

Advanced Separator Modifications for Lithium-Sulfur Batteries: Multifunctional Organic Frameworks and Nanostructured Composites to Mitigate the Polysulfide Shuttle Effect

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This thesis consists of materials from two published papers and three submitted manuscripts, in which I, Razieh Fazaeli, am the first author. All authors reviewed and provided feedback on the manuscripts.

The content in **Chapter 1** is based on the article: “*Advancements in Glass Fiber Separator Technology for Lithium-Sulfur Batteries: The Role of Transport, Material Properties, and Modifications*”, Razieh Fazaeli, Hamid Aliyan, Zhe Huang, Yonglin Wang, and Yuning Li, *ACS Omega*, **2025**, *10*, 3228–3261. I collaborated with Dr. Yuning Li to define the manuscript’s scope. I conducted an extensive literature review, organized and validated the information, and contributed significantly to the manuscript’s writing. Hamid Aliyan, Zhe Huang, and Yonglin Wang assisted by gathering relevant literature. Dr. Yuning Li provided overall guidance, editorial oversight, and ensured the clarity and quality of the manuscript.

The content in **Chapter 3** is based on the published article: “*Melamine-based nanoscale porous organic frameworks as multifunctional separator modifiers to mitigate the polysulfide shuttle effect in lithium–Sulfur batteries*”, Razieh Fazaeli, Zhe Huang, Yonglin Wang, Hamid Aliyan, and Yuning Li, *Applied Materials Today*, **2024**, *41*, 102490. I conceived the research idea with Dr. Yuning Li. I designed and conducted the experiments and co-wrote the manuscript with Dr. Yuning Li. Zhe Huang performed XRD characterizations, Yonglin Wang conducted SEM characterizations, and Hamid Aliyan provided technical advice.

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Abstract

This thesis explores innovative approaches to addressing critical challenges in lithium-sulfur (Li-S) battery technology through the development of modified separator materials. The escalating concerns surrounding climate change, pollution, and fossil fuel depletion are propelling a global transition toward renewable energy sources like wind, solar, and hydropower. Alongside this shift is an increasing demand for efficient, high-capacity, and cost-effective energy storage systems that support these sustainable energy technologies, especially for applications in electric vehicles. Various rechargeable battery technologies, such as lithium-ion, sodium-ion, potassium-ion, magnesium-ion, zinc-ion, and aluminum-ion batteries, have garnered significant research attention due to their high efficiency, reversibility, light weight, and environmental friendliness. Although lithium-ion batteries have achieved widespread success in portable electronics and electric vehicles, they have limitations when it comes to the growing demand for energy density, long cycle life, and affordability. Consequently, next-generation batteries—particularly those based on sulfur chemistry—are being developed to meet these requirements. This thesis specifically investigates how functional materials for separator modification can address the main issues of polysulfide shuttle and conductivity in Li-S batteries, aiming to make these batteries more feasible for next-generation energy storage applications.

The first study in this thesis focuses on designing a series of melamine-based porous organic frameworks (POFs) as efficient polysulfide reservoirs to modify glass fiber (GF) separators in Li-S batteries (LSBs). Despite the promising energy density of Li-S systems, the polysulfide shuttle effect—where lithium polysulfides (LiPSs) dissolve and migrate between electrodes—remains a significant barrier to achieving stable cycling and high capacity retention. To tackle this challenge, we synthesized a series of POF materials (POF-C₄, POF-C₈, and POF-C₁₂) by reacting melamine with dibromoalkanes of varying chain lengths (C₄, C₈, and C₁₂). The resulting POFs displayed distinct nanoscale pore sizes and solubility properties, which are critical for effective LiPS trapping and utilization. These POFs were then combined with conductive Super P (SP) and polyvinylpyrrolidone (PVP) binder to create a composite layer (POF-C_n/SP/PVP) that was coated onto GF membranes, forming modified separators that enhance the electrochemical performance of Li-S batteries. The batteries incorporating these modified separators were evaluated through various electrochemical tests, and the POF-C₈/SP/PVP-modified separator, in particular, demonstrated outstanding performance. It delivered an initial specific capacity of 1392 mAh g⁻¹ at 0.1C and retained 90% capacity over 300 cycles at 0.5C. This enhanced performance can be attributed to the optimal pore structure of POF-C₈ and its high nitrogen content, which work in tandem to capture soluble LiPSs and limit their migration toward the lithium anode. Furthermore, the good solubility of POF-C₈ ensures uniform dispersion

and strong interactions with LiPSs, enabling efficient redox reactions. This study highlights the potential of functional polymer-based separator modifications to mitigate polysulfide migration, improving the stability and longevity of Li-S batteries.

The second study investigates the use of Congo Red (CR), a redox-active organic compound, in conjunction with cetyltrimethylammonium bromide (CTAB), a cationic surfactant, to modify GF separators for improved LSB performance. CR has a unique capability of engaging in redox reactions, which aids in suppressing the polysulfide shuttle by capturing LiPSs at the separator interface. The CR-CTAB/SP/PVP-modified GF separators demonstrated enhanced ion transport properties and higher sulfur utilization, addressing core issues that commonly degrade Li-S battery performance. Electrochemical performance tests revealed that LSBs with these CR-CTAB-modified separators achieved an initial specific capacity of 1161.9 mAh g⁻¹ and maintained 994.1 mAh g⁻¹ after 300 cycles at 0.5C, showing significant improvement over the baseline unmodified GF separators. The CR molecules in the separator modification layer serve as efficient adsorbents for polysulfides, while the CTAB molecules aid in stabilizing the structure and enhancing ion transport across the separator. This work emphasizes the importance of incorporating redox-active molecules into separator designs, showing that such molecules can effectively reduce the shuttle effect, enhance performance, and create more durable energy storage systems.

The third study delves into the incorporation of a nanocomposite composed of CR and tin dioxide (SnO₂) nanoparticles for further improvement of polysulfide-trapping capability and redox kinetics in GF separators. The CR-SnO₂/SP/PVP-modified separators were synthesized by combining CR, SnO₂ nanoparticles, conductive SP, and PVP binder. This approach resulted in a composite layer with enhanced surface interactions and improved electron transport pathways. Structural characterization using techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM) confirmed the uniform dispersion of CR and SnO₂, indicating strong cooperative interactions between these components. Electrochemical tests demonstrated that LSBs incorporating the CR-SnO₂-modified separators exhibited exceptional performance, with an initial specific capacity of 1377 mAh g⁻¹ at 0.1C and capacity retention of 91% over 300 cycles at 0.5C. The CR-SnO₂ composite material provides dual benefits: CR molecules effectively capture LiPSs, while SnO₂ nanoparticles act as catalysts, promoting redox reactions and enhancing ion transport. This synergy between CR and SnO₂ in the separator layer contributes to stable cycling performance and mitigates capacity loss due to polysulfide migration, making this composite a promising solution for improving Li-S battery stability.

The fourth study addresses the shuttle effect challenge by employing cysteine and layered double hydroxides (LDHs) as 2D materials to create an innovative 2D heterostructure (Cys/FeNi-LDH). This

heterostructure serves as a robust support for immobilizing V_2O_5 nanoparticles (NPs). Incorporating $\text{V}_2\text{O}_5/\text{Cys}/\text{FeNi-LDH}$ (VCFN) into a GF separator ensured stable electron and ion pathways, significantly enhancing long-term cycling capabilities. The use of L-cysteine, a cost-effective and readily available amino acid, played a crucial role in enhancing the Li-S battery performance. The remarkable enhancement in electrochemical performance is attributed to the synergistic effects of VCFN nanoparticles, cysteine, and SP. A Li-S battery featuring the VCFN GF separator demonstrated an impressive initial capacity of $1036.8 \text{ mAh g}^{-1}$ and, after 300 cycles at 0.5C , retained a capacity of 920.1 mAh g^{-1} .

This thesis demonstrates that modifying the separator is a highly effective strategy for addressing the primary challenges in Li-S batteries, particularly the polysulfide shuttle effect. By tailoring the physical and chemical properties of the separator layer, significant improvements in capacity retention, cycling stability, and rate performance have been achieved. Each of the materials that used for modification of GF separators demonstrates the potential to enhance battery performance through unique mechanisms. The melamine-based POF- C_8 -modified separator leverages a nanoscale porous framework to trap polysulfides and improve LiPS utilization. Meanwhile, the CR-CTAB and CR- SnO_2 composites add a redox-active element to the separator, aiding in polysulfide trapping and catalyzing redox reactions at the interface. A novel composite of V_2O_5 nanoparticles on Cys/FeNiLDH sheets (VCFN) was synthesized and used to modify GF separators, enhancing the electrochemical stability of LSBs. This research contributes to the field of LSBs by providing insights into the design of multifunctional separators that simultaneously address multiple performance issues, including polysulfide retention, ion transport, and redox catalysis.

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List of Abbreviations

Abbreviation	Definition
COF	Covalent organic frameworks
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DMSO	Dimethylsulfoxide
EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier-transform infrared spectroscopy
GF	Glass fiber
HRTEM	High resolution transmission electron microscopy
LDH	Layered double hydroxide
LPSs	Lithium poly sulfides
LIBs	Lithium-ion batteries
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
LSBs	Lithium-sulfur batteries
LUMO	Lowest uoccupied molecular orbital
MIBs	Metal-ion batteries
MOFs	Metal organic frameworks

List of Abbreviations (*Continued...*)

Abbreviation	Definition
MGF	Modified glass fiber
OCP	Open-circuit potential
PP	Polypropylene
POFs	Porous organic frameworks
PVDF	Poly(vinylidene fluoride)
PXRD	Powder x-ray diffraction
PVP	Polyvinylpyrrolidone
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SERS	Surface-enhanced Raman scattering
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-visible spectroscopy
XPS	X-Ray photoelectron spectroscopy
XRD	X-Ray diffraction

Chapter 1. Introduction

This chapter is based on the following *publication*:

R. Fazaeli, H. Aliyan, Z. Haung, Y. Wang, Y. Li, *ACS Omega* **2025**, 10, 4, 3228–3261.

The biggest obstacle facing humanity in the twenty-first century is energy. Fossil fuels that are not renewable are running out quickly. Their excessive use and exploitation have also caused serious environmental issues due to greenhouse gas emissions (such as CO₂, CO, and CH₄). As a result, harvesting of sustainable energy becomes crucial. Energy storage is crucial for a green and sustainable civilization because of the temporal mismatch between the supply and demand of sustainable energy.¹

Since 1991, lithium-ion batteries (LIBs), a type of energy storage device, have changed the world by making portable electronics possible. However, their short durability, low safety at high current, susceptibility to overcharge or overheating,² insufficient gravimetric [240 Wh kg⁻¹ of NCA, NCA meaning layered lithium metal oxides (nickel, cobalt, aluminium)] and volumetric (670 Wh L⁻¹ for LIBs) energy densities, and high cost³ are the main obstacles to their large-scale applications in transportation and power grids. It is critical to build next-generation high-power electronic devices due to the growing energy demand and the resulting environmental problems.⁴ High-power battery technologies are in high demand due to the requirement for electrical power sources not only for electric vehicles and grids but also for artificial satellites, biomedical devices, and electric power tools.^{5,6} One of the most promising options for the upcoming generation of rechargeable batteries is lithium-sulfur (Li-S) batteries, which are expected to meet the high theoretical gravimetric energy density (2600 Wh L⁻¹) and volumetric energy density (2800 Wh L⁻¹) (Figure 1.1), improved safety, and cost-effectiveness.⁷

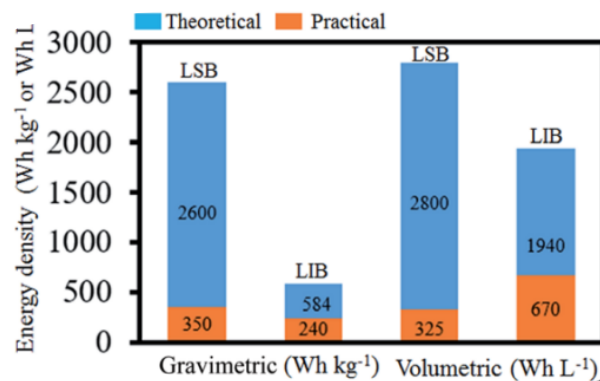


Figure 1.1 Comparison of the theoretical and practical gravimetric energy density and volumetric energy density of LSBs and LIBs.⁷ Reprinted with permission from ref 7, copyright 2019. The Royal Society of Chemistry.

1.1 Electrochemistry and challenges of Li-S batteries

1.1.1 Electrochemistry

The LSB is an energy storage device which converts chemical energy into electrical energy through electrochemical reactions between the negative lithium electrode and the positive sulfur electrode. The main functional components and the internal operating environment of a Li-S cell is shown in Figure 1.2. In the majority of published LSB research, lithium metal has been utilized as the anode.⁷

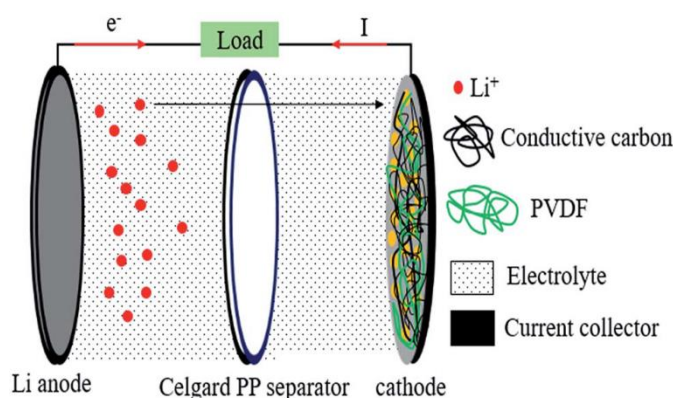


Figure 1.2 Different functional components of LSBs.⁷ Reprinted with permission from ref 7, copyright 2019. The Royal Society of Chemistry.

As seen in Figure 1.3, the charge/discharge process of LSBs often exhibits two distinctive voltage plateaus, which are commonly referred to as higher and lower voltage plateaus. The higher and lower voltage plateaus contribute 25% (418 mA h g⁻¹) and 75% (1254 mA h g⁻¹) of the total theoretical specific capacity (1672 mA h g⁻¹) of sulfur, respectively.⁸ During these two plateaus, LSBs adopt four steps of electrochemical reactions as shown in Figure 1.3. At the beginning of the higher voltage plateau, the sulfur in the cathode is lithiated by Li⁺—forming highly soluble high order PSs (Li₂S₈). At the beginning of the lower voltage plateau, the lithiation process is repeated to produce low order PSs (Li₂S₂) and an insoluble PS (Li₂S) at the end of the second voltage plateau. During the subsequent charging, Li₂S is reconverted to elemental sulfur through the formation of intermediate polysulfides, resulting in a reversible cycle.⁹

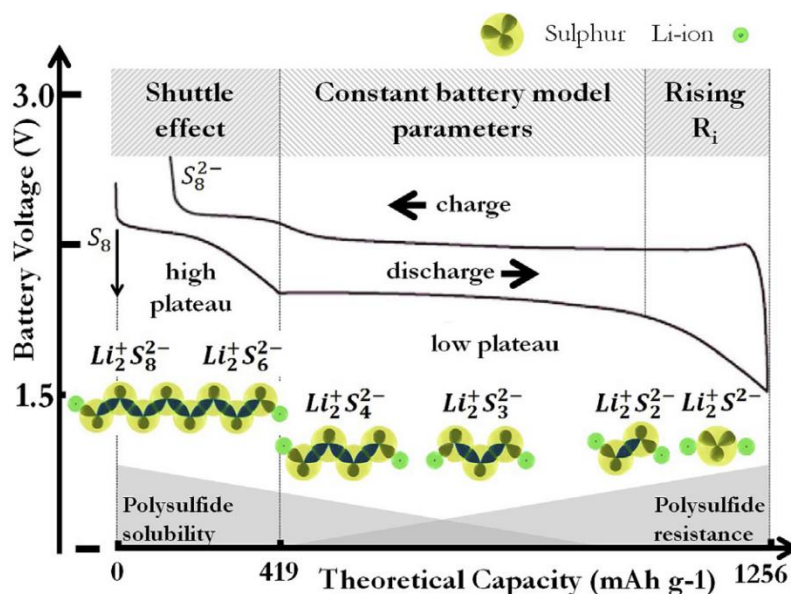


Figure 1.3 Discharge/charge behaviour of a Li-S battery.⁹ Reprinted with permission from ref 9, copyright 2017. Elsevier B.V.

1.1.2 Challenges

Despite the potentially high energy density of Li-S batteries, several key challenges persist and must be addressed for performance improvement and future commercialization.

(1) The insulating nature of sulfur and Li_2S

The challenge with Li-S batteries lies in the insulating nature of both sulfur and Li_2S for electrons and lithium ions, limiting electrochemical reactions and leading to low material utilization. Achieving the theoretical capacity of 418 mAh g^{-1} is difficult due to the presence of unreacted sulfur even after repeated cycles.¹⁰ To improve performance, it is crucial to uniformly disperse sulfur and ensure good electrical contact with conductive additives. The conversion of sulfur to long-chain polysulfides and then to Li_2S in the upper discharge plateau is hindered by sluggish reaction kinetics. In the lower discharge plateau, the conversion of Li_2S_2 to Li_2S involves a solid-solid process, making it challenging to reduce polysulfides completely.¹¹ While the capacity ratio of the lower discharge plateau to the upper discharge plateau is theoretically 3, a value of around 2.5 is more realistic. Incorporating sulfur into a conductive matrix is often necessary, but this reduces specific capacity. The common Li-S voltage profiles exhibit higher polarization in the lower discharge plateau due to limited kinetics for both electrons and lithium ions, resulting in a decrease in practical energy density.¹²

(2) High solubility of intermediate polysulfides in the electrolyte

The presence of lithium polysulfides in Li-S batteries' electrolytes poses several challenges, including low Coulombic efficiency, rapid capacity decay, and high self-discharge rates. These polysulfides migrate to the lithium anode, where they are reduced to insoluble Li_2S , leading to active material loss and anode passivation. During charging, some long-chain polysulfides are partially reduced to short-chain polysulfides by the lithium anode, which then shuttle back to the cathode, causing the "shuttle effect" and reducing charging efficiency. The repeated dissolution and redeposition of these species rearrange sulfur within the cathode, passivating it and increasing impedance. Despite these issues, polysulfide dissolution is crucial for achieving high sulfur utilization. Since sulfur is not conductive, its reduction can only occur on the surface of the conductive matrix. Therefore, controlling the dissolution of polysulfides is essential for balancing high sulfur utilization and cycling stability.¹³

(3) The use of a metallic lithium anode

Lithium metal is an attractive anode for high-energy-density batteries due to its high specific capacity (3860 mAh g^{-1}) and low reduction potential (-3.04 V vs a standard hydrogen electrode).¹⁴ However, its use in Li-S batteries faces challenges for commercialization. Firstly, the formation of lithium dendrites caused by an uneven current distribution and lithium ion concentration gradient at the electrode/electrolyte interface raises safety concerns due to potential short circuits.¹⁵ Secondly, the repeated plating/stripping process during cycling causes the lithium anode to undergo large volume changes and crack, leading to the formation of inactive "dead Li," which lowers lithium utilization rates.¹⁶ Thirdly, metallic lithium reacts with organic electrolytes to form an unstable solid electrolyte interphase (SEI), continuously consuming active lithium.¹⁷ Finally, the "shuttle effect" reduces the efficiency of the lithium anode by forming a Li_2S passivation layer on its surface, limiting battery cycling stability.¹⁸ Protecting the lithium anode or exploring alternative anodes are potential solutions to these challenges. The failure of Li metal anodes induced by uneven plating/stripping and the effect of soluble lithium polysulfides are concretely demonstrated in Figure 1.4.¹⁹

(4) The volume expansion during lithiation from sulfur to Li_2S :

The lithiation of sulfur to Li_2S results in a significant volume expansion of approximately 80%, as the density of octasulfur is higher than that of Li_2S .²⁰ This repeated volume change causes the cathode to pulverize and sulfur to detach from the conductive matrix, leading to permanent capacity fade. Providing appropriate void space to accommodate the volume change is crucial to preserve the cathode's structural integrity, but this decreases the cell's volumetric energy density. Despite sulfur's low density, the volumetric

energy density of Li-S batteries is not expected to be much higher than that of state-of-the-art lithium-ion batteries, around 600 Wh L^{-1} .¹⁵ Therefore, controlling the electrode's porosity is essential to balance volumetric energy density and performance. The key problems and challenges of Li-S batteries are summarized in Figure 1.5, with four major topics described in depth.²¹

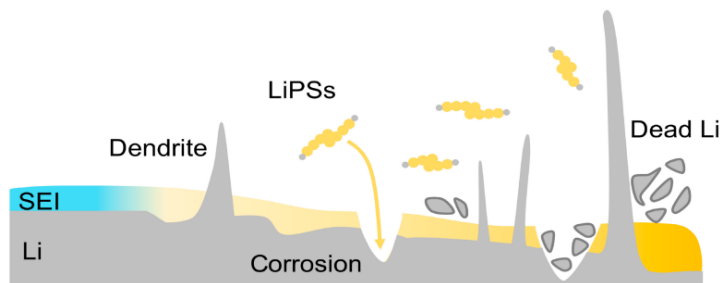


Figure 1.4 Challenges of the Li metal anode in Li-S batteries. Nonuniform Li stripping/plating and corrosion reactions with lithium polysulfides contribute to anode instability.¹⁹ Reprinted with permission from ref 19, copyright 2023. Exclusive Licensee Beijing Institute of Technology Press.

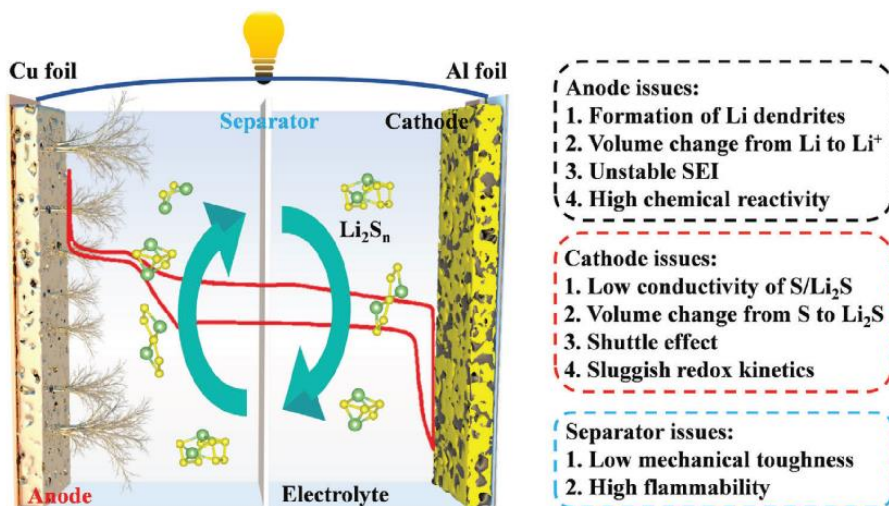


Figure 1.5 The schematic illustration of the Li-S batteries and the challenges of anode, cathode, and separator. The inside red line is the charge-discharge curve of Li-S batteries.²¹ Reprinted with permission from ref 21, copyright 2021. Wiley-VCH GmbH.

1.2 Key criteria for separator design

In order to address these challenges, especially the shuttle effect, recent research efforts have been directed toward constructing functional cathode that could physically or chemically restrain polysulfides dissolution.²² Despite enormous progress has been achieved, it is difficult to completely inhibit the dissolution of lithium polysulfides by cathode optimization and the shuttle effect still exists in the batteries. Meanwhile, the expensive and power-consuming preparation processes of these composites also hinder

their practical application. As an essential component in the lithium-sulfur battery, the separator plays the role of avoiding short circuit and maintaining ion channels between anode and cathode. Recently, introducing a functional layer on the separator has been recognized as another encouraging method to boost the performance of the lithium sulfur batteries. Particularly, some ion-selective separators are introduced to inhibit the shuttle of soluble lithium polysulfides while hardly affecting the diffusion of lithium ion.²³ Separators in lithium batteries must meet several critical requirements to ensure optimal performance and safety. A few key requirements that will be discussed separately are categorized in Figure 1.6.²⁴

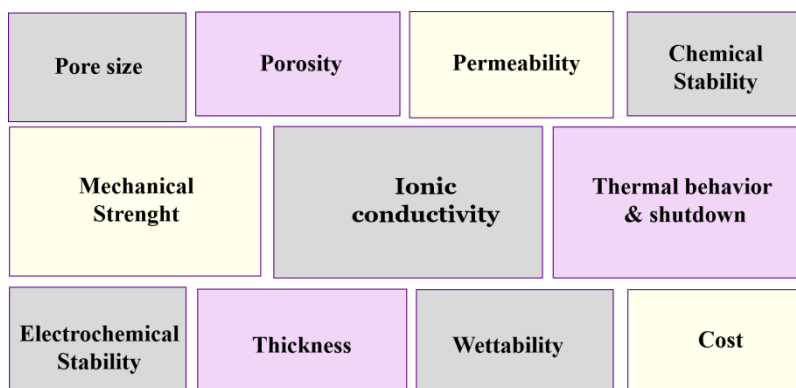


Figure 1.6 Some key criteria for separators in Li batteries.²⁴ Reprinted with permission from ref 24, copyright 2025. American Chemical Society.

1.2.1 Porosity and pore size

Porosity, in the context of battery separators, is a crucial parameter that defines the volume of pores within the separator material relative to its total volume. This ratio directly impacts the performance and safety of the battery. Porosity is generally expressed as a percentage and calculated by:²⁵

$$\text{Porosity (\%)} = \left(1 - \frac{\rho_M}{\rho_P}\right) \times 100 \quad (1.1)$$

where ρ_M and ρ_P represent the density of the separator and the polymer (or other material), respectively. Porosity in a separator enables gas flow and retains liquid electrolyte, impacting battery capacity and cycle life. Adequate porosity provides space for electrolyte, supporting ionic conductivity, while low porosity increases internal resistance, hindering ion flow and performance. Excessive porosity, however, weakens mechanical strength, risking shrinkage with temperature changes and compromising stability and safety. High porosity can also lead to separator damage. Uneven pore distribution causes non-uniform current

density across electrodes, reducing battery efficiency. Polyolefin separators in rechargeable batteries usually maintain a porosity range of 40-50%.²⁶ The techniques used to manage the porosity of separators often involve the following: vacuum impregnation, soaking media, microscopic analysis, direct weighing, and floating.^{27,28} The soaking medium and direct weighing are the two most often utilized ones among them.

In practical applications, controlling and measuring the porosity of separators is essential and the porosity is determined by weighing the separator before and after absorbing the liquid electrolytes by:

$$\text{Porosity (\%)} = \left(\frac{W - W_0}{\rho_L V_0} \right) \times 100 \quad (1.2)$$

where W_0 and W are the separators weights before and after adsorbing the liquid electrolyte. ρ_L is the density of the liquid electrolyte, and V_0 is the separator volume. Direct weighing and soaking methods ensure precise control of porosity, optimizing battery performance by allowing stable ion flow through uniformly sized, submicron pores. Larger pores enhance conductivity, but excessive size increases short-circuit risk, making tight pore size control (0.03 to 0.12 μm) essential for consistent performance and safety.²⁹

The tortuosity (τ) of the electrolyte membrane conduction pathways (pores), e.g., the ratio between the thickness sample and the effective pore length, was determined by the relation:¹⁶

$$\tau = \sqrt{\frac{\sigma_0 \phi}{\sigma_i}} \quad (1.3)$$

where σ_0 is the conductivity of the liquid electrolyte and σ_i and ϕ represent the conductivity and the porosity of the membrane, respectively.

Sousa et al.³⁰ developed polymer electrolyte membranes based on the P(VdF-HFP) copolymer with various polymer/DMF ratios, demonstrating promising properties for lithium battery separators. These membranes achieve optimal porosity and tortuosity when the solvent content is 90% or higher. They can retain up to 77% liquid and exhibit conductivities above $10^{-3} \text{ S cm}^{-1}$ at room temperature, aiming to enhance rate capability by improving pore distribution and interconnection. Further investigations into the effect of separator thickness and porosity on the performance of Lithium Iron Phosphate batteries were conducted.³¹ The study found that the porosity of the separator significantly influences cell performance, with higher porosity separators leading to lower performance. Four different separators were tested: a polypropylene (PP) monolayer and a polypropylene/polyethylene/polypropylene (PP/PE/PP) trilayer, each with thicknesses of 20 μm and 25 μm , and porosities of 41%, 45%, 48%, and 50%. It was determined that the PP separator with 41% porosity and the PP/PE/PP separator with 45% porosity performed better than the

others. Additionally, lignin/polyacrylonitrile composite fiber-based nonwoven membranes (L-PANs) were fabricated through electrospinning by incorporating varying amounts of lignin into polyacrylonitrile (PAN) solutions (Figure 1.7i).³² The L-PANs achieved a porosity of 74%, significantly higher than the 42% porosity of the commercial PP separator. When exposed to 150°C for 15 minutes, the L-PANs maintained their dimensions without wrinkling (Figure 1.7ii), whereas the commercial PP separator shrank by 32%.

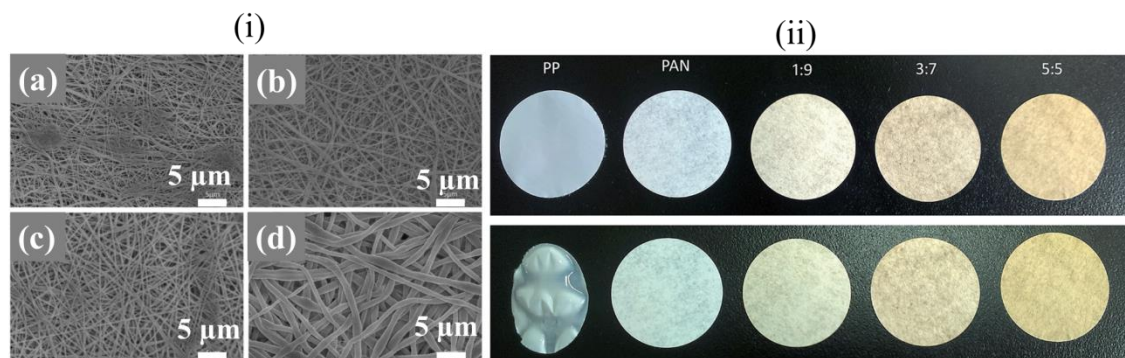


Figure 1.7 (i) SEM of membranes with different lignin/PAN weight ratio. (a) PAN (b) 1:9 (c) 3:7 (d) 5:5. (ii) Photographs of the separators before and after thermal exposure at 150°C for 15 min.³² Reprinted with permission from ref 32. Copyright 2015 The Royal Society of Chemistry.

1.2.2 Permeability

Permeability in battery separators controls electrolyte ion movement, impacting charging speed and overall efficiency. It depends on factors like thickness, porosity, and pore structure, and is often measured by the Gurley value following ASTM standards.^{33,34} The Gurley value measures how quickly air passes through a separator, with rechargeable battery separators typically below 0.025 sμm⁻¹, indicating high permeability. Factors like tortuosity and thickness impact permeability; increased tortuosity lengthens ion paths, while thinner separators generally enhance ion flow, making optimal permeability vital for battery performance and longevity, especially in non-aqueous systems where tailored polymer membranes can significantly improve ion conductivity.³⁵ Tailored separators play a key role in boosting battery performance, as demonstrated by Jiang et al., who developed a high-throughput permeability separator for Li-S batteries using a crumpled MXene/MoS₂ heterostructure (Figure 1.8) on a polypropylene separator. This design effectively immobilizes lithium polysulfides, enhances catalytic conversion kinetics, and accelerates lithium-ion diffusion, thereby significantly improving battery performance.³⁶

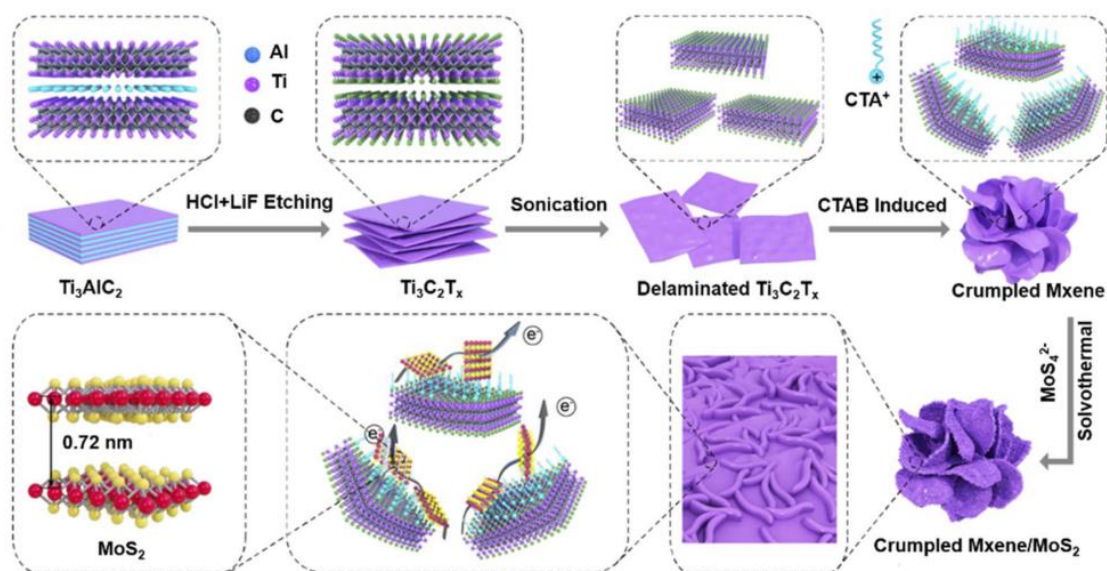


Figure 1.8 Schematic illustration of the synthesis of a 3D hierarchical crumpled MXene/MoS₂ heterostructure.³⁶ Reprinted with permission from ref 36, copyright 2022. Royal Society of Chemistry.

1.2.3 Thickness

The thickness of the separator in a battery is crucial because it directly impacts several key aspects of battery performance and safety. A thinner separator allows for quicker passage of lithium ions between the cathode and anode, reducing internal resistance. This low internal resistance enables the battery to deliver power more efficiently, resulting in higher power density. In simpler terms, thinner separators facilitate faster charging and discharging of the battery. Furthermore, thinner separators enable higher energy density because they allow for more active material (such as lithium ions) to be packed into the same volume of the battery. This means that for a given size, a battery with a thinner separator can store more energy.²² However, if the separator becomes too thin, it may struggle to retain the electrolyte (liquid component of the battery) effectively. Additionally, a thin separator might compromise its ability to provide electronic insulation between the cathode and anode. Both of these factors are critical for the safe and efficient operation of the battery.

1.2.4 Chemical stability

In the realm of battery technology, the chemical stability of separators plays a pivotal role in ensuring the efficient and safe operation of batteries. Separators serve as the physical barrier between the positive and negative electrodes in a battery cell, preventing short circuits while allowing the flow of ions

during the charge and discharge cycles. However, beyond mere physical integrity, separators must exhibit high chemical stability to withstand the harsh conditions within the battery environment, including exposure to reactive lithium,³⁷ corrosive electrolytes,³⁸ and elevated temperatures. These conditions can cause thermal stress, degradation, or failure if the separator is not robust enough.

1.2.5 Mechanical strength

Mechanical strength is a critical aspect of separator performance in batteries, as it ensures the structural integrity of the separator under various conditions encountered during battery operation. The mechanical strength of separators is typically evaluated in terms of tensile strength and puncture strength in the machine direction (MD) and the transverse direction (TD).³⁹ Tensile strength measures the ability of the separator to withstand stretching forces, while puncture strength assesses its resistance to penetration. These properties are crucial for maintaining the structural integrity of the separator during battery assembly and operation.

1.2.6 Wettability

In lithium-ion batteries, the wettability of separators is a crucial factor influencing the overall performance and efficiency of the battery system. A separator with good wettability facilitates easy penetration of electrolyte into its porous structure, ensuring sufficient electrolyte retention during battery operation.⁴⁰ This is essential for maintaining high ionic conductivity within the battery and maximizing its capacity. When a separator exhibits poor electrolyte wettability, it hinders the efficient impregnation of electrolyte into its pores. As a result, the interface resistance between the separator and electrodes increases, leading to reduced charge and discharge efficiency, as well as compromised cycle performance of the battery.

Under low-temperature and discharge coupling conditions, lithium-ion batteries face significant performance degradation, particularly due to the evolving wettability of the separator. This deterioration affects cycling stability and safety.⁴¹ The separator wettability varies significantly with discharge ambient temperature and current. Microstructure and chemical analysis reveal that electrochemical reaction products deposit on the separator, reducing wettability. Lower temperatures and higher currents increase contact angles, leading to particle agglomeration, sediment formation, and reduced separator-ion compatibility.⁴²

1.2.7 Electrochemical stability

In the context of lithium-ion batteries (Li-ion), the electrochemical stability of separators is a critical consideration for ensuring the reliability and safety of battery systems. Li-ion batteries operate within a highly oxidative and reductive environment, particularly during the charge and discharge processes, where lithium ions shuttle between the electrodes. To withstand this extreme redox environment, separators must exhibit robust electrochemical stability. During battery operation, the voltage across the electrodes can vary significantly, with the maximum voltage often reaching up to 4.5 volts. This wide voltage range necessitates separators that remain stable and inert within the 0 to 5.0 volts range. Maintaining stability within this voltage window is crucial to prevent unwanted reactions between the separator material and the electrolyte or electrodes, which could lead to degradation of battery performance or even safety hazards. Cyclic voltammetry (CV) is a commonly employed technique to assess the electrochemical stability of separators within the operational voltage range of Li-ion batteries.

1.2.8 Thermal behavior and shutdown

The thermal behavior of separators in lithium-ion batteries is a critical aspect that directly impacts the safety and reliability of battery systems. Maintaining stability at high temperatures is paramount to prevent internal short circuits and thermal runaway, which can lead to catastrophic failures. During battery assembly, separators must withstand mechanical stresses such as bending and tilting without compromising their structural integrity. Any deformation of the separator that results in electrode contact can trigger an internal short circuit.

1.2.9 Cost

The cost of separators in lithium-ion batteries constitutes a significant portion of the total production expenses, currently amounting to over 20% of the overall cost. This cost encompasses various factors, including expenses related to production equipment, energy consumption during manufacturing, and the raw materials used in separator fabrication. Therefore, finding ways to develop a low-cost production process for separators is crucial for reducing the overall cost of rechargeable batteries.

1.3 Properties of glass fiber (GF) separators

Glass fiber (GF) is an inorganic, nonmetallic material with excellent properties like high aspect ratio, low thermal conductivity, strong corrosion resistance, stable chemical performance, and electrical insulation. It is used in insulation,⁴³ fire prevention,^{44,45} heat insulation^{46–48} and sound insulation,^{49–51} adsorption,^{52,53} and as a polymer precursor,^{54–56} finding applications in plastics, rubber, chemicals, and aerospace. The commonly used polyolefin microporous membrane, like polypropylene (PP), has limitations

such as low porosity, poor wettability to electrolyte, and instability at high temperatures.^{57,58} On the other hand, GF membranes offer better properties like electronic insulation, high thermal (550 °C) and chemical stability, cost-effectiveness, and good affinity to electrolyte, making them promising for Li-S batteries.⁵⁹ Additionally, the hydroxyl groups in GF facilitate the deposition of functional nanostructures like metal-organic framework (MOF), and the structure of GF accommodates functional materials well. Recent studies show GF-based separators in batteries, including Li-S, hold great potential for efficiency.⁶⁰⁻⁶²

PP separator shrinks significantly when exposed to high temperature due to its poor thermal stability, stemming from the low melting point of PP (Figure 1.9a). In contrast, GF separator maintains its dimensions, attributed to its borosilicate structure's intrinsic thermal resistance, enhancing battery safety under high charge/discharge rates or elevated temperatures.⁶³ A separator needs good electrolyte wettability for faster electrolyte filling and efficient retention during battery operation. PP separator has a contact angle of 37°, indicating poor wetting by the electrolyte, while GF separator shows complete wetting with a 0° contact angle, owing to its interconnected microporous structure and lyophilic nature, ensuring superior electrolyte wettability (Figure 1.9b). The highly porous structure of the GF separator increases intake of soluble polysulfide intermediates, slows down their diffusion to the Li anode, improving active material utilization, and protecting the Li anode surface from diffused polysulfides. This leads to better electrochemical performance. Additionally, The high porosity facilitates electrolyte permeation and ion transport, enabling efficient diffusion of lithium ions (Li^+) between the cathode and anode during charge and discharge cycles. FE-SEM analysis (Figure 1.9c) reveals that the PP separator has uniform slit-like pores, designed to prevent short circuits from dendritic lithium growth. In contrast, the GF separator consists of randomly arranged fibers, creating a highly porous structure with pores in the macroscopic range. The GF separator exhibits significantly higher porosity (66%) compared to the PP separator (41%), which enhances its ionic conductivity, facilitating rapid ionic transportation in the electrolyte. Before cycling, the metallic lithium anode surface appeared smooth. However, after cycling with a PP separator, significant corrosion damage and cracks were observed on the lithium anode surface due to side reactions with soluble lithium polysulfides. On the other hand, after cycling with a GF separator, the surface of the lithium anode stayed comparatively smooth and less damaged, suggesting that the GF separator can inhibit polysulfide diffusion to the lithium anode, leading to better cycling performance.

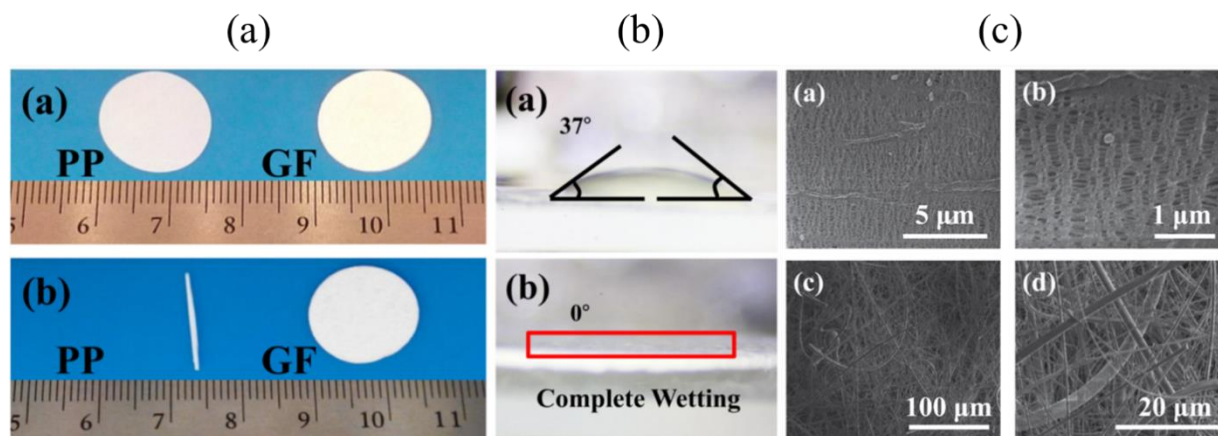


Figure 1.9 (a) Photographs of PP and GF separators before (top) and after (below) thermal treatment at 150 °C for 2h, (b) Contact angle photographs of PP (top) and GF (below) separators using liquid electrolyte. (c) SEM images of PP (top) and GF (below) separators with different resolutions.⁶³ Reprinted with permission from ref 63, copyright 2016. Elsevier.

The thermal shrinkage behavior of GF and Celgard 2400 membranes was evaluated by heating them to 25°C, 150°C, and 200°C for 30 minutes (Figure 1.10a). Celgard 2400 wrinkled significantly at 150°C and melted further at 200°C. In contrast, no obvious morphology change was seen for GF membrane at 200°C, indicating excellent battery safety with GF separators. This nonflammable property is crucial for preventing safety hazards during thermal runaway. The wettability of separators significantly affects electrolyte uptake and ion conductivity. Two separators (GF and Celgard 2400) were evaluated using a spreading test (Figure 1.10b). GF membranes immediately absorbed the electrolyte and laterally diffused it within about 5 seconds. In contrast, Celgard 2400 maintained its shape and had an inferior contact angle of 55° even after several hours, indicating poor wettability. The fast soaking process prevented capturing the contact angle for GF separator, demonstrating its excellent wettability. In Figure 1.10c, Celgard 2400 melts and catches fire quickly when exposed to fire due to its combustible polyolefin components. In contrast, GF separator demonstrate excellent flame resistance and no shrinkage when exposed to fire.⁶⁴

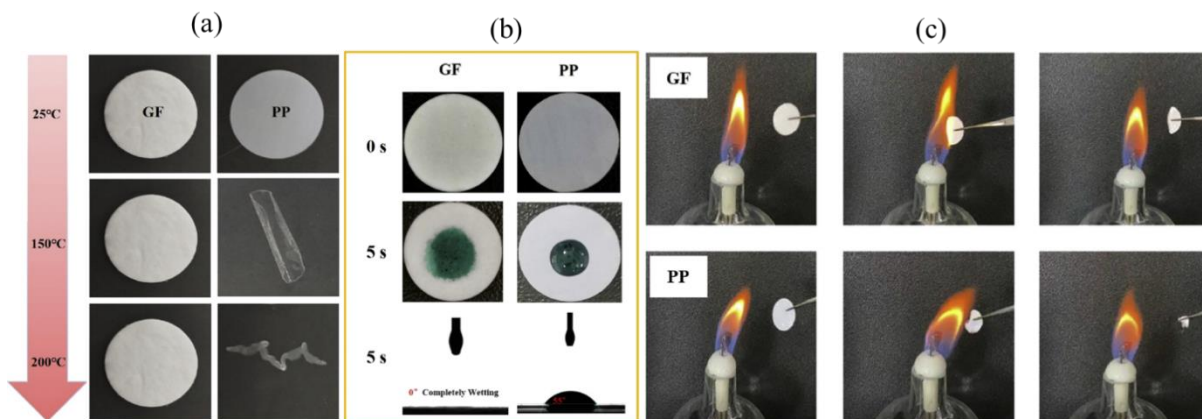


Figure 1.10 (a) Photographs of GF and Celgard 2400 (PP) separator heated at 25°C, 150°C, 200°C in vacuum oven. (b) Contact angle characterization of GF and Celgard 2400 (PP) separator; (c) Flame resistant behavior of GF and Celgard 2400 (PP) separator.⁶⁴ Reprinted with permission from ref 64, copyright 2020. Elsevier.

GFs have good mechanical properties, providing good support for electrodes and preventing deformation and short circuits in Li-S batteries. Their chemical inertness ensures compatibility with various electrolytes, preventing degradation and enhancing battery longevity. Additionally, GFs are cost-effective and readily available, making them suitable for large-scale Li-S battery production; however, it is worth to mention that GFs have limitations as battery separators, such as poor retention of soluble polysulfides leading to capacity fading, susceptibility to pore clogging which impedes ion transport, and fragility that complicates handling and manufacturing. Additionally, their limited thickness variations can restrict battery design flexibility. GFs are modified in order to get around these restrictions; this is covered in more detail in the section that follows.

1.4 Modification techniques for GF separators

There are numerous studies on the modification of GF membranes used in lithium-oxygen batteries,⁶⁵ surface-enhanced Raman scattering (SERS) detection,⁶⁶ oil/water separation,⁴² biological detection⁶⁷ and microfluidics.⁶⁸ GF's brittleness and poor wear resistance limit its direct use. To overcome these issues, physical and chemical modification methods are employed to enhance its compatibility and binding ability with polymer matrices, expanding its application range. GF's main component, amorphous silicon dioxide, forms a highly inert three-dimensional network, necessitating surface functionalization to produce modified GF (MGF).^{69–71}

1.4.1 Common techniques for separator modification

Several techniques have been employed for the modification of separators, including surface functionalization⁷², chemical coating deposition⁷³, vacuum filtration^{74–76}, functional nanoparticle incorporation⁷⁷, spray method⁷⁸, dip coating⁷⁹, impregnation⁷⁵, in-situ polymerization⁸⁰ and the doctor blade casting method. Given that this study employs the doctor blade casting method, the subsequent section of this thesis will focus on a detailed investigation of this specific technique.

1.4.2 The doctor blade casting method

This technique involves preparing slurries containing desired materials (carbon, carbon nanotube, conductive carbon, and polyvinylidene fluoride) in a solvent (like N-methyl-2-pyrrolidone (NMP)) and then coating the GF separators with these slurries using a doctor blade. The process begins with coating separators under vacuum to create carbon-modified GF separators. These separators, enhanced with porous carbon derived from biomass, significantly improve the performance of LSBs. They exhibit higher initial capacity and lower charge transfer resistance compared to uncoated separators, indicating effective inhibition of polysulfide shuttling.⁸¹ The glass platelets are successfully integrated into the GF nonwoven in a single tape-casting step, influenced by the viscosity of the slurry, platelet dimensions, and fiber interspaces.⁸² Figure 1.11 a,b shows of the separator and a demonstration of its flexibility. An illustration of the platelet integration process is shown in Figure 1.11c. Larger platelets than fiber interspaces hinder integration. The process involves three stages: no specific alignment in the slurry, horizontal alignment by the doctor-blade, and pushing into the nonwoven.⁷⁶

1.5. Innovative materials for battery performance enhancement

1.5.1 Porous polymers

Separators are critical components in LSBs, playing a key role in improving cycling performance. They need suitable channels for polysulfide trapping and rapid Li⁺ transport, along with high Young's modulus to suppress dendritic Li growth. Porous polymers including covalent organic frameworks (COFs), metal organic frameworks (MOFs) or porous organic frameworks (POFs) are promising for high-performance separators due to their tunable pores that can accommodate sulfur and its products, preventing polysulfide shuttle effect.⁸³ Porous structures in natural materials have been extensively studied for their applications in various fields. These structures are made of linked spaces that permit the passage of gases or liquids, and they can be found in materials like charcoal and rocks. Advanced porous materials, which can be classified as microporous (<2 nm), mesoporous (>2 nm and <50 nm), and macroporous (>50 nm) materials, have undergone significant advancement in recent times. Common examples include porous

organic polymers (POPs) and MOFs, where POPs are created by network reactions and MOFs via coordinate bonds. POPs have drawn interest for uses including gas separation, energy storage, and pollution degradation because of their consistent pore diameters and large surface areas. Their morphologies, such as those of nanospheres and nanotubes, are manipulable by synthetic techniques. POPs usually have larger surface areas than MOFs.⁸⁴

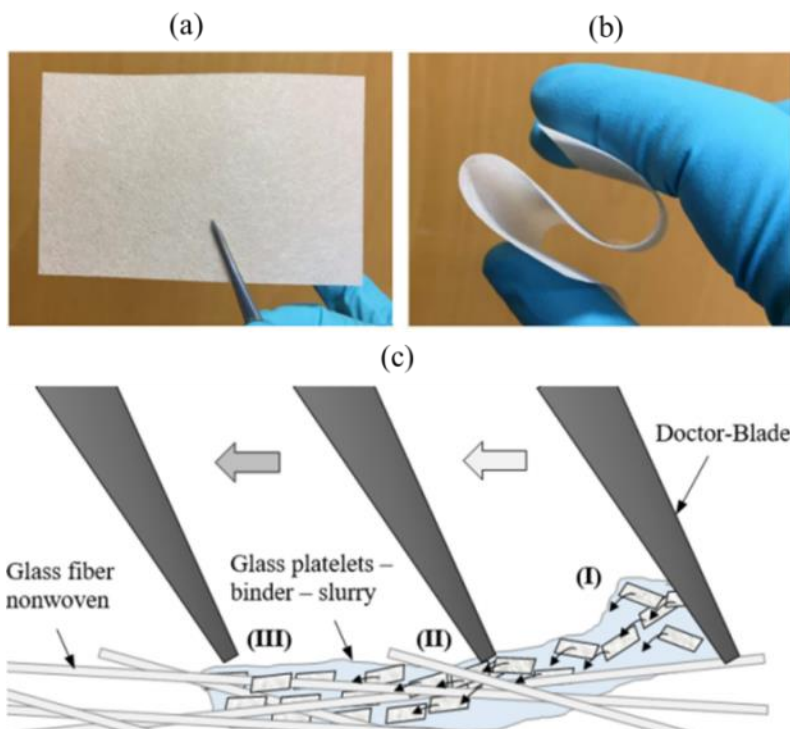


Figure 1.11 Pictures of a glass fiber nonwoven/glass platelet composite separator, (a) top view; (b) demonstration of the separators flexibility, (c) Illustration of the integration process of micrometer-sized glass platelets in a glass fiber nonwoven by tape casting.⁷⁶ Reprinted with permission from ref 76, copyright 2018. MDPI.

There are various benefits to using POFs as sulfur's host material in LSBs. First off, the sulphur content may rise due to their big pore volume and high specific surface area. Second, the cathode's volumetric growth may be constrained by the stiff scaffold of POFs. Thirdly, LiPSs can be efficiently trapped via the chemisorption of polar links and the physisorption of intrinsic pores, which lessens the shuttle effect and enhances battery performance. Ultimately, the ability to customize the pore environment, surface area, and functionality of POFs through modular synthesis is crucial for attaining optimal performance in lithium-sulfur batteries. Studies have demonstrated the potential effectiveness of sulphur cathodes made using POFs as the host material.⁸⁵

Porous polymers with controllable pore structures can encapsulate liquid electrolytes, providing rapid Li^+ transport pathways and improving Li^+ conductivity, especially in solid-state batteries. Including

liquids in MOFs/COFs can also enhance interfacial contact for active materials, further improving battery performance.⁸⁶ Compared to liquid electrolytes where ions move easily, solid conductors have higher diffusion energy barriers. MOFs/COFs, with their nanochannels, allow ions to hop between ion-conducting sites, resulting in lower diffusion energy barriers compared to inorganic or polymer solid conductors. This is due to their high porosity and active sites for ionic transfer. The rigid continuous nanochannels in MOFs/COFs provide enough free volume for fast ionic conduction and stability over a wide temperature range (Figure 1.12).⁸⁷

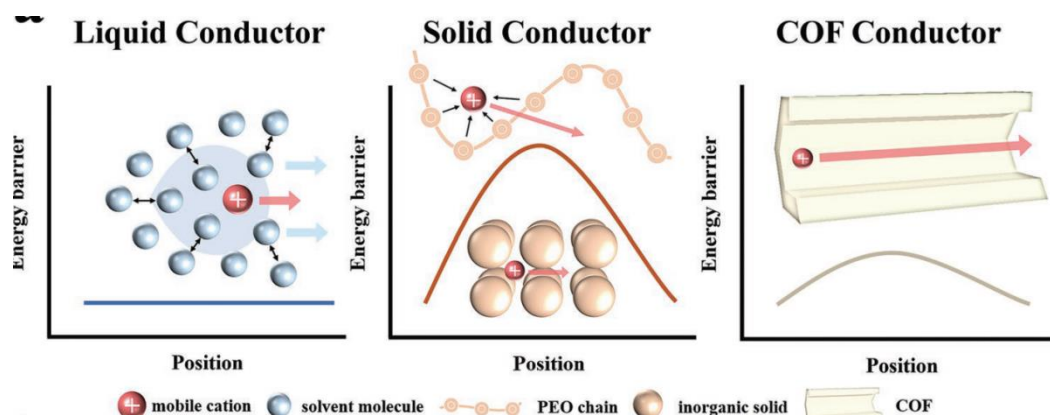


Figure 1.12 Schematics of the ion-conducting behavior and diffusion energy barrier in (a) liquid conductor, (b) typical solid conductor, and (c) COF conductor, respectively.⁸⁷ Reproduced with permission from Ref. 87, copyright 2022. Wiley-VCH GmbH.

To gain deep insights into the ion-conducting mechanisms and establish the property–function relation between COFs and ion-conducting process, herein, we summarize a series of design principles for the construction of ion-conducting COFs, which pave the foundation for the optimization and application of COFs in rechargeable batteries. The six strategies including pore size regulation, pore wall decoration, crystallinity regulation, crystallographic orientation, exfoliation, and guest promoting transport are systematically proposed and analyzed based on the fundamental understanding of COF features and rechargeable batteries (Figure 1.13).⁸⁷



Figure 1.13 Schematics of strategies for ion-conducting COF design.⁸⁷ Reproduced with permission from Ref. 87, copyright 2022. Wiley-VCH GmbH.

1.5.2 Metal oxides

A wide range of nanostructured metal oxides have been shown to exhibit enhanced electrochemical properties as promising electrode materials for high-performance LIBs. Tin dioxide (SnO_2), a polar material, effectively mitigates the polysulfide shuttle effect through strong chemical adsorption.⁸⁸ It is cost-effective, environmentally friendly, and commonly used as a sulfur carrier in Li-S batteries. Studies have shown that SnO_2 , when combined with other materials like 1T-MoS₂ or polypyrrole, enhances sulfur's performance by trapping polysulfides and facilitating their redox reactions. However, due to SnO_2 's low conductivity, it requires pairing with conductive matrices or 3D frameworks to improve sulfur electrode conductivity and accommodate volume changes during cycling.⁸⁹ V_2O_5 is a widely used layered transition metal oxide in energy storage, particularly in Li batteries,⁹⁰ with various architectures like nanorods, nanofibers, and nanotubes developed for enhanced performance⁹¹. V_2O_5 has gained attention for its role in modifying sulfur cathodes, showing strong adsorption of LiPSs and catalytic effects.⁹² Liu et al. demonstrated that V_2O_5 -coated carbon membranes effectively suppress LiPSs shuttling and improve electrochemical performance. Despite this, the semiconductive V_2O_5 nature increases interfacial impedance, limiting capacitance retention at high current densities. To maximize its potential as an interlayer material, a strategy focusing on efficient LiPSs utilization and stable electron/ion pathways is necessary.⁹³

1.5.3. Layered double hydroxides (LDHs)

Layered double hydroxides (LDHs) are a class of two-dimensional anionic clays characterized by the general chemical formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n} zH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, respectively, A^{n-} is an interlayer anion, and zH_2O denotes water molecules (Figure 1.14) ^{94,95}. This structure is formed by positively charged metal hydroxide layers interspersed with negatively charged interlayer anions and water molecules, which stabilize the structure and impart unique properties. LDHs exhibit several attractive features, including a large specific surface area, chemical and thermal stability, tunable composition of metal cations within the layers, and environmental compatibility. These features make LDHs highly versatile and suitable for various applications. The layered structure can incorporate a variety of di- and trivalent metal cations, as well as organic or inorganic anions (e.g., hydroxide (OH^-), carbonate (CO_3^{2-})) in the interlayer space, along with water molecules ⁹⁶. The potential of LDHs has been widely explored in different fields. For example, they have been studied for their catalytic properties, where their large surface area and tunable chemistry make them ideal for supporting active catalytic sites. In electroactive and photoactive materials, LDHs are recognized for their ability to facilitate charge transfer processes due to their semiconductor properties ⁹⁷.

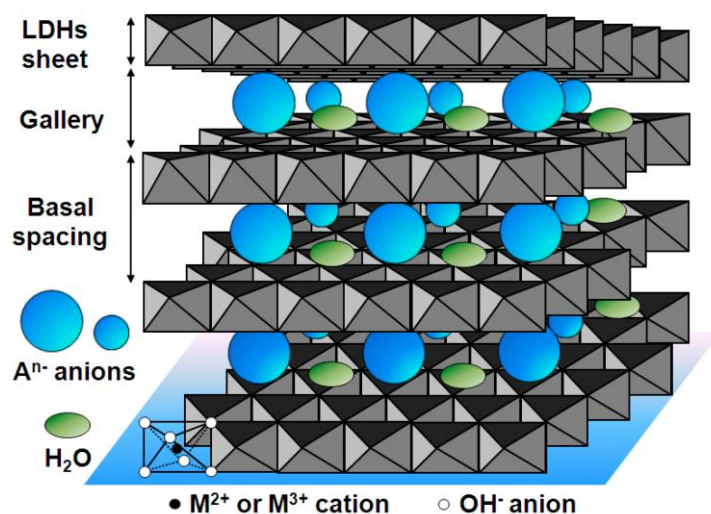


Figure 1.14 Schematic representation of the structure of layered double hydroxides (LDHs).⁹⁵ Reprinted with permission from ref 95, copyright 2014. MDPI.

A specific example of LDH materials is NiFeLDH, which consists of layers of edge-shared nickel oxide octahedra. In these materials, some of the nickel (Ni^{2+}) ions are replaced by ferric (Fe^{3+}) ions. This substitution creates an excess positive charge on the layers, which is balanced by interlayer anions. The

interlayer space contains hydroxide groups and water molecules, which contribute to the stability and functionality of the material ⁹⁸.

Rechargeable metal-ion batteries (MIBs) are pivotal energy storage devices due to their high energy density, voltage, and safety. Effective energy storage in MIBs depends on the reversible insertion and removal of cations (e.g., H^+ , Li^+) within electrode materials, accompanied by metal-ion redox reactions and phase transformations.⁹⁹ Layered double hydroxides (LDHs) were historically overlooked for cation intercalation until a 2017 breakthrough showed that electrochemical activation could create 2D channels and hydrogen vacancies (HV) in LDHs, enabling high cation-storage capacities.⁹⁹ LDHs also excel as battery separator modifiers,⁹⁴ improving the mechanical strength, ionic conductivity, and stability of separators in lithium-based batteries¹⁰⁰. For example, MgAl-LDH coatings enhance thermal stability and suppress dendrite growth in lithium-metal batteries (LMBs), while LDH/graphene oxide composites in lithium-sulfur batteries (LSBs) inhibit polysulfide shuttling and improve cycling stability.⁶¹ Liu et al. synthesized CoAl-LDH quantum dots on nitrogen-doped graphene to modify PP separators, enabling effective polysulfide capture through polar interactions and quantum confinement. This highlights the broad potential of LDHs as separator modifiers in advanced batteries.¹⁰¹ Metal-based batteries, utilizing metal anodes, offer high theoretical capacity but face challenges like dendrite growth and interface side reactions. Controlling metal nucleation is key to preventing dendrites and enhancing metal loading. LDHs promote uniform nucleation of anode metals, with atomically exposed active oxygen aiding Li adsorption and uniform deposition. Their lithiophilic terminal-O and ultrathin structure enhance Li nucleation and electron transfer.¹⁰² In aqueous zinc batteries, LDHs facilitate Zn^{2+} adsorption and matching with the Zn (002) plane, improving Zn-metal deposition, electrode stability, and performance.¹⁰³

1.6 Objective and the structure of this thesis

The objective of this thesis is to investigate the development of modified separator materials to address critical challenges in LSB technology, particularly the polysulfide shuttle effect and conductivity issues. With the growing demand for efficient energy storage systems, this research aims to enhance the electrochemical performance and long-term stability of LSB through functional modifications of GF separators. By incorporating novel materials, such as porous polymers, Congo Red, metal oxides, and LDHs, the work explores their potential to improve battery performance. The structure of this thesis is organized into several chapters, each focusing on a different aspect of separator modification and the impact of the chosen materials on Li-S battery performance.

Chapter 1 explores the electrochemistry, challenges, and performance-enhancing strategies for LSBs, focusing on separator properties, modification techniques, and the role of porous polymers, metal oxides, and LDHs.

The objective of Chapter 2 is to provide a comprehensive overview of the characterization techniques employed, including physical characterization methods and electrochemical evaluation indexes, to assess the properties and performance of the modified separators.

Chapter 3 is dedicated to the development of melamine-based porous organic frameworks (POFs) as functional materials for the modification of separators. This study examines a series of POFs (POF-C₄, POF-C₈, and POF-C₁₂), synthesized by reacting melamine with dibromoalkanes of varying chain lengths. The chapter investigates the influence of dibromoalkane chain length on the solubility and pore size of the resulting POFs, and explores how these properties affect the modification of glass fiber separators. Additionally, the study evaluates how the solubility of the POFs contributes to their ability to effectively trap polysulfides and, ultimately, improve the overall performance of the battery.

In Chapter 4, the incorporation of CR, a redox-active organic compound, in combination with CTAB, a cationic surfactant, for the modification of GF separators is investigated. The structural properties of the CR-CTA compound are characterized using XRD, FTIR, TEM, and ¹H NMR. This chapter also examines the synthesis of CR-CTA/SP/PVP-modified GF separators and compares their electrochemical performance with cells incorporating bare GF, CR/SP/PVP, and CTAB/SP/PVP -modified GF separators. The study focuses on the effects of particle size and uniform distribution on the modification of GF separators and their subsequent impact on electrochemical properties.

Chapter 5 examines the role of SnO₂/CR/SP/PVP-modified GF separators in LSBs. SnO₂ nanoparticles were synthesized through the thermal decomposition of a Sn-MOF. Composite mixtures of CR and SnO₂ were prepared by grinding SnO₂ with CR at various molar ratios to optimize the composite for enhanced electrochemical performance. The cooperative interactions and crystalline structure of the composites were characterized using XRD. The specific capacity, cycling stability, ionic conductivity, and rate performance of LSBs incorporating CR-SnO₂/SP/PVP-modified separators were investigated.

Chapter 6 investigates the use of cysteine as a cheap amino acid and LDHs in the development of a novel composite (VCFN) for the modification of GF separators. The VCFN composite is characterized using XRD, FTIR, SEM, EDS, TEM, TG-DTG and XPS. The synergistic effects of cysteine, LDHs, and V₂O₅ on the electrochemical performance of the VCFN/SP/PVDF-modified GF separators are thoroughly examined and compared with VCFN/SP/PVDF-modified PP separators.

In Chapter 7, the work of this thesis is concluded, and future directions are given to further study on the topic.

Chapter 2. Characterization Techniques

In this chapter, the basic principles and the instrumentation for the main characterization techniques adopted to characterize the physicochemical properties of electrode materials and evaluate their electrochemical performance are described.

2.1 Physical characterization

2.1.1 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) is used to analyze the crystal structure of materials, including in Li-S batteries to understand their electrochemical behavior and performance. It identifies phases of sulfur and lithium sulfides formed during cycling, aiding in understanding electrochemical reactions. PXRD also provides information on particle size in cathode materials, crucial for electrode optimization. Using Bragg's Law,

$$n\lambda = 2d\sin\theta \quad (2.1)$$

when the wavelength λ is set, the angle θ can be measured to confirm the interplanar spacing, unit cell size and type. The measurement result was compared with the XRD standard card (PDF card), and the phase composition was confirmed. XRD is used to study structural changes in electrode materials during cycling in Li-S batteries. This includes phase transitions, crystallinity changes, and variations in lattice parameters. XRD can also examine the content and structure of the SEI layer, aiding in understanding its role in battery performance. Additionally, XRD can analyze interactions between electrode materials and electrolytes, including the formation of new phases or compounds at the interface.¹⁰⁴

2.1.2 X-ray photoelectron spectroscopy (XPS)

One of the great strengths of XPS is that it can be used not only for elemental analysis, but also for quantitative analysis.¹⁰⁵ XPS peak areas are proportional to the amount of material present because the photoionization cross-section of core levels is virtually independent of the chemical environment surrounding the element. XPS is a crucial instrument for analyzing the components of the various nitrogen types in nitrogen-modified samples, including pyridinic-N, graphitic-N, pyrrolic-N, and pyrazole-N, of which pyridinic-N has high chemical adsorption and catalytic properties toward LPSs.¹⁰⁶

2.1.3 Energy-dispersive X-ray spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS or EDX) is a technique used to analyze the elemental composition of materials, often in conjunction with electron microscopes like SEM or TEM. In Li-S batteries, EDS is valuable for studying elemental composition and distribution, such as mapping elements like sulfur, lithium, and carbon in electrodes. It can identify sulfur species in the cathode, analyze the SEI layer, study electrolyte penetration, and examine lithium dendrites on the anode. These analyses provide insights into battery behavior, performance, and stability.¹⁰⁷

2.1.4 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) is used to study how a sample's mass changes with temperature. In Li-S batteries, TGA can determine sulfur content by heating the cathode material to measure sulfur's mass loss. This helps calculate sulfur utilization efficiency by comparing initial and final masses. TGA also assesses thermal stability of cathode materials and electrolytes, identifying temperatures of decomposition or reactions. It studies SEI layer formation on electrodes, revealing layer composition and stability. Additionally, TGA analyzes electrolyte thermal decomposition, aiding in understanding electrolyte stability and its effects on battery performance.¹⁰⁸

2.1.5 Ultraviolet–visible spectroscopy (UV-Vis)

UV-Vis spectroscopy is utilized in LSBs for several purposes. It can analyze sulfur species in the electrolyte, including polysulfides, aiding in understanding electrochemical reactions and degradation mechanisms. UV-Vis is also used to study electrolyte degradation, SEI formation on electrodes, and optical properties of cathode materials, providing insights into structural changes and degradation processes. Additionally, it has potential for lithium dendrite detection, crucial for battery safety and performance. Care is needed during analysis, especially regarding polysulfide adsorption capabilities, as different species can complicate the interpretation of results. LPS species such as Li_2S_6 can undergo disproportionation reactions to form other species such as Li_2S_4 and Li_2S_8 , adding complications to the analysis with Li_2S_6 no longer being the sole species present.¹⁰⁹

2.1.6 Scanning electron microscope (SEM)

SEM is valuable in Li-S battery research, aiding in electrode microstructure analysis including the distribution and morphology of sulfur, carbon, and other components to optimize performance. It helps identify sulfur loss mechanisms, crucial for mitigating cathode sulfur loss. SEM also characterizes interfaces between components in the battery, such as the sulfur-carbon composite cathode, electrolyte, and

lithium anode, understanding their impact on performance. Additionally, it studies lithium dendrite formation, which can cause short circuits and degrade battery performance, electrolyte penetration into the electrode structure, and interfacial reactions, providing insights into battery behavior and stability.¹¹⁰

2.1.7 Transmission electron microscopy (TEM)

In addition to assisting other analytical methods, Transmission electron microscopy (TEM) offers comprehensive information about the nanoscale chemistry and structure of Li-S batteries, enabling researchers to maximize the performance and durability of these batteries. It characterizes sulfur species and electrode morphology as well as identifies various sulfur allotropes' distribution, aiding in understanding electrode structure evolution. TEM studies interfaces between electrode materials and electrolyte, including SEI layer development. It provides detailed insights into lithium dendrite formation and growth, crucial for preventing dendrite growth. TEM also analyzes the crystalline structure of electrode materials, aiding in understanding phase transitions and structural changes. Additionally, TEM allows for cross-sectional analysis, providing insights into electrode structure and interfaces' 3D morphology.¹¹¹

2.2 Evaluation indexes

For LSBs, there are several evaluation indexes of battery performance, including:

(1) Specific capacity

In LSBs, specific capacity is a crucial performance metric. It measures the amount of electricity a material can deliver per unit mass or volume of the electrode active material under a specified current density. The theoretical mass specific capacity is calculated using the formula:

$$C_o = \frac{nN_A q}{3.6 M} = \frac{nF}{3.6 M} \quad (2.2)$$

Where:

- n is the number of electrons acquired or lost in the reaction
- N_A is Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$)
- q is the charge of an electron ($1.6 \times 10^{-19} \text{ C}$)
- M is the molar mass of the active material
- F is Faraday's constant ($9.65 \times 10^4 \text{ C mol}^{-1}$)

The theoretical mass specific capacity of sulfur ($M = 32.07 \text{ g mol}^{-1}$) is 1672 mAh g^{-1} .

(2) Rate performance

The rate of a battery, typically measured in C (where 1 C corresponds to the current required to discharge or charge the battery in 1 hour), indicates how fast the battery can be charged or discharged. The rate performance and high-current charge-discharge performance of a battery are influenced by the electrochemical reaction kinetics of the electrode. Faster rates require more rapid ion transport and surface reactions within the electrode materials, which can impact the battery's overall efficiency and cycling stability. Improving rate performance is crucial for applications that require fast charging or high power output, such as electric vehicles or grid energy storage.¹¹²

(3) Cyclic stability

Cycle performance is a critical metric for evaluating the lifespan of a rechargeable battery. It refers to how well a battery maintains its capacity over multiple charge and discharge cycles. The cycling performance is influenced by two main factors:

(i) **Electrochemical Reversibility:** This refers to how easily the active materials in the battery can reversibly undergo the charging and discharging process without significant degradation. In a LSBs, for example, the sulfur cathode should efficiently convert back and forth between lithium sulfide (Li_2S) and elemental sulfur (S_8) during charge and discharge cycles. If this process is not reversible, the battery's capacity will degrade over time.

(ii) **Structural Stability:** The structural stability of the battery's components, particularly the electrodes, is crucial for maintaining cycling performance. In the case of LSBs, the volume expansion and contraction of the sulfur cathode during cycling can lead to mechanical stress and structural degradation. This can result in the loss of active material and decrease in battery capacity over time. Characterizing structural stability in LSBs involves multiple techniques, including:

1. Electrochemical methods assess capacity retention and internal resistance.
2. Microscopy provides insight into morphology and nanostructure changes.
3. X-ray techniques identify phase changes and surface chemistry.
4. Spectroscopy detects polysulfide formation and chemical bonds.
5. Thermal analysis assesses material stability under temperature changes.
6. Mechanical testing evaluates mechanical properties.
7. Chemical analysis monitors gaseous products and dissolved metals.

Combining these methods allows for a comprehensive assessment and improvement of LSB performance and longevity. Improving the electrochemical reversibility of the active materials and enhancing the

structural stability of the battery components are key strategies for enhancing the cycle performance of LSBs and ensuring their long-term reliability.¹¹³

2.2.1 Coin cell

Coin cells are commonly used in laboratory settings for their simplicity and ease of use in testing new battery materials and configurations. They are also used as a preliminary step before scaling up to larger battery formats for commercial applications. Figure 2.1 depicts the structure of a typical coin cell.¹¹⁴ The diameter and thickness of a CR2032 type coin cell are 20 mm and 3.2 mm, respectively. Here are the key components of a coin cell in a Li-S battery: Anode, Cathode, Separator, Electrolyte, Coin cell casing, Current collectors. To assemble a coin cell for a Li-S battery, researchers typically prepare the electrodes by coating the active materials (sulfur for the cathode and lithium metal or other lithium-containing materials for the anode) onto the current collectors. The electrodes are then assembled with a separator soaked in the electrolyte, and the entire assembly is enclosed in the coin cell casing.

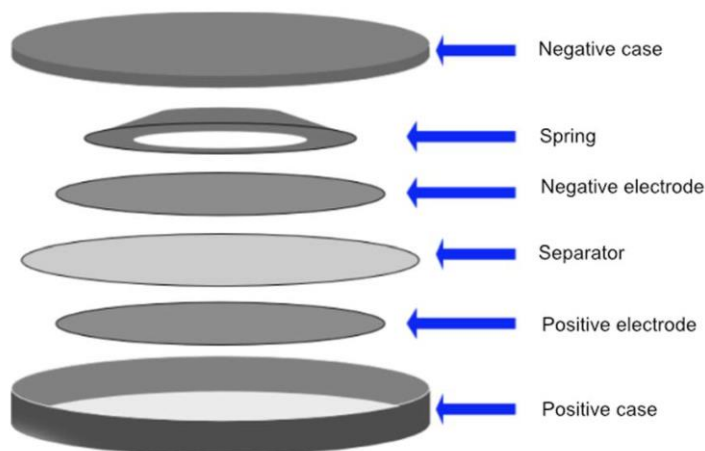


Figure 2.1 Schematic diagram of the CR2032 coin cell configuration.¹¹⁴ Reprinted with permission from ref. 114, copyright 2019. ECS.

2.2.2 Galvanostatic charge and discharge

Galvanostatic charge and discharge is a common technique used to characterize the performance of LSBs.¹¹⁵ In this technique, the battery is charged or discharged at a constant current, allowing researchers to study the electrochemical behavior of the battery over time.

During a galvanostatic charging measurement, a constant current from the outer circuit is applied to cathode in order to drive Li^+ ions out of the cathode and towards the anode, while the responding voltage of the cell is simultaneously monitored and recorded. Once the voltage of the cell reaches the cut-off potential, a constant potential is then applied to the cell with a decreasing current as a result. The discharging process is operated in the opposite direction.

Two different graph types are produced by galvanostatic charge/discharge. One is a voltage versus time or specific capacity plot that can identify voltage plateaus related to different electrochemical processes that occur during charge and discharge. On the other hand, data regarding long-term cycling stability can be found by plotting specific capacity vs. cycle number. Examining the rate performance at various rates (e.g., 0.1 C, 0.5 C, 2 C) for an equivalent number of cycles allows one to additionally assess the specific capacity vs. cycle number plot. A cell can be charged or discharged rapidly without losing capacity when it operates well at high rates. The standard for comparing a battery's charge and discharge rates is known as the C-rate. A battery that charges or discharges in n hours is indicated by a C-rate of $1/n$ C. For example, a battery with a C-rate of 1 C is designated to be fully charged or drained in one hour. In order to discharge a battery with a capacity of 100 A h in one hour, a discharging current of 100 A is needed. Furthermore, 0.5 C means using a 50 A discharge current to drain the same battery in two hours.

2.2.3 Electrochemical impedance spectroscopy (EIS)

One effective electrochemical method for examining the electrical characteristics of electrochemical systems is electrochemical impedance spectroscopy (EIS). It involves applying a small amplitude alternating current (AC) signal to a system over a range of frequencies and measuring the resulting AC response. Because EIS can give precise information on the electrochemical processes taking place inside the battery, it is widely employed in the study of LSBs. Among the most important uses of EIS in Li-S batteries are: Charge transfer kinetics, sulfur utilization, electrode/electrolyte interface, degradation mechanisms and battery state-of-charge (SoC) estimation.¹¹⁶

EIS data are commonly plotted either in a Nyquist plot (Figure 2.2a) or in a Bode plot (Figure 2.2b). The Bode plot shows how the absolute value of the impedance $|Z|$ and the phase (ϕ) shift varies with the logarithm of the frequency. A more frequently representation of impedance data is the Nyquist Plot, which contains both the real part (x-axis) and the imaginary part (y-axis) of the impedance Z .¹¹⁷

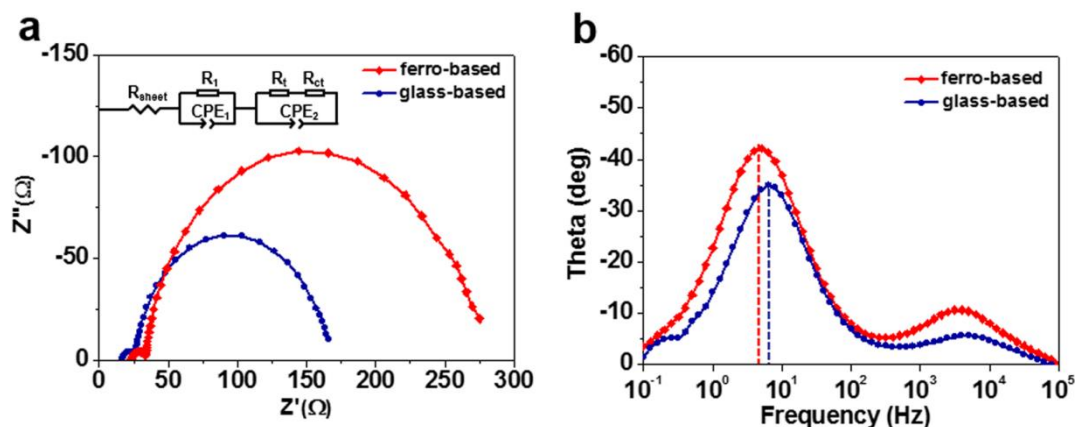


Figure 2.2 The same EIS data plotted in (a) Nyquist Plot and (b) Bode Plot.¹¹⁷ Reprinted with permission from ref. 117, copyright 2018. Springer Nature.

EIS data are commonly interpreted by fitting with an equivalent electrical circuit model as shown in Figure 2.3. A common electrical circuit model consists of a uncompensated resistance in the solution between the electrode surface and the reference electrode (R_e), a charge transfer resistor (R_{ct}), a double layer capacitor (C_d). The intersection of the semicircle and Z_{real} axis defines R_e , which is attributed to the equivalent series resistance, also known as internal resistance.¹¹⁸

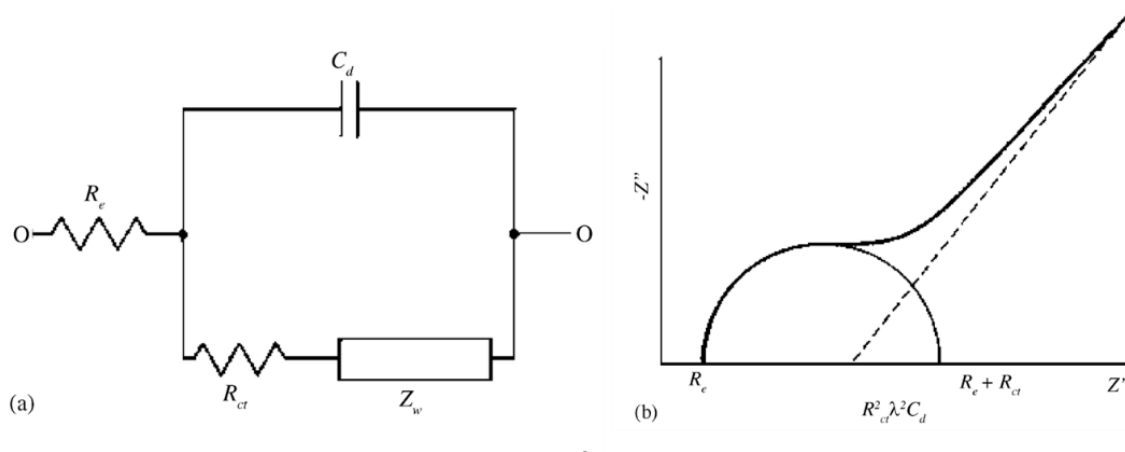


Figure 2.3 (a and b) Randles equivalent circuit for a charge transfer reaction at an electrode surface. R_e is the uncompensated resistance in the solution between the electrode surface and the reference electrode, R_{ct} is the charge transfer resistance, and C_d is the double layer capacitance.¹¹⁸ Reprinted with permission from ref 118, copyright 2005. Elsevier.

2.2.4 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is a common electrochemical technique used to study the behavior of redox reactions happening at the interface between the electrode and the electrolyte. It involves applying a

voltage to an electrochemical cell and measuring the resulting current. In a typical CV experiment, the potential is swept linearly between two limits (the limits are called the forward and reverse potential limits) at a constant rate. One generic cyclic voltammogram of a reversible dissolved redox system is exemplified in Figure 2.4. E_a is termed the anodic peak potential, at which point shows the maximum anodic current and interprets that the analytes near the electrode are oxidized. The corresponding current is called anodic current, i_a . After that, the current declines because the analytes need to diffuse towards the electrode and continue the oxidation until the point the applied voltage switches to negative scanning. Thereafter, reduction of the analytes occurs on the working electrode and at E_c , cathodic peak potential, with the related cathodic current i_c .¹¹⁹

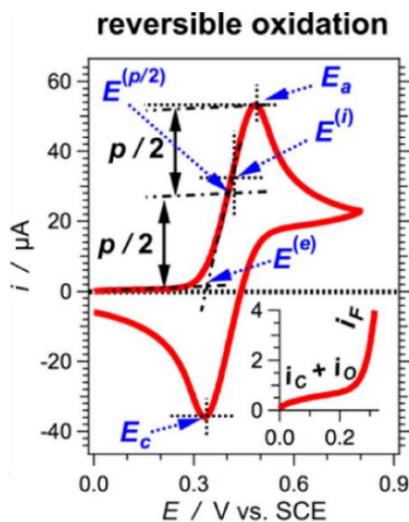


Figure 2.4 A generic cyclic voltammogram of a reversible redox system.¹¹⁹ Reprinted with permission from ref 119, copyright 2019. ECS.

CV is commonly used in the study of LSBs due to its ability to provide valuable information about the electrochemical behavior of sulfur and LiPS in the battery system. Some specific applications of CV in Li-S battery experiments include: redox behavior, electrode kinetics, cycling stability, electrode design and electrolyte optimization.¹²⁰

Chapter 3. Melamine-Based Nanoscale Porous Organic Frameworks as Multifunctional Separator Modifiers to Mitigate the Polysulfide Shuttle Effect in Lithium–Sulfur Batteries

This chapter is based on the following publication:

R. Fazaeli, Z. Haung, Y. Wang, H. Aliyan, Y. Li, *Applied Materials Today* 41, **2024**, 102490-102501.

3.1 Introduction

LSBs hold great potential for energy storage due to their low cost, high energy density, and environmental friendliness. However, lithium polysulfide intermediates dissolve into the electrolyte during charge/discharge, causing a notorious "shuttle effect" that leads to capacity loss and inadequate cycle stability. Consequently, tremendous efforts have been made to tackle this issue over the past decade. While research has primarily focused on incorporating various functional additives and binders in the cathode composite to trap LiPSs, increasing efforts have been directed toward developing functional separators to inhibit the shuttle effect.^{121–129} A simple and efficient approach has been to coat separators with barrier layers that are capable of trapping and utilizing LiPSs. For instance, modifying the separator with microporous or mesoporous materials can physically trap LiPSs and reduce their diffusion, thereby enhancing discharge capacity and cycle performance.^{130,131} Active species such as metal oxides,^{132–135} bimetallic nitride,⁵⁷ sulfides,¹³⁶ and various nanoparticles are incorporated in the modifying layer to trap LiPS through the strong interactions of transition metal and heteroatoms with LiPSs,¹³⁷ while various conductive carbonaceous materials have also been included to efficiently utilize the trapped LiPSs.^{138–146} Compared to commonly used PP separators, GF separators offer several advantages. First, they are highly porous and exhibit excellent wettability, allowing for greater electrolyte intake and higher ionic conductivity, which enhances ionic transport.¹⁴⁶ Second, GF separators provide more stable capacity and better rate capability than the PP separators.¹⁴⁷ Additionally, due to their high thermal resistance, they undergo minimal dimensional changes when exposed to high temperatures, which is beneficial for battery safety at high charge/discharge rates or elevated temperatures.¹⁴⁸

Porous materials can be classified into microporous (<2 nm), mesoporous (between 2 nm and 50 nm), and macroporous (>50 nm) materials.^{149–152} Recently, POFs¹⁵³ and MOFs^{122,154–156} have received significant attention for various applications. POFs, known for their consistent pore sizes and large surface areas, have been explored in gas separation, energy storage, and pollutant degradation. Their morphologies,

such as nanospheres and nanotubes, can be tailored using appropriate synthetic techniques. Additionally, POFs typically have larger surface areas than MOFs.³⁹ There are several advantages to using POFs as sulfur's host material for lithium-sulfur batteries. First, their large pore volume and high specific surface area can accommodate increased sulfur content. Second, the rigid scaffold of POFs can constrain the volumetric expansion of the cathode. Third, LiPSs can be effectively trapped through the chemisorption by embedded functional groups and physisorption on the large pore surface area, reducing the shuttle effect and enhancing battery performance. Finally, the pore environment, surface area, and functionality of POFs can be conveniently adjusted through synthesis, which is crucial for achieving optimal performance of lithium-sulfur batteries. Studies have demonstrated the effectiveness of using POFs as the host material to enhance the performance of sulfur cathodes.^{136,157,158}

Herein, we introduce novel flexible GF separators modified with melamine-based POFs, synthesized through condensation of melamine and dibromoalkanes (1,4-dibromodibutane, 1,8-dibromooctane and 1,12-dibromododecane) with different alkyl chain lengths (denoted as POF-C_n, n=4,8,12). The alkyl chain length in POF-C_n materials influences their pore size, surface chemistry, mechanical properties, and electrochemical performance, affecting their ability to trap polysulfides, conduct ions, and cycling stability. These POFs have mesoporous pores (~15-17 nm), large surface areas (~420-470 m² g⁻¹), and abundant nitrogen atoms, which are beneficial for effectively trapping LiPSs.^{159,160} The Li-S battery using the GF separator modified with POF-C₈, namely, POF-C₈/SP/PVP, exhibited an initial discharge specific capacity of 1035 mAh g⁻¹ at 0.5C and maintained a capacity of 883.5 mAh g⁻¹ after 300 cycles. These results represent significant improvements compared to batteries using non-modified PP and GF separators. This modified separator not only mitigates the shuttle effect but also enhances the transport of lithium ions, thereby improving the cycling stability and rate performance of LSBs.

3.2 Experimental

1,4-Dibromobutane, 1,8-dibromooctane, and 1,12-dibromododecane (Sigma-Aldrich), Li foils (Shenzhen Poxon Machinery Technology Co. Ltd.), N-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich), polyvinylpyrrolidone (PVP) (Sigma-Aldrich), polyvinylidene difluoride (PVDF) (with a molecular weight of ~1,000,000 g mol⁻¹), and Super P (IMERY) were used as received. Borosilicate glass fiber filter paper (GF, diameter of 18 mm, thickness of 550±10 µm and filtration rating of 0.2 µm, OMICRON) was evenly split into two films, each approximately 275 µm thick, to serve as battery separators.

3.1.1. Material characterization

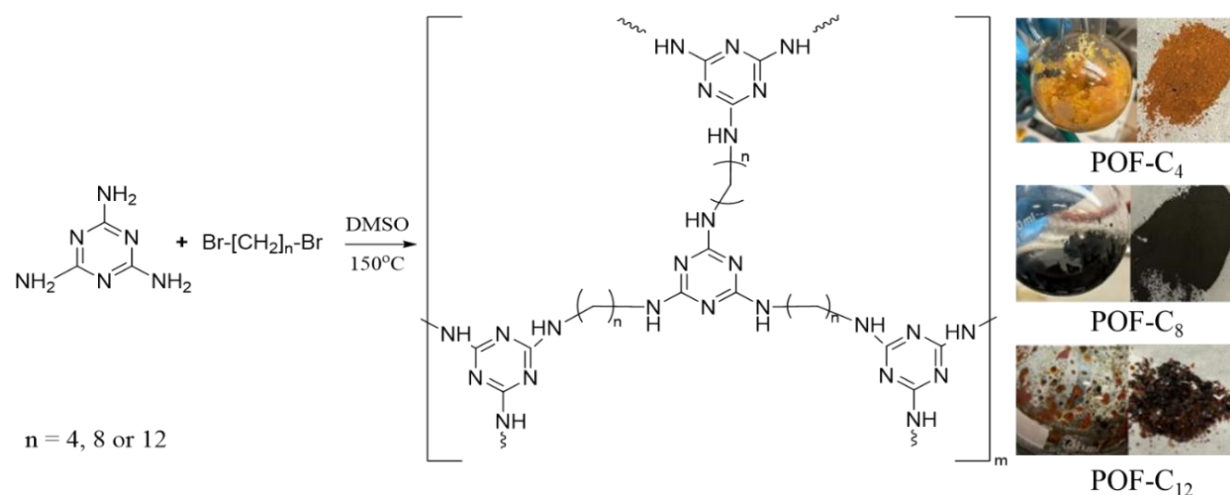
XRD patterns were recorded on a Bruker D8 Advance X-Ray diffractometer with a Cu K α anode ($\lambda = 0.1542$ nm) operating at 40 kV and 30 mA. SEM images were acquired with a Zeiss Sigma HD microscope. The Brunauer-Emmett-Teller (BET) specific surface areas and pore volumes of the catalysts were determined by nitrogen adsorption-desorption at liquid nitrogen temperature (-196 °C) using a Micromeritics TriStar II Series instrument. The samples were degassed at 623 K for 12 h at a reduced pressure of 10^4 Pa before carrying out the adsorption measurements. FT-IR spectra were taken on a PerkinElmer Spectrum 65 FT-IR spectrometer.

3.1.2. Synthesis of melamine-based POFs

Three melamine-based POFs were synthesized following the method described in the literature (Fig. 1).¹⁵⁷ Melamine (1.26 g, 0.010 mol) and a dibromoalkane (0.015 mol) (1,4-dibromobutane (3.24 g), 1,8-dibromooctane (4.08 g), or 1,12-dibromododecane (4.92 g)) were dissolved in 50 mL of dimethyl sulfoxide (DMSO) in a 250 mL flask. The mixture was heated at 150°C under a nitrogen atmosphere with stirring for 10, 14, or 18 h for 1,4-dibromobutane, 1,8-dibromooctane, or 1,12-dibromododecane reactions, respectively. The resulting melamine-based POFs, designated as POF-C₄, POF-C₈, and POF-C₁₂, were precipitated by adding excess ethanol to the reaction mixture. The precipitates were dispersed in a 50:50 acetone-ethanol mixture and then centrifuged. This process was repeated 10 times to remove any residual DMSO and other soluble impurities. The final precipitates were dried in a vacuum oven at 60°C overnight to obtain POF-C₄ (1.95 g), POF-C₈ (2.16 g), and POF-C₁₂ (2.44 g) as orange, black, and dark red solids, respectively (Scheme 3.1). POF-C₈ is soluble in DMSO, whereas POF-C₄ and POF-C₁₂ are insoluble in DMSO and other common solvents.

3.1.3. Modification of separators

A slurry was prepared by mixing a mixture of POF-C_n, SP, and PVP in a weight ratio of 6:3:1 in DMSO solvent. The slurry was applied to one side of the GF or PP membrane using the doctor blading technique and dried overnight in an oven at 60 °C in air. The resulting membrane, with a POF-C_n/SP/PVP loading of 1.58 mg cm⁻², was then cut into 19 mm diameter disks to function as separators. The thickness of the POF-C_n/SP/PVP coating on the GF or PP separators is about 30 $\pm$ 2 μ m. For comparison, GF and PP separators modified with SP and PVP in a weight ratio of 3:1 were also prepared using the same method.



Scheme 3.1 Schematic presentation of the synthesis of melamine-based porous organic frameworks (POFs): POF-C₄, POF-C₈ and POF-C₁₂.

3.1.4. Electrochemical measurements

A sulfur/Super P (S/SP) composite was prepared grinding a mixture of sulfur (600 mg) and SP (400 mg) in a mortar for 30 min. The resulting mixture was pressed into pellets, which were placed in a glass vial and heated at 155 °C for 12 h to facilitate sulfur infiltration into SP pores. Next, a slurry was prepared by grinding a mixture of the S/SP composite (90 wt.%) and PVDF (10 wt.%) in NMP. The slurry was applied onto a carbon-coated aluminum foil using a doctor-blading technique and then dried overnight at 60°C in a vacuum oven. The dried film was cut into 12 mm diameter disks to serve as cathodes, with a sulfur loading of 1.67 mg cm⁻², for Li-S batteries.

For the electrolyte, a commercial 1 M bis(trifluoromethane) sulfonimide lithium (LiTFSI) solution in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume) with 1 wt.% LiNO₃ was used. GF and PP membranes modified with POF-C_n/SP/PVP were utilized as the separators for their respective cells. For comparison, the non-modified GF and PP separators were also tested. The Li-S batteries were assembled into 2032-type coin cells using lithium foil as the anode inside an argon-filled glove box (both O₂ and H₂O concentrations are < 0.1 ppm). The assembly process involved adding 15 μL of electrolyte onto the lithium foil, placing the modified separator with the modification layer facing up, adding an additional 15 μL of electrolyte, and then positioning the cathode on top. The electrochemical performance of batteries was measured galvanostatically on a Land 2001A battery test system. Electrochemical impedance spectra (EIS) were recorded at the open-circuit potential (OCP) using a Bio-

logic electrochemical potentiostat/galvanostat (VSP) in a frequency range from 1000 kHz to 0.1 Hz with an AC amplitude of 10 mV.

3.3 Results and discussion

The FTIR spectra of melamine and the synthesized melamine-based POFs are presented in Figure 3.1a and Figure 3.1b. The FTIR spectrum of melamine (Figure 3.1a) shows distinct peaks attributed to various vibrations.¹⁶¹ The most prominent bands, observed in the range of 3121-3467 cm^{-1} , correspond to N-H stretching vibrations. Additionally, peaks around 1550-1650 cm^{-1} are associated with Ar-C=N stretching, while C-N stretching vibrations appear at 1525, 1465 and 1427 cm^{-1} . In the POFs (Figure 3.1b), the absence of these distinct stretching vibration peaks indicates that the N-H functional groups of melamine have reacted with dibromoalkanes. Furthermore, the increasing intensity of the CH_2 stretching vibration peaks at 2917 and 2836 cm^{-1} from POF-C₄ to POF-C₁₂ confirms the incorporation of longer alkyl chains within the POFs. It was anticipated that longer alkane chains would result in larger pore sizes, thereby increasing the average interchain distance in the resulting POFs. Figure 3.1d presents the XRD patterns for POF-C_n samples, which display a broad peak in the 2θ range of 20.0–26.5°, indicating their amorphous nature, unlike crystalline melamine, which shows sharp diffraction peaks (Figure 3.1c). Specifically, the 2θ values for POF-C₄, POF-C₈, and POF-C₁₂ are 22.4°, 20.0°, and 21.3°, respectively, corresponding to d-spacings of 0.396 nm, 0.443 nm, and 0.417 nm, reflecting the average interchain distances in these crosslinked networks (Figure 3.1d). The unexpected decrease in d-spacing for POF-C₁₂ compared to POF-C₈ is likely due to the folding of the longer dodecane linkages between melamine units, leading to tighter packing and smaller pores, consistent with circuit theory.^{161,162}

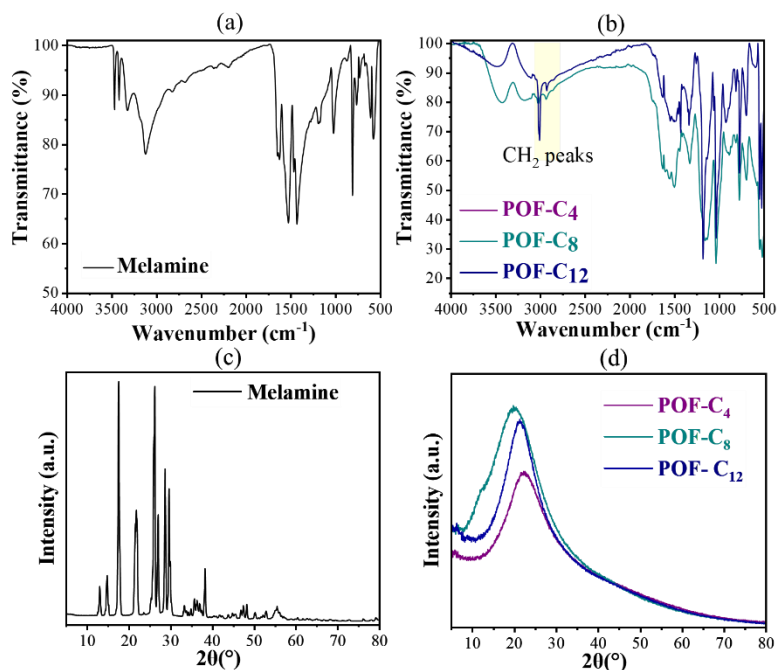


Figure 3.1 FTIR spectrum of (a) melamine and (b) POF- C_n samples. XRD patterns of (c) melamine and (d) POF- C_n samples.

N_2 adsorption-desorption measurements were conducted to acquire information on the pore size and distribution in these POFs (Figure 3.2). The adsorption isotherms exhibited characteristics typical of Type IV isotherm, with noticeable hysteresis during desorption, indicating a mesoporous structure.¹⁶³ The pore sizes were determined to be 15.6 nm for POF- C_4 , 17.3 nm for POF- C_8 , and 16.8 nm for POF- C_{12} . Additionally, the specific Brunauer–Emmett–Teller (BET) surface areas were found to be 468 $m^2 \cdot g^{-1}$ for POF- C_4 , 462 $m^2 \cdot g^{-1}$ for POF- C_8 , and 419 $m^2 \cdot g^{-1}$ for POF- C_{12} . These pore size and surface area data align with the XRD results, suggesting that the longer dodecane chains may fold, causing pore collapse in the POFs. Consequently, the octane linkage appears to have the optimal chain length for achieving the largest pore size and surface area.

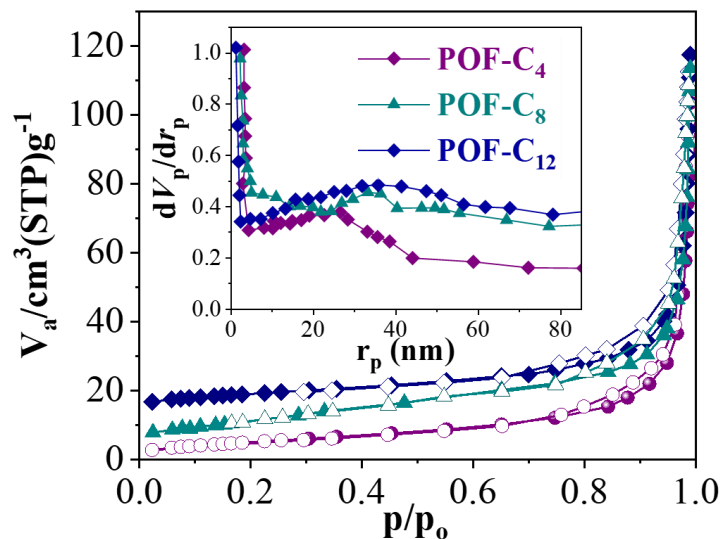


Figure 3.2 BET nitrogen adsorption isotherms of POF-C_n samples.

To evaluate the polysulfide trapping capability of POF-C_n, visual adsorption tests were conducted by soaking POF-C_n powders in Li₂S₆ solutions (Figure 3.3a). The brownish-red Li₂S₆ solution in DOL/DME turned nearly colorless upon the addition of POF-C_n at a mass equivalent to Li₂S₆, demonstrating the strong polysulfide trapping capability of POF-C_n. To quantitatively evaluate the Li₂S₆ trapping capability of POF-C_n, UV-vis measurements^{164–167} were conducted on Li₂S₆ solutions before and after treatment with POF-C_n at a mass equivalent to Li₂S₆. As shown in Figure 3.3b, the absorbance of the Li₂S₆ solution decreased significantly after the addition of POF-C_n. Based on the absorbance changes at the wavelength of maximum absorption at 264 nm, the trapping efficiency of POF-C_n for Li₂S₆ was calculated to be 0.61 g(Li₂S₆)/g(POF-C₄), 0.64 g(Li₂S₆)/g(POF-C₈), and 0.63 g(Li₂S₆)/g(POF-C₁₂) (Table 3.1). Based on the molecular weight of the repeat units, their molar efficiencies for Li₂S₆ was calculated to be 0.61 mol(Li₂S₆)/mol(POF-C₄), 0.90 mol(Li₂S₆)/mol(POF-C₈), and 1.15 mol(Li₂S₆)/mol(POF-C₁₂). This trend indicates that the polysulfide trapping capacity per melamine unit increases with longer alkane spacer length. The deviation from the interchain distance trend observed in the XRD analysis suggests that, despite the reduced pore size in POF-C₁₂ due to chain folding, the collapsed pores can expand and effectively accommodate polysulfides, allowing each melamine unit to absorb up to 1.15 Li₂S₆ molecules. However, when considering mass trapping efficiency, which is more relevant for battery energy density, POF-C₈ demonstrates the highest effectiveness as a polysulfide trapper for separator modification. Compared to other polysulfide trapping agents reported in the literature, POF-C_n appear to be among the most effective.¹⁶⁷

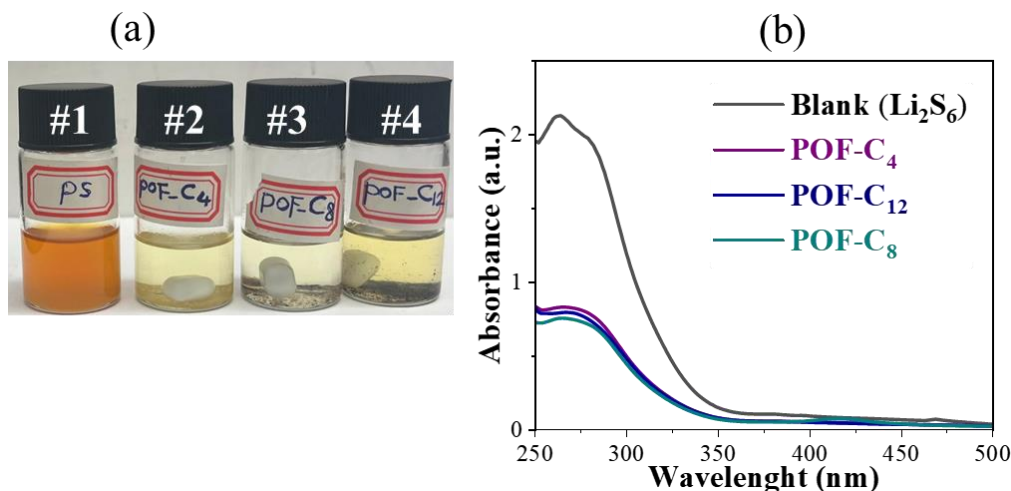


Figure 3.3 (a) Photos of (1) a 0.008 M Li₂S₆ solution in DOL/DME (v/v = 1/1) and (2)-(4) solutions prepared by stirring a 0.024 M Li₂S₆ solution in DOL/DME with POF-C₄, POF-C₈, and POF-C₁₂ at a mass equivalent to Li₂S₆ overnight, followed by a threefold dilution with DOL/DME (v/v = 1/1). (b) UV-vis absorption spectra of a blank 0.008 M Li₂S₆ solution in DOL/DME (v/v = 1/1) and solutions prepared by stirring a 0.024 M Li₂S₆ solution in DOL/DME with POF-C₄, POF-C₈, and POF-C₁₂ at a mass equivalent to Li₂S₆ overnight, followed by a threefold dilution with DOL/DME (v/v = 1/1).

Figures 3.4 a-c shows TEM images of POF-C_n samples with distinct morphologies. The POF-C₄ sample displays layered structures hundreds of nanometers in size, while POF-C₈ consists of nanoparticles tens of nanometers in size. In contrast, POF-C₁₂ adopts a nanotube structure. These varying morphologies reflect differences in their polymerization and growth mechanisms as illustrated in Scheme 3.2. With the shorter 1,4-dibromobutane, POF-C₄ grows horizontally under the guidance of the rigid melamine template, forming a two-dimensional (2D) flat sheet. For POF-C₈, the longer 1,8-dibromooctane promotes backbiting of the peripheral bromooctyl chains with unreacted NH₂ groups on melamine units, resulting in defect sites and the formation of zero-dimensional (0D) nanoparticles. When using the longest 1,12-dibromododecane, backbiting is suppressed, allowing 2D growth in POF-C₁₂. However, the longer and more flexible alkane spacer enables the 2D sheets to fold, resulting in one-dimensional (1D) tubular structures. These morphologies are also related to their solubilities: POF-C₈, with its particulate form, disperses well in DMSO, while the larger POF-C₄ and POF-C₁₂ structures are insoluble in any solvent. Additionally, structural defects in POF-C₈ may contribute to its larger interchain distance compared to POF-C₄ and POF-C₁₂.

Table 3.1 Li_2S_6 trapping efficiencies of POF- C_n calculated from UV-vis spectra of Li_2S_6 solutions treated with POF- C_n at a mass equivalent of to Li_2S_6 .^a

Trapper	A_0^b	A^b	$\Delta A (A-A_0)$	$\Delta A/A_0 \times 100\%$	$\Delta C/C_0 \times 100\%$	η_m^c	η_n^d
#1: Blank	2.12856	2.12856	-	-	-	-	-
#2: POF- C_4	2.12856	0.83118	-1.29738	-61%	-61%	0.61	0.61
#3: POF- C_8	2.12856	0.75654	-1.37202	-64%	-64%	0.64	0.90
#4: POF- C_{12}	2.12856	0.79365	-1.33491	-63%	-63%	0.63	1.15

^aSample #1 is a blank solution of 0.008 M Li_2S_6 in DOL/DME (v/v = 1/1), while Samples #2–#4 are prepared by stirring a 0.024 M Li_2S_6 solution in DOL/DME (v/v = 1/1) with POF- C_n at a mass equivalent to Li_2S_6 overnight, followed by threefold dilution with DOL/DME (v/v = 1/1) and filtration before UV-Vis measurement.

^b A_0 and A are the absolute absorbances of the sample solution before and after POF- C_n treatment (refer to Figure 3.5b in the main text).

^c(g(Li_2S_6)/g(POF- C_n)).

^d(mol(Li_2S_6)/mol(POF- C_n)).

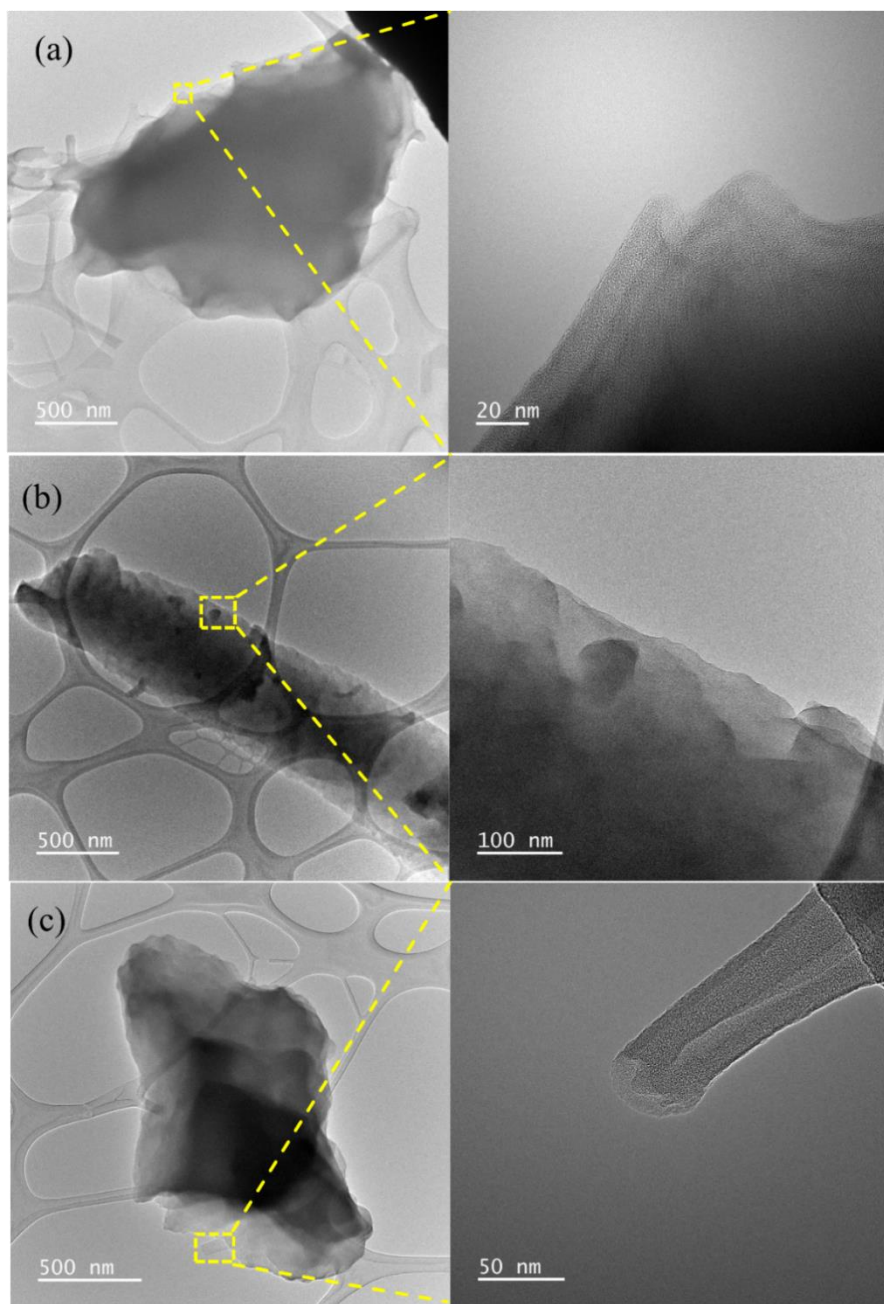
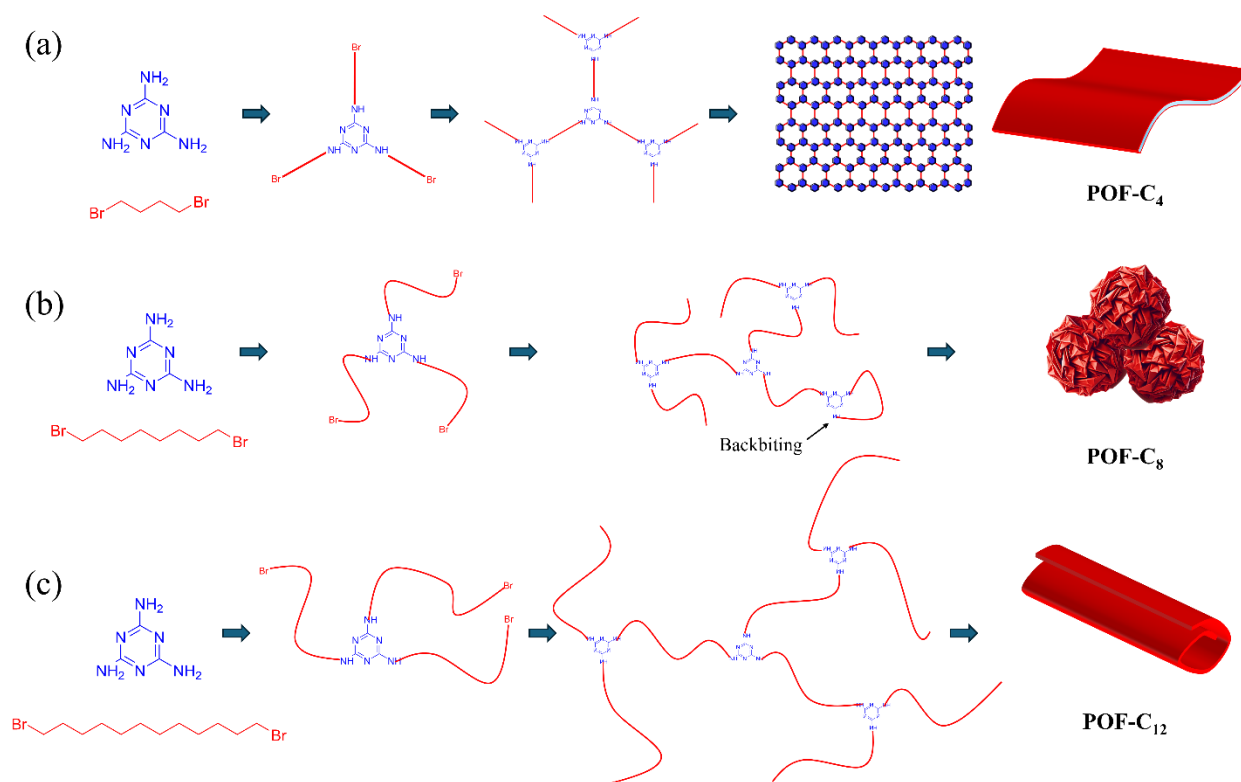


Figure 3.4 TEM images of (a) POF-C₄, (b) POF-C₈ and (c) POF-C₁₂.



Scheme 3.2 Polymerization and morphology formation mechanisms for (a) POF-C₄, (B) POF-C₈ and (c) POF-C₁₂.

Various solvents were tested to dissolve POF-C_n, and only DMSO was able to dissolve POF-C₈, while POF-C₄ and POF-C₁₂ were insoluble in any solvent. Consequently, PVP, which is soluble in DMSO, was chosen as a binder to prepare POF-C_n/SP/PVP slurries for modifying GF separators. SEM analysis was performed to evaluate the morphology of both the bare and modified GF separators. As depicted in Figure 3.5a the bare GF separator exhibits a three-dimensional network with large pores around 2 μm , allowing for the free movement of LiPSs, which can lead to LiPS shuttle. Figures 3.5b-d, show that after coating with the POF-C_n/SP/PVP layer, the glass fibers are covered by SP and POF particles. In Figure 3.5c, the GF separator modified with POF-C₈/SP/PVP shows uniformly dispersed POF-C₈ particles. Conversely, the GF separators modified with POF-C₄/SP/PVP and POF-C₁₂/SP/PVP display large POF-C₄ and POF-C₁₂ particles greater than 10 μm . The uniform distribution of POF-C₈ in the coating is attributed to its good solubility in the processing solvent DMSO, while the poor solubility of POF-C₄ and POF-C₁₂ in DMSO results in their poor dispersion within the coatings.

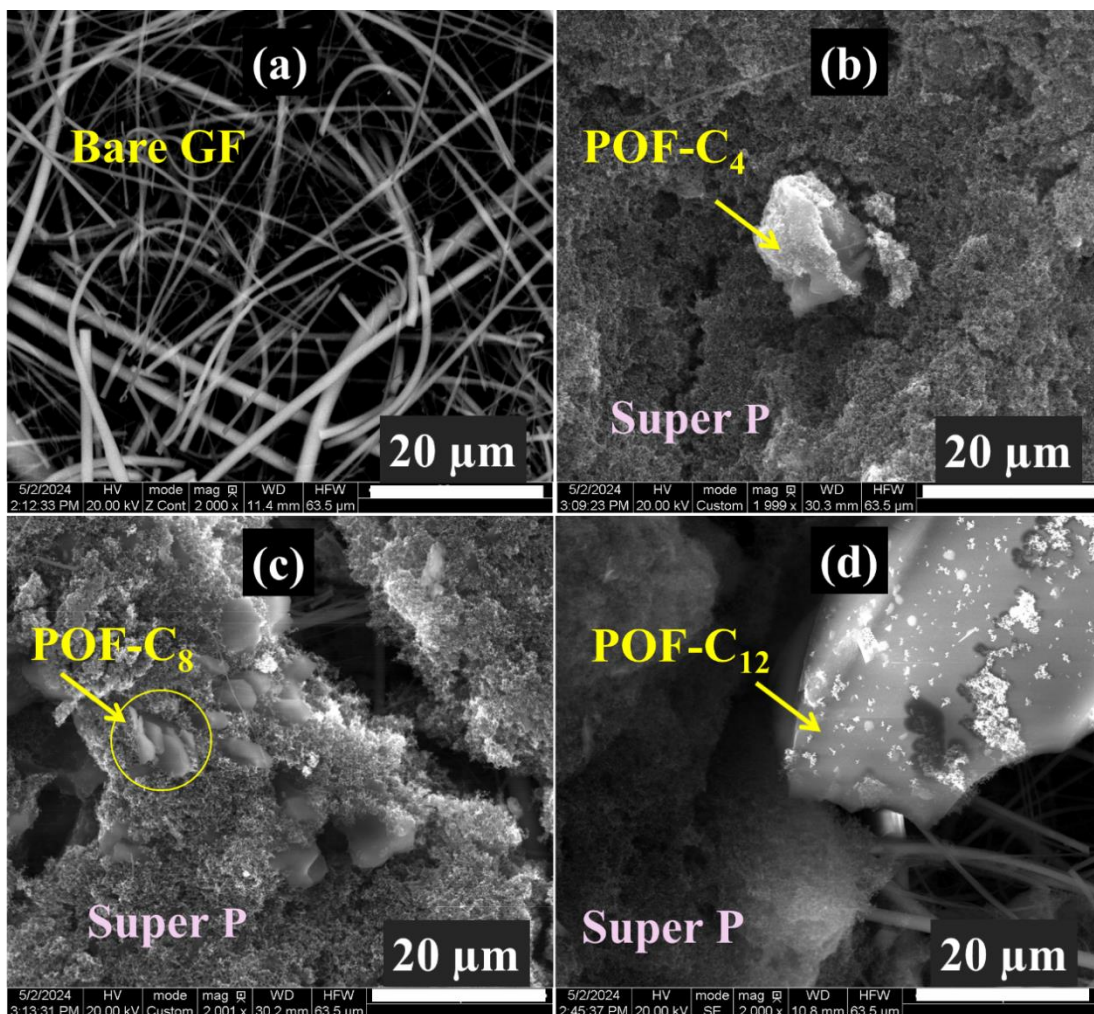


Figure 3.5 SEM images of (a) the bare GF; and the modified separator with POF- C_n /SP/PVP: (b) POF- C_4 ; (c) POF- C_8 ; (d) POF- C_{12} .

Galvanostatic charging/discharging tests on the Li-S cells were conducted in the voltage range of 1.7–2.8 V. Figures 3.6a and 3.6b compare the initial charging/discharging curves under 0.1C for the cells with the bare and modified PP and GF separators. The cell with the bare PP separator delivered a discharge capacity of 839 mAh g⁻¹, while the one with the bare GF separator showed a higher capacity of 1070 mAh g⁻¹ at the end of the second discharge plateau. Additionally, the cell with the bare GF separator exhibited smaller polarization, indicated by higher discharge voltages and lower charge voltages, compared to the cell with the bare PP separator. The superior performance of the GF separator can be attributed to its higher porosity, improved wettability, enhanced thermal stability (Figure 3.7), and lower tortuosity, all of which facilitate ion transport and contribute to better charge/discharge profiles. These results suggest that the bare GF separator is superior to the bare PP separator. After modification with SP/PVP (3:1), both PP and GF separators resulted in increased capacities, achieving 965 mAh g⁻¹ and 1228 mAh g⁻¹, respectively. These

improvements are attributed to the conductive SP in the modification layer, which aids in utilizing LiPSs that have migrated out of the cathode.

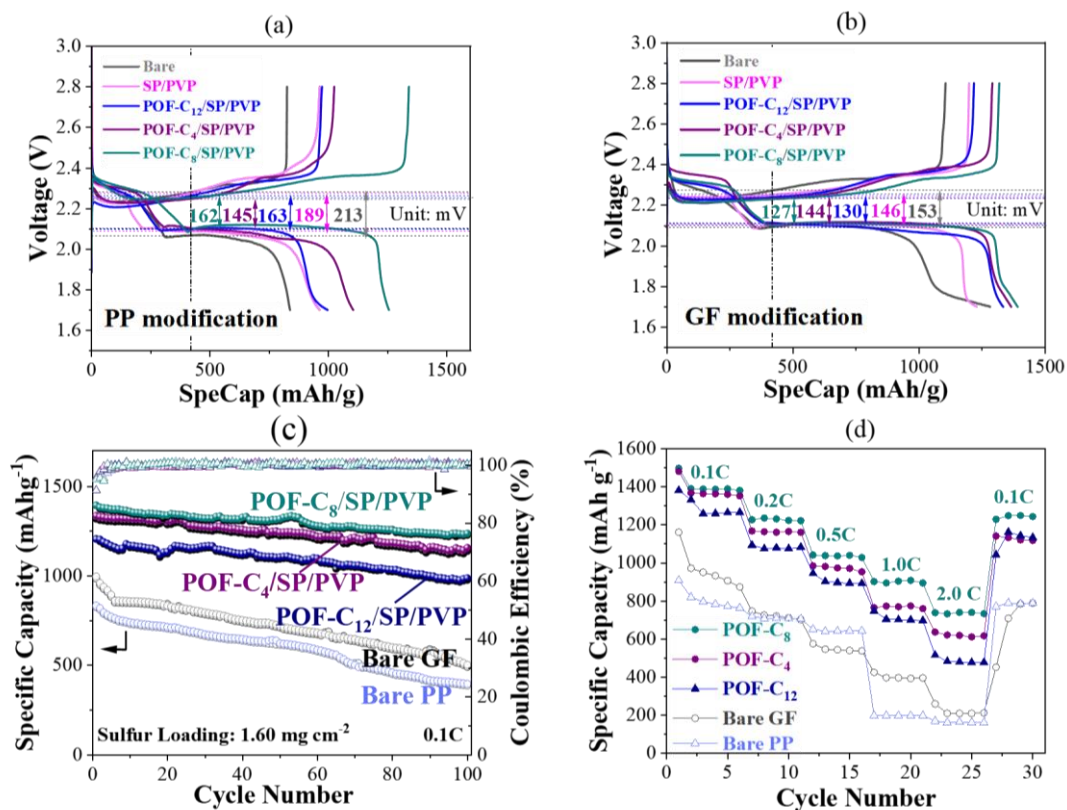


Figure 3.6 Charge/discharge curves at 0.1C for Li-S batteries with (a) bare and modified-PP separators and (b) bare and modified-GF separators; (c) cycling stability of cells with different separators over the first 100 cycles at 0.1C; (d) rate performance of cells with different separators.



Figure 3.7 Photographs of (a) modified PP separators and (b) modified GF separators at 50°C in a vacuum oven.

Cells with PP and GF separators modified with POF-C₈/SP/PVP displayed significant increases in discharge capacity, achieving values of 1257 mAh g⁻¹ and 1396 mAh g⁻¹, respectively. These enhancements

are due to the efficient capture of LiPSs by POF-C₈ in the modification layer. The large surface area of POF-C₈ exposes abundant nitrogen atoms to interact strongly with LiPSs, while the nanopores help retain LiPSs. Furthermore, the uniform dispersion of POF-C₈ within SP facilitates the conversion of captured LiPSs into shorter lithium sulfides with the assistance of adjacent SP particles, leading to increased capacity. The cell with the POF-C₈/SP/PVP modified GF separator exhibited better performance than the one with the modified PP separator, likely due to better ion transport and superior adhesion of the modification layer on the hydrophilic GF surface compared to the hydrophobic PP. Cells with GF separators modified with POF-C₄/SP/PVP and POF-C₁₂/SP/PVP also showed noticeable improvements in capacity, although slightly lower than the cell with the POF-C₈/SP/PVP-modified GF separator, most likely due to the poor dispersion of POFs as observed in their SEM images. Cells with PP separators modified with POF-C₄/SP/PVP and POF-C₁₂/SP/PVP showed limited improvements, attributable to the poor adhesion of the modification layer to the PP surface. In addition, the cell with the bare GF separator exhibits lower polarization (ΔE) than its PP counterpart, indicating its more efficient ion transport.

Figure 3.6c illustrates the cycling performance of Li-S batteries after 100 charge/discharge cycles at a rate of 0.1C. The bare PP and GF cells exhibited initial capacities of 833 mAhg⁻¹ and 995 mAhg⁻¹, respectively. After 100 cycles, the capacities dropped to 396 mAhg⁻¹ for the bare PP cell and to 503 mAhg⁻¹ for the bare GF cell. In contrast, cells with modified-GF separators exhibited high initial capacities and maintained high capacities after 100 cycles. Notably, the cell with the POF-C₈/SP/PVP GF-modified separator provided a high initial capacity of 1393.8 mAh g⁻¹ and retained a capacity of 1236.5 mAh g⁻¹ (89% retention) after 100 cycles. The abundant nitrogen atoms, large surface area, small pore size, and uniform dispersion of POF-C₈ in the modification layer all contribute to retaining and utilization of LiPSs, effectively suppressing LiPS shuttle and leading to improved cycle stability of the battery. Figure 3.6d shows the rate performance of cells with different separators. All cells with POF-modified separators demonstrated improved rate performance compared to those with bare PP and bare GF separators. The POF-C₈/SP/PVP modified GF separator showed the best rate performance, followed by the POF-C₄/SP/PVP and POF-C₁₂/SP/PVP modified separators.

Achieving a low electrolyte-to-sulfur (E/S) ratio is crucial for maximizing the energy density of Li-S batteries. Additionally, the E/S ratio significantly impacts the battery's specific capacities and cycling stability.¹⁶⁸ In our study, we maintained a constant electrolyte volume of 30 μ L while varying the sulfur loading to achieve cathodes with different E/S ratios. As shown in Figures 3.8 a-c, among three E/S ratios tested, 12 μ L mg⁻¹, 16 μ L mg⁻¹, and 20 μ L mg⁻¹, the cell with E/S = 16 μ L mg⁻¹ demonstrated the best initial cycling performance. At E/S = 12 μ L mg⁻¹, limited electrolyte availability and thicker active layer hindered ion transport, adversely impacting overall performance. Conversely, at E/S = 20 μ L mg⁻¹, all cells exhibited

significantly reduced capacities, likely due to a higher proportion of dissolved polysulfides in the electrolyte. Notably, compared to POF-C₈, cells with POF-C₄ and POF-C₁₂ showed more severe performance deterioration, characterized by reduced capacity and increased polarization. This could be attributed to the trapping of polysulfides by POF-C₄ or POF-C₁₂ particles that isolated or poorly interconnected with SP, resulting in lower sulfur utilization and increased electrical resistance. The 16 $\mu\text{L mg}^{-1}$ ratio balanced optimal electrolyte availability with efficient sulfur utilization, resulting in enhanced electrochemical performance, improved cycle stability, and superior capacity retention.^{168,169} For POF-C₈, we further increased the sulfur loading to 3.0 and 4.5 mg cm^{-2} , corresponding to E/S ratios of 9 and 6 $\mu\text{L mg}^{-1}$, respectively. The cells maintained high initial capacities of 953 mAh g^{-1} and 877 mAh g^{-1} at 0.5C for sulfur loadings of 3.0 and 4.5 mg cm^{-2} , respectively, while demonstrating decent cycling stability (Figure 3.9).

We also increased modification layer thicknesses from 30 μm to 45 μm while maintaining the same E/S ratio of 6 $\mu\text{L mg}^{-1}$) (Figures 3.8b and 3.8d). The results demonstrate that the 30 μm separator outperforms the 45 μm variant. The thinner modification layer facilitates more efficient ion transport, reducing the overall resistance within the cell, thereby improving electrochemical kinetics.

The long-term cycle performance of the cell with a POF-C₈/SP/PVP GF-separator at 0.5C is shown in Figure 3.8e. The cell achieved an initial capacity of 1035 mAh g^{-1} and retained 90% of its capacity (883 mAh g^{-1}) after 300 cycles, corresponding to a capacity decay rate of 0.03% per cycle.

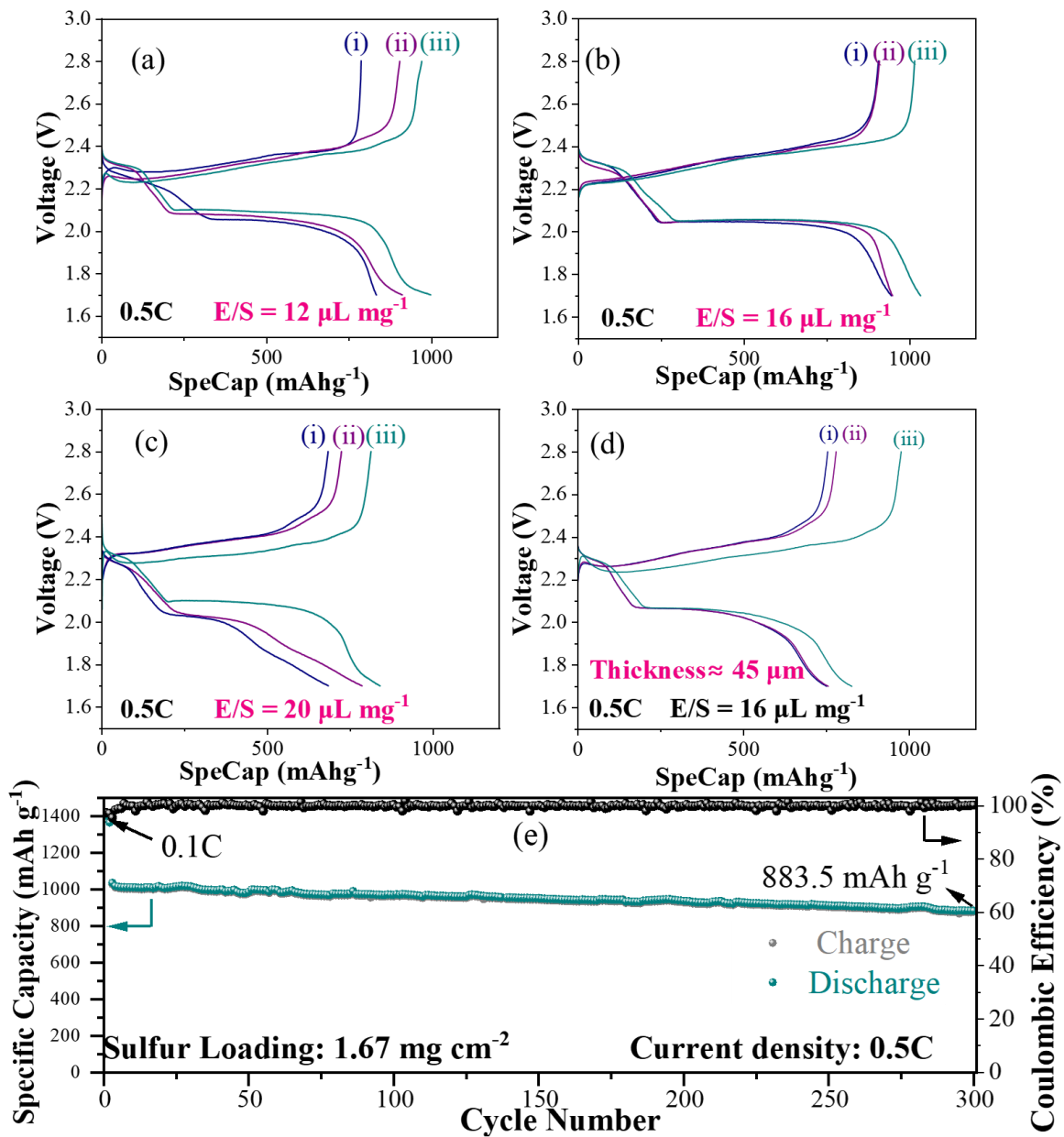


Figure 3.8 Effect of E/S ratio on the cycling performance of Li/S cells using a POF-C₈/SP/PVP-modified GF separator with a thickness of 30 μm : (a) E/S = 12 μLmg^{-1} ; (b) E/S = 16 μLmg^{-1} ; (c) E/S = 20 μLmg^{-1} ; (d) cycling performance of Li/S cells with thickness of 45 μm for modified layer with E/S ratio of 16 μLmg^{-1} ; In panels (a–d), (i) represents POF-C₁₂/SP/PVP, (ii) denotes POF-C₄/SP/PVP, and (iii) corresponds to POF-C₈/SP/PVP GF-modified separators. (e) cycling performance at 0.5C over 300 cycles for the cell with E/S ratio of 16 μLmg^{-1} .

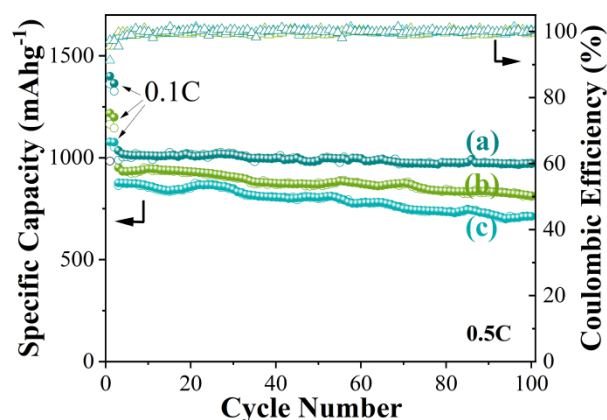


Figure 3.9 Cycling performance of the cell incorporating the POF-C₈/SP/PVP modified glass fiber composite at a current density of 0.5C, with different sulfur loadings: (a) 1.67 mg cm⁻² (E/S = 16 μL mg⁻¹) (b) 3.0 mg cm⁻² (E/S = 9 μL mg⁻¹), and (c) 4.5 mg cm⁻² (E/S = 6 μL mg⁻¹).

Figure 3.10a presents the Nyquist plots of the cells with bare GF and POF-modified GF separators prior to cycling, obtained via electrochemical impedance spectroscopy (EIS). The inset shows the corresponding equivalent circuit, where R_e represents the bulk ohmic resistance, R_{ct} signifies the charge transfer resistance, and W is associated with Warburg impedance, reflecting Li⁺ ion diffusion. Notably, the R_{ct} values for cells with POF-C_n/SP/PVP-modified GF separators (17.1, 20.8, and 29.23 Ω for POF-C₈, POF-C₄, and POF-C₁₂, respectively) are significantly lower compared to that with the bare GF separator (72.4 Ω), indicating that the presence of POF-C_n/SP/PVP reduces R_{CT} , facilitating rapid reaction kinetics. After 100 cycles at 0.1C, two semicircles are observed (Figure 3.10b). After 100 cycles, the Nyquist plots (Figure 3.10b) for all batteries exhibit two distinct semicircles. The semicircle appearing at lower frequencies is linked to the charge transfer resistance (R_{ct}) and its corresponding constant phase element (CPE2) in the cathode. Conversely, the semicircle at higher frequencies represents the interfacial contact resistance (R_f) and capacitance (CPE1) between the current collector and the active reaction sites within the cathode.^{170–172} Additionally, it includes contributions from the formation of the solid electrolyte interface (SEI) on the lithium anode.¹⁷¹ Notably, the first semicircle of the cell with the POF-C_n/SP/PVP GF-modified separator is less prominent, confirming its efficacy in reducing the shuttle effect.

The ionic conductivity (σ) of the separators were calculated using Equation 3.1:

$$\sigma = \frac{d}{R_e S} \quad (3.1)$$

where, d is the thickness of the separator, R_e is the electrical resistance, and S is the geometric area of the stainless steel (SS) electrode.^{173–175} The R_e values were obtained from the x-axis intercepts of the Nyquist

plot (Fig. 3.10a). While the conductivity of all cells with modified separators decreased compared to the cell with the bare GF separator, it remained in the 10^{-2} S cm^{-1} range. Among the GF separators modified with SP/PVP/POF- C_n , the POF- C_8 -modified separator exhibited the highest conductivity, even surpassing the SP/PVP-modified separator (Table 3.2). This superior conductivity is attributed to POF- C_8 's excellent solubility in DMSO, which ensures its uniform dispersion in the modification layer, along with its larger pore size that facilitates efficient Li^+ ion transport.

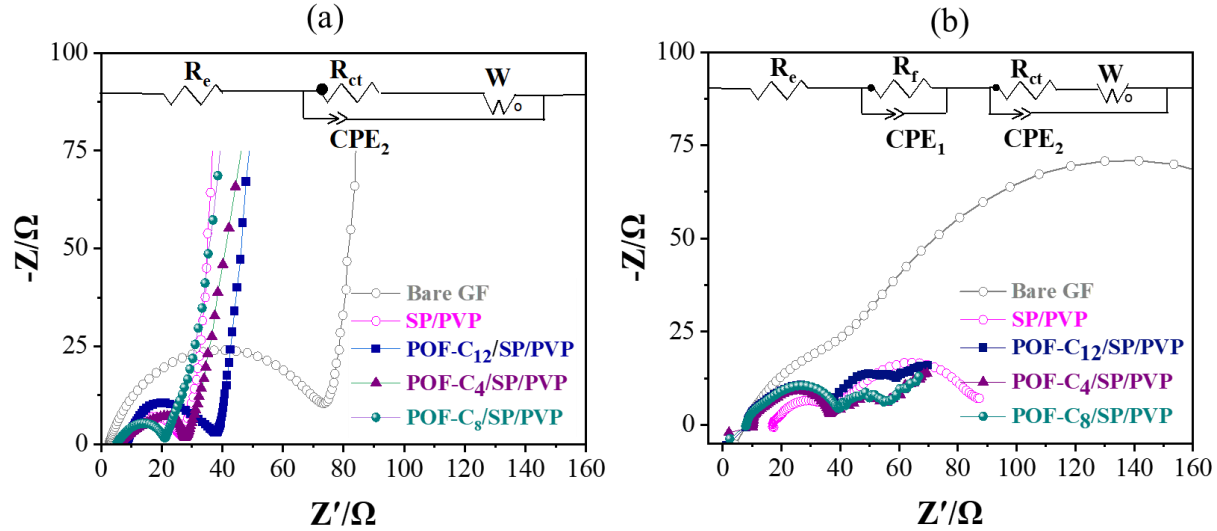


Figure 3.10 (a) Comparison of the capacity decay rate (per cycle) of the modified GF separator with POF- C_8 /S/SP versus previously reported materials. The dashed line indicates a decay rate of 0.030%, with numbers in parentheses showing the cycle numbers. (b) EIS before cycling and (c) after 100 cycles (inset: equivalent circuit).

Table 3.2 The values of EIS fitting and the conductivity measurement of the separators

Modifier	R_e (Ω)	R_{ct} (Ω)	d (μm)	σ (S, cm^{-1})
bare GF	2.69	70.95	280	3.7×10^{-2}
SP/PVP	6.51	20.25	310	1.7×10^{-2}
POF- C_4 /SP/PVP	8.86	19.01	308	1.2×10^{-2}
POF- C_8 /SP/PVP	5.01	16.15	310	2.2×10^{-2}
POF- C_{12} /SP/PVP	8.66	29.36	312	1.3×10^{-2}

CV measurements were conducted to evaluate the electrochemical properties and redox behavior of the LSB. Figure 3.11a shows the CV analysis of the cells with bare and POF-modified SF separators, conducted at a scan rate of 0.1 mV s^{-1} within a voltage range of 1.7–2.8 V. The CV curves of all cells display the typical characteristic of a sulfur cathode, featuring two distinct cathodic peaks: Peak A at $\sim 2.2\text{--}2.3 \text{ V}$, corresponding to the conversion of S_8 into long-chain LiPSs (Li_2S_n , $4 \leq n \leq 8$), and Peak B at $\sim 1.9\text{--}2.0 \text{ V}$, indicating the conversion of these long-chain LiPSs into short-chain LiPSs (Li_2S_n , $1 \leq n < 4$). The subsequent oxidation process shows Peak C at $\sim 2.4\text{--}2.5 \text{ V}$, representing the conversion of $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ to LiPSs and S_8 .¹⁷⁶ Notably, the cell with the POF-C₈/SP/PVP-modified separator exhibits the highest reduction and lowest oxidation potentials, reflecting faster redox reaction kinetics in this cell.

CV curves at higher scan rates of 0.2 to 0.6 mV s^{-1} were obtained (Figures 11b-e), and the Li^+ ion diffusion coefficients were calculated using the Randles–Sevcik equation (2) at 25°C :

$$i_p = (2.69 \times 10^5) n^{1.5} A C_0 D_0^{0.5} v^{0.5} \quad (3.2)$$

where n is the total number of electrons reacted per mole in the electrochemical process, A is the electrode area (cm^2), v is scan rate in V s^{-1} , C_0 is the concentration of the electrode material at surface in mol cm^{-3} , and D_0 is the diffusion coefficient in $\text{cm}^2 \text{ s}^{-1}$.

Figure 3-11i displays the Li^+ ion diffusion coefficients in the cells, calculated from the slopes of the linear fits shown in Figures 3-11 f-h. Cells with POF-modified GF separators exhibit higher diffusion coefficients compared to the cell with a bare GF separator, indicating improved Li^+ ion migration. This enhancement is due to the increased electrolyte uptake and better interface wettability provided by the POF-C_n/SP/PVP layer on the GF separator. Notably, the cell with the POF-C₈/SP/PVP-modified GF separator shows the highest Li^+ diffusion coefficients at all three peaks, demonstrating a significant improvement in Li^+ ion diffusion during the charge and discharge processes.

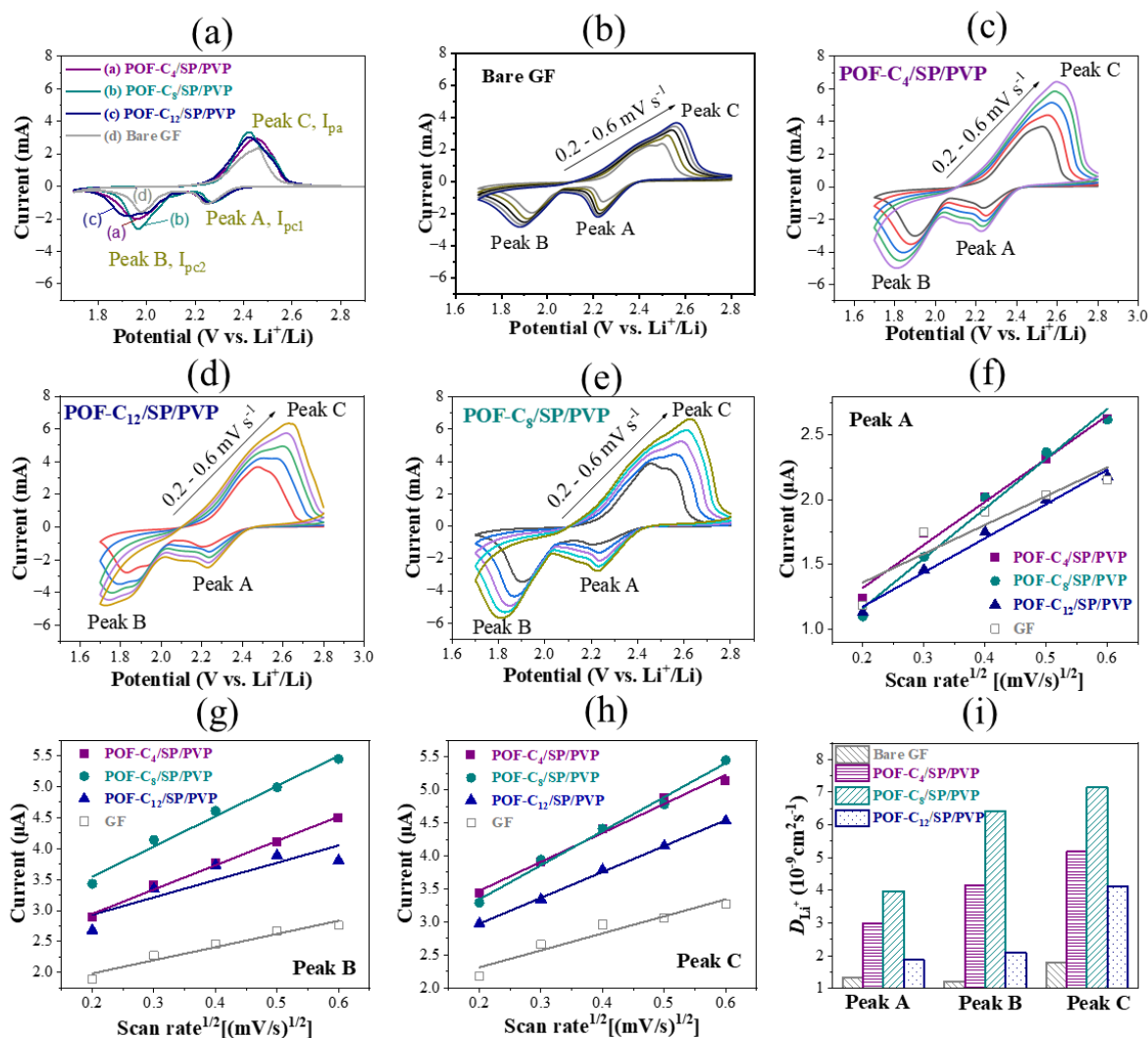


Figure 3.11 (a) CV curves at a scan rate of 0.1 mV s⁻¹ for Li-S batteries for the bare GF and POF-C₄/SP/PVP, POF-C₈/SP/PVP and POF-C₁₂/SP/PVP-modified GF separators; (b-e) CV curves at scan rates of 0.2-0.6 mV s⁻¹; (f-h) Linear fits of peak currents (I_A, I_B and I_C) versus the square root of the scan rate. (i) Li⁺ ion diffusion coefficients calculated from the slopes of the linear fits in (f-h).

To investigate changes in POF-C_n during extensive battery cycling, cells POF-C_n/SP/PVP-modified GF separators were subjected for the post-mortem analysis after 100 charge-discharge cycles. Inside a glove box, the cycled cells were disassembled, and the separators were removed from the cathodes and then dried in a vacuum oven at 50°C for 5 hours to remove solvents. SEM images (Figures 3.12 a-c) of the cycled modification layers reveal a more cohesive network of POF-C_n and SP particles compared to their uncycled states. Notably, the cycled POF-C₈/SP/PVP exhibited the highest degree of integration between POF-C₈

and SP. These results suggest that, instead of being damaged, the morphology of the modification layer was actually enhanced during cycling.

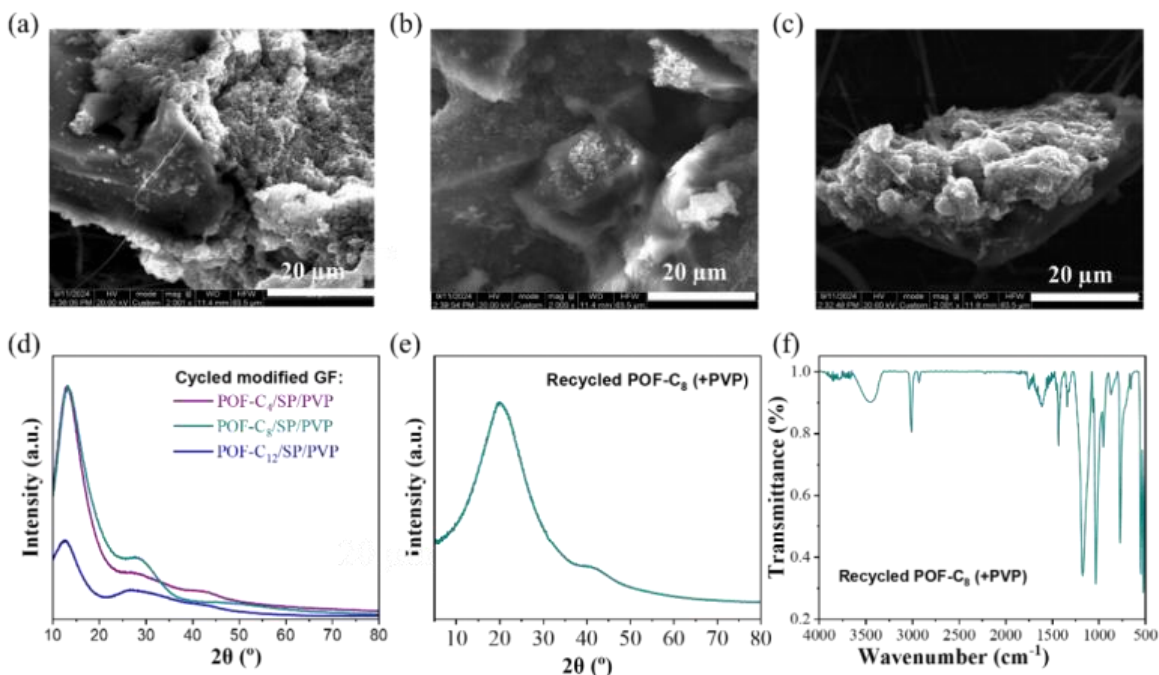


Figure 3.12 SEM images of GF separators modified with (a) POF-C₄/SP/PVP, (b) POF-C₈/SP/PVP, and (c) POF-C₁₂/SP/PVP after 100 charge/discharge cycles at 0.1C; (d) XRD patterns of cycled POF-C_n/SP/PVP-modified GF separators after 100 cycles; (e) XRD pattern of recycled POF-C₈ (and PVP) from the cycled POF-C₈/SP/PVP-modified GF separator after 100 cycles; (f) FTIR spectrum of recycled POF-C₈ (and PVP) from the cycled POF-C₈/SP/PVP-modified GF separator after 100 cycles.

The XRD patterns of the side of the separators with the modification layer exhibited the strongest peak at $\sim 12^\circ$, corresponding to a d-spacing of ~ 0.74 nm, which are much larger than that of ~ 0.36 nm ($2\theta = \sim 25^\circ$) for the pristine modification layer before cycling (Figures 3.13b, c). Since this d-spacing represents the average interchain distance of POF-C_n, its increase indicates the effective trapping of polysulfides (in the elemental sulfur form in the charged state), which enlarges the interchain distance in POF-C_n. The FTIR spectrum (Figure 3.13d) of the recovered material showed no significant shifts in the characteristic absorption bands of POF-C₈, indicating that its chemical structure remained essentially intact.

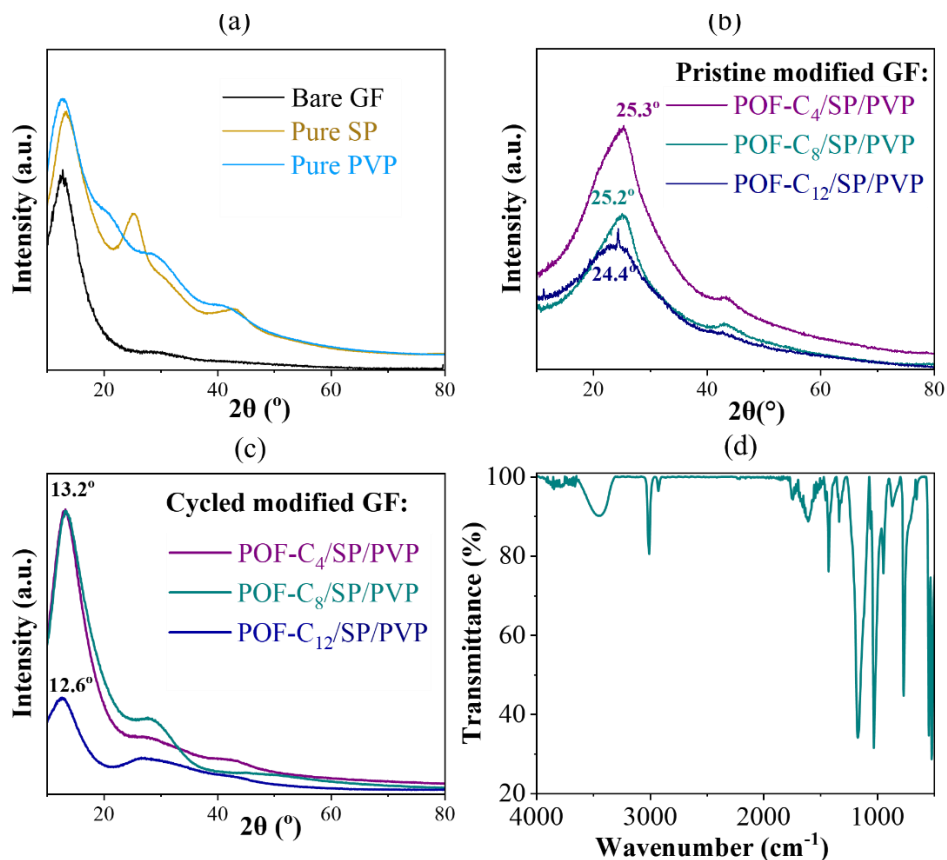


Figure 3.13 XRD patterns of (a) bare GF, pure SP, and pure PVP; (b) Pure POF-C_n powders; (c) Pristine (unused) GF separators modified with POF-C_n/SP/PVP; (d) Cycled GF separators modified with POF-C_n/SP/PVP disassembled from batteries after 100 cycles.

3.4 Conclusion

This study demonstrates the effectiveness of melamine-based nanoscale POFs in enhancing the performance of Li-S batteries through the modification of GF separators. The POF materials, synthesized by reacting melamine with dibromoalkanes of varying carbon chain lengths, significantly improved the initial capacity, rate performance, and long-term cycling stability of the batteries. Among the tested POF composites, POF-C₈/SP/PVP demonstrated superior performance, achieving an initial specific capacity of 1392 mAh g⁻¹ at 0.1 C and retaining 90% of its capacity after 300 cycles at 0.5 C. The enhanced electrochemical performance is attributed to the nanoporous structure and high nitrogen content of POF-C₈, which effectively traps soluble LiPSs and reduces their diffusion toward the lithium anode. The solubility of POF-C₈ ensures uniform dispersion in the modifying layer, facilitating efficient LiPS trapping and maximizing their utilization in electrochemical reactions, assisted by the conductive SP in the

composite. The coating layer on the separator in our experiments exceeds the sulfur loading. However, the benefits of the modified separators—despite the heavier coating—include enhanced polysulfide trapping, extended cycle life, increased ionic conductivity, improved mechanical stability, higher sulfur utilization, reduced lithium dendrite formation, optimized surface interactions, and improved thermal stability. These findings suggest that POF-modified GF separators can mitigate the LiPS shuttle effect, improve lithium-ion transport, and enhance the overall stability and efficiency of Li-S batteries, offering a promising pathway to realizing Li-S batteries as next-generation energy storage technologies.

Chapter 4. Enhanced Cycling Stability in Li-S Batteries: CR-CTA Modified GF Separators with Mechanistic Insights and Performance Evaluation

This chapter is based on the following submitted manuscript:

R. Fazaeli, Z. Haung, Y. Wang, H. Aliyan, Y. Li, *J. Power Sources*.

4.1 Introduction

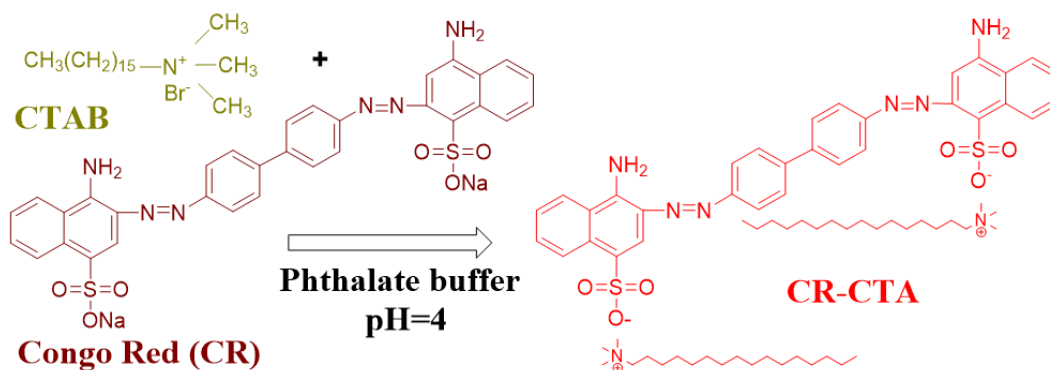
Significant progress in alternative energy storage technologies has been driven by the search for high-energy-density battery systems to meet the growing needs of portable devices, electric vehicles, grid energy storage,^{177–180} Lithium-sulfur batteries (LSBs) are particularly promising among the several options because of several benefits. Compared to many current battery technologies, they can store more energy per unit mass due to their exceptionally high theoretical energy density. They are also economical because sulfur is cheap and plentiful. Furthermore, compared to many other battery materials, sulfur is non-toxic and has a smaller environmental impact, making LSBs more environmentally benign.¹⁸¹ Despite their potential, there are certain barriers to the widespread application of LSBs,¹⁸² including poor cycling stability and sluggish reaction kinetics under lean electrolyte conditions¹⁸³ and at low temperatures.^{184,185} A major challenge is the dissolution of polysulfide intermediates into the electrolyte during battery operation. This process leads to the loss of active material and triggers the "shuttle effect," where polysulfides migrate between the electrodes, leading to low active material utilization and unwanted side reactions. Over repeated charge-discharge cycles, these issues cause capacity fading and poor cycling stability, ultimately limiting the long-term performance of LSBs^{113,129,186–189}. To mitigate these shuttle effects, several strategies have been developed to confine polysulfides within the sulfur cathode. These include the use of mesoporous carbon materials,^{12,159,190} polysulfide-trapping additives^{191–194} and functional binders,^{160,195–197} and the development of all-solid-state Li–S batteries.^{198,199} In this context, modifying separators with functional materials has gained increasing attention as a straightforward and effective approach to enhancing Li–S battery performance and stability^{122,154,156,200–204}. By tailoring the properties of separators, such as wettability, porosity, and affinity for polysulfides, it is possible to mitigate polysulfide shuttling

and improve sulfur utilization, thereby prolonging battery lifespan and enhancing overall performance.^{205,206}

Congo red (CR) serves as an indicator in analytical chemistry, particularly in determining pH changes. It shifts its color from red to blue in the transition from acidic to basic conditions²⁰⁷. In Alzheimer's disease research, CR is utilized to study protein aggregation and fibril formation due to its ability to bind to proteins and form complexes.²⁰⁸ CR contains an aromatic chromophore which contributes to its vivid coloration. This structure makes it suitable for use as a dye in textile industries and as a staining agent in biological applications. The redox-active nature of CR allows it to participate in electron transfer reactions, making it suitable for applications such as dye-sensitized solar cells.²⁰⁹ Nitrogen atoms are well known for their strong affinity to polysulfides, and various nitrogen-containing materials have been employed to trap polysulfides.^{160,210,211} Accordingly, the nitrogen-containing amino ($-NH_2$) and azo ($-N=N-$) groups in CR are expected to contribute to polysulfide trapping. CR also contains sulfonate groups ($-SO_3^-$), which enhance its solubility in water and facilitate its use in aqueous solutions for staining and dyeing purposes. Additionally, the sulfonate groups contribute to CR's hydrophilicity, enhancing its interactions with polar substrates such as cellulose fibers and biological tissues.²¹² Separators modified with sulfonate-containing materials have demonstrated multiple benefits in enhancing Li-S battery performance. Lu et al. reported that sulfonated reduced graphene oxide (SRGO) coated on a separator effectively mitigates the polysulfide shuttle effect, resulting in improved cycling stability and capacity retention.²¹³ This enhancement is attributed to the strong polysulfide anchoring provided by the sulfonate groups. Xu et al.²¹⁴ developed a sulfonate-rich COF (SCOF-2) to modify the separator, enhancing Li^+ migration and reducing dendrite formation. SCOF-2's strong electronegativity and larger interlayer spacing improve battery performance. Hu et al. demonstrated that the polar sulfonate groups of Sulfophenylated Poly (Ether Ether Ketone Ketone) (SPEEKK) in the composite separator greatly increases the separator's wettability by the electrolyte, which in turn improves lithium-ion conductivity.²¹⁵ Better ion movement within the separator is made possible by this enhanced wettability. Furthermore, SPEEKK exerts electrostatic repulsion to the anionic components of the lithium salt in the electrolyte due to the presence of anionic sulfonic groups on its side chains. The effective passage of lithium ions through the separator is further aided by this electrostatic contact. Additionally, sulfonate groups can enhance

the ionic conductivity of the separator. This facilitates better ion transport between the electrodes, contributing to improved battery performance and higher rate capabilities. A covalent organic framework (TpPa-SO₃Li) film was fabricated on a Celgard separator, featuring nanochannels and negatively charged sites that enhance lithium ion conduction and suppress polysulfide diffusion.²¹⁶ Shi et al. constructed a stable and lightweight imide-based covalent organic framework (COF-TpPa@rGO) with functionalities like -SO₃H and -Cl. These functional groups and tailored pores effectively absorb and restrict Li₂S_n, reducing the shuttle effect.²¹⁷

In this study, we present an innovative method for enhancing the performance of lithium-sulfur (Li-S) batteries by modifying glass fiber (GF) separators with a compound CR-CTA synthesized from CR and cetyltrimethylammonium bromide (CTAB). This redox-active organic compound is integrated into the separator to boost the battery's efficiency and longevity. As illustrated in Scheme 4.1, a key element in this modification is the electrostatic interaction between the cationic cetyltrimethylammonium (CTA) of CTAB and the anionic CR core. These interactions ensure that the negatively charged CR core is uniformly distributed and well-absorbed on the separator's surface.²¹⁸ Additionally, the quaternary ammonium CTA cation is expected to have a strong adsorption capability to a negatively charged polysulfide anion, improving the battery cycling stability.^{201,219} This dual-modification approach leverages the strengths of both CR and CTAB, resulting in a significant enhancement of the Li-S battery's performance.



Scheme 4.1 Synthesis of CR-CTA.

4.2 Experimental

4.2.1 Materials

The materials used in the experiment including polyvinylpyrrolidone (PVP), Congo red (CR, disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)diazenylphenyl]phenyl]diazenyl-naphthalene-1-sulfonate), cetyltrimethylammonium bromide (CTAB), polyvinylidene fluoride (PVDF), super P (SP), N-methyl-2-pyrrolidone (NMP), polypropylene separators (PP, Celgard 2400 with 40% porosity), and lithium foils were obtained from Sigma-Aldrich, Sinopharm, Shenzhen Poxon Machinery Technology, and other commercial sources. Before use, lithium perchlorate (LiClO_4) and lithium iodide (LiI) were dried at specific temperatures (LiClO_4 at 160 °C and LiI at 200 °C) in a vacuum oven for 12 hours to remove any moisture. Additionally, the Li plates underwent a preparation step where they were immersed in a propylene carbonate (PC) solution containing 0.1 M LiClO_4 for a minimum of two days. This treatment likely aimed to condition the Li plates before further experimentation, ensuring they were properly prepared for their intended use in the study.

4.2.2 Synthesis of cetyltrimethylammonium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)diazenylphenyl]phenyl]diazenyl-naphthalene-1-sulfonate (CR-CTA)

A mixture of CR (6.97 g, 0.010 mol) and CTAB (7.29 g, 0.020 mol) in a molar ratio of 1:2 was ground using a mortar and pestle for 30 minutes and added to a phthalate buffer solution at pH 4 (BDH5018 BUFFER). The mixture was stirred for 1 hour. The pH was adjusted to be around with the buffer if necessary. After stirring for an additional 30 minutes, the reaction mixture was subjected to centrifugation to remove the buffer solution, followed by washing the resulting precipitate with deionized water. The obtained solid was dried in an oven vacuum at 40-50°C under reduced pressure to afford the product CR-CTA, which was stored in a desiccator to prevent moisture absorption.

4.3 Results and discussion

CR-CTA was conveniently synthesized by reacting CR with CTAB at a 1:2 molar ratio, where the two sodium ions in CR are replaced by two cetyltrimethylammonium ions (Scheme 4.1). Figure 4.1 (a) shows the ^1H -NMR spectra of CTAB, CR, and CR-CTA. Compared to CTAB and CR, the ^1H -NMR spectrum of CR-CTA exhibits characteristic peaks corresponding to both CTA

and CR at a molar ratio of 2:1. As CR-CTA is insoluble in water, unlike the water-soluble CR, it is proposed that CR-CTA adopts the chemical structure depicted in Figure 4.1a, where each sodium ion in CR is replaced by a cetyltrimethylammonium ion.

Figure 4.1b displays the XRD patterns of CR, CTAB, their physical mixture (CR+CTAB, prepared by mixing for 30 minutes with a mortar and pestle), and the synthesized compound CR-CTA. The XRD pattern of CR reveals its monoclinic crystalline structure, belonging to the space group P2. This crystallinity is attributed to the presence of both intramolecular and intermolecular hydrogen bonding. These bonds occur between the amino and sulfonate groups located on the outer regions of the CR molecule and the azo group situated in its interior, stabilizing the overall structure. The X-ray diffraction (XRD) pattern of CR reveals sharp peaks at 2θ values of 27.25° , 32.18° , 37.84° , 44.91° , and 45.33° , corresponding to the $(11\bar{1})$, (111) , $(11\bar{7})$, (124) , and $(13\bar{4})$ planes, respectively.^{220,221} The physically mixed CR+CTAB exhibited distinct diffraction peaks corresponding to CR and CTAB, respectively. In contrast, CR-CTA displayed a significantly different diffraction pattern, including new peaks absent in CR or CTAB. Additionally, the peaks in the CR-CTA pattern were noticeably weaker and broader, indicating its creased crystallinity compared to CR and CTAB. The crystallite size of CR-CTA is estimated to be about 28 nm according to the Debye–Scherrer equation.²²²

Figures 4.1c and 4.1d show FTIR spectra of CR, CTAB and CR-CTA. For CR-CTA, the N-H stretching peak appeared at 3341 cm^{-1} , significantly shifted from that of CR and CR+CTAB (3466 cm^{-1}).²²³ Additionally, the asymmetric stretching vibration of S=O in SO_3^- ^{224–226} shifted to a higher wavenumber of 1365 cm^{-1} , compared to 1346 cm^{-1} for CR and CR+CTAB (at) (Figure 4.1d). Moreover, the stretching vibration of the C–N bond exhibited a shift from 1035 cm^{-1} in CR to 1061 cm^{-1} in the CR-CTA compound, indicating significant interaction between the components. These FTIR data strongly suggest that CR-CTA is not a simple mixture of CR and CTAB but rather a distinct compound.

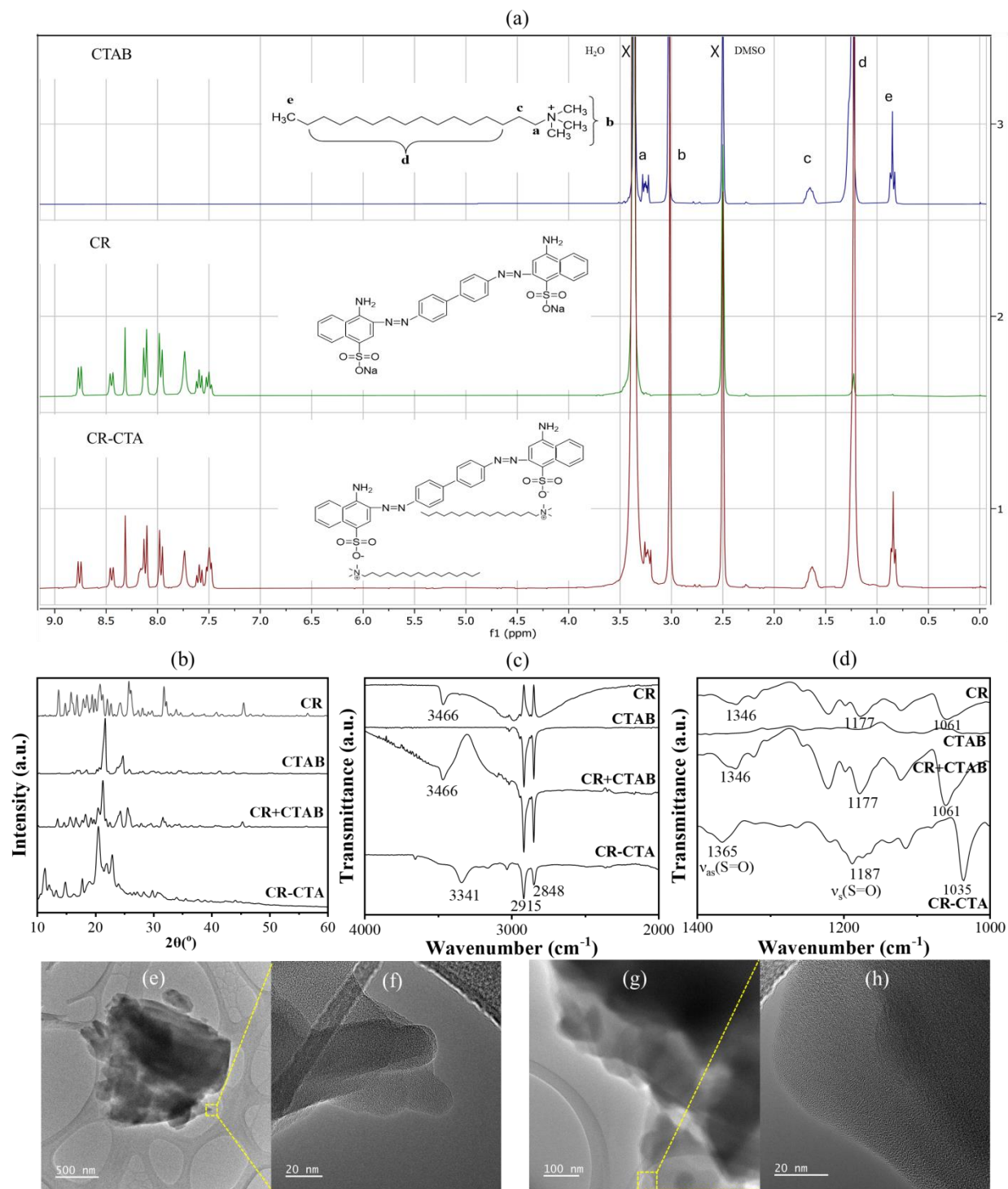


Figure 4.1 (a) ^1H NMR spectra of CTAB, CR, and CR-CTA measured in DMSO-d_6 . (b) XRD patterns and (b, c) FTIR spectra in the ranges for CR, CTAB, CR+CTAB (physically mixed) and CR-CTA; (e-h) TEM images of pristine CR-CTA.

High-Resolution Transmission Electron Microscopy (HRTEM) images (Figures 4.1e-4.1h) reveal that CR-CTA consists of nanoparticles with sizes on the order of tens of nanometers, which agree with the crystallite size determined from the XRD data. No lattice structures were observed, likely due to the damage to the crystal structure of CR-CTA caused by the high-energy electron beam during the measurement.

The CR-CTA/SP/PVP-modified GF separator exhibits excellent wettability to the electrolyte, rapidly absorbing it upon contact. Additionally, it demonstrates good flexibility, as it can be folded multiple times without noticeable damage or mechanical failure (Figure 4.2). The morphology of unmodified (bare) and modified GF separators was examined using SEM to investigate their structural differences and their influences on the performance of LSBs (Figure 4.3). The SEM image of the bare GF separator (Figure 4.3a) reveals a network of loosely arranged fibers with large inter-fiber gaps ranging from approximately 5 to 10 μm . This porous structure promotes efficient ion transport by facilitating electrolyte movement. However, it also enables the unrestricted diffusion of lithium polysulfides (LiPSs), which contributes to the LPS shuttle effect and leads to performance degradation in the battery.¹⁸⁹ After modification, Super P particles are clearly visible on the GF surfaces (Figures 4.3b and 4.3c). The CR/SP/PVP-coated GF separator displays large CR particles, whereas the CR-CTA/SP/PVP-modified GF separator exhibits a more uniform coating. The cross-sectional SEM image of the CR-CTA/SP/PVP-modified GF separator (Figure 4.3d) reveals a coating layer thickness of $\sim 16 \mu\text{m}$.

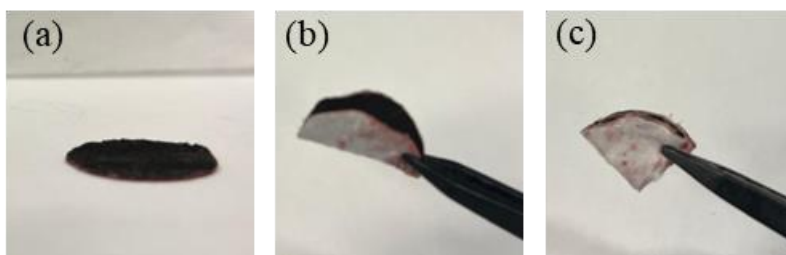


Figure 4.2 Flexibility assessment of the CR-CTA/SP/PVP-modified GF separator: (a) without folding, (b) folded once, and (c) folded twice.

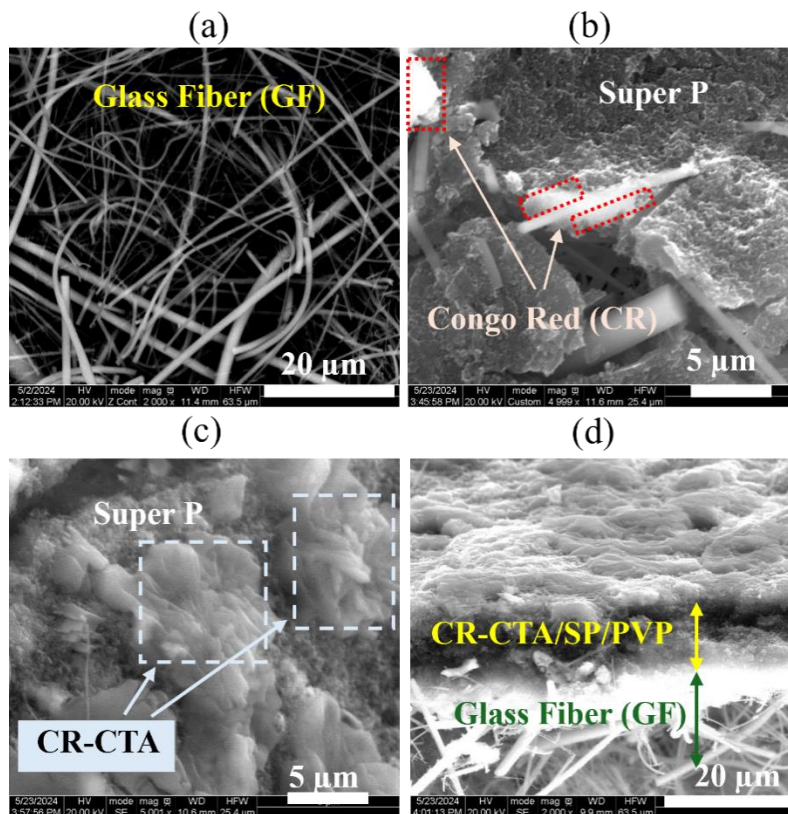


Figure 4.3 SEM top-view images of (a) the bare GF separator, (b) the CR/SP/PVP-coated GF separator, (c) the CR-CTA/SP/PVP-modified GF separator, and (d) a cross-sectional view of the CR-CTA/SP/PVP-modified GF separator.

Figure 4.4a display the galvanostatic discharge/charge profiles for modified PP and GF separators at 0.1C. The CR-CTA/SP/PVP-modified GF separator shows superior performance, with an initial discharge capacity of $1366.4 \text{ mAh g}^{-1}$, significantly higher than the other separators: bare PP (838.9 mAh g^{-1}), bare GF ($1060.1 \text{ mAh g}^{-1}$), CR/SP/PVP (PP) ($1210.6 \text{ mAh g}^{-1}$), CR/SP/PVP ($1256.6 \text{ mAh g}^{-1}$) and CTAB/SP/PVP ($1320.4 \text{ mAh g}^{-1}$). Cells with GF separators outperform those with PP separators due to GF's higher porosity, better thermal stability (supporting modification layer coating), and improved electrolyte retention. These factors promote efficient ion transport and help mitigate the polysulfide shuttle effect.¹⁸⁹ The presence of CR likely enhances cell performance due to its promotion of redox activity and LPS trapping effect through its nitrogen atoms (amino and azo groups)^{160,210,211} and sulfonate groups.²¹³ All discharge curves exhibit a two-step process: a high-discharge plateau linked to higher-order soluble polysulfides and a low-discharge plateau corresponding to insoluble Li_2S_2 and Li_2S .¹⁴⁸ The CR-CTA/SP/PVP-

modified GF separator shows a longer second discharge plateau than other separators, indicating superior redox activity. Figure 4.4b present the cycling stability at 0.1C for the modified separators. Figure 4.4b shows the cycling stability at 0.1C, with the CR-CTA/SP/PVP-modified GF separator retaining 90.2% of its initial capacity after 100 cycles and nearly 99.18% coulombic efficiency, surpassing other separators in LiPS shuttle effect suppression. The rate performance of cells with various separators is shown in Figure 4.4c. The cell with the CR-CTA/SP/PVP-modified GF separator consistently delivers higher capacities than the other cells at all tested rates. Specifically, it achieves capacities of 1366.4, 1221.9, 1066.2, 959.0, and 813.1 mAh g⁻¹ at rates of 0.1, 0.2, 0.5, 1, and 2C, respectively. The enhanced performance of the CR-CTA/SP/PVP-modified separator compared to the SP/PVP-modified separator is attributed to the dual beneficial effects of CR-CTA: improved dispersion of CR-CTA on the separator's surface²¹⁸ and the strong polysulfide adsorption capability of CTA's functional nitrogen-containing amino and azo groups,^{160,210,211} sulfonate groups,^{214,215} and quaternary ammonium cations.^{219,227,228}

In this study, the electrolyte volume was kept constant at 30 μ L while sulfur loading was varied to examine the effect of the electrolyte to sulfur (E/S) ratio on cell performance (Figure 4.4d). The best cycling performance was achieved at an E/S ratio of 16 μ L mg⁻¹. At E/S = 12 μ L mg⁻¹, limited electrolyte and a thicker active layer restricted ion transport, while at E/S = 20 μ L mg⁻¹, excessive dissolved polysulfides led to reduced capacities. A thinner modification layer (28 μ m) outperformed its thicker counterpart (45 μ m) by providing enhanced ion transport and lower resistance, leading to improved overall cell performance. Additionally, Figure 4.4d shows that the cell with the CR-CTA/SP/PVP-modified GF separator has higher and flatter voltage platforms at various current densities, indicating its enhanced lithium-ion transport and redox kinetics.^{217,229,230}

The cycling performance of cells with bare PP, bare GF, and CR-CTA/SP/PVP-modified GF separators at a current rate of 0.5C is displayed in Figure 4.4e. With a low decay rate of 0.051% per cycle, the CR-CTA/SP/PVP-modified GF separator first yields 1153.3 mAh g⁻¹ and maintains 86.2% (993.9 mAh g⁻¹) after 300 cycles.

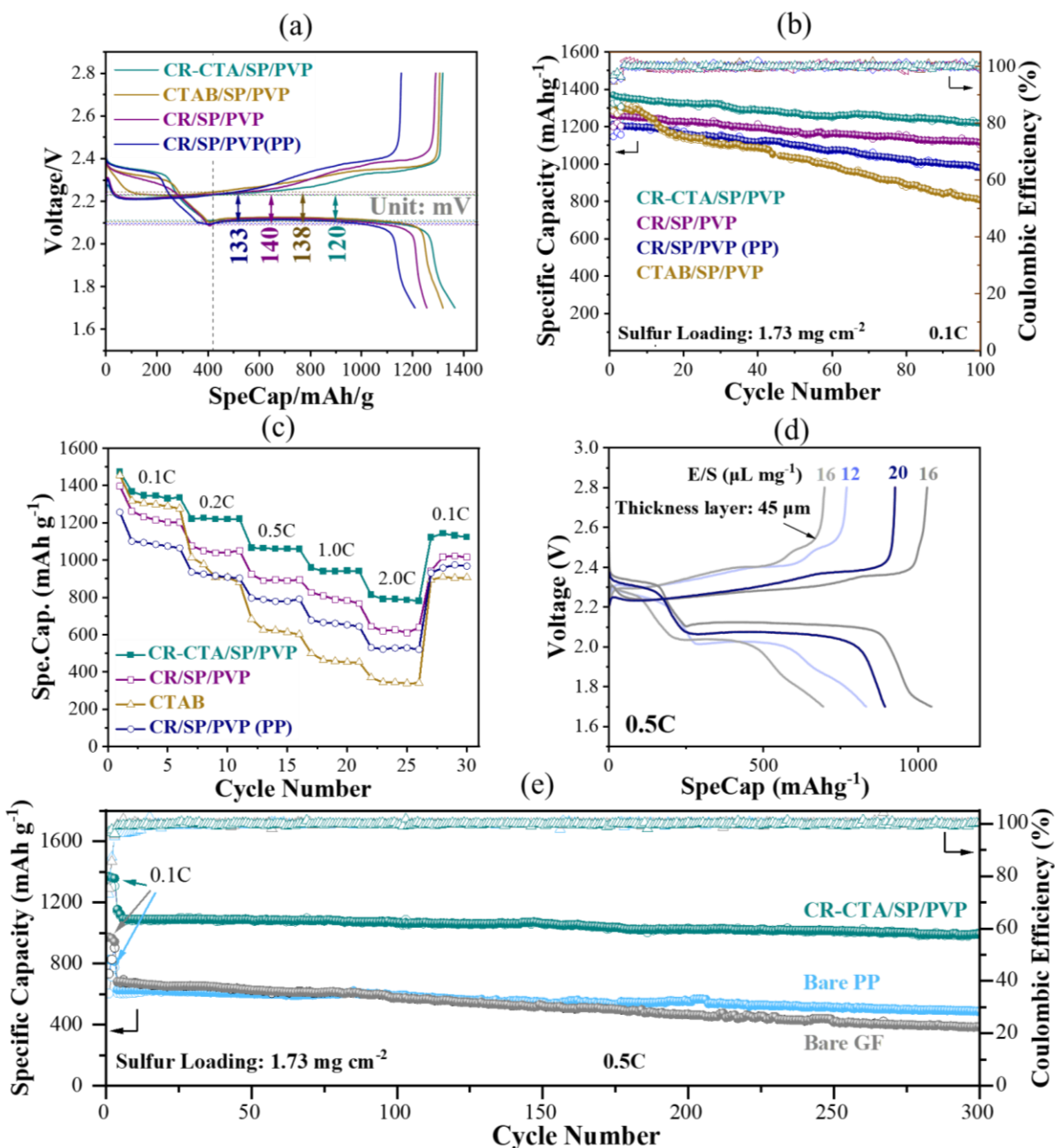


Figure 4.4 (a) Discharge/charge curves of cells with different separators; (b) cycling performance of cells with different separators over 100 cycles at 0.1C; (c) rate performance of cells with different separators; (d) Effect of E/S ratio on the discharge/charge curves of cells with thickness of 28 μm with E/S of 12, 16 and 20 μLmg^{-1} and thickness of 45 μm with E/S of 16 μLmg^{-1} and (e) cycling stability comparison of bare PP, bare GF, and CR-CTA/SP/PVP-modified GF separators at 0.5C for 300 cycles.

Because CR-CTA effectively suppresses LiPS shuttling, it performs better than cells with bare PP and GF separators and outperforms the majority of reported modified GF separators (Table 4.1).^{81,144,231–236} For Li-S batteries to have a high energy density, high sulfur loading is vital. To

evaluate the effect of increased sulfur content, we tested sulfur loadings of 3.0 mg cm^{-2} and 4.5 mg cm^{-2} using the CR-CTA/SP/PVP-modified GF separator (Figure 4.5). While the cell with 1.73 mg cm^{-2} sulfur showed an initial capacity of 1161 mAh g^{-1} at 0.5C , the higher sulfur loadings of 3.0 mg cm^{-2} and 4.5 mg cm^{-2} resulted in reduced initial capacities of 984 and 883 mAh g^{-1} , respectively, confirming efficient sulfur utilization.

Table 4.1 Comparison of the capacity decay rate (per cycle) of CR-CTA/SP/PVP-modified GF separator and previously reported materials.

GF modification	Binder	Thickness (μm) of layer on GF	Decay per cycle (%)
Bare GF ¹⁴⁸	No binder	260*	0.27
UiO-67 ²²⁹	No binder	19	0.04
Cu-MOF ²³⁰	PVDF	18	0.08
Fe-MOF ²³⁰	PVDF	22	0.06
KB/MTiO ₂ ²³⁶	PVDF	10	0.11
B/TiO ₂ ²³²	PVDF	46	0.11
Ti ₃ C ₂ ²³⁴	PVDF	-	0.13
ACGF ⁸¹	PVDF	-	0.25
PCFN ²³³	PVDF	25	0.31
CR-CTA/SP/PVP (This work)	PVP	28	0.05

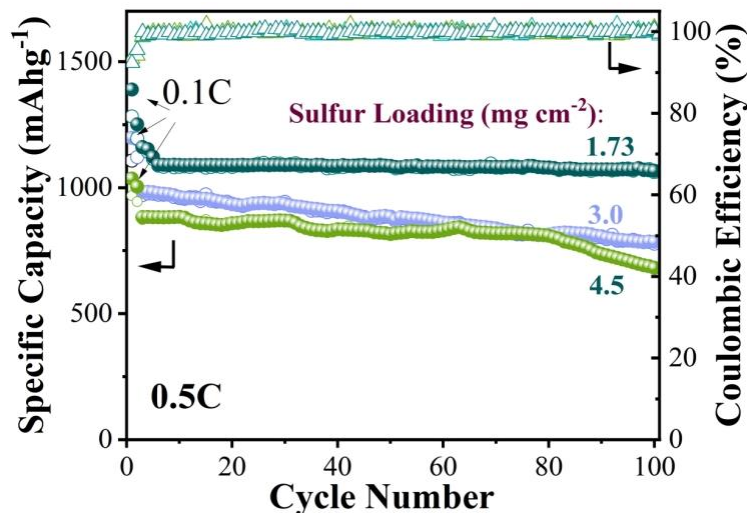


Figure 4.5 Cycling performance of Li-S batteries with the CR-CTA/SP/PVP-modified GF separator at a current density of 0.5C, with sulfur loadings of (a) 1.73 mg cm⁻² (E/S = 16 μ L mg⁻¹), (b) 3.0 mg cm⁻² (E/S = 9 μ L mg⁻¹), and (c) 4.5 mg cm⁻² (E/S = 6 μ L mg⁻¹).

The separators were characterized using electrochemical impedance spectroscopy (EIS) to assess ion transport properties (Figures 4.6a and 4.6b). The medium-frequency semicircle in the EIS spectra represents the charge transfer resistance (R_{ct}) at the electrode-electrolyte interface. The low-frequency linear Warburg region corresponds to lithium-ion diffusion within the electrode, while the high-frequency intercept on the real axis signifies the cell's ohmic resistance (R_e) due to the electrolyte.^{237,238} The EIS data (Figure 4.6a and Table 4.2) reveal that the fresh Li-S battery with the CR/CTA-modified GF separator exhibits a lower R_{ct} (34.09 Ω) compared to cells with CR-PP-modified (39.58 Ω) and CR-GF-modified (42.14 Ω) separators. After 100 cycles at 0.1 C, all cells exhibit a new semicircle in the intermediate frequency range (Figure 4.6b), which is attributed to increased interfacial resistance and a decline in charge transfer efficiency. All batteries' Nyquist plots (Figure 4.6b) show two different semicircles after 100 cycles. The charge transfer resistance (R_{ct}) and its associated constant phase element (CPE2) in the cathode are connected to the semicircle that appears at lower frequencies. On the other hand, at higher frequencies, the semicircle symbolizes the capacitance (CPE1) and interfacial contact resistance (R_f) between the cathode's active reaction sites and the current collector. It also incorporates contributions from the solid electrolyte interface (SEI) development on the lithium anode.^{170–172} Notably, the second semicircle, representing R_{ct} , for the cell with the CR-CTA/SP/PVP-modified GF separator is the smallest and shows minimal change compared to its pristine state. This result

highlights the effectiveness of this modified separator in facilitating sulfur redox reactions, attributed to the nitrogen-containing amino and azo groups and sulfonate groups^{214,215} in CR, as well as the CTA quaternary ammonium anions.^{219,227,228}

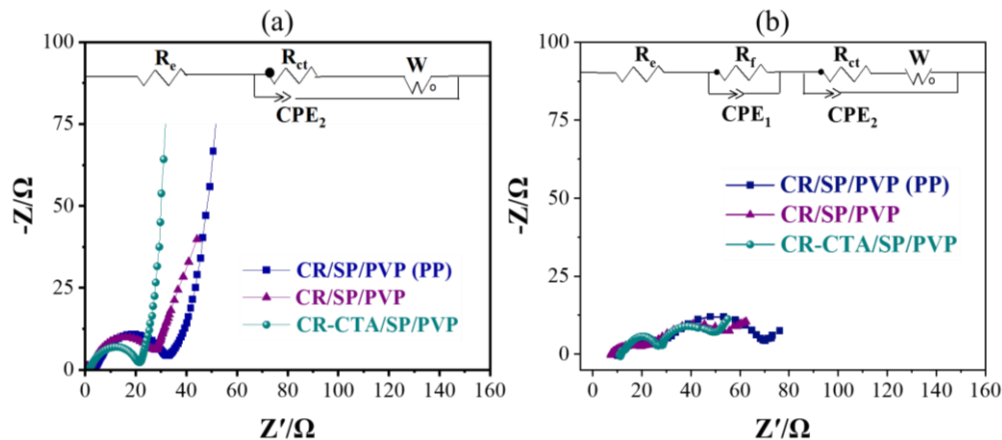


Figure 4.6 Nyquist plots from EIS for cells utilizing various modified GF separators, displayed for (a) initial measurements and (b) after 100 cycles (insets: corresponding equivalent circuit models).

We determined the ionic conductivity (σ) of the separators by employing electrochemical impedance spectroscopy (EIS) on cells with the separator positioned between two stainless steel electrodes.¹⁷³ The bulk resistance (R_e) was calculated from the intersection points on the x-axis of the Nyquist plot (Figure 4.6a). As shown in the data summarized in Table 4.2, the CR-CTA/SP/PVP-modified GF separator exhibits superior conductivity compared to both CR/SP/PVP (PP) and CR/SP/PVP. The high conductivity can be attributed to the presence of CTA ions, which effectively facilitates the movement of Li^+ ions across the separator.²³⁹

Table 4.2 Fitted EIS parameters and ionic conductivity values of the separators.

Samples	R_e (Ω)	R_{ct} (Ω)	d (μm)	σ (S cm^{-1})
Bare GF	2.69	70.95	280	3.7×10^{-2}
SP/PVP ^a	6.51	20.25	310	1.7×10^{-2}
CR/SP/PVP (PP) ^b	10.54	39.54	55	1.8×10^{-3}
CR/SP/PVP ^a	6.16	42.14	308	1.8×10^{-2}
CR-CTA/SP/PVP ^a	3.57	34.09	308	3.0×10^{-2}

^aA GF separator with a thickness of $\sim 280 \mu\text{m}$ was used.

^bA PP separator with a thickness of $\sim 25 \mu\text{m}$ was used.

The electrochemical processes in cells with different separators were investigated using cyclic voltammetry (CV) at a scan rate of 0.1 mV s^{-1} between 1.7 and 2.8 V (Figure 4.7a). The reduction of S_8 to long-chain (Li_2S_n , $4 \leq n \leq 8$) and short-chain (Li_2S_n , $1 \leq n < 4$) polysulfides is represented by two cathodic peaks at 2.30 V and 2.03 V, respectively. The re-oxidation of $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ to polysulfides and S_8 is shown by an oxidation peak at 2.4 V.²⁴⁰ The peak potentials observed in the CV curves reflect the charge transfer barrier, providing a qualitative assessment of the electrochemical reaction kinetics.²⁴¹ The cell incorporating the CR-CTA/SP/PVP-modified GF separator shows lower polarization and enhanced polysulfide conversion, as evidenced by higher reduction peaks and lower oxidation potentials compared to CR(PP) and CR(GF) separators (Figure 4.7a). The lithium-ion diffusion coefficient (D) can be calculated using the Randles–Sevcik equation.²⁴² CV curves for different cells were recorded at scan rates ranging from 0.2 to 0.6 mV s^{-1} (Figures 4.7b - 4.7d). The slopes of the I_p vs. $v^{0.5}$ curves, derived from the peak currents I_A , I_B , and I_C at different scan rates (Figures 4.7e-4.7g), were used to calculate the D values (Figure 4.7h). The results reveal that the D values at all three peak positions are higher for the cell with the cell using the GF separator modified by CR-CTA/SP/PVP compared to those with other separators, confirming a faster lithium-ion diffusion rate in this cell. This result further confirms the high effectiveness of CR-CTA in enhancing sulfur redox reactions, attributed to its functional nitrogen-containing amino and azo groups,^{160,210,211} sulfonate groups,^{214,215} and quaternary ammonium cations.^{219,227,228}

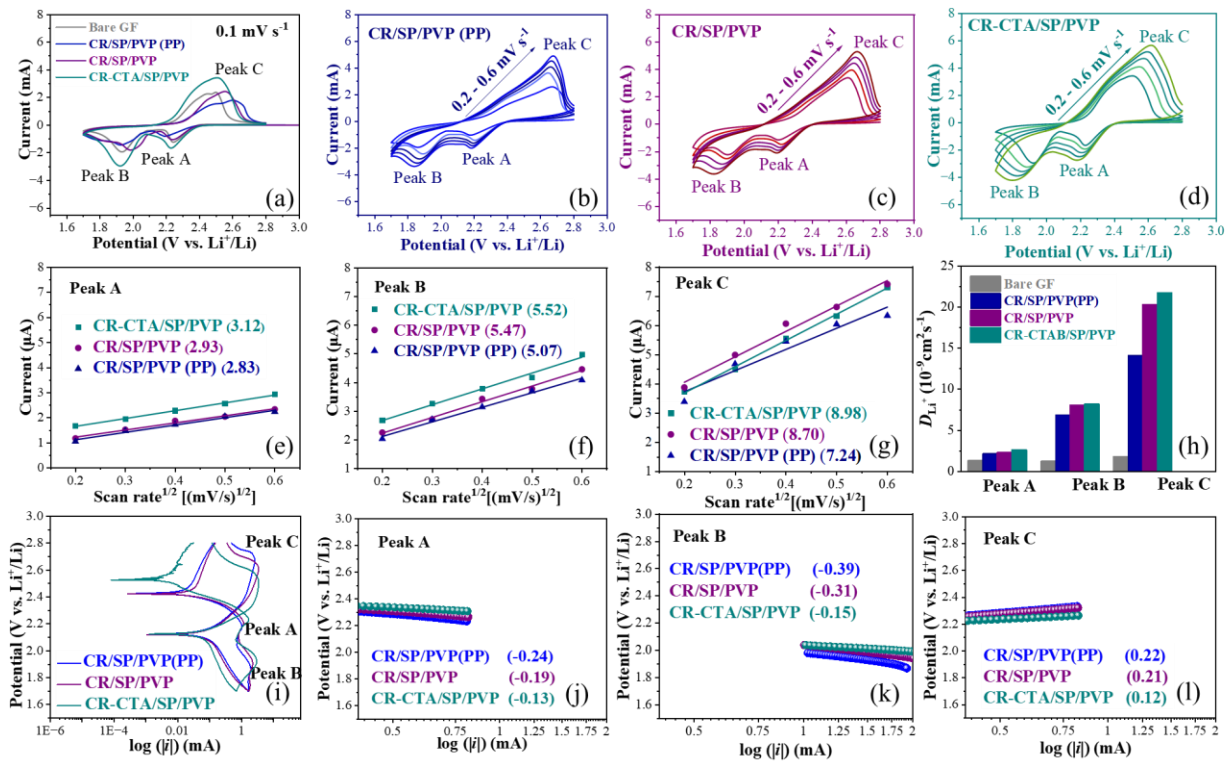


Figure 4.7 (a) CV curves recorded at a scan rate of 0.1 mV s^{-1} and (b-d) at varying scan rates ($0.2\text{--}0.6 \text{ mV s}^{-1}$) for LSBs for the bare GF, CR/SP/PVP(PP), CR/SP/PVP and CR-CTA/SP/PVP, respectively; (e-g) peak current dependence on scan rate, with values in parentheses indicating the respective slopes; (h) Li diffusion coefficients at different peak positions calculated using the Randles-Sevcik equation. (i) Tafel plots of Li-S batteries with various separators obtained from CV measurements at a scan rate of 0.2 mV s^{-1} ; (j-l) corresponding Tafel plots of peak A, peak B, and peak C, with values in parentheses representing the respective Tafel slopes.

The reaction kinetics of the batteries were further analyzed using Tafel plots (Figure 4.7i-4.7l) derived from the CV curves measured at 0.2 mV s^{-1} , providing detailed insights into the sulfur redox reaction (SROR) kinetics.^{243–245} Peak A corresponds to the reduction of high-order polysulfides (Li_2S_n , $n = 6\text{--}8$) to lower-order polysulfides (Li_2S_4), Peak B represents the further reduction to solid-phase Li_2S , and Peak C corresponds to the oxidation of Li_2S back to high-order polysulfides and sulfur. For the cell with the CR-CTA/SP/PVP-modified GF separator, the Tafel slopes were -0.13 , -0.15 , and 0.12 mV dec^{-1} for Peaks A, B, and C, respectively, which are lower than those observed with other separators. These reduced slopes reflect enhanced reaction kinetics in the cell with the CR-CTA/SP/PVP-modified separator, aligning with the CV data obtained at varying scan rates (Figure 4.7a-4.7d).

The superior polysulfide adsorption capacity of CR-CTA was visually verified and compared with CTAB and CR, as evidenced by the dramatic color change from dark brown to almost colorless of a Li_2S_6 solution after addition of CR-CTA. This observation is further supported by the significant reduction in Li_2S_6 absorbance (or concentration) in the UV-vis spectra (Figure 4.8a). While both CR and CTAB demonstrate notable polysulfide adsorption, CR-CTA exhibits enhanced capability based on a molar basis. These findings confirm the strong polysulfide trapping effect of the CR-CTA/SP/PVP-modified GF separator, which contributes to enhanced battery performance. As mentioned earlier, the nitrogen-containing amino and azo groups,^{160,160,210} sulfonate groups,²¹³ and CTA cations^{219,227,228} in CR-CTA contribute to its polysulfide trapping effect.

After 100 charge-discharge cycles, the CR-CTA/SP/PVP-modified GF separator was disassembled for SEM analysis to examine morphological changes. As shown in Figure 4.8b, the modification layer demonstrates a denser and more integrated network of CR-CTA and SP particles relative to its pre-cycled condition (Figure 4.3c and 4.3d), indicating that the structure of the layer was enhanced rather than degraded during cycling. The XRD pattern of the CR-CTA/SP/PVP-modified separator after 100 cycles remains similar to that of the fresh separator (Figure 4.8c), demonstrating the excellent stability of the modification layer, which contributes to the battery's long-term cycling performance.

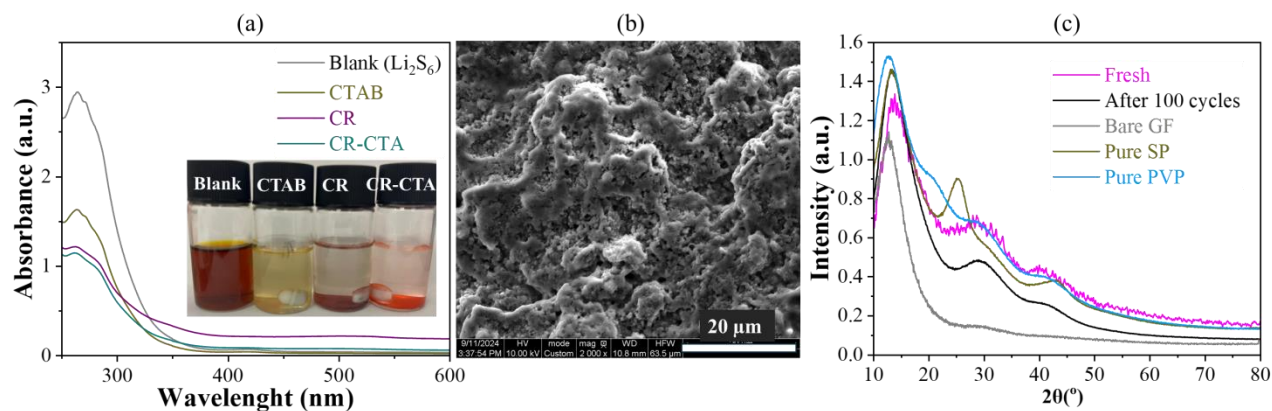


Figure 4.8 (a) UV-Vis spectra of a blank 0.025 M Li_2S_6 solution in DOL/DME (v:v = 1:1, 5 mL) and after adsorption by CTAB (36 mg, 0.1 mmol), CR (70 mg, 0.1 mmol) and CR-CTA (122 mg, 0.1 mmol) with the inset photo illustrating the color change in the Li_2S_6 solution. The solutions were diluted tenfold with DOL/DME (v:v = 1:1) prior to UV-Vis measurements. (b) SEM image of the CR-CTA/SP/PVP-modified GF separator after 100 charge-discharge cycles; (c) XRD patterns of the CR-CTA/SP/PVP-modified SF separators in their initial state (fresh) and after 100 cycles, bare GF (fresh), pure SP, and pure PVP.

4.4 Conclusion

A new compound, CR-CTA synthesized from CR and CTAB, was employed to modify the GF separator, effectively mitigating the polysulfide shuttle effect of Li-S batteries. The cell utilizing the CR-CTA/SP/PVP-modified GF separator exhibited superior initial capacity, cycling stability, and redox kinetics, significantly outperforming cells with bare GF, CR/SP/PVP-modified GF, and CTAB/SP/PVP-modified GF separators. The enhanced performance of CR-CTA is attributed to its ability to anchor polysulfides and facilitate lithium-ion transport. The amino (NH_2), azo ($-\text{N}=\text{N}-$), and sulfonate ($-\text{SO}_3^-$) groups in CR interact with lithium polysulfides via chemical bonding and electrostatic forces, effectively trapping polysulfides and mitigating the shuttle effect, as confirmed by UV-vis spectroscopy. Additionally, the quaternary ammonium cations in CTA enhance ionic conductivity and lithium-ion transport while further contributing to polysulfide retention. The synergy between these functionalities results in a robust modification layer that effectively suppresses polysulfide migration and enhances sulfur utilization. A key factor in the improved performance of the CR-CTA/SP/PVP-modified GF separator is the uniform dispersion of CR-CTA within the modification layer. Unlike the highly crystalline structures of CR and CTAB, CR-CTA forms small nanoparticles, allowing for a more homogeneous distribution. The synergy of CR and CTA ensures the formation of a high-quality modification layer capable of effectively trapping polysulfides and improving sulfur utilization.

In summary, CR-CTA achieves a balance between suppression of polysulfide shuttle effect, efficient ion transport, and redox kinetics, leading to a significant enhancement in the overall performance of Li-S batteries. This simple and effective strategy offers a promising approach for utilizing other industrial dyes and pigments with functional groups such as NH_2 and SO_3^- to modify separators in Li-S batteries, enabling improved capacity, rate performance, and cycling stability.

Chapter 5. Enhancing Lithium-Sulfur Battery Performance through the Synergistic Effects of Congo Red and SnO₂ Nanoparticles in Separator Modification Layers

This chapter is based on the following submitted manuscript:

R. Fazaeli, Z. Haung, Y. Wang, Y. Li, *Surfaces and Interfaces*.

5.1 Introduction

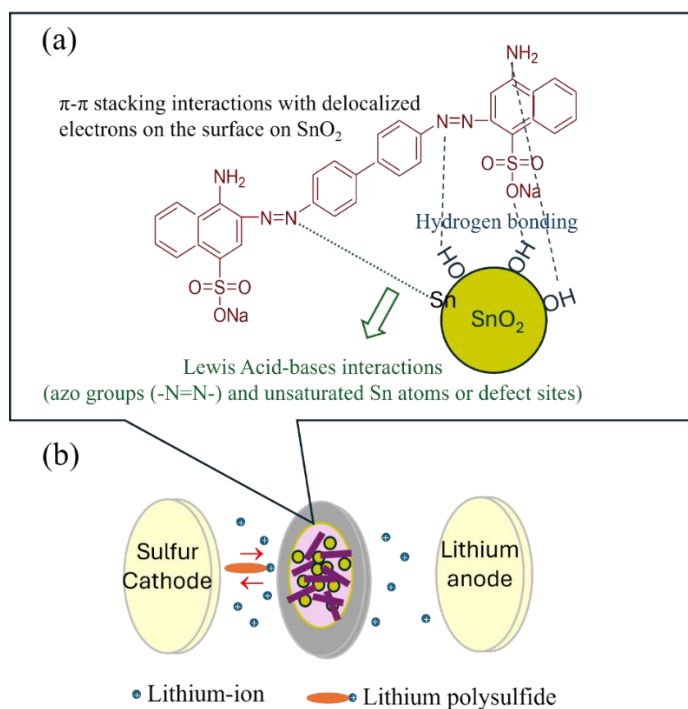
The escalating demand for high-energy-density storage systems has driven extensive research into lithium-sulfur batteries (LSBs), which hold significant promise due to their high theoretical energy density and cost-effectiveness.¹¹³ Despite these advantages, the widespread adoption of LSBs is hampered by several critical challenges.¹⁸⁷ Among these, polysulfide shuttling and limited cycle life are the most prominent, severely undermining the performance of LSBs.²⁴⁶ Polysulfide shuttling refers to the migration of soluble lithium polysulfide intermediates from the cathode to the anode during the discharge-charge cycles, which leads to active material loss, low Coulombic efficiency, and rapid capacity fading. Additionally, the insulating nature of sulfur and its reduction products, lithium sulfide (Li₂S) and lithium disulfide (Li₂S₂), exacerbates the problem by impeding electron and ion transport, thereby limiting the electrochemical performance of the battery.²⁴⁷ To solve these issues, efforts have focused on modifying battery components to enhance polysulfide confinement and improve overall battery stability.²⁴⁸

Various nanostructured metal oxides, typically below 10 wt%, have been incorporated into the sulfur host or separator materials in lithium-sulfur batteries. These additives offer numerous polar active sites that effectively absorb lithium polysulfides, helping to mitigate the shuttle effect.²⁴⁹ SnO₂ plays a significant role in reducing the dissolution of lithium polysulfides in LSBs by forming S-SnO chemical bonds, thereby minimizing the shuttle effect during charge and discharge cycles. It has been applied to enhance the sulfur cathode, anode, separator, and electrolyte and has also been integrated into interlayers to control polysulfide migration. Recent applications of SnO₂-decorated sulfur hosts, separators, and interlayers in LSBs include nanoparticles (0D) nanowires,^{89,250,251} nanorods, nanotubes (1D),^{252,253} ultra-thin layered materials (2D),^{254–257} and interconnected carbon aerogels (3D).^{258–260}

Separators are crucial in LSBs, maintaining the physical separation between the cathode and anode while allowing ion transport. Modifying separators to capture and block polysulfides and enhance ionic conductivity is a more convenient strategy for improving the performance of LSBs compared to altering

cathode compositions.^{205,260–262} Congo Red (CR) contains sulfonate groups ($-\text{SO}_3\text{Na}$) that enhance its solubility in water, hydrophilicity, and interactions with polar substrates. Sulfonate groups enhance ionic conductivity, improving ion transport and electrolyte wettability. While no previous reports have documented the utilization of CR for trapping polysulfides in lithium batteries, several studies have shown that incorporating sulfonate-rich materials into separators enhances lithium-ion migration, reduces dendrite formation, and suppresses polysulfide diffusion, collectively improving overall battery performance. Xu et al.²¹⁴ utilized a sulfonate-rich COF (SCOF-2) to modify the separator. SCOF-2's strong electronegativity and wider interlayer spacing facilitate Li^+ movement and suppress dendrite formation, resulting in improved battery performance. Hu et al.²¹⁵ demonstrated that the strong electrostatic repulsion of sulfonate groups can significantly enhance Li^+ transport efficiency in the SPEKK separators. This effect arises from the sulfonate groups facilitating phase separation between the hydrophobic main chain and hydrophilic side chains, creating continuous ion transport channels. Additionally, the interaction between the sulfonate groups and anions in LiTFSI prevents anion accumulation, further boosting the conductivity of lithium ions within the porous electrospun membrane. Cao et al.²¹⁶ incorporated a covalent organic framework (TpPa- SO_3Li) film with negatively charged sites and nanochannels on a Celgard separator to promote lithium ion conduction and inhibit polysulfide diffusion. Congo Red (CR) contains amino ($-\text{NH}_2$) groups, which are believed to strongly contribute to polysulfide adsorption through their interaction with lithium polysulfides. Similarly, a polyethyleneimine (PEI) binder, composed of both $-\text{NH}_2$ and $-\text{NH}$ groups, has been shown through density functional theory (DFT) simulations and lithium polysulfide (LPS) absorption tests to exhibit a strong affinity for LPS.¹⁶⁰

In this study, we investigate the synergistic effects of CR dye and SnO_2 nanoparticles on glass fiber (GF) separators to mitigate the LPS shuttle effect of LSBs by utilizing the LPS-absorbing sulfonate groups on CR and the strong $\text{S}-\text{SnO}$ chemical bonds of SnO_2 nanoparticles (Scheme 5.1). Additionally, SnO_2 provides excellent ionic conductivity, facilitating lithium ion transport and maintaining efficient charge-discharge cycles.^{89,253,263–273} The GF helps prevent physical deformation or damage during battery operation, thereby extending the lifespan of the battery.²⁷⁴ The combined properties of CR and SnO_2 , along with the support of GF, enable effective polysulfide adsorption, high ionic conductivity, and suppression of the polysulfide shuttle effect, leading to higher initial discharge capacities, reduced capacity fading, and extended cycle life.



Scheme 5.1 Schematic illustration of the interaction between Congo Red (CR) and SnO_2 nanoparticles; (b) Diagram of a Li-S cell incorporating a CR-CTA/SP/PVP-modified GF separator.

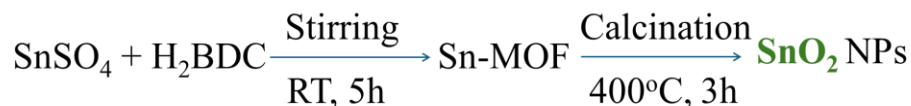
5.2 Experimental

5.2.1 Materials

Congo red (CR), terephthalic acid (H_2BDC) and SnSO_4 (Sigma-Aldrich), Li foils (Shenzhen Poxon Machinery Technology Co. Ltd.), polyvinylpyrrolidone (PVP) (Sigma-Aldrich, MW~1,300,000 by LS), polyvinylidene difluoride (PVDF) (MW~1,000,000), Super P (IMERY) were purchased from commercial sources and used as received.

5.2.2 Synthesis of SnO_2 nanoparticles

The SnO_2 nanoparticles (NPs) were synthesized through thermal decomposition of a tin-based metal-organic framework (Sn-MOF). Specifically, H_2BDC (1.992 g, 0.012 mol) and NaOH (0.960 g, 0.024 mol) were dispersed in 300 mL of deionized water. This solution was then combined with 60 mL of a 0.25 M SnSO_4 solution and vigorously stirred for five hours at room temperature. The precipitates were collected by filtration and dried to yield the Sn-MOF. The SnO_2 NPs were obtained by subjecting the Sn-MOF to thermal treatment at 400 °C in air for three hours (Scheme 5.2).



Scheme 5.2 Synthesis of SnO₂ NPs.

5.3 Results and discussion

TEM image of the CR-SnO₂ composite, displayed in Figure 5.1a, reveals the presence of SnO₂ nanoparticles embedded within the CR matrix. The observed SnO₂ nanoparticles have an average size of approximately 5 nm and are uniformly dispersed across the matrix. Additionally, Figure 5.1b presents Energy Dispersive X-ray (EDX) spectroscopy data for the CR-SnO₂ composite, confirming the presence of key elements, including C, N, O, Sn, and S. Figure 5.1c further illustrates the elemental mapping of the CR-SnO₂ composite, showing a homogeneous distribution of these elements across the sample.

Figure 5.2 displays the XRD patterns of pure CR, bare GF and modified GF with CR/SP/PVP, SnO₂/SP/PVP and CR-SnO₂/SP/PVP, respectively. Congo Red exhibits sharp, well-defined peaks, indicating its crystalline nature. In contrast, the bare GF demonstrates an amorphous structure, as reflected by the absence of distinct peaks in its XRD spectrum (Figure 5.2a). The XRD patterns of the CR/SP/PVP modified-GF separator reveal the characteristic sharp peaks associated with the crystalline structure of CR (Figure 5.2b). This suggests that the modification process effectively integrates the CR within the glass fiber matrix while maintaining its crystalline properties. The diffraction peaks of SnO₂ NPs (Figure 5.2c) are analyzed in comparison with JCPDS data #41-1445, and the corresponding crystalline planes are indexed accordingly. The XRD patterns of SnO₂/SP/PVP and CR-SnO₂/SP/PVP-modified GF separators (Figure 5.2d and Figure 5.2f) confirm the presence of SnO₂ polycrystalline phase, which corresponds to a tetragonal crystal system with a P42/mnm space group, consistent with previously reported data for similarly synthesized SnO₂ NPs.²⁷⁵ Furthermore, the XRD patterns of the CR-SnO₂/SP/PVP modified-GF separator (Figure 5.2f) exhibit distinct diffraction peaks corresponding to both CR and SnO₂. The presence of these characteristic peaks confirms the successful physical integration of the two components within the composite, indicating that the SnO₂ NPs are well incorporated into the CR matrix without any chemical alterations or phase transformations.

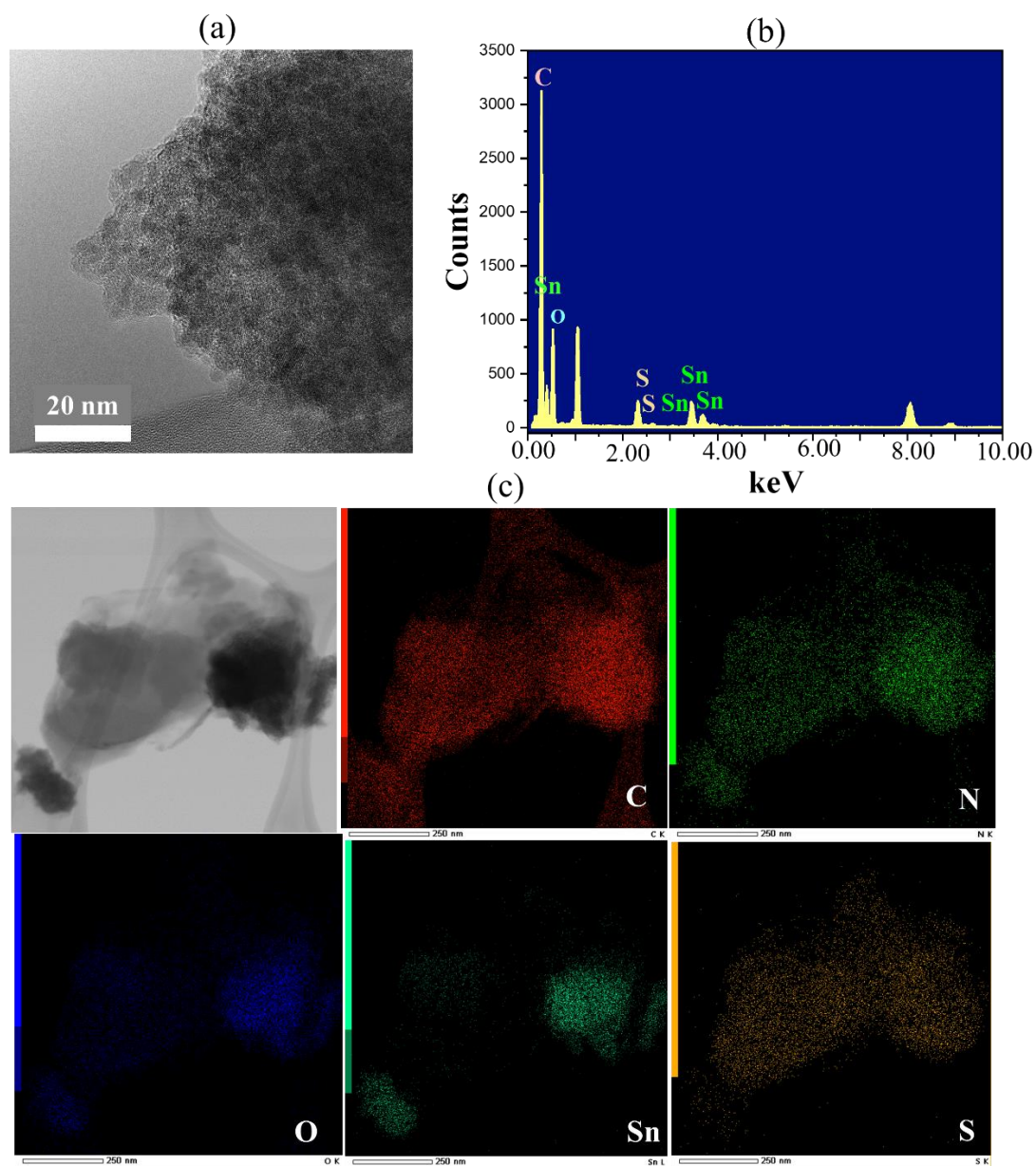


Figure 5.1 (a) TEM images; (b) EDX and (c) mapping-TEM analysis of CR-SnO₂.

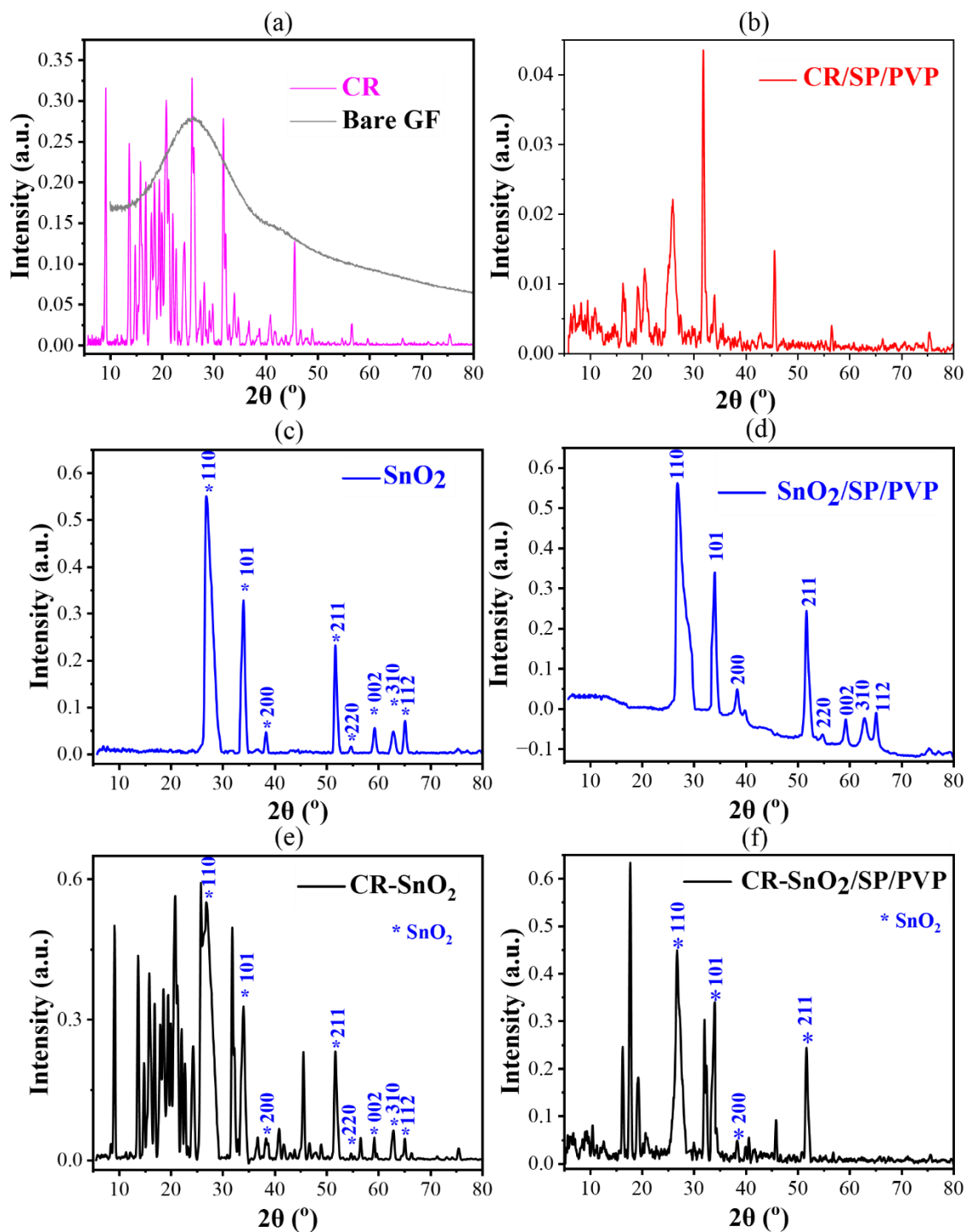


Figure 5.2 XRD patterns of (a) pure CR and the bare GF, (b) CR/SP/PVP GF-modified separator (CR/ SnO_2 molar ratio of 1:3), (c) SnO_2 NPs; (d) SnO_2 /SP/PVP GF-modified separator (CR/ SnO_2 molar ratio of 1:3); (e) CR- SnO_2 and (f) CR- SnO_2 /SP/PVP GF-modified separator (CR/ SnO_2 molar ratio of 1:3).

Dimethyl sulfoxide (DMSO) was utilized as the solvent for dissolving CR, facilitating the preparation of CR-SnO₂/SP/PVP slurries for the modification of GF separators. Polyvinylpyrrolidone (PVP) was selected as the binder due to its solubility in DMSO, ensuring effective dispersion and strong adhesion of CR and SnO₂ in the slurry formulation. The polar PVP can also ensure uniform coating of the GF separators, providing sufficient mechanical integrity. To characterize the morphology of the modified GF separators, SEM analysis was conducted. Figures 5.3a and 5.3b show the surface and cross-sectional SEM images of the CR/SP/PVP-coated GF separator, respectively. In Figure 5.3a, the presence of CR and SP on the surface of the GF separator is clearly visible, confirming successful deposition of the modification materials. The cross-sectional image (Figure 5.3b) reveals a distinct layer of CR/SP/PVP formed on the surface of the GF substrate, indicating a uniform coating. Similarly, the surface and cross-sectional SEM images of the CR-SnO₂/SP/PVP-modified GF separator are shown in Figures 5.3c and 5.3d, respectively. As observed in Figure 5.3c, CR and SnO₂ are homogeneously distributed across the surface of the GF separator, demonstrating effective modification. The cross-sectional image (Figure 5.3d) shows a continuous coating layer with a thickness of approximately 35 μm . Notably, a comparison between the cross-sectional SEM images of the CR/SP/PVP-modified separator (Figure 5.3b) and the CR-SnO₂/SP/PVP-modified separator (Figure 5.3d) reveals that the latter exhibits more complete penetration of the modification materials into the interior of the GF matrix. This enhanced penetration is likely attributable to the presence of SnO₂ NPs, which may facilitate deeper incorporation of the slurry components into the fibrous structure of the GF separator through the strong interaction between the similar SnO₂ and SiO₂.

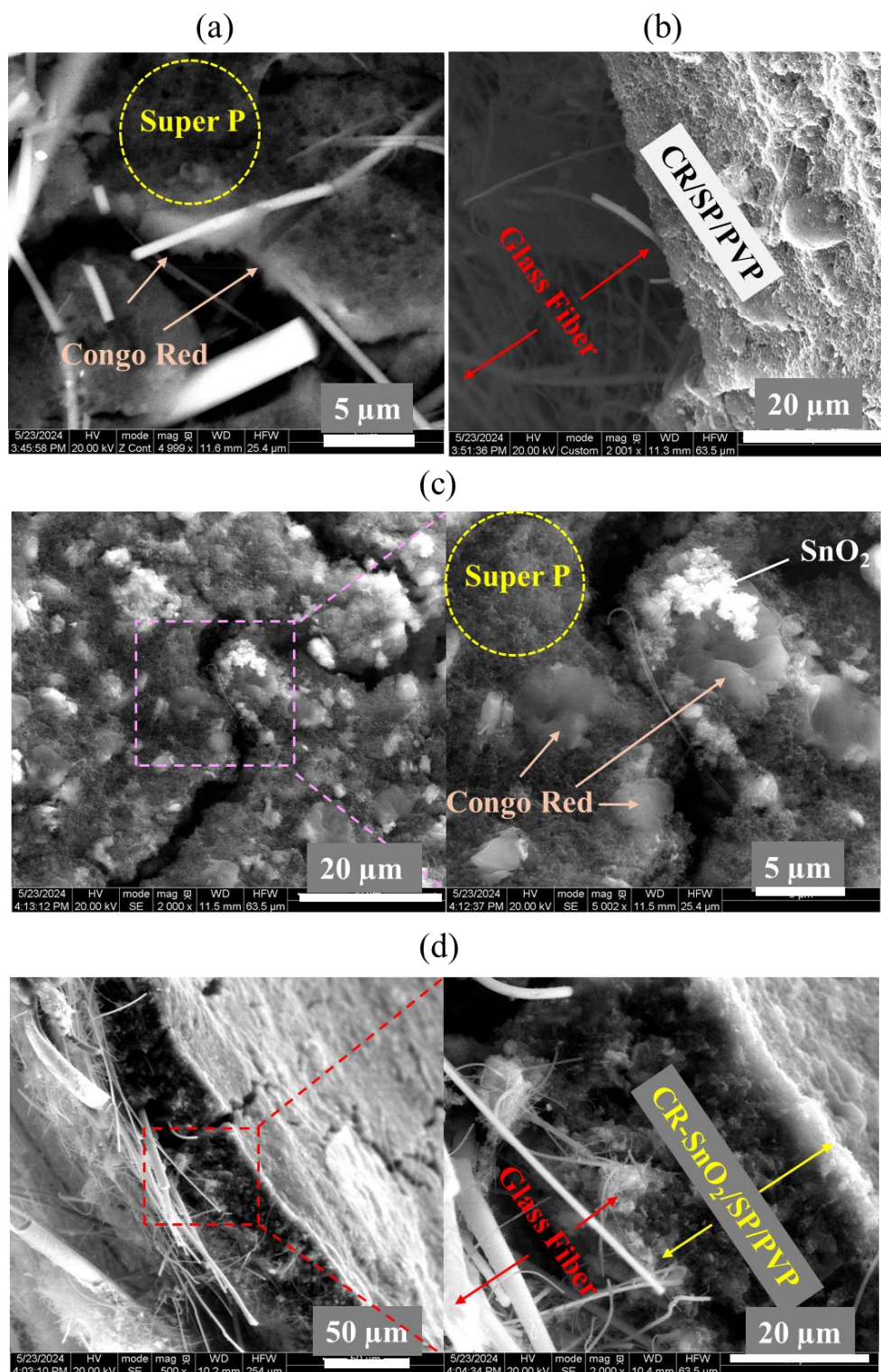


Figure 5.3 (a) SEM images and (b) cross-sectional SEM image of CR /SP/PVP-coated GF separator; (c) SEM images and (d) cross-sectional SEM image of CR-SnO₂/SP/PVP-coated GF separator.

The electrochemical performance of LSBs during galvanostatic cycling at 0.1C in a voltage range of 1.8–2.7 V (vs. Li/Li⁺) reveals distinct discharge and charge characteristics. As shown in Figure 5.4a, the discharge profile features a potential peak around 2.3 V, indicating the reduction of elemental sulfur (S₈) to long-chain polysulfides (Li₂S_x, 4 ≤ x < 8), followed by a second plateau at approximately 2.1 V, corresponding to the further reduction to shorter polysulfides (S₂²⁻/S²⁻). On charging, a plateau above 2.2 V reflects the reverse oxidation back to sulfur. A comparison between cells employing a bare separator and that with a CR-SnO₂/SP/PVP-modified separator (Figure 5.5) reveals a notable reduction in the energy barrier at the onset of the second discharge plateau²⁷⁶, decreasing from 22 mV for the bare GF separator to 13 mV for the modified separator. This reduction highlights the catalytic effect of the modified separator, likely due to the enhanced interactions between the CR-SnO₂ composite and polysulfides, facilitating the conversion of soluble polysulfides into insoluble Li₂S₂. Additionally, the catalytic effect of the modification layer on the redox reactions of the sulfur species can be assessed by the reduced polarization, which is reflected by the potential difference (ΔE) between the charge and discharge plateaus at 50% discharge capacity²⁷⁷. While the ΔE for the bare GF separator-based battery is 216 mV, it reduced to 134 mV in the case of the CR-SnO₂/SP/PVP-modified separator (Figure 5.5), indicating the strong catalytic effect of CR-SnO₂.

Cells with CR-SnO₂/SP/PVP-modified GF separators, at CR:SnO₂ ratios of 1:3, 1:4, and 1:2, demonstrated higher discharge capacities of 1377, 1342, and 1334 mAh g⁻¹, respectively, compared to SnO₂/SP/PVP and CR/SP/PVP separators, which delivered 1294 and 1260 mAh g⁻¹. This performance highlights the superior electrochemical properties of the CR-SnO₂/SP/PVP modification in enhancing cycling stability and capacity retention while reducing polarization, making it more effective than other tested separators. Figure 5.4b illustrates the cycling stability of the batteries over the first 100 cycles at current densities of 0.1C and 0.5C. The battery with the CR-SnO₂/SP/PVP-modified separator (CR/SnO₂ molar ratio of 1:3) exhibits an impressive initial discharge capacity of 1377 mAh g⁻¹, retaining 92% of this capacity after 100 cycles at 0.1C. In comparison, batteries with CR/SP/PVP and SnO₂/SP/PVP separators display lower performance. The enhanced cycling stability and capacity retention of the CR-SnO₂/SP/PVP-modified separator result from the synergistic effects of CR and SnO₂, which optimize both electronic conductivity and ionic diffusion and mitigate polysulfide shuttling. At a sulfur loading of 1.84 mg cm⁻², the modified separator achieves an initial capacity of 1079 mAh g⁻¹ 0.5C, maintaining 91% retention after 100 cycles. Even at higher sulfur loadings of 3.04 and 4.53 mg cm⁻², the cells achieve impressive initial capacities of 963 mAh g⁻¹ and 852 mAh g⁻¹, respectively (Figure 5.6). To evaluate the rate capability of the cells, their specific capacities were measured at current rates ranging from 0.1C to 2.0C, as shown in Figure 5.4c. Among all tested separators, the CR-SnO₂/SP/PVP-modified GF separator exhibited superior rate

performance, delivering specific capacities of 1377, 1227, 1079, 943, and 918 mAh g⁻¹ at current rates of 0.1, 0.2, 0.5, 1.0, and 2.0C, respectively. These results reflect excellent sulfur utilization and fast kinetics. This suggests that the incorporation of CR-SnO₂ into the interlayer significantly enhances the rate capability and longevity of LSBs. The improved performance is likely attributed to the enhanced ionic and electronic conductivity of the CR-SnO₂/SP/PVP composite, which facilitates faster charge transfer and stable cycling under high current conditions. Achieving a high energy density in LSBs requires an optimized electrolyte-to-sulfur (E/S) ratio. In this study, the electrolyte volume was fixed at 30 μL, while sulfur loading was adjusted to modify the E/S ratio (Figure 5.4d). Among the tested E/S ratios of 12, 16, and 20 μL mg⁻¹, 16 μL mg⁻¹ exhibited the best cycling performance. A lower electrolyte volume restricted ion transport, whereas excessive electrolyte resulted in capacity loss due to increased polysulfide dissolution. Additionally, increasing the modification layer thickness from 30 μm to 45 μm hindered ion mobility, adversely impacting overall electrochemical performance (Figure 5.4d).

To evaluate the long-term cycling stability of the cells with CR-SnO₂/SP/PVP GF modified separators, extended cycling tests were performed. As illustrated in Figure 5.4e, after 300 cycles at 0.5C, the cells exhibited an initial discharge capacity of 1084 mAh g⁻¹ and stable and highly reversible cycling with a low capacity decay rate of only 0.063% per cycle, or a 91% capacity retention, and nearly 100% coulombic efficiency. The results demonstrate the synergetic effects of CR and SnO₂ nanoparticles in the modification layer in enhancing the efficiency and lifespan of LSBs.

The Nyquist plots of fresh batteries (Figure 5.7a) display a semicircle at high frequencies and an inclined line at low frequencies. These features can be modeled using a Randles equivalent circuit (inset of Figure 5.7a).²⁷⁸ The intercept of the semicircle with the real axis (Z') at high frequencies represents the electrolyte resistance (R_e). The semicircle itself corresponds to the charge-transfer resistance (R_{ct}) and its associated capacitance (CPE₂) at the cathode. The inclined line at low frequencies is indicative of lithium-ion diffusion, known as Warburg impedance (W).²⁷⁸ The battery with a CR-SnO₂/SP/PVP modified-GF separator exhibits a notably low R_{ct} of 9.56 Ω. This value is lower than those of other modified separators, including 9.61 Ω for the SnO₂ modified-GF separator and 31.59 Ω for the CR-modified GF separator, with the unmodified GF separator showing the highest R_{ct} at 70.95 Ω. The CR-SnO₂ modification enhances both electrical conductivity and lithium-ion diffusion, while effectively reducing polysulfide diffusion. Among the GF separators, the CR-SnO₂/SP/PVP-modified one exhibited the highest conductivity (Figure 5.7c and Table 5.1). The enhanced performance is again linked to the synergetic effects of CR and SnO₂ nanoparticles, which improve Li⁺ ion transport and cycle stability.

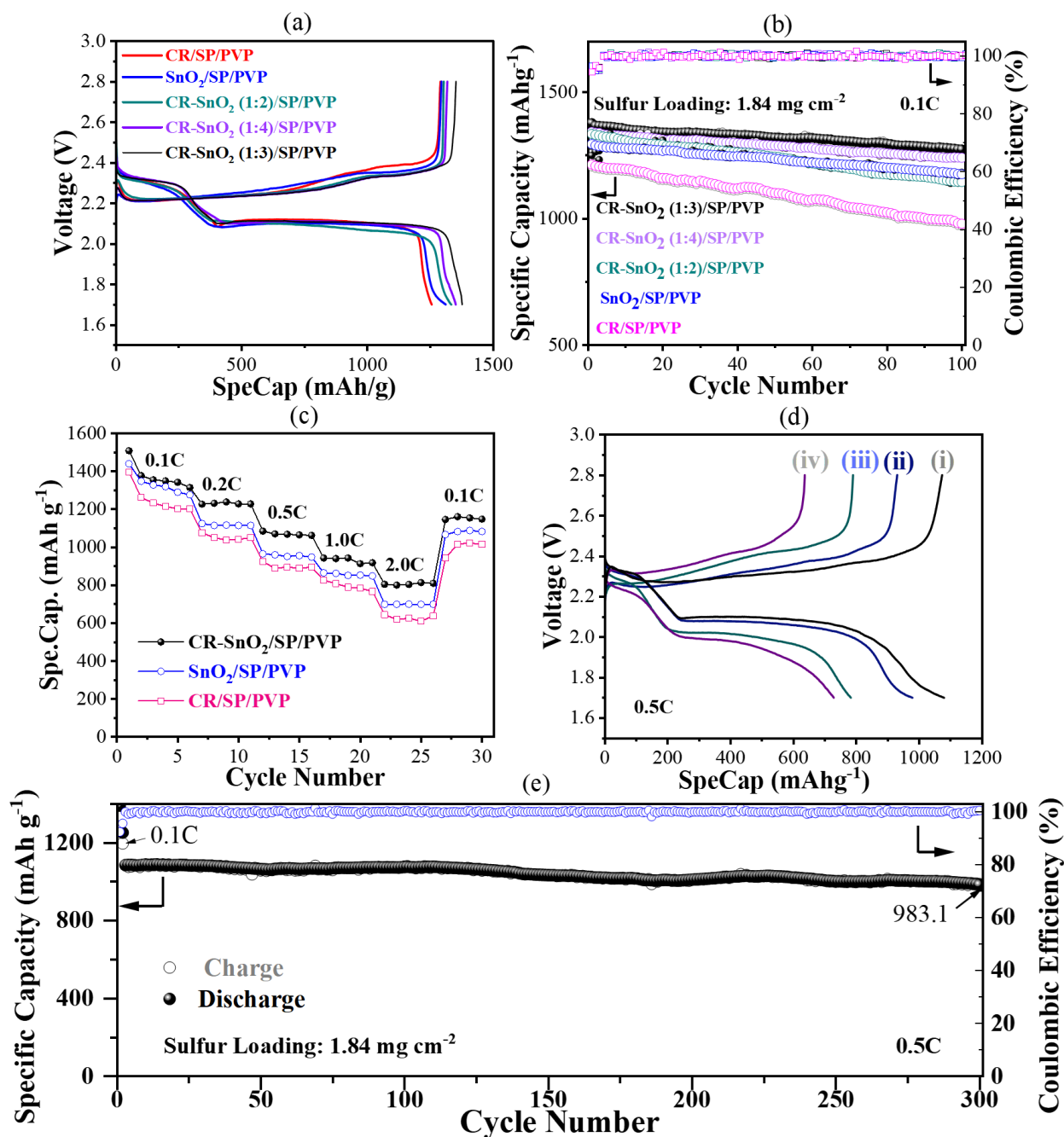


Figure 5.4 (a) Discharge/charge curves at 0.1C of LSBs with CR/SP/PVP, $\text{SnO}_2/\text{SP/PVP}$ and CR- $\text{SnO}_2/\text{SP/PVP}$ -modified separators with different CR/ SnO_2 molar ratios; (b) comparison of cycling stability for cells with various separators during the first 100 cycles at 0.1C; (c) comparison of rate performance for cells with various separators; (d) effects of E/S ratio and modification layer thickness on the cycling performance of LSBs: (i) 12 $\mu\text{L mg}^{-1}$, thickness 30 μm (ii) 16 $\mu\text{L mg}^{-1}$, thickness 30 μm , (iii) 20 $\mu\text{L mg}^{-1}$, thickness 30 μm ; and (iv) 16 $\mu\text{L mg}^{-1}$, thickness 45 μm ; and (e) Cycling stability at 0.5C over 300 cycles for the cell using a CR- SnO_2 (1:3)/SP/PVP-modified GF separator.

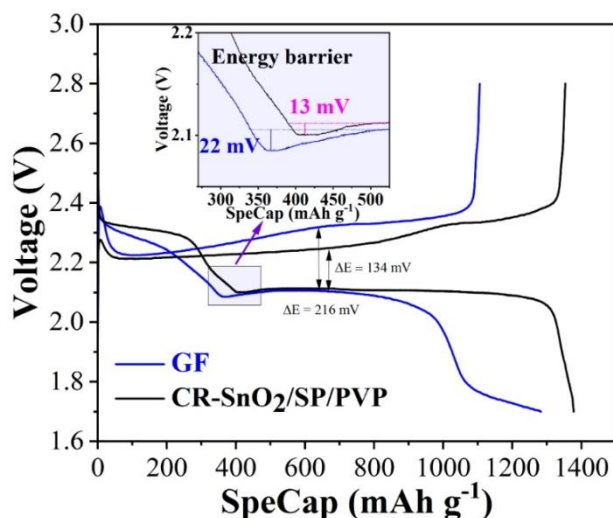


Figure 5.5 Comparison of the discharge/charge curves for cells equipped with a bare GF separator and a CR-SnO₂/SP/PVDF-modified GF separator. The polarization, defined as the potential difference (ΔE) between the charge and discharge plateaus at 50% discharge capacity, is depicted. Inset: Energy barrier of the potential well at the onset of the second plateau.

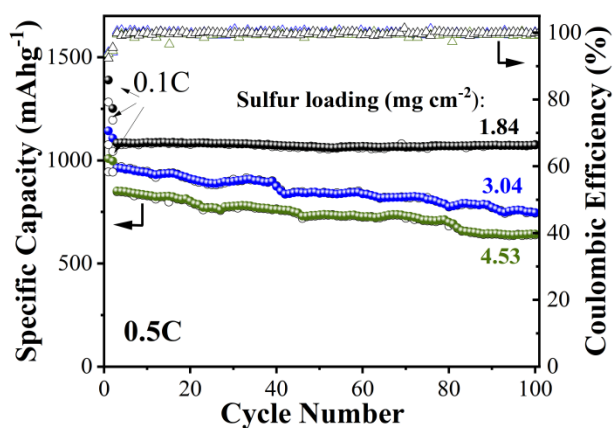


Figure 5.6 Cycling performance of cells with the CR-SnO₂/SP/PVDF-modified GF separator at a current density of 0.5C, with sulfur loadings of 1.84 mg cm⁻² ($E/S = 16 \mu\text{L mg}^{-1}$), 3.04 mg cm⁻² ($E/S = 9 \mu\text{L mg}^{-1}$), and 4.53 mg cm⁻² ($E/S = 6 \mu\text{L mg}^{-1}$).

After 100 cycles, the Nyquist plots (Figure 5.7b) of all batteries display two semicircles. The semicircle at lower frequencies corresponds to the R_{ct} and associated CPE_2 of the cathode. The semicircle at higher frequencies is attributed to the interfacial contact resistance (R_f) and capacitance (CPE_1) between the current collector and the reaction sites in the cathode¹⁷⁰ and the solid electrolyte interface (SEI) at the lithium anode.^{172,279} Among the tested separators, the SnO₂/SP/PVP-modified GF separator demonstrated

the lowest R_f , indicating superior interfacial properties. In contrast, the CR/SP/PVP modified GF separator exhibited the highest R_f , while the CR/SP/PVP-modified GF separator containing a mixture of CR and SnO_2 showed an intermediate R_f value. This trend aligns with the electrical conductivity hierarchy of the materials: $\text{SnO}_2 > \text{CR-SnO}_2 > \text{CR}$ since SnO_2 is highly conductive, whereas CR is insulating. Consequently, the observed order of R_f reflects the varying degrees of electrical conduction between the redox sites and the conductive pathways (SP and current collector) in the different separator modifications. On the other hand, while the R_{ct} values of the cycled CR/SP/PVP and SnO_2 /SP/PVP-modified GF separators increased significantly, the CR- SnO_2 /SP/PVP-modified GF separator remained small, indicating its excellent charge transfer capability even after extensive cycling. It is noticed that the Warburg tail disappeared for all cycled batteries, which suggests lithium-ion diffusion within the separator has been hindered,²⁸⁰ likely due to the accumulation of polysulfides. Among the GF separators, the CR- SnO_2 /SP/PVP-modified one exhibited the highest conductivity (Fig. 5.7c and Table 5.1). The enhanced performance is again linked to the synergetic effects of CR and SnO_2 nanoparticles, which improve Li^+ ion transport and cycle stability.

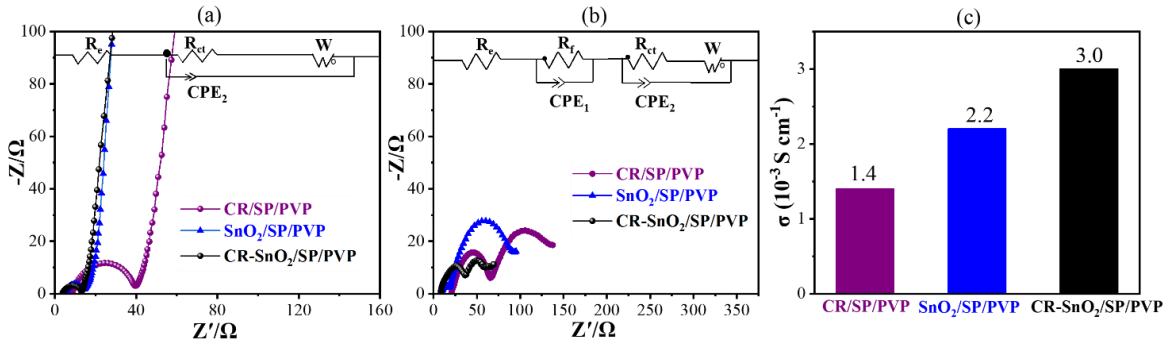


Figure 5.7 EIS (Insert: equivalent circuit plot) of (a) fresh cells and (b) cells after 100th cycling; (c) The ion conductivity values of the cells with difference modified GF separators.

Table 5.1 The values of EIS fitting and the conductivity measurement of the separators.

	Modifier	R_e (Ω)	R_f (Ω)	R_{ct} (Ω)	d (μm)	σ (S cm^{-1})
Fresch	Bare GF	2.69	-	70.95	280	3.7×10^{-3}
	CR/SP/PVP	8.03	-	31.77	308	1.4×10^{-3}
	SnO_2 /SP/PVP	4.63	-	9.58	312	2.2×10^{-3}
	CR- SnO_2 /SP/PVP	3.67	-	9.56	311	3.0×10^{-3}
After 100 th cycling)	Bare GF	8.54	31.98	211.28	280	1.2×10^{-3}
	CR/SP/PVP	20.7	44.8	71.56	308	0.53×10^{-3}
	SnO_2 /SP/PVP	8.80	8.98	74.99	312	1.3×10^{-3}
	CR- SnO_2 /SP/PVP	8.46	27.95	20.95	311	1.3×10^{-3}

To evaluate the electron transfer kinetics between redox species and the electrodes, we performed cyclic voltammetry (CV) measurements over a potential window of 1.8 to 2.7 V, employing a scan rate of 0.1 mV s^{-1} , as depicted in Figures 5.8a–5.8c. The current-potential curves obtained from these CV measurements illustrate near-reversible electrode reactions across the different separator configurations employed in the cells. The cell with the CR-SnO₂/SP/PVP-modified GF separator exhibits more pronounced and sharper peaks in its CV curves compared to the cell with the CR/SP/PVP-modified GF separator. These characteristics suggest more efficient redox reactions, indicating improved electron transfer kinetics and a more favorable electrochemical environment within the cell. This improvement can be attributed to the unique properties of the CR-SnO₂/SP/PVP GF-modified separator, which facilitate the interactions between the redox species and the electrodes, enhancing overall cell performance. In the anodic sweep of the cyclic voltammetry (CV) curve, a distinct peak is observed at 2.44 V, which corresponds to the oxidation of polysulfide species into elemental sulfur. This peak signifies the transition from longer polysulfides to sulfur during the charging process. In the cathodic sweep, an initial reduction peak emerges at 2.28 V, indicating the transformation of elemental sulfur into soluble polysulfide species S_x^{2-} ($8 \geq x \geq 4$), signifying the transition from solid to liquid phase. A second cathodic peak at 2.03 V is associated with the further reduction of S_4^{2-} to lower-order species such as S_2^{2-} and S^{2-} , indicating the liquid-to-solid phase transition where solid lithium sulfides are formed. The CV curves of cells equipped with CR-SnO₂/SP/PVP and SnO₂/SP/PVP separators exhibit nearly identical current responses, indicating that the SnO₂ component facilitates efficient and rapid discharge-charge kinetics. This suggests that the SnO₂ plays a crucial role in enhancing the electrochemical performance by enabling faster and more consistent redox reactions within the cell.

Diffusion coefficients of lithium ions (Figure 5-8j) were determined by analyzing the slopes of the linear fits obtained from the CV data (Figures 5.8g–5.8i), which were recorded at scan rates from 0.2 to 0.6 mV s^{-1} (Figures 5.8d–5.8f). The results clearly indicate that the CR-SnO₂/SP/PVP modification layer significantly enhances Li^+ ion migration, as evidenced by the steeper slopes observed in the batteries with CR-SnO₂/SP/PVP modified GF separators compared to those with SnO₂/SP/PVP or CR/SP/PVP modified GF separators. The improvement in Li^+ ion migration can be attributed to the introduction of the CR-SnO₂ layer, which increases the electrolyte absorption capacity and improves interface wettability, thereby facilitating more efficient ion transport.

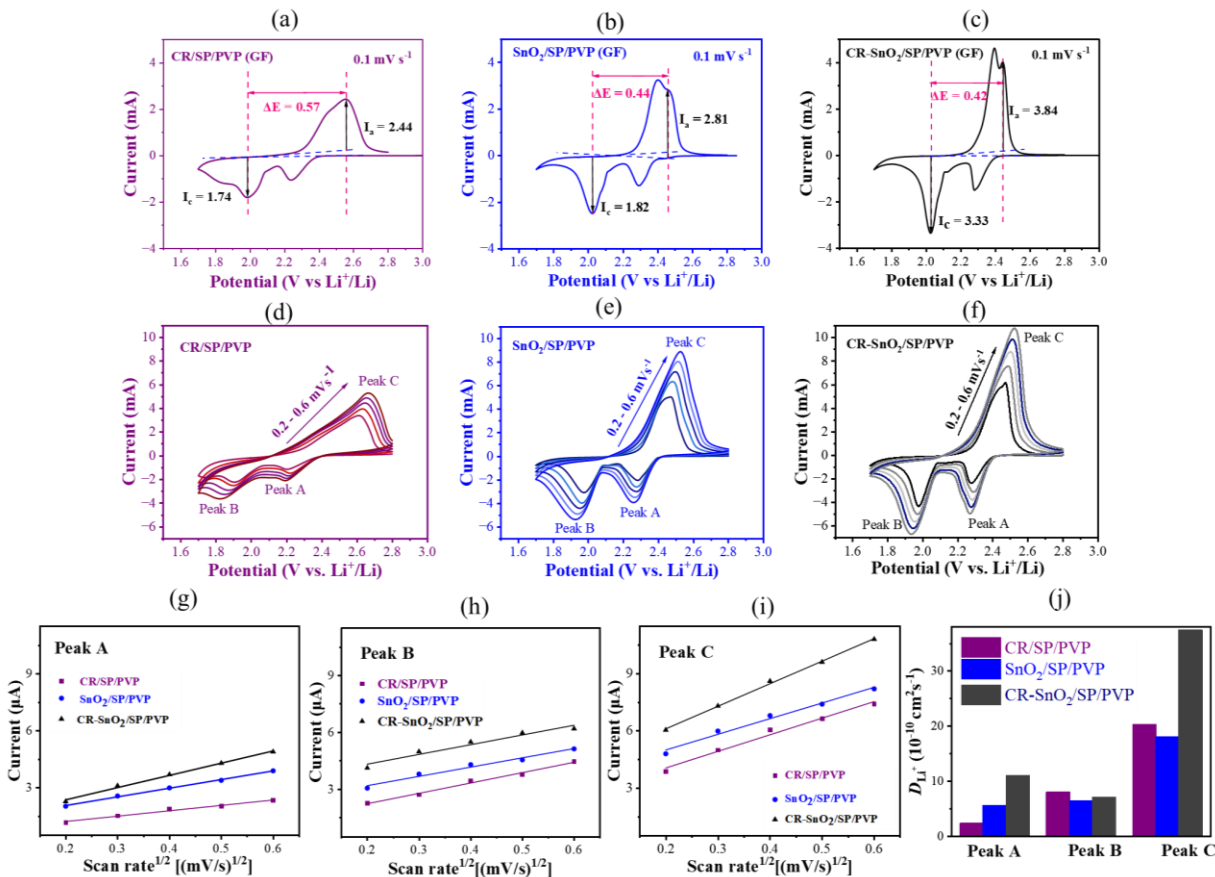


Figure 5.8 Electrochemical analysis of Li-S batteries with various modified separators: (a–c) CV profiles at a scan rate of 0.1 mV s⁻¹ for cells incorporating CR/SP/PVP, SnO₂/SP/PVP, and CR-SnO₂/SP/PVP-modified GF separators, respectively; (d–f) CV profiles at scan rates ranging from 0.2 to 0.6 mV s⁻¹; (g–i) Linear regressions of peak currents (I_A, I_B and I_C) plotted against the square root of the scan rate; (j) Calculated Li⁺ ion diffusion coefficients derived from the slopes of the linear fits in panels (g–i).

The polysulfide adsorption capability of the CR-SnO₂ composite was evaluated by mixing it with a Li₂S₆ solution overnight, resulting in a color shift from brown to nearly colorless, as shown in the inset of Figure 5.9a. This was compared to the adsorption abilities of CR and SnO₂ alone. The UV-Vis spectrum of the Li₂S₆ solution following treatment with CR-SnO₂ exhibited approximately a 74% reduction in the Li₂S₆ absorption peak, indicating substantial polysulfide adsorption by the composite. An analysis of the cell after 100 discharge-charge cycles showed that the CR-SnO₂/SP/PVP-modified GF separators maintained structural integrity, with minimal degradation. The cells were disassembled in an argon atmosphere, and the separators were subsequently dried at 50°C to eliminate residual solvents. SEM images (Figure 5.9b) reveal strong cohesion between the CR-SnO₂ and SP layers, suggesting that the composite structure supports long-term separator stability and enhances battery performance during cycling.

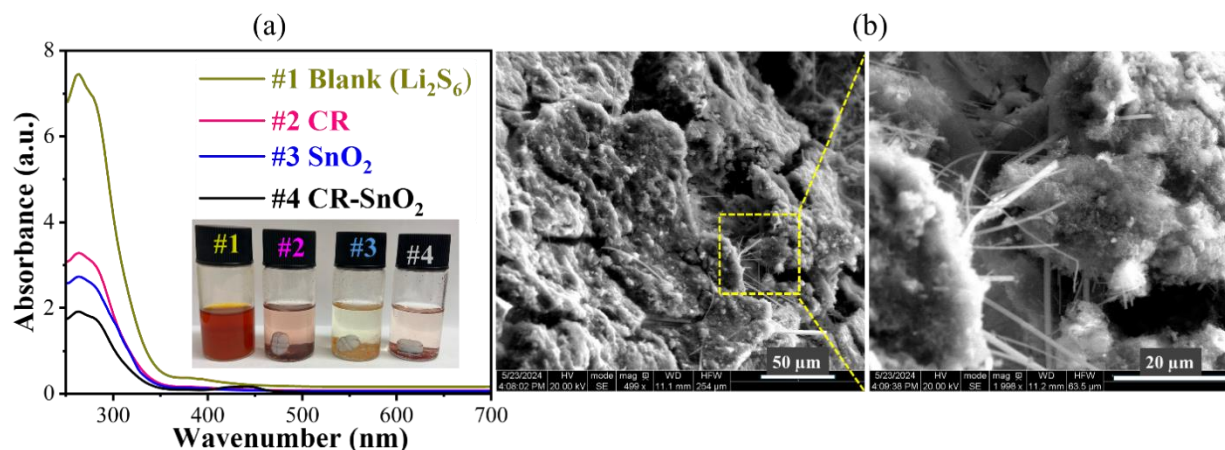


Figure 5.9 (a) UV-vis absorption spectra of a 0.025 M Li_2S_6 solution in DOL/DME (v:v = 1:1, 5 mL) before and after treatment with various adsorbents: CR (70 mg, 0.1 mmol), SnO_2 (15 mg, 0.1 mmol), and a CR- SnO_2 composite (30 mg, CR/ SnO_2 molar ratio = 1:3, total 0.1 mmol: CR 0.026 mmol, SnO_2 0.079 mmol). The inset photograph displays the corresponding color changes in the Li_2S_6 solutions. Prior to UV-vis analysis, the solutions were diluted sixfold with DOL/DME (v:v = 1:1). (b) SEM image of a CR-CTAB/SP/PVP-modified GF separator after 100 discharge-charge cycles at 0.1C.

5.4 Conclusion

This study presents a new approach for enhancing the electrochemical performance of LSBs by modifying GF separators with a CR- SnO_2 composite, which effectively mitigates the polysulfide shuttle effect while enhancing lithium-ion transport. The synergistic interaction between the sulfonate groups in CR and the active surface of CR- SnO_2 enables strong polysulfide adsorption and conversion, leading to reduced active material loss and improved sulfur utilization. Additionally, SnO_2 contributes to enhanced ionic conductivity and charge transfer kinetics, reducing polarization and improving redox efficiency. These combined effects result in superior electrochemical performance compared to separators modified with either CR or SnO_2 alone. LSBs employing CR- SnO_2 /SP/PVP-modified separators achieve an initial discharge capacity of 1377 mAh g^{-1} at 0.1C, with 92% capacity retention after 100 cycles and 91% retention after 300 cycles at 0.5C, demonstrating excellent cycling stability. Furthermore, the modified separator supports high rate capability, retaining substantial capacity even at increased current densities.

EIS confirms reduced charge transfer resistance, while CV demonstrates improved redox kinetics and sulfur species reversibility in CR- SnO_2 /SP/PVP-modified separators. Polysulfide adsorption tests highlight the CR- SnO_2 composite's superior adsorption capability, emphasizing its unique surface interactions. These findings advance interface engineering strategies for enhancing LSB performance.

While this study significantly improves LSB performance, the high thickness and loading of the CR-SnO₂/SP/PVP-modified GF separator negatively impact the battery's specific energy and energy density. This issue stems from the rough surface and large pores of GF, which hinder uniform thin coatings. Attempts to use smoother polypropylene (PP) separators failed due to poor adhesion of the modification layer. Future research will optimize the coating process and explore alternative separators with better surface compatibility to achieve thinner coatings, enhancing energy density and real-world applicability.

Nonetheless, this study establishes CR-SnO₂ as a highly effective multifunctional separator modification, demonstrating both strong polysulfide immobilization and enhanced ion transport. By bridging the fields of battery materials, surface chemistry, and interfacial engineering, this work provides new insights into functional separator design for next-generation LSBs. The promising performance enhancements suggest that further optimizations of CR-SnO₂-based separators could play a key role in advancing high-energy, long-cycle LSB technology.

Chapter 6. Modification of Glass Fiber Separators with a Ternary V₂O₅/Cysteine/FeNi-LDH Composite to Enhance the Performance of Lithium-Sulfur Batteries

This chapter is based on the following submitted manuscript:

R. Fazaeli, H. Aliyan, M. Javadi, Z. Haung, Y. Wang, Y. Li, *Inorganic Chemistry Communication*.

6.1 Introduction

Lithium-sulfur (Li-S) batteries are emerging as promising candidates for next-generation high-energy-density secondary batteries due to their high theoretical energy density, the environmental friendliness of sulfur as an active material, and the low production cost.^{189,281–283} However, despite these advantages, several challenges—such as sluggish reaction kinetics and the solubility of polysulfides—have hindered their practical application.^{284,285} In ether-based electrolytes, soluble polysulfides are formed, which activate sulfur particles during discharge and oxidize insoluble sulfides during charging. The high solubility of these polysulfides, however, leads to their diffusion and migration, triggering parasitic reactions and causing capacity loss, a phenomenon commonly referred to as the shuttle effect. One promising strategy to mitigate the shuttle effect is through separator modification to block the migration of polysulfides.^{150,286} While separators themselves do not participate in the cell's chemical reactions, they play a critical role in preventing electrical contact between the anode and cathode while allowing ionic movement. This significantly impacts the cycle life, energy density, and power density of Li-S batteries^{122,285}. The selection of an appropriate separator involves several key considerations, including its ability to absorb and retain liquid electrolyte to ensure low internal resistance and high ionic conductivity. Additionally, the separator must exhibit chemical and electrochemical stability across varied operating conditions.^{205,287,288}

Metal oxide nanoparticles have been widely applied as modifiers to improve the wettability and thermal stability of separators with liquid electrolytes.^{289,290} Composite separators coated with such nanoparticles not only exhibit superior mechanical strength but also maintain excellent electrochemical properties.²⁹¹ Among the commonly used metal oxides, nanoparticles of Al₂O₃,²⁹² SiO₂,²⁹³ and ZrO₂²⁹⁴ have been dispersed onto separators to enhance polysulfide adsorption and improve battery cycling performance. Particularly, V₂O₅ has demonstrated a strong affinity for lithium polysulfides (LiPSs), exhibiting catalytic properties that enhance battery performance^{295,296}. These characteristics make it an excellent candidate for

use in Li-S battery separators, similar to other metal oxides.²⁹⁷ Various topologies of V₂O₅—such as nanorods, nanofibers, and nanotubes—have been developed and used for modifying sulfur cathodes to further improve performance.^{92,298–300}

Layered double hydroxides (LDHs), 2D anionic clays with the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n}] \cdot m H_2O$, represent a promising class of materials for broad applications.^{97,298,301} LDHs exhibit a strong ability to trap polysulfide anions, which enhances reaction kinetics in Li-S batteries.^{302–306} Their capacity for anion exchange further prevents the dissolution of polysulfides into the organic electrolyte, effectively mitigating the shuttle effect.^{237,307} LDHs consist of positively charged metal hydroxide layers with interlayer anions, making them ideal 2D hosts that can interact with LiPSs through electrostatic and hydrogen bonding interactions. Despite the weaker nature of S···H bonds compared to traditional O···H bonds, the abundance of hydroxyl groups on LDH surfaces reinforces these interactions, improving the immobilization of LiPSs during battery cycling.³⁰⁸

In this study, we present the development of a novel V₂O₅/Cys/FeNi-LDH (VCFN) ternary heterostructure composite for modifying glass fiber (GF) separators to suppress the shuttle effect in Li-S batteries by harnessing the combined advantages of V₂O₅ and LDHs. The GF separator was selected for its excellent wettability and highly porous structure, which allows for increased electrolyte absorption and higher ionic conductivity, thereby facilitating faster ionic transport.⁶³ Cysteine, a thiol-containing amino acid incorporated into the ternary composite, provides versatile chemical properties. Its carboxylic acid (COOH) and amino (NH₂) groups are capable of forming hydrogen bonds, while its thiol group (SH) is highly reactive, enabling the formation of disulfide linkages.³⁰⁹ These functional groups not only facilitate the formation of the desirable VCFN heterostructure through strong coordination with Fe, Ni, and V,³¹⁰ but also effectively trap lithium polysulfides (LiPSs) via strong interactions with lithium cations^{160,311} contributing significantly to the performance enhancement of Li-S batteries.

6.2 Experimental

6.2.1 Materials and characterization

The materials used including sodium borohydride (NaBH₄), sodium metavanadate (NaVO₃), vanadium (V) oxide (V₂O₅), nickel chloride hexahydrate (NiCl₂·6H₂O), iron chloride hexahydrate (FeCl₂·6H₂O), L-cysteine (Cys), polyvinylidene fluoride (PVDF), Super P (SP), N-methyl-2-pyrrolidone (NMP), polypropylene separators (PP, Celgard 2400 with 40% porosity and a thickness of 25 μm), and lithium foils were obtained from Sigma-Aldrich, Sinopharm, Shenzhen Poxon Machinery Technology, and other commercial sources. FeNi-LDH was synthesized using a reported procedure³¹²; further details can

be found in the Supporting Information. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Discover X-Ray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm). Fourier transform infrared (FTIR) spectra were recorded using a PerkinElmer Spectrum 65 spectrophotometer. For imaging, field-emission scanning electron microscopy (FESEM) images were captured using a MIRA3LMU scanning electron microscope. Transmission electron microscope (TEM) images were recorded using a Philips EM 208s microscope operating at 100 kV. The Brunauer–Emmett–Teller (BET) surface area analysis was conducted using nitrogen adsorption-desorption measurements performed at liquid nitrogen temperature with a Micromeritics TriStar II Series instrument. Prior to these measurements, the samples were degassed at 350°C for 12 hours under a reduced pressure of 10^{-4} Pa to eliminate any adsorbed gases or contaminants. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Bahr-STA-504 instrument. These thermal analyses were conducted over the temperature range of 25–800 °C at a heating rate of 10 K·min $^{-1}$ to assess the thermal stability and decomposition behavior of the samples.

6.2.2 Synthesis of Cys/FeNi-LDH

NiCl $_2$ ·6H $_2$ O (1.7827 g, 0.0075 mol) and FeCl $_2$ ·6H $_2$ O (0.6758 g, 0.0025 mol) were dissolved in a mixture of 40 ml of deionized water and absolute ethanol at a 3:1 molar ratio. L-Cysteine (0.178 g, 0.0015 mol) was added to this solution, which was then continuously stirred for 10 minutes. Subsequently, 10 ml of ~30% aqueous ammonia solution was added and stirred for another 10 minutes. The mixture was transferred to a 100 ml Teflon-lined steel autoclave and heated at 180°C for 12 hours in an oven. After cooling to room temperature, the precipitate formed was collected, washed several times with deionized water and ethanol, and finally dried at 60°C. This process yielded hierarchically porous Cys/FeNi-LDH microspheres (1.42 g).

6.2.3 Synthesis of V $_2$ O $_5$ /Cys/FeNi-LDH (VCFN)

A mixture of 0.10 g (0.82 mmol) of NaVO $_3$ and 1.0 g of Cys/FeNi-LDH microspheres was placed in a 25 ml round-bottom flask. Then, 5 ml of methanol was added, and the mixture was kept stirring under reflux for 24 hours. After the reaction was complete, the mixture was cooled to room temperature, filtered, and thoroughly washed with methanol to remove any residual impurities. The resulting product was dried at 80°C under vacuum (*in vacuo*) to remove any remaining solvent, yielding 0.63 g of the target material (Figure 6.1).

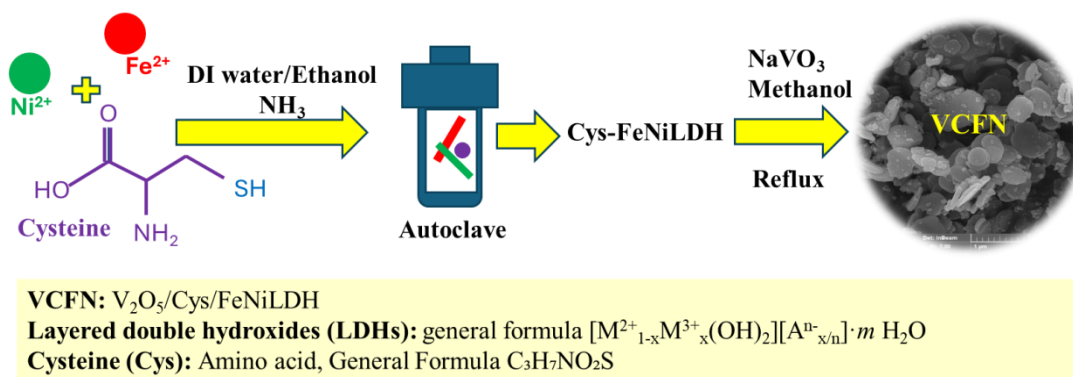


Figure 6.1 Synthesis of $\text{V}_2\text{O}_5/\text{Cys}/\text{FeNi-LDH}$ (VCFN).

6.2.4 Modification of separators

A slurry was prepared by mixing VCFN, SP, and PVDF in a 6:3:1 weight ratio in NMP. The slurry was applied to one side of either GF or PP membranes using the doctor blade method, followed by air-drying in an oven at 60 °C overnight. The modified separators, with a VCFN/SP/PVDF coating weight of 1.43 mg/cm², were then punched into circular disks measuring 19 mm in diameter for use as separators. The coating thickness on the GF and PP separators was approximately 31±2 μm and 29±2 μm, respectively. Separators modified with other materials (as listed in Table 6.1) were fabricated using the same procedure for comparative analysis.

6.2.5 Battery fabrication and electrochemical measurements

To prepare the S/SP composite, 600 mg of sulfur and 400 mg of SP were mixed in a mortar for 30 minutes and pressed into pellets. These pellets were placed in a sealed vial and heated at 155 °C for 12 hours in an oven to facilitate sulfur infiltration. A slurry was then prepared by combining 90 wt.% of the S/SP composite with 10 wt.% PVDF, using NMP as the dispersing solvent. The resulting slurry was uniformly coated onto a carbon-coated aluminum foil and dried overnight at 60 °C under vacuum. After drying, the foil was cut into 12 mm diameter disks to serve as cathodes for Li-S batteries, with a sulfur loading of approximately 1.67 mg cm⁻². The electrolyte used was 1 M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) which was dissolved in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 by volume) with 1 wt% LiNO₃. Li-S batteries were assembled in 2032-type coin cells inside an argon-filled glove box (O_2 and H_2O < 0.1 ppm), using lithium foil as the counter electrode and a VCFN/SP/PVDF-modified GF separator (or an alternative separator type, as listed in Table 6.1). The electrochemical performance of batteries was measured galvanostatically on a Land 2001A battery test

system. Electrochemical impedance spectra (EIS) were recorded at the open-circuit potential (OCP) using a Bio-logic electrochemical potentiostat/galvanostat (VSP) with a frequency range from 1000 kHz to 0.1 Hz and an AC amplitude of 10 mV. Cyclic voltammetry (CV) measurement was carried out in the potential range of 1.7–2.8 V (vs. Li/Li⁺) at different scan rates (0.1–0.6 mV s⁻¹).

Table 6.1 Materials used for the modification of separators and their corresponding total specific capacity (mAh g⁻¹) during the discharge/charge cycles at 0.1C.

Separator	First plateau/Total specific capacity, mAh g ⁻¹ (0.1C)	$R = \frac{C_{second}}{C_{first}}$	$x = \frac{R-1}{2}$
Bare GF	364.9/1282.6	2.51	0.755
(FeNi-LDH)/SP/PVDF	369.2/1230.7	2.33	0.665
(Cys/FeNi-LDH)/SP/PVDF	389.2/1284.9	2.30	0.650
(V ₂ O ₅ /FeNi-LDH)/SP/PVDF	406.5/1307.8	2.22	0.609
VCFN/SP/PVDF	395.4/1401.3	2.54	0.770

^aPhysical mixture of cysteine and FeNi-LDH in a weight ratio of 1:5 (cysteine: FeNi-LDH).

^bPhysical mixture of V₂O₅ and FeNi-LDH in a weight ratio of 1:5 (V₂O₅: FeNi-LDH).

6.3 Results and discussion

6.3.1 Characterization of VCFN composite

Figure 6.2a shows the XRD patterns of VCFN, which exhibits major peaks of the FeNi-LDH (pdf number: 40-0216) at 11.70°, 22.96°, 34.40°, 38.80°, 46° and 60.66°. These peaks can be assigned to (003), (006), (012), (015), (018), (110) and (113) planes³⁰². XRD patterns also confirm that V₂O₅ exhibits an orthorhombic structure assigned to the space group *Pnma*. The primitive unit cell consists of 14 atoms, comprising four vanadium and ten oxygen atoms, organized into puckered layers of edge-sharing, deformed V₂O₅ pyramids. Depending on the specific atomic arrangements and structural frameworks, the crystals display distinct space groups and adopt either orthorhombic or monoclinic configurations. Numerous polymorphs of V₂O₅ have been documented, including hydrated V₂O₅ (V₂O₅·nH₂O) as well as the α-, β-, δ-, γ-, ζ-, and ε-V₂O₅ variants³¹³. The structure's lattice constants for V₂O₅ in VCFN are a = 9.946 Å, b = 3.585 Å, and c = 10.042 Å, and a=b=g=90°, which correspond to α-V₂O₅ (orthorhombic, layered structure,

the most stable phase at room temperature) (Figure 6.3a). The interplanar distance (d), crystallite size (D), the dislocation density (δ) and strain (ϵ) of the synthesized sample were determined, respectively (Figures 6.3b-6.3e) ^{314,315}. These factors provide information about the material's structural properties. The dislocation density and strain were found to decrease as the crystallite size increased, as depicted in Figures 6.3c and 6.3d. The crystallite size of V_2O_5 was determined using the Debye-Scherrer method to be 309 nm, which closely aligns with the value obtained through the Williamson-Hall method, approximately 301 nm (Figure 6.3e). This consistency between the two methods indicates that the broadening observed in the diffraction peaks is predominantly due to the crystallite size, with minimal influence from microstrain effects ³¹⁶. However, it should be noted that these methods are generally optimized for crystallite sizes below 200 nm. For larger particles, such as those reported here, the peak broadening becomes significantly smaller, leading to reduced accuracy and potential errors due to the limitations of instrumental resolution and the diminishing contribution of crystallite size to broadening.

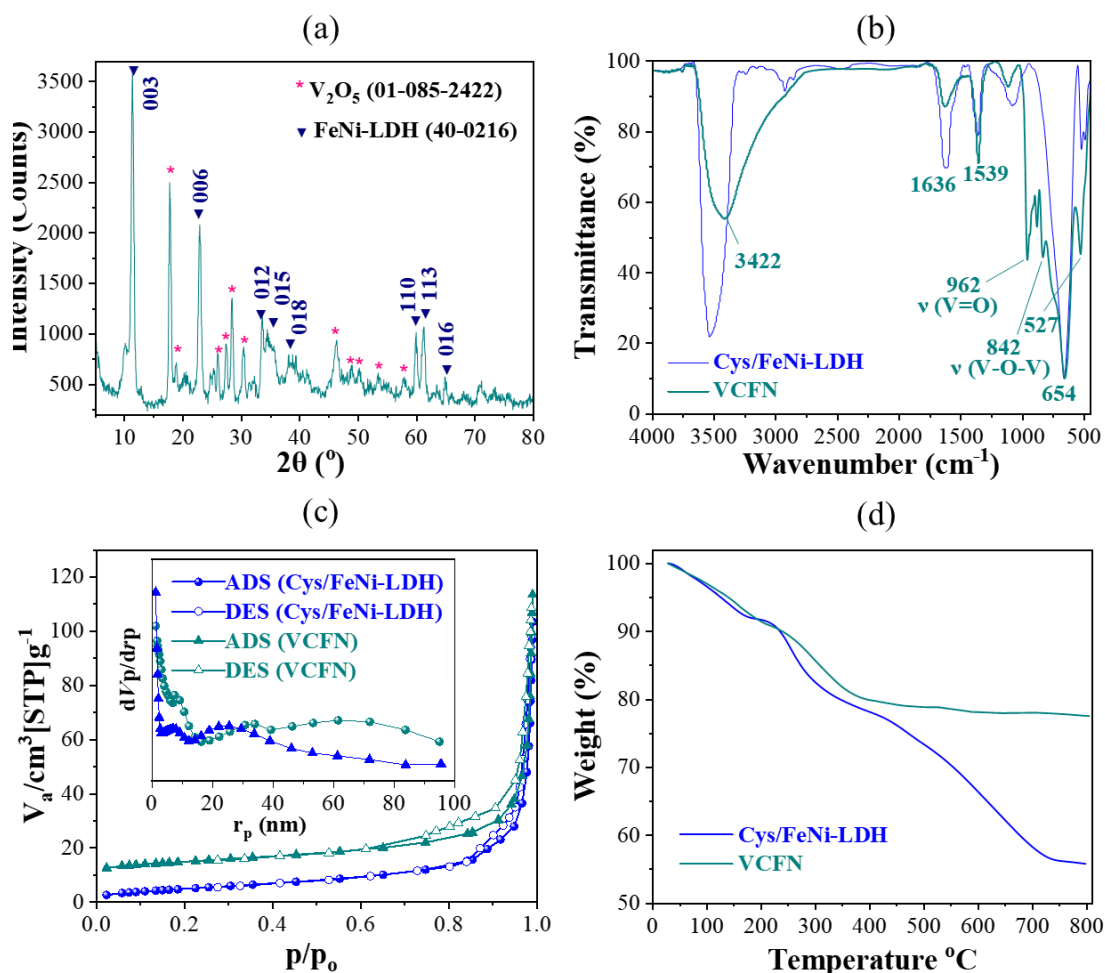


Figure 6.2 (a) XRD patterns of VCFN; (b) FTIR spectra; (c) N_2 adsorption-desorption (inset: pore size distribution); and (d) TGA curves of Cys/FeNi-LDH and VCFN.

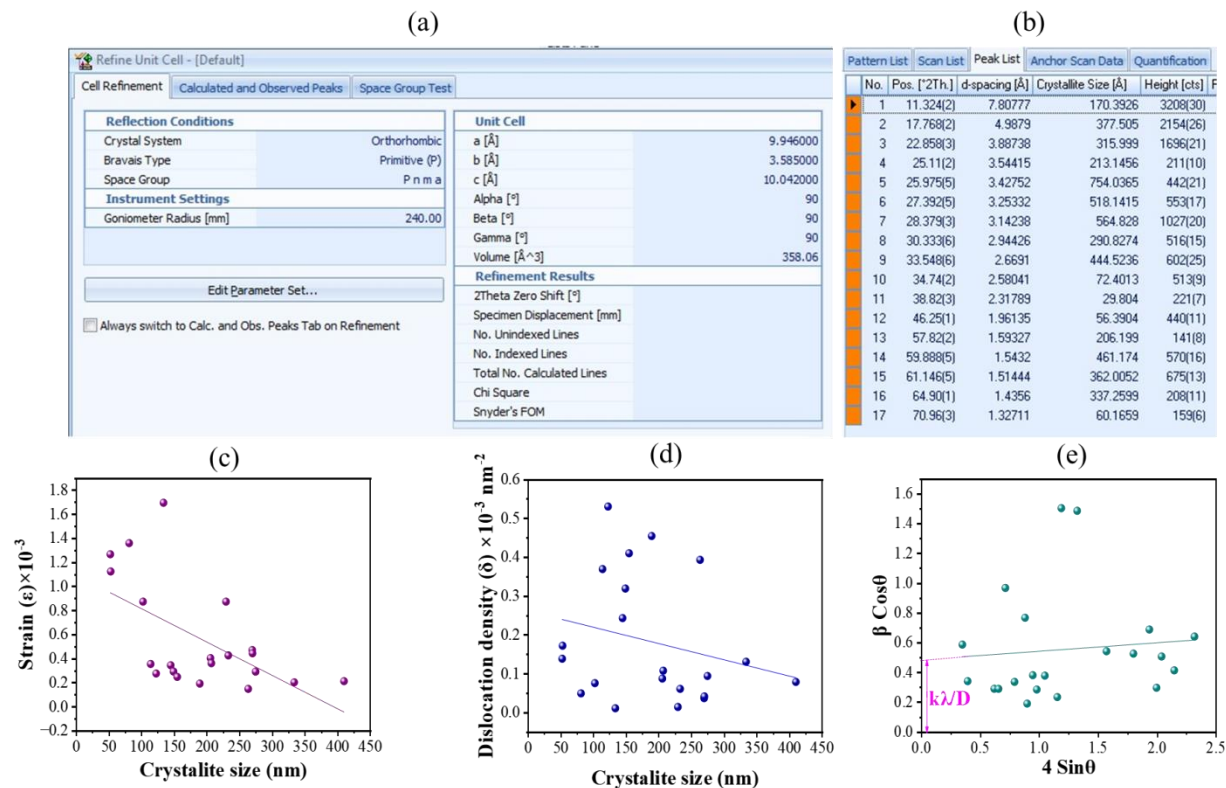


Figure 6.3 (a) Cell refinement information for V_2O_5 in VCFN; (b) d-spacing and crystallite size; (c) strain; (d) dislocation density with respect to crystallite size and (e) Williamson- Hall plot for VCFN.

The FTIR spectra of VCFN, shown in Figure 6.2b, displays distinctive bands that are very similar to those described for compounds that resemble hydrotalcite⁹⁷. The stretching vibrations of the hydroxyl groups (O-H) in FeNi-LDH and the NH_2 groups in cysteine are responsible for the broad and intense band that is centred about 3422 cm^{-1} . This suggests that the composite contains both cysteine and FeNi-LDH³¹⁷. The observation of a weak band at roughly 1636 cm^{-1} is ascribed to the bending vibrations of water molecules inside the FeNi-LDH complex³¹⁸. The lattice vibrations of metal-oxygen-metal (M-O-M), metal-oxygen (M-O), and oxygen-metal-oxygen (O-M-O) links in the brucite-type layer are linked to the peaks detected below 1000 cm^{-1} . Furthermore, distinct bands are seen at 962 cm^{-1} and 527 cm^{-1} , which are associated with the vibrations of vanadium-oxygen double bonds (V=O) and vanadium-oxygen-vanadium (V-O-V) bonds, respectively³¹⁹. This in-depth spectral research sheds light on the structural elements of the VCFN composite and validates its existence.

The VCFN sample's N_2 adsorption-desorption isotherms, which are shown in Figure 6.2c, offer important new information about the composite material's textural characteristics. Based on the

International Union of Pure and Applied Chemistry (IUPAC) classification scheme, the sample's isotherms show Type IV behaviour, which is typical of materials that are mesoporous. Furthermore, the mesoporous character of the material is further confirmed by the occurrence of an H1-type hysteresis loop at high relative pressures. Type IV isotherms show that the VCFN composite has a porous structure with pores in the range of 2 to 50 nm³²⁰. These isotherms are generally associated with materials that have well-defined mesopores. Mesoporous materials with narrow pore size distributions and high pore connectivity are frequently linked to the Type H1 hysteresis loop, which is observed at high relative pressures and is indicative of a uniform pore size distribution and cylindrical pore shape³²¹. According to the IUPAC classification, Figure 6.2c (inset) shows that the VCFN samples consist of two porous materials: macro (>50 nm) and meso (2-50 nm)³²⁰.

The thermal stability and decomposition behaviour of the synthesized hybrids up to 800 °C in an air atmosphere were evaluated by thermogravimetric analysis (TGA) as shown in Figure 6.2d. The weight loss pattern in the Cys/FeNi-LDH composite (Figure 6.2d) is three-staged: The first phase of weight loss has an approximate 8% weight loss and happens between 25 °C and 200 °C. The removal of physically adsorbed (physisorbed) and intercalated water molecules from the composite is the cause of this loss. The second stage, which accounts for a 15% weight loss, happens between 200 and 450 °C. During this phase, functional groups in FeNi-LDH undergo dehydroxylation and decarboxylation, which releases CO³²². The last stage begins beyond 450 °C, resulting in an additional 28% weight loss. The substantial weight loss can be attributed to the further decarboxylation and decarbonation, which ultimately result in the creation of mixed metal oxides. Decarbonation is the process of removing carbon dioxide (CO₂), which, in conjunction with decarboxylation, denotes the disintegration of organic components and the production of stable metal oxides at higher temperatures. These stages highlight the composite's decomposition pattern and thermal stability, revealing the loss of water, organic functional groups, and the subsequent formation of metal oxides as the temperature increases³²³. The VCFN composite (Figure 6.2d) exhibits a similar three-stage weight loss trend. However, the formation of V₂O₅ on Cys/FeNi-LDH enhances the thermal stability of the VCFN composite, as illustrated in Figure 6.2d.

The scanning electron microscopy (SEM) images of the VCFN samples, shown in Figures 6.4a, 6.4b reveals that V₂O₅ nanoparticles are positioned on the surface of the round, disk-like structures of Cys/FeNi-LDH, likely due to strong interactions between vanadium and cysteine molecules on the FeNi-LDH surface, which promote the growth and attachment of V₂O₅ particles. Cysteine, a thiol-containing amino acid, strongly coordinates with transition metals through one or more functional groups, such as thiol (-SH), carboxylic acid/carboxylate (-COOH or -COO⁻), and amino groups³¹⁰. It is hypothesized that cysteine molecules coordinate with Fe and Ni on the surface of Fe-Ni layered double hydroxides (Cys/FeNi-

LDH), potentially leaving one or two functional groups unutilized. During the synthesis of VCFN, V_2O_5 particles nucleate and grow by interacting with the remaining functional groups of cysteine molecules attached to the Cys/FeNi-LDH surface, enabling a stable and uniform distribution of V_2O_5 within VCFN.

Figure 6.4c presents the EDX (energy dispersive X-ray) spectrum of VCFN, indicating the presence of vanadium (V), iron (Fe), nickel (Ni), sulfur (S), nitrogen (N), and oxygen (O) within the VCFN structures. The EDX spectrum confirms that a substantial amount of vanadium has been successfully incorporated into the Cys/FeNi-LDH composite. Transmission Electron Microscopy (TEM) images of the VCFN sample, shown in Figure 6.4d, reveal the presence of nanodisk structures observed either in random groups or bundles. The particle size distribution of the VCFN sample is depicted in Figure 6.4e indicating the size range of the nanodisks. Furthermore, elemental mapping (Figure 6.4f) demonstrates the uniformity of the elemental composition and distribution across the VCFN samples. This mapping confirms that the elements are evenly distributed throughout the sample, highlighting the homogeneity of the composite material.

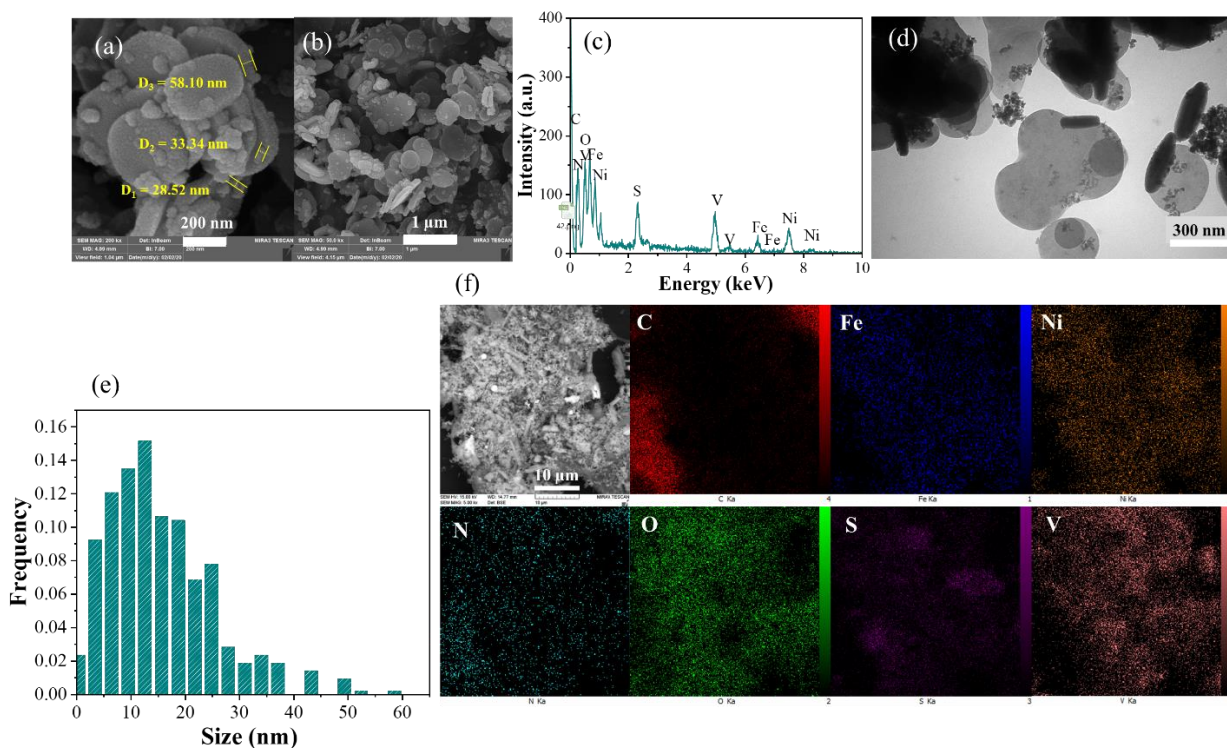


Figure 6.4 (a, b) SEM images; (c) EDX spectrum; (d) TEM image; (e) particle size distribution of V_2O_5 ; and (f) EDS-mapping image of VCFN.

X-ray photoelectron spectroscopy (XPS) was utilized to investigate the surface characteristics and chemical states of the VCFN composite, as shown in Figure 6.5. The full-scan XPS spectra of VCFN (Figure 6.5a) confirm the presence of carbon (C), iron (Fe), nickel (Ni), nitrogen (N), oxygen (O), sulfur (S), and vanadium (V). High-resolution XPS peaks were deconvoluted using CasaXPS and Origin software to further examine the oxidation states of these elements, revealing interactions between the components of the heterostructure. The N1s spectrum (Figure 6.5b) exhibits a main peak at 399.3 eV, associated with sp^3 -hybridized nitrogen atoms in amine (NH_2) functional groups,³²⁴ indicating the presence of nitrogen in these functional groups within the composite. The deconvoluted C1s spectrum (Figure 6.5c) reveals peaks at 284.6 eV (C–C), 287.4 eV (C–O), and 288.3 eV (O–C=O), indicative of the presence of cysteine in the VCFN composite.³²⁵ The O1s spectrum (Figure 6.5d) shows two distinct peaks at 531.1 and 533.3 eV, corresponding to the cysteine C=O group and the M–O bonds (M = Fe, Ni, or V), respectively.³²⁶ The S2p spectrum appears as a doublet, indicating the presence of two distinct sulfur environments in the VCFN composite (Figure 6.5e). The first doublet, at binding energies (BE) of 159.98 eV and 161.18 eV, corresponds to the S 2p_{3/2} and S 2p_{1/2} states, while the second doublet, at 166.84 eV and 168.04 eV, is attributed to sulfur in cysteine.^{327,328} The V2p spectrum (Figure 6.5f) shows peaks at 517.0 eV and 524.2 eV, corresponding to the 2p_{3/2} and 2p_{1/2} levels of V^{5+} , respectively (Figure 6.5f).³²⁹ The Fe2p spectrum (Figure 6.5g) displays two prominent peaks at 712.5 eV and 725.9 eV, assigned to the Fe2p_{3/2} and Fe2p_{1/2} states, respectively.³³⁰ The Ni2p spectrum (Figure 6.5h) shows Ni2p_{3/2} and Ni2p_{1/2} peaks at 856.5 eV and 873.5 eV, respectively. These peaks are accompanied by two spin-orbit doublets and two prominent shake-up satellites at 861.2 eV and 873.5 eV, characteristic of the high-spin Ni^{2+} state in the VCFN composite.³⁰¹ This comprehensive XPS analysis provides detailed insights into the chemical states and interactions of the elements within the VCFN composite, confirming the successful incorporation and interaction of the constituent elements.

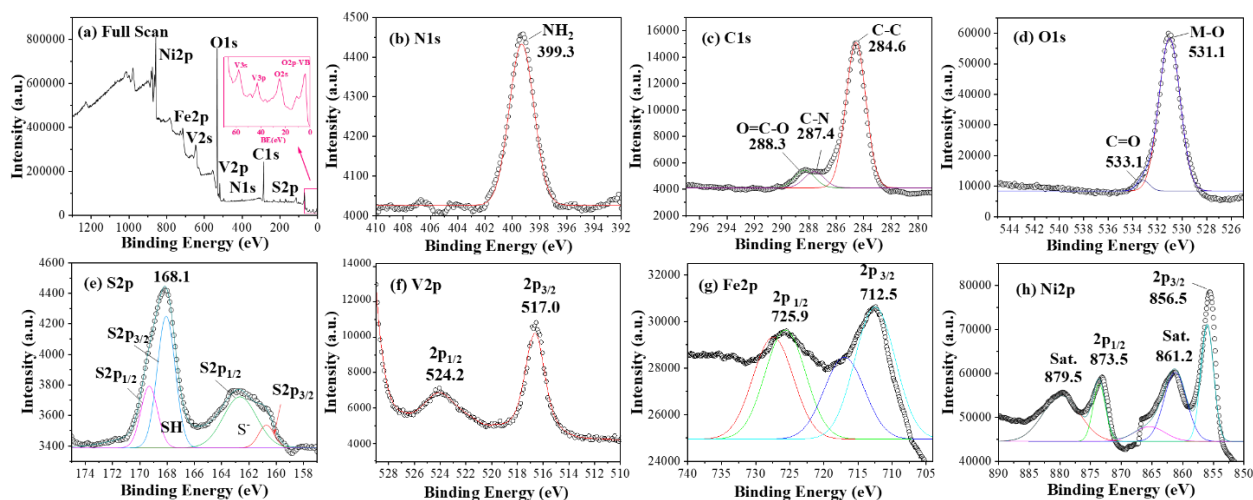


Figure 6.5 XPS spectra of the VCFN sample: (a) Full spectrum, (b) N1s; (c) C1s; (d) O1s; (e) S2p; (f) V2p; (g) Fe2p and (h) Ni2p.

6.3.2 Characterization of glass fiber separator modified with VCFN composite

Figure 6.6a shows the XRD patterns of the bare GF and VCFN/SP/PVDF-modified GF separators. As shown in Figure 6.6a, major peaks corresponding to V_2O_5 and FeNi-LDH (Fig. 1a) are clearly observed. The morphology of both the bare and modified GF separators was analyzed using SEM (Figures 6.6b and 6.6c). The GF separator's three-dimensional network (Figure 6.6b) contains wide gaps measuring a few micrometers, which facilitate the easy diffusion of LiPSs. In contrast, the SEM image of the VCFN/SP/PVDF-modified GF separator (Figure 6.6c) reveals a distinctly altered surface morphology, with the gaps effectively covered and filled by the dense modification material.

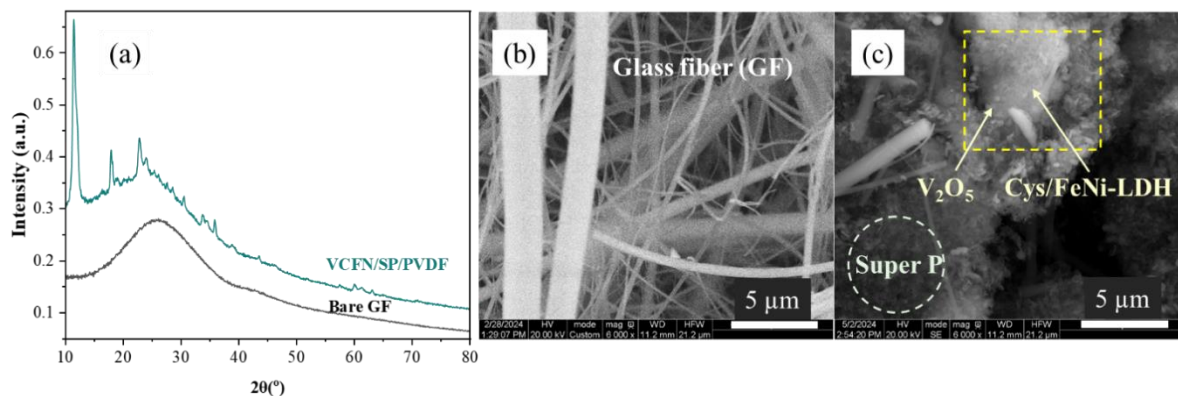


Figure 6.6 (a) XRD patterns; and (b, c) SEM images of the bare GF VCFN/SP/PVDF-modified GF separators.

6.3.3 Electrochemical performance

Figures 6.7 (a) and 6.8a display the discharge/charge voltage profiles for Li-S batteries using bare and modified PP and GF separators at 0.1 C ($1C = 1675 \text{ mA g}^{-1}$). The VCFN/SP/PVDF-modified GF separator exhibits the best performance, delivering an initial discharge capacity of $1401.3 \text{ mAh g}^{-1}$, significantly surpassing bare PP (838.9 mAh g^{-1}) and GF ($1070.1 \text{ mAh g}^{-1}$) separators, and ones modified by SP/PVDF ($1229.3 \text{ mAh g}^{-1}$), (FeNi-LDH)/SP/PVDF ($1230.7 \text{ mAh g}^{-1}$), (Cys/FeNiLDH)/SP/PVDF ($1284.9 \text{ mAh g}^{-1}$) and (V_2O_5 /FeNi-LDH)/SP/PVDF ($1307.8 \text{ mAh g}^{-1}$). Discharge curves exhibit two steps: a high plateau for soluble polysulfides and a low plateau for insoluble Li_2S_2 and Li_2S formation. The formation of the final product, Li_2S , can be estimated using the ratio (R) of the second plateau capacity to the first plateau capacity, where $R = 2x + 1$. Here, x represents the molar fraction (or degree of formation) of Li_2S in the final discharge product mixture of Li_2S and Li_2S_2 . For a complete discharge forming Li_2S as the sole product, $x = 1$ and $R = 3$. The R values calculated from the first discharge curves of the batteries are 2.54, 2.22, 2.30, and 2.33 for the VCFN/SP/PVDF, (V_2O_5 /FeNi-LDH)/SP/PVDF, (Cys/FeNi-LDH)/SP/PVDF, and (FeNi-LDH)/SP/PVDF-modified GF separators, corresponding to degrees of Li_2S formation of 0.770, 0.609, 0.650, and 0.665, respectively (Table 6.1). Clearly, the degree of Li_2S formation is the highest for the cell with the VCFN/SP/PVDF-modified separator. Interestingly, the cell with the bare GF separator also shows a relatively high R value of 2.51, corresponding to a degree of Li_2S formation of 0.755. However, its discharge curve exhibits a long low-voltage tail after $\sim 1077 \text{ mAh g}^{-1}$, and the subsequent charging capacity (1106 mAh g^{-1}) is much lower than the discharge capacity ($1282.6 \text{ mAh g}^{-1}$) (Figure 6.8b). This behavior suggests the formation of relatively large Li_2S_2 particles, leading to a substantial overpotential for the conversion of Li_2S_2 to Li_2S within the particle core. As a result, the reaction is inhibited above the cutoff voltage of 1.7 V at the later stage. During charging, the $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ formed in the core cannot be fully oxidized due to poor electrical and ionic transport, leading to a significantly reduced charge capacity.

In contrast, the cells with modified GF separators do not exhibit pronounced low-voltage discharge tails, and their subsequent first charge capacities closely match their respective discharge capacities (Figure 6.7a). This suggests a more uniform distribution of sulfur species. Particularly, the cell with the VCFN/SP/PVDF-modified GF separator achieves the highest degrees of Li_2S formation during discharge and dissolution during charge. This indicates the most uniform distribution and efficient electrochemical reactions of sulfur species, attributed to the beneficial effects of the modification layer, such as polysulfide trapping and catalytic activity. Additionally, the energy barrier at the onset of the second discharge plateau²⁷⁶ is significantly reduced from 22 mV for the bare GF separator to 7 mV for the VCFN/SP/PVDF-modified GF separator (Figure 6.8b). This reduction underscores the catalytic effect of VCFN, attributed to the strong

interactions of transition metals (V, Fe, and Ni) with sulfide species (S_n^{2-} , $n = 1$ to 8).^{295,296} These interactions effectively lower the activation energy required for converting soluble polysulfides at the end of the first plateau (e.g., Li_2S_4) into insoluble Li_2S_2 and Li_2S .

Figures 6.7b and 6.8c illustrate the cycling stability of the cells at 0.1C. The cell using the VCFN/SP/PVDF-modified GF separator retains 89.1% of its initial capacity after 100 cycles while maintaining a high coulombic efficiency of 99.77%. This performance significantly surpasses that of cells with bare PP and bare GF separators (Figure 6.8), underscoring the effectiveness of the VCFN/SP/PVDF-modified GF separator in mitigating the LiPS shuttle effect. However, the VCFN/SP/PVDF-modified PP separator exhibits inferior performance compared to the VCFN/SP/PVDF-modified GF separator, likely due to poor adhesion of the modification layer on the nonpolar surface of the PP separator. Figures 6.7c and 6.8d show the rate performance of cells with different separators. Cells with VCFN/SP/PVDF-modified GF separators demonstrated improved rate performance compared to other separators, indicating the enhanced redox kinetics of the battery.

Cells with the VCFN/SP/PVDF-modified GF separator were fabricated and tested at elevated sulfur loadings of 3.0 and 4.5 $mg\ cm^{-2}$ (Figure 6.7d). Compared to a cell with a sulfur loading of 1.67 $mg\ cm^{-2}$, which achieved an initial capacity of 1035.2 $mAh\ g^{-1}$ at 0.5C, the higher-loading cells still exhibited impressive initial capacities of 951.2 and 905.3 $mAh\ g^{-1}$, respectively. These results show the effectiveness of the modified separator in enhancing battery performance at increased sulfur loadings, a critical factor for achieving high energy density.

Figures 6.7e and Figure 6.8g shows the long-term cycling performance of cells with bare PP, bare GF and VCFN/SP/PVDF-modified GF separators at 0.5 C. The VCFN/SP/PVDF-modified GF separator delivers 1035.2 $mAh\ g^{-1}$ initially and retains 920.1 $mAh\ g^{-1}$ (88.9%) after 300 cycles, with a low capacity decay rate of 0.039% per cycle. This performance is significantly superior to cells with bare separators and surpasses most previously reported Li–S batteries utilizing modified GF separators¹⁸⁹ (Figure 6.8e). The enhanced specific capacity and long-term stability of cells with VCFN/SP/PVDF-modified GF separators can be attributed to the synergistic effects of V_2O_5 , cysteine, and FeNi-LDH in VCFN. The FeNi-LDH/SP/PVDF-modified separator exhibits notable catalytic activity and LiPS trapping due to the presence of Fe, Ni, and functional hydroxyl groups [35]. Incorporating V_2O_5 ($(V_2O_5/FeNi-LDH)/SP/PVDF$) or modifying FeNi-LDH with cysteine ($(Cys/FeNi-LDH)/SP/PVDF$) enhances performance (Figure 6.7a, Figure 6.8, and Table 6.1), largely due to catalytic and LiPS-trapping effects of V_2O_5 and the amino and carboxylate groups in cysteine^{160,311}.

In VCFN, the thiol, carboxylic acid/carboxylate, and amino groups of cysteine on the surface of Cys/FeNi-LDH strongly interact with vanadium atoms on V_2O_5 , promoting its stable and uniform

dispersion within VCFN (Figures 6.4a, 6.4b). This improved dispersion enhances V_2O_5 's capacity to trap LiPSs and catalyze the reduction of sulfur and LiPSs, further boosting electrochemical performance.

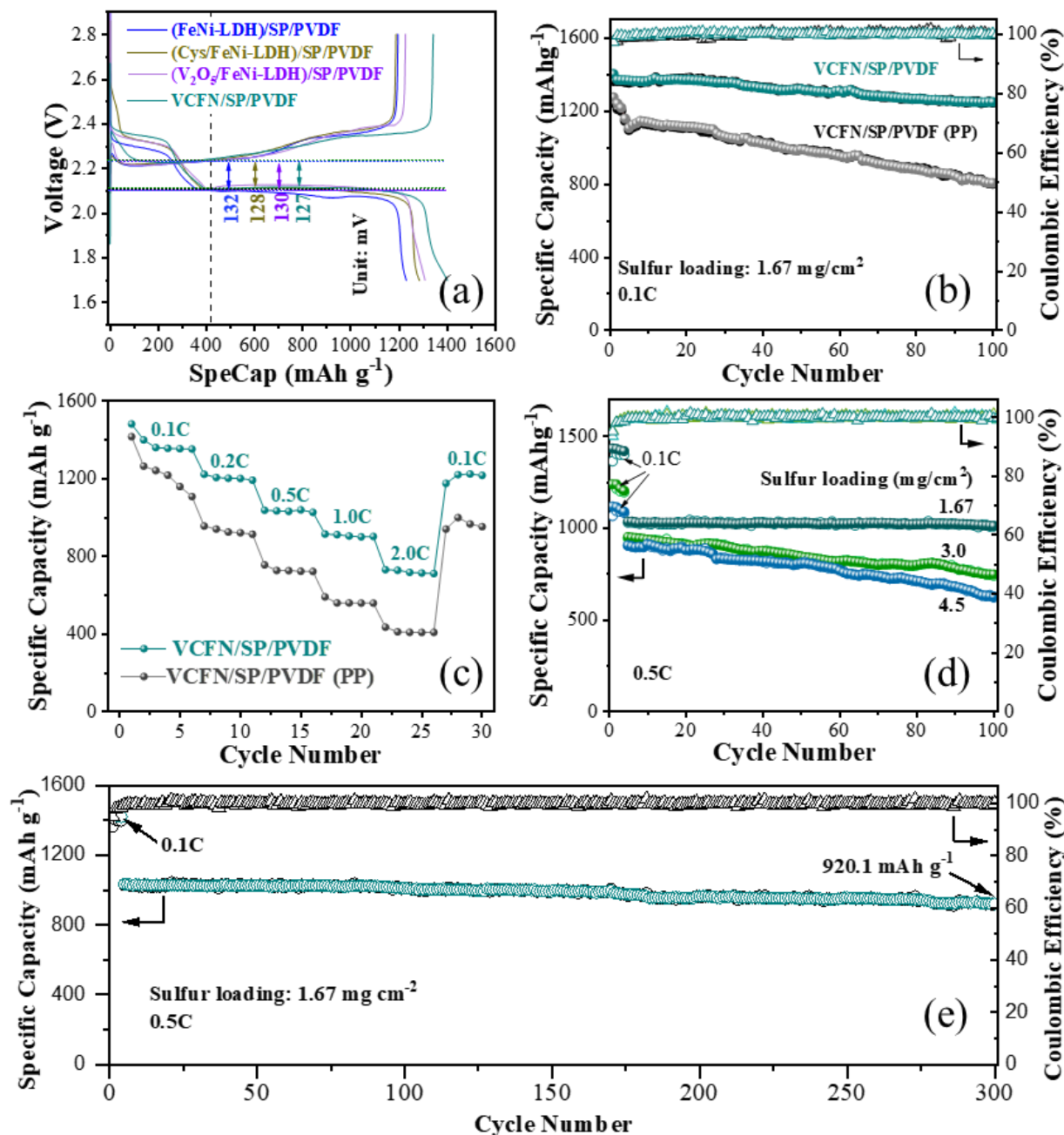


Figure 6.7 (a) Discharge/charge curves of cells with different separators at 0.1C; (b) cycling performance of cells with VCFN/SP/PVDF-modified GF and pp separators over 100 cycles at 0.1C; (c) rate performance of cells with VCFN/SP/PVDF-modified GF and pp separators; (d) cycling performance of cells with the VCFN/SP/PVDF-modified GF separator at a current density of 0.5C, with sulfur loadings of 1.67 mg cm⁻² (E/S = 16 μ L mg⁻¹), 3.00 mg cm⁻² (E/S = 9 μ L mg⁻¹), and 4.50 mg cm⁻² (E/S = 6 μ L mg⁻¹); (e) long-term cycling performance of the cell with the VCFN/SP/PVDF-modified GF separator at 0.5C for 300 cycles.

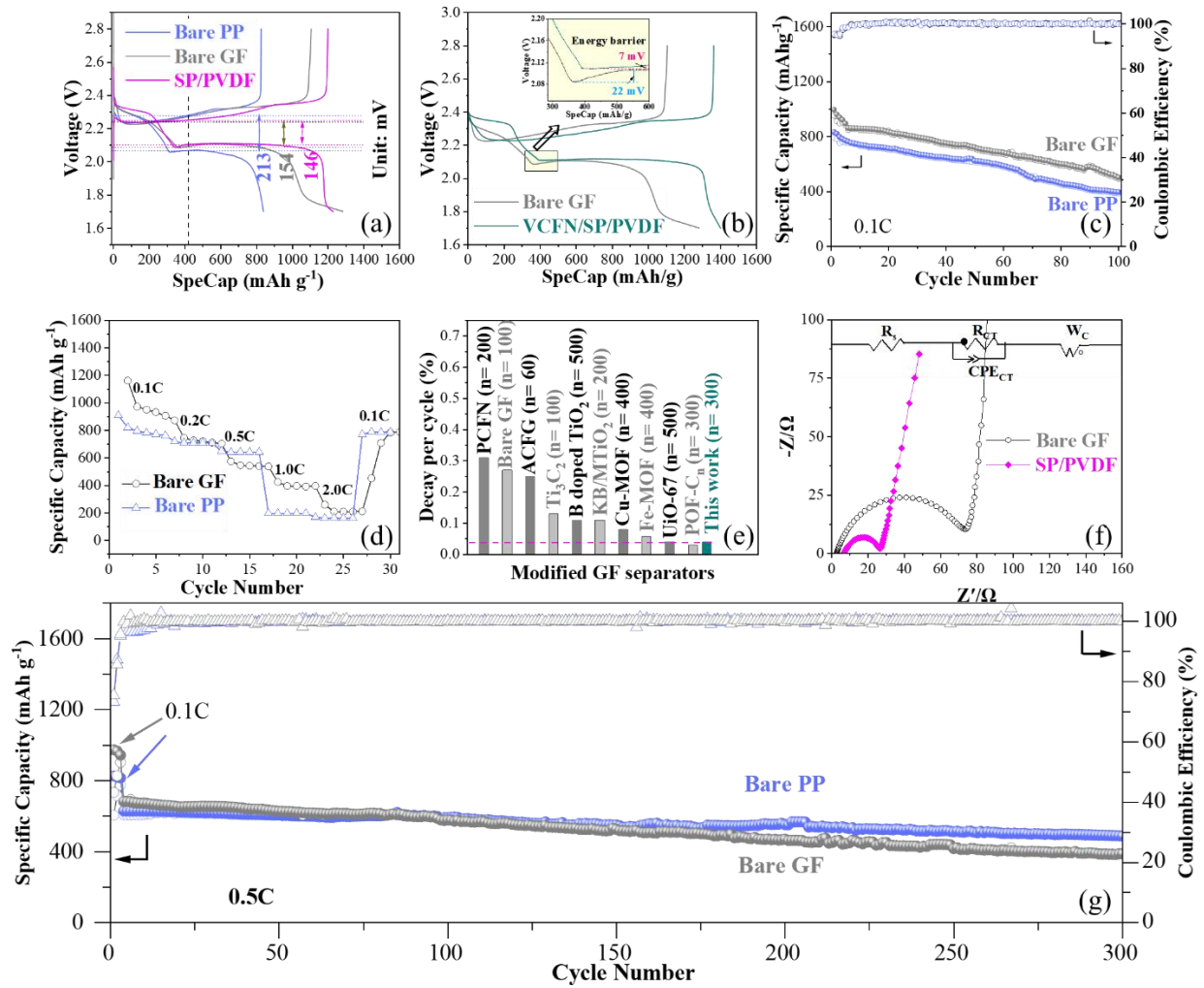


Figure 6.8 (a) Discharge/charge curves of cells with different separators at 0.1C; (b) comparison of the discharge/charge curves for cells equipped with a bare GF separator and a VCFN/SP/PVDF-modified GF separator. (Inset: Energy barrier of the potential well at the onset of the second plateau.) (c) cycling performance of cells with bare pp and GF separators over 100 cycles at 0.1C; (d) rate performance of cells with bare pp and GF separators; (e) comparison of the capacity decay rate (per cycle) of VCFN/SP/PVP-modified GF separator and previously reported materials^{63,81,189,231,232,234–236,331}; (f) EIS Nyquist plots of cells with bare GF and SP/PVDF-GF modified separators and (g) cycling stability comparison of bare PP and bare GF separators at 0.5C for 300 cycles.

Electrochemical impedance spectroscopy (EIS) was employed to evaluate the ion transport properties of the separators (Figures 6.9a and Figure 6.8f). The medium-frequency semicircle in the EIS spectra represents charge transfer resistance (R_{ct}), while the low-frequency linear region corresponds to Li-ion diffusion, and the high-frequency intercept indicates the cell's ohmic resistance (R_s)¹⁸⁹. EIS data show

that the VCFN-modified GF separator achieves the lowest R_{ct} (15.30 Ω) among all separators. The ionic conductivity (σ) values of separators of the cells with different separators were calculated³²⁹ using the bulk resistance (R_s) obtained from the x-axis intercepts of the Nyquist plot (Fig. 6a and Fig. S11f). Among all the modified GF and PP separators, the VCFN/SP/PVDF-modified GF separator demonstrated the highest conductivity (Table 6.2), comparable to that of the bare GF separator. This exceptional ion transport property is likely attributed to the partial coverage of the disk-like Cys/FeNi-LDH structures with V_2O_5 particles, which prevents disk stacking and facilitates the formation of channels for efficient Li-ion transport through the VCFN/SP/PVDF modification layer. Although the bare GF separator shows high ion conductivity, its high charge transfer resistance (R_{ct}) results in significant overpotentials during operation, which decreases energy efficiency¹⁷³.

Figure 6.9b shows cyclic voltammetry (CV) analysis of cells with bare and VCFN/SP/PVDF-modified GF separators at 0.1 mV s^{-1} (1.7–2.8 V). Both cells display redox peaks characteristic of sulfur cathodes: Peak A (~2.2–2.3 V), corresponding to the reduction of S_8 to long-chain LiPSs; Peak B (~1.9–2.0 V) representing the conversion of long-chain to short-chain LiPSs; and Peak C (~2.4–2.5 V), associated with the oxidation of Li_2S to S_8 . The cell with the VCFN/SP/PVDF-modified separator exhibits reduced polarization and enhanced polysulfide conversion, as indicated by its higher reduction peak intensities and lower oxidation potentials compared to the bare GF separator. To assess the Li-ion diffusion of the cells, we compared the CV curves obtained from the cells with the bare GF and VCFN/SP/PVDF-modified GF separator at scanning rates ranging from 0.2 to 0.6 mV s^{-1} , as shown in Figures 6.9c and 6.9d. The Li-ion diffusion coefficients were calculated using the Randles–Sevcik equation, based on the slopes derived from linear fitting of the CV curves (Figures 6.9e–6.9g). For both cells, distinct pairs of redox peaks were observed, indicating the electrochemical reactions involving sulfur (S_8), long-chain lithium polysulfides (Li_2S_x , $3 \leq x \leq 8$), and the insoluble short-chain Li_2S_2/Li_2S species³³². Notably, the VCFN/SP/PVDF-modified GF separator exhibited higher Li-ion diffusion coefficients across all peaks compared to the bare GF (Figure 6.9h). This indicates that this modified separator enables faster Li-ion diffusion, likely due to the presence of channels in VCFN that promote efficient Li-ion transport, as discussed earlier.

Tafel analysis of CV curves has been used to investigate the electrochemical kinetics of Li-S batteries²⁴³. The Tafel plots for cells using the bare and VCFN/SP/PVDF-modified GF separators (Figure 6.10a), derived from their CV scans at 0.2 mV s^{-1} , show that the thermodynamic potential for the reduction of S_8 to lithium polysulfides (Peak A) is higher for the modified separator (2.57 V) compared to the bare GF separator (2.39 V). This indicates that V_2O_5 facilitates the reduction of S_8 by stabilizing (or trapping) the lithium polysulfides formed³³³. The Tafel slope for Peak A is larger for the cell with the modified separator (Figure 6.10b), likely due to the overlapping of two reaction pathways: one involving sulfur

species in contact with V_2O_5 within the modification layer, which occurs at higher potentials, and the other involving species in the cathode that are not in contact with V_2O_5 , proceeding at lower potentials similar to the bare GF separator.

Conversely, the thermodynamic potential for the oxidation of Li_2S (Peak C) remains unchanged for both separators (2.12 V), indicating that V_2O_5 does not facilitate this process. For the modified separator, the Tafel slope for Peak C is slightly larger (Figure 6.10c), and peak position shifts to a higher potential, suggesting that V_2O_5 may make the oxidation of Li_2S thermodynamically more difficult due to its stabilizing (or trapping) effect on Li_2S , Li_2S_2 , and polysulfides²⁹⁶. The presence of these sulfur species in two distinct environments, within the modification layer (in contact with V_2O_5) and the cathode, results in different thermodynamic potentials. This leads to the broadening of Peak C and a larger apparent Tafel slope for the cell with the modified separator. Consequently, the Tafel slopes for the cell with the modified separator may not accurately reflect the true reaction kinetics due to the varied environments of the sulfur species within the cathode and modification layer.

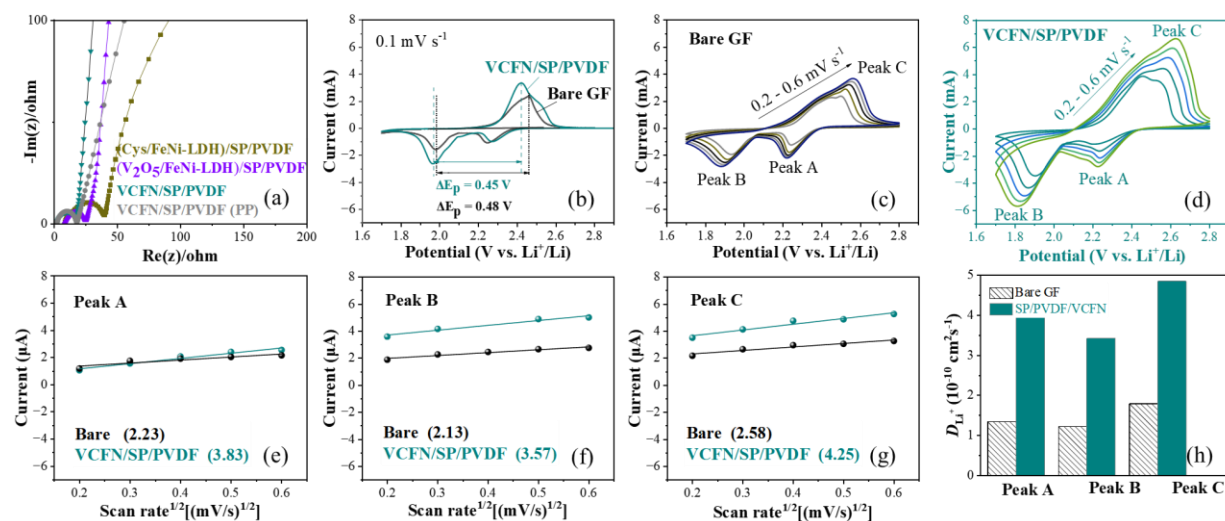


Figure 6.9 (a) EIS Nyquist plots of cells; (b) CV curves of cells at a scan rate of 0.1 mV s^{-1} ; (c, d) CV curves of cells recorded at varying scan rates ($0.2 - 0.6 \text{ mV s}^{-1}$) for bare GF and VCFN/SP/PVDF-modified GF separator; (e-g) peak current dependence on scan rate; (h) Li diffusion coefficients at different peak positions calculated using the Randles-Sevcik equation.

Table 6.2 The values of EIS fitting and the conductivity measurement of the separators.

Modified separator		R_s (W)	R_{ct} (W)	d (mm)	s (S, cm^{-1})
GF	Bare ^a	2.69	70.95	280	3.7×10^{-2}
	(Cys/FeNi-LDH)/SP/PVDF ^a	8.20	31.38	311	1.3×10^{-2}
	(V ₂ O ₅ /FeNi-LDH)/SP/PVDF ^a	7.91	17.20	310	1.4×10^{-2}
	VCFN/SP/PVDF ^a	2.70	15.30	311	4.1×10^{-2}
PP	VCFN/SP/PVDF ^b	6.24	15.71	54	3.1×10^{-3}

^a A GF separator with a thickness of ~ 280 μm was used.

^b A PP separator with a thickness of ~ 25 μm was used.

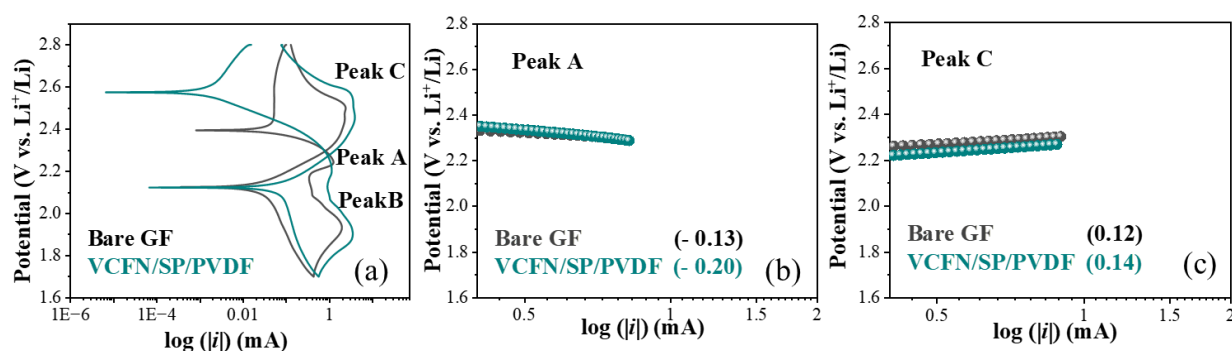


Figure 6.10 (a) Tafel plots for cells with bare and VCFN/SP/PVDF-modified GF separators, derived from their CV scans at 0.2 mV s^{-1} ; (b, c) corresponding Tafel plots for Peak A and Peak C, respectively, with slope values indicated in parentheses.

Vanadium in V_2O_5 in VCFN is in a high oxidation state and may potentially be reduced to lower oxidation states during battery operation.³³³ To investigate this possibility, a Li-S battery using the VCFN/SP/PVDF-modified GF separator was disassembled in an argon-filled glove box after the first discharge at 0.1C. The separator was carefully removed and dried in a vacuum oven at 50°C for 5 hours. XPS measurements were performed on the separator to analyze its chemical composition and compare it with the fresh state (Figure 6.11a and Figure 6.12). In comparison to pure VCFN, which displays $\text{V}2\text{p}_{3/2}$ and $\text{V}2\text{p}_{1/2}$ peaks at 517.0 eV and 524.2 eV for V_2O_5 , respectively, the fresh VCFN/SP/PVDF-modified GF separator shows a notable positive shift in these peaks to 518.6 eV and 526.0 eV. This shift is primarily attributed to interactions between the fluorine atoms in the PVDF binder and vanadium atoms, which alters the local electronic environment and binding energy. After the first discharge, the $\text{V}2\text{p}_{3/2}$ and $\text{V}2\text{p}_{1/2}$ peak of the separator shifted to 517.7 eV and 525.5 eV, which are still characteristic $\text{V}2\text{p}$ peaks,³²⁹ indicating that V_2O_5 was not reduced into lower oxidation states. The observed shift in the peak positions is most likely due to the displacement of PVDF on the V_2O_5 surface by Li_2S and other sulfide species.

To assess structural changes in the modification layer after extensive cycling, the separator from a Li-S battery cycled 100 times at 0.1C was examined. XRD analysis (Figure 6.11b) of the cycled separator shows characteristic diffraction peaks of V_2O_5 and NiFe-LDH, confirming that the bulk structures of V_2O_5 and NiFe-LDH remain intact. Additionally, the SEM image of the cycled separator (Figure 6.11c) shows that the VCFN particles remain intact on the glass fiber surface, along with the SP particles. The LiPS trapping ability of VCFN was evaluated using a Li_2S_6 solution as a representative for LiPSs. As shown in Figure 6.11d, the brown color of the Li_2S_6 solution changed noticeably to nearly colorless upon the addition of VCFN, indicating its strong capacity to adsorb LiPSs. This observation is further supported by the UV-Vis spectra, which show a significant decrease in the absorption peak at 265 nm for Li_2S_6 after the addition of VCFN. The strong LiPS trapping capability of VCFN contributes to the remarkable specific capacity and cycling stability of the Li-S battery using the VCFN/SP/PVDF-modified GF separator.

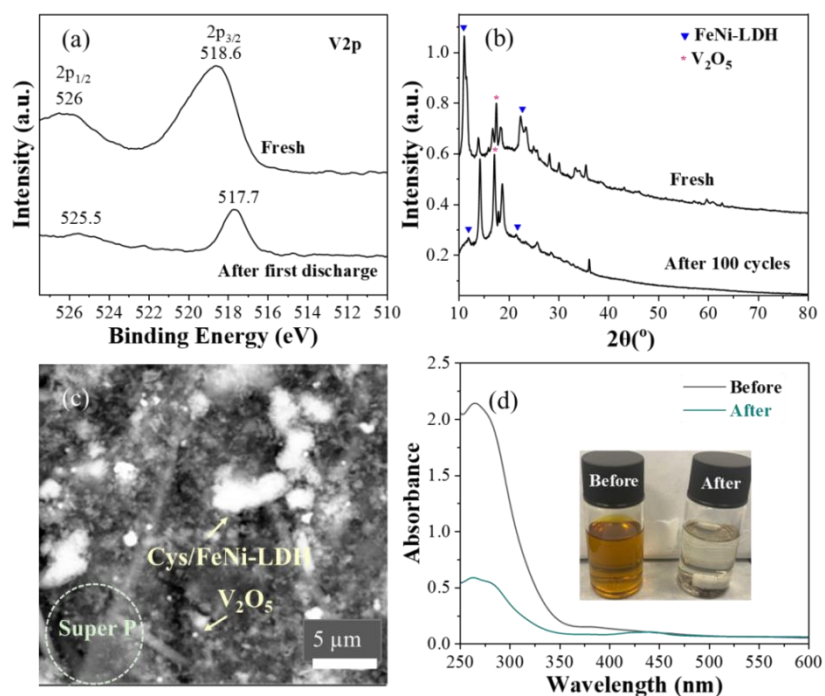


Figure 6.11 (a) High-resolution XPS spectra of V2p and (b) XRD patterns of the VCFN/SP/PVDF-modified GF separators: fresh and after first discharge at 0.1C; (c) SEM image of VCFN/SP/PVDF-modified GF separator after 100 charge-discharge cycles at 0.1C in the discharged state; (d) UV-vis spectra of the Li_2S_6 solution before and after adsorption by VCFN. Inset photo shows the color change of Li_2S_6 solution (4 mL, 0.02 M in DOL/DME) before and after adding 100 mg VCFN.

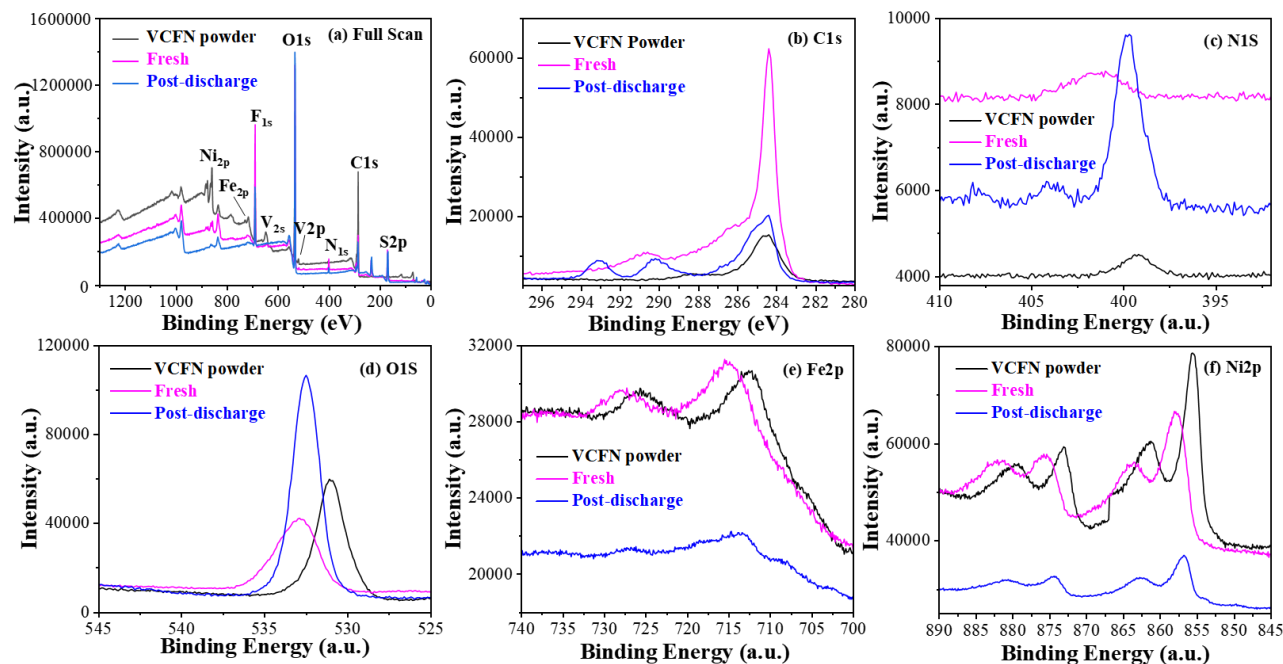


Figure 6.12 Comparison of XPS spectra of the powder VCFN, modified separator (fresh and after the first discharge): (a) Full spectrum, (b) N1s; (c) C1s; (d) O1s; (e) S2p; (f) V2p; (g) Fe2p and (h) Ni2p.

6.4 Conclusions

In this study, we developed a novel ternary composite, $\text{V}_2\text{O}_5/\text{Cys}/\text{FeNi-LDH}$ (VCFN), as a separator modifier to enhance the performance of Li-S batteries. The synthesis of VCFN involved the uniform deposition of V_2O_5 nanoparticles onto cysteine-modified FeNi-LDH nanodisks, facilitated by the strong coordination between cysteine's functional groups and vanadium atoms. The resulting heterostructure provided multiple synergistic benefits: effective LiPS trapping, catalytic conversion of LiPSs, and improved Li-ion transport, all contributing to significant enhancements in the electrochemical performance of Li-S batteries.

Electrochemical evaluations revealed that cells incorporating the VCFN-modified GF separator exhibited an impressive initial discharge capacity of $1035.2 \text{ mAh g}^{-1}$ at 0.5C and retained 920.1 mAh g^{-1} after 300 cycles, corresponding to a low capacity decay rate of 0.039% per cycle. The superior performance of the VCFN-modified separator was further demonstrated in high sulfur loading cells (up to 4.5 mg cm^{-2}), where stable capacities were maintained, highlighting its potential for high-energy-density applications. Compared to bare and other modified separators, the VCFN-modified separator showed reduced overpotential, improved rate capability, and higher Li-ion diffusion coefficients. These enhancements are

attributed to the synergistic effects of V_2O_5 's catalytic activity, FeNi-LDH's high surface area, cysteine's essential role as a linker between V_2O_5 and FeNi-LDH, the polysulfide trapping capability of all three components, and the unique porous structure of VCFN that promotes efficient Li-ion transport. Structural and compositional analyses, including XPS, XRD, and SEM, confirmed the stability of the VCFN composite after prolonged cycling, indicating the durability of the modification layer under operational conditions. The ability of VCFN to adsorb LiPSs was confirmed by UV-vis spectroscopy, which demonstrated its strong LiPS trapping capability.

Overall, the successful application of VCFN as a separator modifier in Li-S batteries offers a promising approach to mitigating the LiPS shuttle effect and improving long-term cycling stability. This work provides valuable insights into the rational design of advanced separator materials for next-generation high-performance Li-S batteries. Future research could explore optimization of the VCFN structure and its application in other battery systems.

Chapter 7. Conclusions and Future Outlook

7.1 Conclusions

This thesis presents the development of a diverse array of innovative materials, including polymers, surfactants, and metal oxides, for the modification of GF separators to enhance the electrochemical performance of LSB. A primary focus of this research is mitigating the polysulfide shuttle effect—a critical challenge in LSB technology. This effect arises from the dissolution and migration of lithium polysulfides (Li_2S_4 – Li_2S_8) between the cathode and anode, resulting in severe capacity fading and posing significant obstacles to the commercial viability of LSBs. The modifications introduced in this study were strategically designed to enhance polysulfide retention, improve electron transport, and ensure the structural stability of the glass fiber separators:

In Chapter 3, a melamine-based nanoscale porous organic framework (POF) was synthesized and used as a separator modifier. The intrinsic porosity and chemical functionality of the POF allowed it to act as a physical barrier while providing abundant adsorption sites for polysulfides. This adsorption ability was attributed to the nitrogen-rich framework of the POF, which creates strong interactions with lithium polysulfides through Lewis acid-base interactions and hydrogen bonding. This modification led to significant improvements in specific capacity and cycling stability, as the POF effectively suppressed polysulfide migration, preserving active material within the cathode region.

In Chapter 4, the separator was modified with CR-CTA, aiming to create a multi-functional layer capable of simultaneously adsorbing and blocking polysulfides. CR, a dye with multiple sulfonate groups, interacts strongly with lithium ions, providing a chemical “trap” for polysulfides, while CTAB, a surfactant, enhances the uniformity and stability of the coating on the GF separator. Together, these components form a synergistic layer that blocks the physical passage of polysulfides.

Chapter 5 expanded on this approach by incorporating SnO_2 nanoparticles alongside CR as a separator modification. SnO_2 , known for its catalytic properties, provided additional functionality to the separator by promoting the conversion of lithium polysulfides back to their insoluble forms. The CR/ SnO_2 -modified GF separator exhibited high capacity retention over long cycling periods, suggesting that the synergistic combination of adsorptive and catalytic effects is a promising strategy for improving Li-SB performance.

In Chapter 6, a ternary composite of V_2O_5 , cysteine, and FeNi-LDH (called VCFN) was applied to the GF separator to create a highly functionalized and structurally robust layer. Each component within the

VCFN composite contributed distinct properties: V_2O_5 enhanced electronic conductivity, cysteine provided sites for polysulfide binding, and FeNi-LDH, with its layered double hydroxide structure, added mechanical stability and further adsorptive capability. The VCFN-modified separators showed considerable improvements in cycling stability and specific capacity, as the composite layer efficiently trapped polysulfides, prevented their migration, and maintained structural integrity over prolonged cycling.

These cells demonstrate superior long-term stability compared to most previously reported LSBs with GF separators modified with other materials (Table 7.1), including UiO-67,²³¹ Fe-MOF and Cu-MOF,³³⁴ Ketjen Black & mesoporous TiO_2 (KB/MTiO₂),²³⁶ B-doped TiO_2 ,²³² Ti_3C_2 ,²³⁴ activated porous carbon on glass fiber (ACGF),⁸¹ and porous carbon nanofibers (PCNFs)³³¹ (Table 7.1).

Table 7.1 Comparison of the capacity decay rate per cycle of modified GF separators developed in this study with previously reported materials.

GF modification	Binder	Thickness (μm) of layer on GF	Decay per cycle (%)
Bare GF ¹⁴⁸	No binder	260*	0.27
UiO-67 ²²⁹	No binder	19	0.04
Cu-MOF ²³⁰	PVDF	18	0.08
Fe-MOF ²³⁰	PVDF	22	0.06
Ketjen Black & mesoporous TiO_2 (KB/MTiO ₂) ²³⁶	PVDF	10	0.11
B doped TiO_2 ²³²	PVDF	46	0.11
Ti_3C_2 ²³⁴	PVDF	-	0.13
Activated porous carbon on glass fiber (ACGF) ⁸¹	PVDF	-	0.25
Porous carbon nanofibers (PCFN) ²³³	PVDF	25	0.31
POF-C _n (This work, Chapter 3)	PVP	28	0.03
CR-CTA (This work, Chapter 4)	PVP	28	0.05
CR-SnO ₂ (This work, Chapter 5)	PVP	28	0.06
VCFN (This work, Chapter 6)	PVDF	31	0.04

To evaluate the performance of the GF-modified separators developed in this study, two critical parameters were analyzed: the long-term stability of the cells and their ionic conductivity, both of which are pivotal for the efficiency and commercial viability of LSBs. Among the materials tested, the POF-C₈-modified separator demonstrated the best long-term stability, with the lowest capacity decay per cycle

(Table 7.1). This superior performance is attributed to its robust structural and electrochemical properties, which effectively minimize degradation during extended charge-discharge cycling, ensuring consistent and reliable electrochemical behavior.

In contrast, the CR-SnO₂/SP/PVP-modified separator emerged as the best-performing material in terms of ionic conductivity, as revealed by EIS measurements (Figure 7.1a). This separator exhibited the lowest R_s , highlighting its efficiency in facilitating ionic transport. The enhanced conductivity results from the synergistic contributions of its components: SnO₂ nanoparticles and CR provide high-surface-area pathways for lithium-ion transport, while the SP/PVP matrix improves structural stability and wettability. Additionally, a detailed analysis of the lithium-ion diffusion coefficient (D) derived from peak currents at varying scan rates showed that the CR-SnO₂/SP/PVP-modified separator achieved significantly higher D values at all measured positions (Figure 7.1b). These findings confirm its superior capacity for lithium-ion transport and faster diffusion compared to other separators.

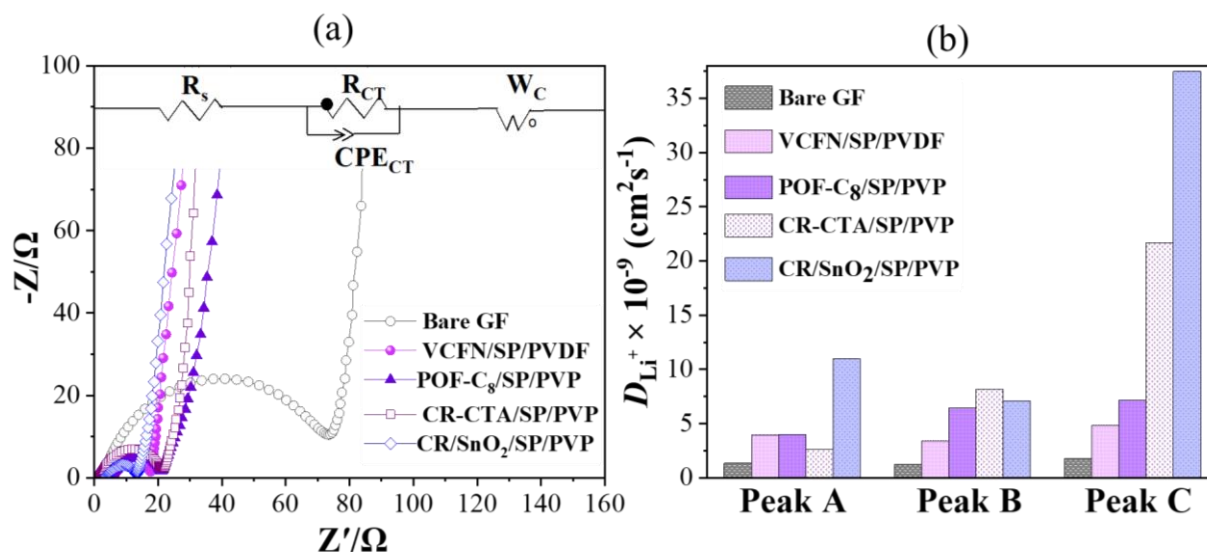


Figure 7.1 Comparison of (a) Nyquist plots and (b) lithium-ion diffusion coefficients for cells with different modified GF separators in this study.

7.2 Future outlook

The successful development of these separator modifications suggests several avenues for further enhancing the performance of Li-S batteries through separator design. Future research should aim to optimize the structure, composition, and integration of separator modification layers to better balance

polysulfide retention, electron conduction, and cycling stability. Several specific areas for exploration are proposed below.

One promising area for future research is the development of advanced porous organic frameworks (POFs) or covalent organic frameworks (COFs) with tailored pore sizes and surface chemistries. Such frameworks could maximize polysulfide adsorption without compromising ion and electron transport across the separator. Customizing the pore structure and functional groups within these frameworks could enable selective adsorption of polysulfides while facilitating the free movement of lithium ions, potentially enhancing both capacity retention and rate performance.

Another direction lies in the incorporation of catalytic materials within separator modification layers. Materials such as metal oxides or sulfides have shown potential to not only adsorb polysulfides but also promote their conversion back to sulfur, reducing their availability for diffusion and shuttle. Building on the promising results with SnO_2 in Chapter 5, future studies could explore alternative catalysts, including manganese oxides, molybdenum disulfide, and cobalt oxides, which have shown efficacy in polysulfide redox catalysis. Such catalytic layers could be integrated with adsorptive frameworks to create hybrid separators that actively manage polysulfide chemistry while supporting high-rate cycling.

The exploration of multifunctional composites—such as VCFN—opens additional possibilities for separator design. These composites can offer a balance of adsorption, catalytic activity, and structural reinforcement, making them highly suitable for high-performance LSBs. Future research could focus on refining these composites by adjusting component ratios, exploring alternative materials (e.g., different transition metals or layered hydroxides), and examining their interaction mechanisms with polysulfides. These studies could provide a deeper understanding of the roles each component plays, leading to optimized hybrid materials that meet the challenges of LSB operation.

Lastly, advancements in deposition techniques could play a critical role in the practical application of separator modifications. Methods such as CVD, or electrochemical in-situ polymerization offer ways to form thin, uniform coatings on separator surfaces. By achieving precise control over thickness, uniformity, and porosity, these methods could help realize separator layers that minimize polysulfide crossover while remaining cost-effective for large-scale production.

Through these avenues, the insights and methodologies developed in this thesis offer a foundation for next-generation lithium-sulfur batteries. By continuing to explore innovative separator materials and modification strategies, there is a strong potential to overcome current limitations and bring Li-S batteries closer to practical and commercial applications, with a focus on high energy density, extended cycle life, and environmental sustainability.

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