathode additives are then systematically evaluated and compared with Co/CN and Bi/CN reference electrocatalysts. Experimental results identify Ni-Bi/CN and particularly Co-Bi/CN as the most effective TM-Bi/CN catalysts for improving cathode performance. Detailed analysis of the charge and discharge processes reveals that these best-performing catalysts significantly enhance the electrochemical $S_8 \rightarrow Li_2S_8$ conversion at relatively high voltage, effectively suppressing the simultaneous formation of Li_2S_4 and the chemical comproportionation reaction to Li_2S_2 . Additionally, cathodes incorporating these catalysts exhibit faster activation of the Li_2S phase, enabling the maintenance of high capacities at elevated charge/discharge rates. To further elucidate the catalytic mechanisms, first-principles calculations are employed to correlate the electronic interactions within the coupled 3d-6p atomic pairs with their electrocatalytic performance. Overall, this work provides valuable insights for the rational

design of practical Li-S catalysts, particularly DACs, unlocking their potential to advance LSB technology, optimize other conversion-type cathodes, and expand application in various electrocatalytic processes.

6.2 Experimental Section

6.2.1 Synthesis of TM-Bi/CN

Chloroanilic acid (417.96 mg, 2 mmol) was placed into a three-necked round-bottom flask under an argon atmosphere, and the flask was cooled in an ice bath. N-methyl-2-pyrrolidone (NMP) (12 mL) was used as the solvent, and melamine (504.48 mg, 4 mmol), 20 mg BiCl₃, and the same amount of the selected transition metal chloride (MnCl₂, CoCl₂, NiCl₂) were introduced into the mixture at around 0 °C. While stirring vigorously, a few drops of concentrated sulfuric acid were slowly added. After 20 minutes of continuously stirring, the ice bath was removed, and the reaction mixture was allowed to warm to room temperature. The solution was then heated to 170 °C for 24 hours under an argon atmosphere. Upon cooling to room temperature, the mixture was vacuum-filtered, washed with ethanol and water three times, and freeze-dried for 24 hours. The resulting black solid was annealed at 700 °C for 3 hours under an argon atmosphere, with a temperature ramp of 5 °C/min.

A series of CN-supported TM-Bi atomic pairs, including Mn-Bi/CN, Co-Bi/CN, and Ni-Bi/CN was produced through the pyrolysis of a mixture of chloroanilic acid and melamine containing small amounts of the corresponding metal chlorides (Figure 6.1). Additionally, reference Bi/CN, Co/CN, and CN materials were synthesized using the same procedure and evaluated as control samples. Chloroanilic acid exhibits a distinctive molecular structure, featuring a six-membered carbon ring decorated with highly electronegative groups, including -Cl, =O, and -OH, which contribute to its unique chemical reactivity and versatility. When combined with melamine, these electronegative groups interact with hydrogen (-H) from the Lewis base group (-NH₂) on melamine. This interaction promotes the detachment of small molecules, which, upon pyrolysis, results in the formation of a nitrogen-enriched carbon framework with numerous nitrogen-terminated structural voids. These voids provide abundant sites for metal-N bonding, enabling the incorporation of a high loading of Lewis acid atoms, such as Bi and 3d TMs, with excellent dispersion. This high density of trapping sites is crucial for synthesizing atomically dispersed catalysts, effectively suppressing the formation of metal-based nanoparticles.^[30]

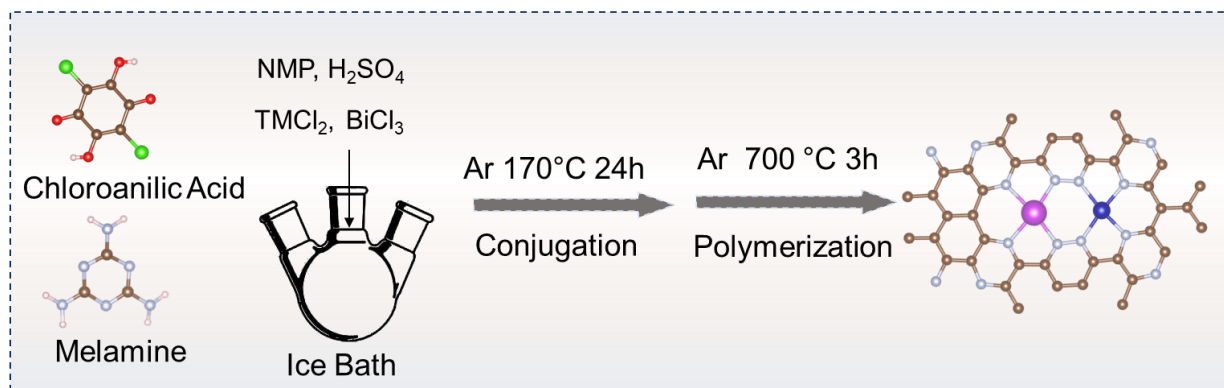


Figure 6.1. Scheme of the TM-Bi/CN DACs synthesis mechanism.

6.2.2 Preparation of TM-Bi/CN/S

TM-Bi/CN/S was prepared through a three-step process. First, the cathode host material was mixed with sulfur powder in a 1:3 ratio. The mixture was then ground thoroughly using a mortar and subjected to heat treatment at 155°C for 12 hours. Finally, the resulting product was collected for subsequent analysis.

6.3 Results and Discussion

6.3.1 DAC synthesis and physicochemical characterization

SEM images show that all samples feature irregular nanosheet-like structures (Figure 6.2). XPS further corroborates the presence of these elements (Figure 6.3). It is noteworthy that the relative signal intensities of TM and Bi significantly differ, which is attributed to their notably distinct photoionization cross-sections. Specifically, heavier elements such as Bi have larger cross-sections than lighter TMs, resulting in stronger XPS signals at comparable concentrations. Atomic-resolution AC-HAADF-STEM images (Figures 6.4a-d) display a high density of metal atoms distributed as single atoms across the CN matrix, validating the synthesis process's ability to trap different elements in single-atom form.

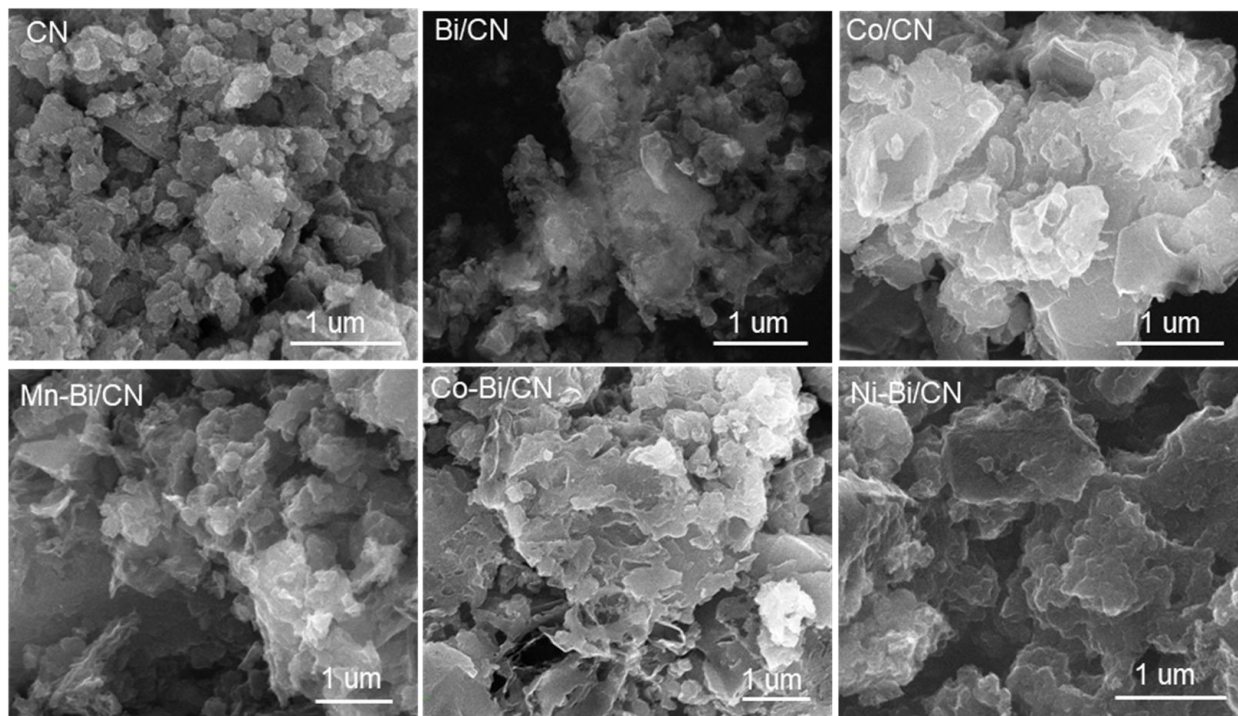


Figure 6.2. SEM images of CN, Bi/CN, Co/CN, Mn-Bi/CN, Co-Bi/CN, and Ni-Bi/CN.

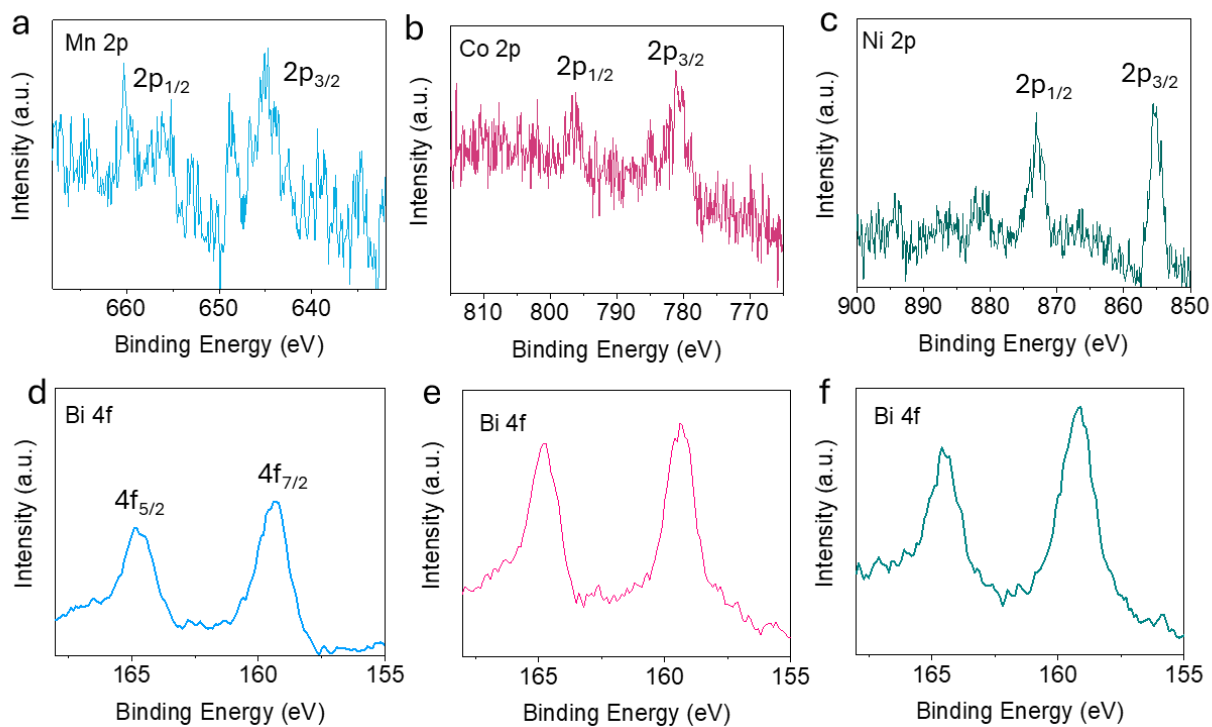


Figure 6.3. (a,d) High-resolution Mn 2p (a) and Bi 4f (d) XPS spectra of Mn-Bi/CN. (b,e) High-resolution Co 2p (b) and Bi 4f (e) XPS spectra of Co-Bi/CN. (c,f) High-resolution Ni 2p (c) and Bi 4f (f) XPS spectra of Ni-Bi/CN.

Using the Co-Bi/CN sample as a representative case, atomic-resolution AC-HAADF-STEM images were analyzed with a Laplacian of Gaussian algorithm to identify regions of rapid intensity variation, thereby detecting metal atoms. The intensity values of the identified metal atoms exhibit a bimodal distribution, indicating the presence of two distinct intensity levels corresponding to two different atomic species (Figure 6.5a). Given that atomic-resolution AC-HAADF-STEM intensity scales approximately with the atomic number (Z),^[31] the position of the two peaks aligns well with the atomic numbers of Co and Bi when taking into account an underlying 3 nm-thick C/CN layer contributed by the CN matrix and the ultrathin carbon grid used for STEM characterization. Furthermore, the ratio of the integrated peak areas matches the atomic ratio of Co and Bi detected by EDS analysis (Table 6.1), validating the algorithm's ability to differentiate between the two metal atoms (Figure 6.4e). Building on this differentiation, we conducted a detailed analysis of the spatial organization of Co and Bi atoms within the CN matrix (Figures 6.5b-c). Statistical results indicate that approximately 32% of the metal atoms form coupled Co-Bi pairs, as those shown in Figure 6.4f, another 31% were organized as either Bi-Bi or Co-Co pairs, and the remaining 37% existed as isolated Co or Bi atoms. Inductively coupled plasma mass spectrometry (ICP-MS) showed the atomic metal concentration to be about 1% with a TM/Bi ratio of ca. 1 (Table 6.2).

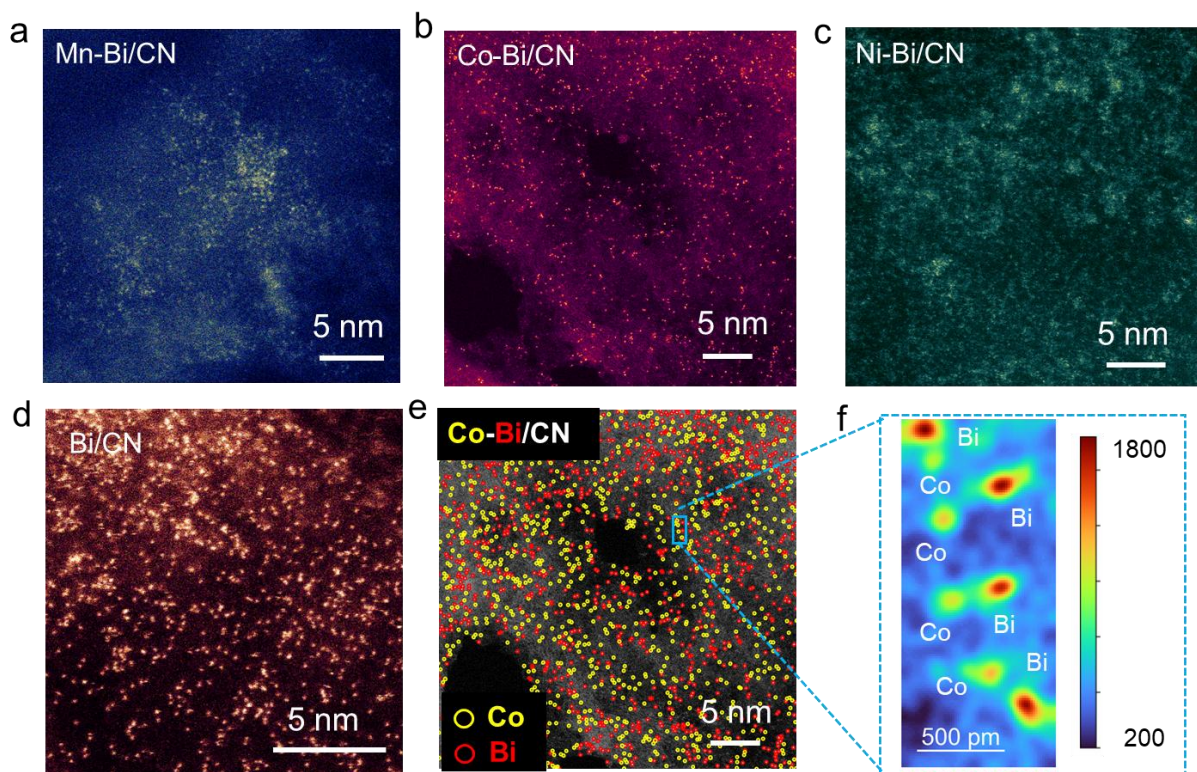


Figure 6.4. (a-d) Atomic-resolution AC-HAADF-STEM images (false-colors) of TM-Bi/CN: Mn-Bi/CN (a) Co-Bi/CN (b), Ni-Bi/CN (c), and Bi/CN (d). (e) Co-Bi/CN AC-HAADF-STEM image identifying Co (yellow) and Bi (red) atoms. (f) 3D plot of a magnified region of the Co-Bi/CN AC-HAADF-STEM image.

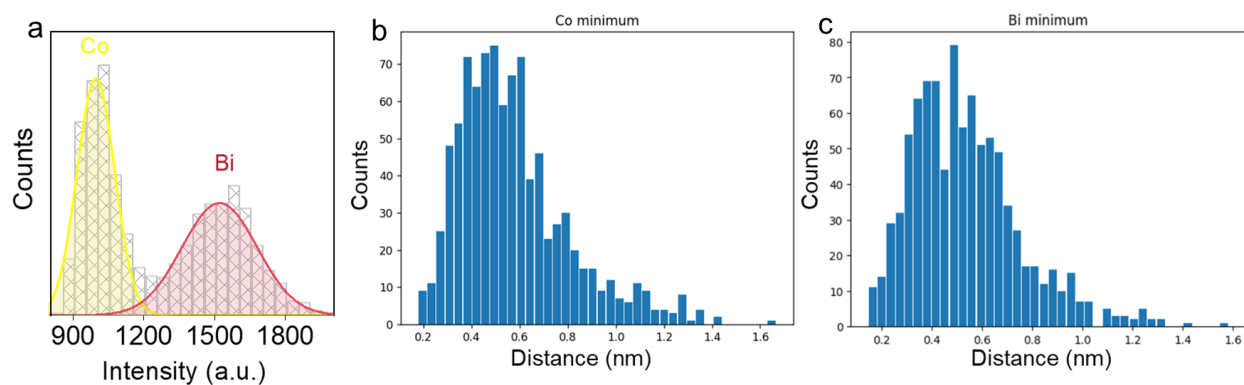


Figure 6.5. (a) Histogram of all the intensity spikes detected in the Co-Bi/CN AC-HAADF-STEM image using Laplacian of Gaussian algorithm. (b,c) Histograms of the minimum distance's distribution from Co and Bi atoms within Co-Bi/CN

Table 6.1. Atomic quantification EDS results.

Samples / Relative Content	TM (%)	Bi (%)
Mn-Bi/CN	0.55	0.46
Co-Bi/CN	0.56	0.47
Ni-Bi/CN	0.41	0.25

Table 6.2. Concentrations of metal ions in various samples measured by inductively coupled plasma mass spectrometry (ICP-MS).

Relative Content	TM Concentration (%)	RSD (%)	Bi Concentration (%)	RSD (%)
Mn-Bi/CN	0.468	2.74	0.551	0.63
Co-Bi/CN	0.517	8.64	0.622	3.97
Ni-Bi/CN	0.541	5.02	0.680	2.62

RSD: Relative Standard Deviation

XAS was used to identify the local geometry of the TMs. EXAFS analysis of the TM *K*-edges allowed us to extract interatomic distances of the first coordination shell for TM-Bi systems and construct a series of DFT atomic structure models for TM-Bi/CN complexes. XANES spectra and the generated molecular structure models are shown in Figure 6.6. The peak around 2.0 Å in the Fourier-transformed (FT) EXAFS spectrum corresponds to the TM–N bond. The length of this bond is influenced by the TM chemical environment, particularly the presence of Bi, which should be evident in the experimental data, offering a means to verify the formation of coupled TM-Bi pairs. First shell Fourier analysis revealed the interatomic TM–N distances to be $R_{\text{Mn-N}}=2.192$ Å, $R_{\text{Co-N}}=1.963$ Å, and $R_{\text{Ni-N}}=1.871$ Å (Table 6.2). The experimental TM–N bond lengths align with those simulated for the TM–Bi/CN model, confirming the presence of a substantial amount of asymmetric coupled metal pairs, consistent with atomic resolution AC-HAADF-STEM analysis.

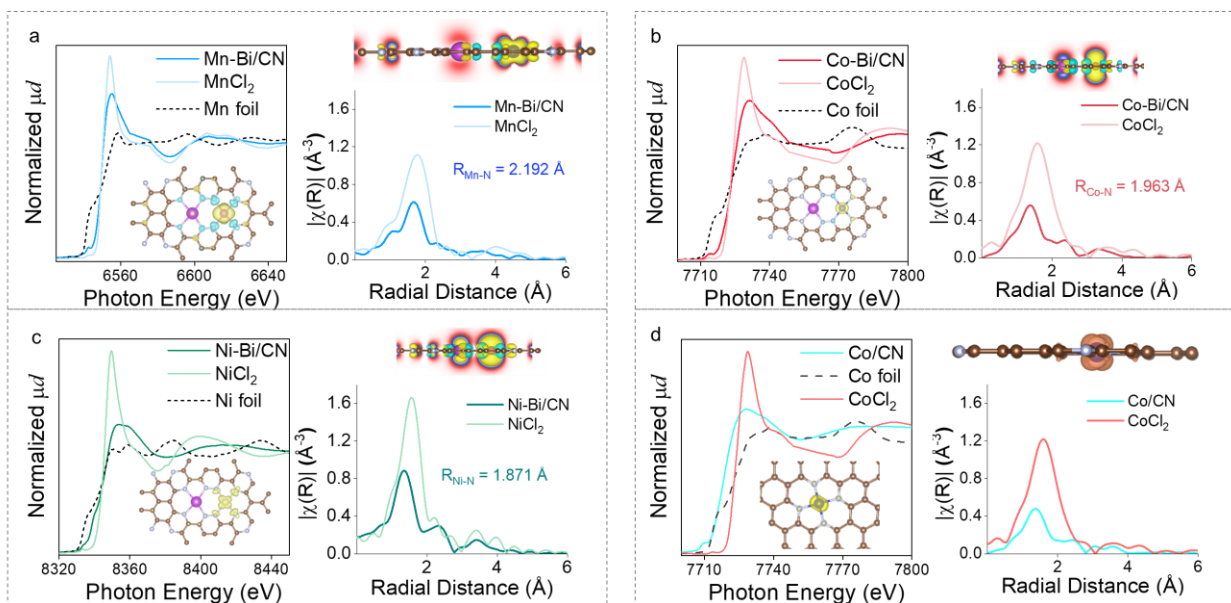


Figure 6.6. (a-d) TM K-edge XANES spectra (left) and FT of the EXAF spectra (right) of Mn-Bi/CN (a), Co-Bi/CN (b), Ni-Bi/CN (c), and Co/CN (d). The spectra of the corresponding metal foils and metal(II) chlorides are also included as references. Structural parameters extracted from the 1st shell Fourier analysis are shown in Table 6.3. Insets show the ball and stick structure models, where brown = C; grey = N; pink = Bi; and other colors = TMs. The models include electronic density data obtained from DFT calculations, where cyan = spin down electron cloud, and yellow = spin up electron cloud. The isosurface level is 0.001 e/a_0^3 .

Table 6.3. Structural parameters extracted from 1st shell Fourier analysis

Name	Bonding	R ($\text{\AA}$)	R error ($\text{\AA}$)	N	σ^2	σ^2 error
Mn-Bi/CN	Mn-N	2.1918	0.0408	4	0.0069	0.0028
Co-Bi/CN	Co-N	1.9634	0.0138	4	0.0101	0.0023
Ni-Bi/CN	Ni-N	1.8726	0.0327	4	0.0077	0.0020

6.3.2 DAC performance in LSBs

To assess the electrochemical performance of DACs as catalytic additives in sulfur-based cathodes, CR2032 coin-type full cells were assembled using a 1.0 M LiTFSI and 0.2 M LiNO₃ in a DOL/DME electrolyte, a Li foil anode, and a TM-Bi/CN/S cathode. The cathode was prepared

by casting a mixture with an 8:1:1 mass ratio of TM-Bi/CN/S, conductive carbon (Super P, SP), and polyvinylidene fluoride binder. TM-Bi/CN/S was produced by heating a 1:3 mixture of TM-Bi/CN and S at 155 °C. The cells were cycled within the voltage range of 1.7-2.8 V. Cells based on Bi/CN/S, Co/CN/S, CN/S, and SP/S were also assembled and tested as a reference.

In the commonly used DOL/DME electrolyte, the galvanostatic discharge profiles of LSBs typically display two distinct plateaus separated by a gradual transition. The combined capacity of the first plateau and the transition region (Q_1) is usually attributed to the four-electron reduction of S_8 to Li_2S_4 . The initial plateau is generally associated with the conversion of S_8 to Li_2S_8 , a two-electron process with an equilibrium potential of 2.41 V that contributes to 50% of Q_1 .^[12] The subsequent sloped transition represents the reduction of Li_2S_8 to Li_2S_4 , which involves two additional electrons and occurs at a lower potential (2.24 V).^[12] The sloped nature of this transition arises from the multiple disproportionation and comproportionation reactions that can occur in this region, particularly considering the relatively low solubility of Li_2S_4 in the DOL/DME electrolyte. The second discharge plateau, Q_2 , overall accounts for the conversion of Li_2S_4 to Li_2S , a process that is assumed to occur through the precipitation of soluble $LiPS$ into Li_2S_2 , followed by its crystallization into Li_2S . This step involves the transfer of 12 electrons, accounting for 75% of the cell's total capacity, and it is governed by sluggish liquid-solid and solid-state reactions, making it a critical bottleneck in LSB performance.

All the cells incorporating catalytic additives achieved high capacities approaching the theoretical limit, indicating a high sulfur utilization (Figure 6.7). In contrast, the catalyst-free SP/S cell displayed significantly lower capacity, highlighting the critical role of catalysts in the activation of the electrochemical process. While all catalysts promoted the cell rate performance and stability, notable differences among the tested DAC-based electrodes were observed, further demonstrating their substantial influence on sulfur redox kinetics and overall battery performance.

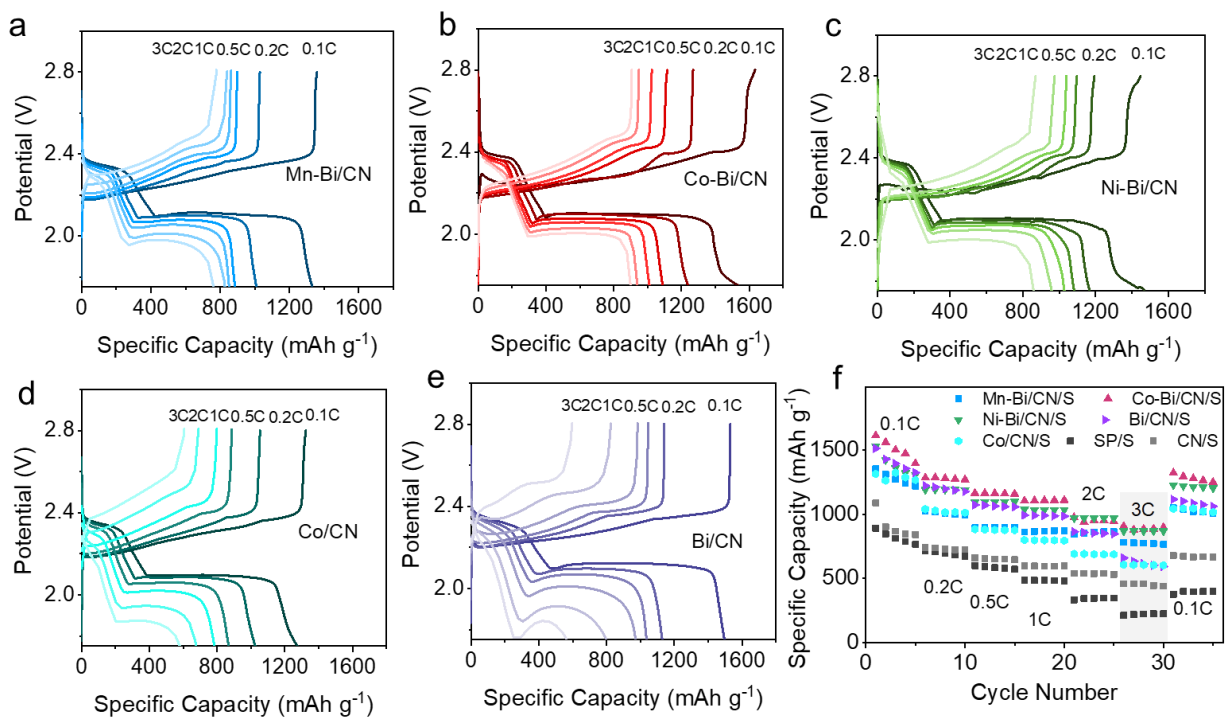


Figure 6.7. (a–e) GCD profiles of Mn–Bi/CN/S (a), Co–Bi/CN/S (b), Ni–Bi/CN/S (c), Co/CN/S (d), and Bi/CN/S (e) at different current densities. (f) Rate performance of TM–Bi/CN/S, Co/CN/S, Bi/CN/S, CN/S and SP/S full cells.

As consistently observed in previous literature, all tested LSBs experience capacity loss during the initial cycles at low GCD rates, primarily due to the dissolution and redistribution of LiPS throughout the cell. However, while some of the LSBs continue to suffer significant capacity degradation during high-rate cycling, the cells based on Ni–Bi/CN/S and Co–Bi/CN/S demonstrate minimal capacity loss at high rates. These electrodes also exhibited the best rate performance (Figure 6.7), achieving high specific capacities at the highest current rates tested. Specifically, at 3C, Co–Bi/CN/S delivered a discharge specific capacity of 906 mAh g⁻¹, i.e. 56 % of the capacity delivered at 0.1C, significantly outperforming the Mn–Bi/CN/S electrode and most previously reported cathodes.^[3,5,32–35] The rate performance of the Co–Bi/CN/S-based cell also surpassed that of the Co/CN/S and Bi/CN/S reference electrodes, which retained only 46% and 42% of their capacities for Co/CN/S for Bi/CN/S, respectively, when the current density was increased from 0.1C to 3C.

A closer examination of the galvanostatic discharge profiles at the lowest tested current density (0.1C) reveals two differentiated behaviours (Figure 6.8a). On the one hand, the best-performing cathodes, those based on Ni-Bi/CN/S and Co-Bi/CN/S, exhibit the highest first discharge plateau, at an average potential of around 2.38 V. This plateau contributes approximately 50% of the first-step capacity (Q_1), which represents roughly one-quarter of the total discharge capacity, yielding a Q_2/Q_1 ratio of approximately 3. This aligns with the simplified interpretation of the sulfur redox pathway, where the first plateau corresponds to the 2-electron $S_8 \rightarrow Li_2S_8$ transition, the sloped region accounts for the subsequent 2-electron $Li_2S_8 \rightarrow Li_2S_4$ conversion, and the second plateau represents the 12-electron $Li_2S_4 \rightarrow Li_2S$ transformation.

On the other hand, Mn-Bi/CN/S, Co/CN/S, and Bi/CN/S demonstrate substantially superior performance compared to SP/S, rivalling that of previously reported high-performance catalysts (Figure 6.8a).^[3,5,32–35] However, their performance was inferior to that of the best-performing DACs developed in this study, particularly in terms of rate performance and stability. These relatively less-performing electrodes display initial discharge plateaus at a lower average voltage (~ 2.34 V), indicating limitations in the activation of the $S_8 \rightarrow Li_2S_8$ conversion, thereby requiring additional overpotential. Notably, the Mn-Bi/CN/S and particularly Bi/CN/S electrodes display a significantly extended first plateau that accounts for 60% of Q_1 , reaching approximately three electrons per S_8 molecule. This suggests that the initial plateau involves sulfur electrochemical reduction beyond Li_2S_8 , probably activated by the lower potentials reached during the initial discharge required by the inefficient $S_8 \rightarrow Li_2S_8$ conversion. Although the first plateau in these catalysts remains above the equilibrium potential of further Li_2S_8 electrochemical reduction reactions (≤ 2.24 V), this reaction can be facilitated by the additional driving force provided by the chemical disproportionation or comproportionation conversion of the Li_2S_8 reduction products, such as Li_2S_4 . Additionally, Q_1 exceeds the theoretical limit of the four-electron $S_8 \rightarrow 2Li_2S_4$ reaction and results in low $Q_2/Q_1 \approx 2.0$. This implies that the first sulfur reduction step extends beyond Li_2S_4 , involving the formation of some Li_2S_2 . Since the equilibrium potential for the electrochemical formation of Li_2S_2 or Li_2S is too low to be effective (≤ 2.1 V) at this discharge stage, Li_2S_2 needs to be formed via a chemical comproportionation reaction involving additional production of S_8 or Li_2S_8 to further fuel the Q_1 electrochemical process and sustaining the extended first plateau, e.g. $Li_2S_8 + Li_2S_4 \rightarrow S_8 + 2Li_2S_2$. This reaction is likely activated in these specific electrodes, but not in the best-performing Ni-Bi/CN/S and Co-Bi/CN/S cathodes, due to the slow $S_8 \rightarrow Li_2S_8$ conversion

that enables the coexistence of a richer variety of sulfur species in the presence of S_8 , thereby facilitating comproportionation reactions that generate additional S_8 capable of heterogeneously precipitating. Since the formation of Li_2S_2 through chemical comproportionation can occur away from the electrode surface, part of the active sulfur may become electrochemically isolated and be lost during each cycle, contributing to capacity fade and reduced long-term cycling stability. This capacity loss may be masked by the LiPS migration-induced losses at slow discharge rates, but it becomes evident at higher discharge rates (Figure 6.7).

When normalizing the discharge profile to the capacity achieved at 1.9 V (Figure 6.8b), we observe that all the less-performing LSBs, including the SP/S cell, exhibit a relatively longer first plateau, along with a relatively low Q_2/Q_1 ratio. This suggests that the commonly observed low Q_2/Q_1 ratio in these systems is not solely attributable to incomplete LiPS reduction, as often assumed. Instead, it may also result from a relatively extended Q_1 step beyond four electrons per S_8 participating in the reaction, likely caused by the inefficient $S_8 \rightarrow Li_2S_8$ conversion that facilitates additional electrochemical reactions followed by chemical comproportionation processes, ultimately leading to the precipitation of some Li_2S_2 .

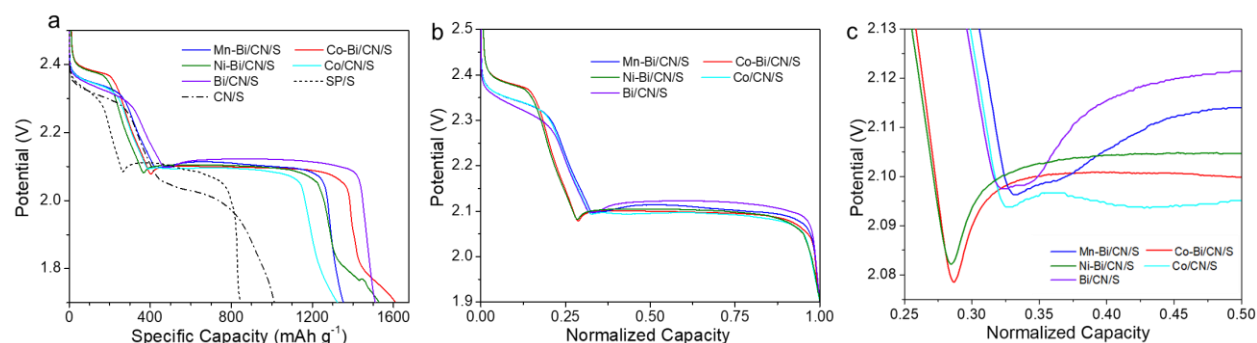


Figure 6.8. (a) Galvanostatic discharge profiles of Mn-Bi/CN/S, Co-Bi/CN/S, Ni-Bi/CN/S, Co/CN/S, Bi/CN/S, SP/S, and CN/S at 0.1C, with the y-axis displayed over the voltage range of 1.7–2.5 V. (b) Normalized galvanostatic discharge curves of Mn-Bi/CN/S, Co-Bi/CN/S, Ni-Bi/CN/S, Co/CN/S, and Bi/CN/S at 0.1C, with the y-axis displayed over the voltage range of 1.9–2.5 V. (c) Galvanostatic discharge curves at 0.1C at the transition between the two plateaus.

At the onset of the second discharge plateau, the Ni-Bi/CN/S and Co-Bi/CN/S electrodes exhibit a distinct sharp potential dip, which is attributed to the Li_2S_2/Li_2S nucleation barrier and remains relatively unaffected when increasing the discharge rate (Figure 6.8c). No additional

features are observed within this plateau. *Operando* XRD (Figure 6.9a-b) shows that the Li_2S phase appears immediately after the dip, indicating that Li_2S forms either directly from or concurrently with the Li_2S_2 through the reduction of solution-phase precursors from the very start of the second plateau. Conversely, for the Mn-Bi/CN/S sample, Li_2S formation becomes evident only some time after the voltage reaches 2.1 V, followed by a progressive growth until the end of discharge (Figures 6.9c-d).

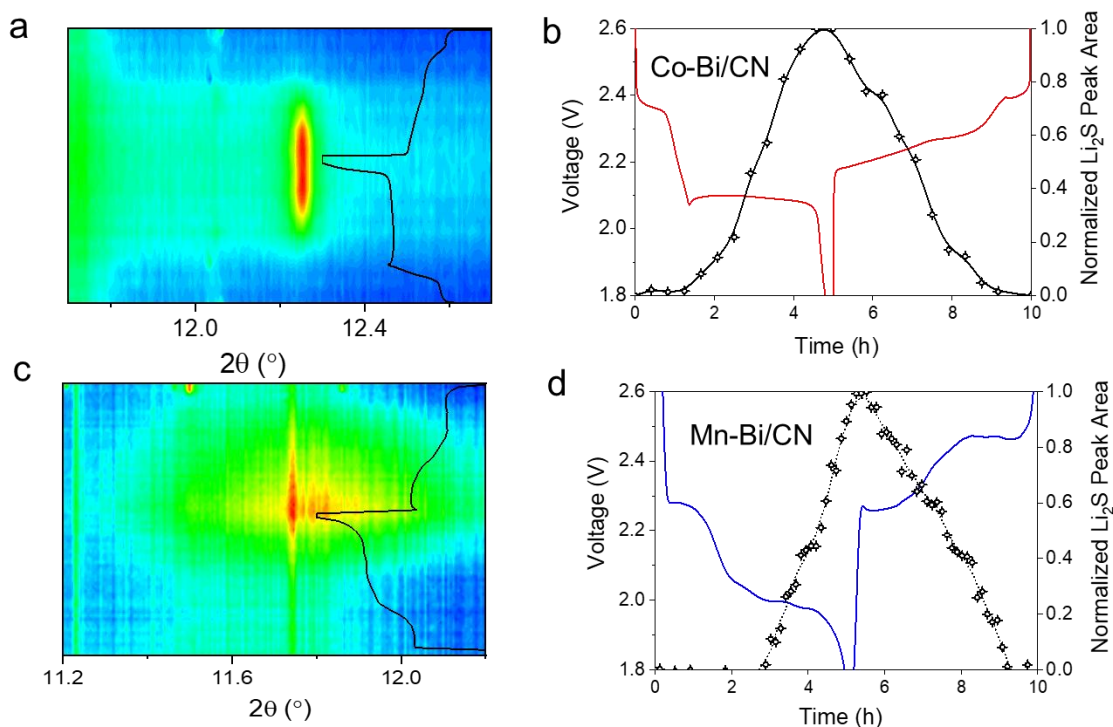


Figure 6.9. (a) Operando XRD patterns of Co-Bi/CN/S and GCD profile. (b) Normalized Li_2S (220) XRD peak area obtained from operando XRD analysis and GCD profile. (c) Operando XRD patterns of Mn-Bi/CN/S and GCD profile. (d) Integrated Li_2S (331) peak area and GCD profile for Mn-Bi/CN/S.

In contrast, at 0.1C, the Mn-Bi/CN/S and Bi/CN/S electrodes exhibit a less pronounced yet significantly more extended potential dip at the onset of the second plateau, characterized by two distinct steps (Figure 6.8c). Co/CN/S electrodes exhibit an even more pronounced two-step potential dip. This dip and the overall plateau overpotential strongly increase with the discharge rate for all these electrodes. The reduced depth of the potential dip at 0.1C obtained for these catalysts is consistent with the formation of Li_2S_2 precipitates in the previous step (Q_I), which

subsequently facilitates the electrochemical deposition of short-chain polysulfides on the pre-nucleated Li_2S_2 at the onset of Q_2 . However, this shadow dip comes at the cost of an extended prolongation that suggests a delayed Li_2S nucleation. This delayed onset of the Li_2S nucleation occurs either because the activated Li_2S_2 growth prevents reaching the lower potentials required for Li_2S nucleation at the onset of Q_2 or because the catalyst surface is covered by a solid Li_2S_2 layer that requires the less favourable solid-to-solid phase nucleation over the more accessible liquid-to-solid pathway. In the best cases, the dip extends for approximately 1000 seconds, which constitutes only a small fraction of the total discharge time at 0.1C (36,000 s). Consequently, a nearly complete conversion of S_8 to Li_2S remains attainable at these low rates. However, at higher rates, such as 1C (3,600 s full discharge) and above, this extended nucleation time becomes a critical bottleneck, significantly restricting Li_2S crystallization and thereby strongly limiting the capacities obtained at relatively high rates. Post-mortem SEM analysis of the discharged cathodes confirmed that the reference Co/CN and Bi/CN catalysts failed to promote Li_2S nucleation even at moderate current densities, resulting in irregular Li_2S_2 deposits rather than well-defined Li_2S crystals (Figure 6.10). In contrast, the Co-Bi/CN/S cathode displayed clear crystalline features after discharging at 0.5C and 2C current densities (Figure 6.10).

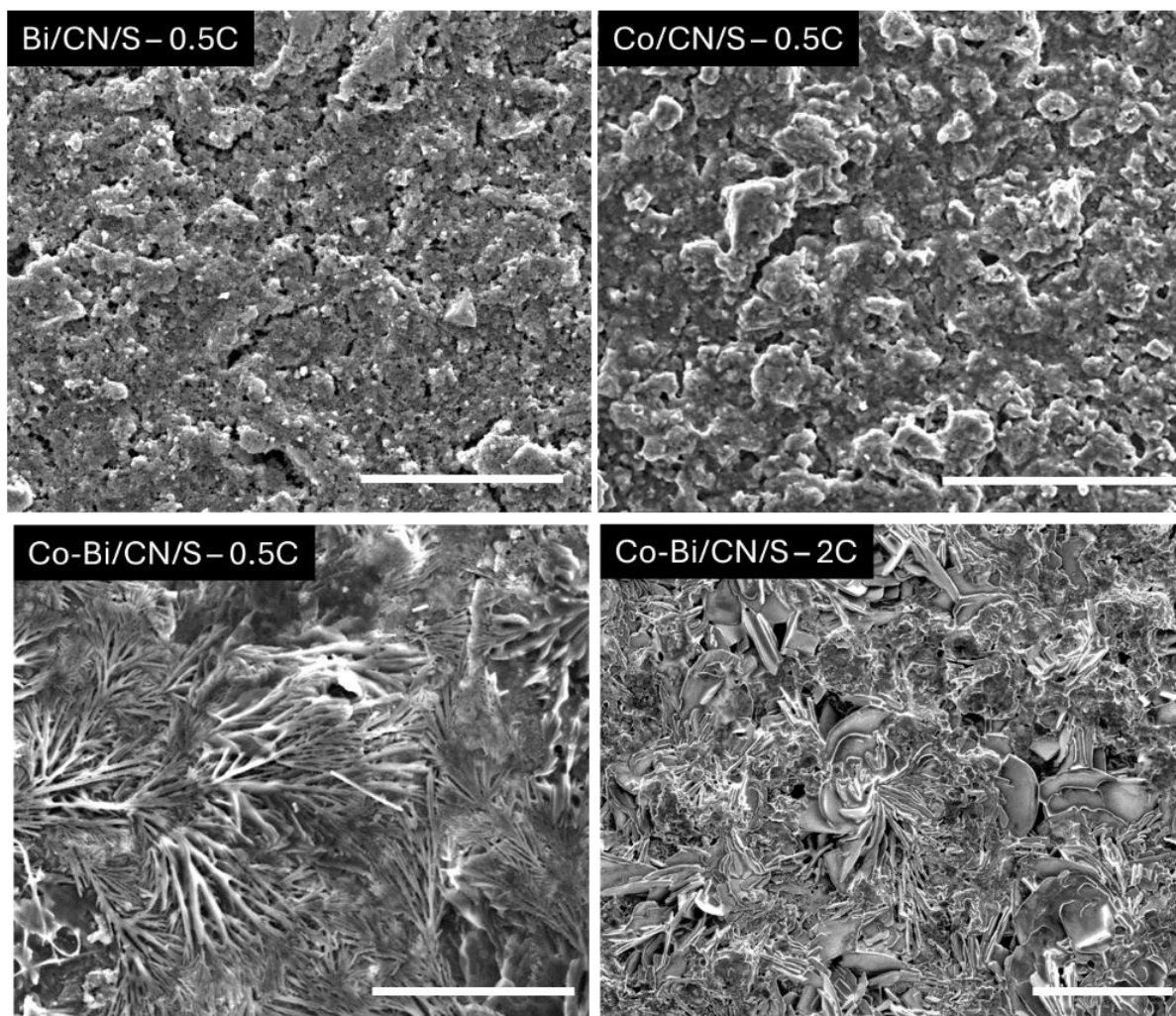


Figure 6.10. SEM images of Bi/CN/S, Co/CN/S, and Co-Bi/CN/S cathodes after discharging at 0.5C and a Co-Bi/CN/S cathode discharged at 2C, as noted in labels. Scale bars = 100 μm .

Upon normalizing the discharge profiles to the maximum capacity of each step (Q_1 and Q_2 , Figure 6.11) and using the 0.1C discharge profile as a reference, we observe that the Co-Bi/CN/S electrode exhibits minimal overpotential increase with the current rate during the first plateau, corresponding to the formation of Li_2S_8 . This indicates fast reaction kinetics and an absence of diffusion limitations, as the reactant is initially in the solid state, and Li_2S_8 dissolution likely occurs rapidly at the beginning of discharge when no LiPSs are yet present in solution (Figure 6.11). A noticeable overpotential increase appears midway through the first step, coinciding with the transition between the first and second plateaus. This is attributed to diffusion limitations, as a significant fraction of the generated Li_2S_8 fueling this second reaction is now dissolved in solution.

However, the overpotential stabilizes during this transition and remains steady throughout the second plateau, where Li_2S_2 and Li_2S form and crystallize from solution-phase precursors, encountering the same diffusion constraints as in the $\text{Li}_2\text{S}_8 \rightarrow \text{Li}_2\text{S}_4$ conversion. The Co/CN/S electrode exhibits a similar overpotential trend with increasing cycling rates, showing a moderate initial rise that becomes more pronounced at the transition between the two plateaus before stabilizing in the second plateau. However, the overpotential increase in Co/CN/S is higher than that in Co-Bi/CN/S, suggesting lower catalytic activity or a reduced ability to interact with LiPSs in solution due to a lower LiPS adsorption energy, as discussed later. In contrast, the Bi/CN/S electrode exhibits a lower initial increase in overpotential compared to the Co/CN/S electrode during the first step, attributed to enhanced interactions with LiPS. However, as sulfur reduction progresses, the overpotential gradually increases throughout the first plateau and continues to rise into the second plateau. This behavior suggests increasing difficulties in breaking additional S-S bonds as the LiPS chain shortens, likely due to the strong interaction between Bi and S within LiPS, as shown below.

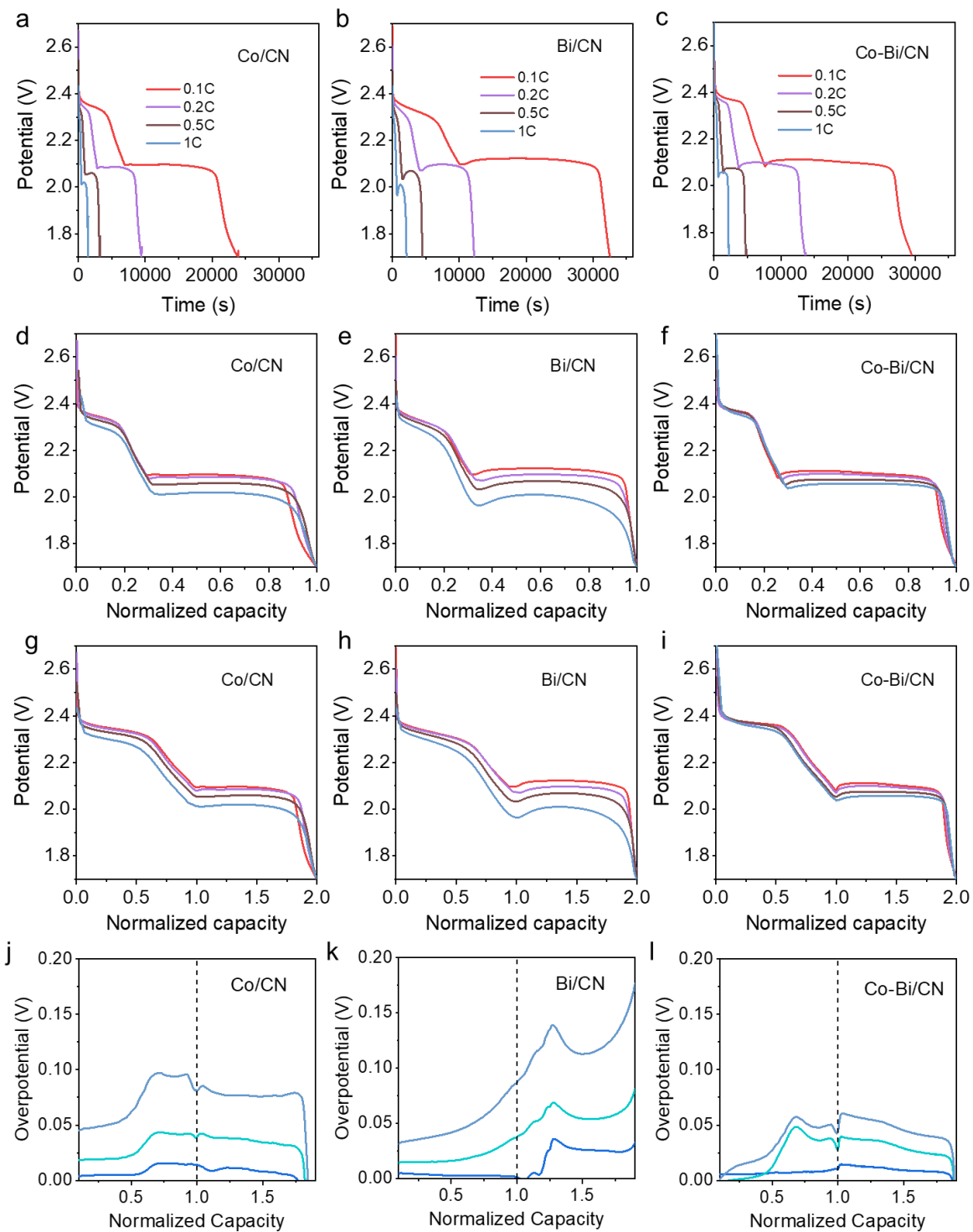


Figure 6.11. Galvanostatic discharge profiles (a-c), profiles normalized to the total capacity (d-f), profiles normalized for both Q_1 and Q_2 steps (g-i), and relative overpotential at 0.2C, 0.5C and 1C,

referred to the 0.1C profiles (j-i) of Co/CN/S (a,d,g,j), Bi/CN/S (b,e,h,k) and Co-Bi/CN/S (c,f,i,l) based cells.

Focusing on the galvanostatic charge curves, distinct charging profiles for the two types of catalysts discussed above are observed (Figures 6.12 a-b). The Ni-Bi/CN/S and Co-Bi/CN/S electrodes show a pronounced initial overpotential peak, followed by a steady rise in charging potential, eventually reaching a plateau at approximately 2.40 V. This plateau, extending for two electrons per S_8 molecule, corresponds to the final $Li_2S_8 \rightarrow S_8$ step. Interestingly, as the charge rate increases, the initial overpotential peak decreases, suggesting different dominant mechanisms at low and high cycling rates. This initial overpotential is associated with an additional discharge plateau observed at around 1.8 V (Figures 6.7a-e), which can accommodate up to two electrons per S_8 molecule. Notably, this additional plateau is pronounced only in high-performing electrodes and exclusively at low discharge rates ($<1C$). The disappearance of this discharge plateau correlates with the vanishing of the overpotential peak at the onset of charging.

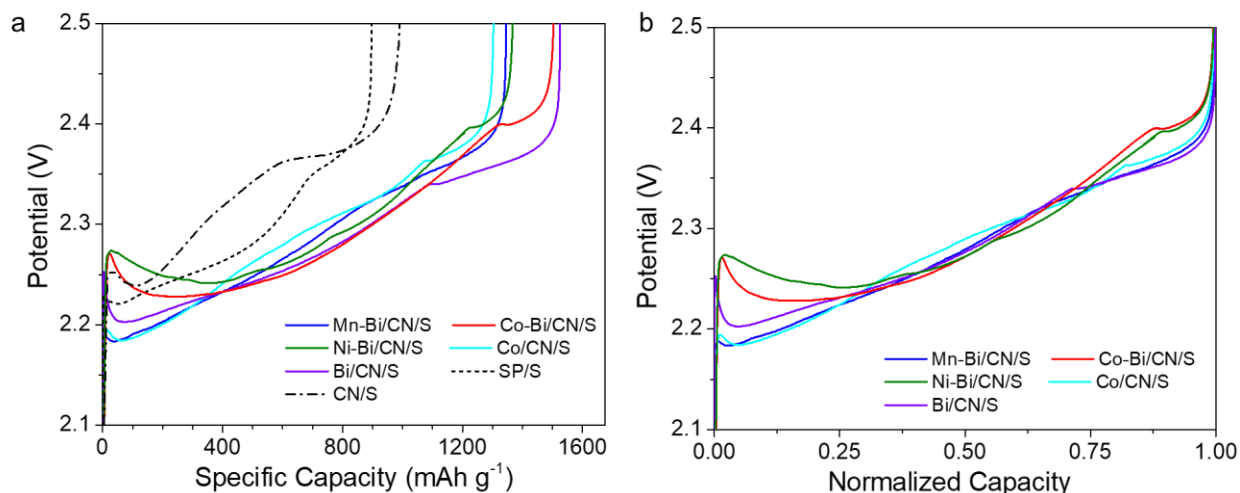


Figure 6.12. (a) Galvanostatic charge curves of Mn-Bi/CN/S, Co-Bi/CN/S, Ni-Bi/CN/S, Co/CN/S, Bi/CN/S, SP/S, and CN/S at 0.1C, with the y-axis displayed over the voltage range of 2.1–2.5 V. (b) Normalized galvanostatic charge profiles of Mn-Bi/CN/S, Co-Bi/CN/S, Ni-Bi/CN/S, Co/CN/S, and Bi/CN/S at 0.1C, with the y-axis displayed over the voltage range of 2.1–2.5 V.

Discharge plateaus within this voltage range have been attributed to reactions involving $LiNO_3$ electrolyte additives.^[36] However, in the present study, the selective appearance of this plateau for certain catalysts, its confinement to low discharge rates, indicative of a diffusion-

limited process, and its persistence even after returning to 0.2C, imply a different underlying mechanism. A plausible explanation is the direct reduction of residual, highly soluble Li_2S_6 into Li_2S , which would occur at a lower potential than the 2.1 V of the second plateau.^[12] This extended reduction process not only increases the discharge capacity but also depletes the electrolyte of LiPS, thereby preventing undesirable reactions with the anode and enhancing the cell's stability. However, this mechanism also introduces a trade-off. The extensive consumption of LiPS during discharge impedes the dissolution of Li_2S at the onset of the subsequent charge process, leading to the observed initial overpotential peak.

In contrast, all the other electrodes exhibit only a minor initial overpotential at 0.1C, which rapidly increases with the charge rate. This behavior suggests the sufficient presence of LiPS at the discharge onset but a limited ability to interact with them effectively. These electrodes also show a steeper voltage rise, with a lower potential (around 2.36 V) more extended final plateau, corresponding to the transfer of approximately four electrons per S_8 . Similar to the discharge process, these electrodes facilitate the simultaneous and premature formation of Li_2S_8 and S_8 from Li_2S_4 or other short-chained LiPSs formed during the electrochemical dissolution of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$. The coexistence of these species promotes chemical comproportionation reactions, resulting in both homogeneous and heterogeneous sulfur nucleation within the solution and at the electrode and separator surfaces. This uncontrolled chemical formation of S_8 leads to the precipitation of some electrically isolated sulfur (Figure 6.13), rendering it inactive for subsequent cycles. While this chemical S_8 precipitation can contribute to capacity loss, especially at high rates, it also facilitates S_8 growth at lower charge potentials. In contrast, the best-performing catalysts effectively confine the electrochemical growth of S_8 to the electrode surface, preventing uncontrolled sulfur precipitation and enhancing the cycling stability of the battery.

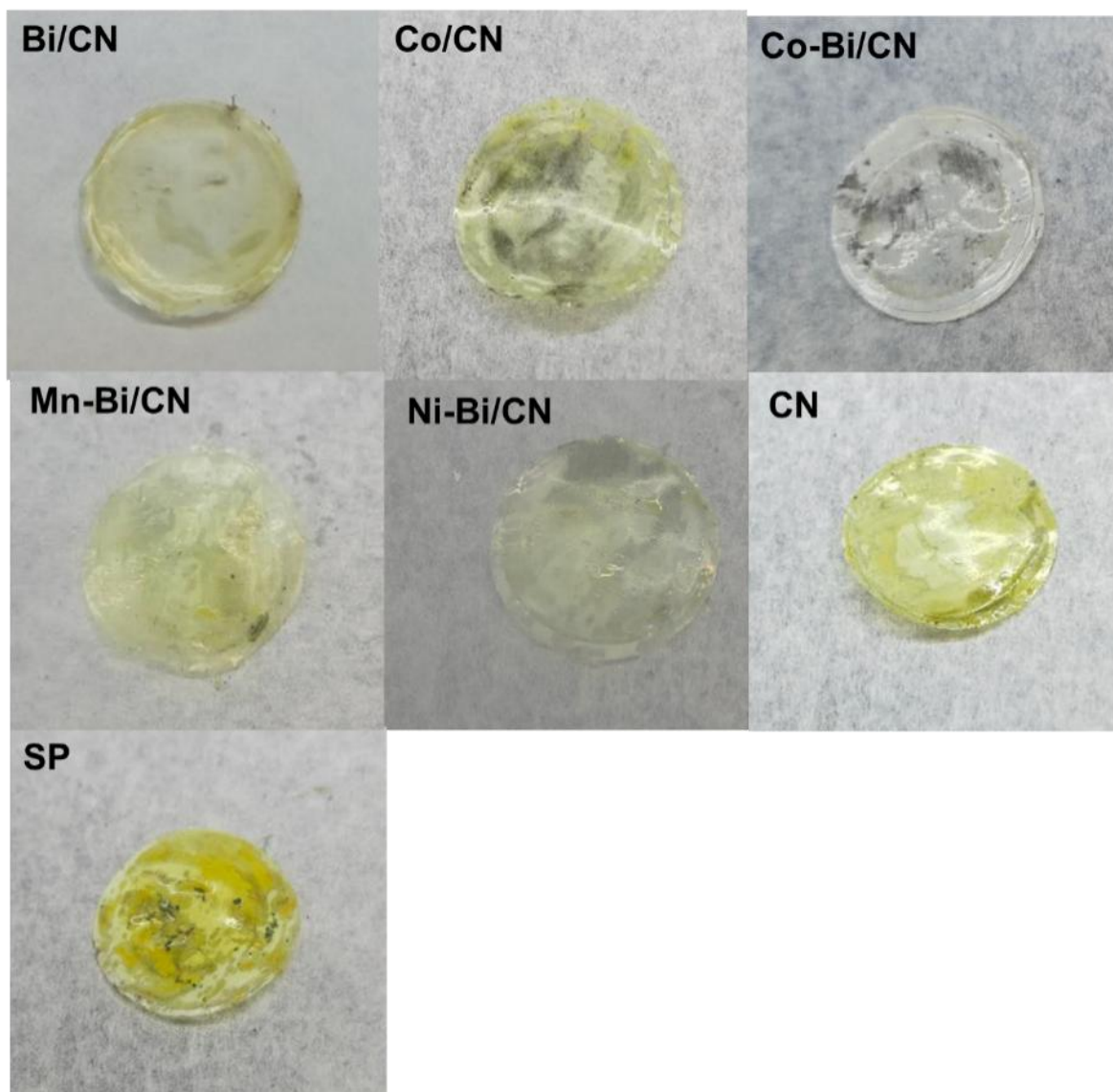


Figure 6.13. Digital images of coin cell separators after one charge/discharge cycle with sulfur cathodes incorporating different catalysts: Bi/CN/S, Co/CN/S, Co-Bi/CN/S, Mn-Bi/CN/S, Ni-Bi/CN/S, CN/S, and SP/S.

As an overview, Figure 6.14 compares the normalized GCD curves of the Co-Bi/CN/S and Mn-Bi/CN/S cells at 0.1C, highlighting the key features that influence their performance, including rate capability and cycling stability.

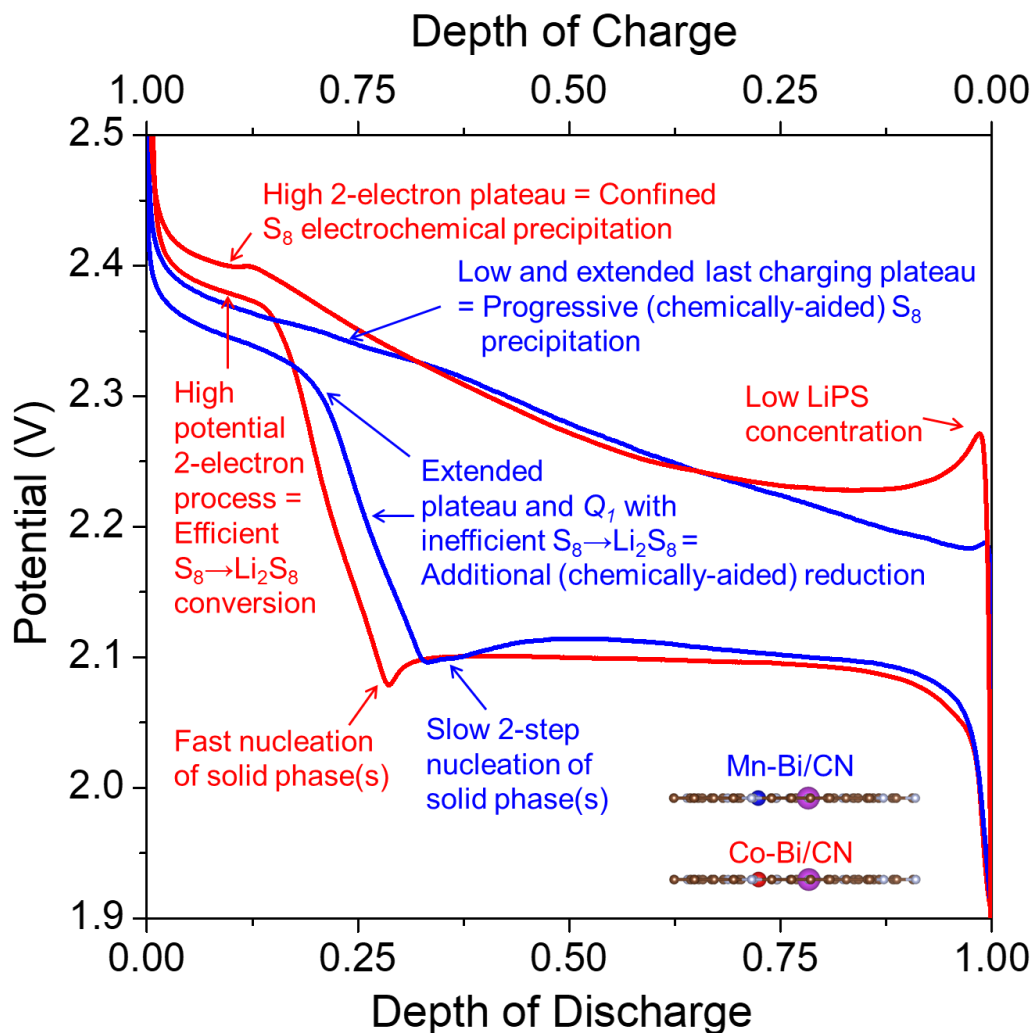


Figure 6.14. GCD profiles of Co-Bi/CN/S (red) and Mn-Bi/CN/S (blue) cells labelled with the key mechanisms determining rate performance and stability.

Figure 6.15a displays the long-term cycling performance of the TM-Bi/CN/S full cells tested at 1C. Among the different catalysts, the Co-Bi/CN/S and Ni-Bi/CN/S cells exhibited significantly improved capacity retention over 1000 cycles, maintaining 86% (1153 mAh g⁻¹) and 89% (1070 mAh g⁻¹) of their initial capacities, respectively, along with a stable and high Coulombic efficiency exceeding 99.5%. In contrast, the Mn-Bi/CN/S-based cell retained only 43% of its capacity under the same conditions.

Co-Bi/CN/S cells also exhibited the highest initial specific capacitance and the highest capacity retention rate over 500 cycles at 2C (1268 mAh g⁻¹ and 84.5%), well above that of

Bi/CN/S (973 mAh g⁻¹ and 51.0%), and Co/CN/S (1167 mAh g⁻¹ and 62.6%), as displayed in Figure 6.15b.

To further evaluate the catalytic activity under practical conditions, several coin cells using Co-Bi/CN/S cathodes with a high sulfur loading of 4.3 mg cm⁻² were assembled and tested (Figure 6.15c). Remarkably, even after 500 cycles, the best electrodes retained 952 mAh g⁻¹, and all cells demonstrated capacity retention rates above 85%. Notably, the specific capacity at 0.5C under high sulfur loading is lower than the capacities observed at higher current rates (1C and 2C) with lower sulfur loadings (~1.2 mg cm⁻², Figures 6.15a-b). This is attributed to increased electrode thickness and reduced electrolyte-to-sulfur ratio at high loading, which limit ion and electron transport and enhance polysulfide shuttle effects, thereby reducing sulfur utilization despite the lower current rate. These findings demonstrate that our DAC catalysts maintain high catalytic activity and durability under realistic high-loading and limited-electrolyte conditions, highlighting their promise for practical high-energy-density LSBs. Finally, to demonstrate commercial potential, pouch cells incorporating Co-Bi/CN/S cathodes were assembled and evaluated. As shown in Figure 6.15d, the pouch cell delivers an initial discharge capacity of 1372 mAh g⁻¹ at 0.05C. After the activation process, the second discharge capacity stabilizes at 890.7 mAh g⁻¹. When cycled at 0.2C for 300 cycles, it maintained 698.6 mAh g⁻¹, corresponding to a low capacity decay rate of approximately 0.08% per cycle after activation, demonstrating excellent cycling stability. Additionally, Figure 6.15e presents a practical demonstration of the pouch cell powering an LSB sign containing 46 light-emitting diodes (LEDs), highlighting its robust performance and potential for real-world energy storage applications.

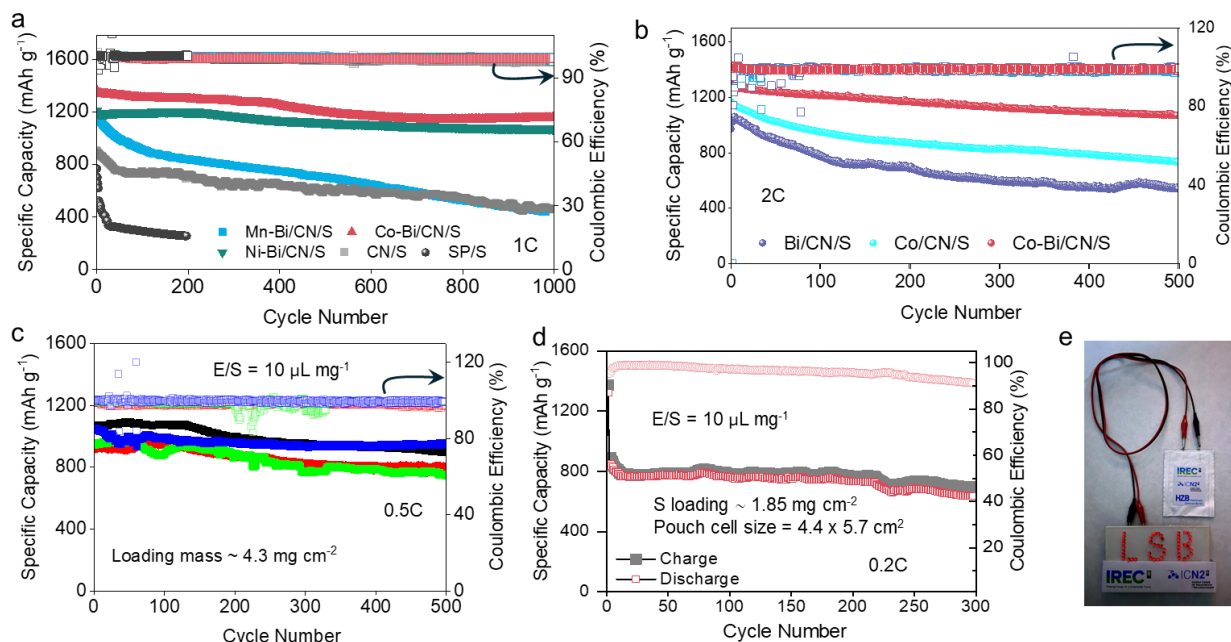


Figure 6.15. (a,b) Long-term cycling performance at 1C of TM-Bi/CN/S cells (a), and at 2C of Bi/CN/S, Co/CN/S, and Co-Bi/CN/S cells (b). (c) Cycling performance at 0.5C of four coin cells equipped with Co-Bi-CN/S-cathodes containing a sulfur loading of about 4.3 mg cm⁻². (d) Cycling performance of a Co-Bi/CN/S-based pouch cell with 1.85 mg cm⁻² sulfur loading at 0.2C current density and (d) photograph of the pouch cell powering an LED sign.

Post-cycling XPS analysis (Figures 6.16-6.17) revealed that Co-Bi/CN and Ni-Bi/CN cathodes contained higher proportions of fully reduced sulfur species (Li₂S) and exhibited markedly lower residual polysulfide content compared with other catalysts, confirming their sustained catalytic promotion of complete SRR. The N 1s spectra showed well-preserved pyridinic-N and pyrrolic-N environments with only minor losses, indicating robust atomic coordination structures. F 1s and C 1s signals further suggested that DAC-based electrodes formed more stable electrode-electrolyte interfaces, with reduced carbonate/SO_xF_y species relative to SP/S.^[37-42]

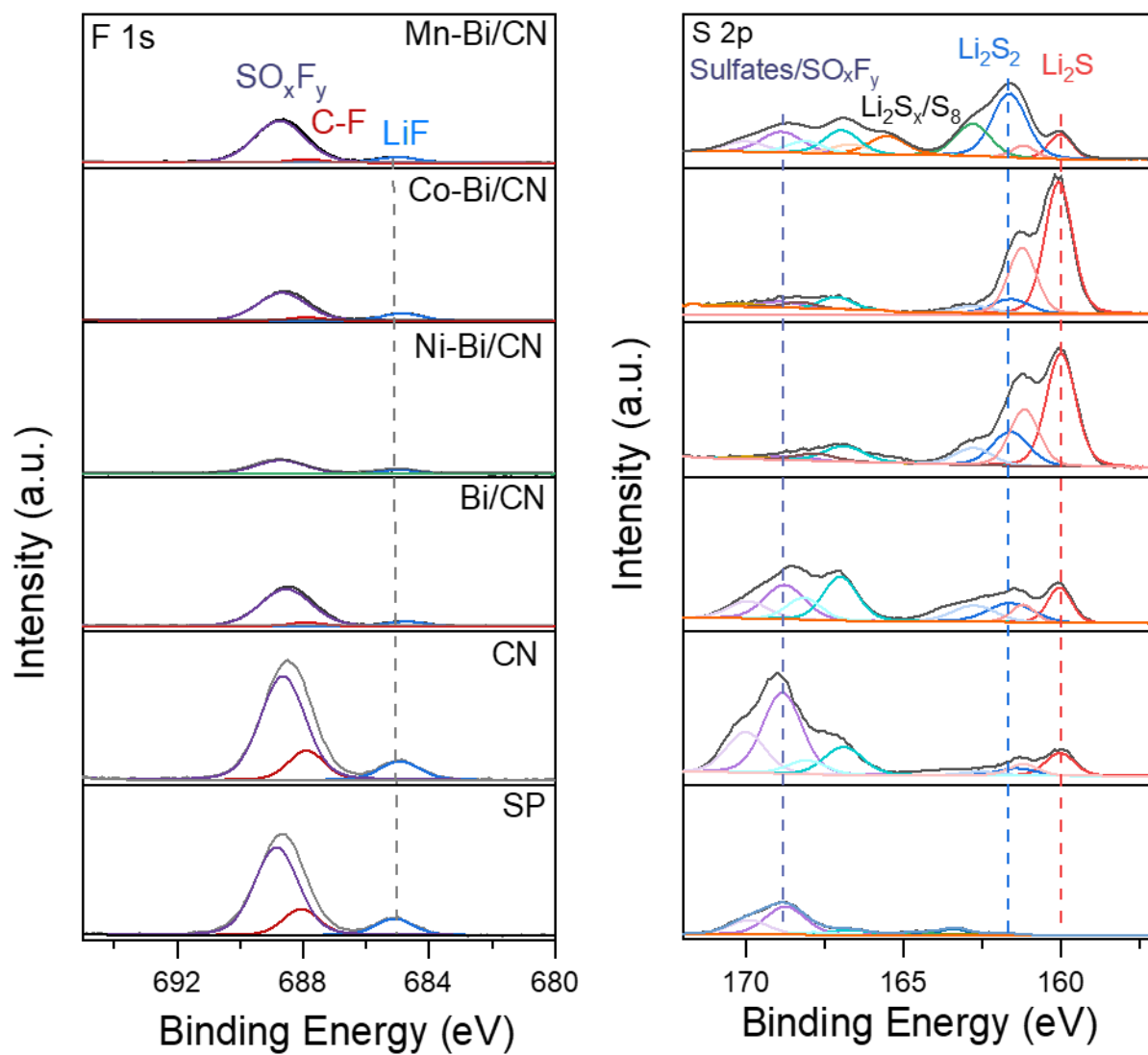


Figure 6.16. High-resolution F 1s (left) and S 2p (right) XPS spectra of the different electrode after 100 cycles at 1C.

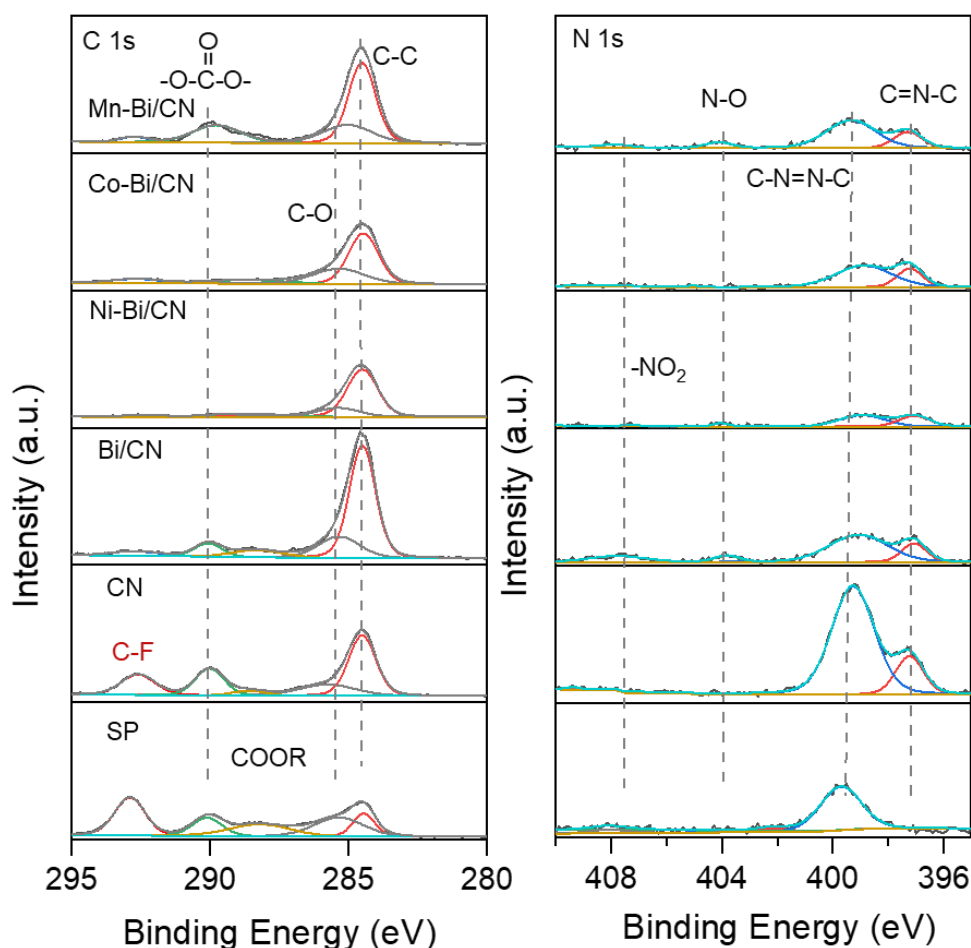


Figure 6.17. High-resolution C 1s (left) and N 1s (right) XPS spectra of the different electrodes after 100 cycles at 1C.

Post-mortem separator and lithium anode SEM analyses (Figure 6.18) supported these findings: separators from cycled Co–Bi/CN and Ni–Bi/CN cells displayed much lighter coloration, indicating more effective polysulfide confinement, while SEM images of Li anodes showed smoother surfaces without severe dendrite growth, in contrast to control electrodes. These results demonstrate that Co–Bi/CN and Ni–Bi/CN DACs maintain catalytic efficiency, structural integrity, and effective polysulfide management over prolonged cycling—critical factors for achieving durable, high-performance LSBs.

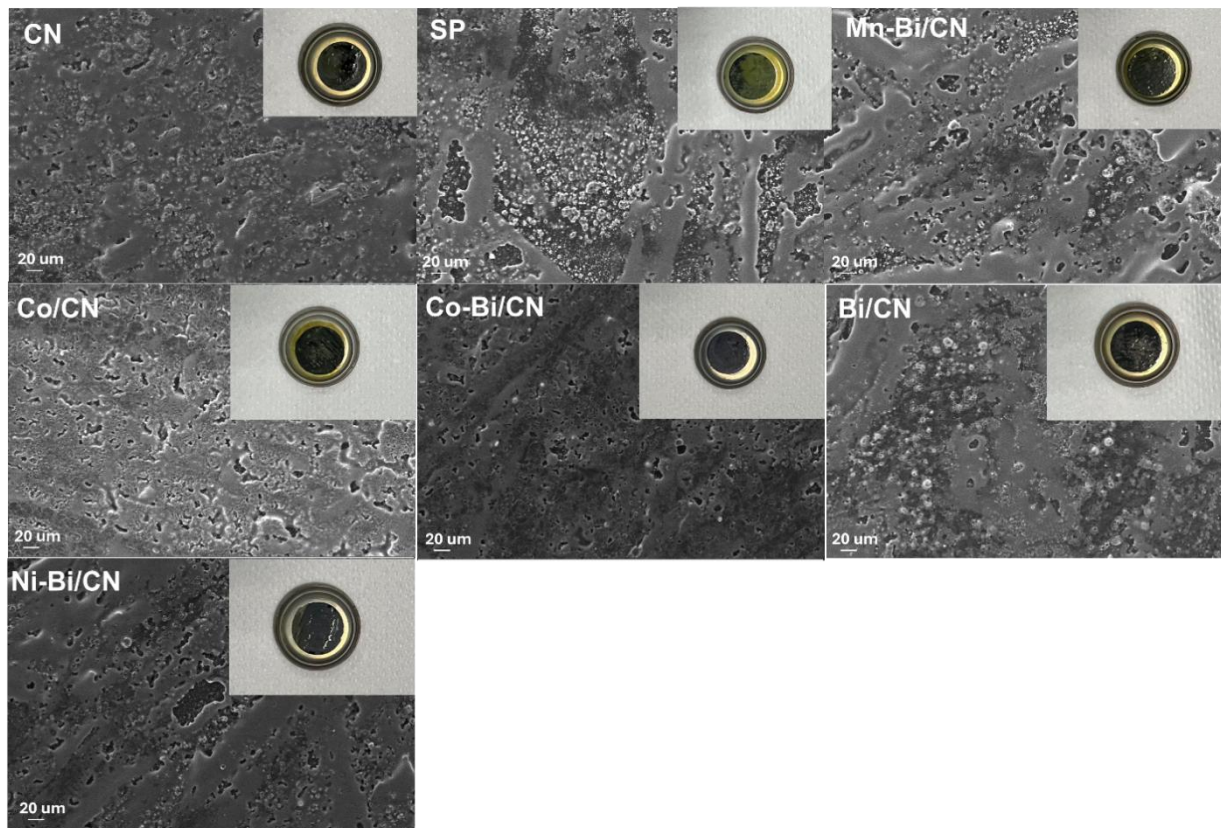


Figure 6.18. SEM images of Li anode and corresponding digital photographs of the Li anode with the separator after 100 charge/discharge cycles with different catalysts: Bi/CN/S, Co/CN/S, Co-Bi/CN/S, Mn-Bi/CN/S, Ni-Bi/CN/S, CN/S, and SP/S.

6.3.3 TM-Bi electronic interaction

DFT calculations were performed to explore the electronic structure and charge redistribution within coupled heteroatom pairs. As discussed earlier, Co and Ni possess partially filled asymmetrical 3d orbitals close to the Fermi level, making them highly effective for orbital overlap and bonding with adsorbed species. These elements, even as isolated atoms, can exhibit indirect exchange interactions via the Ruderman–Kittel–Kasuya–Yosida (RKKY) mechanism within the CN framework, leading to ferromagnetic spin alignment. In contrast, Mn, with its half-filled symmetric 3d shell, offers higher stability and has its 3d orbital center positioned further from the Fermi level. These distinctions partially account for the superior catalytic performance observed in Ni and Co-based systems compared to Mn-based ones. However, this explanation falls short of accounting for the significantly enhanced performance of the Co-Bi/CN system relative

to Co/CN, suggesting that additional factors, likely linked to the synergistic effects between Co and Bi, contribute to the observed improvement.

Upon combination, the 3d orbitals of the TM (Mn, Co, Ni) and the half-filled Bi 6p³ orbitals^[29] may undergo hybridization to σ , π , σ^* , and π^* orbitals, as visualized in the scheme in Figure 6.19a and the top and side views of the electron cloud diagram of the generated models in Figure 6.6. The d_{z^2} of TM 3d can selectively hybridize with the pz orbital of Bi 6p, forming σ and σ^* orbitals due to their compatible orbital symmetries. Meanwhile, the d_{xz}/d_{yz} orbitals of TM 3d interact directionally with the $p_{x/y}$ orbitals of Bi 6p, resulting in the generation of π and π^* orbitals. On the other hand, the d_{xy} and $d_{x^2-y^2}$ orbitals of TM 3d are considered nonbonding, as their orbital orientations do not align effectively with the Bi 6p orbitals.^[43,44] d-p hybridization significantly reduces the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As an example, the energy gap decreases from 0.84 eV for Bi/CN and 1.04 eV for Co/CN single atom models to just 0.34 eV for Co-Bi/CN (Figure 6.19b). The higher HOMO level facilitates electron transfer from the catalyst to sulfur species during the reduction process, while a lower LUMO level promotes electron acceptance from sulfur species during the oxidation process. This effect aligns with the significantly enhanced performance observed for the DACs, particularly for Co-Bi/CN, compared to the single-metal systems, Co/CN and Bi/CN.

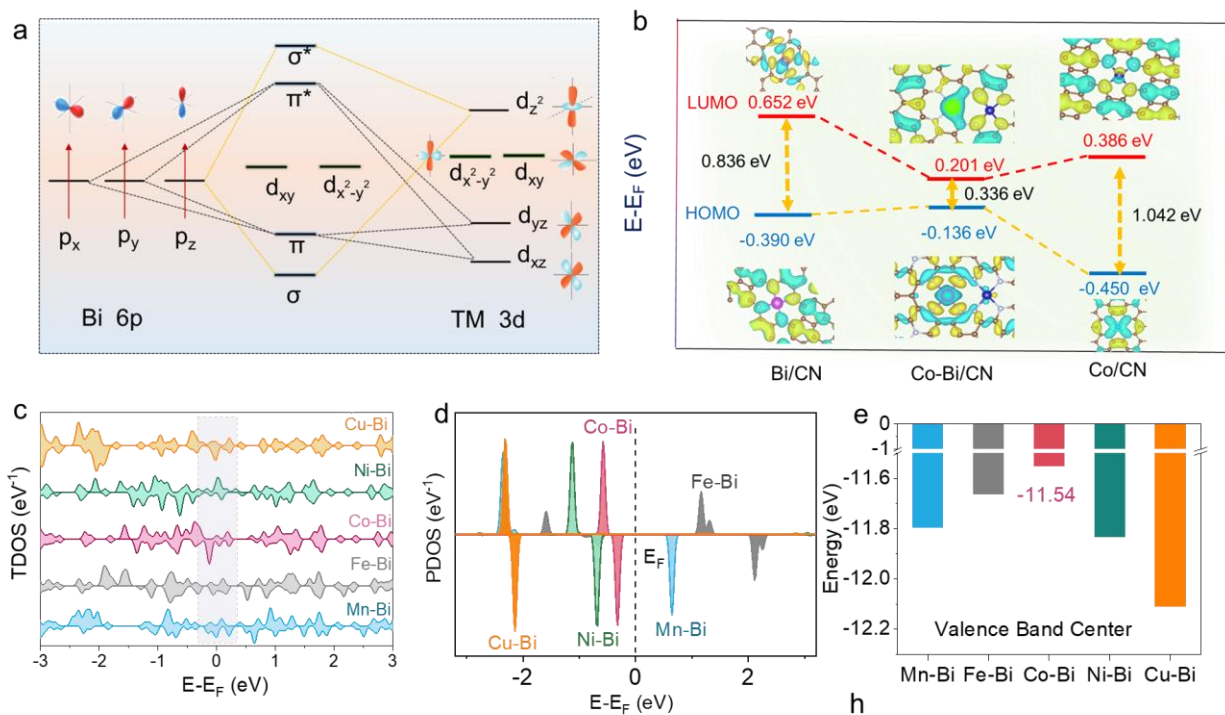


Figure 6.19. (a) Scheme of the Bi 6p - TM 3d orbital hybridization. (b) HOMO and LUMO schemes for Co/CN, Bi/CN, and Co-Bi/CN. (c) TM TDOS for the different TM-Bi/CN DACs. (d) TM d_{z^2} PDOS and (e) valence band center in TM-Bi/CN.

According to Marcus' theory^[45], the electron transfer rate is primarily governed by the electronic coupling between donor and acceptor states. The diverse electron configurations of 3d TMs result in distinct hybridization with Bi atoms, leading to differences in their electron capture and donation capabilities. The TM total density of states (TDOS) and the d_{z^2} contribution to the hybridized orbitals in the Mn-Bi/CN, Co-Bi/CN, and Ni-Bi/CN, systems are displayed in Figures 6.19c-d. Among these heteroatom pairs, the Co 3d orbitals exhibit a d_{z^2} partial density of states (PDOS) positioned closest to the Fermi level, followed by the Ni-based system. In addition, Co-Bi/CN has the lowest valence band center (VBC) for the entire system.(Figure 6.19e). This favourable electronic alignment partially explains why Ni-Bi/CN and particularly Co-Bi/CN possess the most well-suited electronic structure for enhanced catalytic performance.

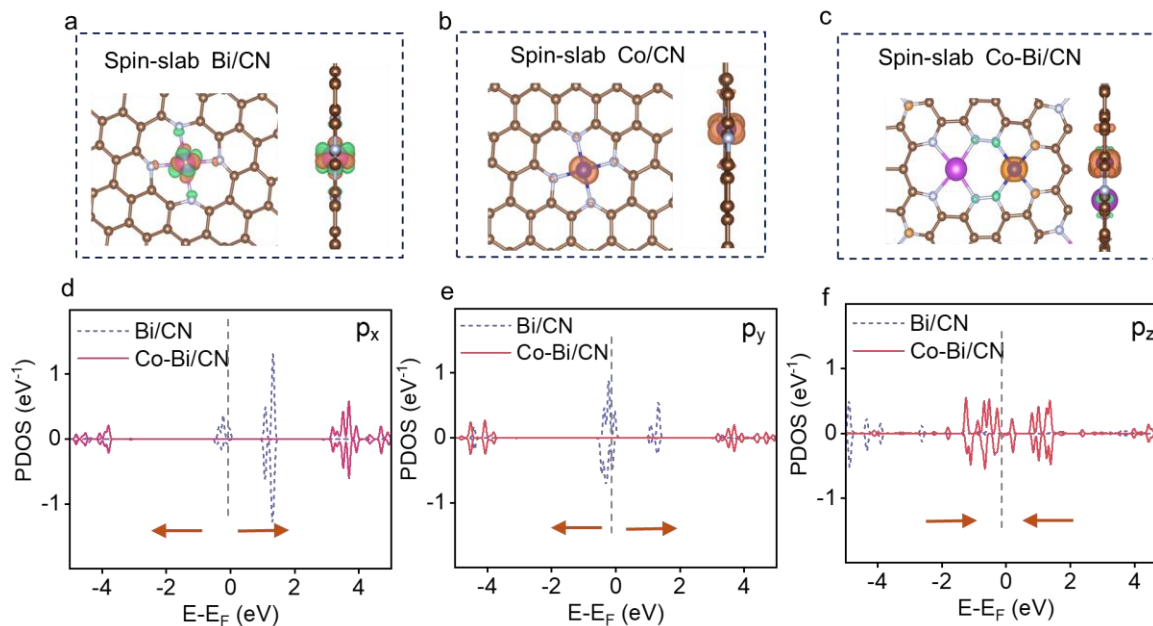


Figure 6.20. (a-c) Top and cross views of the spin slabs of Bi/CN (a), Co/CN (b), and Co-Bi/CN (c). (d-f) Bi 6p orbitals (p_x , p_y , and p_z) PDOS from Bi/CN (dash line) and Co-Bi/CN (solid line) models.

DFT analyses also reveal significant differences in the electron cloud distribution around the metal atoms in Co-Bi/CN compared to the Bi/CN and Co/CN single-atom models (Figures 6.20a-c). The PDOS of the different Co 3d orbitals within Co-Bi/CN and Co/CN shows the filled d_{z^2} orbital contribution to shift 0.26 eV closer to the Fermi level after hybridization with Bi atoms (Figure S6.21). Concurrently, the PDOS of the Bi 6p orbitals in Co-Bi/CN shows a substantial rearrangement in the electron cloud distribution around the Bi atom (Figures 6.20d-f). Specifically, the p_x and p_y orbital electrons are displaced further from the Fermi level, while the p_z orbital electron density increases significantly near the Fermi level.

The adsorption energies of Li_2S_4 on various TM-Bi/CN catalysts are presented in Figure 6.21a, indicating that Mn-Bi/CN exhibits the weakest adsorption strength, while Co-Bi/CN shows the strongest. These results are consistent with the experimental LiPS adsorption findings shown in Figure 6.21b. The LiPS adsorption capability of the DACs was experimentally assessed by dispersing equal amounts of each TM-Bi/CN catalyst in vials containing a Li_2S_4 solution. After 1.5 hours, the UV-vis spectra revealed a substantial reduction in the characteristic UV absorption

peak of Li_2S_4 for the vials containing Co-Bi/CN and Ni-Bi/CN, indicating their relatively high LiPS adsorption capacities (Figure 6.21b). In contrast, Mn-Bi/CN exhibited significantly lower adsorption abilities. These observations were visually supported by optical photographs of the vials after Li_2S_4 adsorption (inset Figure 6.21b). The strong affinity of Ni-Bi/CN/S and Co-Bi/CN/S for Li_2S_4 can promote effective solid phase growth from solution, being Li_2S_4 a key species bridging the solid-liquid-solid reaction.^[46]

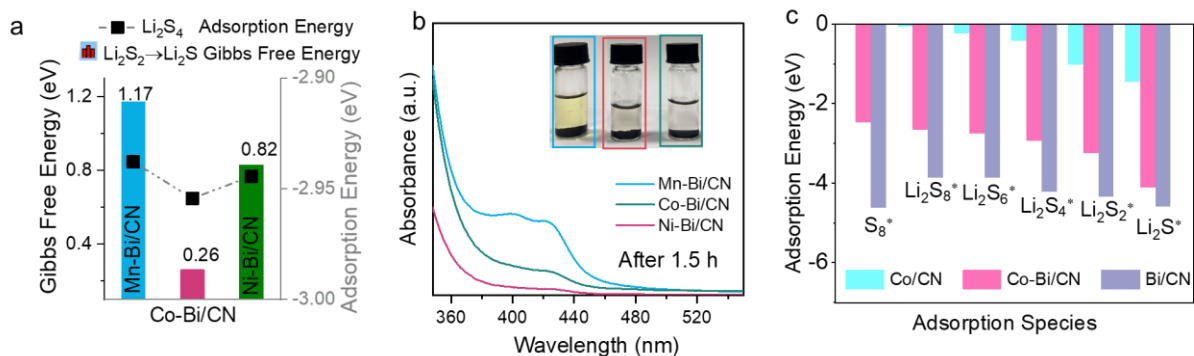


Figure 6.21. (a) Adsorption energy of Li_2S_4 and Gibbs free energy change for the conversion of Li_2S_2 to Li_2S on the surface of Mn-Bi/CN, Co-Bi/CN, and Ni-Bi/CN catalysts. (b) UV-vis absorption spectra of the supernatant of the vials containing the different catalysts and a Li_2S_4 solution after 1.5 h adsorption. The inset shows an optical photograph of the vials after 1.5 h adsorption. (c) Adsorption energies of S_8 , Li_2S_8 , Li_2S_6 , Li_2S_4 , Li_2S_2 , and Li_2S on Bi/CN, Co/CN, and Co-Bi/CN catalysts.

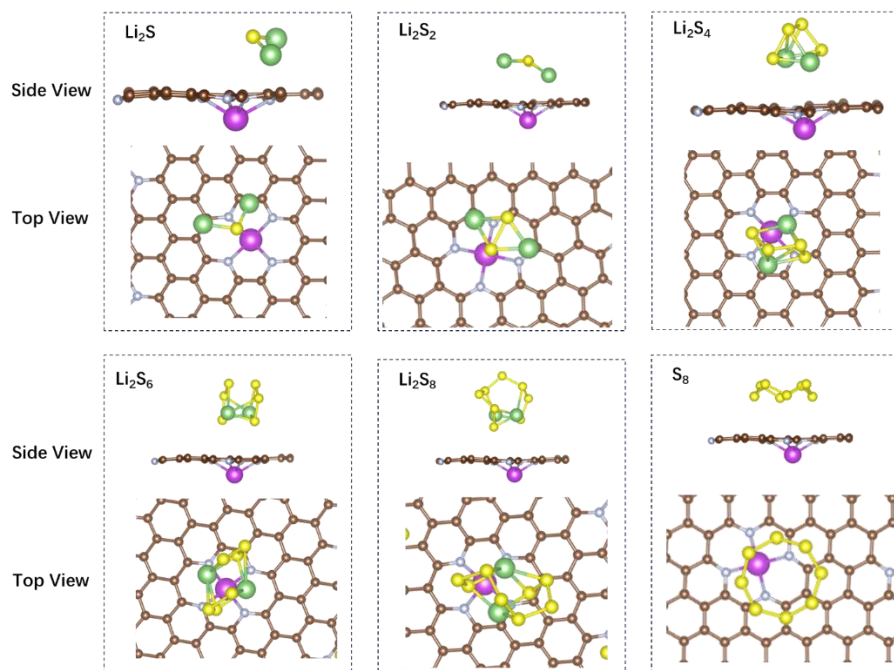


Figure 6.22. DFT optimized geometrical configuration of Bi/CN with LiPS.

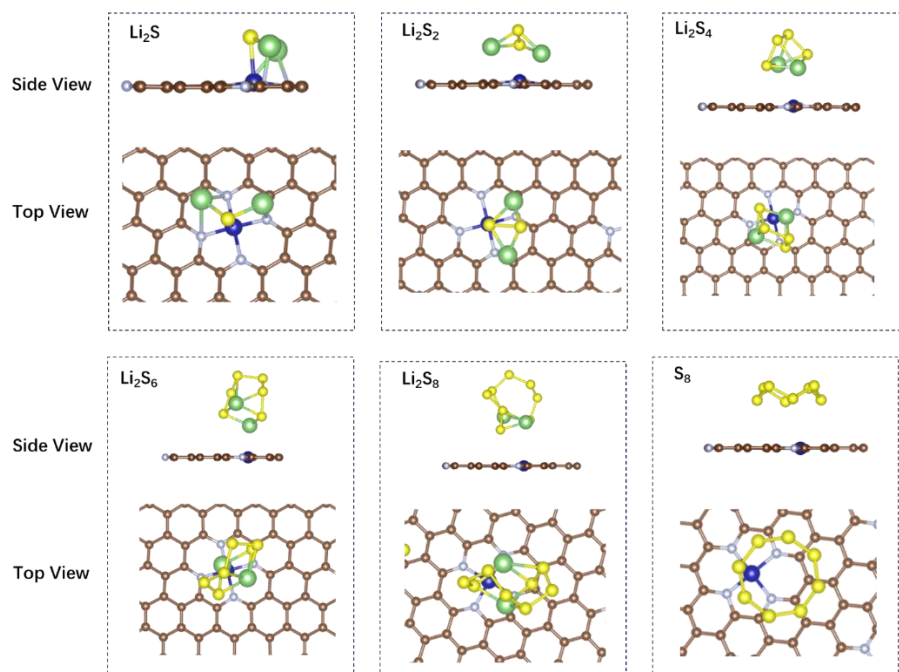


Figure 6.23. DFT optimized geometrical configuration of Co/CN with LiPS.

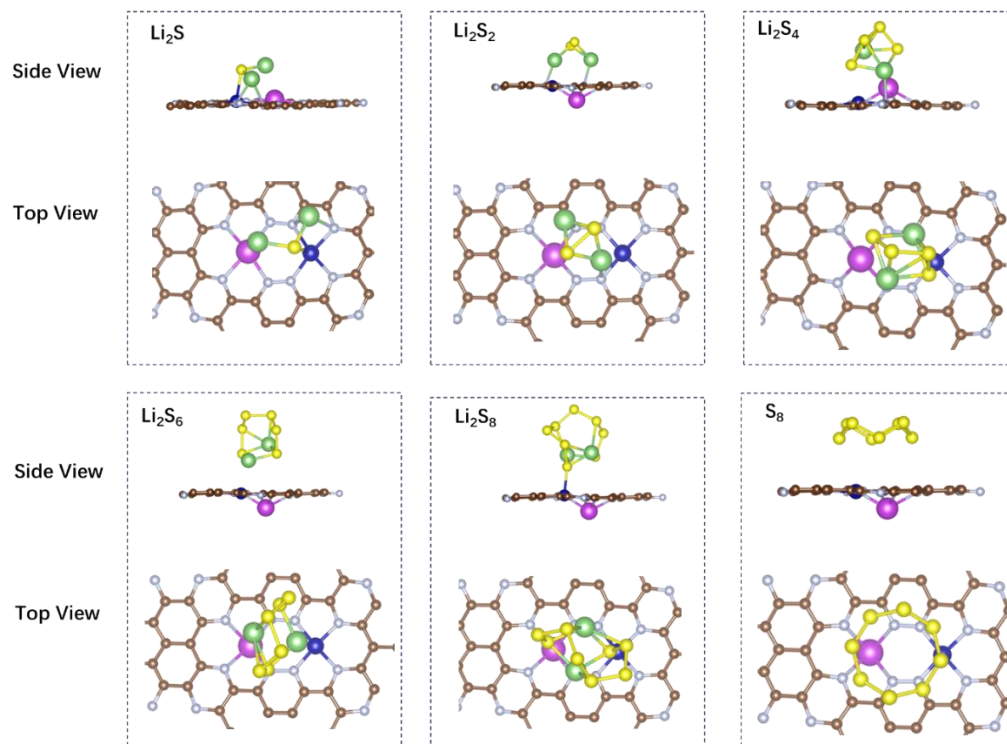


Figure S6.24. DFT optimized geometrical configuration of Co-Bi/CN with LiPS.

The corresponding adsorption energies for the DFT-optimized configurations of diatomic Co-Bi/CN, single-atom Bi/CN, and Co/CN models with adsorbed S_8 , Li_2S_8 , Li_2S_6 , Li_2S_4 , Li_2S_2 , and Li_2S species are summarized in Figure 6.21c. Side and top views of the corresponding geometrical configurations are displayed in Figures 6.22-6.24. The spin-slab side view in Figure 6.25 illustrates the electron cloud distributions for the three systems. Among these, Bi/CN exhibits strong adsorption capacities for all sulfur species, Co/CN demonstrates significantly weaker adsorption, and Co-Bi/CN displays intermediate adsorption energies. The notable affinity of the Co-Bi/CN DAC for polysulfides aligns with the observed low increase in overpotential at higher discharge rates. In contrast, Co/CN exhibits relatively weak interactions with LiPS, which is consistent with the notable rise in overpotential as the discharge rate increases, as previously noted. Interestingly, while Bi demonstrates a strong affinity for polysulfides, it struggles to sustain the reaction pace at high discharge rates. This observation suggests the presence of additional underlying mechanisms that hinder its performance under rapid cycling conditions.

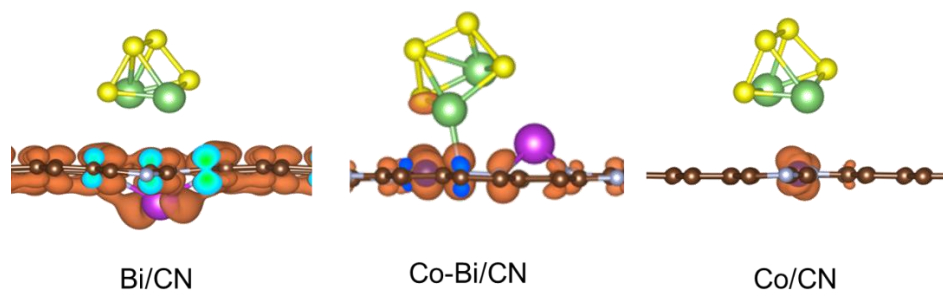


Figure 6.25. Side view of spin slabs of a Li_2S_4 molecule adsorbed on Bi/CN (left), Co/CN (right), and Co-Bi/CN (middle). The isosurface level is 0.001 e/a_0^3 .

Figure 6.26a presents the Gibbs free energy evolution of the sulfur reduction reaction on the surfaces of Co-Bi/CN, Bi/CN, and Co/CN catalysts at the molecular level. Bi/CN shows high overpotentials for the formation of both Li_2S_2 and Li_2S , while Co/CN exhibits a very low Gibbs free energy change for Li_2S_2 formation but a significant energy barrier for Li_2S formation. Although these results are obtained at the molecular level and do not account for the energy of formation or crystallization of solid phases, they align with the observed extended dip at the onset of the second discharge plateau, the rapid increase in overpotential with rising rates during the second plateau, and the absence of Li_2S formation at high current densities observed for the less performing catalysts. In contrast, Co-Bi/CN displays a notable energy barrier for Li_2S_2 formation, consistent with the observed dip, but a significantly lower energy barrier for the Li_2S_2 -to- Li_2S conversion. This finding is well-supported by experimental data indicating more facile Li_2S nucleation in this material.

During the reverse process of charging, compared with Co/Cn and Bi/CN, Co-Bi/CN exhibits a particularly large Gibbs free energy barrier for the $\text{Li}_2\text{S}_8 \rightarrow \text{S}_8$ oxidation step. This is experimentally reflected in the relatively higher potentials required towards the end of the charging process for this final two-electron step. Notably, this characteristic might actually be advantageous as it could help prevent chemical S_8 precipitation outside the electrode, thereby enhancing the LSB cycling stability.

To experimentally verify the transfer of charge within the coupled metal atoms at the origin of the DACS enhanced performance and analyze its evolution with the reaction process, *operando* Co *K*-edge XAS spectra were obtained. The *operando* Co *K*-edge spectra of Co/CN/S and Co-

Bi/CN/S cathodes revealed subtle yet analyzable spectral changes during cycling. As shown in Figures 6.26b-f, within the battery environment, the average oxidation state of Co in Co-Bi/CN/S was slightly lower during the entire cycle than in Co/CN/S, denoting a higher interaction with S in the former cathode. Principal component analysis was used to highlight the evolution of spectral features during the reaction. Two principal components were identified and deconvolved using the multicurve resolution (MCR) technique, implemented in the MCR-ALS Python library (Figure 6.26b).^[47] In both Co/CN/S and Co-Bi/CN/S, the relative concentration of the 1st MCR component, associated with the highest oxidation state, decreased during charging and increased during discharging, while the 2nd MCR component exhibited the opposite trend (Figures 6.26e-f). These concentration profiles match the gradual formation of Co-S bonds and thus the decrease of Co-N structural bonds during the discharge process, when S₈ is converted into progressively shorter chain polysulfides, and the reversal of this process during charging. This evolution and the lower valence state of Co in the Co-S bond compared to the Co-N bond, due to nitrogen's higher electronegativity, allowed us to assign the 1st MCR component to Co-N and the 2nd MCR component to Co-S. Notably, the concentration of Co-S was significantly higher in Co-Bi/CN/S than in Co/CN/S, and the evolution of these two components was more reversible in Co-Bi/CN/S, aligning with the higher catalytic activity and improved cycling stability.

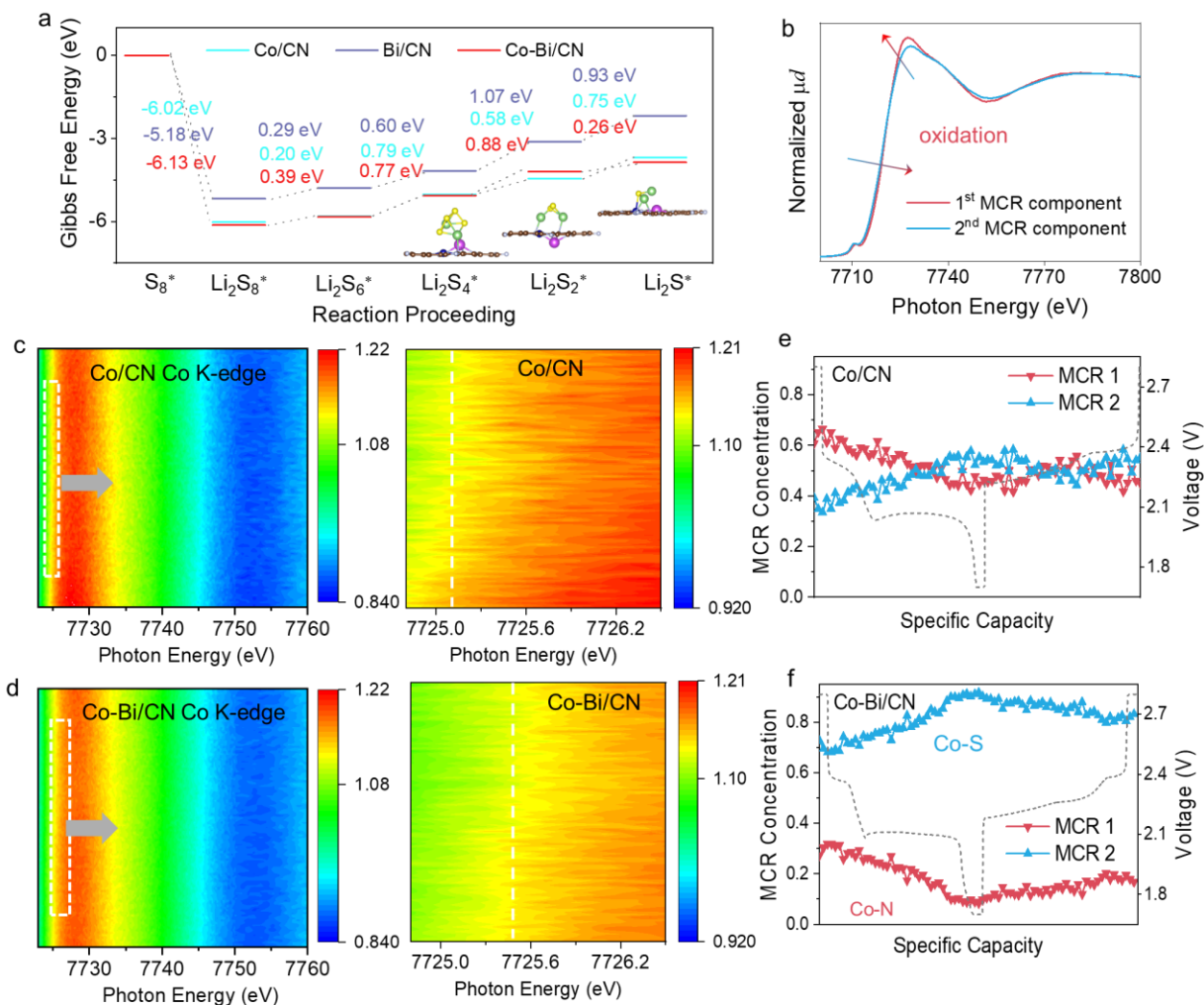


Figure 6.26. (a) Gibbs free energy of S_8 , Li_2S_8 , Li_2S_6 , Li_2S_4 , Li_2S_2 , and Li_2S on Bi/CN, Co/CN, and Co-Bi/CN catalysts. (b) MCR-retrieved XANES spectra for the operando XAS Co K-edge dataset. (c-f) *Operando* XAS 3D map of Co K-edge results for Co/CN/S and Co-Bi/CN/S, the second rows show enlarged details of the spectra to more clearly show the different oxidation states. *Operando* concentration profiles of the 2 identified Co-species of (c,e) Co/CN /S and (d,f) Co-Bi/CN/S.

6.4 Conclusions

In conclusion, a series of TM-Bi DACs supported on a CN substrate, namely Mn-Bi/CN, Co-Bi/CN, and Ni-Bi/CN, were successfully synthesized using a simple and low-cost process. While all DACS demonstrated notable performances, the fastest sulfur redox kinetics were obtained in Co-Bi/CN/S and Ni-Bi/CN/S, which displayed the highest first discharge plateau

(~2.38 V) and a balanced Q_2/Q_1 ratio. In contrast, Mn-Bi/CN/S, Co/CN/S, and Bi/CN/S exhibited an extended first discharge plateau at a lower voltage (~2.34 V) with a low Q_2/Q_1 ratio, attributed to the inefficient $S_8 \rightarrow Li_2S_8$ conversion. This inefficient conversion lowers the voltage of the first discharge plateau, thereby facilitating additional electrochemical reactions and subsequent comproportionation processes. As a result, some Li_2S_2 is chemically formed early in the reaction, during the Q_1 step. The premature Li_2S_2 precipitation, indicated by the extended Q_1 beyond the four-electron S_8 - Li_2S_4 process and the corresponding Q_2 reduction, may occur outside the electrode, leading to active material loss and ultimately poor cycling stability. Additionally, the early formation of Li_2S_2 is linked to prolonged Li_2S nucleation times in the less effective catalysts. This is associated with a low overpotential at the onset of the second discharge plateau, which reflects the facile heterogeneous growth of preformed Li_2S_2 and/or the challenging nucleation of Li_2S through solid-state transformation of the preformed Li_2S_2 . The extended nucleation time observed in the less-performing electrodes accounts for their relatively poor rate performance, as these systems struggle to initiate Li_2S nucleation and thus fail to promote extensive Li_2S crystallization at high rates ($>1C$). This stands in stark contrast to the Ni-Bi/CN/S and Co-Bi/CN/S electrodes, which sustain high capacities even at elevated discharge rates. Similarly, during charging, Ni-Bi/CN/S and Co-Bi/CN/S exhibited a steady potential increase with a final two-electron plateau, effectively confining the electrochemical LiPS to S_8 conversion to the electrode. In contrast, other cathodes showed lower potential and prolonged final plateaus, which could reflect the chemical formation of electrically isolated sulfur, thereby diminishing cycling stability. DFT calculations reveal that the asymmetric coordination configuration of Co-Bi significantly modulates the local electronic structure and introduces additional electron density to Co within the Co-Bi/CN framework. This modification enhances the interaction between Co and polysulfides, facilitates Co-S bond formation, improves electron transfer, and ultimately boosts the catalytic activity of the Co sites. Consequently, this leads to Co-Bi/CN/S-based LSBs with superior rate performance and long-term stability. Overall, this study not only elucidates the mechanisms of metal interaction, LiPS adsorption, and catalytic enhancement in TM-Bi DACs but also establishes a robust platform for the rational design of optimized DACs. These advancements hold significant potential for improving conversion-type cathodes, particularly sulfur cathodes in LSBs, as well as other electrocatalytic applications.

6.5 References

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Chapter 7 Conclusions and Outlook

7.1 Conclusions

To enhance the kinetics of LiPSs conversion during the operation of LSBs and to mitigate the detrimental effects of the shuttle phenomenon, this dissertation focuses on optimizing the catalytic conversion processes of LiPS through rational design and engineering of catalytic materials. The research systematically explores catalyst development from two fundamental perspectives: (i) spin control to tune the local coordination environment and electronic structure, and (ii) atomic-level active site engineering of catalytic centers to tailor contact exposure. Specifically, the study investigates how spin manipulation through compositional modulation, vacancy engineering, and dual-atom dispersion influences the adsorption, conversion, and stabilization of LiPS intermediates, as well as their corresponding electrochemical behavior within working LSB systems. By integrating advanced structural characterization with electrochemical evaluation, this work provides a comprehensive understanding of LiPS catalytic conversion mechanisms, establishing fundamental design principles that connect atomic-scale structure to macroscopic battery performance.

The overall findings reveal that accelerating the conversion kinetics of lithium sulfide species significantly improves the rate capability of LSBs while simultaneously suppressing the diffusion and migration of soluble LiPS intermediates. These effects mitigate the shuttle phenomenon and contribute to remarkable improvements in the long-term cycling stability of the batteries. The results collectively highlight that strategic manipulation of electronic structure, defect states, and atomic coordination is a powerful and versatile approach to achieve high-efficiency sulfur redox catalysis. This dissertation thus lays the groundwork for next-generation catalytic sulfur hosts and provides guiding principles for advanced energy storage systems beyond lithium–sulfur chemistry.

The main conclusions and scientific contributions of each chapter are summarized as follows:

In Chapter 4, compositional tuning for electronic structure optimization. This chapter establishes Fe-doped NiSe₂ as a highly efficient bifunctional catalyst capable of accelerating both the reduction and oxidation reactions of sulfur species. Through combined experimental and theoretical analyses, it demonstrates that Fe doping effectively tailors the electronic configuration

and optimizes the adsorption energy of polysulfide intermediates, thereby enhancing both redox kinetics and structural stability. The study further reveals that compositional modulation in transition-metal selenides can precisely tune the d-band center and electron density distribution, offering a generalizable strategy for designing catalytic hosts with improved activity and durability in LSBs.

In chapter 5, spin-state modulation via vacancy engineering. This chapter highlights the crucial yet often overlooked role of electron spin configuration in determining catalytic behavior. By introducing cationic vacancies into transition metal-based catalysts, the study manipulates local spin states to optimize orbital hybridization between the catalyst and polysulfide species. The results uncover a direct correlation between spin polarization and catalytic activity, showing that controlled spin-state engineering can significantly enhance redox kinetics and suppress side reactions. This work establishes spin modulation as a new and powerful dimension in the design of high-performance LSB catalysts, broadening the conceptual framework of catalyst optimization beyond conventional compositional and structural approaches.

In chapter 6, atomic-level control through dual-atom catalyst engineering. This chapter demonstrates the potential of DACs to control sulfur redox reaction pathways with atomic precision. By stabilizing isolated dual-metal sites within a conductive carbon framework, the study achieves synergistic electronic effects that lower energy barriers for LiPS adsorption and conversion. The work elucidates the cooperative mechanisms between heteronuclear metal pairs, revealing how dual-atom dispersion enhances both catalytic activity and structural robustness.

In summary, this dissertation provides a coherent and systematic exploration of the catalytic mechanisms governing LiPS conversion in lithium–sulfur batteries. By integrating defect engineering, spin manipulation, and atomic-scale catalyst design, it contributes fundamental insights into structure–property relationships that underpin catalytic sulfur chemistry. These findings not only deepen the understanding of sulfur redox catalysis but also pave the way toward the rational design of advanced, durable, and high-performance energy storage systems that can support future sustainable energy technologies.

7.2 Outlook and future work

As the demand for clean energy rises, traditional energy storage and power batteries face challenges in meeting this need due to their limited theoretical energy density. This has spurred extensive research into next-generation rechargeable battery technologies, with LSBs gaining increasing attention due to their exceptionally high theoretical capacity, energy density, and relatively low cost. This paper focuses on improving the high-rate charge-discharge performance and cycling stability of LiS batteries by optimizing the conversion of lithium polysulfides during operation. For the sake of controlled experimentation, this study primarily investigates the structural design and catalytic properties of the cathode material, deliberately excluding variables such as the electrolyte composition and sulfur cathode volumetric energy density. However, these factors are crucial for the practical application of LiS batteries.

(1) To maintain the energy density advantage of lithium-sulfur batteries over lithium-ion batteries, the overall design of LiS batteries requires a low E/S ratio. Typically, the E/S ratio should be less than 5. However, in this study and most of the published research, the E/S ratio exceeds 10. Excessively high E/S values not only reduce the effective energy density of lithium-sulfur batteries but, from a basic research perspective, fail to fully capture the catalytic effect of catalysts on lithium polysulfides under realistic operational conditions. Future studies should explore the catalytic effects on the anchoring and conversion processes of lithium polysulfides under lower E/S conditions.

(2) The catalytic conversion of lithium polysulfides is influenced by the electrolyte environment, and new electrolyte systems need to be investigated for their impact on polysulfide conversion. Currently, the DME/DOL system is the standard electrolyte for lithium-sulfur batteries, but under low E/S conditions, novel electrolyte systems may be required. These new systems should aim to regulate factors such as the solubility of lithium polysulfides, the ionic potential near the sulfur electrode, and the potential barrier that affects the kinetics of polysulfide conversion.

(3) Volumetric energy density is critical for the practical application of lithium-sulfur batteries. To enhance the mass energy density, the catalyst materials used in this study, and most published research, typically require the addition or combination with carbon materials. However, carbon materials have relatively low density, which can decrease the overall tap density and volumetric energy density of the sulfur electrode. This also poses challenges in the assembly process of lithium-sulfur batteries. To improve the volumetric energy density of LiS batteries, the following strategies could be explored: (1) selecting catalysts and sulfur carrier materials based on factors

like density, specific surface area, and catalytic activity; (2) applying secondary treatments to the "sulfur/catalyst" composites after sulfur loading to increase their tap density; and (3) utilizing non-carbon-based nanomaterials, such as MXene, as catalysts and sulfur carriers for lithium polysulfide conversion.

With the continuous advancement of in situ and operando characterization techniques, many long-standing bottlenecks in lithium–sulfur batteries can now be more accurately monitored and addressed. In my future research, I aim to employ advanced in situ and operando characterization techniques to gain a more comprehensive understanding of the electrochemical and catalytic mechanisms in lithium–sulfur batteries. In particular, I plan to use operando liquid-phase (S)TEM to directly monitor the nucleation, dissolution, and conversion of lithium polysulfides at the cathode–electrolyte interface in real time. By correlating these dynamic structural and chemical evolutions with electrochemical performance, I expect to reveal the intrinsic relationships between catalyst design, polysulfide conversion kinetics, and battery stability. In addition, complementary in situ spectroscopic techniques such as synchrotron XAS will be employed to track oxidation state changes and local coordination environments during charge–discharge processes. Through these multi-modal operando studies, I aim to establish a mechanistic framework that bridges atomic-scale observations with macroscopic electrochemical behavior, thereby guiding the rational design of high-performance catalysts and electrode architectures for next-generation lithium–sulfur batteries.

Compendium of publications and additional works

This thesis is based on five research studies. Chapters 4, 5 and 6 are published works that form part of the compendium, while Chapter 1 is adapted from the published review work.

Chapter 1 adapted from: **J. Yu**, I. Pinto-Huguet, C. Zhang, Y. Zhou, Y. Xu, A. Vizintin, J. Jesús Velasco-Veléz, X. Qi, X. Pan, G. Oney, A. Olgo, K. Märker, L. Morais Da Silva, Y. Luo, Y. Lu, C. Huang, E. Härk, J. Fleming, P. Chenevier, A. Cabot, Y. Bai, M. Botifoll, A. P. Black, Q. An, T. Amietszajew, J. Arbiol, *Mechanistic Insights and Technical Challenges in Sulfur-Based Batteries: A Comprehensive In situ/Operando Monitoring Toolbox*. **ACS Energy Lett.** 2024, 9, 12, 6178–6214. <https://doi.org/10.1021/acsenergylett.4c02703>

Chapter 4: J. Li, **J. Yu**, Y. Zhang, C. Li, Y. Ma, H. Ge, N. Jian, L. Li, C. Y. Zhang, J. Y. Zhou, J. Arbiol, A. Cabot, *Boosting Polysulfide Conversion on Fe-Doped Nickel Diselenide Towards Robust Lithium-Sulfur Batteries*, **Adv. Funct. Mater.**, 2025, 2501485. <https://doi.org/10.1002/adfm.202501485>

#Equal Contribution

Chapter 5: **J. Yu**, C. Huang, O. Usoltsev, A. P. Black, K. Gupta, M. Spadaro, I. Pinto-Huguet, M. Botifoll, C. Li, J. Herrero-Martín, J. Zhou, A. Ponrouch, R. Zhao, L. Balcells, C. Y. Zhang, A. Cabot, J. Arbiol, *Promoting polysulfide redox reactions through electronic spin manipulation*, **ACS Nano** 2024, 18, 19268-19282. <https://doi.org/10.1021/acsnano.4c05278>

Chapter 6: **J. Yu**, O. Usoltsev, I. Martynova, C. Huang, Z. Liang, I. Pinto-Huguet, C. Li, L. Lu, C. Zhang, X. Lu, K. Gupta, M. Botifoll, L. Simonelli, F. Fauth, J. Yuan Zhou, J. Llorca, Y. Lu, C. Yue Zhang, J. Arbiol, A. Cabot, *Promoting Electrochemical Reactions with Dual-Atom Catalysts for High-Rate Lithium-Sulfur Batteries*, **Adv. Mater.** DOI: 10.1002/adma.202511345 (2025). <https://doi.org/10.1002/adma.202511345>

List of Publications

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