MITIGATING POLYSULFIDE SHUTTLING IN LI-S BATTERY

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ABSTRACT

Mitigating Polysulfide Shutting in Li-S Battery

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The energy source shortage has become a severe issue, and solving the problem with renewable and sustainable energy is the primary trend. Among the new generation energy storage, lithium-sulfur (Li-S) battery stands out for its low cost, high theoretical capacity (1,675 mAh g⁻¹), and environmentally friendly properties. Intensive researches have been focusing on this system and significant improvement has been achieved. However, several problems still need to be resolved for its practical application, especially for the “shuttle effect” issue coming from the dissolved intermediate polysulfides, which could cause rapid capacity decay and low Coulombic efficiency (CE). Several methods are proposed to eliminate this issue, including using interlayers, modifying separators, and protecting the lithium anode.

A carbon interlayer is first introduced to compare the function of the graphene and carbon nanotubes (CNTs), while the CNTs performs better with its higher conductivity and 3D network structure. The following study is conducted based on this finding.

A more efficient method is to modify the separator with functional materials. 1) The dissolved polysulfide (Sn₂⁻) could be repelled by electrostatic forces. With the Poly(styrene sulfonate) (PSS), the separator could function as an anion barrier to the intermediate polysulfides. 2D ultra-thin zinc benzimidazolate coordination polymer has the OH⁻ functional groups and works with the same mechanism. 2) A novel covalent organic framework (COF) has a relatively small
pore size, which can block the polysulfide and restrain them at the cathode side. 3) Metal-organic framework (MOF) materials have the adjustable pore size and structure, which can absorb and trap polysulfides within their cavities. Moreover, the dense stacking of the MOF particles creates a physical blocking for the polysulfides, which efficiently suppresses the diffusion process.

Protection of the lithium surface directly with an artificial layer or a solid electrolyte interphase (SEI) can inhibit the polysulfide deposition and suppress the lithium dendrite. A polyvinylidene difluoride (PVDF) membrane is used as an artificial film on lithium anode, which could greatly enhance the battery cyclability and CE. Future work will be conducted based on this concept, especially building an artificial SEI.
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May the force be with me.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAO</td>
<td>Anodic aluminum oxide</td>
</tr>
<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>COF</td>
<td>Covalent organic framework</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DOL</td>
<td>Dioxolane</td>
</tr>
<tr>
<td>DME</td>
<td>Dimethoxyethane</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EV</td>
<td>Electronic vehicle</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GF</td>
<td>Glass fiber (separator)</td>
</tr>
<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium-ion battery</td>
</tr>
<tr>
<td>Li-S</td>
<td>Lithium-sulfur (battery)</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-organic framework</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PS</td>
<td>Polysulfides, Li$_2$S$_n$ ($2 \leq n \leq 8$)</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly (styrene sulfonate)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SSE</td>
<td>Solid-state electrolyte</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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Chapter 1: Introduction

1.1 Rechargeable Lithium-Sulfur Battery

This proposed project is inspired by the depleting condition of fossil fuel energy and severe environmental and air pollution. Thanks to the development of modern science and technology, people have found replacing clean energy, e.g., wind power, solar power, and electrochemical storage such as batteries. First commercialized in the 1990s, the conventional lithium-ion battery (LIB) has tremendously transformed the way that people live. However, with continuous development, the LIB is reaching its theoretical capacity limit and cannot fulfill the increasing demand for higher specific energy and energy density.\(^1,^2\) The lithium-sulfur (Li-S) battery is considered to be a promising replacement mainly because it has the high theoretical specific capacity (1675 mAh g\(^{-1}\)) and energy density (2500 Wh kg\(^{-1}\)),\(^3,^4\) which are much larger than the traditional LIBs (e.g., 387 Wh kg\(^{-1}\) for LiCoO\(_2\) battery). Moreover, the sulfur element is cheap and has a rich reserve, making it a low-cost, commonly affordable technology.

1.1.1 Mechanism

The configuration of a Li-S battery consists of a lithium anode, a sulfur/carbon cathode, the ionic-conductive electrolyte in between, and an electrical-insulating separator, which is usually the glass fiber (GF) or polypropylene (PP), showing in Figure 1.1.\(^5\)

When discharging, the S\(_8\) cathode will open the cyclo-ring and form the long-chain lithium polysulfides (PS) Li\(_2\)S\(_n\) (6 ≤ n ≤ 8) at around 2.4 V. Further reduction will produce intermediate short-chain Li\(_2\)S\(_n\) (2 ≤ n ≤ 4) at around 2.1 V, and the ultimate product is the insoluble Li\(_2\)S.
The overall reaction is given as follows:

$$S_8 + 16Li \leftrightarrow 8Li_2S$$

While the reduction going on the cathode is:

$$S_8 + 2Li^+ + 2e^- \leftrightarrow Li_2S_n (2 \leq n \leq 8)$$

And the oxidation reaction going on the anode is:

$$2Li \leftrightarrow 2Li^+ + 2e^-$$

The electrochemical process and the typical charge-discharge profiles are shown below.
Figure 1.2 Typical galvanostatic charge and discharge profiles of a Li-S battery.

Reproduced from the online figure.

Seen in Figure 1.2, there are two plateaux and a sloping range for the discharge process. The commonly agreed mechanism is that the sulfur will react with lithium ions and transforms to Li$_2$S$_6$ at the first plateau at around 2.4V. Further reduction will continue as the Li$_2$S$_6$ becomes Li$_2$S$_4$ (sloping zone) and Li$_2$S (second plateau). The charge process is the opposite reaction. However, one thing must be noted that the whole reaction process is complex, and each procedure is composed of multiple PS species transformation. The Li-S battery system still needs in-depth exploration and has many mysteries that are yet to be unveiled.

1.1.2 Applications and Challenges

Because of its low cost, environmental abundant and friendly properties, Li-S battery is considered an alternative to the current LIB in many fields. For the portable laptop and mobile phones, Li-S battery can offer longer operation hours than the commercial LIB. According to the latest data, the electric automobile using Li-S battery is supposed to reach an 800 km driving
distance with less than 35,000 USD vehicle cost, which is almost half of the price for the one using LIB (55,000 USD per vehicle). It is thus considered as the most promising alternative for electric vehicle (EV) and hybrid electric vehicle (HEV).

Although Li-S battery has many benefits, it also suffers from several issues. 1) The sulfur is an insulating material with high electrical resistivity, which will lead to low active utilization and low capacity. Thus, a proper conductive material (mostly carbon) is desired to enhance cathode conductivity. 2) Another severe disadvantage is the so-called “shuttle effect”. During the discharge process, PS will dissolve in the liquid electrolyte, which can migrate between the cathode and anode. When the intermediate pass through the separator and reach the anode, they can react with lithium and form insoluble Li$_2$S$_2$/Li$_2$S on the anode surface directly, which will consume extra sulfur and lithium, thus result in low sulfur utilization, large electrode impedance, low coulombic efficiency (CE), and degraded battery performance. 3) Lithium anode gives the great advantage of high energy and low working voltage for the battery; however, it may also be attacked by the PS and forms an inactive film, which could hinder the following reaction. Moreover, the lithium anode is well known for the growth of dendrites, which may penetrate the separator and cause battery shortage and exploration.

### 1.2 Solutions to Challenges

#### 1.2.1 Cathode Engineering

In recent years, various strategies have been continuously investigated to overcome the mentioned issues for Li-S battery. Most of the attention is focused on the cathode modification to enhance the sulfur conductivity with well-designed structures. Carbon materials are regarded as good conductive regent with lightweight and adjustable porous
structures. Carbon black,\textsuperscript{14} macro-, meso-, micro-porous carbon,\textsuperscript{15-18} carbon nanotubes (CNTs),\textsuperscript{19} graphenes,\textsuperscript{20, 21} and nanofibers\textsuperscript{22} have been profoundly and widely investigated as the sulfur host. There are also plenty of synthesis methods for the carbon/sulfur composites, such as simple mixing, ball milling,\textsuperscript{23} melting infiltration,\textsuperscript{24, 25} solution-based synthesis\textsuperscript{26, 27}. Metal oxides materials are the previous options used for trapping the PS, which are preferentially absorbed within the pores or on the material surface.\textsuperscript{28} The commonly used materials include ZnO,\textsuperscript{23, 29} TiO\textsubscript{2},\textsuperscript{30, 31} and SiO\textsubscript{2},\textsuperscript{17} for their stable chemical nature and adjustable pore parameters. The conductive polymer with the \(\pi\)-electronic conjugate system is another option. They can be modified with unique structures and different functional groups to alleviate sulfur aggregation or diffusion. Commonly used polymers are polypyrrole (PPy),\textsuperscript{32, 33} poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT: PSS),\textsuperscript{34} polyanilines (PANI)\textsuperscript{35, 36}, and so on. The conductive materials can help to increase sulfur conductivity and utilization, and the precisely designed structures can store sufficient sulfur and accommodate the PS inside its network. In this way, the sulfur loading is largely increased, and the battery capacity is enhanced.

1.2.2 Separator Modification

In LIB, the primary function of the separator is physically separating the anode and cathode to avoid short cut. In Li-S batteries, an additional requirement for the separator is to prevent the PS diffusion, which can be resolved by modifying the separator with functional materials.\textsuperscript{37, 38} The carbon materials are the most commonly used because of their excellent conductivity and great variety to satisfy different requirements. The carbon family employed are carbon powders (including Super P, Ketjen black, etc.), graphene, CNTs, and their hybrids.\textsuperscript{39-43} Polymers are good choices because they can be doped with O, N, S or have a cation-selective function (e.g.,
In addition, metal oxides and ceramic materials are applied as a physical obstacle to block the polysulfides, such as Al₂O₃ and TiO₂. Besides, the materials mentioned above are combined to enhance battery performance as a multi-functional separator. The preparation ways are also diverse, including vacuum filtration, casting, sputter coating, directly growth, and so on to form a layer on either or both sides of the separator. This layer can act as a trapper or barrier to the diffusion of polysulfides, but should facilitate the transport of lithium ions in the battery. Modifications of the separator are generally easy yet effective, thus developing an advanced separator is a hot research topic.

1.2.3 Anode Protection

Lithium has the properties of ultra-high specific capacity (3,860 mAh g⁻¹) and low redox potential (-3.04 V), which is considered as an essential anode for the new generation lithium battery. However, lithium dendrites will grow unevenly during the reduction/oxidation process, which will become “dead” Li and decrease Coulombic Efficiency (CE). Moreover, the PS generated from the cathode will diffuse to the anode and react with Li metal, continuously consuming the limited lithium. These issues make lithium anode protection becomes a great challenge. The strategies proposed are mainly about adding electrolyte additives, building artificial solid electrolyte interphase (SEI), using solid-state electrolyte (SSE), and utilizing composite anode. These strategies are designed to build or facilitate the stable SEI formation, reduce the lithium dendrites, and suppress the shuttling PS, which gives a long-lifespan Li anode, increased battery safety, and enhanced cycling performance.
1.2.4 Electrolyte

The electrolyte is a critical component in the battery system, which will significantly influence the electrochemical performance. The mainstream electrolytes used in Li-S batteries are composed of ethers, such as 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME). Meanwhile, the common salts are LiN(CF₃SO₃)₂ (LiTFSI) and LiNO₃. Commercial LIB salts such as LiPF₆ cannot be used in Li-S battery system, because they will react with PS and induce ring-opening polymerization of the DOL solvent. The LiNO₃ has the function of passivating the lithium surface and form a protective SEI, which can prevent the PS deposition on the lithium anode surface.⁶², ⁶³ However, the liquid electrolyte will have severe PS dissolution problem; thus the gel polymer and solid-state electrolyte are believed to be the promising solutions.⁶⁴ Several attempts have already been made and displayed fascinating results, including using poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), Li₂S-P₂S₅,⁶⁵ and poly(ethylene oxide) (PEO) compounds.⁶⁶ These gel polymer or solid-state electrolytes make PS diffusion impossible, but substantial improvements are still needed to be made to increase the electrolyte ionic conductivity and battery rate capability.

1.3 Objectives for the Dissertation

The primary objective of this dissertation is to mitigate the PS-caused shuttle effect in Li-S battery, which is the toughest issue remaining. Various functional materials, different material structures, and novel battery configurations have been and will be continuously adapted to tackle the problem.

Chapter 2 lists the general materials preparation or synthesis procedures and characterizations used for material analysis.
Chapter 3 introduces an interlayer with a facile synthesis method to compare the effect of different carbon materials (e.g., graphene, carbon nanotube, and their mixture). This result has proved the superior ability of CNT than graphene, which is used as the base for the following studies.

Separator modification with PSS and CNT mixture is shown in Chapter 4. Polysulfides are negatively charged species, thus can be repelled by electrostatic forces. The PSS has the functional $\text{SO}_3^{2-}$ groups and restrains the PS at the cathode side, which could effectively suppress the PS diffusion.

An ultrathin two-dimensional coordination polymer has been firstly synthesized and decorated with the $\text{OH}^-$ group, which also acts as the anion barrier for the PS species. A combination of the CNTs material further provides the conductivity for the sulfur species and can trap them within the 3D network. Details are shown in Chapter 5.

A novel covalent organic framework (COF) modified separator is presented in Chapter 6. The COF material has a small pore size, which can block the Li$_2$S$_n$ ($n \geq 6$) from diffusing to the anode.

Several MOF materials functioning as PS trappers are utilized and compared carefully in Chapter 7. The MOF materials can absorb the PS in their internal cages due to their high surface area. Meanwhile, the blocking effect with the stacking MOF particles is also critical. Attention should be paid when using Cu-containing materials, which will react with sulfur and lithium and make the battery die directly.

As lithium is vulnerable in the Li-S battery, the more efficient strategy to enhance battery performance is to protect the lithium anode by solid electrolyte interphase (SEI) or artificial films. Discussed in Chapter 8, a novel polyvinylidene difluoride (PVDF) membrane is prepared
to cover the lithium surface. With the PVDF membrane, less PS is deposited on the anode and fewer dendrites are grown, leading to enhanced battery stability and safety. This method shows the promising application and will be further studied in-depth.

Finally, the summary of all projects and the further study plan are presented in Chapter 9.
Chapter 2: General Experimental Procedures

The general experimental procedures are described below, which will not be further included in the following chapters.

2.1 Materials Preparations

2.1.1 Electrodes Preparation

The cathode materials were prepared as follows. Sulfur (99.8%, Sigma) and Super P carbon were first mixed at a weight ratio of 70:30 and then sealed in a glass bottle. This bottle was heated up to 200 °C, and the mixture was taken out and grounded into powders. This procedure was repeated three times.

The as-prepared S/C composite was mixed with polyvinylidene fluoride (PVDF, Mw=70,000) binder at a weight ratio of 90:10 in N-Methyl-2-pyrrolidone (NMP) to form a slurry and then cast on the aluminum foil. After drying at 40 °C in a vacuum oven overnight, the electrode was punched into circular discs with a diameter of Ø12 mm and used as the cathode. The general active material mass loading was around 1 mg cm⁻². The anode was prepared from lithium foil (Sigma) and was cut into the same size as the anode.

2.1.2 Electrolyte

The liquid electrolyte used for Li-S battery was 1.0 M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) and 0.4 M LiNO₃ in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (v:v=1:1).
2.2 Material Characterizations

The general characterization procedures are listed below, while the specific requirements are described in detail in the respective chapter sections.

2.2.1 X-ray Diffraction (XRD)

XRD data were collected with Bruker D8 Advance Diffractometer with Cu Kα radiation under 40 kV, 40 mA.

2.2.2 Thermogravimetric Analysis (TGA)

The amount of sulfur in the composites was determined with a Perkin-Elmer TGA Thermogravimetric Analyzer at a fixed heating rate under the flow of nitrogen gas.

2.2.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS)

The sample morphology and composition were investigated with Zeiss Merlin Gemini or FEI Quanta 600 equipped with EDS.

2.2.4 Raman Spectroscopy

The Raman spectrum was collected on a Witec alpha 300R Raman spectrometer at the excitation wavelength of 514 nm.
2.2.5 X-ray Photoelectron Spectroscopy (XPS)

The samples were examined by XPS with a Kratos Axis Ultra spectrometer, utilizing a monochromated Al Kα X-ray source, while the instrument base pressure controlled below $1 \times 10^{-7}$ Torr. All spectra were fitted by the Gaussian-Lorentzian (30% Gaussian) function and a Shirley-type background using the CasaXPS software.

2.3 Electrochemical Characterization

2.3.1 Battery Configuration and Assembly

The electrochemical properties of the samples were evaluated with CR2032-type coin cells. The cells were assembled with the S/C composite cathode, prepared Li-S battery electrolyte, interlayers (if any), glass fiber separators (Advantec, with and without modification), and lithium foil anodes (Sigma Aldrich). The operation was conducted inside an Ar-filled glovebox (Mbraun), in which the moisture and oxygen levels were controlled below 0.5 ppm.

2.3.2 Cycle Performance and Rate Capability Measurements

All electrochemical cycling tests were performed with an Arbin (USA) or Neware (China) battery testing instrument. Different voltage windows and current rates were used depending on the experimental settings. Cycle performances were evaluated by discharging and charging the cells at a fixed current density within a fixed voltage window or charge capacity. Rate capability tests were evaluated by cycling the cells at various C rates within a fixed voltage window.
2.3.3 Cyclic Voltammograms (CV) and Electrochemical Impedance Spectroscopy (EIS)

The CV and EIS data were collected with a Biologic VMP3 electrochemical station. The CV plots were measured at a fixed scan rate with a voltage window from 1.8-2.8 V, and EIS data were measured from 200 kHz -10 mHz.
Chapter 3: A Scalable Approach to Construct Free-Standing and Flexible Carbon Networks for Lithium-Sulfur Battery

3.1 Introduction

The application of the carbon nanomaterials, such as graphene and carbon nanotubes (CNTs), has covered wide industrial fields including water treatment, gas separation, and energy storage devices due to their unique morphological and electronic properties. Therefore, it would be necessary to develop one feasible strategy to fabricate the nano-units into a hierarchical one with satisfying performances. However, among the reported methods for preparing the multi-dimensional films or membranes, most synthetic strategies begin with preparing a uniform solution of carbon materials and then form a layer by filtration. The thickness and uniformity cannot be controlled precisely during the filtration because carbon materials may precipitate from the suspension. Thus, it remains a challenge to fabricate thin films with a large surface area to date, especially in industrial production. In this work, multi-dimensional carbon networks are prepared simply by casting carbon suspension on a sacrificial template followed by carbonization. This approach is universally applicable for all carbon materials, as well as any other solid materials that can form a uniform suspension. The scalable approach with controllable lightweight and binder-free characteristics are the key advantages.

Ever since developed, considerable attention has been paid on the interlayers for lithium-sulfur battery, which is usually inserted in between sulfur electrodes and separators. The interlayer can efficiently suppress the dissolution and migration of polysulfides as a blocking wall. The most commonly used materials are carbon, especially the graphene and carbon nanotubes (CNTs). However, very limited reports have compared these materials with detailed characterization. With the proposed scalable approach, the carbon network-based interlayers
were prepared and compared in-depth from morphological, electrical, and microscopic aspects to understand their effects in Li-S battery.

### 3.2 Experimental

#### 3.2.1 Scalable Interlayers Preparation

Multi-walls CNTs and graphene pastes were purchased from CNano Company (5 wt% in NMP). The suspensions of CNTs, graphene, and their mixture (mass ratio = 1:1) were prepared by mixing with NMP using a Thinky mixer, Japan, and then cast on both sides of the flexible cellulose paper with controlled thickness. After drying at room temperature, the samples were calcined at 450 ºC for 3 h under steady Ar flow, giving rise to the free-standing carbon networks.

#### 3.2.2 Electrochemical Measurement

The battery with the configuration of S/C cathode | interlayer | separator | lithium anode was assembled using the CR2032-type coin cell, while the interlayer and separator were Ø18 mm round discs. The batteries were tested under the voltage window of 1.5-3.2 V with an Arbin instrument, USA.

#### 3.2.3 Characterizations

The morphology of the interlayers and the sulfur distribution after the discharge were characterized by the scanning electron microscope (SEM, FEI Quanta 600) and energy-filtered transmission electron microscopy (EFTEM).
3.3 Results and Discussion

3.3.1 Preparation and Characteristics of Carbon Networks

The schematic illustration in Figure 3.1a shows the preparation process for the free-standing carbon interlayers. The suspension of carbon nanomaterials was cast on the surface of a cellulose paper uniformly by a doctor blade. The thickness of the layer can be precisely controlled by the height of the blade within the micrometers. Note that both sides of the template can be cast by the same or different carbon materials, thereby giving rise to the free-standing films with the flexibility of combining various carbon nanomaterials. The cellulose paper template could offer a bendable feature to the film (Figure 3.1b-d). A lightweight (i.e., 1.69 mg cm\(^{-2}\)) and highly flexible CNTs interlayer with a large area over 50 mm\(^2\) (e.g., > 10 mm \(\times\) 5 mm) can be obtained after carbonization. The surface morphology and structure of all the carbon networks were characterized by SEM (Figure 3.1e-g). This method offers a simple and scalable approach to construct the free-standing carbon films with controllable areal density (even below 1.0 mg cm\(^{-2}\)), which is also applicable to various materials, such as forming a metal (oxide)/C composite.
Figure 3.1 Schematic illustration of the preparation and characterization of the networks.

(a) Schematic illustration of the preparation process. (b, c) Flexible template after casting with CNTs and the enlarged SEM images for the surface and cross-sectional area. (d) Carbon networks after the carbonization. Interlayer photos, structure schematic drawings, surface and cross-sectional SEM images of (e) graphene, (f) CNTs, and (g) CNTs-graphene mixture.

3.3.2 Applications of the Carbon Network in Lithium-Sulfur Battery

The prepared carbon interlayers were inserted between the cathode and separator (inset of Figure 3.2a), and the electrochemical performance of the batteries with and without the interlayers were investigated. Under 0.25 C (1C = 1675 mA g⁻¹), the battery with CNTs interlayer shows an initial capacity of 1658 mAh g⁻¹, which is much higher than 1285 mAh g⁻¹, 1131 mAh g⁻¹, and 543 mAh g⁻¹ of CNTs-graphene, graphene and pristine (no interlayer), respectively, demonstrating the highest sulfur utilization in the presence of CNTs network. Its capacity can maintain at 556 mAh g⁻¹ after 100 cycles with a perfect charge-discharge profile and good coulombic efficiency (CE) of around 98% (Figure 3.2c), which is still higher than 306 mAh g⁻¹ of graphene and 92 mAh g⁻¹ of the pristine electrode, respectively. Figure 3.2b displays that the battery with CNTs interlayer has a longer charge/discharge platform and the
lowest polarization of 191 mV than 251, 337 and 436 mV of the CNTs-graphene, graphene, and pristine electrode, respectively. The benefit of using the CNTs interlayer is more pronounced under C-rate tests. Figure 3.2d shows that the capacities of 1301, 924, 756, 630, 466 mAh g$^{-1}$ were obtained using CNTs interlayer under the rates of 0.1, 0.25, 0.5, 1, 2.5C, which are higher than 1112, 731, 586, 471 and 317 mAh g$^{-1}$ of the CNTs-graphene, not to mention those with graphene and without interlayers (inset of Figure 3.2d). After the C-rate test, the battery with the CNTs interlayer can recover to 738 mAh g$^{-1}$ under the rate of 0.25C, confirming its excellent rate capability.

**Figure 3.2** Illustration of battery configuration and battery electrochemical performance.

(a) Cycling performance and (b) charge-discharge profiles of the Li-S battery with and without the interlayers. The inset of (a) shows the battery configuration with the interlayer. (c) The 1$^{\text{st}}$, 25$^{\text{th}}$, 50$^{\text{th}}$, 75$^{\text{th}}$, and 100$^{\text{th}}$ cycles profiles for the battery with CNTs interlayer. (d) C-rate performance of the battery using the CNTs interlayer and the inset is the comparative rate
capabilities of batteries with and without different carbon interlayers. Color black: CNTs; Red: CNTs-graphene mixture; Green: graphene; Blue: pristine electrode.

3.3.3 Electrochemical Analysis

The electrochemical behaviors of batteries were further studied with cyclic voltammetry (CV) (Figure 3.3). In Figure 3.3a-c, all batteries display two typical anodic peaks (i, the reaction of S\textsubscript{8} to Li\textsubscript{2}S\textsubscript{6}; ii, further reduction to Li\textsubscript{2}S\textsubscript{3}/Li\textsubscript{2}S) and one broad cathodic peak (iii, reversible oxidation reactions from Li\textsubscript{2}S/Li\textsubscript{2}S\textsubscript{2} to Li\textsubscript{2}S\textsubscript{x}, 2 < x \leq 8).\textsuperscript{74} These phenomena are consistent with the discharge plateaus at around 2.40 V/2.08 V and the charge plateau at about 2.22-2.42 V (Figure 3.2b). The CV curves are similar for all the samples, but the CNTs-based one has two unique features: (a) two clearly separated discharge peaks (i) and (ii) even at high cycling rate, which is due to the lower polarization, demonstrating the stronger trapping ability for polysulfide in networks; (b) a small peak around 2.43 V appears under the slow scan rate (e.g., 0.075 mV s\textsuperscript{-1}) but not in the other two cells, confirming the reduction of long-chain polysulfides into elemental sulfur step-by-step with the help of CNTs.

To make a more intuitive demonstration, the lithium-ion diffusion coefficient is calculated using the Randles-Sevcik equation, which describes the relationship between peak current and the scan rate as below:

\[
i_p = 2.69 \times 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} C^{\frac{1}{2}} v^{\frac{1}{2}},
\]

where \(i_p\) is the maximum peak current (A), \(n\) is the number of electrons transferred in the reaction (here is 2, corresponding to the reaction of S\textsubscript{8} to Li\textsubscript{2}S\textsubscript{6}), \(A\) is the electrode area (cm\textsuperscript{2}), \(C\) is the change in concentration of Li\textsuperscript{+} (mol cm\textsuperscript{-3}), \(v\) is the scan rate (V s\textsuperscript{-1}) and \(D\) is the diffusion coefficient (cm\textsuperscript{2} s\textsuperscript{-1}).\textsuperscript{75} A plot of normalized peak current (\(i_p\) value vs. the square root of the
scan rate \((v^{1/2})\) is shown in Figure 3.3d. The results reveal that the lithium-ion diffusion coefficient for the battery with the CNTs interlayer is the highest, \(1.93 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}\), over four times than \(4.15 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}\) of the pristine one (Table 1). It is also higher than \(1.39 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}\) of CNTs-graphene and \(7.69 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}\) of graphene, which is in accordance with the battery cycling and rate test results.

**Figure 3.3** Typical CV profile of different interlayers and diffusion coefficient.

CV profiles of batteries with (a) pristine electrode, (b) graphene interlayer, and (c) CNTs interlayer under different scan rates from 0.075 mV s\(^{-1}\) to 1 mV s\(^{-1}\). (d) Graph of normalized peak current vs. square root of the scan rate.
To get a better understanding of the interlayers, electrochemical impedance (EIS) was investigated after battery cycling. The Nyquist plots are fitted with an equivalent circuit, shown in the inset of Figure 3.4a.\textsuperscript{76} $R_e$ represents the electrolyte ohmic resistance, corresponding to the intercept of the x-axis at high-frequency regions. The similar $R_e$ value for different batteries at around 1.4-2.1 Ω confirms the uniformity of the battery assembly procedure. $R_1$, $R_2$, and $R_3$ are the relative charge-transfer resistance at the interfaces of anode/electrolyte, cathode/electrolyte, and interlayer/electrolyte, respectively.\textsuperscript{77} The sums of these resistances are 41.1 Ω (CNTs), 56.1 Ω (CNT-graphene), 61.3 Ω (graphene) and 52.9 Ω (pristine electrode), respectively (Table 1). The electrical resistance using CNTs interlayer is much lower than that of graphene. Note that the charge transfer resistance of CNTs-based battery decreased significantly to 2.6 Ω after the cycling, which was much lower than 14.8 Ω of CNTs-graphene, 6.9 Ω of graphene and 10.3 Ω of pristine one. The reason should be ascribed to the better conductive pathways along CNTs for Li\textsuperscript{+} and its naturally good conductivity, thereby giving rise to the superior performance. Furthermore, the sharper slope of CNTs-based battery at the low frequencies (i.e., Warburg Impedance $Z_w$) directly confirms the fastest lithium diffusion rate among the studied batteries (Figure 3.4c).
Figure 3.4 Nyquist plots and resistances comparison of the batteries with and without using the interlayers (a, b) before and (c, d) after the cycling.
**Table 1** Lithium diffusion constant and impedance value.

<table>
<thead>
<tr>
<th>Battery w/o interlayer</th>
<th>Slope</th>
<th>(D) (cm(^2) s(^{-1}))</th>
<th>(R_e)</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>(R_{1+2+3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>0.2394</td>
<td>(1.93 \times 10^{-7})</td>
<td>1.972</td>
<td>3.275</td>
<td>10.34</td>
<td>27.53</td>
<td>41.1</td>
</tr>
<tr>
<td>Cycled CNTs</td>
<td>2.135</td>
<td>0.505</td>
<td>1.031</td>
<td>1.05</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNTs-Graphene</td>
<td>0.2033</td>
<td>(1.39 \times 10^{-7})</td>
<td>2.035</td>
<td>3.926</td>
<td>28.55</td>
<td>23.62</td>
<td>56.1</td>
</tr>
<tr>
<td>Cycled CNTs-Graphene</td>
<td>1.950</td>
<td>0.662</td>
<td>3.617</td>
<td>10.50</td>
<td>14.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphene</td>
<td>0.1512</td>
<td>(4.15 \times 10^{-8})</td>
<td>1.783</td>
<td>4.325</td>
<td>32.95</td>
<td>24.04</td>
<td>61.3</td>
</tr>
<tr>
<td>Cycled graphene</td>
<td>1.817</td>
<td>1.300</td>
<td>3.317</td>
<td>2.318</td>
<td>6.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pristine Electrode</td>
<td>0.1111</td>
<td>(7.69 \times 10^{-8})</td>
<td>1.438</td>
<td>26.89</td>
<td>26.010</td>
<td>--</td>
<td>52.9</td>
</tr>
<tr>
<td>Cycled battery</td>
<td>1.499</td>
<td>5.77</td>
<td>4.649</td>
<td>--</td>
<td>--</td>
<td>10.3</td>
<td></td>
</tr>
</tbody>
</table>

3.3.4 Internal Structural Analysis

The function of the interlayers in suppressing polysulfide diffusion was further characterized by the energy-filtered transmission electron microscopy (EFTEM) (Figure 3.5) after the first cycle discharge process. The cross-sectional area of the carbon layer is rich in sulfur, demonstrating the holding ability of interlayers for the polysulfides. Intensive sulfur distribution was found at the locations with CNTs, revealing the capability of the CNTs network for trapping the polysulfides. The tubular structure of CNTs in a knitted frame may be favorable for holding the polysulfide in comparison to the two-dimensional graphene.
Figure 3.5 EFTEM of elemental sulfur distribution on (a, b, c) CNTs and (d, e, f) graphene interlayers after the 1st cycle discharge. Blue and red colors represent elemental carbon and sulfur, respectively.

3.4 Conclusions

In summary, we present a new and versatile sacrificial template method for constructing flexible carbon networks in industrially scalable production. The different effects of carbon networks as interlayers in Li-S battery have been investigated in detail. The in-depth analysis of lithium diffusion constant, electrochemical impedance, and elemental sulfur distribution confirmed that CNTs network performs better than graphene. With the CNTs interlayer, the battery's initial capacity has risen from 543 mAh g⁻¹ (pristine) to 1658 mAh g⁻¹ under 0.25 C and maintains 556 mAh g⁻¹ after 100 cycles. These results serve as a base level for future research on the Li-S battery, and the CNTs network is chosen as a coating layer on the separator afterward.
Chapter 4: Taming the Polysulfides with Functionalization Polymers

Modified Separator in Li-S Battery

4.1 Introduction

With the emerging energy demand worldwide, lithium-sulfur (Li-S) battery has attracted much attention because it is considered as the most promising next-generation energy storage. However, its commercialization has been plagued by several intrinsic drawbacks, while the polysulfide shuttle effect being one of the main reasons for battery decay. Much research has been conducted to overcome this issue in recent years, including synthesizing sulfur/carbon-based composites cathode, protecting of the lithium anode, and adjusting of the electrolyte composition with additives. These methods can, to some extent, solve the problem and improve the battery’s electrochemical performance, but most of them require complicated preparation procedure or expensive materials, which lacks commercialization value.

A separator is a decisive element in Li-S battery to stop the shuttling of the polysulfides. However, general commercial separators (e.g., PP or PE) could not satisfy this desire mainly because of the relatively large pores of the membrane. Thus, many efforts focusing on the modification of the separator have been conducted and have achieved outstanding results. Here, we report a simple strategy by casting the poly(styrene sulfonate) (PSS) and the carbon nanotubes (CNTs) mixture on the separator. The dissolved polysulfide (Sn²⁻) in the electrolyte is known to be negatively charged and could be repelled by electrostatic forces. The PSS has the same negatively charged sulfonate groups (-SO₃⁻), thus the separator could function as an anion barrier and hinder the shuttle of the intermediate polysulfide. Considering the excellent electrical conductivity of the CNTs, they were mixed with PSS with different weight ratios to study the impact on separator properties. This method not only gives rise to enhanced
cycling stability and Coulombic efficiency, which approaching almost 100%, but also offers a facile, scalable, and cheap strategy to be applied to the industrial field.

4.2 Experimental

Different weight ratios of PSS vs CNT (90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 10:90) were first mixed with a Thinky mixer, Japan. The formed slurries were further mixed with 10 wt% of PVDF binder in NMP and coated on glass fiber separator by a doctor blade with the same height. The coated separator was dried at 100 ℃ in the air-flowing oven for 1 h and cut into ϕ18 mm round separators, and further dried in a vacuum oven at 80 ℃ overnight.

4.3 Results and Discussion

4.3.1 Morphology Characterizations

Different weight ratio PSS polymer and CNTs were mixed and coated on glass fiber separator. The surface of the coated glass fiber separator was characterized by scanning electron microscope (SEM), shown in Figure 4.1. With the increase of the PSS content, more polymers tend to aggregate on the separator surface, wrapped by the CNTs network. But the CNTs cannot hold all the big polymer particles, and cracks can be noticed when the PSS content reached 70% (Figure 4.1d). When PSS reached 90 wt%, the polymers covered most of the surface and the CNTs could barely be seen (Figure 4.1e). The surface displays a non-porous structure morphology, proving that the substrate glass fiber separator was fully coated.
Figure 4.1 SEM surface images of the PSS/CNT separator with different weight ratios.

The ratio of PSS:CNT is (a) 10:90, (b) 30:70, (c) 50:50, (d) 70:30, (e) 90:10, (f) 0:100.

4.3.2 Electrochemical Analysis

Preliminary galvanostatic cycling tests were performed and compared to demonstrate the ability of the functional separators to stop the polysulfide diffusion. The red plot shown in Figure 4.2 represents the cell with pure CNT coated separator, which is the reference for the other samples. It is observed that a high capacity of 1258 mAh g⁻¹ was initially achieved with the CNT separator, but it has lower CE (< 90% for the first cycle, Figure 4.3b) and severe
capacity fading. This phenomenon suggests that CNTs can help to increase the conductivity and improve the sulfur utilization, but the polysulfide shuttling issue remains. With the incorporation of the PSS polymer, it is apparent that the battery cycling stability was improved, especially with PSS:CNT=5:5 (w/w) separator, which displayed more remarkable stability than others, reaching 1078 mAh g⁻¹ at the beginning and maintained 908 mAh g⁻¹ after 100 cycles. Moreover, the CE steadily increased and reached almost 100% (Figure 4.3b), further confirming the ability of the sulfonate functional group to stabilize the polysulfide at the cathode side. However, as the PSS content increases, it is also noticed that higher PSS content did not result in higher capacity, which could be attributed to its insulating nature. The disadvantage of the insulating property could overwhelm the advantage of conductivity brought by CNT, leading to a bigger internal resistance and a worse battery performance.

**Figure 4.2** Cycling performance of batteries with different weight ratios of PSS/CNT separators under 0.25C.
4.4 Conclusions

In summary, the separator of the Li-S battery was modified by PSS/CNT composite to enhance battery performance. It was found that the PSS/CNT composite played a dual function of suppressing the polysulfide diffusion by SO$_3^-$ functional group and enhancing the electric conductivity of the sulfur by CNT. Without PSS polymer, the battery based on CNTs separator has a high capacity of 1258 mAh g$^{-1}$ but a low CE of 88% and a fast stability decrease under 0.25 C. After adding the PSS, when PSS/CNT ratio reaches 5:5, the Li-S battery has achieved a slightly lower initial capacity of 1058 mAh g$^{-1}$ with a much enhanced electrochemical performance and high Coulombic efficiency approaching 100%. This method offers a simple
but efficient way to commercialize Li-S battery using a cheap PSS polymer, which could also be extended to other functional polymers based on the charge-repulsion mechanism.
Chapter 5: Functional Two-Dimensional Coordination Polymeric Layer
as a Charge Barrier in Li-S Batteries

5.1 Introduction

Two dimensional (2D) coordination polymeric layer has become a fascinating research topic owing to their unique physical properties and potential applications.90, 91 Among the numerous coordination structures, Zn\(^{2+}\) (or Co\(^{2+}\)) ions can coordinate with organic imidazole in tetrahedron units, making it feasible to form 2D zeolite-like structures.92, 93 However, a simple method to introduce functional groups to the structure without changing the 2D geometry is still not available. Here, we demonstrate a simple, room-temperature and scalable method to synthesize free-standing and nanometer-thin zinc benzimidazolate coordination polymer (ZBCP) layers on water surfaces, where the desired hydroxyl (-OH) group with a charge functionality are stoichiometrically coordinated into the 2D structure, characterized as Zn\(_2\)(Bim)\(_2\)(OH)\(_2\). In various separation technologies, the electrostatic shield is a noticeable mechanism. Therefore, the incorporation of hydroxyl groups introduces electrostatic charges into the 2D layers, making it an effective charge barrier to the transport of negative ions in solutions, a robust functionality which had not been achieved to date in ultra-thin 2D layers.94-96 These 2D ZBCP layers are applied to modify the separator in the next-generation Li-S battery and significantly enhance the battery performance and stability, where the notorious sulfur shuttling effect is shown to be suppressed in our experiments.

5.2 Experimental

5.2.1 Synthesis of ZBCP
Zinc(II) acetylacetonate (263.6 mg, 1 mmol) was dissolved in deionized water (500 ml), and the solution (pH ≈ 8) was poured into the Langmuir trough. A saturated benzimidazole/toluene solution was prepared by dissolving the benzimidazole in toluene and was centrifugated to remove the excessive benzimidazole precipitates. Then, 500 μl clear benzimidazole/toluene solution was gently dropped onto the surface of the zinc (II) acetylacetonate solution. After resting for a few minutes, the fast solvent evaporation of toluene created a confinement space for the ligands on the aqueous surface, where the polymerization occurred. The packed ZBCP thin film was formed by compressing the surface pressure-area isotherm to 30 mN/m.

5.2.2 Characterizations

Atomic force microscopy (AFM) was performed in the tapping mode with a commercial multifunction atomic force microscope (Asylum Research Oxford Instruments, Cypher ES). Scanning transmission microscopy (STM) imaging was operated in a variable temperature VT-STM, Omicron under the UHV condition (5.0×10^{-10} bar). Chemically etched polycrystalline tungsten STM tip was used, which was further cleaned by electron bombardment in situ under UHV. The ZBCP nanosheets were transferred on gold (111)/mica substrates for STM measurements. Infrared spectroscopy (IR) spectra of the studied samples were recorded in the wavenumber range 4000–400 cm^{-1} with an FT-IR spectrometer (Thermo Scientific, Nicolet iS10) using samples dispersed in pure KBr pellets. X-ray fluorescence (XRF) spectra were measured with an X-ray analytical microscope (Horiba Scientific, XGT-7200) under vacuum condition with Rh X-ray tube (50 kV/1 mA). Elemental analysis of the ZBCP nanosheets was obtained by the organic elemental analyzer (Thermo Scientific, FLASH 2000). GI-XRD was performed at 23 A SWASX beamline with a beam length of 1.24 Å at 0.2° or 2.0° incidence using a CMOS flat panel X-ray detector C9728DK. Transmission electron microscope (TEM)
images were taken on a Cs-corrected FEI Titan Cube transmission electron microscope operated at 300 kV. Selected area diffraction (SAED) patterns were collected by a Gatan Ultra-scan 1000xp CCD camera. Low-dose TEM images were acquired by a Gatan K2 direct-detection camera operated in electron-counting mode. To prepare samples for TEM analysis, the ZBCP nanosheets were deposited on lacey carbon-supported copper grids (TED PELLA, Inc.) and dried overnight. The BET surface area of the polymers was measured by nitrogen sorption at 77 K (Micrometrics ASAP 2020) and helium sorption (Horiba SA-9601 Surface Area Analyzer); the sample was degassed at 100~150 °C for 24 hours before testing. Zeta potential measurements were performed in Zetasizer Nano ZS (Malvern Instruments Ltd.) under room temperature. The ZBCP \([\text{Zn}_2(\text{Bim})_2(\text{OH})_2]\) nanosheets (40 mg, 0.1 mmol) were dispersed in de-ionized water (100 mL) in an ultrasonic bath for 1 hour. Nitric acid and ammonium hydroxide were used for conventional pH adjustment of aqua suspensions. The analysis was processed using a DTS1070 disposable folded capillary cell. To verify the origin of surface charges, magnesium sulfate (6 mg, 0.05 mmol) was dissolved in the aqua suspension of ZBCP (100 mL) before the measurement.

5.2.3 Separator Coating

The glass fiber separator was first coated with CNT paste (CNT: PVDF binder = 90:10, w/w) on one side and dried in an air oven at 80 °C. After drying, the separator was cut into \(\phi 18\) mm diameter round discs. The ZBCP was transferred on the other side of the separator to form a ZBCP/GF/CNT structure (or the CNT side for ZBCP/CNT/GF structure). The transfer process was repeated three times to make an approximate 10 nm thick ZBCP thin film on the glass fiber separator. Then the separator was dried at 60 °C under vacuum for one day.
5.3 Results and Discussion

5.3.1 Synthesis and Morphology of ZBCP

Figure 5.1a illustrates the method for synthesizing the two-dimensional, large-area, and free-standing polymeric layers based on zinc(II) benzimidazolate using a Langmuir trough. A toluene solution of benzimidazole (Hbim) was gently spread on top of an aqueous solution of zinc(II) acetylacetonate [Zn(acac)2]. The polymerization of Zn$^{2+}$ ion and Hbim can occur in an ambient condition, and then the products were compressed to a surface pressure of 30 mN/m, which promoted the formation of a large-area film. It is noticed that some coordination structures of Zn$^{2+}$ ions with Hbim have been reported, but most of the results were single-phase solvent synthesis.\textsuperscript{93, 97} Here, we utilize the water/toluene heterogeneous phase and fast solvent evaporation of the toluene to constrain the reaction in two dimensions, resulting in large-area 2D zinc benzimidazolate coordination polymer (ZBCP) layers at the air/water interface. Furthermore, since the reaction occurs in an alkaline environment resulting from the dissociation of Zn(acac)$_2$, the hydroxyl groups (-OH) are also coordinated to zinc as part of the coordination system. The thickness of the ZBCP layer depends on the quantity of the added Hbim solution, which was optimized to achieve a large-area, continuous and transferrable 2D film, as shown in the scanning electron microscopy (SEM) image Figure 5.1b. The atomic force microscopy (AFM) topographical image (Figure 5.1c) reveals that the typical thickness of the obtained ZBCP layers is around 3.2±0.2 nm. The scanning tunneling microscopy (STM) images of these small islands transferred onto a gold (111) substrate (Figure 5.1d and 5.1e) reveal that the obtained ZBCP film has a stacked structure composed of a few 2D monolayers (apparent thickness ~1 nm for each monolayer).
Figure 5.1 Synthesis and morphological characterizations of the ZBCP layers.

(a) Schematic illustration for the preparation process of the ZBCP layers at the air/water interface using a Langmuir trough. (b) SEM image of the ZBCP layer on a 300 nm SiO₂/Si substrate. The wrinkles were formed during the transfer process. Scale bar: 50 μm. (c) The AFM topographical image of the ZBCP layer on a 300 nm SiO₂/Si substrate and the corresponding cross-sectional height profile (~3 nm). Scale bars: 10 μm. (d) STM image of a small domain ZBCP layer on a gold (111) substrate. Scale bars: 75 nm and (e) the relative height profile along the marked red line.

5.3.2 Spectroscopic and Structure Characterization of the ZBCP Layer

To explore the chemical structure of the obtained ZBCP film, techniques including Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and elemental analyzer analysis were adopted. Most of the IR vibrational modes in Figure 5.2a are attributed to the benzimidazolate (Bim) including the whole ring stretching or bending at 600-1500 cm⁻¹, the =C-H stretching of aromatics at 3068 and 3032 cm⁻¹, and the C-C stretching of
the aromatic ring at 1611 and 1465 cm⁻¹. The presence of the Zn-N stretching at 421 cm⁻¹ and the translation mode of Zn-OH at 465 cm⁻¹ prove that zinc (II) ions formed coordination bonds with Bim and hydroxyl groups. The observation of bending modes at 850 cm⁻¹ and 1015 cm⁻¹ and the single Zn-OH deformation band at around 1520 cm⁻¹ further corroborated the formation of the Zn-OH bonds. Furthermore, the N-H vibration mode of free Hbim located at 628 cm⁻¹ disappeared after coordination with the zinc (II) ions. These results suggest that the ZBCP layer is a coordinated system consisting of zinc (II), benzimidazolate, and hydroxyl groups. Figure 5.2b displays the XPS spectra of N 1s and O 1s for the ZBCP layers. The two N 1s peaks from Hbim are corresponding to the non-protonated (399 eV) and protonated (401 eV) nitrogen. The non-protonated nitrogen dominates the whole peak (96.53%), indicating that the pyrrole nitrogen (-NH-) in Hbim has been deprotonated and coordinated to zinc(II) ions. This conclusion is supported by the absence of N-H vibration mode in the FTIR spectrum (Figure 5.2a). The predominant peak in the O 1s spectrum with a binding energy of 532 eV is originated from the zinc hydroxide bond (Zn-OH) in the ZBCP layer, while the weak peak at 533.3 eV is correlated to a trace amount of residual moisture. Elemental analysis was performed to quantitatively define the chemical composition of the ZBCP layer. Zinc was the major metal component, while the other components are C (42.11%), H (3.34%), N (13.66%), and O (8.46%) (Table 2). The atomic composition matches well with the proposed chemical formula Zn₂(Bim)₂(OH)₂.

Table 2 C, H, N, and O elemental analysis of the ZBCP layer.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass(%)</th>
<th>Mass(%) of Zn₂(bim)₂(OH)₂ (expected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>42.10942</td>
<td>42.21106</td>
</tr>
<tr>
<td>H</td>
<td>3.33754</td>
<td>3.015075</td>
</tr>
<tr>
<td>N</td>
<td>13.66156</td>
<td>14.07035</td>
</tr>
<tr>
<td>O</td>
<td>8.458052</td>
<td>8.040201</td>
</tr>
</tbody>
</table>
Taking the FTIR and XPS results together with the confirmed formula Zn$_2$(Bim)$_2$(OH)$_2$, the structure of ZBCP is proposed in Figure 5.2c. Each Zn$^{2+}$ ion is coordinated with two benzimidazolates and two hydroxyl groups, forming a tetrahedral unit. The extension of the unit allows the formation of a planar polymer (Figure 5.2d), as evidenced by the STM image in Figure 5.1d.
**Figure 5.2** Spectroscopic characterization and molecular structure of ZBCP.

(a) Full (blue) and zoom-in (red) FTIR spectra of the ZBCP film. (b) XPS spectra of N 1s (left) and O 1s (right) of the ZBCP film. (c) The tetrahedral unit and (d) top and side views of the proposed Zn2(Bim)2(OH)2 structure.
5.3.3 Electrostatic Charge Property of ZBCP

To demonstrate the synthesized ZBCP material has a charged surface, the surface electrostatic potential was probed by the zeta potential measurements: the higher the zeta potential, the larger the surface potential. The measurement was performed by breaking the ZBCP layers into small pieces and suspended in deionized water subjected to different pH values (Figure 5.3a). The intrinsic ZBCP (pH ≈ 7) is negatively charged likely due to the amphotericism of zinc-hydroxides, where the zinc-hydroxides behave as Lewis acids and receive electron pairs from other hydroxides in basic solutions. To verify the origin of negative charges, a small amount of Mg$^{2+}$ ions were introduced into the solution, while the pH value of the system was maintained at around 7. As shown in the inset of Figure 5.3a, the zeta potential of ZBCP decreased with the addition of Mg$^{2+}$ due to the affinity of OH$^{-}$ groups to Mg$^{2+}$ ions, meaning that the Mg$^{2+}$ ions can passivate the hydroxyl groups in ZBCP and diminish the surface charges. The formation of the Mg-OH bond was also proved by FTIR measurements (Figure 5.3b). Two peaks at 830 cm$^{-1}$ and 625 cm$^{-1}$ are assigned to the Mg-OH stretching mode and the combination modes of Eu (368 cm$^{-1}$) and Eg (280 cm$^{-1}$), respectively. The zeta potential dependence on pH value and the Mg$^{2+}$ passivation results confirm that the surface electrostatic property is attributed to the amphoteric property of hydroxyl groups in ZBCP.
**Figure 5.3** The electrostatic charge property of ZBCP.

(a) The zeta potential values of ZBCP dispersed in deionized water with various pH values. The inset figure shows that the intrinsic Zeta potential of ZBCP decreases after adding Mg$^{2+}$ ions. (b) FTIR spectra of ZBCP before and after adding Mg$^{2+}$ ions, where the formation of Mg-OH bonds results in a reduction of net electrical charges in ZBCP.

### 5.3.4 The electrochemical Performance of Li-S Batteries

The inclusion of a vast number of -OH groups in the layered ZBCP provides a great potential in applications that require charge filters, such as an ultrathin charge barrier for Li-S batteries to mitigate the notorious polysulfide shuttle effect. The shuttle effect is a significant issue due to the migration of dissolved (negatively charged) polysulfides to the lithium anode, which forms the insoluble Li$_2$S$_2$/Li$_2$S and causes significant capacity decay. Figure 5.4a displays the configuration of the battery and the mechanism for stopping the polysulfides with a charged ZBCP barrier. One side of the glass fiber (GF) separator (facing the cathode) was first coated with a layer of carbon nanotubes (CNT), which can enhance the conductivity of the insulating sulfur and also help to suppress the polysulfide migration as the first barrier. The ZBCP layers (around 10 nm thick) were transferred onto the other side of the GF separator to form a
ZBCP/GF/CNT structure. The electrochemical characteristics of the Li-S batteries with and without the ZBCP charge barrier were examined. With the ZBCP layer, the battery’s initial capacity can reach 1272 mAh g\(^{-1}\), and maintained a relatively high capacity of 738 mAh g\(^{-1}\) after 200 cycles (Figure 5.4b). In contrast, the one without ZBCP showed a lower capacity of 927 mAh g\(^{-1}\) at the beginning and decayed fast to 412 mAh g\(^{-1}\) after cycling. The excellent performance of the battery with the ZBCP barrier suggests that more polysulfides have been effectively utilized with the help of the negatively charged ZBCP barrier layer, which can help to reduce both self-discharge and loss of S to the electrolyte at the anode side due to efficient blocking of polysulfides from the cathode to the anode. Both batteries exhibited two typical discharge platforms at 2.3 V and 2.1 V, suggesting that the ZBCP layer did not involve in the battery internal reactions (Figure 5.4c). In the C-rate tests, the battery with the ZBCP separator delivered capacities of 1407 mAh g\(^{-1}\), 1130 mAh g\(^{-1}\), 987 mAh g\(^{-1}\), 842 mAh g\(^{-1}\) and 610 mAh g\(^{-1}\) at 0.1 C, 0.25 C, 0.5 C, 1 C, and 2.5 C, respectively, which are much higher than the one without ZBCP (Figure 5.4d). Note that under a high rate of 2.5 C, the battery with ZBCP had a similar capacity with the one without ZBCP due to its ultrathin property. The outstanding capacity retention and stability proved the ability of the ZBCP layers for suppressing the polysulfide shuttling.
Figure 5.4 Electrochemical performance of the Li-S batteries with and without ZBCP.

(a) Schematic illustration of the Li-S battery using the ZBCP/GF/CNT separator and the charge repulsion of the ZBCP layer to the polysulfides. (b) Cycling performance and (c) first cycle charge-discharge curves of the batteries using the separator with and without ZBCP coating at 0.25 C. (d) Rate capability and cycling retention of the battery using the separator with and without ZBCP coating.

After the galvanostatic cycling, the batteries were disassembled and the separators were examined by SEM and FTIR (Figure 5.5). It can be seen that the ZBCP layers remained attached to the GF (Figure 5.5c) and the structure was not destroyed (Figure 5.5d), proving its chemical stability. Several cracks were observed, which could be induced by (i) the stress induced by the sputtering coating for SEM imaging; (ii) the mechanical force involved when
disassembling and taking the separator from the battery. The sulfur elemental mapping in the cross-sectional SEM image of the ZBCP separator (Figure 5.5e) reveals a distinct sulfur depletion region right underneath the ZBCP layer, suggesting a robust blocking effect by the ZBCP layer.

**Figure 5.5** Characterization of the separators before and after cycling.

The top-view SEM images of the GF separators (a) before and (b) after coating the ZBCP layers. (c) The SEM image of ZBCP/GF/CNT separator after cycling. (d) The FTIR spectra of the ZBCP/GF/CNT separator before and after cycling. Red dash lines represent the characteristic IR absorption peaks of the ZBCP. (e) The elemental mapping of sulfur in the cross-sectional SEM image of the ZBCP/GF/CNT separator.
5.4 Conclusions

In summary, we proposed a novel strategy to synthesize a large-area and ultra-thin Zn-coordination 2D polymer, which contains a large number of OH functional groups and played an active role in the separation application. It has the charge barrier feature and is integrated into the separator of the Li-S battery to mitigate the polysulfide shuttle effects as an electrostatic shield, largely promoting the battery capacity and cycle performance. The cell with the ZBCP layers reached 1272 mAh g⁻¹ for the initial cycle, while the one without ZBCP was only 927 mAh g⁻¹. After 200 cycles, the battery with ZBCP maintained a relatively high capacity of 738 mAh g⁻¹, while the one without ZBCP decayed dramatically to 412 mAh g⁻¹. Moreover, the synthesis process is simple, scalable, and cost-saving, which is anticipated to be adopted for practical use.
Chapter 6: Two-Dimensional Covalent Organic Framework as an Efficient Polysulfide Barrier for Li-S Battery

6.1 Introduction

The lithium-sulfur battery was first introduced in the early 1980s, but it hasn’t attracted enough attention until the emerging requirement for the next-generation storage system with high capacity, abundant natural source, and cheap cost. The development for the Li-S battery mainly focusing on increasing its active material utilization, suppressing the polysulfide diffusion process, and protecting the anode from the dendrites and polysulfide deposition. The sulfur utilization could be enhanced by combining with the conductive agents, such as carbon materials or conductive polymers. While the lithium anode protection could be realized by forming the protection layer on the anode, or adjusting the electrolyte composition to form a SEI. The most severe issue is the so-called “shuttle effect”, which is caused by the intrinsic properties of the Li-S battery. During the discharge process, the sulfur molecules will form soluble polysulfide intermediates (Li2Sx, 2<x≤8), which could shuttle between the cathode and anode through the liquid electrolyte. This will not only cause low Coulombic efficiency, and the polysulfides may also deposit on the lithium anode (Li2S and Li2S2), leading to a rapid capacity fading.

To address the shuttling issue, intensive researches have been devoted to trap the polysulfides within the electrodes, such as building a carbon matrix or coating with metal oxides or conductive polymers. Moreover, an alternative way to prevent the diffusion is to add physical blocking, including the insertion of an interlayer or modification of the separators. Two dimensional material, with its flexible, ultra-thin, and adjustable nanopore sizes, has been selected as a novel and promising material to be applied to the separator. Herein, we introduce a 2D covalent organic framework (COF) material with tailored nanopore size on the
separator, which could block the diffusion of the polysulfides and eventually contributing to enhanced cycling performance and capacity in Li-S battery.

6.2 Experimental

6.2.1 Synthesis of COF thin film

The COF was prepared from two kinds of precursors, 1,3,5-triformylphloroglucinol (TFP) and 2,7-diamino-9,9-dihexylfluorene (DHF), by interfacial polymerization through a Langmuir-Blodgett (LB) trough (Kibron MicroTrough X). During the preparation, the LB trough was first filled with deionized water, and the two precursors were dissolved in toluene separately to form a 0.009 M solution for TFP and a 0.006 M solution for DHF. Then, an equal amount of TFP and DHF solutions (~150 µL) were mixed and spread on the water surface using a syringe. After evaporation of toluene for 30 min, the surface layer was compressed at a rate of 3.0 mm/min until the surface pressure reached 17 mN/m. 500 µL trifluoroacetic acid was further added to the trough to act as a reaction initiator, and the mixture was left undisturbed for 48 h at room temperature. A yellow-colored TFP-DHF 2D thin film was formed at the water-air interface. The film was transferred on the anodic aluminum oxide (AAO) supports for morphology characterization and on glass fiber separators for Li-S battery studies.

6.2.2 Characterizations

The Brunauer-Emmett-Teller (BET) surface area analysis was carried by nitrogen physisorption using ASAP2020, Micromeritics instrument.
6.3 Results and Discussion

6.3.1 Synthesis and Morphology of the COF Film

The COF structure was formed through a two-step condensation reaction from the precursors, shown in Figure 6.1a. Both precursors have a rigid and planar molecular structure, which tends to bond along the well-defined directions to form a 2D hexagonal porous structure with pore size around 1.5 nm. Figure 6.1b shows the side view SEM image of the COF film supported on an AAO support. A continuous and uniform film was formed with a thickness of around 73 nm. Figure 6.1c displays the top-view SEM image of the film. The surface is smooth with no defects. From the adsorption isotherm, the BET surface area and the pore size were estimated to be $\sim285 \text{ m}^2/\text{g}$ and $\sim1.41 \text{ nm}$ (Figure 6.1d), respectively. The pore size estimated from the COF porous structure is around 1.28 nm (Figure 6.1e), which is consistent with the pore size measured by BET. This pore size value is believed to be smaller than the Li$_2$S$_8$ (~2.2 nm) and Li$_2$S$_6$ (~1.6 nm) species in the Li-S battery. Thus, this COF thin film could be applied as the blocking wall for the polysulfides with the size exclusion functionality and mitigates the shuttling effect.
Figure 6.1 The synthesis process and characterizations of the COF film.

(a) Schematic illustration of the polycondensation reaction for the formation of the TFP-DHF COF structure. SEM images of (b) cross-section and (c) surface morphology for the COF film. (d) The pore size distribution of the TFP-DHF calculated by the NLDFT method from the N\textsubscript{2} adsorption isotherm data. (e) Pore size estimation from the simulated COF structure.
6.3.2 Electrochemical Performance of the Li-S Battery with the COF Membrane

To study the effect of the COF membrane in Li-S battery, two cells with the COF coated separator and the pristine separator (glass fiber separator without COF film) was measured under 0.25 C (1C = 1,675 mAh g\(^{-1}\)). The battery with the COF separator delivered a high specific capacity of 1208 mAh g\(^{-1}\) for the first cycle (Figure 6.2a), while the one with pristine separator was only 960 mAh g\(^{-1}\) (Figure 6.2b). After 200 cycles, the battery with COF membrane maintained a capacity of 925 mAh g\(^{-1}\) with Coulombic efficiency of 99% (Figure 6.2c), the one with pristine separator, however, decreased quickly to only 423 mAh g\(^{-1}\), confirming the superior ability of the COF membrane to block the polysulfides. Furthermore, the rate capabilities of the batteries were examined and exhibited in Figure 6.2d. The battery with the COF separator delivered discharge capacities of 1323, 1009, 865, 708, and 423 mAh g\(^{-1}\) at the rate of 0.1 C, 0.25 C, 0.5 C, 1 C, and 2.5 C, respectively. These values are much higher than the pristine one, which further proves that the COF membrane played a significant role in blocking the polysulfides.

Moreover, EIS was conducted together with the galvanostatic tests (0.25 C) to evaluate the conductivity variation of the batteries with two types of separators. As shown in Figure 6.2e and 6.2f, both cells present similar ohmic resistance (R\(_{e}\)) before cycling, demonstrating the uniformity during the battery assembly process, and the COF membrane does not introduce much internal resistance. The semicircle located at the medium-high frequency region is corresponding to the charge-transfer resistance (R\(_{ct}\)), which distinguished greatly for two batteries after cycling. The battery using COF separator displays a much lower R\(_{ct}\) than the pristine one, which can be attributed to the suppressed polysulfide diffusion by the COF membrane with nanometer-sized pores.
Figure 6.2 Electrochemical performances of the battery with COF and pristine separator.

The charge-discharge profiles of batteries using (a) COF separator and (b) pristine separator for the 1\textsuperscript{st}, 2\textsuperscript{nd}, and 100\textsuperscript{th} cycles under 0.25 C. (c) Cycling performance comparison under 0.25 C and (d) C-rate performance comparison for batteries using COF and pristine separators. Nyquist plots for batteries with (e) COF separator and (f) pristine separator.

6.3.3 Visualization of the Polysulfide Diffusion with the COF Membrane

To demonstrate the effect of the 2D COF membrane on suppressing the polysulfide diffusion, a visualization experiment was conducted with a specially designed set. As displayed in Figure 6.4, one small vial containing brown colored polysulfide electrolyte (0.05 M Li$_2$S$_8$ in...
DOL/DME, v:v=1:1) is placed top-down inside of a big vial that contains transparent DOL/DME (v:v=1:1) solvent mixture. The small vials were covered with the COF and pristine separators on the cap. It is observed that after 30 h, the color of the out vial had almost no change for the COF separator, but turned yellow for the pristine separator, which indicates that the COF membrane has effectively limited the transport of polysulfides through the separator due to its nanometer-sized pores.

**Figure 6.3** Demonstration of the COF ability to suppress polysulfide diffusion.

### 6.4 Conclusions

In summary, we proposed a novel COF ultrathin polymer coating layer on the separator in the Li-S battery, which has a smooth surface and a small pore size of around 1.28 nm. The modified separator with small pore size has an excellent polysulfide blocking effect, which greatly
enhanced the electrochemical performance and stability of the Li-S battery. The battery with the COF separator delivered a high specific capacity of 1208 mAh g\textsuperscript{-1} and maintained a capacity of 925 mAh g\textsuperscript{-1} after 200 cycles. While the initial capacity for the one with pristine separator was only 960 mAh g\textsuperscript{-1} and decreased quickly to only 423 mAh g\textsuperscript{-1}. This study demonstrates the possibility of utilizing the 2D COF material in Li-S batteries, which can intrigue future works on combining feasible membrane material with the battery technology.
Chapter 7: Mechanism Study of Metal-Organic Framework-Based Separators for Enhanced Li-S Battery Stability

7.1 Introduction

Pursuing high energy density storage system with the sustainable features are being one of the main trends in rechargeable battery research, where the limited capacity and high cost of traditional Li-ion batteries (LIBs) cannot fulfill the ever-increasing demand for the long-life handheld device and electric vehicle.\textsuperscript{1,2,123} Alternatively, the lithium-sulfur (Li-S) battery has attracted much attention because of the abundant sulfur resource on earth, the extremely high theoretical capacity (1675 mAh g\(^{-1}\)), and environmental benignity for sustainability. However, it also suffers from several major issues which significantly hinder its commercialization: (i) the low utilization of sulfur resulted from its non-conductive nature; (ii) the severe capacity fading caused by the polysulfide intermediates shuttling; (iii) the safety issue of applying metallic lithium anode due to the lithium dendrites formation during the cycling.\textsuperscript{124,125} To date, efforts have been made to design carbon-sulfur composite cathodes to increase the cathode conductivity and minimize the shuttle effects;\textsuperscript{126, 127} however, it remains challenging to suppress the dissolution and migration of polysulfides in the electrolyte.\textsuperscript{128} Recently, the modification of separator using different kinds of carbon, polymers or 2D materials has been demonstrated as an effective approach to improve the cycle performance of Li-S batteries,\textsuperscript{38, 129, 130} in which the modified separator can significantly reduce the polysulfide migration to the anode. These reports have suggested that the characteristics of the added materials on separators, including their inner structure, interfacial properties, wettability with electrolytes, surface areas, and porosity are all crucial factors to determine the battery performance.

Metal-organic framework (MOF) is of great interest for their unique properties, such as high porosity, sufficient reaction area, and tunable cavity size. They have been widely investigated
in the fields of gas separation, catalysis, and energy storage systems including the Li-S battery.\textsuperscript{49, 131, 132} Although the MOF layer is considered as a molecular sieve to trap or block the polysulfides benefiting from its internal voids; the polysulfides may also diffuse through the inter-granular channels of the MOF films.\textsuperscript{133, 134} Thus, the operation mechanism of the MOF-based separators has not fully reached an agreement yet. Herein, we perform a systematic comparison between the Li-S batteries using separators deposited with different types of MOFs including Y-FTZB, ZIF-7, ZIF-8, and HKUST-1, which have various pore sizes and chemical structures. With the MOF-based separators, the Li-S battery cycle performance is greatly improved, particular with the Y-FTZB. However, the formation of large-scale and grain boundary-free MOFs is still very challenging, where a large number of grain boundaries of MOF particles may also allow the diffusion of polysulfides. Different from previous reports, we found that the packing morphology of MOF particles also plays a critical role together with the size exclusion effect. In addition, selecting the appropriate cut-off voltage is also crucial for minimizing the degradation of MOFs and the occurrence of side reactions, especially when the MOFs contain metal ions that can react with lithium or sulfur, e.g., the Cu$^{2+}$ from the HKUST-1.

7.2 Experimental

7.2.1 Preparation of MOFs

Preparation of Y-FTZB: H$_2$FTZB (68.0 mg, 0.3265 mmol), Y(NO$_3$)$_3$·6H$_2$O (83.5 mg, 0.3265 mmol), DMF (2.50 mL), C$_2$H$_5$OH (1.25 mL), and chlorobenzene (1.25 mL) were mixed in a 20 mL scintillation vial, then sealed and heated to 115 °C for 72 h. After cooling down to room temperature, colorless polyhedral crystals of fcu-MOF were collected and washed with DMF.
The products were then immersed in 10 mL methanol for 3 days, where the methanol was replaced three times per day.

Preparation of ZIF-7: Zinc(II) acetylacetonate hydrate (13.2 mg, 0.5 mmol) and benzimidazole (118 mg, 1 mmol) were dissolved in 100 ml deionized water and mixed with the aid of ultrasonication, where the solution turned into a milk-like suspension quickly. It was kept under ultrasonic treatment for 3 h at room temperature for complete crystallization. The as-synthesized product of ZIF-7 (phase-III) was collected by filtration and washed with ethanol three times and then dried at 50 ºC for 24 h.

Preparation of ZIF-8: Zn(NO₃)₂·6H₂O (405 mg) and 2-methylimidazole (263 mg) were dissolved in 20 mL methanol, respectively. Then, the Zn(NO₃)₂·6H₂O solution was added into the 2-methylimidazole solution. The solution was mixed under 1000 rpm stirring for 5 min and kept static at room temperature for 24 h. The formed particles were collected by centrifugation at 8000 rpm for 10 min and washed twice by ethanol, followed by drying at room temperature.

Preparation of HKUST-1: 0.6 g Cu(Ac)₂·H₂O and 7.4 g propionic acid were dissolved in 60 mL deionized water. Later, a 75 mL DMF solution containing 2 g H₃BTC was added dropwise to the Cu(Ac)₂·H₂O/propionic acid solution with a speed of 2 ml min⁻¹ using a syringe pump under vigorous stirring. The mixture was stirred for 1 h, and the precipitate was centrifuged and washed at 8000 rpm for 10 min using ethanol. The powder was finally dried at room temperature.

7.2.2 Preparation of the Modified Separators

Carbon nanotubes (CNTs, Cnano, China) and the polyvinylidene fluoride (PVDF) binder with a weight ratio of 90:10 were mixed in N-Methyl-2-Pyrrolidone (NMP, Sigma-Aldrich) to form
a uniform slurry and was cast onto one side of the glass fiber (GF, Advantec Co., Japan) by a
doctor blade. The separator was then dried in an air-drying oven at 120 ºC for 2 h to remove
the solvent. The MOF powders were dispersed and sonicated in the NMP solvent first and then
filtrated onto the opposite side of the GF separator, which was then dried in the vacuum oven
at 60 ºC for 24 h followed by punched to Ø18 mm MOF/CNTs separator. The loading and the
thickness of CNT and MOFs are about 0.3 mg cm⁻², 4 μm, and 1.2 mg cm⁻², 10 μm, respectively.

7.2.3 Characterizations

The permeation experiments were performed using two types of specially designed glassware.
The first device has components of two bottles. One small bottle was filled with the brown
electrolyte of 1.0 M LiTFSI, 0.4 M LiNO₃, 0.05M Li₂S₈ in DOL/DME. It was sealed by a blue
cap with a hole in the middle that was covered by the MOF-based separator. The small bottle
was placed upside-down inside of the big bottle, which was filled with the transparent
electrolyte (1.0 M LiTFSI, 0.4 M LiNO₃ in DOL/DME). The brown polysulfide electrolyte can
diffuse into the transparent electrolyte through the MOF-based separators under the force of
the concentration gradient. The second device is for evaluating the filtration speed of the MOF-
based separator, where the polysulfide-based electrolytes are placed on the top side of the
separators to allow the filtration driven by the gravity.

7.3 Results and Discussion

7.3.1 MOF-based Separator in Li-S Battery

The configuration of the battery using the MOF-based separator is illustrated in Figure 7.1a.
The carbon nanotubes (CNTs) facing the cathodic side can act as a conductive layer to promote
the sulfur utilization and also to trap part of the dissolved polysulfides. The MOFs deposited on the other side of the separator behave as an additional blocking barrier to inhibit the shuttle effect of polysulfides. It should be noted that the stacking morphology of MOFs and the interfacial structures with the separators are quite different due to the variations in the sizes and shapes of the MOF particles (Figure 7.1b-e). The XRD results (Figure 7.2) of the MOFs on separators matched well with their reference patterns, which proved that their crystal structures were well reserved.135-138

Figure 7.1 (a) Schematic illustration of the Li-S battery with the MOF-based separator. SEM images of the stacking structure of (b) Y-FTZB, (c) ZIF-7, (d) ZIF-8, and (e) HKUST-1. The scale bar is 200 nm.
7.3.2 Comparison of Electrochemical Performance

The capability to mitigate the polysulfide diffusion by the MOF-based separators was evaluated by the capacity and cycle performance of the Li-S batteries. The initial discharge capacity of the battery with a Y-FTZB-coated separator was the highest, followed by those with HKUST-1, ZIF-7, ZIF-8, and pristine (without MOF), which were 1101, 1032, 1025, 989, and 925 mAh g⁻¹, respectively (Figure 7.3a). The observed voltage plateaus are consistent with the typical profiles in the Li-S batteries, which are related to the conversion from the sulfur to the long-chain lithium polysulfide (Li₂Sn₄, 4 ≤ n ≤ 8) at around 2.4 V and the further reduction to Li₂S₂/Li₂S at 2.1 V.¹³⁹,¹⁴⁰ However, it was observed that the slope zone following the first plateau has varied in the battery using the separator coated with HKUST-1 separator. Moreover, the coulombic efficiency was only 90% for the initial cycle and decreased further with cycling,
indicating the occurrence of side chemical reactions (Figure 7.3b). After 300 cycles, the capacity of the Li-S battery using a Y-FTZB-based separator maintained around 557 mAh g\(^{-1}\), demonstrating the efficient blocking of polysulfide ability by the Y-FTZB. Meanwhile, the value for batteries with ZIF-7, ZIF-8, and pristine (with only CNTs) separators decreased to around 452, 403, and 380 mAh g\(^{-1}\), respectively. The capacity and cycle stability of the battery using the HKUST-1 separator was much worse than that using a pristine separator, demonstrating that HKUST-1 may not be suitable for mitigating the polysulfide diffusion, which is in clear contrast to the previous report.\(^{132}\) The differences become more evident in the C rate tests (Figure 7.3c). The battery with the Y-FTZB separator can deliver a high capacity of 1480 mAh g\(^{-1}\) at 0.1C and showed excellent capacity retention of 987 mAh g\(^{-1}\) when it cycled back to 0.25C. By contrast, low Coulombic efficiency and a dramatic capacity decay were observed in the battery using the HKUST-1 separator, suggesting a severe shuttle effect. The reason is related to its chemical stability, which is discussed in section 7.3.4.
Figure 7.3 Comparison of galvanostatic electrochemical performance of the batteries using different MOF-based separators.

(a) Cycling performance comparison of the batteries using different MOF-based separators under 0.25C, and (b) the relative 1st cycle charge-discharge profiles. (c) C rates performance comparison with different MOF-based separators from 0.1C to 2.5C then back to 0.25C.

To explore the electrochemical behaviors, the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the cells using different MOFs separators were investigated (Figure 7.4a-d). Each battery demonstrated two characteristic cathodic peaks, but the one at around 2.3 V was very weak for the battery using the HKUST-1 separator in the first scan (Figure 7.4d), which is consistent with the observation in the galvanostatic curves that the first plateau was deformed (Figure 7.3b). The CV curves of the battery with the Y-FTZB separator displayed relatively sharp peaks, while the ones with ZIF-7 and ZIF-8 separators showed a
more obvious change in voltage position and distorted peak at around 1.8 V particularly at the high rates, suggesting the decreased suppressing effect for the polysulfide redox process.

The EIS plots and the equivalent circuit used for fitting the Nyquist plot are shown in Figure 7.4e-f. The intersection for the semicircle with the X-axis represents the Ohmic resistance $R_e$ between the electrode and the electrolyte, while the semicircle of the Nyquist plot is the overlap of two semicircles consisting of the charge-transfer resistance ($R_{ct}$) and interfacial layer resistance ($R_{sl}$). After 1st charge to 2.8 V, the battery with the Y-FTZB separator showed the lowest $R_e$ value of 3.8 Ω, demonstrating that the polysulfides can return to the cathode rather than accumulating at the anode side. While for the ZIF-7 and ZIF-8 separators, relatively larger amounts of polysulfides diffused to the anode side due to their relatively weak effect. As a result, solid Li$_2$S$_2$/Li$_2$S was formed and deposited on the lithium surface, leading to increased resistance. The HKUST-1 layer is denser than ZIF-7 and ZIF-8, where more polysulfides can be blocked and thus give rise to a lower $R_e$. Apparently, the semicircle for the Y-FTZB separator had the smallest diameter, confirming a low charge-transfer resistance existed in the battery. While the battery with ZIF-8 separator exhibited the highest resistance, leading to poor battery performance.
7.3.3 Mechanism Study of the MOF-based Separator

The mechanism of MOF based separators in polysulfide suppressing is in a debate. Zhou et al.\textsuperscript{132} have suggested that MOF materials could repel the polysulfide due to its ion sieve property, and hence the performance is expected to decrease with an increasing pore size; i.e. in the sequence of 2.9 Å (ZIF-7), 3.4 Å (ZIF-8), 6 Å (Y-FTZB) and 9 Å (HKUST-1) in our case (Figure 7.5a-d). However, the electrochemical performance of these batteries in our experiments did not exactly follow the sequence, while the Y-FTZB being the best, followed by ZIF-7, ZIF-8 and HKUST-1. The results suggest that the pore size exclusion effect in MOFs is not the only determining factor for polysulfide migration. Besides, it is rational to speculate that the polysulfide can easily penetrate through the grain boundaries.

Park et al.\textsuperscript{133} used density functional theory calculation to study the molecular structure, claiming that the MOF material can trap the PS species by adsorption. Experiment was
conducted to prove this proposal with the four types of MOFs (Figure 7.5e). Small vials were filled with the 10 mL DOL/DME mixture (1:1, v/v). 104 µL 0.05M Li2S8 brown electrolyte was added into the bottle, which amount equals to the sulfur loading on the cathode. With the PS electrolyte, the original transparent solution turned into yellow color, and the same amount of MOF particles were further added to adsorb the PS. It was noticed that there was no obvious color variation among these samples, meaning that the adsorption may take a very limited effect in minimizing the polysulfide shuttling.

![Figure 7.5 MOF structure and adsorption visualization.](image)

The chemical structure of (a) Y-FTZB, (b) ZIF-7, (c) ZIF-8, and (d) HKUST-1. (e) The visualization experiment for the MOF adsorption effect. The polysulfide electrolyte and MOF amount equal to the amount used in the Li-S battery.

Seen from the SEM images, the structure of the Y-FTZB-based layer looks generally dense, where the large particles cover most of the surface area, and the boundary gap can be further filled with small particles. The ZIF-7 layer has a well-packed structure with its relatively large
particles. By contrast, the ZIF-8 layer has a loose stacking form. The HKUST-1 also displayed a loose-packed morphology as shown in Figure 7.1e. It is thus reasonable to suspect that a more densely packed structure may have a superior effect in stopping the diffusion process. To obtain the direct insights of the polysulfide physical blocking capability of various MOFs, two types of specially designed devices were constructed to visualize the effect. First shown in Figure 7.6a, a small bottle containing a brown polysulfide electrolyte (0.05 M Li2S8) was separated from the standard clear electrolyte by the MOF-based separators. The driving force of the polysulfide diffusion is the concentration gradient. The transparent electrolyte in the bottle with the pristine separator become light yellow color within 1 h, while the others with MOF separators remained clear. This phenomenon directly proved that all the MOFs have a certain ability in blocking the polysulfides. After 4 h, the bottle with the Y-FTZB separator demonstrated the lightest electrolyte color, followed by HKUST-1, ZIF-7, and ZIF-8, while the pristine being the darkest. The superior blocking capability of Y-FTZB could be attributed to its high packing density, which also corresponds well to its superior cycle stability as discussed in Figure 7.3. The HKUST-1 has a loose surface but dense bulk packing, while the ZIF-7 being just the opposite, which results in their similar blocking effect. The ZIF-8 has both loose-packed surface and bulk structure, leading to the worst performance. The filtration rate experiment as demonstrated in Figure 7.6b also showed the consistent trend that the MOF with a slower filtration rate results in better cycle performance in Li-S batteries. For example, the Y-FTZB separator demonstrated the longest diffusion time and proved its best capability to suppress the polysulfide diffusion. Based on the above results, it is confirmed that the physical blocking plays an important role in the suppression of polysulfides diffusion for the MOF materials.
Figure 7.6 Comparative visualization of the polysulfide diffusion process.
(a) The polysulfide electrolyte containing 0.05 M Li$_2$S$_8$ with 1 M LiTFSI and 0.4 M LiNO$_3$ in DOL: DME (1/1, v/v), and the standard clear electrolyte is the same as that used in the battery test. The separator was fixed on the cap of the small bottle to examine the polysulfide diffusion from the small bottle into the big bottle. (b) The separator was placed between two glass tubes and the upper one has a scale to record the volume variation of electrolyte. The polysulfide electrolyte can pass through the separator to the bottom glass tube, and the total time for the diffusion of 10 mL electrolyte was recorded.

7.3.4 Discussion for the HKUST-1 MOF and Material Selection

Although the HKUST-1 separator is dense and exhibits slow diffusion and filtration features, the poor battery performances with low coulombic efficiency resulted from its chemical instability. The sulfur cathode would self-discharge and react with Cu from the HKUST-1 cluster to form CuS, which can further react with Li$^+$ and transform into Cu$_2$S and Li$_2$S when discharged to 2.1 V.$^{141-143}$ Considering that the HKUST-1 is facing the anode side, the formed Cu$_2$S and Li$_2$S can deposit on the lithium surface and inhibit the SEI formation, leading to the low Coulombic efficiency. The problem is more pronounced at a low C-rate because of the full
side reactions. With further charge and discharge, the reaction may be reversible when the
discharge voltage was stopped at 1.8 V, although the capacity was not high due to the loss in
the first few cycles. Unfortunately, if the discharged voltage was set at 1.5 V, together with the
decomposition of the electrolyte, the battery will suffer severe degradation and a tremendous
capacity fading (Figure 7.7a, b). This mechanism also explained the lower EIS for the battery
using the HKUST-1 separator. The copper sulfide and/or Cu, resulting from the side reaction
of the sulfur and Cu ions, can cover the lithium surface and incorporate into the SEI layer,
thereby giving rise to a lower Rsl and Rct (Figure 7.4e). The observation and speculation were
confirmed by the XRD analysis of the separator coated with HKUST-1. As shown in Figure
7.7c, the HKUST-1 can maintain its primary crystal structure even after 100 cycles when the
discharged voltage of battery was cut at 1.8 V but was almost destroyed after cycling with the
discharge voltage of 1.5 V. Thus, the stability and the selection of MOFs is also important to
guarantee the battery performance, where the appropriate charge/discharge voltage is also
critical.
Figure 7.7 Mechanism study of the battery using HKUST-1 based separator.

(a) Comparative cycle performance of batteries using HKUST-1 separator when the battery was discharged to 1.8 V and 1.5 V, respectively. (b) Typical galvanostatic charge-discharge profiles of the battery at the 1st, 2nd, 10th and 100th cycles using HKUST-1 separator when it was discharged to 1.5 V. (c) Variation of XRD patterns of the HKUST-1 on separator before and after cycling.

7.4 Conclusions

In this study, we modified the separators with various MOFs to reveal their functionality of mitigating polysulfide diffusion in Li-S batteries. The MOF-based separators can suppress the polysulfide shuttling effect and improve battery performance, which is caused by the combined effects of MOFs’ chemical and physical properties. The chemical side reaction of HKUST-1 with lithium primarily degraded its battery performance. Meanwhile, selecting a proper charge-discharge voltage window is critical to maintain the stability of MOFs, avoid electrolyte decomposition and other side reactions.
Chapter 8: Protection of Lithium Anode by a Highly Porous PVDF Membrane for High-Performance Li-S Battery

8.1 Introduction

With the global electrification process, it is commonly acknowledged that building the modern world requires high-performance rechargeable batteries. The lithium-ion battery (LIB), developed in 1991, has been widely utilized and occupied the majority of the electric industry market. However, the demand for higher battery capacity has kept growing, and the state-of-art LIB cannot fully satisfy the request. Thus, the high capacity lithium-sulfur (Li-S) battery has caught great attention in recent years. This attractive advantage depends mostly on the utilization of lithium metal as an anode material because it is not only the most lightweight metal but also containing an extremely high theoretical specific capacity (~3,860 mAh g⁻¹) and a low redox potential (-3.04 V).

Despite the benefits, however, there are several issues that hinder the practical application of lithium metal in Li-S batteries. The first is the formation of uncontrollable dendrites on the lithium anode surface during the dissolution/deposition processes, which may penetrate the separator and cause a battery short circuit. Also, unlike the graphite anode, the solid electrolyte interphase (SEI) formed on lithium surface will be continuously destroyed by the consumption of lithium anode and electrolyte, leading to poor cycling performance. Moreover, the cross-over of the soluble polysulfides caused by the so-called “shuttle effect” during cycling will lead to the deposition of insulating species (i.e., Li₂S and Li₂S₂) on the anode surface that will quickly decrease the electrical capacity and the Coulombic efficiency (CE). To overcome these issues, various techniques have been utilized. One method is to modify the separator by carbon, metal oxides, polymers, or two-dimensional materials, to suppress the shuttle effect. However, this approach cannot sufficiently restrict
lithium dendrites growth. Recently, a more straightforward yet efficient strategy has been developed. By directly protecting the lithium anode with an artificial layer or SEI, the lithium surface can be insulated from the polysulfide intermediates, and the formation of dendrites can be minimized as well.\textsuperscript{110, 152-154} However, most reported methods involved either complicated processes or hazardous and expensive materials, which is not well suitable for practical applications. A low-cost, stable, and easily processable layer is thus highly desirable.

Polyvinylidene difluoride (PVDF) is known to have excellent electrochemical and thermal stability and has been used as a universal binder and the separator in lithium/lithium-ion batteries.\textsuperscript{155, 156} In our previous work, we developed a novel “mixed solvent phase separation” (MSPS) method to prepare highly porous PVDF membranes.\textsuperscript{157} The membrane has an ultrathin skin layer containing a super high density of uniform surface pores with pore size around 30 nm and a sponge-like bulk layer with pore size in hundreds of nanometers. Such an asymmetric porous structure is formed in one process and has a great advantage in separation since it meets the requirements for both high selectivity and high permeability. The unique porous structure also stimulates us to apply it as a protection layer for lithium anode in Li-S battery. It is expected that the porous PVDF membrane can block the deposition of polysulfide species and inhibit the growth of lithium dendrites. While from the other hand, the highly porous structure, particularly the high-density surface pores, will allow fast transport of lithium ions, which ensure high rate cyclability. As expected, a high specific capacity of around 850 mAh g\textsuperscript{-1} over 200 cycles under 0.5 C with a Coulombic efficiency of 98\% is reported here for the Li-S battery.

\textbf{8.2 Experimental}

\textbf{8.2.1 Preparation of PVDF membrane and Anode}
The PVDF membrane was prepared by mixing 11.5 wt% PVDF in 65.8 wt% DMF and 22.7 wt% of octane at 90 °C to form a homogeneous casting solution. A thin film was cast on a glass plate by a doctor blade with 60 mm air gap inside a hot chamber at 85 °C. The film was covered by a glass container and left at room temperature. The surface temperature was monitored by an IR thermometer (TRACEABLE® VWR). After 60 s, the membrane was immersed in a room temperature DI water coagulation bath until it was detached. The membrane was then taken out and kept in another fresh DI water for 24 h to remove any trace of solvent, further washed with IPA several times and then dried at ambient conditions. The dry membrane showed a white color and was opaque.

The prepared PVDF membrane was dried under 60 ℃ under vacuum before transferring into the Ar-filled glovebox, where the moisture and oxygen were controlled below 0.5 ppm. The PVDF membrane was further roll-pressed on lithium foil, cut into φ12 mm round discs, and used as the anode.

8.2.2 Electrochemical measurements

For Li migration measurements, symmetric Li coin cells were assembled with and without the PVDF membrane on one side of the lithium foil in the CR2032-type coin cell. The typical Li-S battery electrolyte is 1M bis(trifluoromethyl sulfonyl)amine lithium salt (LITFSI, Sigma) and 0.4M LiNO₃ in 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME, 50:50, v/v, Sigma). And the commercial LIB electrolyte is 1M LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC, 50:50, v/v, Sigma). An areal current density of 1 mA cm⁻² was applied for Li stripping/plating tests. For Li-S battery, the cathode, glass fiber separator (Advantec) coated with a thin layer of carbon nanotubes (CNTs, Cnano), and lithium anode (w/o PVDF membrane) were assembled.
The battery cycling cut-off voltage is 1.8-2.8 V under different C rates, where 1 C = 1,675 mAh g⁻¹.

8.2.3 Characterizations

The cycled lithium anodes were disassembled after 100 cycles and washed with DME electrolyte before doing the SEM. The prepared PVDF membrane was characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet iS10) equipped with a smart OMNI transmission ranging from 400 to 4000 cm⁻¹. The contact angle of the membrane with 2 µL water or liquid electrolyte was carried out by a contact angle goniometer FM40, KRUSS GmbH, Germany. The electrolyte uptake was calculated based on (M₁-M₀) / M₀ × 100, where M₁ and M₀ represent the mass of the electrolyte absorbed membrane and dry membrane, respectively.

8.3 Results and Discussion

8.3.1 Physical Properties of the PVDF Membrane

The SEM images of the PVDF membrane are shown in Figure 8.1a and 8.1b. It can be seen that the membrane surface contains a high density of circular pores with a narrow pore size distribution centered at 30 nm (Figure 8.1c). The surface porosity is more than 20%. However, the bulk of the membrane has a sponge-like porous structure with pore size in hundreds of nanometers that is much bigger than the surface pores. The surface layer is very thin and interconnected with the bulk layer. The asymmetric porous structure is formed in one-step through the novel MSPS process. The detail membrane preparation procedure and the pore-forming mechanism can be found in previous work.¹⁵⁷ The membrane thickness can also be
tuned by adjusting the amount of PVDF used in the preparation (e.g., Figure 8.1d, 29.82 µm), and the thinnest film of around 19 µm (Figure 8.1b) was used in the battery.

![Figure 8.1 SEM image of the PVDF membrane and pore size distribution plot.](image)

(a) Surface and (b) cross-section SEM images of the prepared PVDF membrane, while the thickness of the membrane is about 19.08 µm. (c) Relative pore size distribution curves. (d) The cross-section SEM for the PVDF membrane, which thickness is 29.82 µm.

The Fourier transform infrared spectra (FTIR) in Figure 8.2a revealed that the PVDF membrane contained α, β, and γ three types of crystalline phases. Figure 8.2b shows the
uptake curve of the PVDF membrane versus time with the electrolyte of 1 M LiTFSI in DOL/DME. The electrolyte uptake ratio increased with time and reached a saturated capacity of 700% after 30 min. This value is substantially higher than other hosts benefitting from the highly porous sponge-like structure, and a high electrolyte uptake is beneficial for achieving a high conductivity.\textsuperscript{159, 160} Figure 8.2c and 8.2d show that the PVDF membrane has a contact angle of 84.3° for water and 28.6° for electrolytes. This is expected as PVDF is well known to be hydrophobic and oleophilic. The wettability is critical for the battery’s electrochemical performance because a poor wettability will increase the internal resistance and reduce the rate capability.\textsuperscript{161} A low contact angle to electrolyte indicates that the electrolyte can easily penetrate through the membrane, which can guarantee the fast transport of lithium ions.

Figure 8.2 (a) FTIR spectra of the PVDF membrane. (b) Electrolyte uptake plots of the PVDF membrane. The contact angles of the membrane with (c) water and (d) liquid electrolyte.
8.3.2 Lithium Cyclability with the PVDF Membrane

To investigate the reversibility of lithium during the deposition/dissolution process, two symmetric cells containing Li/PVDF|PVDF/Li and bare Li|Li were assembled and cycled at 1mA cm\(^{-2}\). Figure 8.3a shows the voltage vs. time profiles of the two cells, while the magnified profiles of 2-10 h and 100-110 h (which equal to about 1-15 and 181-200 cycles) are shown in Figure 8.3b and 8.3c. Initially, both cells displayed a decreased voltage trend, but the cell containing the PVDF membrane exhibited a little lower polarization than the pristine one. For the pristine cell, the overpotential varied significantly during the Li migration process, especially reaching around 25 h (which equals to about 40 cycles), indicating the poor reversibility and uneven growth of the ‘dead’ Li. In clear contrast, the battery with the PVDF protecting film maintained steadily decreased potential for more than 250 h, which is equivalent to more than 450 cycles, proving its superiority in suppressing the Li dendrite. Moreover, commercial LIB electrolyte (1M LiPF\(_6\) in EC/DEC) was examined and shown in Figure 8.3d-f. It is more evident to see that the pristine lithium metal performed worse in the commercial LiPF\(_6\) electrolyte, which is in agreement with the previous report\(^{162}\). The cell with PVDF membrane coated Li, however, demonstrated a much lower Li migration voltage and better retention performance than the pristine Li cell. This result also indicates the stability of the PVDF membrane in a different environment and its applicability in commercial LIB.
Figure 8.3 Lithium stripping-plating profiles with different electrolytes.

(a) Galvanostatic charge-discharge voltage profiles for pristine Li and PVDF/Li symmetric cells at a constant current density of 1 mA cm$^{-2}$ in LiTFSI electrolyte. Magnified voltage profiles from (b) 2-10 h and (c) 100-100 h. (d, e, f) Relative profiles with the LiPF$_6$ electrolyte.
8.3.3 Electrochemical Performance of the Li-S Battery

The Li-S battery electrochemical performance was studied with coin cells assembled with the simple sulfur/carbon composite cathode and the lithium anode with and without the PVDF membrane. As shown in Figure 8.4a, the battery cycling performance distinguishes significantly under 0.5 C (1 C = 1675 mAh g⁻¹). For the pristine battery, the initial discharge capacity was only 601 mAh g⁻¹ and dropped to 194 mAh g⁻¹ after 200 cycles. Such a quick capacity decay is normal for Li-S batteries that have no protection, attributing to the severe shuttle effect of the polysulfide species. As a comparison, the battery with PVDF/Li delivered an initial capacity of 968 mAh g⁻¹. After 200 cycles, the capacity slowly decreased to 850 mAh g⁻¹, and a high CE of around 98% was maintained. The enhanced battery capacity and excellent cycling stability of the PVDF/Li battery demonstrate that the PVDF membrane has effectively suppressed the shuttle effect as well as lithium dendrites. Fig. 3b shows the galvanostatic charge-discharge profiles of the first cycle. Both batteries exhibited two characteristic reduction peaks at ~2.3 V and ~2.0 V, which are associated with the reduction of the elemental sulfur to dissoluble long-chain polysulfides (Li₂Sn₄, 4 ≤ n ≤ 8) and further to short-chain insulating polysulfides (i.e., Li₂S₂ and Li₂S). These peak voltage values are consistent with the reported results.¹⁶³,¹⁶⁴ The result also proves that the PVDF membrane did not react inside the battery or hinder the lithium diffusion process. It is further noticed that the second stage of the charge-discharge curve of the pristine battery is much shorter, which indicates that the polysulfide species have migrated to the anode side and could not undergo further reactions.

The cycled Li-S batteries were further disassembled, and the anodes were characterized by SEM and EDS (Figure 8.4c-g). The pristine anode displayed a rough morphology with congregated dendrites (Figure 8.4d) and was full of polysulfide deposition (Figure 8.4e). In contrast, the PVDF protected lithium anode is relatively smooth (Figure 8.4f) and remained
similar to the uncycled one (Figure 8.4c). The formed dendrites were small and hardly visible. Moreover, the EDS results indicated a much less deposition of sulfur element than the unprotected one (Figure 8.4g). These observations confirm that the PVDF membrane can efficiently inhibit the Li dendrite growth and suppress the polysulfide shuttling.

**Figure 8.4** Cycling performance of the Li-S battery and comparison of the cycled lithium anode morphologies.

(a) Cycling performance comparison of Li-S cells with PVDF/Li and pristine Li anode at 0.5 C and relative (b) first cycle charge-discharge curves. (c) SEM images of bare Li foil surface before cycling. SEM image and EDS mapping of sulfur element for (d, e) bare Li and (f, g) PVDF protected Li after 200 cycles in Li-S batteries. The scar bar is 2 µm.

To investigate the battery rate capability in-depth, the batteries were cycled from 0.1 C to 2.5 C, and each C rate tests were followed with electrochemical impedance spectroscopy (EIS) measurements (Figure 8.5). As cycling from low to high rates, the battery with PVDF/Li anode
delivered the capacity of 1390, 1137, 1015, 883 and 660 mAh g\(^{-1}\) under the rate of 0.1 C, 0.25 C, 0.5 C, 1 C, and 2.5 C, respectively. The one with pristine Li, however, decreased almost linearly at the first five cycles under 0.1 C and exhibited less than half the value of the capacity compared to the PVDF/Li battery. The excellent rate capability and cycle stability confirm that the PVDF layer can effectively enhance battery performance. Furthermore, after each five rate tests, electrochemical impedance spectroscopy (EIS) measurements were conducted for two cells, shown in Figure 8.5b and 8.5c. The intercept of the compressed semicircle with the x-axis at the high-frequency range corresponds to the ohmic resistance (Re), which value (around 5 \(\Omega\)) was very close for the batteries with and without the PVDF protective layer before cycling, demonstrating that the PVDF layer does not introduce much internal resistance. With the rising of the C rate and cycles, the pristine cell demonstrated an increasing Re. It has a noticeable change that when reaching 0.5 C, the Re value increased to around 7 \(\Omega\) and an extra semicircle has appeared from 1 C (Figure 8.5b). The addition of the Re comes from the redistribution of the insulating sulfur during the charge-discharge process, and the appearance of the second semicircle suggests a much larger charge transfer resistance and the formation of an SEI film. The insulating polysulfides will shuttle and deposit on the surface of cathode and anode during the reduction/oxidation process, which will form the SEI. In comparison, the Li-S battery with the protected Li anode revealed a smaller interfacial resistance even at high rate cycling, implying the PVDF layer functions as a stable and less resistive protective film that facilitate lithium ion transfer at the interfaces during cycling. No appearance of additional semicircle also indicates that the insulating polysulfides during the charge/discharge process are suppressed effectively, further proving the capability of suppressing the shuttle effect of the PVDF membrane. Based on the impedance results, the ionic conductivity are further calculated using relation \(\sigma = \frac{L}{RA}\), while \(\sigma\) is the ionic conductivity, R is the intercept of the semicircle with the real \(Z'\) axis, L is the distance between the electrode, and A is the contact area. We
could simply consider the thickness of the separator and separator with the membrane as the L. In the Li-S battery, the glass fiber separator used is around 190 µm while the PVDF membrane is around 20 µm. The contact area for the electrode is 1.13 cm². After cycling under 0.1C, the R values for pristine and PVDF protected membrane are 7.99 Ω and 9.19 Ω, respectively, and the relative calculated ionic conductivities are $2.1 \times 10^{-3}$ S cm⁻¹ and $2.02 \times 10^{-3}$ S cm⁻¹. The values are almost the same, suggesting that the ionic conductivity will not be affected by adding the PVDF membrane.

**Figure 8.5** Battery C-rate performance and Nyquist plots after each rate test.

(a) Rate capabilities of Li-S batteries with PVDF/ Li and bare Li anode tested at 0.1 C, 0.25 C, 0.5 C, 1 C and 2.5 C. 1 C = 1,675 mAh g⁻¹. Nyquist plots for cells using (b) pristine Li and (c) PVDF/Li after every five cycles of rate tests.
8.4 Conclusions

In conclusion, we have developed a novel porous PVDF membrane and utilized it as a Li anode protection layer in Li-S battery. The PVDF membrane can restrain the Li dendrite and block the polysulfide deposition on the anode. It also exhibits high chemical and physical stability during the battery cycling process. For the pristine battery, the initial discharge capacity was only 601 mAh g\(^{-1}\) and dropped to 194 mAh g\(^{-1}\) after 200 cycles. But with the help of the protective layer, the Li-S battery enhanced greatly in Coulombic efficiency and electrochemical stability, delivering an 968 mAh g\(^{-1}\) initial capacity and 850 mAh g\(^{-1}\) capacity and 98% CE after 200 cycles at 0.5 C. The preparation of the PVDF membrane is easy, scalable, and cheap, which make it a promising approach to improve the Li-S battery performance.
Chapter 9: Summary and Perspective

Several methods have been developed and studied in this dissertation, and each conclusion is summarized in the “conclusions” section in each chapter. A comparison of battery performance including capacity and cycling stability is presented in Table 3.

<table>
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<tr>
<th>Method</th>
<th>Material used</th>
<th>Properties</th>
<th>1st cycle capacity / mAh g⁻¹</th>
<th>100th cycle capacity / mAh g⁻¹</th>
<th>Capacity retention / %</th>
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<td>/</td>
<td>/</td>
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<td>16.9</td>
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<td>968</td>
<td>822</td>
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</table>

* Only the PVDF was tested under 0.5 C, while the others were tested under 0.25 C.

Overall, the techniques have been proven effective in suppressing the polysulfide shuttling effect, which can be generalized as below.

- Separator modification with functional materials: As the barrier between cathode and anode, the separator is the essential wall to block the PS, and its modification is necessary. There are several principles that can be applied: 1) Absorbing or trapping the PS in 3D networks,
which can eliminate the PS deposition on the anode. This aspect is discussed in Chapter 3.

2) Repelling negative charged PS by electrostatic force is an effective way, as discussed in Chapter 4 and Chapter 5. 3) The PS species size varies from long-chain to short-chain. Finding a material with a smaller pore size or material with dense stacking can help to block them at the cathode size. Materials such as COF can be designed to satisfy the request, as shown in Chapter 6. 4) Sometimes, using materials combining two (or more) mechanisms will also be quite effective, such as MOF materials which possess physical blocking and size exclusion functions as in Chapter 7.

- Anode protection: Employing lithium anode has great benefits but also brings a safety concern due to the lithium dendrites. The insulating Li$_2$S and Li$_2$S$_2$ will attack and poison the lithium, leading to capacity decay and low coulombic efficiency. Therefore, the protection layer or artificial SEI is critical to solving the problem. The method has been risen in Chapter 8 and will be further studied in the future.

- Solid-state battery: The sulfur species will dissolve into the electrolyte and diffuse, thus currently liquid electrolytes will never be practical to fully stop the shuttle issue. A more reliable answer is to use the gel polymer and solid-state electrolyte, which will successfully anchor the PS at the cathode side. This aspect will be studied further as well.
REFERENCES


155. Costa, C. M.; Silva, M. M.; Lanceros-Mendez, S., Battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium ion battery applications. RSC Adv. 2013, 3 (29), 11404-11417.


APPENDICES

List of Selected Publications


   *This work forms the majority of the basis for Chapter 7.*


   *This work forms the majority of the basis for Chapter 3.*


   *This work forms the majority of the basis for Chapter 8.*

4. J. Huang†, **M. Li†**, Y. Wan, S. Dey, M. Ostwal, D. Zhang, Z. Lai, Y. Han, S. Li, L.J. Li. Functional Two-Dimensional Coordination Polymeric Layer as a Charge Barrier in Li-S Batteries. *ACS Nano*, 2018, 12, 836. († **Contributed equally**)

   *This work forms the majority of the basis for Chapter 5.*


13. M. Li, J. Ming, L.J. Li, KCC. Lithium and sodium batteries with polysulfide electrolyte.