ZHU, JIADENG. Advanced Separator Selection and Design for High-Performance Lithium-Sulfur Batteries. (Under the direction of Dr. Xiangwu Zhang).

Sulfur (S) has received much attention recently as a promising cathode material for high-specific energy rechargeable lithium batteries due to its high theoretical capacity (1,675 mAh g$^{-1}$), which is calculated based on the complete reduction from S to lithium sulfide (Li$_2$S). Moreover, S is inexpensive and nontoxic. Despite these significant advantages, the practical applications of Li-S batteries are hindered by the short cycle life, severe capacity fading and low Coulombic efficiency. All of these challenges are related to the dissolution of reduction intermediates, lithium polysulfides, in the electrolyte, resulting in parasitic reactions. Therefore, it is essential to suppress the diffusion of polysulfides in order to obtain high performance Li-S batteries.

To address the abovementioned challenges for Li-S batteries, the main approach has been to perform nanomaterials (including porous hollow carbon, carbon nanofiber, carbon nanotubes, graphene oxide, graphene, yolk-shell TiO$_2$ spheres, conductive polymers, etc.) as conductive frameworks for sulfur cathodes. These conductive frameworks help sulfur cathodes achieve high capacity and long cycle life by enhancing the electrical conductivity of the cathode and minimizing the loss of soluble polysulfide intermediates during cycling. However, those methods generally involve complex, multi-step synthetic processes, which hinder the practical application of Li-S batteries. Moreover, the severe self-discharge induced by polysulfides has not been fully solved.
As a critical component in battery systems, the separator plays an important role in all batteries because its main function is to prevent electrical short circuiting by separating positive and negative electrodes while simultaneously transporting the ions. An ideal separator for Li-S batteries is expected to not only have a good ionic conductivity but also to suppress the migration of polysulfides during cycling. Recently, glass fiber (GF) and as-spun polymer nanofiber membranes have received attention for use as battery separators because they have a relatively higher porosity compared to polypropylene (PP) or polyethylene (PE) membranes. The higher porosity results in higher electrolyte intake and consequently greater ionic conductivity when placed in an electrolyte, facilitating rapid ionic transportation.

In this work, glass fiber and polymer nanofiber membranes were investigated as superior separators for Li-S batteries. In order to further improve the electrochemical performance of the Li-S cells, different approaches were utilized, including carbon-coating on the separators, incorporating particles into polymer nanofibers, and insertion of multi-walled carbon nanotube interlayer. The improved performance is likely due to the suppression of polysulfide migration by these methods, not only enhancing the utilization of the active materials but also protecting the Li anode as well.
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Advanced Separator Selection and Design for High-Performance Lithium-Sulfur Batteries

by

Jiadeng Zhu

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Fiber and Polymer Science

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DEDICATION

To my beloved parents and my wife,

without their continuous encouragement, this is impossible to be accomplished.
BIOGRAPHY

Jiadeng Zhu was born in Rugao, Jiangsu Province, China. He received his Bachelor degree in Macromolecular Materials & Engineering and Master degree in Textile Engineering, respectively, from Soochow University (China) and Chonbuk National University (Korea). After one and half years’ research work in Korea Institute of Science and Technology (KIST), he started to pursue his Ph.D. in Fiber and Polymer Science at North Carolina State University in August 2013.
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CHAPTER 1 OVERVIEW OF LITHIUM-SULFUR BATTERIES

1.1 Introduction

With the continuously increasing demand for energy around the world along with the extensive development of electric vehicles and portable electronic devices, advances in energy storage systems are essential.\(^1\)-\(^{13}\) It is clear that the intensive use of petroleum for transportation has significantly influenced the environment, negatively affecting the quality of life.\(^{14}\)-\(^{18}\) Therefore, clean energy sources such as solar and wind energies are becoming more and more important. Unfortunately, the application of solar and wind energies are less viable without energy storage, thus it is critical for efficient and economical storage of electricity produced by renewable sources to be competitive.

Rechargeable lithium-ion batteries have been the subject of intense research over the past three decades due to their relatively higher energy density, longer cycle life, and low environmental impact compared to the well-known Ni-Cd and Ni-MH battery systems.\(^{19}\)-\(^{34}\) As highlighted in Figure 1.1, the comparison between specific and volumetric energy densities for rechargeable battery technologies shows these differences.\(^{35}\) The general goal for battery development is to increase energy density. For example, the huge demand for portable electronics by consumers means that researchers are pursuing both smaller and lighter batteries which need less time to charge, but without minimizing usage time or cycling life. However, it is very hard to further improve the energy density of Li-ion batteries since the limited electrochemically-stabile
working window for the currently available liquid electrolytes makes it difficult to increase the cathode operating voltage beyond ~4.5 V. In addition, the capacities of the insertion-oxide cathode and the graphite anode are limited to ~250 mAh g\(^{-1}\) and ~370 mAh g\(^{-1}\), respectively. Therefore, alternative cathodes and anodes offering higher capacities need be developed.

Figure 1.1 Comparison of the different battery systems in terms of energy density.\(^{35}\)

Lithium-sulfur (Li-S) batteries are prospective candidate in this regard not only because S has a high theoretical capacity of 1,675 mAh g\(^{-1}\) which is an order of magnitude higher than those of the insertion-oxide cathodes but also due to their low cost and environmental friendliness.
In terms of the energy density of Li-S batteries, the theoretical value is ~2500 Wh kg\(^{-1}\) (or ~2800 Wh L\(^{-1}\)) calculated based on the Li anode and the S cathode (shown in Figure 1.2).\(^{37}\) The practical energy density of packaged Li-S batteries would be as high as 500 Wh kg\(^{-1}\) which is two or three times higher than the current commercial LIBs, as exhibited in Figure 1.3.\(^{38}\)

![Figure 1.2 Theoretical energy densities of various rechargeable batteries based the active materials only.\(^{37}\)](image)
Figure 1.3 Practical energy densities of various rechargeable batteries.\textsuperscript{38}
1.2 Mechanism

A Li-S cell is an electrochemical storage device through which electrical energy can be stored in sulfur electrodes. Figure 1.4 shows a schematic of the components in a single Li-S cell.39

![Schematic image of a conventional Li-S cell.](image)

Like LIBs, a Li-S cell also includes cathode, separator, anode, and electrolyte in between. As shown in Figure 1.4, Li metal and S are used as the anode and cathode, respectively. The microporous polyolefin (e.g. polypropylene) is generally applied as the separator. The operating principle of Li-S battery relies on electrochemical reactions between S and Li,
supported by the electrolyte as a conductive medium for Li ions. Since S is in the charged state, the cell operation starts with discharge. The typical discharge-charge profile for the first cycle of the Li-S cell is shown in Figure 1.5.\(^\text{40}\)

![Figure 1.5 Typical voltage profiles of a Li-S cell.\(^\text{40}\)](image)

During the discharge process, Li metal is oxidized at the negative electrode to produce Li ions and electrons. The produced Li ions move to the positive electrode through the electrolyte while the electrons go to the positive electrode through the external electrical circuit.\(^\text{41}\) S reduction is a multistep electrochemical process that involve several various intermediate species.\(^\text{42-50}\) As shown in Figure 1.5, the discharge process are divided into four regions.
Region I: A solid-liquid two-state reduction from S to Li$_2$S$_8$. The high solubility of Li$_2$S$_8$ in the electrolyte results in a big volume change.

\[ S_8 + 2Li \rightarrow Li_2S_8 \]  \hspace{1cm} (1.1)

Region II: A liquid-liquid single-state reduction from Li$_2$S$_8$ to low-order polysulfides (Li$_2$S$_x$, 4 \leq x < 8). The solution’s viscosity achieves a maximum value at the end of this region.

\[ Li_2S_8 + 2Li \rightarrow Li_2S_{8-x} + Li_2S_x \]  \hspace{1cm} (1.2)

Region III: A liquid-solid two-state reduction from low-order polysulfides to solid Li$_2$S$_2$ or Li$_2$S.

\[ 2Li_2S_x + (2x-4) Li \rightarrow xLi_2S_2 \]  \hspace{1cm} (1.3)

\[ Li_2S_x + (2x-2) Li \rightarrow xLi_2S \]  \hspace{1cm} (1.4)

Region IV: A solid-solid single-state reduction from Li$_2$S$_2$ to Li$_2$S.

\[ Li_2S_2 + 2Li \rightarrow 2Li_2S \]  \hspace{1cm} (1.5)

During the charge process, the oxidation reactions of lithium sulfides to polysulfides and finally to sulfur occur.

As shown in Figure 1.5, there are two arrows. Arrow 1 is ascribed to a point at which the polysulfide solution has the highest viscosity as a combined result of the S-S chain length and
concentration of polysulfide anions. Arrow 2 presents a reduced polarization as a result of the phase transition from solid Li$_2$S$_2$ and Li$_2$S to the soluble polysulfides.

The theoretical capacities of S and Li are 1,675 and 3,862 mAh g$^{-1}$, respectively, which lead to a theoretical cell capacity of 1,168 mAh g$^{-1}$ for the Li-S cell. And the discharge reaction has an average cell voltage of 2.1 V, hence, the theoretical gravimetric energy density for a Li-S cell is ~2500 Wh kg$^{-1}$. 
1.3 Challenges

The practical applications of Li-S batteries are hindered by many factors that need to be addressed.

1.3.1 Sulfur Cathode and Its Intermediates

The first challenge comes from the S and its various intermediate polysulfides formed during the discharge which show poor ionic and electronic conductivities, causing the internal resistance of the battery to increase and limiting of the active material utilization efficiency and rate capability. The increase of internal resistance also leads to a large polarization that reduces the energy efficiency of the battery. In addition, the intermediate products of lithium polysulfides (Li$_2$S$_x$) formed during the cycling along with their structural and morphological changes results in unstable electrochemical contact with sulfur electrodes.

The second challenge lies in the electrochemical process of the Li-S battery. As discussed above, the discharge process of the Li-S battery contains four regions. S element (S$_8$) is reduced by Li step-wisely to form soluble Li$_2$S$_8$ and Li$_2$S$_6$, semi-solid Li$_2$S$_4$, and then solid Li$_2$S$_2$ and Li$_2$S. During the reverse charging process, Li$_2$S is first oxidized to polysulfides and finally to sulfur. It is demonstrated that the polysulfides (mainly Li$_2$S$_4$-Li$_2$S$_8$) produced during cycling can easily react with or dissolve into the organic solvent of electrolyte, leading to irreversible capacity fade of the solid cathode. Moreover, the dissolved polysulfides can migrate onto
the Li anode by a so-called shuttle effect (shown in Figure 1.6) and thereby form an electrochemically inactive layer, consisting mainly of Li$_2$S$_2$ and Li$_2$S, further reducing the battery efficiency.$^{41}$

![Figure 1.6 Schematic image of the shuttle mechanism in a Li-S cell.](image)

The third challenge is related to volume change during the cycling process, as shown in Figure 1.7.$^{61}$ The densities of S and its final reduction product Li$_2$S are 2.07 and 1.66 g cm$^{-3}$, respectively, which result in a volumetric increase by $\sim$79% in a full discharge. The big volume change makes Li$_2$S lose their electrical contacts with the conductive substrate or the current collector, leading to a fast capacity fading.$^{62,63}$
1.3.2 Electrolyte

Electrolyte is also an important component of Li-S batteries, and the selection of each part in the electrolyte directly affects the battery performance. Polysulfide anions and anionic polysulfide radicals are extremely reactive and they participate in many types of reactions. It appears that the suitable solvents for the Li-S cell electrolytes are only limited within the linear and cyclic ethers, such as dimethyl ether (DME) and 1,3-dioxolane (DOL).

Abruna et al. studied the effects of solvents with 1 M lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) on the performance of the Li-S batteries. As shown in Figure 1.8a, two distinct voltage plateaus were seen at around 2.4 and 2.1 V, respectively, for the tetra(ethylene glycol) dimethyl ether (TEGDME) and DOL/DME electrolytes. The slight difference of the voltage window for the plateaus between these two systems were probably ascribed to the difference in their viscosities. Only one plateau was observed at 2.4 V for the electrolyte with the existence of propylene carbonates (PC)/ethylene carbonate (EC)/diethyl carbonate (DEC)
which was because carbonates can react with polysulfides through possible nucleophilic attack at either the ether or carbonyl carbon atoms on the carbonate molecules.\textsuperscript{69}

Figure 1.8 (a) Discharge and (b) charge profiles of the first cycle for the Li-S cell in 1 M LiCF$_3$SO$_3$ with different solvents by volumetric ratios.\textsuperscript{67}
Figure 1.9 Cycling performance for the Li-S cells with different solvents.\textsuperscript{67}

The first charge profiles for the Li-S cells with various electrolytes are shown in Figure 1.8b. It could be seen that the charge capacities were both higher than 1000 mAh g\textsuperscript{-1} for the TEGDME and DOL/DME. In contrast, there was almost no capacity for the PC/EC/DEC electrolyte. It is obvious that the cell with electrolyte solvents of DOL/DME displayed the best electrochemical performance, as shown in Figure 1.9.

It concludes that the linear DME offers higher polysulfide solubility and faster polysulfide reaction kinetics, whereas the cyclic DOL forms more stable solid electrolyte interface (SEI) on the surface of the Li anode while providing lower polysulfide solubility and slower reaction kinetics. Although the dissolution of polysulfides causes parasitic redox shuttle reactions, the
solvents with high polysulfide solubility and low viscosity are greatly favorable for the cycling performance of the Li-S cells.

In addition, lithium salt in the electrolytes is playing an important role. It is selected based on the chemical compatibility with polysulfides. The conventional lithium salts, such as lithium hexafluorophosphate (LiPF$_6$), and lithium tetrafluoroborate (LiBF$_4$), are not suitable for the electrolyte of the Li-S cells due to the following reactions:

$$\text{LiPF}_6 + \text{Li}_2\text{S}_n \rightarrow \text{LiPS}_n\text{F}_4 + 2\text{LiF} \quad (1.6)$$

$$\text{LiBF}_4 + \text{Li}_2\text{S}_n \rightarrow \text{LiBS}_n\text{F}_2 + 2\text{LiF} \quad (1.7)$$

It is necessary to note that lithium perchlorate (LiClO$_4$) is also not a good choice due to its oxidative property although no safety issue has been reported yet. So far, bis(trifluoromethane)sulfonamide lithium (LiTFSI, LiN(SO$_2$CF$_3$)$_2$) is the mostly used as the lithium salt for Li-S cells because it provides higher ionic conductivity and less corrosion to the aluminum (Al) substrate.$^{40,70}$

1.3.3 Anode

Li anodes are widely used for Li-S batteries and they also suffer from several problems although these issues are not as severe as those observed in other lithium cell systems. This can be ascribed to the dissolved polysulfides, which prevents the growth of Li dendrites.
The electrolytes can be reduced on the surface of the Li anode to form a SEI layer, causing a significant irreversible capacity loss and low deposition efficiency of Li upon charging.\textsuperscript{71}

The problem of the Li anode also comes from the shuttle effect of polysulfides. The high-order polysulfides diffusing throughout of the separator could react with Li to form insoluble sulfides (Li\textsubscript{2}S\textsubscript{2}, Li\textsubscript{2}S) which further retards the rapid access of Li, resulting in poor rate capability.\textsuperscript{72-74}

1.3.4 Separator

It is well known that separators also play a key role in all batteries. Their main function is to prevent electrical short circuits by keeping the positive and negative electrodes apart, while simultaneously allowing the rapid transport of ionic charge carriers that are needed to complete the path during the passage of current in an electrochemical cell.\textsuperscript{75} There are many property requirements for separators used in batteries: high electronic insulation, excellent chemical resistance, good wettability with electrolyte, etc. Microporous polyolefin membranes are currently the most commonly-used separators for lithium batteries since they have good chemical stability and mechanical strength, but they suffer from low porosity and poor wettability with liquid electrolyte which increase the cell resistance, resulting in poor kinetics and low rate capability of the batteries. In addition, polyolefin-based separators exhibit large thermal shrinkage at high temperatures which may cause internal short circuits, fire and even explosions in case of overcharge or overheating.
1.4 Solutions

As discussed above, most of the problems faced by the Li-S batteries are due to the dissolution of polysulides, which result in parasitic reactions. Many approaches have been applied to solve this issue. The details are discussed as followings.

1.4.1 Sulfur Cathode

Since sulfur is an insulator with a resistivity of ~$10^{30} \, \Omega \, \text{cm}$, a key approach is to provide a proper electrically conductive framework (conductive carbon/polymer) for the active material to ensure smooth electron transport between the electrical conductor and the active material. Based on the composition and structure of the electrodes, we separate them into several types: (1) porous carbon-sulfur composites, (2) graphene (oxide)-sulfur composites, (3) one-dimensional carbon-sulfur composites, and (4) conductive polymer-sulfur composites. In addition, binder, a key component in the cathode, is also playing an important role in determining the final performance of batteries.

1.4.1.1 Porous Carbon-Sulfur Composites

Briefly, a porous carbon-sulfur composite is a mixture of porous carbon and sulfur where most of sulfur exists inside the carbon pores. Those carbon pores not only improve the electrical conductivity of the composite but help trap dissolved polysulfides during the cycling.
In 2002, Wang et al. reported that a sulfur-carbon nano-composite with elemental sulfur incorporated in porous carbon could deliver a reversible capacity of 440 mAh g\(^{-1}\) at a current density of 0.3 mA cm\(^{-2}\), as shown in Figure 1.10.\(^{84}\) The utilization of the active sulfur was up to 90% assuming a complete reaction to the product of Li\(_2\)S.

![Discharge-charge profiles for the composite containing 30 wt% sulfur and pure carbon.\(^{84}\)](image)

Later, Ji et al. demonstrated that the electrochemical performance of the Li-S cells could be significantly improved by using ordered CMK-3 mesoporous carbon to trap polysulfides.\(^{85}\) As shown in Figure 1.11a, CMK-3 carbon consists of an assembly of hollow 6.5 nm-thick carbon rods separated by empty 3 nm-wide channel voids. The intermediates, polysulfides, can be efficiently trapped by those small pores which can facilitate fast electronic and ionic transport.
The electronic contacts were provided by the numerous carbon interconnects that span the channels (Figure 1.11b).

Figure 1.11 (a) A schematic diagram of the sulfur (yellow) incorporated in the interconnected pore structure of CMK-3. (b) Procedure of the composite syntheses and the lower diagram shows the chemical reaction with Li during cycling.  

As a result, shown in Figure 1.12, a high initial discharge capacity of 1005 mAh g\textsuperscript{-1} could be achieved for the composite CMK-3/S, and it was further increased to 1320 mAh g\textsuperscript{-1} by linking the carbon surface with polyethylene glycol (PEG) which helps trap polysulfides. It is important to note that these values are much higher than earlier results which demonstrates that incorporating S into porous carbon is an effective approach to achieve high-performance Li-S batteries.
To enhance the long-term stability of sulfur cathode for a high energy lithium-sulfur system, Gao et al. used porous carbon sphere composite to encapsulate sulfur by thermal treatment of a mixture of sublimed sulfur and microporous carbon sphere. The surface area of the carbon sphere significantly decreased from 843.5 to 6.5 m\(^2\) g\(^{-1}\), demonstrating the successful embedding of sulfur into the carbon sphere. As shown in Figure 1.13a, the lithium-sulfur cell with a sulfur content of 42 wt% could obtain a much higher capacity compared to that of 51 wt% at a low current density of 40 mA g\(^{-1}\). The capacities were ~900 and ~300 mAh g\(^{-1}\) after 50 cycles, respectively, for 42 and 51 wt% sulfur electrodes. This was probably due to the pore-narrowing and full saturation of the micropores, preventing passage of solvated electrolyte molecules. The high performance can be achieved by such design not only because the carbon framework improves the conductivity of the cathode but the migration of the
polysulfides can be minimized, enhancing the utilization of the active material and resulting in a much better performance (Figure 1.13b).

Figure 1.13 (a) Cycling performance of the sulfur-carbon composites with 42 and 51 wt% sulfur at a current density of 40 mA g\(^{-1}\). (b) A schematic of the electrochemical reaction inside the micropores of the sulfur-carbon sphere.\(^{86}\)

Archer and his coworkers presented a template-based method for synthesizing hollow carbon particles for incorporating with S (63 wt% S loading).\(^{87}\)

As shown in Figure 1.14a, a capacity of ~970 mAh g\(^{-1}\) with a Coulombic efficiency of 94% could be still obtained at the 100\(^{th}\) cycle under a current density of 0.5C. For the rate capability test (Figure 1.14b), it could deliver a capacity of 450 mAh g\(^{-1}\) at 3C and 891 mAh g\(^{-1}\) with the current density went back to 0.5C. This confirmed that the unique structure is able to suppress
the shuttle effect as well as to enhance electron transport based on the close contact between S and the carbon framework.

![Figure 1.14](image)

**Figure 1.14** (a) Cycling performance at a current density of 0.5C. (b) Rate capability.\(^{87}\)

1.4.1.2 Graphene (Oxide)-Sulfur Composites

Graphene has a single-atom thickness and it is made up of sp\(^2\)-boned carbon atoms that are densely packed in a honeycomb crystal lattice. It has attracted much attention due to its high surface area and excellent electrical conductivity.\(^{94-105}\)

In 2010, Wang *et al.* synthesized sulfur-graphene nanosheets (S-GNS) by heating a mixture of graphene nanosheets and elemental sulfur.\(^{97}\) According to scanning electron microscopy image with energy dispersive X-ray mapping, it was demonstrated that the sulfur was distributed uniformly in the graphene matrix, as shown in Figure 1.15.
Figure 1.15 (a) SEM image of the S-GNS and EDS mapping for (b) sulfur and (c) carbon.\textsuperscript{97}

Figure 1.16 Cycling performance of the cells with pure sulfur and S-GNS as cathodes.\textsuperscript{97}

With the addition of the GNS, the initial discharge capacity increased from 1100 to \~1611 mAh g\textsuperscript{-1} at a current density of 50 mA g\textsuperscript{-1}. Meanwhile, the cycling stability of the cell with S-GNS was also improved (Figure 1.16). Those improvements were ascribed to high electrical conductivity of the S-GNS composite which was provided by the graphene.
Recently, Li et al. demonstrated an easy electrochemical assembly method to obtain sulfur-graphene (S-G) nanowalls, which were controllably and vertically aligned onto the surface of the electrically conductive substrates during the tunable cyclic voltammetry (CV) process, shown in Figure 1.17.¹⁸

Figure 1.17 (a) Schematic explanation of the fabrication procedure. (b) CV curves at different cycles during the electrochemical assembly process. (c) Schematic image of the final product.¹⁸
Figure 1.18 Rate capability of the lithium-sulfur cell with vertically aligned sulfur-graphene nanowalls as cathode.98

The rate capabilities of vertically aligned sulfur-graphene nanowalls were further investigated at various current densities from C/8 to 4C. As shown in Figure 1.18, the capacity decreased slowly with the increase of the current density. Even at the highest current density of 8C, a capacity of 410 mAh g⁻¹ was still achieved. It is confirmed that such unique structure is favorable for the fast ion and electron transport, resulting in good electrochemical performance.

Obviously, graphene oxide is oxidation of graphene and it contains many oxygen-functional groups and it can be used as a sulfur immobilizer to improve the electrochemical performance of the lithium-sulfur batteries.106-109
Ji et al. prepared a sulfur/graphene oxide composite by depositing nano-sulfur on the surface of GO by chemical reaction in a micro-emulsion system. Then, the as-prepared sample was further treated at 155 °C for 12 h in an argon atmosphere to remove the bulk sulfur which was not directly attached to the GO layers.

As shown in Figure 1.19, it could get an initial capacity of 1320 mAh g⁻¹ with a Coulombic efficiency of 96.4% at 0.02C. A high reversible capacity of 1247 mAh g⁻¹ with a Coulombic efficiency of 97.5% could be achieved at the second cycle, corresponding to 94.5% capacity retention. It was probably ascribed to the strong GO-sulfur interaction, which could suppress the dissolution of the lithium polysulfides into the electrolyte and minimize the shuttle effect, further enhancing utilization of the active material.

Figure 1.19 Discharge/charge profiles of the Li-S cells at 0.02C.
Zhou et al. discovered that a three-dimensionally cross-linked structure prepared by an amylopectin wrapped graphene oxide-sulfur composite could stabilize the lithium-sulfur batteries. The synthesis procedure was shown in Figure 1.20.

Figure 1.20 Schematic of the procedure for preparing three-dimensionally structure.
In Figure 1.21, it was clear that the cell with a sulfur loading of 2 mg cm$^{-2}$ delivered higher capacity and efficiency compared to that of 6 mg cm$^{-2}$. Low capacity for the high sulfur loading was due to worse ionic transportation and contact in thicker electrode film, but it is important to note that it is still much better than the pure sulfur electrode.

1.4.1.3 One-Dimensional Carbon-Sulfur Composites

One-dimensional structural materials possess short diffusion distance for ions and effective transfer pathway for electrons, which are beneficial for improving the electrochemical performance of the batteries.$^{110-121}$
Yuan et al. carried out the sulfur coating of multi-walled carbon nanotubes (MWCNTs) and further investigated their electrochemical performance. Figure 1.22 shows TEM images of pure sulfur, MWCNTs and their composites. It is clear that the diameter of the sulfur coated MWCNTs was larger than that of the pure MWCNTs and the sulfur was uniformly coated on the surface, demonstrating good connection between components.

Figure 1.22 TEM images of (a) pure sulfur, (b) MWCNTs, (c) sulfur-coated MWCNTs (50 wt% sulfur), and (d) sulfur-coated MWCNTs (80 wt% sulfur).

In Figure 1.23, the initial discharge capacities of the cell with S-coated-CB and S/MWCNTs were 480 and 655 mAh g\(^{-1}\). In contrast, the capacity increased to 1075 mAh g\(^{-1}\) for the cell with S-coated-MWCNTs. The electrochemical impedance spectroscopy (EIS) measurements
were carried out to characterize the batteries before discharge and after 40 cycles. The corresponding Nyquist plots are shown in Figures 1.24(a) and (b), respectively. The semicircle in the high frequency is corresponded to the charge transfer resistance. Before discharge, the charge transfer resistance of the cell with S/MWCNTs was smaller compared to the other two samples. However, after 40 cycles, the charge transfer resistances of the cell with S-coated-MWCNTs and S-coated-CB were 16 and 28 Ω, respectively, which were both lower than that of S/MWCNTs. This is because the surface of MWCNTs and CB uncovered to the electrolyte increased with the phase change of sulfur from solid to the dissolved polysulfide state during the cycling.

Figure 1.23 First discharge profiles of the cell with sulfur coated carbon black (S-coated-CB), mixture of sulfur and MWCNTs (S/MWCNTs), and sulfur coated MWCNTs (S-coated-MWCNTs).
Zheng et al. introduced amphiphilic polymers to modify the surface of the CNTs, rendering strong interactions between the nonpolar carbon and the polar Li$_x$S compounds. The cycling performance of the cells with unmodified and modified electrodes is shown in Figure 1.25. A fast capacity fading could be seen for the cell with unmodified electrode. In contrast, the capacity retention was over 80% for more than 300 cycles after the modification which was probably because the amphiphilic polymers could supply anchoring points, allowing lithium sulfides to bind strongly with the carbon surface (shown in Figure 1.26).
Figure 1.25 Cycling performance of the sulfur and polymer modified sulfur cathodes.\textsuperscript{124}

Figure 1.26 Schematic images of the polymer modified sulfur cathode before (left) and after discharge (right).\textsuperscript{124}
1.4.1.4 Conative Polymer-Sulfur Composites

Besides conductive carbon matrices, conductive polymers are also used as the framework for the sulfur electrode not only to improve the electrode conductivity but also to suppress the migration of the lithium polysulfides during cycling.125-130

A conductive polymer/sulfur composite was prepared by heating a mixture of polyacrylonitrile (PAN) powder and sublimed sulfur at 280 to 300 °C for 6 h under an atmosphere of argon.128 At 300 °C, PAN and sulfur made contact at the molecular level in the melt state. Sulfur dehydrogenated PAN formed a conductive main chain. Meanwhile, the –CN function groups cyclized in the melt state to form a highly thermally stable compound where sulfur was intercalated. A capacity of over 600 mAh g⁻¹ was achieved after 50 cycles (Figure 1.27).

Figure 1.27 Cycling performance of the composite cathode.128
Xiao et al. used polyaniline as the conductive polymer matrix. The polymer and sulfur were treated at 280 °C and a fraction of sulfur reacted with the polymer to fabricate three-dimensional cross-linked stable sulfur-polyaniline nanotubes (SPANI-NT). This novel framework provided strong physical and chemical confinement to the sulfur and the resident polysulfide at molecular level. Figure 1.28 shows a possible structure for the SPANI-NT composite and it illustrated the morphology change during the discharge/charge process.

Figure 1.28 Schematic illustration of cycling process of the SPANI-NT/S composite.
In Figure 1.29a, the capacities at different current densities almost stabilized and displayed relatively slow fading rates. The capacities of 837, 614, and 568 mAh g⁻¹ could be obtained after 100 cycles at 0.1, 0.5, and 1C, respectively. A capacity as high as 432 mAh g⁻¹ was achieved at 1C even after 500 cycles, as shown in Figure 1.29b.

Hollow sulfur nanospheres coated by different conductive polymers were synthesized and investigated by Li et al. Briefly, monodisperse hollow sulfur nanospheres were dispersed in water with different monomers (aniline, pyrrole, or 3,4-ethylenedioxythiophene (EDOT)), then a small amount of acid (hydrochloric acid for aniline; no acid for pyrrole; camphorsulfonic acid for EDOT) and oxidant (iron chloride for pyrrole; ammonium persulfate for aniline and EDOT) were added. The procedure is shown in Figure 1.30. The as-prepared three samples were designated as PANI-S, PPY-S, and PEDOT-S, respectively.
Figure 1.30 Schematic image of the experimental procedure.

Figure 1.31 shows the cycling performance of the cells made from PANI-S, PPY-S, and PEDOT-S with conductive polymer coatings of ~20 nm at a current density of C/2. The initial capacities of the cells made from PANI-S, PPY-S, and PEDOT-S were 1140, 1201, and 1165 mAh g\(^{-1}\), respectively. The cells made from PPY-S and PEDOT-S could still deliver high capacities of 726 and 780 mAh g\(^{-1}\) even after 500 cycles. The cell made from PANI-S showed a relatively faster capacity fading with a capacity of 516 mAh g\(^{-1}\) at the 500\(^{\text{th}}\) cycle. EIS measurements were carried out to further investigate the electrode kinetics. The charge transfer resistances of the three electrodes are in the order of PEDOT-S < PPY-S < PANI-S, revealing the conductivities of the three polymers are in the order of PEDOT-S > PPY-S > PANI-S.
Several alternative electrode binders, such as polyethylene oxide (PEO), gelatin, polyvinylpyrrolidone (PVP), Na-alginate, gum arabic (GA), etc., have been studied as alternatives to the common polyvinylidene difluoride (PVDF). The ideal binder is required to create a more robust conductive framework and improve the strength and structural stability of the entire sulfur electrode. Li et al. presented Acacia senegal-inspired binder, GA, which is nontoxic and sustainable, for high performance of lithium-sulfur batteries. The structure of the GA was described in Figure 1.32.
Figure 1.32 Schematic image of the chemical structure of GA with the background of Acacia senegal.\textsuperscript{135}

Figure 1.33a shows the discharge/charge profiles of the cell with GA binder at C/5. It was clear that there were two typical plateaus during the discharge, corresponding to the formation of soluble long-chain polysulfides and insoluble short-chain Li$_2$S$_2$/Li$_2$S. As shown in Figure 1.33b, the S@GA could deliver an initial capacity of 1386 mAh g$^{-1}$ which was much higher than that of S@Gelatin and S@PVDF. A high capacity of 1090 mAh g$^{-1}$ could still be achieved after 50 cycles for S@GA, indicating the excellent electrode integrity of the cell with GA. On the other hand, the capacities of the cell with Gelatin and PVDF decreased to 452 and 312 mAh g$^{-1}$, respectively.
Figure 1.33 (a) Discharge/charge profiles of the cell with GA binder at C/5. (b) Cycling performance of the cells with various binders.\textsuperscript{135}

Even though those alternative binders have been demonstrated to have positive effects for lithium-sulfur batteries, there are still many limitations for their practical applications due to a lack of understanding of how these binders interact with the sulfur cathode to improve performance. Therefore, more work needs to be done to understand the mechanism behind them.
1.4.2 Electrolyte Additives

Since the solvents and the lithium salts for the Li-S batteries are fixed, we only focus on the additives in the electrolytes which can affect the bulk electrolyte properties such as ionic conductivity, viscosity, wettability, etc. Different additives have been demonstrated to protect Li electrodes by forming a surface protective film and suppressing the shuttle effect. Several additives are discussed below.

1.4.2.1 Lithium Nitrate

One of the most commonly used additives in Li-S electrolytes is lithium nitrate (LiNO₃) which is able to form a stable passivation SEI layer on the surface of Li electrodes. This protective film effectively improves the stability of the Li anode and further suppresses the shuttle effect of the polysulfides and self-discharging of the Li-S cells, enhancing the capacity as well as Coulombic efficiency of the cells.

Aurbach et al. reported that the additional LiNO₃ in the electrolyte could improve the discharge capacity, which increased from ~650 to ~1150 mAh g⁻¹, as shown in Figure 1.34. It was obvious that the upper discharge plateau was greatly shortened in the absence of LiNO₃ which was ascribed to the loss of long-chain polysulfides, decreasing the utilization of active materials.
The mechanism of the LiNO$_3$-induced SEI for preventing the shuttle effect in Li-S batteries was further studied by Xiong et al. Based on the characterizations of scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), it is believed that both LiNO$_3$ and polysulfides play important roles in forming stable SEI layers on the Li electrode, shown in Figure 1.35. A SEI film is produced and grows during cycling in an electrolyte with LiNO$_3$ as additive which is due to the strong oxidative nature of LiNO$_3$. 

Figure 1.34 Typical discharge/charge profiles of the Li-S cells (a) without and (b) with LiNO$_3$ additive.
1.4.2.2 Polysulfides

Long-chain polysulfides are also used as additive in the electrolyte to eliminate the formation of insoluble Li$_2$S$_2$ and Li$_2$S inside the carbon matrix and generate a protective SEI layer on the Li electrode. As shown in Figure 1.35, for the electrolyte with polysulfides additive, a stable SEI film is also formed during the cycling, which mainly consists of solid Li$_2$S$_2$ and Li$_2$S.

Xiong et al. also used two additives together, LiNO$_3$ and lithium polysulfides, to investigate SEI film formation of the Li-S cells. The results shows that the SEI film possesses two sub-layers. First, the reduced products of LiNO$_3$ and polysulfides are deposited on the Li electrode, which results in a compact bottom layer composed of Li$_2$S$_2$, Li$_2$S, and LiN$_x$O$_y$. The subsequent
layer comes from the reaction between LiNO$_3$ and lithium polysulfides, forming stable compounds Li$_2$S$_2$O$_3$ and LiSO$_4$ (shown in Figure 1.35). This top layer is able to block direct contact between the polysulfides in the electrolyte solution and reductive species on the Li electrode during the cycling.

1.4.2.3 Phosphorus Pentasulfide

Liang’s group found that phosphorus pentasulfide (P$_2$S$_5$) could be used as a novel additive in the organic electrolyte for Li-S batteries, which demonstrated that P$_2$S$_5$ can react with the Li electrode to form a dense passivation layer between the Li electrode and the electrolyte.$^{147}$ This passivation layer can help prevent polysulfides from accessing and reacting with the Li electrode.
As shown in Figure 1.36, a capacity of ~900 mAh g\(^{-1}\) could be achieved after 40 cycles with the additive of P\(_2\)S\(_5\). In contrast, the capacity of the cell without P\(_2\)S\(_5\) additive was less than 300 mAh g\(^{-1}\). This poor cycling performance was probably due to the direct reduction of polysulfides on the Li electrode surface and formation of a SEI film mainly composed of Li\(_2\)S, which is a poor Li-ion conductor.
1.4.3 Anodes

The anode is an important part of the Li-S battery system because the long-term cycle stability of Li-S batteries is determined by the stability of the anode. Metallic lithium is widely used as the anode material for Li-S batteries due to its low potential and high capacity, resulting in higher energy density. Nevertheless, metallic lithium is unstable in organic electrolytes, which may produce safety issues for the rechargeable batteries. The limitations of metallic lithium anodes and its possible alternative anodes are discussed in the following sections.

1.4.3.1 Lithium Anode

Metallic lithium has a high theoretical capacity of ~3800 mAh g\(^{-1}\), however, it suffers from degradation upon cycling, forming dendrites which negatively affect the cycling performance and introduce the safety issue of rechargeable batteries.\(^{148-151}\)

The dendrite formation and low lithium cycling efficiency were due to the instability of the SEI film on its surface, which couldn’t suppress the shape and volume changes of the lithium electrode during charge/discharge process and resulted in lithium dendrite formation. The intermediate polysulfides in Li-S batteries can be dissolved in an organic electrolyte which causes severe parasitic reactions on the lithium surface, making it hard to form a stable SEI film. Some approaches have been used to solve this issue, including the usage of additive (e.g. LiNO\(_3\), polysulfides, P\(_2\)S\(_5\)) in the electrolytes.
Recently, Cui’s group reported that a thicker and less sharp morphology (shown in Figure 1.37 a-c) of lithium filaments deposited in the electrolyte with LiNO$_3$ compared to the absence of LiNO$_3$ even though LiNO$_3$ alone is not sufficient to prevent dendrite growth.$^{152}$ In comparison, a lower density of nucleated lithium particles was produced when Li$_2$S$_8$ and LiNO$_3$ were added to the electrolyte together, as shown in Figure 1.37 d-e. No long filaments or dendrites could be found even at a high deposition capacity of 6 mAh cm$^{-2}$ (Figure 1.37 f).
Figure 1.37 Scanning electron microscopy (SEM) images of lithium metal deposited onto the bare stainless steel for the electrolyte with addition of only LiNO₃ (a-c) and with addition of LiNO₃ and Li₂S₈ (d-f) at different deposition capacities.¹⁵²
1.4.3.2 Silicon Anode

Silicon is a promising alternative for lithium metal as an anode for Li-S batteries due to its high theoretical capacity of ~3580 mAh g$^{-1}$ ($\text{Li}_{15}\text{Si}_4$). It is well known that the practical application of Si-based anodes is limited by the severe capacity fade which is ascribed to the mechanical failure of the active material of high volume change of >300% during the cycling.\textsuperscript{153-157} Fortunately, this major issue has been solved by using nanosized Si as anode which can not only control the volume change but also shorten the Li-ion diffusion length.\textsuperscript{158}

It is important to note that either the cathode (S) or the anode (Si) needs to be prelithiated when making a full battery. Cui and his coworkers presented a prelithiated silicon nanowire anode by an easy self-discharge mechanism and constructed a full battery using prelithiated silicon nanowire and sulfur as anode and cathode, respectively.

![Graph](image)

Figure 1.38 (a) Voltage profiles of the first, second, and tenth cycles of the full cell. (b) Cycling performance of the full cell.\textsuperscript{158}
Figure 1.38a shows the voltage profiles of the first, second, and tenth cycles of the sulfur/prelithiated silicon nanowire. A retention of ~80% could be achieved after 10 cycles (Figure 1.38b) and severe capacity fading was obvious within the first 20 cycles. But it is demonstrated that a full battery can be fabricated with a prelithiated anode materials and a Li-free sulfur cathode, which eliminates the safety issues associated with the lithium metal.
1.4.4 Interlayers

As discussed previously, the main approaches for achieving high-performance lithium-sulfur batteries are using conductive frameworks (carbon/polymer) for sulfur. All those methods not only improve the electrical conductivity of the cathode but suppress the migration of the polysulfide intermediates during cycling, enhancing the utilization of the active material.

Since Manthiram’s group introduced a microporous carbon (MPC) interlayer into the cell which was inserted between the cathode and separator, the study on interlayers for the Li-S batteries has attracted more attention.\(^{159-169}\) The schematic image of the first work of Manthiram’s group is shown in Figure 1.39.\(^{159}\) This electrolyte-permeable microporous carbon paper could trap the polysulfide intermediates and was treated as a second current collector, resulting in a significant improvement for the lithium-sulfur batteries.

![Figure 1.39 Schematic image of the Li-S cell with a microporous carbon interlayer.\(^ {159}\)](image-url)
In Figure 1.40a, with the insertion of the MPC interlayer, the charge transfer resistance of the cell remarkably decreased by about 79% compared to that of the cell without MPC interlayer. As shown in Figure 1.40b, the retained capacity was higher than 1000 mAh g\(^{-1}\) with a Coulombic efficiency of 97.6% even after 100 cycles at the current density of 1C. A capacity as high as 846 mAh g\(^{-1}\) could be achieved at a higher current density of 2C after 150 cycles.

![Figure 1.40 (a) EIS plots of Li-S cells with and without the carbon interlayer. (b) Discharge/charge profiles of the cell with carbon interlayer at different cycles.](image)

Recently, Singhal et al. used activated carbon nanofibers (ACNF) as the interlay for high-performance lithium-sulfur batteries.\(^{170}\) As exhibited in Figure 1.41, the cycling performance of the cell with ACNF interlayer significantly improved. The initial discharge capacity of the cell with conventional sulfur cathode increased from 1226 to 1519 mAh g\(^{-1}\) at a current density of C/5 with the insertion of the ACNF interlayer. It displayed a relatively stable capacity during cycling. The capacity retentions after 100 and 200 cycles were \(~80%\) and \(~60%\), respectively.
When the sulfur content increased to 70 wt%, a capacity of 810 mAh g$^{-1}$ could still be obtained after 200 cycles.

![Graph showing cycling performance of the cell with and without ACNF.](image)

Figure 1.41 Cycling performance of the cell with and without ACNF.$^{170}$

However, this carbon interlayer generally requires a further heat-treatment which is energy consuming. Meanwhile, the thickness (hundreds of micrometers) and the mass (several milligrams) of the carbon interlayers are large, which results in a reduced energy density of the cell, limiting the practical applications of lithium-sulfur batteries.
1.4.5 Separators

Compared with the intensive studies on the electrode material designs, there are only few researchers working on Li-S battery separators, which are considered to be a critical component in the battery system.171-173

As discussed before, the main function of separators in batteries is to permeate ions and block electrons to realize reversible charge/discharge, and avoid the direct contact between the cathode and anode electrodes. An ideal separator for Li-S batteries is expected to not only have a good ionic conductivity but suppress the migration of polysulfides during cycling.174-176

Yao et al. reported a conductive coating on the separator to prevent the accumulation of inactive sulfur-related species at the cathode.171 The cycling performance of the cell with pristine separator (polypropylene, PP) and different materials coated on the separator are shown in Figure 1.42. A initial capacity of 1100 mAh g\(^{-1}\) could be achieved for the cell with the Ketjenblack and multi-wall carbon nanotube coated separator. In contrast, it was only ~700 mAh g\(^{-1}\) for the cell with the super P coated separator. It was probably due the higher conductivity of Ketjenblack and multi-wall carbon nanotube compared to that of super P. It is important to note that a big improvement was achieved for the cell with super P coated separator compared to the pristine separator.
Figure 1.42 Cycling performance of the cells with pristine separator and different materials coating on separator at C/5 with a sulfur content of 60 wt%.

Even though microporous polyolefin membranes are currently the most commonly-used separators for lithium batteries, their low porosity and poor wettability with liquid electrolyte increase the cell resistance, resulting in poor kinetics and low rate capability of the batteries.

A poor rate capability of the cell with pristine polypropylene is shown in Figure 1.43. Even for the cell with the super P coated separator, a capacity of ~300 mAh g\(^{-1}\) could only be obtained at a current density of 1C. This was probably due to low porosity and poor wettability with liquid electrolyte of the microporous polyolefin membranes, resulting in poor kinetics of the batteries.
Figure 1.43 Rate capability of the cell with the pristine separator and super P coated separator.\textsuperscript{171}

Therefore, to achieve better rate capability for lithium-sulfur batteries, the proper separator should not only have highly porous structure and excellent electrolyte wettability but also be able to trap sulfur-related species during cycling, enhancing the utilization of the active material.
CHAPTER 2 RESEARCH OBJECTIVES

The objective of this work is to explore and design advanced separators for high-performance Li-S batteries. Our main research work includes:

2.1 Separator Selection

Microporous polyolefin membranes are currently the most commonly-used separators for lithium batteries since they have good chemical stability and mechanical strength, but they suffer from low porosity and poor wettability with liquid electrolyte which increases the cell resistance, resulting in poor kinetics and low rate capability of the batteries. In addition, polyolefin-based separators exhibit large thermal shrinkage at high temperatures which may cause internal short circuits, fire and even explosions in case of overcharge or overheating.

Glass fiber (GF) membranes have received attention because of their highly porous structure and excellent wettability, which can lead to large electrolyte intake and consequently high ionic conductivity when placed in the electrolyte, facilitating rapid ionic transportation. In this study, a highly porous GF membrane was investigated as the separator for Li-S batteries. Experimental results showed that the GF membrane not only had higher thermal stability and larger ionic conductivity but also possessed superior electrochemical performance compared to microporous polypropylene (PP). It is, therefore, demonstrated that a GF membrane with
superior thermal stability and excellent electrolyte wettability is a promising separator candidate for high-performance Li-S batteries.

2.2 Carbon Coated Glass Fiber Separator

Although GF has been considered as a promising separator candidate for Li-S batteries, the performance of the Li-S cell needs to be further improved. Herein, we introduced a conductive carbon coating on the GF separator. The carbon coating layer not only provides sufficient contact with the cathode surface, offering a high active material utilization, but also inhibits the migration of polysulfide intermediates, avoiding shuttle reactions.

More importantly, the improved cells involve only a simple adjustment of the cell configuration by introducing a carbon coating on the separator instead of complex carbon-sulfur composite structure design or sulfur-conductive polymer modification.

2.3 Polyacrylonitrile/Graphene Oxide Nanofiber Membrane Separator

Nanofiber membranes are attractive for use as battery separators because they have highly porous structure and excellent electrolyte wettability, which can lead to large electrolyte intake and consequently high ionic conductivity when placed in the electrolyte, facilitating rapid ionic transportation. Many polymers can be used to prepare nanofiber membranes. Among them,
polyacrylonitrile (PAN) is believed to be a suitable polymer for battery separator application because of its easy processability and excellent resistance to oxidative degradation.

In addition to PAN, graphene oxide (GO) membrane was demonstrated to be able to block the polysulfide diffusion which was due to the electrostatic interactions between the negatively charged species ($S_{n^2}$) and the oxygen-containing groups on GO. We reported an effective PAN/GO nanofiber membrane separator that could provide Li-S cells with significantly enhanced cycle stability and rate capability without complex cathode structure design.

2.4 Polyacrylonitrile/Silica Nanofiber Membrane Separator with Carbon Nanotube Sheet

Silica nanoparticles were used as an adsorption agent for polysulfides. The combination of PAN and SiO$_2$ could lead to a nanofiber membrane separator that can effectively inhibit the diffusion of polysulfides in Li-S batteries. Moreover, the performance of Li-S batteries can be further improved by introducing a conductive carbon interlayer.

Therefore, a hierarchical multi-component PAN/SiO$_2$ nanofiber membrane separator with an ultralight and thin MWCNT sheet was prepared and used to improve the electrochemical performance of Li-S cells without introducing a complicated cathode architecture. These results are also supported by molecular modeling studies designed to investigate the molecular origins of this improved performance.
CHAPTER 3 SEPARATOR SELECTION

Abstract

Glass fiber (GF) membrane is evaluated as a potential separator for lithium-sulfur batteries. It is found that GF membrane has a highly porous structure with superior thermal stability, resulting in high liquid electrolyte uptake and enhanced electrochemical performance. Li-S cells using GF membrane as the separator can retain a capacity of 617 mAh g\(^{-1}\) after 100 cycles at a current density of 0.2C, which is 42% higher than that of cells using commercial microporous polypropylene separator. During rate capability tests, the capacity of Li-S cells using GF membrane decreases slowly from the reversible capacity of 616 mAh g\(^{-1}\) at 0.2C to 505, 394 and 262 mAh g\(^{-1}\) at 0.5C, 1C, and 2C, respectively. It should be noted that these cells can still deliver a high capacity of 587 mAh g\(^{-1}\) with a high retention of 95% when the current density is lowered back to 0.2C. The improved cycling and rate performance are ascribed to the fact that the highly porous GF membrane can increase the intake of soluble polysulfide intermediates and slow down their rapid diffusion to the Li anode side, which can not only improve the utilization of active material, but help protect the Li anode surface as well.

Keywords: Separators; Glass fiber; Lithium-sulfur batteries; Rate capability; High capacity
3.1 Introduction

Demand is increasing for rechargeable lithium batteries with higher energy density and longer cycle life since they are widely used in portable electronic devices, electric vehicles, etc. Sulfur (S) is considered to be one of the most promising candidates in this regard because it has the advantages of high theoretical capacity (1,675 mAh g⁻¹), low cost, and environmental friendliness. However, the practical application of Li-S batteries is hindered by the low utilization of the active material, severe capacity fading, and low Coulombic efficiency.

Many efforts have been made to overcome the challenges faced by Li-S batteries. The main approaches focus on design various nanomaterials as conductive frameworks for sulfur cathodes to achieve high capacity and improve cycle life. The active material utilization and cyclability can be improved because these conductive frameworks can enhance the electrical conductivity of the cathodes and minimize the loss of soluble polysulphide intermediates during cycling. However, those methods always involve complicated, multi-step synthetic processes, which limit their application in practical Li-S batteries.

Compared with the intensive studies on the electrode material designs, there are only few researchers working on Li-S battery separators, which are considered as a critical component in the battery system. It is well known that separators play a key role in all batteries since their main function is to keep the positive and negative electrodes apart to prevent electrical short circuit and meanwhile allow the rapid transport of ionic charge carriers that are needed to complete the path during the passage of current in an electrochemical cell. There are
many property requirements for separators used in batteries: high electronic insulation, excellent chemical resistance, good wettability with electrolyte, etc. Microporous polyolefin membranes are currently the most commonly-used separators for lithium batteries since they have good chemical stability and mechanical strength, but they suffer from low porosity and poor wettability with liquid electrolyte which increase the cell resistance, resulting in poor kinetics and low rate capability of the batteries. In addition, polyolefin-based separators exhibit large thermal shrinkage at high temperatures which may cause internal short circuits, fire and even explosions in case of overcharge or overheating.

Glass fiber (GF) membrane has received attention because it has highly porous structure and excellent wettability, which could lead to large electrolyte intake and consequently high ionic conductivity when placed in the electrolyte, facilitating rapid ionic transportation. For example, Luo et al. introduced a glass fiber fabric separator into Li-ion batteries and achieved a capacity retention of 60% for more than 100 cycles at a current density of 40 mA g\(^{-1}\). Zhu et al. used polyvinylidene fluoride (PVDF) coated GF as the separator for Li-ion batteries. They found that a reversible capacity of 125 mAh g\(^{-1}\) could be achieved for the LiFePO\(_4\) electrode at 0.2C when the PVDF-coated GF separator was used. Recently, a hybrid separator composed of GF membrane and Celgard microporous polypropylene (PP) membrane was developed for Li-S batteries by Wang et al. Their results showed that the cell with this hybrid separator delivered a specific capacity of 1050 mAh g\(^{-1}\) at the 10\(^{th}\) cycle with a current density of 0.2C, which was significantly higher than that (450 mAh g\(^{-1}\)) achieved by the cell with PP membrane. However, they did not report any result on the use of GF membrane directly as the
separator in Li-S batteries. In our study, we directly used the GF membrane (without the introduction of PP) as the separator for Li-S cells since the excess weight from the microporous PP membrane can decrease the gravimetric energy density as well as the volumetric energy density of the cells. In addition, the extra PP membrane can also increase the resistance of the cell and negatively affect the ionic transportation, resulting in reduced electrochemical kinetics, especially at high current densities. Experimental results showed that the GF membrane not only had higher thermal stability and larger ionic conductivity but also provided Li-S cells with more stable capacity and better rate capability as compared to microporous PP membrane. It is, therefore, demonstrated that GF membrane with superior thermal stability and excellent electrolyte wettability is a promising separator candidate for high-performance Li-S batteries when it is used alone without the introduction of another PP layer. More importantly, the contribution of this manuscript to the scientific community is to provide a new route to further improve the electrochemical performance of Li-S batteries by using a simple GF membrane separator without introducing complex electrode structure designs, enhancing the practical application of Li-S batteries.

3.2 Experimental

3.2.1 Materials

Sulfur (S, 99.5-100.5%, Sigma-Aldrich), bis(trifluoromethane) sulfonamide lithium (LiTFSI, Sigma-Aldrich), lithium nitrite (99.99% trace metals basis, Sigma-Aldrich), n-butyl alcohol
(99%, Sigma-Aldrich), N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich), 1,3-dioxolane (DOL, Sigma-Aldrich), 1,2-dimethoxyethane (DME, Sigma-Aldrich), super P carbon black (C-65, TIMCAL Graphite & Carbon Ltd.) and polyvinylidene fluoride (Solef® PVDF-5130, Solvay) were used as received.

GF membrane (Whatman, thickness of 260 µm) made from borosilicate microfibers was investigated as the separator in this study. Microporous polypropylene (PP) separator (Celgard 2400, thickness of 25 µm) was used as a comparison to the GF membrane.

3.2.2 Structural Characterization

The morphology of PP and GF separators was studied by using a field-emission scanning electron microscopy (FESEM, FEI Verios 460L, USA).

The porosities of the separators were measured by conducting n-butyl alcohol uptake tests. In an uptake test, the porosity was calculated based on the following equation:

$$\text{Porosity (\%)} = \left( \frac{w_w - w_d}{\rho_b \times V} \right) \quad (3.1)$$

where $w_w$ and $w_d$ are the weights of wet and dry separators, respectively; $\rho_b$ is the density of n-butyl alcohol, and $V$ is the geometric volume of the separator.
3.2.3 Performance Evaluation

The dimensional stability of the separators was determined by thermal shrinkage tests at 150 °C for 2 h. The electrolyte contact angle test was carried out by using a Canon EOS camera which was attached to a microscope (Meiji Techno America).

Liquid electrolyte uptakes were measured by soaking weighed separators in the liquid electrolyte of 1 M LiTFSI and 0.1 M LiNO$_3$ in a mixture of DOL and DME (1: 1 by volume) for 2 h at room temperature. The electrolyte uptake (EU) was then calculated by:

$$\text{EU (})\%\text{) }= \frac{(w_1 - w_0)}{w_0} \times 100$$

(3.2)

where $w_0$ and $w_1$ are the weights of the dry and wet separators, respectively.

Electrochemical impedance spectroscopy (EIS) was performed to investigate the ionic conductivity of liquid electrolyte-soaked separators by using Reference 600 Potentiostat/Galvanostat/ZRA (Gamry) over a frequency range from 1 MHz to 1 Hz under an AC voltage of 10 mV. During the measurement, the liquid electrolyte-soaked separators were sandwiched between two stainless steel electrodes. The ionic conductivity was calculated by using the following equation:

$$\sigma = \frac{L}{(R_b \times A)}$$

(3.3)

where $L$ is the thickness of separator, $A$ is the contact area between the separator and the stainless steel electrode, and $R_b$ is the bulk resistance of the electrolyte, defined as the intercept of the semicircle with the real axis.
The electrochemical performance of Li-S cells containing PP and GF separators was evaluated by using coin-type cells. The sulfur cathode was prepared by mixing 70 wt% active material (S), 20 wt% Super P and 10 wt% PVDF binder in solvent NMP and coating the slurry onto the carbon-coated aluminum foil, following by drying at 60 °C in vacuum oven overnight to remove the solvent. Lithium metal foil was used as the anode. Li-S cells were assembled by sandwiching liquid electrolyte-soaked separator between lithium anode and sulfur cathode in an argon-fill glove box. The electrolyte used was the same as the one for electrolyte uptake measurement and its amount was controlled as 40 µL per 1 mg S. A programmable battery cycler (Arbin Instruments) was used to record discharge/charge profiles and cycling performance with a voltage range between 2.8 V and 1.7 V at ambient temperature. Cyclic voltammetry (CV) measurements were carried out by using a Gamry reference 600 device with a scan rate of 0.1 mV s\(^{-1}\) in a potential range of 2.8 – 1.7 V. Several coin cells were disassembled in the charged state for further analysis after cycling. Morphological characterization of the lithium anodes before and after cycling was carried out with a field-emission scanning electron microscopy (FE-SEM, FEI Verios) after they were washed using DOL and dried in the argon-filled glovebox. The sulfur loading was around 0.7-1 mg cm\(^{-2}\) and all the cells’ capacities were calculated based on the mass of sulfur.
3.3 Results and Discussion

3.3.1 Morphology

FE-SEM is performed to examine the morphology of the GF separator, and the resultant SEM images are shown in Figure 3.1. For comparison, the SEM images of the PP separator are also shown. It is seen that slit-like pores are uniformly distributed in the PP separator (Fig. 1a and b). Such a micro-porous membrane with tortuous structure is designed for rechargeable lithium batteries in order to avoid short circuit resulting from dendritic lithium growth during the charge/discharge process. On the other hand, the GF separator consists of randomly arranged fibers with diameters less than 2 µm, which create a network structure with pores in the macroscale range (Fig. 1c and d). This highly porous structure is further confirmed by porosity testing results, as shown in Table 1. The porosity (66%) of GF separator is significantly higher than that (41%) of PP separator. This unique porous structure of GF separator could lead to high ionic conductivity when placed in the electrolyte, facilitating rapid ionic transportation.
Figure 3.1 SEM images of (a, b) PP and (c, d) GF separators with different resolutions.

Table 3.1 Physical and electrochemical parameters of PP and GF separators.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Electrolyte Uptake (%)</th>
<th>Ionic Conductivity (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>41</td>
<td>152</td>
<td>0.60</td>
</tr>
<tr>
<td>GF</td>
<td>66</td>
<td>360</td>
<td>3.83</td>
</tr>
</tbody>
</table>
3.3.2 Thermal Dimensional Stability

Thermal stability of separators is a vital aspect of the battery safety characteristics.\textsuperscript{200} Thermal shrinkage properties of PP and GF separators were investigated by observing their dimensional changes after storage at 150 °C for 2 h. As shown in Figure 3.2, the PP separator displays a significant thermal shrinkage after exposure to high temperature due to its intrinsically poor thermal stability. The substantial thermal shrinkage of the PP separator at high temperature originates from the low melting point of PP. In contrast, the GF separator does not display apparent dimensional change after the thermal exposure. This excellent thermal stability of GF separator can be attributed to the intrinsic thermal resistance of the borosilicate structure, which is beneficial for battery safety, especially when operated at high charge/discharge rates or elevated temperatures.

![Figure 3.2](image)

Figure 3.2 Photographs of PP and GF separators (a) before and (b) after thermal treatment at 150 °C for 2 h.
3.3.3 Electrolyte Wettability and Uptake

A separator should possess good electrolyte wettability to reduce the electrolyte filling time during battery assembly and to retain the electrolyte efficiently in the charge/discharge process. Contact angles were measured using a liquid electrolyte (1 M LiTFSI and 0.1 M LiNO₃ in DOL/DME) to characterize the electrolyte wettability of PP and GF separators. As shown in Figure 3.3a, the contact angle of PP separator is 37°, indicating that it cannot be wetted by the electrolyte. However, the contact angle of the GF separator is 0° (complete wetting, shown in Figure 3.3b), which confirms that GF separator exhibits significantly better electrolyte wettability than PP separator. This remarkable liquid electrolyte wettability of GF separator may be ascribed to the well interconnected microporous structure and the intrinsically lyophilic nature of borosilicate.

![Figure 3.3 Contact angle photographs of (a) PP and (b) GF separators using liquid electrolyte.](image-url)
The electrolyte uptake capacities of PP and GF separators were measured and are shown in Table 3.1. Obviously, the electrolyte capacity (360%) of GF membrane is much higher than that (152%) of PP membrane, which can be ascribed to the larger porosity of GF separator. Generally, high electrolyte uptake is beneficial for improving the cycling stability and rate capability of Li cells.

3.3.4 CV and Discharge-Charge Profiles

Figure 3.4 compares the CV curves of Li-S cells containing PP and GF separators for the first five cycles within a cutoff voltage window of 1.7-2.8 V at a scan rate of 0.1 mV s\(^{-1}\). As shown in Figure 3.4a, the cell with PP separator exhibits two cathodic peaks at around 1.83 and 2.15 V and two overlapped anodic peaks at around 2.41 and 2.47 V, which are typical of Li-S cells. The Li-S cell with GF separator also exhibits similar redox reactions, except for the difference in the peak intensity and slight shifts of the two reduction peaks from 2.28 V and 1.98 V to 2.27 V and 1.97 V from the 2\(^{nd}\) cycle to the 5\(^{th}\) cycle (shown in Figure 3.4b). Compared to the Li-S cell with GF, the larger deviation in the current peaks of the Li-S cell with PP suggests a fast capacity fading during cycling which is due to the diffusion of lithium polysulfide intermediates through the separator.
Figure 3.4 Cyclic voltammograms of Li-S cells with (a) PP and (b) GF separators cycled between 1.7 and 2.8 V at a scan rate of 0.1 mV s\(^{-1}\).

The first discharge-charge profiles of Li-S cells with PP and GF separators are shown in Figures 3.5a and b, respectively. It is obvious that both cells display two discharge plateaus and two closely spaced charge plateaus, which are consistent with the CV plots. The upper discharge plateau (Region 1) represents the transformation of sulfur into long-chain polysulfides (Li\(_2\)S\(_x\), 4 \(\leq x \leq 8\)) and the lower discharge plateau (Region 2) indicates the conversion of the semi-solid phase Li\(_2\)S\(_4\) to solid-phase low-order Li\(_2\)S\(_2\), or even Li\(_2\)S. During the cell charging, the two continuous charge plateaus correspond to the oxidation reactions from lithium sulfides to polysulfides and finally to sulfur. From Figure 3.5, it is also seen that the cell with GF separator has higher capacity than that with PP separator, and the increased capacity for the cell with GF separator is mainly attributed to the extended Region 2. It is
probably because the GF separator slows down the diffusion of dissolved polysulfide intermediates, which improves the utilization of active material.

Fig. 3.5 Discharge/charge profiles in the first cycle of Li-S cells with (a) PP and (b) GF separators at a current density of 0.2C.

3.3.5 Cycling Performance

Figure 3.6a presents the cycling stability of the Li-S cells using PP and GF separators at a current density of 0.2C up to 100 cycles. The initial discharge capacity (with sulfur utilization in parentheses) increases from 781 (47%) to 1033 mAh g\(^{-1}\) (62%) at 0.2C when using GF as the separator instead of PP. Meanwhile, the cell with GF separator shows more stable cycling performance and higher capacity retention ratio than the cell with PP separator. After 100 cycles at a current density of 0.2C, the cell with GF separator can still deliver a high capacity
of 617 mAh g\(^{-1}\), which is 42% higher than that of the cell with PP separator. It is probably because the highly porous structure of the GF separator, which helps increase the intake of soluble polysulfide intermediates and slow down the rapid diffusion of polysulfides to the Li anode side, which can not only improve the utilization of active material, but also protect the Li anode surface from diffused polysulfides, resulting in a better electrochemical performance, as illustrated in Figures 3.6b and c. From Figure 3.6a, it is also seen that both cells display good Coulombic efficiencies, which are 99% and 96%, respectively, for PP and GF in most cycles. Such excellent Coulombic efficiencies are probably due to the existence of LiNO\(_3\) in the electrolyte, promoting the formation of a stable passivation film on the Li anode surface to minimize the redox shuttle of lithium polysulfides.\(^{201}\)
3.3.6 C-Rate Performance

Rate capability is one of the critical parameters for batteries, especially in high power applications. The rate capability of Li-S cells with PP and GF separators was evaluated by increasing the discharge/charge current density stepwise from 0.2C to 2C every 10 cycles. Since the thickness (25 µm) of PP separator is much thinner than that (260 µm) of GF separator,
Li-S cells were assembled by stacking multiple pieces of PP separators to take the consideration of the separator thickness effect. It was found that the Li-S cell with 10 pieces of PP separators was not able to charge or discharge, probably due to the poor electrolyte wettability of PP. Figure 3.7 shows the rate capability of Li-S cells with a single piece of PP separator, three pieces of PP separators stacked together, and a single piece of GF separator. It is seen that the reversible capacities of Li-S cells with 1 and 3 pieces of PP separators decrease from 457 to 302 mAh g\(^{-1}\) and 530 to 111 mAh g\(^{-1}\), respectively, when the current density increases from 0.2C to 1C. The capacity of the cell with 3 pieces of PP is almost totally lost when the current density increases to 2C, indicating that thicker PP separator will definitely result in poorer reaction kinetics of the cell. On the other hand, the capacity of the cell with GF separator decreases slowly from the reversible capacity of 616 mAh g\(^{-1}\) at 0.2C to 505, 394 and 262 mAh g\(^{-1}\) at 0.5C, 1C, and 2C, respectively. Importantly, a high reversible capacity of 587 mAh g\(^{-1}\) (95% of the stable reversible capacity) is achieved when the current density is lowered back to 0.2C, indicating a highly reversible and efficient Li-S cell enabled by using the GF separator.\(^{202, 203}\) As shown in Table 1, when placed in a liquid electrolyte, the ionic conductivity of the GF separator is 3.83 mS cm\(^{-1}\), which is six times higher than that (0.60 mS cm\(^{-1}\)) of the PP separator. This higher conductivity can be attributed to the higher porosity of the GF separator and might be responsible for the good rate capability of the Li-S cell with GF separator.
Figure 3.7 Rate capability of Li-S cells with PP (1 and 3 pieces) and GF separators at various rates.

A comparison of the rate performance between the Li-S cell with GF separator in this work and the Li-S cells with PP separator reported in the literature is given in Figure 3.8.\textsuperscript{171, 204-207} It is obvious that our Li-S cell with GF separator shows a better high-rate capability than the Li-S cells with PP separator.\textsuperscript{204-207} Moreover, Yao \textit{et al.} used a carbon-coated PP separator to further improve the electrochemical performance of Li-S cells.\textsuperscript{171} Although a relatively higher capacity of 705 mAh g\textsuperscript{-1} for the cell with this carbon-coated PP separator could be achieved at 0.2C compared to that (616 mAh g\textsuperscript{-1}) of the Li-S cell with GF separator in this work, the faster capacity fading of the cell with carbon-coated PP separator could be observed as the current density increased. For example, the capacities of the Li-S cell with carbon-coated PP separator at 0.5C and 1C were 420 and 330 mAh g\textsuperscript{-1}, respectively, while the corresponding capacities were 505 and 394 mAh g\textsuperscript{-1} for the cell with GF separator in this work. It is, therefore, indicated that the electrochemical performance of Li-S cells can be improved by simply replacing PP
separator with GF separator even without complicated electrode structure designs or other modifications.

Figure 3.8 Rate capability comparison between the previously reported Li-S cells with PP separator and the Li-S cell with GF separator in this work.

Because the porosity and thickness are the two important structural parameters that directly affect the electrochemical performance of separators and the resultant Li-S cells, two additional GF membranes with different porosities and thicknesses were also investigated. The porosities of these two GF membranes are 51% and 58%, and their thicknesses are 675 and 435 µm,
respectively. The electrochemical performance results of Li-S cells using these two GF membranes are shown in Figure 3.9 and Figure 3.10. At 0.2C, the capacities of Li-S cells using GF separators with thicknesses of 675 µm and 435 µm are 580 and 575 mAh g\(^{-1}\), respectively, which are comparable to that (616 mAh g\(^{-1}\)) of Li-S cell using GF separator with a thickness of 260 µm. However, rapid capacity fading can be observed for the cells using GF separators with thicknesses of 675 µm and 435 µm. For example, at a current density of 2C, the capacities of these two cells are 130 and 149 mAh g\(^{-1}\), respectively, which are much lower than that (262 mAh g\(^{-1}\)) of the cell using GF separator with a thickness of 260 µm. The reduced rate capacities can probably be ascribed to the larger thicknesses and smaller porosities of these two GF separators, which not only increase the cell resistances, but also negatively affect the ionic transportation, resulting in reduced electrochemical kinetics. It should be pointed out that although the electrochemical performance of Li-S cells can be improved by replacing the PP separator with GF separator, the poor mechanical flexibility of the GF separator needs to be addressed before it can be used in practical Li-S cells. One possible strategy is to introduce polymer binders, such as polyvinylidene fluoride (PVDF), polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP), etc., to form flexible polymer/GF hybrid separators, which can combine the good electrochemical performance of GF separator with the flexible nature of polymers.
Figure 3.9 Rate capability of the Li-S cell by using GF separator with a porosity and thickness of 51% and 675 µm, respectively.

Figure 3.10 Rate capability of the Li-S cell by using GF separator with a porosity and thickness of 58% and 435 µm, respectively.
3.3.7 Morphology of the Li Anode after Cycling

To further understand the function of GF separator, Li-S cells were disassembled after 100 cycles (at a current density of 1C) in an argon-filled glove box to examine the surface morphology of the lithium anode. For the purpose of comparison, the metallic lithium anode before cycling was also observed by SEM. It can be seen that the surface of metallic lithium before cycling is smooth, as shown in Figure 3.11a and b. However, after 100 cycles in the Li-S cell containing PP separator (Figure 3.11c and d), obvious corrosion damage can be observed on the Li anode surface with some cracks, which is due to the side reactions between soluble lithium polysulfides and metallic lithium during cycling. In contrast, a relatively smooth, less damaged surface can be found on the lithium anode surface after cycling in the Li-S cell with GF separator (Figure 3.11e and f), which indicates that the GF separator can help suppress the diffusion of polysulfide intermediates to the lithium anode, resulting in an improved cycling performance.
Figure 3.11 SEM images of the surface view of Li anode (a, b) before cycling, (c, d) after cycling with PP separator, and (e, f) after cycling with GF separator at different magnifications (after 100 cycles at a current density of 1C).
3.4 Conclusions

In summary, highly porous GF separator had better electrolyte wettability and higher thermal stability than microporous PP membrane. The GF separator was also able to increase the intake of highly-soluble polysulphide intermediates and slow down the rapid diffusion of polysulfides to the Li anode side, resulting in better electrochemical performance. A high capacity of 617 mAh g\(^{-1}\) was remained for the Li-S cell containing GF separator after 100 cycles at a current density of 0.2C, which was 42% higher than that of PP. In the rate capability test, the capacity of the cell with GF decreased slowly from the reversible capacity of 616 mAh g\(^{-1}\) at 0.2C to 505, 394 and 262 mAh g\(^{-1}\) at 0.5C, 1C, and 2C, respectively. Importantly, it could still deliver a high capacity of 587 mAh g\(^{-1}\) when the current density was lowered back to 0.2C, indicating a high retention of 95%. It is, therefore, demonstrated that GF membrane is a promising separator candidate for high-performance Li-S batteries.
CHAPTER 4 CARBON COATED GLASS FIBER SEPARATOR

Abstract

Lithium-sulfur batteries have received intense attention because of their high theoretical capacity, low cost and environmental friendliness. However, low active material utilization and poor cycle life limit their practical applications. Here, we report a strategy to obtain high capacity with long cycle life and rapid charge rate by introducing a carbon coating on the separator. Excellent cycling performance with a high capacity 956 mAh g$^{-1}$ after 200 cycles and outstanding high-rate response up to 4C are achieved, which are among the best reports so far. High electrochemical performance can be obtained even at a high sulfur loading of 3.37 mg cm$^{-2}$. Such improved results could be ascribed to the conductive carbon coating, which not only reduces the cell resistance but blocks the diffusion of soluble polysulfides avoiding shuttle effect during cycling. This study demonstrates a feasible, low cost and scalable approach to address the long-term cycling challenge for lithium-sulfur batteries.

Keywords: Lithium-sulfur batteries, Carbon coating, Separator, Rate capability, Sulfur loading
4.1 Introduction

With the continuously increasing demand of the world energy consumption, energy storage systems are essential for the extensive development of portable electronic devices, electric vehicle, etc.\textsuperscript{208, 209} Lithium-sulfur (Li-S) batteries are one of the prospective candidates in this regard because S has a high theoretical capacity of 1,675 mAh g\textsuperscript{-1}, and is low cost and environmental friendliness. However, the practical applications of Li-S batteries are hindered by the low utilization of the active material, severe capacity fading, and low Coulombic efficiency. The poor utilization of active material results from the insulating nature of sulfur, which limits the electron transfer during the electrochemical reactions.\textsuperscript{210-212} The fast capacity fading is due to the dissolution of lithium polysulfide intermediates (Li\textsubscript{2}S\textsubscript{x}, 4 ≤ x ≤ 8) in the electrolyte and the low Coulombic efficiency is caused by the internal “shuttle reaction”.\textsuperscript{213, 214}

Many efforts have been made to overcome the challenges faced by Li-S batteries. The main approaches are performing nanomaterials as conductive frameworks for sulfur cathodes to achieve high capacity and improve cycle life, including porous hollow carbon,\textsuperscript{87, 187} carbon nanofiber,\textsuperscript{188, 189} carbon nanotubes,\textsuperscript{190} graphene oxide,\textsuperscript{215} graphene,\textsuperscript{216} yolk-shell TiO\textsubscript{2} spheres,\textsuperscript{61} conductive polymers,\textsuperscript{192} etc. The active material utilization and cyclability are improved because these conductive frameworks are able to enhance the electrical conductivity of the cathode and minimize the loss of soluble polysulfide intermediates during the cycling. These sulfur cathodes with conductive frameworks are often accompanied with electrolyte additives, such as lithium nitrate,\textsuperscript{40} phosphorous pentasulfide\textsuperscript{147} to increase the Coulombic
efficiency. Unfortunately, those structure designs are complex and high cost, which limit the practicality of Li-S batteries. In addition, those cathode systems generally have a relatively low sulfur content and loading which can significantly reduce the energy density of the entire cell. Therefore, it is still urgent to discover a low cost and scalable approach to achieve the high performance for Li-S batteries with a high sulfur content and loading.

Recently, Manthiram, et al. introduced a conductive interlayer to the Li-S battery system.\textsuperscript{159} This conductive interlayers are able to supply fine contact with the cathode surface, offering electron pathways through the insulating S/Li\textsubscript{2}S and preventing the migrating polysulfide intermediates, and this new cell design has shown the promise to improve the performance of the Li-S battery.\textsuperscript{162,170} However, the thickness (hundreds of micrometers) and the mass (several milligrams) of the carbon interlayers are large, which results in a reduced energy density of the cell.

Compared with the intensive studies on the electrode material designs, electrolyte additives and interlayers, there are only a few researchers working on separators, which are considered as a critical component in the battery system. Separators are typically made of insulating materials, such as polypropylene (PP) and polyethylene (PE), and have a porous structure that allows the transportation of ions. Recently, Celgard\textsuperscript{®} PP membranes coated with graphene,\textsuperscript{217} multiwall carbon nanotubes\textsuperscript{172} and carbon nanoparticles\textsuperscript{171} have been investigated for preventing the migration of polysulfides away from the cathode to the Li metal anode in Li-S batteries. With these coated separators, Li-S cells have shown improved cycling stability,
however, the low sulfur content and loading, as well as the poor rate performance and high cost, still make them unsuitable for practical applications.

Glass fiber (GF) membrane has received attention for use as a battery separator because it has a higher porosity (65%) compared to PP or PE membranes (40%), which could lead to higher electrolyte intake and consequently greater ionic conductivity when placed in an electrolyte, facilitating rapid ionic transportation.\textsuperscript{201, 218} In this study, we present an effective approach to achieve a stable and high-performance Li-S battery with exceptional rate capability by simply using carbon-coated GF (CGF) as the separator. It can effectively decrease the cell resistance, resulting in an enhancement of active material utilization. The thin carbon coating used in this work is able to block the shuttling of soluble polysulfides in the electrolyte and makes them available to be reutilized even for prolonged charge/discharge cycling. This conductive carbon coating can be considered as a second current collector for accommodating the migrating active material from sulfur cathodes. Therefore, the originality of our work is related to the use of a simple coating method instead of any complex electrode structure design to achieve excellent electrochemical performance (e.g., high cycling stability and good rate capability \textit{simultaneously}) for Li-S batteries. In addition, the cell configuration suggested by this work can be fabricated in large scale with low cost, further enhancing the practicality of Li-S batteries.
4.2 Experimental

4.2.1 Carbon-Coated Separator Fabrication

A super P (TIMCAL, Graphite & Carbon Ltd., C-65)/polyvinylidene fluoride (PVDF) slurry was prepared by mixing 70 wt% super P with 30 wt% PVDF in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) solvent, which was coated onto one side of a Glass Fiber mat (GF, GE healthcare) by the doctoral blade casting method. The carbon-coated separator was dried in a vacuum oven at 60 °C for 12 h.

4.2.2 Material Characterizations

The morphology of the samples was characterized using a filed-emission scanning electron microscopy (FESEM, Quanta 3D FEI, USA) with an energy dispersive X-ray spectroscopy (EDS) detector and a transmission electron microscopy (TEM, JEOL 2010F). X-ray Diffraction (XRD) patterns were recorded on a Rigaku D/Max 2400 (Japan) type X-ray spectrometer with Cu Kα radiation (λ=1.5418 Å).

4.2.3 Electrode Fabrication and Cell Assembly

The sulfur electrodes were prepared by casting a slurry containing 70 wt% pure sulfur (Sigma-Aldrich), 20 wt% conductive additive (TIMCAL, Graphite & Carbon Ltd., C-65), and 10 wt%
PVDF binder in NMP (Sigma-Aldrich) on the carbon-coated aluminum foil, followed by drying in a vacuum oven at 60 °C for 12 h. The areal loading of sulfur for the as-prepared electrodes ranged from 0.70 to 3.37 mg cm⁻². To test the electrochemical properties, 2032 type coin cells were assembled using the sulfur electrodes, PGF/CGF separators, and Li metal (Sigma-Aldrich) as the counter electrode. The electrolyte was prepared by dissolving 1 M bis(trifluoromethane)sulfonamide lithium (LiTFSI, Sigma-Aldrich) and 0.1 M lithium nitrite (99.99% trace metals basis, Sigma-Aldrich) in a mixture of 1,3-dioxolane (DOL, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, Sigma-Aldrich) (1:1 by volume). The amount of the electrolyte used in this work was 40 µL per 1 mg S. The cell assembly process was done in an argon-filled glove box and all capacity values were calculated based on the sulfur mass.

4.2.4 Electrochemical Measurement

Electrochemical impedance spectroscopy data were obtained with a device from 100,000 to 1 Hz with an AC voltage amplitude of 5 mV. A programmable battery cycler (Arbin Instruments) was used to record discharge/charge profiles cycle data. The cyclic voltammetry (CV) measurements were carried out by using a Gamry reference 600 device with a scan rate of 0.1 mV s⁻¹ in a potential range of 2.8 – 1.7 V. Several coin cells were disassembled in the charged state for further analysis after cycling. Morphological characterization and elemental mapping of the Li electrodes before and after cycling were carried out with a FE-SEM equipped with an EDS. X-ray photoelectron spectroscopy (XPS, SPECS FlexMod, Germany) was performed to execute elemental analysis at room temperature by using a Kratos Analytical spectrometer.
and monochromatic Mg Kα X-ray source. The lithium electrodes were washed using DOL and dried in the argon-filled glove box. A pure lithium plate before cycling was used as a comparison.

4.2.5 Polysulfide Diffusion Test

Li$_2$S$_8$ was synthesized by adding Li and S into the electrolyte (in volumetric flask) with a proper molar ratio under an intensive stirring at 80 °C for 24 h. The concentration of Li$_2$S$_8$ in the electrolyte was adjusted to 0.1 M. A vial with a hole on its cap combined with an O-ring and a beaker were used as the Li$_2$S$_8$ solution and blank electrolyte containers, respectively. The diffusion images were recorded by a camera.

4.3 Results and Discussion

The conductive carbon coating was applied onto one side of the GF separator (toward the cathode side). The main interaction mechanism of carbon coating in Li-S cell is that the conductive carbon coating can act as an interlayer to suppress the diffusion of the lithium polysulfides, which in turn minimizes the shuttle effect and enhances the active material utilization. In addition, this conductive carbon coating on the separator surface may also act as a current collector for low-conductivity sulfur and thus enhance the utilization of active materials, raising the specific capacity of the cell. In this work, the conductive carbon coating was prepared by a facile slurry coating of carbon nanoparticles and polyvinylidene fluoride.
(PVDF) binder with an optimized weight ratio of 7:3 (as shown in Figure 4.1). It is noted that severe cracking is obvious when the carbon/PVDF weight ratios are 9:1 (Figure 4.1b) and 8:2 (Figure 4.1c). The final mass loading of the carbon coating on the separator is ~0.61 mg cm\(^{-2}\) and the thickness of coating is ~60 μm when the carbon/PVDF weight ratio is 7:3 (as shown in Figures 4.1d and e).

Figure 4.1(a) SEM images of pristine GF separator. (b-d) SEM images of carbon/PVDF coated GF separators with weight ratios of 9/1, 8/2, and 7/3, respectively. The inserts are their photographs. (e) SEM image of the cross-section area of the carbon/PVDF (7/3 by weight) coated GF.
The configuration of the cell is shown in Figure 4.2a. Here, we employ pure sulfur powder as the active material to fabricate conventional sulfur cathodes instead of using sulfur-carbon composite or applying conductive polymer surface modification to demonstrate that the observed improvement of electrochemical performance is solely contributed from the conductive carbon coating. Figure 4.2b shows the scanning electron microscope (SEM) image of the conductive carbon coating used in this study. It is seen that the nanosized carbon particles (C-65) are uniformly dispersed on the surface of GF separator, which is able to reduce the electrical resistance by providing sufficient surface contact with the sulfur cathode. The highly porous coating structure is beneficial for electrolyte penetration during cycling.\textsuperscript{159} Transmission electron microscope (TEM) was used to evaluate the size of the carbon particles in the coating. The particle size ranges from 30 to 50 nm, as shown in Figure 4.2c. The crystal nature of the carbon particles was identified by high-resolution TEM (Figure 4.2d), which is in good agreement with its XRD pattern (Figure 4.2e). The crystallized carbon structure generally provides good electrical conductivity, which is also helpful for improving the electrochemical performance of battery cells.
Figure 4.2 (a) Schematic configuration of a Li-S cell with CGF as the separator. (b) SEM image of the surface of the CGF (the inset is its photograph). (c) Low-resolution and (d) high-resolution transmission electron microscope images of C-65. (e) XRD spectrum of C-65.

To analyze the impact of the conductive carbon coating, impedance analysis was performed to compare the cells with pristine GF (PGF) and CGF before cycling (Figure 4.3). The diameter of depressed semicircle in the high-frequency region, regarded as the charge transfer resistance of the cell, decreases from 58 Ω cm² to 8 Ω cm² after the introduction of the conductive carbon coating onto the separator surface. This conductive carbon coating can block the diffusion of the lithium polysulfides, avoiding the shuttle effect, enhancing the active material
utilization. The reduced charge transfer resistance is probably because the conductive carbon coating on the separator surface provides a conductive pathway, facilitating the charge transfer for surface reactions, and thus reduces the charge transfer resistance.\textsuperscript{219} Moreover, the charge transfer resistance remarkably decreases for the cell with CGF, indicating a weaker polarization for the Li-S cell with the addition of carbon coating layer.\textsuperscript{220}

![Impedance spectra of Li-S cells with PGF and CGF before cycling. This indicates the charge transfer resistance can be reduced significantly with the introduction of the conductive carbon coating.](image)

Figure 4.3 Impedance spectra of Li-S cells with PGF and CGF before cycling. This indicates the charge transfer resistance can be reduced significantly with the introduction of the conductive carbon coating.

Figure 4.4a shows the cyclic voltammetry (CV) of the cell with CGF for the first five cycles within a cutoff voltage window of 1.7-2.8 V at a scan rate of 0.1 mV s\textsuperscript{-1}. The C rates specified
in this study are based on the mass and theoretical capacity of sulfur (1C = 1.675 mA g\(^{-1}\)). Two cathodic peaks at around 2.3 and 2.0 V, and two overlapped anodic peaks at around 2.38 and 2.45 V are typical of Li-S cells without the carbon coating (Figure 4.4b).\(^{178}\) The cathodic peak in the first cycle appears at 2.2 V, which is probably due to the over potential of the electrode, caused by the morphology and position changes during the discharge. This cathodic peak shifts to a relatively stable value, 2.3 V, from the second cycle, which is due to the rearrangement of the migrating active material to electrochemically favorable positions.\(^{221}\) The discharge/charge profiles in Figure 4.4c, exhibiting two discharge plateaus and two closely spaced charge plateaus, are consistent with the cyclic voltammogram plots. The upper discharge plateau (Region 1) represents the transformation of sulfur into long-chain polysulfides (Li\(_2\)S\(_x\), 4 ≤ x ≤ 8) and the lower discharge plateau (Region 2) represents the conversion of the semi-solid phase Li\(_2\)S\(_4\) to solid phase low-order Li\(_2\)S\(_2\), or even Li\(_2\)S. During the cell charging, the two continuous charge plateaus at 2.38 and 2.45 V correspond to the oxidation reactions from lithium sulfides to polysulfides and finally to sulfur. Additionally, the polarization potential (as shown in Figure 4.4c) of the cell with CGF is significantly reduced to 117 mV, only 40.6% of that of PGF (288 mV), probably due to its small cell impedance, which suggests a kinetically efficient reaction process with a small barrier. It is important to note that the capacities of the cells with CGF and PGF for Region 1 are almost the same (around 410 mAh g\(^{-1}\)), which indicates the sulfur could be fully reacted to form Li\(_2\)S\(_4\) (the theoretical capacity of this reaction is 418 mAh g\(^{-1}\)). Thus, the increased capacity for the cell with CGF is mainly contributed by the extended Region 2. It is probably because the conductive carbon coating acts as a second current collector, therefore, the solid lithium sulfides tend to deposit on the surface of CGF, instead of
being formed on the anode surface (as illustrated in Figure 4.5), which enhances the utilization of active material.

Figure 4.4(a) Cyclic voltammogram scans of the Li-S cell with (a) CGF and (b) PGF. (b) Discharge/charge profiles in the first cycle of Li-S cells with PGF and CGF at a current density of 0.2C.
Figure 4.5 Schematic of polysulfide diffusion in Li-S cells with PGF (left) and CGF (right) during discharge.

Figure 4.6a compares the cycling performance of Li-S cells with PGF and CGF separators, and it demonstrates that the carbon-coated GF allows the successful implementation of a pure sulfur cathode containing 70 wt% sulfur and leads to a high discharge capacity and stable cyclability. After updating the PGF separator to the CGF, the initial discharge capacity (with sulfur utilization in parentheses) increases from 976 (58%) to 1352 mAh g\(^{-1}\) (81%) at 0.2C rate. The Coulombic efficiencies of the Li-S cells with PGF and CGF are 96.7% and 97.6%, respectively, even at the 200\(^{th}\) cycle. Figure 4.6b shows the long-term cycling behavior of Li-S cells containing CGF at higher current densities. When the current density increases to 1C and 2C, the cell still delivers reversible capacities of 721 and 607 mAh g\(^{-1}\) at 200\(^{th}\) cycle with high Coulombic efficiencies of 98.6% and 96.7%, respectively. The electrochemical performance of Li-S cells with PGF at higher current densities are also included, as shown in Figure 4.6c. It is apparent that the electrochemical performance of Li-S cells is improved at high C-rates by the introduction of a conductive coating on the separator surface. The
capacities of the cell with PGF at 1C and 2C are only 44.8% and 31.1% of that of the cell with CGF, respectively, which further indicates the essentiality of the conductive carbon coating in this system.

Figure 4.6 (a) Cycling performance of Li-S cells with PGF and CGF at a current density of 0.2C. Cycling performance of the Li-S cell with (b) CGF and (c) PGF at high rates of 1C and 2C.
Rate capability is one of the critical parameters for batteries, especially for high power applications. The rate capability of the Li-S cells with PGF and CGF is evaluated by increasing the discharge/charge current density stepwise from 0.2C to 4C every 10 cycles. In Figure 4.7a, the first discharge capacity of the cell with CGF is as high as 1352 mAh g\(^{-1}\) (corresponding to 81% utilization of sulfur), which is 60% greater than that of the cell with PGF, demonstrating the effectiveness of the conductive carbon coating in enhancing the conductivity and active material utilization. The capacity becomes stable after the initial decay stage. As the current density increases, the capacity of the cell with CGF decreases slowly from the reversible capacity of 1151 mAh g\(^{-1}\) at 0.2C to 1008, 869, 683, 544 and 417 mAh g\(^{-1}\) at 0.5C, 1C, 2C, 3C, and 4C, respectively. Importantly, a high reversible capacity of 1025 mAh g\(^{-1}\) (89% of the initial reversible capacity) is achieved when the current density is lowered back to 0.2C, indicating a highly reversible and efficient electrode enabled by the introduction of the conductive carbon coating. In contrast, the cathode assembled with PGF exhibits not only much lower capacity at the same discharge rate but also inferior capacity retention ratio of 0.8% (from 487 mAh g\(^{-1}\) at 0.2C to 4 mAh g\(^{-1}\) at 4C). Additionally, Figure 4.7b gives the comparison of the rate performance between the Li-S cell with CGF in this work and Li-S cells reported in literature.\(^{60, 61, 100, 171, 190, 208, 217}\) Our Li-S cell with CGF exhibits a more stable high-rate capability as the current density increases, indicating the electrochemical performance of Li-S cells can be significantly improved even without the complex cathode structure design or modification. However, it should be noted that our rate capability is not the highest among all reported results.\(^{222}\) The high-rate capability should be improved, especially at 4C rate. Some possible approaches can be performed to further improve the high-rate capability, such as
optimizing coating thickness, selecting more conductive carbon filler, introducing more effective polymer binder, modifying sulfur cathode structure, etc.²²³

![Figure 4.7](image_url)

Figure 4.7 (a) Rate cyclability of Li-S cells with PGF and CGF up to 4C. (b) Comparison of rate capabilities of the Li-S cell with CGF in this work and previously reported Li-S cells.

Representative voltage profiles of the Li-S cell with CGF at different rates are shown in Figure 4.8a and all curves show highly reversible capacities with two feature plateaus. However, the discharge/charge plateaus at high current rates obviously shift or even disappear in the cell with PGF, which indicates their high polarization and slow redox reaction kinetics with inferior reversibility (Figure 4.8b). As can be seen in Figure 4.8c, the Li-S cell with PGF has significantly greater polarization potential than the cell with CGF, and the potential difference
remarkably increases from 171 to 507 mV when the current density increases from 0.2 to 2C, indicating a kinetically efficient reaction process with a small barrier for the cell with CGF.

Figure 4.8 Discharge/charge profiles of Li-S cells with (a) CGF and (b) PGF at different current densities. (c) Comparison of the potential difference of Li-S cells with PGF and CGF.
To further understand the function of the CGF, the Li-S cells were disassembled after 100 cycles (at a current density of 1C) in an argon-filled glove box. For comparison, the metallic lithium anode before cycling was first observed by SEM. It can be seen that the surface of metallic lithium before cycling is smooth, as shown in Figures 4.9a and b. However, after 100 cycles in the Li-S cell with PGF (Figures 4.9c and d), obvious corrosion damage can be observed on the lithium anode surface with some cracks and the deposition of complicated sulfur-containing chemicals, such as Li2S2 and Li2S, etc., which is due to the side reactions between soluble lithium polysulfides and metallic lithium during cycling. In contrast, a relatively smooth, less damaged surface was found on the lithium anode after cycling in the Li-S cell with CGF (Figures 4.9e and f). The improvement in lithium surface morphology is in good agreement with the S-mapping analysis by EDS, as showing in Figures 4.9g and h. The S intensity on the Li surface of Li-S cell with PGF is much stronger than that of CGF, demonstrating more lithium sulfide compounds are deposited on the surface, which results in the loss of active materials and corrosion damage of the lithium anode.
Figure 4.9 (a, b) SEM images of the surface view of pristine Li metallic plate before cycling at different magnifications. (c, d) SEM images of the surface view of Li metal anode from the Li-S cell with PGF after 100 cycles at different magnifications. (e, f) SEM images of the surface view of Li metal anode from the Li-S cell with CGF after 100 cycles at different magnifications. (g) S-elemental mapping of Li metal anodes from Li-S cells with PGF (g) and CGF (h). The current density used for the 100 cycles was 1C.
XPS was also performed to characterize the surfaces of lithium anodes from the Li-S cells with PGF and CGF after 100 cycles. As shown in Figure 4.10, the peaks at 167-171 eV and 160-165 eV for the Li anode from the cell with PGF can be attributed to Li\textsubscript{x}SO\textsubscript{y} species, which are due to the reaction of the active material with the LiTFSI, and the discharge product Li\textsubscript{2}S/Li\textsubscript{2}S\textsubscript{2}, respectively.\textsuperscript{224,225} Similar phenomenon is also found for the Li anode from the cell with CGF. However, it is noteworthy noting that the intensity of the peaks at 160-165 eV for the cell with CGF is significantly reduced, indicating less short-chain Li\textsubscript{2}S\textsubscript{2} and Li\textsubscript{2}S are deposited on the Li metal surface with the introduction of the carbon coating layer on the separator. This result demonstrates the ability of CGF in reducing the diffusion of polysulfides to the Li anode, which is critically important for enhancing the active material utilization and protecting the Li anode surface.

Figure 4.10 XPS spectra from the lithium anodes of the Li-S cells with PGF and CGF after 100 cycles at 1C.
Photographic images of the separator surfaces that face the lithium plate are also obtained after 100 cycles at a current density of 1C. The yellowish color on the surface of the PGF indicates that polysulfides could diffuse through the separator and react with the lithium anode during cycling (as shown in Figure 4.11a), leading to shuttling reaction and reduced active material utilization. However, the surface of the CGF remains relatively clean and free of yellowish color (Figure 4.11b), which means the polysulfide migration is well controlled by the conductive carbon coating. All the results demonstrate that the CGF acts as a strong absorbent and an effective barrier to limit the diffusion of polysulfide through the separator and onto the lithium anode during the discharge/charge process, which reduces the polysulfide shuttle phenomenon and lithium surface corrosion.\textsuperscript{226}

![Figure 4.11 Photographs of the lithium anode side of the (a) PGF and (b) CGF separators after 100 cycles at a current density of 1C.](image-url)
In this work, we have presented the electrochemical performance of traditional sulfur electrode using carbon-coated GF as a separator. A simple diffusion model was used to observe the polysulfide diffusion across the separator, as shown in Figure 4.12. The polysulfides were fully blocked by either PGF or CGF at the beginning. The electrolyte with PGF turned to yellow after 15 min, while the color of the electrolyte with CGF did not change. Even after 30 min diffusion, the electrolyte with CGF only showed slight change in color, displaying a good inhibiting effect of polysulfide diffusion due to the carbon coating, which further resulted in better electrochemical performance of the cell.

Figure 4.12 The images of polysulfide diffusion across the PGF (a-c) and CGF (d-f) toward various resting times.
Obviously, the high loading of active material is extremely important for practical applications. The surface loading used in the previous section was 0.7-1.0 mg cm$^{-2}$. Here, we investigated the cycling performance of electrodes with higher sulfur loadings of 2.13 and 3.37 mg cm$^{-2}$, respectively (Figure 4.13). The cell with a sulfur loading of 2.13 mg cm$^{-2}$ can still deliver a reversible capacity as high as 1218 mAh g$^{-1}$ at a current density of 0.2C for the first cycle with a low decay of 0.4% per cycle over 30 cycles. When the sulfur loading increases to 3.37 mg cm$^{-2}$, an excellent retention of 94% can be achieved over 30 cycles with a high reversible capacity of 815 mAh g$^{-1}$. It should be noted that the electrochemical performance of the Li-S cell with CGF is probably related to many factors, such as the type and amount of electrolyte, the porosity and thickness of the GF, the loading and thickness of conductive carbon coating, etc. In addition, S particle size is also essential because the shorter Li$^+$ diffusion lengths could be obtained by using smaller S particles, which further results in better rate capability. What’s more, on one hand, the large amount of electrolyte and thick carbon coating can cause decreased energy density of lithium-sulfur cells; on the other hand, the large amount of electrolyte and three dimensional current collector such as carbon coating will improve the electrochemical performance by reversible dissolution of lithium polysulfides.$^{227}$ Therefore, it is important to determine the appropriate electrolyte amount and carbon coating structure for achieving optimized overall performance. Further work is needed to reduce the carbon content and coating thickness so that the cathode capacity can be further improved.
Figure 4.13 Cycling performance of Li-S cells with CGF at high sulfur loadings at a current density of 0.2C.

4.4 Conclusions

In summary, a carbon coating has been developed to significantly improve the cycle performance of the Li-S batteries. Benefiting from the favorable adsorption properties of the conductive carbon coating on the separator, the sulfur cathodes show high capacity with excellent rate capacity and stable cyclability even with high sulfur content (70 wt%) and high sulfur loading (up to 3.37 mg cm\(^{-2}\)). The conductive carbon coating has multiple roles in enhancing electrochemical performance of the Li-S batteries. Firstly, it provides sufficient contact with the cathode surface, offering a high active material utilization. Secondly, it inhibits the migration of polysulfide intermediates, avoiding shuttle reactions. What’s more, the improved cells involve only a simple adjustment of the cell configuration by introducing a
carbon coating on the separator instead of complex carbon-sulfur composite structure design or sulfur-conductive polymer modification, enhancing the commercial viability of Li-S batteries.
CHAPTER 5 POLYACRYLONITRILE/GRAPHENE OXIDE NANOFIBER MEMBRANE SEPARATOR

Abstract

Lithium-sulfur (Li-S) batteries have been considered as a promising candidate for next-generation energy-storage devices due to their high theoretical capacity and energy density. However, the severe self-discharge behavior of Li-S batteries strongly limits their use in practical applications. Here, we report a sustainable and highly porous polyacrylonitrile/graphene oxide (PAN/GO) nanofiber membrane separator that simultaneously enables large capacity and excellent anti-self-discharge capability for lithium-sulfur batteries. A low retention loss (5%) can be achieved even after a resting time of 24 h. Besides benefitting from the highly porous structure and excellent electrolyte wettability of the nanofiber separator, the improved performance can also be ascribed to the excellent barrier effects caused by the relatively high energy binding between –C≡N and Li$_2$S/polysulfides and the electrostatic interactions between GO and negatively charged species (S$_n^{2-}$). It is, therefore, demonstrated that this GO incorporated PAN nanofiber separator with highly porous structure and excellent electrolyte wettability is a promising separator candidate for high-performance Li-S batteries.

**Keywords:** Graphene oxide; Polyacrylonitrile; Nanofiber; Separator; Lithium-sulfur batteries
5.1 Introduction

Sulfur (S) has recently received attention as a promising cathode material for high-specific-energy rechargeable lithium batteries because it has a high theoretical capacity of 1,675 mAh g\(^{-1}\), which is calculated based on the complete reduction from S to lithium sulfide (Li\(_2\)S).\(^{228-230}\) Moreover, S is inexpensive and nontoxic. However, the use of Li-S batteries in practical applications is currently hindered by their short cycle life, severe self-discharge, and low Coulombic efficiency.\(^{231, 232}\) All these challenges are mainly related to the dissolution of reduction intermediates, lithium polysulfides, in the electrolyte, resulting in parasitic reactions.\(^{233}\) Therefore, it is essential to suppress the diffusion of polysulfides in order to obtain high-performance Li-S batteries.

To address the challenges faced by Li-S batteries, efforts have been focused on the development of electrode materials via introducing conductive frameworks into the cathode, such as porous carbon, graphene, carbon nanotubes, metallic oxides, etc.\(^{234-238}\) For example, Lv et al.\(^{230}\) prepared integrated Ketjen Black/sulfur composite via a solution-polymerization followed by melt-diffusion approach and achieved a discharge capacity of 750 mAh g\(^{-1}\) at 0.1C after 100 cycles. Nazar et al.\(^{234, 235}\) used titanium oxide (Ti\(_4\)O\(_7\), magneli phase) and manganese dioxide (MnO\(_2\)) as efficient polysulfide mediators for Li-S batteries and obtained high rechargeable capacities at practical current densities even with high sulfur loading. Li et al.\(^{53}\) synthesized sulfur impregnated carbon clusters for use as cathode material in Li-S batteries and achieved a stable capacity of over 700 mAh g\(^{-1}\) after 300 cycles. Sulfur cathodes
encapsulated in nitrogen-doped hollow carbon spheres and wrapped graphene were studied by Zhou and his coworkers,\textsuperscript{238} and it was found that sulfur/polysulfides were effectively suppressed in this 3D structure, leading to enhanced utilization of active materials. Although improved cell performance was achieved, the methods used in preparing these composite materials generally involve complex, multi-step synthetic processes. In addition, the severe self-discharge of Li-S batteries induced by polysulfides has not been fully solved.

As a critical component in battery systems, the separator plays an important role in all batteries because its main function is to prevent electrical short circuit by separating positive and negative electrodes and transporting the ions between them.\textsuperscript{239} An ideal separator for Li-S batteries is expected to not only have a good ionic conductivity after absorbing the liquid electrolyte, but also can suppress the migration of polysulfides during cycling. Recently, a cationic selective Nafion modified membrane was used to suppress polysulfide diffusion, enhancing the electrochemical performance of Li-S cells.\textsuperscript{240, 241} Yao et al. performed a thin conductive carbon coating on the polypropylene separator to prevent the migration of polysulfides.\textsuperscript{171} Although the cycling performance of the Li-S cells was improved in their work, the active material concentrations in those systems were relatively low (40-60 wt\%) which significantly reduced the energy density of the cells. In addition, poor rate capability was observed in those systems which was probably due to the slow cell kinetics caused by the low porosity and poor wettability of the microporous polyolefin membranes. In the study of Chang et al., a single-wall carbon nanotube (SWCNT)-modulated polypropylene was utilized
as the separator.\textsuperscript{242} Although a capacity of 501 mAh g\textsuperscript{-1} could be achieved at 0.2C after 300 cycles, the cell using this separator still had a relatively poor rate capability.

Nanofiber membranes are attractive for use as battery separators because they have highly porous structure and excellent electrolyte wettability, which can lead to large electrolyte intake and consequently high ionic conductivity when placed in the electrolyte, facilitating rapid ionic transportation.\textsuperscript{243, 244} Many polymers can be used to prepare nanofiber membranes. Among them, polyacrylonitrile (PAN) is believed to be a suitable polymer for battery separator application because of its easy processability and excellent resistance to oxidative degradation.\textsuperscript{245} Tatsuma \textit{et al.} and Gopalan \textit{et al.} found that the use of PAN separators led to reduced lithium dendrite sizes because the viscoelastic polymer could mechanically suppress dendrite formation.\textsuperscript{246, 247} In addition to PAN, graphene oxide (GO) has received a lot of attention recently.\textsuperscript{248} GO membrane was also demonstrated to be able to block the diffusion of polysulfides which was ascribed to the electrostatic interactions between the negatively charged species (S_n\textsuperscript{2-}) and the oxygen-containing groups on GO.\textsuperscript{163} For example, Zeng \textit{et al.} used electroactive cellulose-supported GO interlayers in Li-S cells, and found that the GO interlayers could minimize the diffusion of polysulfides, enhancing the utilization of active material.\textsuperscript{249} Zhuang \textit{et al.} also reported that the GO sheets could act as physical barriers to suppress the diffusion of polysulfide anions, improving the electrochemical performance of Li-S batteries.\textsuperscript{250}
Based on the abovementioned considerations, we report an effective PAN/GO nanofiber membrane separator that can provide Li-S cells with significantly enhanced cycle stability and rate capability without introducing complicated cathode structure design. More importantly, a low capacity retention loss (5%) can be achieved even after a resting time of 24 h, indicating excellent anti-self-discharge capability of the PAN/GO nanofiber membrane. It is, therefore, demonstrated that this PAN/GO nanofiber membrane can be considered as a promising separator candidate for advanced Li-S batteries.

5.2 Experimental

5.2.1 GO Synthesis

GO was synthesized based on an improved method. Briefly, 1.5 g graphite powder (< 20 micro, Sigma-Aldrich) and 9 g potassium permanganate (KMnO₄, ≥99%, Sigma-Aldrich) were added to a mixture of 180 mL sulfuric acid (H₂SO₄, 95-98%, Sigma-Aldrich) and 20 mL phosphoric acid (H₃PO₄, ≥85%, Sigma-Aldrich). The mixture was then heated to 50 °C followed by mechanical stirring for 12 h. After that, the mixture was cooled to room temperature and poured onto the ice (180 g) with a certain amount of 30 wt% hydrogen peroxide (H₂O₂, 30 wt%, Sigma-Aldrich). The solution color changed from dark green to bright yellow. The solution was then centrifuged at 3500 rpm for 30 min. The obtained material was washed by 100 mL of deionized (DI) water, 100 mL of 37 wt% hydrochloric acid (HCl,
Sigma-Aldrich), and 200 mL of ethanol (EtOH, 99.5%, Sigma-Aldrich). The time for each wash was 15 min. Finally, the as-prepared GO was vacuum-dried at 60 °C for 6 h.

5.2.2 Membrane Preparation

A homogenous solution of 3 g polyacrylonitrile (PAN, $M_w = 150,000$, Sigma-Aldrich) in 27 g dimethylformamide (DMF, >99.5%, Sigma-Aldrich) was prepared and then electrospun to form a PAN nanofiber membrane under a high voltage of 15 kV with a feeding rate of 0.75 mL min$^{-1}$. For the preparation of PAN/GO nanofiber membrane, 0.3 g GO was firstly dispersed into DMF with the assistance of sonication. Then, 3 g PAN was added into the GO dispersed solution. The weight ratio between PAN and GO in the as-spun PAN/GO nanofiber membrane was 10:1, corresponding to a GO content of 9.1 wt%. The average thicknesses of these as-spun membranes were in the range of 65 ± 3 µm. Polypropylene (PP, Celgard 2400) membrane was used for comparison in this study.

5.2.3 Structural Characterization

The size and thickness of GO were evaluated by using atomic force microscopy (AFM, Bruker Dimension 3000, USA). Field-emission scanning electron microscopy (FE-SEM, FEI Verios 460L, USA) was performed to observe the morphology of PAN and PAN/GO nanofiber membranes. X-ray diffraction (XRD, PANalytical Empyrean, Holland) was used to identify the structure of the as-prepared nanofibers. The surface functional groups of PAN and
PAN/GO nanofiber membranes were characterized by using X-ray photoelectron spectroscopy (XPS, SPECS FlexMod, Germany) with Mg Kα X-ray source.

The porosities of the as-prepared membranes were measured by using n-butyl alcohol (99%, Sigma-Aldrich) uptake test and calculated by:

\[
\text{Porosity (\%)} = \frac{(w_w - w_d)}{(\rho_b \times V)} \times 100\%
\]

(5.1)

where \( w_w \) and \( w_d \) are the weights of wet and dry separators, \( \rho_b \) stands for n-butyl alcohol’s density, and \( V \) is the geometric volume of the separator.

The electrolyte uptakes (EU) were determined by soaking weighed separators in the liquid electrolyte of 1 M lithium bis(trifluoromethane)sulfonamide lithium (LiTFSI, Sigma-Aldrich) and 0.1 M lithium nitrite (LiNO₃, 99.99% trace metals basis, Sigma-Aldrich) in a mixture of 1,3-dioxolane (DOL, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, Sigma-Aldrich) (1: 1 by volume) at room temperature for 2 h. The EU values were calculated by:

\[
\text{EU (\%)} = \frac{(w_f - w_0)}{w_0} \times 100\%
\]

(5.2)

where \( w_0 \) and \( w_f \) are the weights of separators before and after soaking in the electrolyte, respectively.

The ionic conductivities (\( \sigma \)) of electrolyte-soaked separators were determined based on the electrochemical impedance spectroscopy (EIS) test. The measurements were carried out after the separators fully adsorbed the liquid electrolyte and reached the equilibrium. The \( \sigma \) values were calculated by:
\[ \sigma = \frac{L}{(R_b \times A)} \]  

(5.3)

where \( R_b \) is the electrolyte’s bulk resistance, \( L \) and \( A \) are the thickness of the separator and the contact area between the stainless steel electrode and the separator, respectively, which are 65 \( \mu \text{m} \) and 1.89 \( \text{cm}^2 \).

5.2.4 Electrochemical Performance Evaluation

Coin-type 2032 Li-S cells were assembled in an argon-filled glove box to evaluate the electrochemical performance of PAN and PAN/GO nanofiber separators. The cathode was prepared by mixing 70 wt% sulfur (99.5-100.5%, Sigma-Aldrich) and 20 wt% Super P (C-65, TIMCAL Graphite & Carbon Ltd.) with 10 wt% polyvinylidene fluoride (Solef®PVDF-5130, Solvay) and certain amount of N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich) to form a slurry which was then coated on the carbon coated aluminum foil and dried under vacuum at 60 \( ^\circ \text{C} \) for 12 h. Lithium metal foil was used as the anode and 1 M LiTFSI with 0.1 M LiNO\(_3\) in a mixture of DOL/DME (1:1 by volume) was used as the electrolyte. The sulfur loading was around 0.7-1 mg cm\(^{-2}\) and the amount of electrolyte in different coin cells was fixed at 40 \( \mu \text{L} \) per 1 mg S. The polysulfide solution with 0.02 M Li\(_2\)S\(_8\) was used for the polysulfide diffusion test. The cycling performance of assembled Li-S cells was evaluated by using Arbin Instruments in a potential range of 2.8-1.7 V. The specific capacities of the cells used in this study were calculated based on the sulfur mass in the cathode.
The cyclic voltammetry (CV) measurement was conducted using a Gamry Reference 600 with different scanning rates in a potential range of 2.8-1.7 V. Lithium-ion diffusion coefficient $D_{Li^+}$ (cm$^2$ s$^{-1}$) was measured by CV with different scanning rates and calculated according to the Randles-Sevick equation:

$$I_p = 2.69 \times 10^5 \ n^{1.5} \ A \ D_{Li^+}^{0.5} \ C_{Li^+}^{0.5} \ v^{0.5}$$  \hspace{1cm} (5.4)

where $I_p$ is the peak current in A, $n$ is the number of electrons in the reaction (it is 2 for Li-S battery), $A$ is the electrode area in cm$^2$, $C_{Li^+}$ and $v$ represent the lithium-ion concentration in the electrolyte in mol mL$^{-1}$ and the CV scanning rate in V s$^{-1}$, respectively.

### 5.3 Results and Discussion

#### 5.3.1 Morphology and Structure

The purpose of this work is to obtain PAN/GO nanofiber separator that is able to minimize the polysulfide diffusion in Li-S batteries. While suppressing the polysulfide diffusion, the PAN/GO nanofiber separator should also have the structure features of high porosity and good electrolyte wettability so that the lithium cations can transport freely between the two electrodes. The scanning electron microscopy (SEM) image of PAN/GO nanofiber separator is shown in Figure 5.1. For comparison, the SEM images of microporous PP membrane separator and PAN nanofiber separator are also shown. Unlike slit-like porous structure of polypropylene (PP) (Figure 5.1a), both PAN (Figure 5.1b) and PAN/GO (Figure 5.1c) nanofiber separators consist of randomly arranged fibers with average diameters of 850 and
600 nm, respectively. The randomly arranged fibers assemble to form a network structure with open pores in the macroscale range. This highly porous structure is further confirmed by the porosity testing results, as shown in Table 1. The porosities of PAN and PAN/GO nanofiber separators are 70% and 72%, respectively, which are significantly higher than that (41%) of PP separator. It should be noted that the use of high-porosity PAN and PAN/GO membranes might increase the risk of short circuit for Li-S cells. Min et al.\textsuperscript{245} used a PAN membrane (porosity = 68%) as Li-ion battery separator and found that the open pores in the membrane disappeared after the uptake of liquid electrolyte, which was caused by the gelation of PAN in liquid electrolyte. This indicated that PAN based separators might reduce the short circuit risk for Li-S batteries. However, efforts are still needed to permanently eliminate the short circuit behavior. One possible approach is to coat the lithium anode with a mechanically-strong, ionically-conductive non-porous layer. Another concern for the use of high-porosity PAN and PAN/GO separators is that Li dendrites might pass through them easily when Li anode is used. However, Tatsuma et al.\textsuperscript{246} found that the use of PAN membrane reduced the size of lithium dendrites because the viscoelastic polymer mechanically suppresses dendrite growth. Similar phenomenon has been discovered by Gopalan et al.\textsuperscript{247} Although PAN-based membranes could potentially inhibit the lithium dendrite growth, this is not a permanent solution. Therefore, other approaches must be studied to avoid the lithium dendrite growth, and the abovementioned non-porous coating layer on lithium anode could be an effect solution to solve the dendrite problem.
Figure 5.1 SEM images of (a) PP, (b) PAN, and (c) PAN/GO separators, the inserts are high resolution images.

Table 5.1 Physical and electrochemical parameters of PP, PAN, and PAN/GO separators.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Electrolyte Uptake (%)</th>
<th>Ionic Conductivity (mS cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>41</td>
<td>152</td>
<td>0.60</td>
</tr>
<tr>
<td>PAN</td>
<td>70</td>
<td>275</td>
<td>1.00</td>
</tr>
<tr>
<td>PAN/GO</td>
<td>72</td>
<td>303</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Figure 5.2 shows the X-ray diffraction (XRD) patterns of pure PAN and PAN/GO nanofiber separators. The XRD spectrum of PAN nanofiber separator displays a sharp intense peak at 16.7° and a weak diffraction peak at 28.5°. The first peak is corresponding to the (100) diffraction of the hexagonal lattice and the second peak is ascribed to the second-order diffraction of the first peak. After the introduction of GO filler, the XRD pattern of PAN/GO
nanofiber separator shows an additional peak at 10.5°, corresponding to the (002) reflection of GO, while still presenting the PAN peaks at 16.7° and 28.5°. The appearance of both PAN and GO peaks indicates that the electrospinning method did not change the structure of GO filler and PAN chains.

![XRD patterns of PAN and PAN/GO separators.](image)

Figure 5.2 XRD patterns of PAN and PAN/GO separators.

XPS was applied to identify the surface functionality of as-spun PAN and PAN/GO nanofiber separators (Figure 5.3). The peaks at 398 and 284 eV for both PAN and PAN/GO membranes are corresponding to N1s and C1s of the –C≡N groups as well as the main chain of polyacrylonitrile. A small oxygen peak can be detected in PAN/GO nanofiber separator (Figure 5.3b) due to the presentence of oxygen-containing functional groups (such as ketone carbonyls,
ester and lactol carbonyls, etc.) in GO. The relatively low intensity of oxygen is ascribed to the low concentration of oxygen in the PAN/GO nanofiber separator. As expected, there is no oxygen detected for the PAN membrane (Figure 5.3a).

Figure 5.3 XPS survey spectra of (a) PAN and (b) PAN/GO separators.

The unique structural features of PAN/GO nanofiber separator can play an important role in improving the overall performance of Li-S cells. As shown schematically in Figure 5.4, when PAN/GO nanofiber separator is used, the lithium cations can transport freely across this high porous network structure, which guarantees the high capacity and excellent rate capability of the Li-S cells. At the same time, the anions of polysulfides are confined on the cathode side and the shuttle of polysulfides between the cathode and anode sides can be significantly minimized due to the relatively high energy binding between the \(-\text{C≡N}\) groups of PAN and
the Li$_2$S/polysulfides in the electrolyte and the electrostatic interactions between the oxygen-containing functional groups of GO and the negatively charged species ($S_n^{2-}$) of polysulfides. As a result, this highly porous PAN/GO membrane can not only block the diffusion of polysulfides but also improve the ionic conductivity which are beneficial for improving the cycling performance, rate capability and anti-self-discharge capability of Li-S cells. The electrochemical performance of Li-S cells using PAN/GO nanofiber separator was characterized and discussed below.
Figure 5.4 Schematic illustration of the Li-S cell with PAN/GO separator.

5.3.2 CV and Discharge-Charge Profiles

CV tests were conducted to investigate the electrochemical behavior of the Li-S cells at a scan rate of 0.1 mV s⁻¹. As shown in Figure 5.5a, the CV curve of the cell with PP separator exhibits
two cathodic peaks at around 2.21 and 1.96 V and two overlapped anodic peaks at around 2.41 and 2.47 V, which are typical of Li-S cells. Similar results have also been found for the Li-S cells with PAN (Figure 5.5b) and PAN/GO (Figure 5.5c) separators.

![CV curves](image)

Figure 5.5 CV curves of Li-S cells with (a) PP, (b) PAN, and (c) PAN/GO separators at a scan rate of 0.1 mV s\(^{-1}\).

The discharge-charge profiles of the first cycle for Li-S cells with PP, PAN, and PAN/GO separators at 0.2C are shown in Figure 5.6. The C-rates specified in this study are based on the
mass and theoretical capacity of sulfur \( (1 \text{C} = 1,675 \text{ mA g}^{-1}) \). In general, there are two discharge regions based on the voltage profile in the reduction process of Li-S battery, which are in the range of 2.4-2.1 V (the first region) and 2.1-1.7 V (the second region), respectively. The first region represents the formation of long-chain polysulfides \( (\text{Li}_2\text{S}_n, 4 \leq n \leq 8) \) by the reduction of elemental sulfur and the second discharge region indicates the conversion of \( \text{Li}_2\text{S}_4 \) to solid-phase low-order \( \text{Li}_2\text{S}_2 \) or \( \text{Li}_2\text{S} \). During the cell charging, the two continuous charge plateaus correspond to the oxidation reactions from lithium sulfides to polysulfides and finally to sulfur. From Figures 5.6a and b, it is seen that both the charge and discharge capacities of the Li-S cell with PAN separator is slightly higher than those with PP separator, which is due to the relatively higher binding energy between the \(-\text{C}≡\text{N}\) and \(\text{Li}_2\text{S}/\text{polysulfides}\) compared with that between \(-\text{CH}_3\) and \(\text{Li}_2\text{S}/\text{polysulfides}\), suppressing the diffusion rate of polysulfides and improving the active material utilization. The binding energies between \(-\text{C}≡\text{N}\) and \(\text{Li}_2\text{S}/\text{polysulfides}\) are 0.60 eV and 0.77 eV, while the binding energies between \(-\text{CH}_3\) and \(\text{Li}_2\text{S}/\text{polysulfides}\) are 0.23 eV and 0.30 eV, respectively.\(^{254}\) As shown in Figure 5.6c, the Li-S cell with PAN/GO separator has the highest charge and discharge capacities among all three cells. This is probably because the electrostatic interactions between GO and negatively charged species \( (\text{S}_n^{2-}) \) help minimize the migration of polysulfide intermediates and further enhance the utilization of active material.\(^{163}\)
5.3.3 Cycling and Rate Performance

Cycling performance of Li-S cells with PP, PAN, and PAN/GO separators was tested at a current density of 0.2C, and the results are shown in Figure 5.7. The initial discharge capacity for Li-S cells with PP, PAN, and PAN/GO separators are 781, 868, and 987 mAh g$^{-1}$, respectively. As discussed above, the higher discharge capacity of the Li-S cell with PAN
separator than that with PP separator is caused by the relatively higher binding energies between the –C≡N and Li₂S/polysulfides compared with those between -CH₃ and Li₂S/polysulfides, suppressing the diffusion rate of polysulfides and improving the active material utilization.²⁴⁸ The Li-S cell with PAN/GO separator has the highest discharge capacity among the three cells because the strong electrostatic interactions between GO and negatively charged species (Sₙ²⁻) further minimize the migration of polysulfide intermediates and enhance the utilization of active material.¹⁶³,²⁵⁰ After 100 cycles, the cell with PAN/GO separator can still deliver a high capacity of 597 mAh g⁻¹ which is 38% higher than that of the cell with PP separator. Such improved cycling performance is due to the relatively high energy binding between –C≡N and Li₂S/polysulfides and the electrostatic interactions between GO and negatively charged species (Sₙ²⁻), effectively blocking the polysulfides transportation and further enhancing the utilization of the active material.

Figure 5.7 Cycling performance of Li-S cells with PP, PAN, and PAN/GO separators at a current density of 0.2C.
Since the rate capability is considered as another essential parameter for batteries, the Li-S cells were also tested under various current densities from 0.2 to 2C rate. As seen in Figure 5.8, the cell with PP separator can deliver specific capacities of 445, 382, and 303 mAh g\(^{-1}\) at current densities of 0.2, 0.5, and 1C, respectively. When the current density increases to 2C, the capacity drops rapidly to 129 mAh g\(^{-1}\). For comparison, the cell with PAN separator shows relatively stabilized and higher capacities of 580, 485, and 391 mAh g\(^{-1}\), respectively, at current densities of 0.2, 0.5, and 1C. A capacity of 257 mAh g\(^{-1}\) can be obtained at the current density of 2C for the Li-S cell with PAN separator. The improved electrochemical performance is probably due to the formation of LiS\(n\cdots\)N interactions via the N lone-pair electrons, which alleviates the dissolution of lithium polysulfides in the electrolyte and enhances the active material utilization.\(^{214}\) For the cell with PAN/GO separator, the capacity gradually decreases from 699 to 591, 448 mAh g\(^{-1}\), respectively, when the current density increases from 0.2 to 0.5, 1C. At a high current density of 2C, the capacity (337 mAh g\(^{-1}\)) achieved by the cell with PAN/GO separator is significantly higher than those (129 and 257 mAh g\(^{-1}\)) of the cells with PP and PAN separators. More importantly, when the current density is switched back from 2C to 0.2C, the Li-S cell with PAN/GO separator can still deliver a reversible capacity of 655 mAh g\(^{-1}\) (a high retention of 94%), which is 80% and 25% higher than those (364 and 525 mAh g\(^{-1}\)) of the cells with PP and PAN separators. The excellent rate capacity of the Li-S cell with PAN/GO separator can be ascribed not only to the highly porous structure of the separator, resulting in good ionic conductivity (1.36 mS cm\(^{-1}\), as can be seen in Table 5.1), but also to the relatively high energy binding between –C≡N and Li\(_2\)S/polysulfides and the electrostatic
interactions between GO and negatively charged species ($S_n^{2-}$), availably suppressing the diffusion of polysulfides.

![Graph showing rate performance of Li-S cells with PP, PAN, and PAN/GO separators under varying current densities.](image)

**Figure 5.8** Rate performance of Li-S cells with PP, PAN, and PAN/GO separators under varying current densities.

5.3.4. Lithium-Ion Diffusion Coefficients

It is necessary to investigate the impact of GO on lithium-ion diffusion since the rate performance is closely associated with the diffusion of lithium ions in the cells. The lithium-ion diffusion coefficients were evaluated by a series of cyclic voltammetry (CV) measurements.
with different scan rates (shown in Figures 5.9a-c) and calculated by the Randles-Sevick equation.\textsuperscript{255,256} Here, the cathodic perks at ~2.2 V and ~1.95 V and the anodic peak at ~2.45 V were defined as peaks A, B, and C, respectively. According to Equation (4), the plot of the reduction peak current $I_p$ versus the square root of the scan rate should result in a straight line which is confirmed by Figures 5.9d-f. From the slope of the linear fit, the lithium diffusion coefficients are calculated to be $D_{Li^+}(A) = 2.90 \times 10^{-9}$ cm$^2$ s$^{-1}$, $D_{Li^+}(B) = 6.36 \times 10^{-9}$ cm$^2$ s$^{-1}$, and $D_{Li^+}(C) = 1.07 \times 10^{-8}$ cm$^2$ s$^{-1}$ for the Li-S cell with PP separator. The diffusion coefficients increase to $D_{Li^+}(A) = 5.51 \times 10^{-9}$ cm$^2$ s$^{-1}$, $D_{Li^+}(B) = 6.71 \times 10^{-9}$ cm$^2$ s$^{-1}$, $D_{Li^+}(C) = 1.55 \times 10^{-8}$ cm$^2$ s$^{-1}$ when PAN separator was used. After the addition of GO in PAN, the diffusion coefficients further increase to $D_{Li^+}(A) = 8.25 \times 10^{-9}$ cm$^2$ s$^{-1}$, $D_{Li^+}(B) = 1.15 \times 10^{-8}$ cm$^2$ s$^{-1}$, and $D_{Li^+}(C) = 2.34 \times 10^{-8}$ cm$^2$ s$^{-1}$. It is obvious that the lithium ion diffusion coefficients can be dramatically enhanced when using PAN and PAN/GO separators, which is attributed to their highly porous structure and excellent electrolyte uptake ability. As shown in Table 1, the electrolyte uptake of the PAN and PAN/GO separators are 275% and 303%, respectively, which are significantly higher than that (152%) of the PP separator.
Figure 5.9 CV curves at various voltage scan rates of Li-S cells with (a) PP, (b) PAN, and (c) PAN/GO PP separators; the linear fits of the peak currents for Li-S cells with (d) PP, (e) PAN, and (f) PAN/GO separators.

5.3.5 Anti-Self-Discharge Capability

It should be noted that low self-discharge is another important requirement for determining the practicality of Li-S batteries. Unfortunately, conventional Li-S batteries exhibit severe self-discharge behavior. The evolution of open-circuit voltages (OCV) with time for Li-S cells using PP, PAN and PAN/GO separators are shown in Figure 5.10. It is seen that the OCV value of the cell with PP separator dropped from 2.44 V to 2.39 V after 10 h of storage, while the OCV of the cell with PAN separator kept a stable value of 2.40 V even after 120 h. For the cell
with PAN/GO separator, the OCV is stabilized at a high value of 2.73 V, demonstrating its excellent anti-self-discharge behavior. Since the self-discharge of Li-S batteries is largely caused by the continuous dissolving of sulfur/high-order polysulfides in the electrolyte even in the resting state after charging due to the presence of concentration gradients, in this work, the discharge capacity after resting was also used to describe how the PAN/GO separator contributes to the anti-self-discharge feature. The capacity retention was defined as the capacity ratio between the second cycle and the first cycle. The capacity retention of the Li-S cell with PP separator is 86% without resting (Figure 5.11a). However, the capacity retention decreases to 51% when there is a 24 h rest between the first and second cycle (Figure 5.11d). This indicates that a high retention loss of 35% (86% - 51%) can be observed for the cell using PP separator if there is a 24 h rest between the first two cycles. As shown in Figures 5.11b and e, the retention loss after 24 h rest decreases to 28% (90% - 62%) when PAN separator is used, which is probably because of the relatively higher binding energy between the -C≡N and Li₂S/polysulfides compared to that between -CH₃ and Li₂S/polysulfides.²⁵⁴ After the introduction of GO into PAN, a significantly lower retention loss of 5% (79% - 74%) can be obtained for the cell using PAN/GO separator, indicating the excellent anti-self-discharge behavior (Figures 5.11c and f). Besides benefitting from the binding ability of the -C≡N groups in PAN, the oxygen-containing electronegative groups in GO act as ion-hopping sites of Li⁺ and minimize the transportation of negatively charged species (Sₙ²⁻) through the formation of electrostatic interactions, which in turn enhances the anti-self-discharge capability of Li-S cells.
Figure 5.10 Evolution of open-circuit voltages with time for Li-S cells with PP, PAN, and PAN/GO separators.

Figure 5.11 Discharge-charge profiles and self-discharge behavior of Li-S cells with (a, d) PP, (b, e) PAN, and (c, f) PAN/GO separators at a current density of 0.2C.
In addition, as shown in Figure 5.12, the diffusion of polysulfides through PP, PAN and PAN/GO separators was observed by using a diffusion model. It is clear that polysulfides were totally blocked by all three separators at the beginning. After 30 min, the color of the electrolyte with PP separator turned to yellow. However, there was no color change when PAN and PAN/GO separators were used, indicating their excellent ability of suppressing the polysulfide diffusion.

Figure 5.12 Images of polysulfide diffusion through PP, PAN, and PAN/GO separators in 30 min.
5.4 Conclusions

In summary, PAN/GO nanofiber separator was prepared for Li-S batteries to enhance the cycle stability and rate capacity even with high sulfur content of 70 wt% in the cathode. The improved performance is attributed to a variety of synergic effects, including highly porous structure and good wettability of PAN/GO nanofibers, as well as the physical and chemical barrier effects of PAN chains, which have –C≡N, and GO filler, which contains various oxygen-containing functional groups. The Li-S cell made with PAN/GO separator is able to demonstrate high specific capacity, excellent rate capability, and enhanced anti-self-discharge capability. More importantly, this work offers a general strategy to apply GO-based polymer membrane for use as novel separator to achieve high-performance Li-S batteries, enhancing their commercial viability.
CHAPTER 6 POLYACRYLONITRILE/SILICA NANOFIBER MEMBRANE
SEPARATOR WITH CARBON NANOTUBE SHEET

Abstract

Sulfur (S) has been considered as a promising cathode candidate for lithium batteries due to its high theoretical specific capacity and energy density. However, the low active material utilization, severe capacity fading, and the short lifespan of the resultant lithium-sulfur (Li-S) batteries have strongly hindered their practicality. In this work, a multi-functional polyacrylonitrile/silica nanofiber membrane with an integral ultralight and thin multi-walled carbon nanotube sheet is presented and demonstrates a new approach to significantly improve the overall electrochemical performance of Li-S batteries. The experimental results are in agreement with molecular modeling studies based on density functional theory and Monte Carlo simulations. Remarkably, this design is favorable for the fast diffusion of both lithium ions and electrons, and mitigating the diffusion of polysulfides. As a consequence, a high reversible capacity of 741 mAh g\(^{-1}\) at 0.2C after 100 cycles with excellent cyclability and high-rate performance (627 mAh g\(^{-1}\) at 1C) are achieved even with a high sulfur loading of 70 wt% in the cathode, revealing its great potential for energy storage applications. Moreover, a capacity of 426 mAh g\(^{-1}\) is retained after 300 cycles at a high current density of 2C. These results represent a major step forward in the progress of Li-S battery technologies.

Keywords: Lithium-sulfur batteries, Nanofiber membrane, Carbon nanotube, High performance, Long cycle life
6.1 Introduction

Lithium-ion batteries (LIBs) have been widely used as the main power source for portable electronic devices because they exhibit long cycle life, high power density and energy density.257-261 However, the applicability of LIBs is hindered in large scale applications, such as electric vehicles, stationary energy storage, etc. This has been the driving force for a large number of investigation of new battery technologies. The lithium-sulfur (Li-S) battery is a promising candidate and has attracted lots of attention due to its abundance in nature, relatively low cost, non-toxicity, high theoretical capacity (1,675 mAh g\(^{-1}\)) and high energy density (2,600 Wh kg\(^{-1}\)) which are calculated based on the reduction from S to lithium sulfide (Li\(_2\)S).262

Despite these considerable advantages, the use of Li-S batteries in practical applications has been severely limited by their short cycle life, fast self-discharge, and low Coulombic efficiency.263 All of these challenges are mainly attributed to the dissolution and diffusion of reduction intermediates (lithium polysulfides, Li\(_{2}S_x\), 2 < x ≤ 8) into the organic electrolyte, resulting in a loss of active material from the cathode and a polysulfide shuttle phenomenon. It is extremely important to suppress the diffusion of polysulfides in order to obtain high-performance Li-S batteries.

Many efforts have been made to address the challenges faced by Li-S batteries, which mostly focused on the preparation of composites of S with conductive materials, such as porous carbon,87 graphene,226 carbon nanotubes,264 conductive polymers,130 etc.; and using metal
oxides which have high polysulfide absorption ability, such as TiO$_2$, Ti$_4$O$_7$, and Al$_2$O$_3$, etc. Unfortunately, these efforts resulted in complicated cathode structure designs that definitely hinder the practicality of Li-S batteries.

It is well known that a key component in all batteries is the separator, which should be electronically insulating but ionically conducting. Microporous polypropylene (PP) separators are commercially used for LIBs but their low porosity and poor electrolyte wettability strongly limit the electrochemical performance of Li-S batteries, especially the rate capability. In contrast, nanofiber membranes have been shown to exhibit better performance as the separator for lithium batteries due to their highly porous structure and excellent electrolyte wettability, which result in large electrolyte uptake and high ionic conductivity, facilitating rapid ionic transportation. An ideal separator for Li-S batteries is expected to not only have a good ionic conductivity after absorbing the liquid electrolyte, but also to mitigate the diffusion of polysulfides during cycling. Very recently, we have demonstrated that electrospun polyacrylonitrile (PAN) nanofiber membranes are promising separator candidate for Li-S batteries, because the –C≡N group has higher binding energy with Li$_2$S/polysulfides compared to the –CH$_3$ group in a PP separator. In addition to PAN, silica nanoparticles were studied by Kim et al., and can be used as an adsorption agent for polysulfides. The combination of PAN and SiO$_2$ could lead to a nanofiber membrane separator that can effectively inhibit the diffusion of polysulfides in Li-S batteries. Moreover, the performance of Li-S batteries can be further improved by introducing a conductive carbon interlayer or coating onto the separator. For example, Manthiram et al. used a microporous carbon paper interlayer that is able to
supply fine contact with the cathode surface, offering electron pathways through the insulating S/Li$_2$S and preventing the migration of polysulfides to achieve high-performance Li-S batteries. Even though the electrochemical performance of Li-S batteries can be improved by this design, this conductive interlayer typically has a large thickness of several hundred micrometers and a high areal density of several milligrams per square centimeters, respectively, leading to a significant reduction in the cell’s energy density.

Based on the abovementioned considerations, we report a hierarchical multi-component PAN/SiO$_2$ nanofiber membrane separator with an ultralight (an areal density of ~0.234 mg cm$^{-2}$) and thin (a thickness of ~3 µm) MWCNT sheet that can provide Li-S cells with significantly improved cycle stability and rate capability without introducing a complicated cathode architecture, further enhancing the practicality of Li-S batteries. These results are also supported by molecular modeling studies designed to investigate the molecular origins of this improved performance.

6.2 Experimental

6.2.1 Synthesis of Multi-Walled Carbon-Nanotube Sheets

Vertically aligned multi-walled carbon nanotubes (MWCNT) were grown by chemical vapor deposition (CVD) on a quartz substrate using iron (II) chloride (FeCl$_2$) as the catalyst. FeCl$_2$ and the substrate were placed inside a quartz tube which was loaded into the furnace. After the
chamber was sealed and pumped to as low as 6.5 mTorr, the furnace was heated up to 760 °C. Subsequently, the growth gasses, acetylene (600 sccm), argon (400 sccm) and chlorine (2 sccm), were allowed to flow into the chamber. The MWCNT growth process lasted for 20 minutes under a pressure of 3 torr. After which time the chamber was returned to the ambient temperature and atmospheric pressure. The resulting MWCNT array had an average height of ~ 2 mm. The aligned MWCNT sheets were formed by means of the MWCNT clean surfaces and the sufficient van der Waals interactions between the tubes that allowed for the transferring of the MWCNTs from an aligned vertical orientation on top of the quartz substrate to the aligned horizontal orientation in the MWCNT sheet. The aligned MWCNT sheet was pulled out of 50 mm wide MWCNT arrays by tweezers and drawn by means of double sided tape over a piece of copper foil until the required number of MWCNT layers was reached.

6.2.2 Self-Assembly of Polyacrylonitrile/Silica Nanofiber Membrane with MWCNT Sheet

Two PAN/SiO\textsubscript{2} solutions were prepared by dispersing 0.3 g and 0.9 g SiO\textsubscript{2} (nanopowder, 10-20 nm, Sigma-Aldrich) in 27 g dimethylformamide (DMF, >99.5%, Sigma-Aldrich), respectively, with the assistance of sonication. After that, 3 g of PAN (\(M_w = 150,000\), Sigma-Aldrich) were added into each solution. The well mixed solutions were electrospun to form PAN/SiO\textsubscript{2} nanofiber membranes under a high voltage of 15 kV with a feeding rate of 0.75 mL min\textsuperscript{-1}.\textsuperscript{[29, 30]} The final PAN/SiO\textsubscript{2} nanofiber membranes with 0.3 g and 0.9 g SiO\textsubscript{2} were designated as PAN/SiO\textsubscript{2}-10 and PAN/SiO\textsubscript{2}-30, respectively, according to their SiO\textsubscript{2} contents. The incorporation of SiO\textsubscript{2} into the nanofiber membranes was confirmed by Fourier Transform
Infrared Spectroscopy (FT-IR, Nicolet Nexus 470 Spectrometer with Nicolet OMNI Germanium Crystal ATR sampling head, USA). The average thicknesses of these as-spun membranes were ~65 µm. The assembly of PAN/SiO$_2$-30 with MWCNT was prepared by electrospinning PAN/SiO$_2$-30 directly onto the MWCNT sheet layers that were attached to a copper foil.

6.2.3 Structural Characterization

The morphology and structure of the as-prepared nanofiber membranes were identified by Field-emission scanning electron microscopy (FE-SEM, FEI Verios 460L, USA) and X-ray diffraction (XRD, PANalytical Empyrean, Holland), respectively. The crystal structure of MWCNT was further characterized by transmission electron microscopy (TEM, JEOL 2010F). The porosities of the as-prepared membranes were measured by using a n-butyl alcohol (99%, Sigma-Aldrich) uptake test and calculated by:

\[
\text{Porosity} \, (\%) = \frac{(w_w - w_d)}{(\rho_b \times V)} \times 100\% \quad (6.1)
\]

where \( w_w \) and \( w_d \) are the weights of wet and dry separators, \( \rho_b \) stands for n-butyl alcohol’s density, and \( V \) is the geometric volume of the separator.

The electrolyte uptakes (EU) were determined by soaking weighed separators in the liquid electrolyte of 1 M lithium bis(trifluoromethane)sulfonamide lithium (LiTFSI, Sigma-Aldrich) and 0.1 M lithium nitrite (LiNO$_3$, 99.99% trace metals basis, Sigma-Aldrich) in a mixture of
1,3-dioxolane (DOL, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, Sigma-Aldrich) (1:1 by volume) at room temperature for 2 h. The EU values were calculated by:

\[
EU(\%) = \frac{(w_f - w_0)}{w_0} \times 100\%
\]  

(6.2)

where \( w_0 \) and \( w_f \) are the weights of separators before and after soaking in the electrolyte, respectively.

The ionic conductivities (\( \sigma \)) of electrolyte-soaked separators were determined based on the electrochemical impedance spectroscopy (EIS) test. The measurements were carried out after the separators fully adsorbed the liquid electrolyte and reached the equilibrium. The \( \sigma \) values were calculated by:

\[
\sigma = \frac{L}{R_b \times A}
\]  

(6.3)

where \( R_b \) is the electrolyte’s bulk resistance, \( L \) and \( A \) are the thickness of the separator and the contact area between the stainless steel electrode and the separator, which are 65 µm and 1.89 cm\(^2\), respectively.

6.2.4 Electrochemical Measurements

Sulfur (S, 99.5-100.5%, Sigma-Aldrich), Super P (C-65, TIMCAL Graphite & Carbon Ltd.), and polyvinylidene fluoride (PVDF, 10 wt%, Solef®PVDF-5130, Solvay) binder with a weight ratio of 7 : 2 : 1 in N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich) were mixed into a homogeneous slurry which was then pasted on the carbon-coated aluminum foil and dried under vacuum at 60 °C for 12 h. Lithium metal foil and 1 M LiTFSI with 0.1 M LiNO\(_3\) in a
mixture of DOL and DME (1:1 by volume) were used as the anode and electrolyte, respectively. Electrochemical test cells were assembled in an argon-filled glovebox and evaluated in the voltage window from 1.7 V to 2.8 V by using Arbin Instruments. Lithium-ion diffusion coefficient $D_{Li^+}$ (cm$^2$ s$^{-1}$) was measured by CV with different scanning rates and calculated according to the Randles-Sevick equation:

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

(6.4)

where $I_p$ is the peak current in A, $n$ is the number of electrons in the reaction (it is 2 for Li-S battery), $A$ is the electrode area in cm$^2$, and $C_{Li^+}$ and $\nu$ represent the lithium-ion concentration in the electrolyte in mol mL$^{-1}$ and the CV scanning rate in V s$^{-1}$, respectively.

6.2.5 Molecular Modeling Studies

Computational chemistry methods were employed to elucidate binding and interactions of PP, PAN and SiO$_2$ with Li$_2$S and LiS$^-$ radicals at the molecular level to explain observed macroscale separator properties. Density functional theory (DFT) methods$^{269}$ with B3LYP$^{270}$, 271 and M06-2X$^{272}$ functionals at the 6-31++(d,p) level were used to optimize geometries and calculate binding energies by using Gaussian09 software.$^{273}$

For Monte Carlo simulations, amorphous cells with 3nm x 3nm x 3nm of PP and PAN were constructed by using the Materials Studio 5.5 software.$^{274}$ A 3 nm vacuum slab in the z direction was used to model polymer surfaces after 5000 step molecular mechanics geometry optimization by using the COMPASS force field.$^{275}$ Ewald and group summation method
where interactions between charge groups are calculated by using a group-based sum, were used while all other electrostatic interaction are calculated using an Ewald summation method.\textsuperscript{276} An atomic based method with a 12.5 Å cut-off distance was used to model vdW interactions. SiO\textsubscript{2} surfaces were modeled with a similar process, however surface oxygens were vacuum slab constructed, and were saturated with hydrogens for SiO\textsubscript{2} cells. The first 1 nm depth from the surfaces were targeted as the adsorption region. Low energy adsorption sites were determined by a Monte Carlo type annealing procedure using the same force field with PAN, PP and SiO\textsubscript{2} substrates loaded with Li\textsubscript{2}S adsorbate with a fixed composition and cell volume. Simulations were repeated by increasing the number of Li\textsubscript{2}S adsorbates from one to seven for each surface.

\textbf{6.3 Results and Discussion}

The scanning electron microscopy (SEM) images of PAN/SiO\textsubscript{2} nanofiber separators with different SiO\textsubscript{2} contents of 10 and 30 wt\% (designated as PAN/SiO\textsubscript{2}-10 and PAN/SiO\textsubscript{2}-30) in Figure 6.1 show their highly porous structures, which is different from the slit-like porous structure of a microporous PP separator. Both nanofiber separators consist of randomly arranged fibers with average diameters of \~625 and \~600 nm, respectively. The porosities of PAN/SiO\textsubscript{2}-10 and PAN/SiO\textsubscript{2}-30 nanofiber separators are 72\% and 75\%, respectively, as shown in Table 6.1, which are both significantly higher than that (41\%) of PP separators. PAN/SiO\textsubscript{2}-30 were also directly deposited onto a MWCNT sheet, forming a multi-component separator (i.e., PAN/SiO\textsubscript{2}-30-MWCNT) with a porosity of 76\%. The morphology and structure of the
synthesized MWCNTs were investigated by using SEM and transmission electron microscopy (TEM), shown in Figures 6.1c, d and e. The diameter of each MWCNT is ~50 nm and it has a well crystallized structure which can provide good electrical conductivity, benefiting the electrochemical performance of battery cells because it is in direct contact with the S. Figure 6.1f contains the FT-IR spectra of as-spun PAN, PAN/SiO$_2$-10, and PAN/SiO$_2$-30 nanofiber membranes. Peaks at 1452, 2243, and 2937 cm$^{-1}$, are characteristic of PAN, corresponding to the CH$_2$, bending vibration stretching of C≡N, and C-H stretching in CH$_2$, respectively.$^{277}$ The major peak at 1084 cm$^{-1}$ is assigned to Si-O-Si stretching of SiO$_2$, and the minor peak at 1639 cm$^{-1}$ is suggested to be the result of the O-H bending vibration of the adsorbed water. Moreover, the absence of a strong broad peak near 3450 cm$^{-1}$ indicates that the silanol group (Si-OH) content is low in SiO$_2$. PAN/SiO$_2$-10 and PAN/SiO$_2$-30 show characteristic peaks of both components and their relative peak intensities of Si-O-Si to C≡N increase with increasing SiO$_2$ loading.
Figure 6.1 SEM images of a) PAN/SiO$_2$-10 nanofibers, b) PAN/SiO$_2$-30 nanofibers, and c) MWCNT sheet. d) TEM and e) HRTEM images of MWCNT sheet. f) FT-IR spectra of as-spun PAN, PAN/SiO$_2$-10, and PAN/SiO$_2$-30 nanofiber membranes.

Table 6.1 Physical and electrochemical parameters of PP, PAN/SiO$_2$-10, PAN/SiO$_2$-30, and PAN/SiO$_2$-30-MWCNT separators.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)</th>
<th>Electrolyte Uptake (%)</th>
<th>Ionic Conductivity (mS cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP (Ref.20)</td>
<td>41</td>
<td>152</td>
<td>0.60</td>
</tr>
<tr>
<td>PAN/SiO$_2$-10</td>
<td>72</td>
<td>310</td>
<td>1.20</td>
</tr>
<tr>
<td>PAN/SiO$_2$-30</td>
<td>75</td>
<td>332</td>
<td>1.45</td>
</tr>
<tr>
<td>PAN/SiO$_2$-30-MWCNT</td>
<td>76</td>
<td>330</td>
<td>2.17</td>
</tr>
</tbody>
</table>
Figures 6.2a, b, and c display the cyclic voltammetry (CV) profiles of Li-S cells containing PAN/SiO$_2$-10, PAN/SiO$_2$-30, and PAN/SiO$_2$-30-MWCNT for the first five cycles within a voltage window of 1.7-2.8 V at a scan rate of 0.1 mV s$^{-1}$. It is obvious that there are two cathodic peaks at around 2.25 and 2.00 V for the cell with the PAN/SiO$_2$-10 separator which are corresponding to the transformation of S into long-chain polysulfides (Li$_2$S$_x$, $4 \leq x \leq 8$) (Region 1) and the conversion of the long-chain polysulfides to low-order Li$_2$S$_2$, or even Li$_2$S (Region 2), respectively. Two overlapped anodic peaks at around 2.45 and 2.50 V represent the oxidation reactions from lithium sulfides to polysulfides and finally to S. The Li-S cells with PAN/SiO$_2$-30 and PAN/SiO$_2$-30-MWCNT also exhibit similar redox reactions.

Figures 6.2d, e, and f show the initial discharge-charge profiles of Li-S cells with PAN/SiO$_2$-10, PAN/SiO$_2$-30, and PAN/SiO$_2$-30-MWCNT at a constant current density of 0.2C, respectively. All three cells display two discharge plateaus and two closely spaced charge plateaus, which are in agreement with their CV plots. From Figure 2f, it is seen that the cell with PAN/SiO$_2$-30-MWCNT has the highest capacity among the three samples, and the increased capacity for the cell with PAN/SiO$_2$-30-MWCNT is attributed to both Region 1 and Region 2. It is because the conductive MWCNT sheet acts as a second current collector, therefore, it provides sufficient contact with the cathode surface, offering a high active material utilization. Additionally, this MWCNT sheet inhibits the migration of polysulfide intermediates, avoiding shuttle reactions, as illustrated in Figure 6.3. It is important to note that all of their capacities are higher than that of the cell with PP separator, which is probably
due to the relatively higher binding energy of both –C≡N and SiO$_2$ to Li$_2$S/polysulfides compared to that between -CH$_3$ group and Li$_2$S/polysulfides for the PP separator.

Figure 6.2 CV curves of Li-S cells with a) PAN/SiO$_2$-10, b) PAN/SiO$_2$-30, and c) PAN/SiO$_2$-30-MWCNT at a voltage scan rate of 0.1 mV s$^{-1}$. d-f) Corresponding discharge-charge profiles for the first cycle at a current density of 0.2C.
We performed density functional theory (DFT) calculations to determine possible interaction mechanisms and to compare adsorption performance of Li$_2$S molecules and LiS$^\cdot$ radicals with PP, PAN and SiO$_2$ based separators. Figure 6.4 contains the most stable configuration and the calculated binding energy of Li$_2$S structure with PP, PAN pentamers, and a SiO$_2$ nanoparticle model with the B3LYP functional. The lowest energy structure for PP has a conformation similar to that reported in the literature, with a binding energy value of -5.99 kcal mol$^{-1}$, which is significantly lower than that of the PAN-Li$_2$S interaction (-39.57 kcal mol$^{-1}$); results using the M06-2X meta-GGA functional also have a similar trend for interaction energies (Table 6.2). Our calculations indicate for the first time that PAN can form two bonds with both Li atoms in Li$_2$S at the same time through its nitrogen in the most stable structure, which has
a higher binding energy than the most stable structures determined by Seh et al.\textsuperscript{254} In addition, SiO\textsubscript{2} nanoparticles can coordinate Li atoms with their multiple oxygen atoms in the surface cavities and pores, and thus more than one stable structure can exist for interaction between Li\textsubscript{2}S and the SiO\textsubscript{2} nanoparticle model. The lowest energy conformation is calculated to be the structure that maximizes the Li-O binding and is given in Figure 6.4c. The DFT calculations also reveal that S atoms can interact with Si-O-H groups at the end and surfaces of SiO\textsubscript{2} nanoparticles.

Figure 6.4 Calculated lowest energy structures and binding energies of Li\textsubscript{2}S with a) PP pentamer, b) PAN pentamer, and c) SiO\textsubscript{2} nanoparticle model.
Table 6.2 Binding energy of PP, PAN, SiO$_2$ with LiS$^-$ radical and Li$_2$S calculated by using DFT methods (M06-2X functional results are given in parenthesis).

<table>
<thead>
<tr>
<th>Material</th>
<th>Binding Energy (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$_2$S</td>
</tr>
<tr>
<td>PP</td>
<td>-5.99</td>
</tr>
<tr>
<td>PAN</td>
<td>-39.57</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>-59.75</td>
</tr>
</tbody>
</table>

To calculate LiS$^-$ radical interactions with PP and PAN pentamer and SiO$_2$ nanoparticle models, unrestricted DFT calculations were performed. The calculations reveal two possible stable structures between PAN and LiS$^-$ radicals: one where Li bonds to a single nitrogen atom (PAN1 in Figure 6.5a), which was also reported in the literature,254 and one where Li is coordinated by two nitrogen atoms from separate PAN repeat units (PAN2 in Figure 6.5b). The interaction energy with the LiS$^-$ radical for PAN2 is 11.5 kcal mol$^{-1}$ higher than for PAN1. With PP, LiS$^-$ radical pair has a weaker binding energy as compared to PAN, and both the lowest energy geometry and interaction energy of the PP-LiS$^-$ radical pair in Figure 6.5c are similar to previously reported calculations.254 LiS$^-$ radicals have stronger interaction with PP than Li$_2$S for the same Li-CH$_3$ binding conformation with PP (Figure 6.5c), this has a similar
lowest energy geometry and similar interaction energy to previously reported calculations. It is important to note that the SiO$_2$ nanoparticle model in Figure 6.5d has the strongest interaction (-37.51 kcal mol$^{-1}$) with the LiS· radical through its oxygen rich surface as well as –Si-O-H end groups in interaction with S atoms.

Figure 6.5 Calculated lowest energy structures and binding energies of Li-S· radical with a) PAN pentamer conformer-1 (bonded to LiS with one nitrogen), b) PAN pentamer conformer-2 (bonded to LiS with two nitrogen), c) PP pentamer, and d) SiO$_2$ nanoparticle model.
Possible adsorption configurations and adsorption energies were determined by carrying out force field based Monte Carlo simulations\textsuperscript{278} that search the configurational space for the Li\textsubscript{2}S adsorbate onto PP, PAN and SiO\textsubscript{2} substrate surfaces as the temperature slowly decreased. Averages of five annealing cycles for each Monte Carlo simulation were used to calculate the following quantities: rigid adsorption energy, which is the energy released when the unrelaxed Li\textsubscript{2}S molecules are adsorbed on the substrate; the relaxation energy, which is the energy released when the adsorbed Li\textsubscript{2}S molecules are relaxed on the surface; and the average adsorption energy, which is the sum of the rigid adsorption energy and the relaxation energy.\textsuperscript{279, 280} These quantities are given for each surface with increasing number of Li\textsubscript{2}S molecules in Figure 6.6 and Table 6.3. These results indicate that the total adsorption energy for SiO\textsubscript{2} is higher than those of PP and PAN. The adsorption energies calculated by Monte Carlo simulations (Figure 6.6, Table 6.3) for PAN are higher than those of PP for low numbers of Li\textsubscript{2}S adsorbate molecules, as also observed by DFT calculations for single adsorbate in Figure 6.4. However, this difference decreases with increasing number of Li\textsubscript{2}S adsorbate molecules onto the surface. This trend is also observed for the rigid adsorption energies, where the PP and PAN surfaces exhibit similar adsorption performance for higher numbers of Li\textsubscript{2}S molecules in the system. The rigid adsorption energy to the SiO\textsubscript{2} substrate surface is lower than those of PAN and PP polymer based systems; note that most of the adsorption energy to the SiO\textsubscript{2} surface arises from the relaxation energy due to the geometry optimization of the system. The high relaxation energy for SiO\textsubscript{2} is mainly due to the cavity and pore shape changes on the surface in order to coordinate Li atoms and the conformational change on the –O-H to interact with S atoms, which is also observed in DFT calculations. The relaxation energy for
PP and PAN surfaces has lower contribution to the system as compared to rigid adsorption energy.

Figure 6.6. a) Adsorption, b) rigid adsorption, and c) relaxation energies for PP, PAN, and SiO$_2$ with various numbers of Li$_2$S molecule.
Table 6.3 Adsorption energy, rigid adsorption energy and relaxation energy of Li$_2$S with PP, PAN, and SiO$_2$ surfaces calculated by Monte Carlo simulations.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorbant</th>
<th>Adsorption Energy (kcal mol$^{-1}$)</th>
<th>Rigid Adsorption Energy (kcal mol$^{-1}$)</th>
<th>Relaxation Energy (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
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<td>-53.23</td>
<td>-11.36</td>
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<td></td>
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<td>-138.3</td>
<td>-59.47</td>
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<td>-627.42</td>
<td>-365.72</td>
<td>-257.68</td>
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<tr>
<td>PAN</td>
<td>Li$_2$S</td>
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<td>-104.88</td>
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<td></td>
<td></td>
<td>-653.12</td>
<td>-373.45</td>
<td>-269.76</td>
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<tr>
<td>SiO$_2$</td>
<td>Li$_2$S</td>
<td>-204.21</td>
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<td>-186.22</td>
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<td>-407.82</td>
<td>-35.41</td>
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<tr>
<td></td>
<td></td>
<td>-1008.83</td>
<td>-78.87</td>
<td>-930.96</td>
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<td>-1203.66</td>
<td>-87.94</td>
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<td></td>
<td></td>
<td>-1396.22</td>
<td>-95.32</td>
<td>-1303.87</td>
</tr>
</tbody>
</table>

To explain decreasing total and rigid adsorption energy differences between PP and PAN systems with increasing number of adsorbate molecules, one of the lowest energy cell structures for adsorption of seven Li$_2$S molecules followed by system relaxation were
investigated more closely. As given in Figures 6.7a and b, Li₂S molecules formed aggregate clusters on the PP and PAN surfaces, respectively. DFT calculations reveal that Li₂S bonds to the PAN surface more strongly than to PP. The aggregation and clustering of Li₂S molecules take place with an increasing number of adsorbate, especially for the relatively nonpolar PP surface. However, this clustering and aggregation effect is not observed for the SiO₂ cell surface, which has a higher number of adsorption sites formed by relatively more polar oxygen and hydroxyl rich cavities (Figure 6.7c). The adsorbate molecules prefer to interact with each other instead of the polymer chains on the relatively hydrophobic PP and PAN surfaces. This aggregation effect causes the reduced adsorption energy difference between pure PP and PAN with increasing number of Li-S compounds. In the absence of this aggregation behavior for SiO₂ in Figure 6.7c, a linear increase is observed in the total adsorption energy due to a higher number of adsorption sites. A high relaxation energy via geometry optimization is observed due to the reorganization of cavities and pores after adsorption of Li₂S to SiO₂. Thus, increasing performance can be expected for the systems both with high content of SiO₂ as well as with higher surface area, as demonstrated by our experiments.
Figure 6.7 Surface morphology of a) PP, b) PAN, and c) SiO$_2$ after adsorption and relaxation by seven Li$_2$S molecules.

Figure 6.8a presents the observed cycling stability of the Li-S cells using PAN/SiO$_2$-10, PAN/SiO$_2$-30, and PAN/SiO$_2$-30-MWCNT at a current density of 0.2C up to 100 cycles. The initial discharge capacity increases slightly from 930 to 946 mAh g$^{-1}$ at 0.2C when using PAN/SiO$_2$-30 as the separator instead of PAN/SiO$_2$-10. In contrast, it can be improved to 1182 mAh g$^{-1}$ by using PAN/SiO$_2$-30-MWCNT. The cell with PAN/SiO$_2$-30-MWCNT can still deliver a high capacity of 741 mAh g$^{-1}$ after 100 cycles at a current density of 0.2C. To further study the electrochemical performance of the cell with PAN/SiO$_2$-30-MWCNT, the long-term cycling test was carried out under a higher current density of 2C, as shown in Figure 6.8b. At such a high current density, the cell with PAN/SiO$_2$-30-MWCNT can still deliver an initial capacity as high as 816 mAh g$^{-1}$. More importantly, a capacity of 426 mAh g$^{-1}$ can still be
maintained with a Coulombic efficiency of 96.3% even after 300 cycles, further indicating its excellent electrochemical performance.

As is well known that the rate capability is one of the important parameters for batteries, especially for high-power applications and the ability to quickly recharge. Therefore, the rate performance of Li-S cells with the three different separators was investigated and is presented in Figure 8c. Current density was increased stepwise from 0.1C to 1C for every ten successive cycles and then returned to 0.1C. The stable reversible capacities of Li-S cells with PAN/SiO$_2$-10 and PAN/SiO$_2$-30 decrease from 613 to 317 mAh g$^{-1}$ and 671 to 357 mAh g$^{-1}$, respectively, as the current density increases from 0.1C to 1C. While the capacity of the cell with PAN/SiO$_2$-30-MWCNT decreases slowly from the reversible capacity 960 mAh g$^{-1}$ at 0.1C to 845, 726, 627 mAh g$^{-1}$ at 0.2C, 0.5C and 1C, respectively. Importantly, a high reversible capacity of 842 mAh g$^{-1}$ is achieved when the current density is lowered back to 0.1C, indicating a highly reversible and efficient Li-S cell enabled by using PAN/SiO$_2$-30-MWCNT. When placed in a liquid electrolyte, the ionic conductivities of PAN/SiO$_2$-10 and PAN/SiO$_2$-30 separators as given in Table 6.1 are 1.2 and 1.45 mS cm$^{-1}$, respectively, which are two times higher than that (0.6 mS cm$^{-1}$) of the PP separator. With the additional MWCNT sheet, the ionic conductivity can further increase to 2.17 mS cm$^{-1}$. These higher ionic conductivities are ascribed to their higher porosities, which might be responsible for the good rate capability of their Li-S cells.
Figure 6.8 a) Cycling performance of cells with PAN/SiO$_2$-10, PAN/SiO$_2$-30, and PAN/SiO$_2$-30-MWCNT at a current density of 0.2C. b) Cycling performance of the cell with PAN/SiO$_2$-30-MWCNT at a high current density of 2C. c) Rate capability.
The discharge/charge profiles of Li-S cells with PAN/SiO$_2$-10, PAN/SiO$_2$-30, and PAN/SiO$_2$-30-MWCNT at different C-rates are shown in Figures 6.9a, b, and c, respectively. At low current rates, all the discharge profiles are characterized by a two-plateau behavior of a typical S cathode, while the charge profiles display two platforms, respectively, which are in agreement with their CV plots. The discharge plateau decreases with the increment of C-rates which is attributed to the kinetic overpotentials at high C-rates. It should be noted that the profiles of the cell with PAN/SiO$_2$-30-MWCNT display two longer discharge plateaus even at a current density of 1C compared to that of PAN/SiO$_2$-10 and PAN/SiO$_2$-30, demonstrating its highly reversible capacities and low polarization.

Figure 6.9 Discharge/charge profiles of Li-S cells with a) PAN/SiO$_2$-10, b) PAN/SiO$_2$-30, and c) PAN/SiO$_2$-30-MWCNT at different C-rates.

Meanwhile, it is important to investigate the impact of SiO$_2$ and MWCNT on lithium-ion diffusion since the rate performance is closely related to the diffusion of lithium ions in the cells. The lithium-ion diffusion coefficients were evaluated by a series of CV measurements with different scan rates (Figure 6.10) and calculated by the Randles-Sevcik equation. Here,
the cathodic peaks at ~2.2 V and ~1.95 V and the anodic peak at ~2.45 V were defined as peaks A, B, and C, respectively. According to the Randles-Sevcik equation, the plot of the reduction peak current $I_p$ versus the square root of the scan rate should result in a straight line which is confirmed in Figures 9d-f. From the slope of the linear fit, the lithium-ion diffusion coefficients were calculated to be $D_{Li^+} (A) = 6.17 \times 10^{-9}$ cm$^2$ s$^{-1}$, $D_{Li^+} (B) = 9.56 \times 10^{-9}$ cm$^2$ s$^{-1}$, and $D_{Li^+} (C) = 2.33 \times 10^{-8}$ cm$^2$ s$^{-1}$ for the Li-S cell with the PAN/SiO$_2$-10 separator, given in Table S3. The diffusion coefficients increase to $D_{Li^+} (A) = 1.05 \times 10^{-8}$ cm$^2$ s$^{-1}$, $D_{Li^+} (B) = 2.05 \times 10^{-8}$ cm$^2$ s$^{-1}$, and $D_{Li^+} (C) = 3.66 \times 10^{-8}$ cm$^2$ s$^{-1}$ when the PAN/SiO$_2$-30 separator was used. After the addition of the MWCNT sheet into the PAN/SiO$_2$-30 separator, the diffusion coefficients increase further to $D_{Li^+} (A) = 1.12 \times 10^{-8}$ cm$^2$ s$^{-1}$, $D_{Li^+} (B) = 2.09 \times 10^{-8}$ cm$^2$ s$^{-1}$, and $D_{Li^+} (C) = 4.55 \times 10^{-8}$ cm$^2$ s$^{-1}$. Compared to the PP separator, the lithium-ion diffusion coefficients can be remarkably enhanced when using the three studied separators, which is attributed to their highly porous structure and excellent electrolyte uptake ability. As shown in Table 6.1, the electrolyte uptake of the PAN/SiO$_2$-10, PAN/SiO$_2$-30 and PAN/SiO$_2$-30-MWCNT separators are 310%, 332% and 330%, respectively, which are all significantly higher than that (152%) of the PP separator.
Figure 6.10 CV curves with various voltage scan rates of Li-S cells with a) PAN/SiO$_2$-10, b) PAN/SiO$_2$-30, and c) PAN/SiO$_2$-30-MWCNT; the linear fits of the peak currents for Li-S cells with d) PAN/SiO$_2$-10, e) PAN/SiO$_2$-30, and f) PAN/SiO$_2$-30-MWCNT.

Table 6.4 Li-Ion diffusion coefficient measurement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li-ion diffusion coefficient (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>PAN/SiO$_2$-10</td>
<td>6.17×10$^{-9}$</td>
</tr>
<tr>
<td>PAN/SiO$_2$-30</td>
<td>1.05×10$^{-8}$</td>
</tr>
<tr>
<td>PAN/SiO$_2$-30-MWCNT</td>
<td>1.12×10$^{-8}$</td>
</tr>
</tbody>
</table>
6.4 Conclusions

In summary, we have proposed a PAN/SiO\textsubscript{2} nanofiber membrane with a MWCNT sheet as a hierarchical multi-component separator for achieving high-performance Li-S batteries. The improved performance is ascribed to a variety of synergic effects, including a highly porous structure and good wettability of PAN/SiO\textsubscript{2} nanofibers, as well as the physical and chemical barrier effects of PAN chains (–C≡N) and SiO\textsubscript{2} filler, which mitigate the polysulfide diffusion to the Li side. These results are in agreement with molecular modeling studies that indicate a significant increase for the SiO\textsubscript{2} nanoparticle model compared to PP and PAN both for the interaction calculated with DFT methods and the adsorption energies calculated with Monte Carlo simulations. Additionally, the existence of the MWCNT separator sheet can further enhance the electrochemical performance of Li-S cells, which not only provides sufficient contact with the cathode surface, offering a high active material utilization, but also inhibits the migration of polysulfides, thus avoiding their shuttle reactions. The findings in this work reveal a scalable and effective membrane separator that provides for a significant development and applicability for Li-S batteries.
CHAPTER 7 RECOMMENDED FUTURE WORK

The recommended future work can include but not limited to:

7.1 Polymer Selection

We have demonstrated that PAN-based nanofiber membrane is a promising separator candidate for Li-S batteries. Besides benefitting from its highly porous structure and excellent electrolyte wettability of the nanofiber separator, the improved performance can also be ascribed to the excellent barrier effects caused by the relatively high energy binding between –C≡N and Li₂S/polysulfides. Therefore, it is worth further finding other polymer matrix which has a higher energy binding with Li₂S/polysulfides compared to that of PAN.

Therefore, several polymers, such as polyimide, polyvinylidene fluoride, polyvinylpyrrolidone, polymethyl methacrylate, etc., are selected to compare their energy binding with Li₂S/polysulfides based on the simulation method.

Through this detailed comparison, we can finally choose one or two polymers among them to be used as the separator matrix for Li-S cells to further examine their practical applications. Then, their electrochemical performance will be carried out, such as CV measurement, EIS, cycling performance, rate capability, anti-self-discharge ability, etc.
7.2 Filler Selection

In Chapter 5, we have demonstrated that GO is able to block the diffusion of polysulfides which is ascribed to the electrostatic interactions between the negatively charged species \(S_n^{2-}\) and the oxygen-containing groups on GO. SiO\(_2\) has also been confirmed to have strong ability for polysulfide adsorption which is due to its high energy binding with polysulfides/Li\(_2\)S in Chapter 6.

We may find other fillers which have stronger adsorption ability of polysulfides compared to that of GO and SiO\(_2\) by computational chemistry calculations. Those fillers can be used either or both in the cathode and separator to inhibit the diffusion of polysulfides, avoiding shuttle effect and enhancing the utilization of active material.

7.3 Binder Selection and Modification

As one of the critical components in electrodes, binder, which directly influences the electrochemical performance of Li-S batteries, especially the cell cyclability, rate capability, and lifespan. Therefore, it is necessary to take it into consideration for obtaining high performance Li-S batteries. As discussed above, the ideal binder is required to create a more robust conductive framework and improve the strength and structural stability of the entire sulfur electrode.
Hence, different binders and their modifications, such as PVDF, cyclodextrin, sodium alginites, polyvinylpyrrolidone, etc., will be studied and their electrochemical measurements will be carried out. What’s more important is to understand the mechanism behind them how they work to affect the electrochemical performance of batteries.

7.4 Lithium Anode Protection

It is well known that Li metal has been considered as an ideal anode candidate for lithium batteries due to its high theoretical specific capacity and low negative electrochemical potential. However, uncontrollable dendritic Li growth during Li deposition/stripping inherent in these batteries has prevented their practical applications. It is, therefore, necessary to solve it by using various methods, such as improving the stability and uniformity of the solid electrolyte interphase (SEI) layer on the Li surface by adjusting electrolyte components and additives, coated polymer layers, etc.
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