Designing Physical and Chemical Confinement in Lithium Sulfur Battery Cathode for Suppression of Shuttle Effect

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DESIGNING PHYSICAL AND CHEMICAL CONFINEMENT IN LITHIUM SULFUR BATTERY CATHODE FOR SUPPRESSION OF SHUTTLE EFFECT

by

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M.S. University of Central Florida, 2018

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor Philosophy in the Department of Materials Science and Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

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Major Professor: Akihiro Kushima
ABSTRACT

Lithium sulfur batteries (LSBs) are attracting attention as a next generation energy storage device because of their high energy density (2670WhKg\(^{-1}\)), high specific capacity (1675 mAhg\(^{-1}\)), low cost and environmental friendliness. However, there are several challenges that need to be overcome before LSBs can be implemented in general applications. This is due to the low electric conductivities of sulfur and lithium sulfide and large volume changes during charge/discharge cycling. Also, most importantly, the dissolution of lithium polysulfides into the electrolyte during cycling leads to capacity decay and low coulombic efficiency. Additionally, these lithium polysulfides can diffuse to the lithium anode through the electrolyte and cause parasitic reactions at the anode (shuttle effect). The objective of this dissertation study is to develop LSB cathode composites to suppress the polysulfide dissolution, improve the performance of the LSB, and study the underlying mechanisms. Here, we employed two strategies: 1) physical confinement and 2) chemical adsorption of the polysulfide species. A nano-porous composite was developed using vat dye particles that confined the polysulfides and accommodated the large volume changes during the charge/discharge process. A gallium-based liquid metal was introduced as an electrocatalyst and a self-healing anchor to adsorb lithium polysulfides and prevent the shuttle effect. The electrochemical performance test showed improved performance using these methods. A variety of characterization techniques, such as X-ray photoelectron spectroscopy, in situ transmission electron microscopy, and theoretical modeling, were used to reveal the fundamental effects of the two strategies proposed. The results obtained in this work provide insights and suggest new research directions towards the fundamental understanding and the development of LSB technologies.
I desire to dedicate this dissertation to the memory of my father and to my son, Yousif, who has made me stronger throughout these past six years.
ACKNOWLEDGMENTS

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LIST OF ABBREVIATIONS

APP - Ammonium polyphosphate
CC - Carbon cloth
CMK-3 - Ordered mesoporous carbon
CNTs - Carbon nanotubes
CPE - Composite solid electrolyte
CV - Cyclic voltammetry
DOL - Dioxolane
DME - Dimethoxyethane
EDS - Energy dispersive X-ray spectroscopy
EIS - Electrochemical impedance spectroscopy
GGA - Generalized gradient approximation
GO - Graphene oxide
GOPPA - Graphene oxide-polyacrylic acid
LIB - Lithium ion battery
LM - Liquid metal
LSB - Lithium sulfur battery
MCP - Microporous carbon interlayer
MD - Molecular dynamics
NMP - N-methyl-2-pyrrolidone
PAW - Projected augment wave
PEG - Polyethylene glycol
PS - Polysulfide
PVDF - Polyvinylidene fluoride
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{ct}$</td>
<td>Charge transfer resistance</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid polymer electrolyte</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>VB</td>
<td>Vat black</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna <em>Ab initio</em> Simulation Package</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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CHAPTER 1 INTRODUCTION

There are increasing demands for high energy density batteries with long cycle life and low cost for various applications such as electric vehicles, portable electronic devices, and grid energy storages. Although lithium ion battery (LIB) is a leading technology in the rechargeable battery market, development of next generation energy storage devices is anticipated to meet the requirements for the increasing energy storage demands [1–4]. The lithium sulfur battery (LSB), which first emerged in the 1960s [5], is considered a promising candidate for the next generation energy storage devices due to many advantages such as high theoretical capacity for both the sulfur-based cathode and lithium anode (1675 and 3862 mAhg$^{-1}$, respectively) and the theoretical energy density of 2500 Whkg$^{-1}$ which is 10 times greater than that of traditional LIBs (Figure 1-1a) [6]. In addition, sulfur is a nontoxic byproduct of the crude oil refining process (Figure 1-1b) [7, 8], making its production environmentally friendly and inexpensive, especially compared to the traditional LIB cathodes such as cobalt and nickel [9–12]. However, there are several challenges that need to be overcome before LSBs can be used in practical applications.

![Figure 1-1: (a) Energy densities of LIB and LSB[6]. (b) picture of sulfur byproduct from the crude oil refining[13].](image)
1.1 Principle of Lithium Sulfur Batteries

An LSB consists of a sulfur cathode combined with conductive additives and binder paired with lithium anode separated by a porous polymeric membrane in an ether-based electrolyte [6, 14] (Figure 1-2).

![Figure 1-2: Schematic of an LSB.](image)

During the discharge, oxidation of lithium takes place by loss of electrons forming lithium ions, which are transferred through the electrolyte to the sulfur cathode. The electrons are transported through the external circuit to the sulfur cathode, where reduction takes place at the sulfur surface as it reacts with the incoming lithium ions to form lithium sulfide. During charging, the opposite reaction occurs where the lithium ions travel from the sulfur cathode to the lithium anode. The equations listed below show the reactions in an LSB:

Cathode: \( S_8 + 16 \text{ Li}^+ +16 e^- \rightarrow 8\text{Li}_2\text{S} \)

Anode: \( \text{Li} \rightarrow \text{Li}^+ + e^- \)

Overall: \( S_8 + 16 \text{Li} \rightarrow 8\text{Li}_2\text{S} \)
The discharge and charge profile of an LSB (Figure 1-3) shows two regions. During discharge, the first region is the upper plateau region occurring at about 2.3 V where the S₈ is reduced to Li₂Sₙ (6 < n ≤ 8). These intermediate products dissolve easily into the liquid electrolyte, leading to an increase in the viscosity of the electrolyte that decreases the lithium-ion conductivity. The second region, at about 2.1 V, is where the polysulfide Li₂S₄ converts into insoluble lithium sulfide (Li₂S₂ and Li₂S). Upon charging, the opposite reactions occur where the Li₂S converts back to S [6, 14].

![Diagram of charge and discharge profile of an LSB](image)

**Figure 1-3: Charge and discharge profile of an LSB[15].**

1.2 Challenges of Lithium Sulfur Batteries

Despite the advantages of LSBs, there are several challenges. Figure 1-4 illustrates examples of the factors that limit the practical applications of LSBs. The main challenge that limits their capacity is the dissolution of the long-chain lithium polysulfides into the electrolyte during battery cycling. This results in a loss of active material and capacity fade. The long-
chain lithium polysulfides can diffuse to the lithium anode to be reduced to short-chain lithium polysulfides and diffuse back to the sulfur cathode where it forms the long-chain lithium polysulfide again (shuttle effect). This reaction loop results in a continuous loss of the active material, low coulombic efficiency, and short cycle lifetime. The other issues include the poor electrical conductivities of sulfur and Li$_2$S. The electrical conductivity of sulfur and Li$_2$S are 5 x $10^{-30}$ and 3.6 x $10^{-7}$ Scm$^{-1}$, respectively. Another problem arises from the large volume changes between sulfur and Li$_2$S in charge/discharge processes, causing crack formation and loss of electrical contact of active materials. In addition, sulfur suffers from low vaporization temperature that causes a sulfur loss under drying of the electrodes in the production process [16–20].

On the anode side, formation of lithium dendrites lead to a short circuit resulting in safety risks [21–23]. Lastly, the high reactivity between the lithium metal and the electrolyte forms an unstable solid electrolyte interphase, leading to consumption of both the lithium metal and electrolyte [23].
Over the last decade, there has been a considerable amount of research conducted on LSBs to overcome these issues. Use of carbon materials with sulfur confining pores was the most frequently adopted approach for improving cycling performance due to their high electrical conductivity and large surface areas [24]. Examples include carbon nanotubes [25], porous carbon [26], graphene oxide [27], and carbon spheres [28]. However, the low binding energy between the non-polar carbon and polar lithium sulfide results in the incomplete trapping of the polysulfides [29, 30]. On the other hand, polar materials such as metal oxides, metal carbides, and metal sulfides have proven effective in trapping polysulfides and providing more reaction sites [30–32]. Other modifications were achieved by using solid electrolytes [33], selecting adequate binders [34], employing lithium polysulfide catholyte [35], inserting an interlayer [16], and modifying separators [36, 37].
1.3 Objective

The main objective of this dissertation is to develop high performance cathode composites to suppress the polysulfide diffusion and shuttle effect of LSBs. This is achieved by designing a nanostructured 3D porous host structure with high electronic conductivity and the ability to confine sulfur species to improve the rate performance and cycle lifetime.

The first approach is to fabricate a free-standing nanostructured cathode with vat black decorated carbon cloth infiltrated with a lithium polysulfide catholyte. This cathode was designed for high loading mass of sulfur. Carbon cloth was chosen as a host material due to its high conductivity, high surface area, porous structure, mechanical stability, and flexibility. In addition, vat dyes have amino- and carbonyl-groups, and these functional groups contribute to trapping lithium polysulfide and preventing the shuttle effect.

The second approach is to develop a novel sulfur composite with liquid metal (LM) nanoparticles and reduced graphene oxide (rGO) dispensed on a carbon cloth electrode. This electrode composite was designed to integrate the ability of rGO to trap the lithium polysulfide and the function of gallium-based LM as an electrocatalyst. Here, In and Sn were added to Ga to synthesize a LM with a low melting point that maintains its liquid state at the LSB operating temperature, which plays a central role in this study. The LM allows the electrode composite to accommodate the large volume change of sulfur in the charge/discharge process and prevents the fracture of the electrode that leads to the loss of the active material.

These two designs will be made feasible and desirable by employing simple preparation techniques, and they provide a promising path towards practical applications of LSBs.
1.4 Overview

This dissertation is organized as follows.

In Chapter 2, some of the key approaches used to overcome challenges in LSBs are compiled. Several strategies on LSBs are presented including cathode design, novel electrolyte, and separator modification. In addition to the developments related to the LSB chemistry, improvements in the anode design and the application of solid-state electrolytes are included.

Chapter 3 demonstrates the effectiveness of the nano-porous composite developed in this work for improving the LSB cell performance. The composite uses vat dye nano particles to capture the lithium polysulfides, preventing the shuttle effect. The composite cathode with nanopores enabled high loading mass of sulfur by confining polysulfide species and improved the mechanical stability by accommodating large volume changes of sulfur active materials. In situ transmission electron microscopy experiment was employed to directly observe the reaction process during lithiation and delithiation to confirm the validity of the concept.

In Chapter 4, a novel idea of utilizing a Ga-based liquid metal as an electrocatalyst and self-healing conducting additives to capture the lithium polysulfides and maintain electrical conduction path during the LSB cycling was introduced. The fundamental ability of the LM to anchor the polysulfides was further verified by DFT calculations and XPS characterization.

Finally, Chapter 5 summarizes this dissertation research and discusses the future directions of LSBs.
CHAPTER 2  ADVANCEMENT OF LITHIUM SULFUR BATTERY

2.1 Introduction

This chapter explores the methods of overcoming the challenges in an LSB, opening a discussion for finding solutions to the fundamental issues and addressing potential improvements in an LSB. The solutions are grouped in four categories as summarized in Figure 2-1: 1) cathode design, 2) separator modifications, 3) novel electrolyte development, and 4) anode improvement.

Figure 2-1: Strategies for improving LSBs.
2.2 Methods to Overcome Challenges in LSBs

2.2.1 Cathode Design

Many approaches have been introduced during the past decade to solve the problems of sulfur-based cathodes in LSBs. One of the most widely used methods is to employ sulfur host materials such as carbon-sulfur and metal oxide-sulfur composites. These materials eliminate the shuttle effect by encapsulating sulfur into the host materials and trapping lithium polysulfides, thereby improving the LSB efficiency and the cycle lifetime.

2.2.1.1 Carbon Host Materials for Sulfur Cathodes

One of the first approaches to utilize the cathode design for an LSB cathode was introduced in 1990 by the Nazar’s group [38]. It was achieved by mixing highly ordered mesoporous carbon (CMK-3) with sulfur. The process of a melt diffusion was performed at 155 °C which allows sulfur material to infiltrate through the mesoporous channels (Figure 2-2 a), giving a specific capacity of 1005 mAhg\(^{-1}\) and a good cyclic stability. This confirms that mesoporous carbon can confine the lithium polysulfide. It was further modified by adding polyethylene glycol (PEG) to the carbon surface, resulting in an increase in discharge capacity. The scanning electron microscopy images display the changes before (Figure 2-2 b) and after heating (Figure 2-2 c) which confirm that there was no bulk sulfur after heating. Following this work, many researches have been conducted incorporating the same concept of the porous host structure to develop carbon-based materials for improving the LSB performance [39–42].
2.2.1.2 Polymer Host Materials for Sulfur Cathodes

Carbon materials improved the conductivity of sulfur and were able to partially hinder the polysulfide dissolutions [43]. An example of these carbon materials is reported by Guangyuan et al. [29]. Using a hollow carbon nanofiber/sulfur composite cathode delivered high capacity, but it still experienced capacity fade. Further investigation was conducted by ex situ transmission electron microscopy to address the capacity fade. The results indicated that the loss of electrical contact occurs when the lithium sulfide disconnects from the inner carbon nanofiber walls. This disconnect was caused by the low binding energy between the nonpolar carbon and polar Li$_x$S groups where (0 < x ≤ 2). An improvement in cycling performance was achieved by adding amphiphilic polymers (polyvinylpyrrolidone) resulting in an increased binding energy between the nonpolar carbon and polar Li$_x$S. This prevented the separation of lithium sulfide from the inner hollow carbon nanofiber walls. The TEM images show a hollow carbon nanofiber/sulfur composite cathode before discharge and after first discharge to 1.7 V.
(Figure 2.3 a and b), as well as before and after discharge of a hollow carbon nanofiber/sulfur composite cathode with modified polymer (PVP) (Figure 2.3 c and d).

Following a similar approach, different types of polymers have been studied in sulfur cathode materials such as polyaniline (PANi) [44], polypyrrole (Ppy) [45], poly(3,4-ethylenedioxythiophene) (PEDOT) [46], and polythiophene (PTh) [47].

![Image of Hollow Carbon Nanofiber/Sulfur Composite Cathode](image)

Figure 2-3: Ex situ study of a hollow carbon nanofiber/sulfur composite cathode. (a) before discharge. (b) after first discharge to 1.7 V. (c) and (d) before and after discharge after modified with amphiphilic polymers.

A simple and environmentally friendly method was reported by Xiao et al. Self-assembled, polyaniline nanotubes mixed with sulfur were heated to 280 °C by an in situ vulcanization process [44]. In this process, a small portion of sulfur reacts with the polyaniline to form a “three dimensional, cross linked, structurally stable sulfur-PANI NT polymer backbone with inter- and/ or intra chain disulfide bonds” (Figure 2.4 a) [44]. This structure provides physical and chemical confinement to the sulfur, resulting in good cycling...
performance, high capacity, and good capacity retention at 0.1C (Figure 2.4 b). At higher current density (1C), a good discharge capacity (568 mAhg⁻¹) was observed but a lower capacity retention of 76 % was obtained after 400 cycles (Figure 2.4 c). This capacity decay was attributed to some polysulfide dissolution and shuttling effect.

Figure 2-4: (a) Schematic showing the structure and the charge/discharge process of the sulfur-PANI-NT/S composite. (b) discharge capacity versus cycle number of the electrode at different current densities. (c) cycling performance and coulombic efficiency of the sulfur PANI-NTS composite at 1 C.

2.2.1.3 Yolk Shell Structure

Providing a nanostructure that physically encapsulates the sulfur active material and isolates it from the electrolyte is another effective strategy to prevent the shuttle effect and the capacity decay in LSBs. One example is the sulfur titanium dioxide yolk shell design which
was proposed for the first time by Zhi Wei Seh et al. [48]. The TiO$_2$ was coated on the sulfur nanoparticles, and then a small amount of sulfur was dissolved by using toluene to form void space between the sulfur and the TiO$_2$ shell (Figure 2.5 a). The internal void space that is provided by the unique yolk-shell morphology allowed it to accommodate the large volumetric expansion of sulfur during lithiation. The hydrophilic Ti-O groups and surface hydroxyl bind well with polysulfide anions, preventing the polysulfide diffusion which results in a high capacity with capacity decay 0.033 per cycle and extended cycle life (Figure 2.5 b).

![Diagram of synthesis process and cycling performance](image)

**Figure 2.5:** (a) Schematic of the synthesis process of TiO$_2$ coating on the sulfur nanoparticles (b) cycling performance and coulombic efficiency of sulfur-TiO$_2$ yolk shell at 0.5 C up to 1000 cycles.

Zhu et al. reported a sulfur gallium core shell structure (S/Ga) which was developed by mixing gallium and sulfur nanoparticles as shown in Figure 2-6, resulting in an exceptional electrochemical performance [49]. The S/Ga core shell composite achieved long cycle life and good capacity retention with a loading mass of sulfur (0.45 mg cm$^{-2}$).
Figure 2-6: Schematic showing the fabrication process of a sulfur gallium core shell structure. Li et al. recently fabricated a silica/gallium core shell with a sulfur cathode (SiO$_2$-Ga/S) [50], as shown in Figure 2-7, to facilitate the electrocatalysis of lithium polysulfides during cycling. It achieved a discharge capacity of 927.1 mAh$^{-1}$ at 0.75C, a coulombic efficiency of 95.2%, and a good capacity retention after 600 cycles. The loading mass of sulfur for this composite was 0.7 mgcm$^{-2}$.

Figure 2-7: Schematic showing (a) the cathode design (SiO$_2$-Ga/S). (b) electrons transfer on the surface of Ga.
2.2.1.4 *Metal Sulfides*

Zhou et al. studied the interaction between a series of metal sulfides and polysulfides through the use of polysulfide adsorption experiments by using the following materials (VS$_2$, COS$_2$, TiS$_2$, FeS, SnS$_2$ and Ni$_2$S$_3$) [30]. The Li$_2$S$_6$ solution was prepared by mixing sublimed sulfur with Li$_2$S in a 1:1 volume ratio of DOL and DME. As shown in Figure 2.8a, the results indicated that the control sample has a weak interaction as indicated by the dark yellow color. The nonpolar conductive material (G/CNT) exhibited weak interaction as there was no change in the color of the solution compared to the control. SnS$_2$ and FeS$_2$ showed stronger adsorption as indicated by the lighter color solution while VS$_2$, CoS$_2$ and TiS$_2$ displayed a higher interaction as the solution became colorless. As indicated in Figure 2-8b, these metal sulfides (VS$_2$, COS$_2$ and TiS$_2$) achieved higher capacities at 0.5C and excellent cycling performance compared to FeS, SnS$_2$, Ni$_2$S$_3$, and carbon materials.
Figure 2-8: (a) Adsorption test of carbon and metal sulfides in Li$_2$S$_6$ DOL/DME solution (b). cycling performance and coulombic efficiency at 0.5 C.

2.2.1.5 Novel Binder

The binder also plays an important part in the sulfur cathode by providing a good contact between the active material sulfur and conductive materials, as well as enabling good adhesion between the sulfur cathode and current collector. The use of an inorganic binder ammonium polyphosphate (APP) with flame retardation properties was proposed by G. Zhou et al. [51]. This novel binder has several advantages discussed below. It has a good binding interaction between the lithium polysulfides and APP chain which prevents the dissolution of polysulfides. This binder eliminates the use of the toxic and expensive organic solvents such as N-methyl-2-pyrrolidone (NMP) due to its solubility in water. Also, due to the flame-retardant property (Figure 2-9a), it can improve the safety compared to organic polymer binders. As a result, a
high discharge capacity was obtained (1035 mAhg\(^{-1}\)) at 0.2 C and (520 mAhg\(^{-1}\)) at 4C (Figure 2-9b), compared to the conventional binder (PVDF) (Figure 2-9c).

![Figure 2-9: Schematic of flame retardation properties of the APP binder (b) charge-discharge voltage profiles of the S-APP (c) charge-discharge voltage profiles of the S-APP.](image)

2.2.1.6 **Lithium Sulfide (Li\(_2\)S) Cathode**

Li\(_2\)S is considered a preferred cathode material compared to sulfur due to its comparable capacity (1166 mAhg\(^{-1}\)), high melting point (938 ºC), and its capability to be used with non-lithium metal anodes, such as Si, Sn, Al, and metal oxides, which improves safety by preventing the formation of the lithium dendrites. For an example, Wang et al. developed a binder free nano-Li\(_2\)S/reduced graphene oxide cathode paper [52]. The Li\(_2\)S/rGO was prepared by dissolving Li\(_2\)S in anhydrous ethanol, and then nanosized Li\(_2\)S was drop casted and distributed evenly on the rGO paper (Figure 2-10a). This cathode paper is lightweight due to the elimination of metal substrates and binders. The use of rGO paper has many advantages including its abilities to accommodate volume changes and to trap the polysulfide diffusion. It
also has flexibility and high conductivity. These result in a high discharge capacity \( (597 \text{ mAhg}^{-1}) \) even at a high current density of 7C as shown in Figure 2-10b.

![Figure 2-10](image)

Figure 2-10: (a) Schematic demonstrating the material preparation and structure changes during the charge/discharge process of the nano-Li\(_2\)S/rGO cathode paper. (b) Cycling performance of nano-Li\(_2\)S/rGO cathode paper at 0.5 and 1C (c) rate performance of nano-Li\(_2\)S/rGO cathode paper at different current densities.

2.2.1.7 Polysulfide Lithium Catholyte

Dissolved lithium polysulfide has recently been considered as an alternative to the conventional LSB cathode that uses solid sulfur, conductive additives, polymer binders, and aluminum foil current collectors. To efficiently use sulfur for the improved redox reaction kinetics, a liquid solution containing lithium polysulfides was used to uniformly distribute the active material in the host materials. Different conductive host materials have been used to achieve high sulfur loading and obtain good electrochemical performance [53–56].
Fu et al. reported the use of a binder free multiwalled carbon nanotube paper with lithium polysulfide catholyte (Li$_2$S$_6$) (Figure 2-11 a) as an electrode with sulfur loadings (1.2 to 3.4 mgcm$^{-2}$) [57]. High discharge capacities were obtained at different current densities (Figure 2-11 b). This result was attributed to the high conductivity of CNTs, a large surface area, and fast ion/electron transport.

![Figure 2-11: (a) Schematic illustration of the structure of lithium polysulfide catholyte (b) voltage versus discharge capacity profiles of lithium polysulfide catholyte at different current densities.]

In a similar concept, the use of carbon cotton cathode was reported [58]. The cotton was carbonized at a high temperature to obtain carbon cotton as shown in Figure 2.12a. High discharge capacities of 1137 and 912 mAhg$^{-1}$ were achieved at sulfur loadings of 30.7 and 61.4 mgcm$^{-2}$, respectively, at 0.1 C after 50 cycles (Figure 2.12 b). The advantages of carbon cotton are its high surface area, good mechanical strength and flexibility which result in an improvement in cyclic stability and 70% capacity retention after 100 cycles. Additionally, the carbon cotton macroscopic structure enables a large amount of catholyte to be retained.
Figure 2-12: (a) Schematic of the synthesis process of the carbon-cotton cathode (b) discharge capacity versus cycle number at high sulfur loadings of 30.7 and 61.4 mg cm\(^{-2}\)

Raghunandan et al. developed a modified graphite paper with lithium polysulfide (Figure 2-13), as sulfur cathode, with a high loading mass of sulfur 4.5 mg cm\(^{-2}\) [59]. In their work, high discharge capacity was achieved; 1246 mAh g\(^{-1}\) at 0.1 C. However, during the 100 cycles, rapid capacity decay was recorded as a result of using a very thick electrode.

Figure 2-13: Schematic showing partially oxidized and exfoliated graphite paper with lithium polysulfide.

2.2.2 Separator Modifications

Besides encapsulating and trapping lithium polysulfide at the cathode, shuttle effect can also be eliminated through separator modifications by preventing the polysulfides from migrating between the cathode and the anode in an LSB. Modification of the separator and
addition of an interlayer have been employed recently to physically block the polysulfide from migrating through the electrolytes shuttling between the electrodes. Carbonaceous and polar materials are commonly used for this purpose.

### 2.2.2.1 Carbon Based Interlayer

Carbon based interlayers, such as carbon fiber paper and carbon nanotubes, have provided enhanced electrochemical performance in LSBs due to their high electron conductivity and porosity [60, 61]. Su and Manthiram [62] reported the improvement of the electrochemical performance of LSBs by inserting a microporous carbon interlayer (MCP) between the separator and the cathode (Figure 2.14a). This interlayer results in preventing the diffusion of polysulfide intermediates to the lithium side by confining them to the cathode side and working as an upper current collector, leading to improvements in the utilization of the active material. As a result, a stable discharge capacity (1000 mAhg\(^{-1}\)) at 1 C was obtained after 100 cycles (Figure 2-14b).

![Figure 2-14](image)

Figure 2-14: (a) Schematic of the LSB with a microporous carbon interlayer (b) cycling performance and coulombic efficiency with a MCP interlayer at 1C and 2 C.
2.2.2.2 Metal Oxide Interlayer

Polar oxides have been employed to block lithium polysulfide by providing physical adsorption sites and high binding energies such as a separator coating containing nano titanium dioxide carbon black mixture [36], twinborn TiO$_2$–TiN heterostructure [63], and Al$_2$O$_3$ as an absorbent layer [64].

Kim et al. studied the use of gallium oxide shield (Ga$_2$O$_3$) as a multifunctional interlayer coated on the separator (Figure 2-15) resulting in superior cycling performance by providing adsorption sites for lithium polysulfides, suppressing the shuttle effect, and preventing lithium metal dendrite growth [65].

Figure 2-15: Schematic illustration of Ga$_2$O$_3$ shield as a multifunctional interlayer in an LSB.
2.2.3 Novel Electrolyte Development

2.2.3.1 Solid Electrolyte

Solid state electrolyte (SSE) is considered another attractive method to combat some of the problems in LSBs. SSE provides better safety compared to conventional batteries relying on flammable organic liquid electrolyte. In addition, SSE improves the cycling performance by completely eliminating the polysulfide shuttling [66].

Chen and Fan designed a solid polymer electrolyte (SPE) with polysiloxane, LiTFSI and PVDF [67]. A rigid cellulose acetate membrane provided a framework to form a composite solid electrolyte to enhance the mechanical properties of SPE (Figure 2-16a). The cycling performance of the LSB was improved, demonstrating a high discharge capacity (987.6 mAh$^{-1}$) at 0.1 C and a more stable discharge capacity at higher current density (1 C) compared to liquid electrolyte. These results were attributed to the high ionic conductivity of SPE. In addition, this composite solid electrolyte (CPE) results in preventing the diffusion of polysulfide and growth of lithium dendrite (Figure 2-16b). The use of SSEs with high modulus has another advantage by preventing the lithium dendrite penetrations, which is discussed in the next section.
Figure 2-16: (a) Schematic demonstrating the preparation of composite polymer electrolyte membrane using a solution-casting method. (b) schematic of lithium metal anode during plating/stripping.

2.2.4 Anode Improvement

Lithium metal is considered an ideal anode material for use in energy storage devices such as portable electronics and electric vehicles due to its lowest electrochemical potential (−3.04 V versus standard hydrogen electrode) and its high theoretical capacity (3860 mAhg⁻¹) compared to graphite anodes (370 mAhg⁻¹) [68, 69]. However, lithium metal has some hurdles
that hinder its practical applications, including the formation of sharp lithium dendrites during cycling which lead to short circuits in the cell causing safety concerns [70, 71]. Another issue is the large volume expansion and contraction during plating and stripping of lithium metal which results in a low coulombic efficiency. Lithium is highly reactive with electrolytes which causes an unstable solid electrolyte interface that degrades the cycle lifetime of battery [21, 23, 72]. In recent years, extensive research has been conducted to protect lithium metal including electrolyte additives such as lithium fluoride additive [73], applying a coating layer on the surface of lithium metal [71], designing 3D structure host [74], and solid electrolytes such as Li_{10}GeP_{2}S_{12} and Li_{5}PS_{3}Br [66, 75].

Zheng et al. developed interconnected hollow carbon nanosphere coating on the lithium metal to accommodate the volume expansion of lithium metal, forming a stable solid electrolyte interphase and preventing the formation of dendrites (Figure 2-17b) [71]. The improvement in coulombic efficiency was around 99% for up to 150 cycles at 0.25 mAcm^{-2} and approximately 98.5% at 0.5 mAcm^{-2} (Figure 2-17c). Comparatively, the cells without coating show a rapid decay in coulombic efficiency after 100 cycles at 0.25 mAcm^{-2} and 0.5 mAcm^{-2} (Figure 2-17c). This enhancement is attributed to the chemical stability of amorphous carbon in the presence of lithium metal. Another benefit of the coating is the high mechanical properties which leads to stabilization of the SEI under multiple plating/stripping cycles of lithium metal.
Figure 2-17: (a) Schematic of lithium metal structures without coating showing fracture of the SEI layer due to volumetric expansion. (b) the carbon nanosphere coating to protect the lithium metal. (c) comparison of coulombic efficiency for the cells with and without coating.

Weiyang Li et al. has investigated the combined reaction between lithium nitrite and lithium polysulfides as additives in ether-based electrolytes. This dual effect enables a stable and uniform SEI layer which results in surpassing dendrite growth as shown in Figure 2-18b and minimizing electrolyte decomposition. The protective SEI layer results in longer cycle life and excellent coulombic efficiency [76].
Figure 2-18: SEM images of SEI layers after 10 cycles (a) with only LiNO₃ in the electrolyte (b) with Li₂S₈ and LiNO₃ in the electrolyte.

2.3 Summary

As mentioned above, there are several strategies for overcoming the obstacles to improve the performance of LSBs. Although these strategies showed significant improvements in the rate performance and the capacity retention, commercial utilizations of LSBs are still under development. The key factors that affect the LSB performance are the electrical conductivity, loading mass of the sulfur active materials, mechanical stability of the cathode composite, and, most importantly, the ability to prevent the lithium polysulfide and the shuttle effect. The use of the lithium metal anode paired with the sulfur cathode has its own issues in terms of cycle efficiency, lifetime, and safety. This dissertation research focuses on improving the factors listed above by introducing new strategies to provide physical and chemical confinements for the lithium polysulfides while increasing the electrical conductivity and the mechanical stability of the cathode composites.
CHAPTER 3  NANO-POROUS LITHIUM POLYSULFIDE CATHODE USING VAT DYE NANO PARTICLES

3.1 Introduction

While the approaches mentioned in Chapter 2 showed significant improvements in the rate performance and the capacity retention, in most reported cases, the loading mass of sulfur was less than 2 mgcm$^{-2}$ [77]. A sulfur loading of 4–10 mgcm$^{-2}$ is ideal for electric vehicles that require an areal specific capacity of capacity of 3-7 mAhcm$^{-2}$ [77–80]. The recent trend is to utilize a nanostructured 3D porous host structure with high electronic conductivity and the ability to confine sulfur species to improve the rate performance and cycle lifetime. An organic carbon-based composite using vat dyes was reported to show promising electrochemical performance as an LIB cathode due to its short Li$^+$ diffusion length and good electrical conductivity [81]. Vat dyes have amino-and carbonyl-groups, and these functional groups contribute to trapping lithium polysulfide, preventing the shuttle effect [82, 83]. Therefore, vat dyes have a potential to improve the LSB performance. However, the application of vat dye in LSB has not been reported to date, and its effect on the LSB reaction is unknown. Here, in situ transmission electron microscopy (TEM) is a powerful tool to directly observe the electrochemical reactions on the nano-scale to evaluate the performance of the electrode composite [84, 85].

This chapter discusses the development of a free-standing nanostructured cathode with vat black decorated carbon cloth infiltrated with a lithium polysulfide (VB/CC/PS) composite. The lithium polysulfide infiltrated vat black particles were synthesized, and their electrochemical performance were tested by in situ TEM to confirm that the porous structure of the composite accommodated the large volume changes during conversion reactions between S and Li$_2$S ($\sim$76%) without electrode fracture and enables fast lithiation/delithiation reactions. Based on
this observation, we developed VB/CC/PS cathode composite that improved sulfur loading while maintaining its cyclability. This cathode design improved sulfur loading while maintaining its cyclability. This carbon cloth boasts a large surface area, good electrical conductivity, a porous structure, flexibility, and serves as the current collector with a conductive framework. In addition, the functional groups in vat black (Figure 3-1) helps to trap lithium polysulfide and prevent the shuttle effect for sulfur species which results in desired electrochemical performance.

![Figure 3-1: Structure of vat black](image)

### 3.2 Preparation of Nanostructured Vat Black/Carbon Cloth Electrode

The preparation procedure of the VB/CC/PS electrode is schematically shown in Figure 3-2. First, a carbon cloth (CCP10, Fuel cell earth, MA, USA) was coated with vat black (Vat black 8) to increase its surface area and number of active sites. The vat black coating slurry was prepared by mixing vat black with the PVDF binder in a ratio of 9:1. The mixture was milled in a mortar for an hour. NMP was added to the mixture and stirred overnight and then sonicated for 3 h to form a homogenous solution. Next, the carbon cloth was soaked in the homogenous solution and dried overnight in air and then was cut into a disk with a diameter of 14 mm. The lithium polysulfide solution was prepared in an argon glove box by stirring...
stochiometric amounts of sublimed sulfur (Alfa Aesar, 99.5%) and lithium sulfide (Alfa Aesar, 99.9%) to produce Li$_2$S$_8$ in 4 mL of a 1:1 vol ratio solvent of dimethoxyethane (DME): dioxolane (DOL) at 60 °C for 18 h. Then, 47.5 and 87.5 μL of lithium polysulfide catholyte were added to the coated carbon cloth corresponding to sulfur loadings of 2.47 mg cm$^{-2}$ and 4.55 mg cm$^{-2}$, respectively. The ratio of sulfur to vat black was 2.18. The coated cloth was then completely dried in the glove box for the coin cell assembly.

![Figure 3-2: Schematic illustration of the preparation of coated carbon cloth/lithium polysulfide catholyte (VB/CC/PS).](image)

3.3 **Physical Characterization**

The morphologies of the carbon cloth with the interwoven carbon fibers for the CC, VB/CC and VB/CC/PS were examined by a Zeiss Ultra 55 scanning electron microscope (SEM). SEM image shows that the uncoated carbon fiber had a clean and flat surface as seen in Figure 3-3a. Furthermore, Figure 3-3b shows the vat black particles uniformly distributed on the coated carbon cloth and embedded between the carbon fibers. The SEM images at low and high magnification in Figure 3-3c and d depicted the vat black particles well-bound to the
fiber. These particles filling the pores of the carbon cloth contribute to the increased surface area, providing more sulfur adsorption sites and electrons for the charge/discharge reactions.

Furthermore, energy dispersive spectroscopy (EDS) elemental mapping shows that sulfur and vat black particles are homogeneously distributed in the 3D framework of the carbon fibers (Figure 3-3e and f).

Figure 3-3: SEM images at different magnifications of (a) uncoated carbon cloth (CC) (b,c,d) of coated carbon cloth (VB/CC); (e) and (f) are EDS mapping of coated carbon cloth at different magnifications corresponding to (c) and (d) respectively.
In addition, TEM image and corresponding selected area electron diffraction pattern (Figure 3-4a and b) of the VB/PS cathode confirmed that lithium polysulfide is well confined in the nano-sized pores and has an amorphous structure.

![Figure 3-4: (a) TEM image of the VB/PS and (b) electron diffraction pattern of the VB/PS.](image)

Scanning transmission electron microscopy (STEM) imaging and the corresponding elemental mapping of the VB/PS cathode verified that lithium polysulfide was evenly distributed throughout the vat black particle (Figure 3-5 a–d). It is well-known that sulfur easily sublimates under TEM observation conditions because of its high vapor pressure, making the characterization challenging. In this work, however, the nano-sized pores confined the sulfur and prevented it from sublimating during the observation under high vacuum and enabled the TEM characterizations [86–88].
Furthermore, \textit{In-situ} Transmission electron microscopy (TEM) experiment was performed to clarify the structural changes of VB/PS during battery charge/discharge cycles. Vat black/lithium polysulfide (VB/PS) particles were dispersed in DME solution and drop casted on a halved copper grid as a cathode electrode. A small piece of lithium metal was scratched on a tungsten probe as an anode. The Cu grid and the probe were mounted on a nano-manipulation holder (Hummingbird Scientific) with a 3D-piezo manipulator. The tungsten probe was manipulated inside the TEM to contact Li metal with a VB/PS particle and constant voltages - 3 and 3 V were applied on the Cu grid with respect to the tungsten probe for lithiation and delithiation. An FEI Tecnai F30 operating at 300 kV acceleration voltage was used in the experiment. The electron beam dosage was carefully controlled so that no structural change in the VB/PS particles were observed without applying the bias potentials.
Figure 3-6a shows the TEM micrograph of the sample at the initial state and after each lithiation/delithiation step. No significant change in the shape and volume was observed in the process. The apparent size change in the figure is due to the rotation of the sample. However, the electron diffraction patterns are different at each step indicating that the phase transformation had occurred (Figure 3-6b). The rotation averages of the diffraction patterns compiled in Figure 3-6c clearly show the phase transformations. At initial state (i), VB/PS had very weak peaks with an amorphous-like structure, which agrees well with the reported lithium polysulfide structure for Li$_2$S$_8$ [89]. After the first lithiation (ii), three prominent peaks corresponding to the (111), (200), and (220) planes of Li$_2$S were observed, indicating the PS was fully lithiated to nanocrystalline Li$_2$S. This agrees well with the lithiation of a carbon-sulfur nanocomposite reported [86]. Upon the first delithiation, a change in the diffraction pattern was observed (iii) indicating the delithiation of Li$_2$S. However, the pattern does not match the orthorhombic sulfur, and the peaks near 3.8 and 4.3 nm$^{-1}$ can be assigned to a polymerized sulfur (PDF#24-1251). This indicates that the Li$_2$S was not transformed to $\alpha$-sulfur but instead to other sulfur allotropes. A transformation to Li$_2$S was confirmed after the second lithiation (iv). It is worth noting that a recent study showed that decomposition of Li$_2$S was difficult at room temperature because of the slow Li ion diffusion in the bulk Li$_2$S [90]. In their report, a lithiation/delithiation experiment was performed for sulfur filled inside a CNT with an internal diameter of ~250 nm and a length of >5 μm, which made it difficult to extract lithium from Li$_2$S during lithiation at room temperature. In our work, the polysulfide was confined in the nano-sized pores with a diameter of ~10 nm, which significantly reduced the diffusion distance and increased the surface area to improve the transport of Li ions and electrons. Therefore, the decomposition of Li$_2$S was possible at room temperature in VB/PS.
Figure 3-7 shows the lithiation process of VB/PS. After applying the bias voltage, the reaction front rapidly propagated across the sample, changing the contrast in the image of the VB/PS sample. Here, no significant volume expansion was observed.
Figure 3-7 shows the propagation distance of the reaction front \( df \) as a function of time \( t \). The data points align well with a square root function \( df = at^{1/2} \) shown by the solid line with a standard error of 1.43\% for \( a = 75.0 \text{ nm}\cdot\text{s}^{-1/2} \). Therefore, the reaction was a diffusion limited process. By extrapolating the fitted curve, the reaction time of a typical sulfur infiltrated vat black particle with a 2 \( \mu \text{m} \) radius can be fully reacted within 12 min. These results indicate that PS infiltrating nanopores of the vat black prevented overall volume changes of the material while allowing for an extremely fast reaction, which makes VB/CC/PS a promising LSB cathode material.
3.4 Electrochemical Performance

To evaluate the electrochemical performance of the free-standing nanostructured vat black/carbon cloth sulfur electrode (VB/CC/PS) and CC/PS, coin cells were assembled. A cyclic voltammetry (CV) test was conducted for the fresh CC/PS and VB/CC/PS with a sulfur loading of 2.47 mg cm\(^{-2}\) at a scan rate of 0.1 mVs\(^{-1}\) in the voltage range of 1.0–3.0 V. Figure 3-9a shows the results of the first CV cycle for CC/PS and VB/CC/PS. For CC/PS, two cathodic peaks at 2.25 V and 2.037 V were observed, which attributes to the reduction of long chain lithium polysulfide to Li\(_2\)S\(_4\) and further reduction of Li\(_2\)S\(_4\) to Li\(_2\)S\(_2\) and Li\(_2\)S, respectively. The weak second peak indicates that there were fewer reactions from Li\(_2\)S\(_4\) to Li\(_2\)S due to the polysulfide dissolution. The two oxidation peaks were observed at 2.49 V and 2.43 V. The absolute peak intensity of the VB/CC/PS increased for both cathodic peaks at 2.23 V and 1.90 V and anodic peaks at 2.30 V and 2.40 V. The stronger anodic peaks of the VB/CC/PS correspond to the oxidation of Li\(_2\)S\(_2\) and Li\(_2\)S to S, resulting in a lower polarization, which
indicated faster reaction kinetics, implying that the vat black coating lowers the electrode’s polarization by confining the reaction products in the vat black particles. The multiple cycle CV curves of the VB/CC/PS (Figure 3-9b) show overlapping peaks from the second to the fourth cycle, indicating good reversibility and stability of the free-standing sulfur cathode.

Figure 3-9: Cyclic voltammetry curve at a scan rate of 0.1 mVs$^{-1}$; (a) for the vat black coated (VB/CC/PS) and uncoated (CC/PS) carbon cloth and (b) for the vat black coated (VB/CC/PS) showing the first four cycles.

To further analyze the redox kinetics of lithium polysulfide, electrochemical impedance spectroscopy (EIS) measurements were conducted for the fresh sample of CC/PS and VB/CC/PS at the open circuit potential. Both CC/PS and VB/CC/PS exhibited two semicircles in the high-to-low frequency region and an inclined line that represents lithium-ion diffusion (Warburg impedance) in the electrode (Figure 3-10). The VB/CC/PS had a lower charge transfer resistance at the polysulfide/3D structure electrode interface as well as a smaller semicircle diameter (17 $\Omega$) compared to the CC/PS (38.5 $\Omega$). This indicated lower polarization and fast reaction due to (1) the strong interaction between lithium polysulfide and vat black
particles, which effectively trapped the polysulfide species, as well as (2) the good conductivity and high surface area of the coated carbon cloth.

Figure 3-10: Nyquist plots of the coated and uncoated carbon cloth with an amplitude of 5 mV.

Figure 3-11a exhibits the charge-discharge profiles of the CC/PS and VB/CC/PS at 0.2 C. High discharge capacity exceeding 1350 mAhg\(^{-1}\) with a long discharge plateau was achieved by using the free-standing VB/CC/PS electrode. This discharge capacity is two times larger than that of CC/PS without vat black coating (550 mAhg\(^{-1}\)). Additionally, the VB/CC/PS electrode showed excellent rate performance at different current densities. The reversible capacities were 1394, 1350, 1294, 1148, and 853.7 mAhg\(^{-1}\) at 0.1, 0.2, 0.5, 1.0 and 2.0 C, respectively. These values were higher than those in other literatures involving the polysulfide cathode, as summarized in Table 3-1, and the corresponding capacity retention values are comparable to literature values as well. The capacity was recovered to 1382.89 mAhg\(^{-1}\) when the rate was slowed to 0.1C after 2C cycles (Figure 3-11b), indicating a good electrochemical reversibility.
Figure 3-11: (a) Galvanostatic charge-discharge curves of the CC/PS and VB/CC/PS at 0.2 C rate. (b) rate performance of the CC/PS and VB/CC/PS at different current densities.

The charge-discharge voltage profiles for VB/CC/PS, at different current rates, show two distinct discharge plateaus at 2.3 V and 2.1 V that are clearly seen even at high current density up to 1C, as shown in Figure 3-12a. In contrast, the lower voltage plateau is hardly observable for CC/PS (Figure 3-12b).

Figure 3-12: (a) and (b) charge-discharge profiles of the VB/CC/PS and CC/PS, respectively, at various rates.
Table 3-1: Comparison of electrode performance for lithium polysulfide batteries.

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<th>Electrode</th>
<th>S loading (mgcm$^{-2}$)</th>
<th>Initial Capacity (mAhg$^{-1}$)</th>
<th>Cycle number</th>
<th>C-rate</th>
<th>Capacity retention (mAhg$^{-1}$)</th>
<th>Ref.</th>
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<tr>
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<td>1200</td>
<td>100</td>
<td>0.2</td>
<td>822</td>
<td>[55]</td>
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<td>900</td>
<td>300</td>
<td>0.5</td>
<td>623</td>
<td>[91]</td>
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<tr>
<td>a polyvinylpyrrolidone-modified carbon paper/lithium polysulfide</td>
<td>0.96</td>
<td>1300</td>
<td>100</td>
<td>0.2</td>
<td>1000</td>
<td>[92]</td>
</tr>
<tr>
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<td>1010</td>
<td>400</td>
<td>0.5</td>
<td>~560</td>
<td>[93]</td>
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<td>1100</td>
<td>100</td>
<td>0.1</td>
<td>789</td>
<td>[94]</td>
</tr>
<tr>
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<td>1246</td>
<td>100</td>
<td>0.1</td>
<td>748</td>
<td>[95]</td>
</tr>
<tr>
<td>N-doped graphene paper</td>
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<td>1100</td>
<td>100</td>
<td>0.2</td>
<td>1000</td>
<td>[96]</td>
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<td><strong>1295</strong></td>
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<td>1150, 837</td>
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</tbody>
</table>

The battery cycle tests were performed for VB/CC/PS and CC/PS at 0.2 C with a sulfur loading of 2.47 mgcm$^{-2}$ (Figure 3-13). The initial discharge capacity was 1295 mAhg$^{-1}$, and it maintained a high discharge capacity of 837 mAhg$^{-1}$ even after 220 cycles. However, the capacity of the CC/PS was significantly lower than that of VB/CC/PS from the initial cycle, indicating low sulfur utilization by CC/PS. SEM/EDS analysis after cycling revealed that a large amount of sulfur was still present on the surface of the VB coated carbon cloth (Figure 3-14). On the other hand, CC/PS without VB lost most of the polysulfide after cycling due to the weak bonding between lithium polysulfide and the carbon cloth (Figure 3-15). These observations confirm the effectiveness of the VB coating in trapping the polysulfide, leading
to the long cyclability of VB/CC/PS. The superior electrochemical performance of VB/CC/PS further emphasizes the ability of VB particles to confine the polysulfides inside the nanopores.

Figure 3-13: Cycling performance of the VB/CC/PS and CC/PS at 0.2 C rate with a sulfur loading mass of 2.47 mg cm\(^{-2}\).

Figure 3-14: SEM image of (a) VB/CC/PS after cycling and (b) and (c) EDS mapping and spectrum of VB/CC/PS after cycling respectively.
As mentioned earlier, high loading mass is desired to fully utilize the high energy density of LSBs [97]. Therefore, the loading mass of sulfur was increased to 7 mg on the 14 mm VB/CC disk corresponding to 4.55 mg cm$^{-2}$. It showed a high initial discharge capacity (928 mAh g$^{-1}$) at 0.1 C and maintained a discharge capacity of 603 mAh g$^{-1}$ after 100 cycles (Figure 3-16), with a good coulombic efficiency between 95 and 100%.

![Figure 3-15: SEM images of CC/PS (a) before cycling and (b) after cycling. Scale bars are 20 µm.](image)

![Figure 3-16: Cycling performance of the VB/CC/PS at 0.1 C rate with a sulfur loading mass of 4.55 mg cm$^{-2}$.](image)
Adding vat black particles by a simple process showed distinguished discharge capacity and superior rate performance from 0.1 C to 2C for the VB/CC/PS electrode. This outstanding performance is attributed to the conductive framework of the current collector carbon cloth and increased active sites facilitated by vat black particles, resulting in capturing the polysulfide species and preventing the shuttle effect.

3.5 Summary

A simple method that enables a high loading mass of sulfur by using a free-standing nanostructured vat black/carbon cloth sulfur cathode (VB/CC/PS) was developed. This combination of carbon cloth fiber and vat black particles showed a good electrochemical performance by providing high surface area and high electrochemical conductivity. An accommodation for volume changes was confirmed by the in-situ TEM observations. As a result, a high discharge capacity exceeding 1300 mAhg\(^{-1}\) at 0.2 C, a capacity retention over 200 cycles, and an excellent rate performance was achieved with a sulfur loading mass of 2.47 mgcm\(^{-2}\). This VB/CC framework concept was still valid even when the sulfur loading was increased to 4.55 mgcm\(^{-2}\) with a high discharge capacity of 928 mAhg\(^{-1}\) and a capacity retention over 100 cycles at 0.1 C. Our results demonstrated that the simple vat black particle coating on a carbon cloth can achieve noticeable improvement in the LSB performance and has a potential to make further improvements in combination with other techniques such as modified separators and optimized electrolytes, paving the way toward practical LSBs.
CHAPTER 4  GA-BASED LIQUID METAL ADDITIVE AS ELECTROCATALYST AND ANCHOR FOR POLYSULFIDES

4.1 Introduction

As indicated in the previous chapter, high discharge capacity and good cycling performance of LSB were achieved by lithium polysulfide infiltrated carbon composite cathode at high sulfur loading. As explained in Chapter 2, the use of rGO in the cathode composite improves the capacity and the cycle lifetime of LSBs due to its ability to trap lithium polysulfide which prevents the shuttle effect \( [98, 99] \). Additionally, sulfur/gallium hybrid materials such as a S/Ga core-shell electrode \([49,50]\), 3D porous S/Ga composite cathode \([100]\), and gallium oxide shield layer on the separator \([65]\) were proposed to show exceptional electrochemical performance by providing abundant adsorption and reaction sites for lithium polysulfides on Ga. These materials indicate that rGO and Ga play an important role in improving the cycling life of LSBs. Although Ga is a low melting point metal with a melting temperature \( T_m \) of \( \sim 30 \) °C, it is a solid at operating temperatures of LSBs. By adding other alloying elements, Ga can further reduce \( T_m \) which allows it to maintain its liquid state during charge/discharge cycles \([101]\). This can provide additional stability of the cathode by utilizing the liquid nature of the LM additives that contribute to maintaining the electrical conduction path even with the large volume changes of the sulfur active materials.

In this chapter, we propose a mixture of sulfur, rGO, and Ga-based LM as an LSB electrode composite to integrate the ability of rGO to trap the lithium polysulfide. Additionally, the Ga-based LM acts as an electrocatalyst. In and Sn were added to Ga to synthesize a LM with a low melting point that maintains its liquid state at the LSB operating temperature, playing a central role in this study. The LM allows the electrode composite to accommodate
large volume changes of sulfur in the charge/discharge process and prevents the fracture of the electrode that leads to the loss of the active material.

4.2 Experimental

4.2.1 Synthesis of Reduced Graphene Oxide (rGO)

First, graphene oxide (GO) was synthesized by modified Hummers’ method [102, 103]. Two grams of graphite flakes (Alfa Aesar) were mixed with 50 mL of concentrated H$_2$SO$_4$ in an ice bath. Eight grams of KMnO$_4$ were then slowly added to the mixture. The temperature of the mixture was kept below 10 °C. Then, the mixture was stirred in an ice bath below 5 °C for 1 hour. The oxidation reaction was sped up by heating the mixture to 35 °C for 30 minutes. The exfoliation of oxidized graphite was carried out by adding 500 mL of deionized water to the system followed by 60 °C heating for 30 minutes [104]. H$_2$O$_2$ was added to remove excess KMnO$_4$. The product was first washed by 2 M HCl and then three times by deionized water. The graphene oxide was obtained by lyophilization at 0.040 mbar and -40 °C using a Labconco freeze drying chamber. Reduced graphene oxide (rGO) was then obtained by thermal reduction of GO. GO was heated to 1000 °C in a pure argon atmosphere for 2 hours [105, 106]. The argon flow was kept at 30 SCCM.

4.2.2 Preparation of rGO/S/LM Electrode Composite

Sulfur composite with a LM and rGO was prepared by the following steps (Figure 4-1). First, a gallium-based LM used in this work was synthesized by mixing 68.5% Ga, 21.5 % In and 10% Sn in a petri dish. The mixture became a room-temperature LM alloy within 4 hours (Figure 4-2). Sulfur, rGO, and the LM were then added to ethanol and sonicated in an ice bath to obtain smaller particles for 2 minutes, with 10-minute pauses in between each cycle to
prevent the solution from reaching a high temperature, for a total of 10 cycles. Here, a surfactant (lithium dodecyl sulfate, Sigma Aldrich) was added in the solution to reduce the size of LM to form nanoparticles [107]. After evaporating the ethanol, polyvinylidene fluoride (PVDF) and N-methyl-2-pyrrolidone solvent (NMP) were added to the mixture and stirred overnight to form a homogeneous slurry. Finally, the resultant slurry was dispersed on a carbon cloth with a diameter of 14 mm and dried overnight. Additionally, for comparison, control cells without LM were prepared by mixing sulfur, rGO, and PVDF with NMP solvent and dispersed on a carbon cloth.

Figure 4-1: Schematic illustration of the preparation of rGO/S/LM cathode.

Figure 4-2: Liquid metal (68.5% Ga, 21.5 % In and 10% Sn) at room temperature.

4.3 Structural Characterization

The surface morphologies and elemental distribution on the surface of the rGO/S/LM electrode were characterized by a scanning electron microscope (SEM, ZEISS ULTRA 55) and a transmission electron microscope (TEM, FEI Tecnai F30). The chemical bonding of the
electrode surface was investigated using X-ray photoelectron spectroscopy (XPS). The cells were disassembled in an argon filled glovebox after cycling and washed five times with 1,2 dimethoxyethane to remove excess electrolyte and dried overnight for characterizations. The TEM sample was prepared by dispersing sulfur, reduced graphene oxide and liquid metal nanoparticles in an ethanol solution and drop casting it onto a copper grid.

The SEM images and EDS elemental mapping of the rGO/S/LM electrode before cycling are shown in Figure 4-3a, b. The LM dispersion is generally uniform within the reduced graphene oxide and sulfur and deposited on the 3D conductive framework of the carbon cloth, however aggregated particles of LM are present. The small nano particles indicated by the arrow heads in the magnified SEM image (Figure 4-3a) are LM nano particles that did not spread on the rGO.

Figure 4-3: (a) SEM images and (b) EDS elemental mapping of rGO/S/LM before cycling.
In addition, STEM EDS and electron diffraction analysis of rGO/S/LM were conducted to confirm that these particles were LM (consisting of Ga, Sn, and In) and the presence of LM on rGO (Figure 4-4). These observations confirm that LM was well mixed with sulfur and bound to rGO flakes although there were some agglomerated LM particles.

Figure 4-4: (a) STEM image of rGO/S/LM cathode revealed that LM nanoparticles encapsulated at the edge of the graphene oxide film. (b) Selected area diffraction pattern of the rGO/S/LM showed an amorphous halo from the LM and diffraction rings corresponding to the rGO.

To validate the morphology and elemental distribution on the surface of the electrode after cycling, SEM and energy dispersive X-ray spectroscopy (EDS) analyses were conducted after second (discharge state) and 100 cycles. The SEM images after second (Figure 4-5a) and 100 cycles (Figure 4-5c and d) indicate no obvious changes or cracks in the structure of the electrode. Moreover, EDS mappings after second and 100 cycles (Figure 4-5 b and e) confirm that sulfur, carbon, tin, gallium, and indium were present and uniformly distributed on the surface of the electrode after the charge/discharge cycles. These results further confirm the liquid characteristics of LM to freely alter its shape contributes to accommodating the volume changes during cycling to prevent the detachment of sulfur from the current collector.
Furthermore, X-ray photoelectron spectroscopy (XPS) was conducted to investigate the element composition of the electrode before cycling and after 100 cycles. The XPS spectrum survey before cycling (Figure 4-6) revealed that gallium, sulfur, carbon, nitrogen, oxygen, and fluoride are present on the surface of the electrode.
In Figure 4-7a, the high-resolution spectrum of S 2p before cycling reveals that the peak located at 162.73 eV is composed of Ga$_2$S$_3$ [50, 108] in addition to the peaks from S$_8$. This indicates that sulfur is chemically bound to LM nanoparticles. The peaks located at 166.54 and 168.8 eV are attributed to SO$_3$$^2$ and SO$_4$$^2$ respectively. After 100 cycles (Figure 4-7c), the peaks at 160.3 and 161.6 eV [109–111] confirm that sulfur, after discharge, transforms to Li$_2$S and Li$_2$S$_2$, respectively. The thiosulfate peak [109, 112, 113], located at 167.2 eV is formed by the redox reaction between lithium polysulfides and gallium oxide, indicating the catalytic effect of the LM nanoparticle and its strong binding to lithium polysulfide. The high-resolution spectrums of Ga 5d before and after discharge are shown in Figure 4-7b and d, respectively. The intensity of the GaS peak is higher than that of the Ga peak before cycling which validates the reaction of gallium with sulfur on the surface [50, 100]. These results confirm the strong binding of sulfur particles which promote redox reaction kinetics by enhancing the transformation of lithium polysulfide to lithium sulfide.

Figure 4-6: XPS spectrum of rGO/S/LM cathode before cycling.

Figure 4-7: S 2p spectrum of rGO/S/LM cathode before (a) and after (b) discharge. Ga 5d spectrum of rGO/S/LM cathode before (c) and after (d) discharge.
4.4 Electrochemical Performance

To investigate the effect of liquid metal nanoparticles, cells with rGO/S/LM and rGO/S were tested. The CR2026 coin cells were assembled inside an argon filled glovebox with lithium metal as an anode, rGO/S/LM and rGO/S as cathodes, and polypropylene (Celgard 2400) as a separator. The specific capacity was calculated based on the active weight of sulfur. The ratio that was used of LM to S is 1:3 and the loading mass of the active material was between 0.65-0.78 mg/cm\(^2\). The electrolyte was prepared using 1 M lithium bis (trifluoromethanesulfonyle) imide (LiTFSI) mixed with a 1:1 ratio of DME: DOL. This mixture was then mixed with 2% LiNO\(_3\). The electrochemical measurements of the battery cells were
tested using a multichannel battery tester (Neware, BTS4000). Cyclic voltammetry (CV) was conducted at a scan rate of 0.1 mV/s, with a voltage range of 1.5-3V. The electrochemical impedance (EIS) was carried out using a CHI 760E electrochemical station with an amplitude of 5mV in the frequency range of $10^{-2}$ to $10^6$ Hz.

The cyclic voltammetry (CV) curves of rGO/S/LM and rGO/S cathodes are shown in Figure 4-8a. Two cathodic peaks and one anodic peak of typical LSB reactions are clearly seen for both samples. The two cathodic peaks of rGO/S/LM, located at 2.36 V and ~ 2 V, correspond to the reduction of sulfur to polysulfides and to lithium sulfides $Li_2S_2/Li_2S$, the one sharp anodic peak located at 2.5 V represents the oxidation of $Li_2S_2/Li_2S$ to polysulfides and to sulfur. Compared to the rGO/S cathode, the rGO/S/LM exhibits higher intensity cathodic peaks at higher voltages and sharper anodic peak at lower potential, which demonstrates the lower over potential and enhanced reaction kinetics of the rGO/S/LM cathode. Electrochemical impedance spectroscopy (EIS) measurements were conducted for the rGO/S/LM and rGO/S cathodes to further analyze the reaction kinetics. Both samples showed one semicircle in the high to low frequency region, representing charge transfer resistance ($R_{ct}$) and one sloping line in the low frequency region (Warburg impedance) as shown in Figure 4-8b. In addition, the rGO/S/LM cathode has a smaller semicircle compared to the rGO/S, demonstrating better charge transfer resistance and enhanced reaction kinetics.
Figure 4-8: (a) CV curves of rGO/S/LM and rGO/S cathodes. (b) EIS spectra of rGO/S/LM

Galvanostatic charge-discharge tests were conducted to evaluate the electrochemical performance of the rGO/S/LM and rGO/S cathodes. The charge-discharge profiles of rGO/S/LM and rGO/S at 0.2 C (Figure 4-9a) show two discharge plateaus (corresponding to the formation of the high and low order lithium polysulfides) and one charge plateau. Both plateaus agreed with CV curves. Comparatively, rGO/S/LM shows a longer discharge profile and higher initial discharge capacity. Additionally, the voltage hysteresis between the charge and discharge plateaus for rGO/S/LM was smaller compared to that of rGO/S. The lower polarization of the rGO/S/LM indicates a good reversibility and faster redox reaction kinetics owing to the catalytic effect of LM nanoparticles that accelerate polysulfide conversion reaction.

The rate performance of rGO/S/LM and rGO/S at different current densities are shown in Figure 4-9b. The rGO/S/LM displays higher discharge capacities at 0.1, 0.2, 0.5, 1 and 2C compared to rGO/S, and the capacity was successfully recovered when switched back to 0.1 C, revealing the good reversibility of rGO/S/LM cathode and the good capability of LM nanoparticles to trap lithium polysulfide. The voltage charge discharge profiles at various
current rates (0.1-2 C) of rGO/S/LM and rGO/S are shown in Figure 4-9c, d. As displayed in Figure 4-9c, the two discharge plateaus of the rGO/S/LM are still obvious even at a higher current density (2C).

Figure 4-9: Electrochemical performance of rGO/S/LM and rGO/S cathodes (a) charge-discharge profile at 0.2 C. (b) rate capabilities. (c) and (d) charge-discharge profiles at different rates.

Figure 4-10 shows the cycling performance of rGO/S/LM and rGO/S electrodes at 0.2 C (after five cycles of activation [114] at 0.1C), with the rGO/S/LM cell exhibiting high discharge capacity (943.2 mAhg\(^{-1}\)) and good Coulombic efficiency (over 96%) while rGO/S showed much lower capacity (540 mAhg\(^{-1}\)). Moreover, the rGO/S/LM cell still maintained a
good capacity retention (72.15%) even after 400 cycles, whereas the capacity retention of the rGO/S was only 59%. These results demonstrate the effectiveness of liquid metal nanoparticles to hinder the polysulfide shuttle effect and to enhance the cycling stability of the lithium sulfur battery.

Figure 4-10: Cycling stability at 0.2 C for 400 cycles.

To further verify the catalytic effect of LM towards lithium polysulfide conversion, CV tests were performed using symmetric cells in a voltage range of -1.0 to 1.0 V [115, 116]. Two symmetric cells were assembled using rGO/LM and rGO electrodes. A Celgard separator with 50 µL of 0.5 M Li2S6 electrolyte was used for both cells (Figure 4-11). The rGO/LM electrode exhibited higher redox current density compared to the rGO electrode, revealing the improved redox kinetics of the polysulfide conversion by the catalytic effect of LM.
Figure 4-11: Cyclic voltammetry of symmetric cells using rGO/LM and rGO electrode with a scan speed of 0.1 mVs$^{-1}$. Clear increase in the current density was observed indicating the improvement in the redox kinetics of polysulfide conversion with LM.

To further confirm the ability of LM to prevent polysulfide dissolution, rGO/S/LM and rGO/S electrodes were immersed in 4 ml and 2 ml of 5 mM Li$_2$S$_6$ DOL/DME and left for few hours to discern the color change of the solutions. The color of the solution with rGO/S electrode became darker after immersion in the solution while the one with rGO/S/LM electrode revealed no color change (Figure 4-12). This result indicates the addition of LM inhibited polysulfide dissolution due to its strong binding with S.

Figure 4-12: Polysulfides adsorption test of rGO/S and rGO/S/LM electrodes immersed in (a) 4 ml and (b) 2 ml solution of Li$_2$S$_6$ in DME/DOL. There is no change in the color of the solution for rGO/S/LM, but it becomes darker for rGO/S. This is more obvious when using the smaller amount of the solution. There is almost no change in the one with LM additive for both 4 ml and 2 ml cases, indicating the dissolution of S was minimum.
4.5 *Ab Initio Simulation*

To evaluate the ability of liquid metal to absorb lithium polysulfides, *ab initio* simulations were performed to calculate the adsorption energy of the polysulfides on the LM surface. First, 32 Ga, 9 In, and 5 Sn atoms were randomly placed in a 10 Å x 10 Å x 10 Å unit cell and the molecular dynamics (MD) simulation was performed for 5 ps at 300 ºC, followed by the structural optimization by conjugate gradient method. Then, 15 Å of a vacuum layer was added to the relaxed structure to create a slab model. Then, MD was performed using the slab model for 5 ps at 300 ºC followed by the structural relaxation. Here, atoms in the bottom few layers (3Å total thickness) were fixed for the simulations of the slab models. After the optimization of the surface model was complete, a lithium polysulfide Li$_2$S$_x$ ($x = 1,2,4,6,8$) was placed on the surface followed by MD for 5 ps at 100 ºC and the structural optimization. Finally, the binding energy $E_{\text{binding}}$ was obtained by, $-E_{\text{binding}} = E_{\text{total}} - (E_{\text{LM}} + E_{\text{PS}})$. Where, $E_{\text{total}}$, $E_{\text{LM}}$, and $E_{\text{PS}}$ are energies of the polysulfide on LM surface, the LM surface, and the polysulfide molecule, respectively. Vienna *ab initio* Simulation Package (VASP) [117, 118] was employed in the simulation using the same parameters described elsewhere [36]. The ionic cores were represented with a projected augment wave (PAW) potential [119, 120]. A plane-wave energy cut-off of 500 eV and a generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof [121] were used for the exchange-correlation functional, and only G-point was selected for the k-mesh in the calculation.

The ability of LM to trap polysulfides was evident from the *ab initio* simulation. Figure 4-13a shows the binding energy of the lithium polysulfides on the LM surface in comparison with those on graphene [36]. The binding energies of the polysulfides on graphene is low and almost constant regardless of the polysulfide species. In contrast, the binding energies are much
higher on the LM surface particularly for the long-chained lithium polysulfides (Li$_2$S$_6$ and Li$_2$S$_8$). This can be attributed to the strong binding of S on LM (especially with Ga atoms) as seen in the molecular adsorption structures in Figure 4-13b. It is worth noting that Li$_2$S$_8$ ring was opened and spread on the LM surface leading to the formation of more atomic bonds between them. These results agree well with the XPS analysis showing Ga-S peak. The outcome of the simulation supports the improved polysulfide trapping by adding LM in the electrodes for high S-containing species. On the other hand, binding energy of Li$_2$S$_n$ on TiO$_2$ increases with decreasing $n$ favoring adsorption of low S-containing species [36]. This suggests the possibilities of combining different polysulfide-trapping agents optimized to capture the entire series of the polysulfides.

Figure 4-13: (a) Calculated binding energies of lithium polysulfides on the LM surface, in comparison with graphene (data from Ref. 36). (b) atomic structures of Li$_2$S$_6$ and Li$_2$S$_8$ adsorbed on the LM surface.
4.6 Summary

In conclusion, an LSB electrode composite consisting of LM, sulfur, and rGO (rGO/S/LM) was developed and demonstrated enhancement of the electrochemical performance of LSB battery. Adding of rGO and LM effectively traps polysulfide and prevents the shuttle effect to prolong the cycle lifetime of the battery. LM also contributes to the faster redox reaction kinetics and accommodates large volume changes of the sulfur during the battery cycles. These characteristics of LM enhanced sulfur utilization, reduced reaction overpotentials, and prevented the loss of sulfur due to the electrode fracture, resulting in the improved capacity and cycle lifetime. The cell with rGO/S/LM cathode exhibited a higher discharge capacity of 943.2 mAhg\(^{-1}\) at 0.2C, better coulombic efficiency, and greater rate performance at 2 C, compared with the control electrode without LM. rGO/S/LM maintained a good cycling stability even after 400 cycles. In addition, SEM analysis of the rGO/S/LM electrode after cycling showed no change in the structure from the initial state. The improved catalytic activity for the redox kinetics of the polysulfides was confirmed by the CV of the symmetric cell using rGO/LM and rGO, and the ability of LM to trap the polysulfides were supported by the polysulfide dissolution experiment and the \textit{ab initio} simulation. The dual function of the Ga-based LM to improve the electrochemical performance and mechanical stability is anticipated to open a new path towards practical lithium sulfur batteries. The application of LM is highly effective in overcoming two of the major challenges in LSBs: polysulfide dissolution and large volume changes of sulfur during LSB operations.
CHAPTER 5 CONCLUSION

This dissertation research focused on finding solutions to mitigate the lithium polysulfide dissolution and shuttle effect to make improvements in the performance of lithium sulfur batteries. As described in Chapter 2, many efforts have been made to overcome major challenges in LSBs with particular emphasis on the polysulfide dissolution. Development of the porous host structure is essential to improve the sulfur loading mass to increase the capacity of the battery cell while providing a physical confinement for the polysulfides. On the other hand, various additives have been proposed as electrocatalysts to enhance the charge/discharge reactions and provide adsorption sites for the polysulfides. In this research, Ga was identified as a good electrocatalyst to bind the polysulfides and improve the LSB reactions. This led to the two strategies developed in this dissertation work to overcome the issue of polysulfide dissolutions, physical and chemical confinement.

For the first strategy (physical confinement), a simple and cost-effective method was proposed to fabricate a nano-porous composite for the lithium polysulfide battery by employing a nanostructured vat black/carbon cloth electrode that exhibits high electrical conductivity, good mechanical properties, and a high surface area (Chapter 3). These benefits enabled a high sulfur loading mass, captured the lithium polysulfide intermediate reaction products, and avoided structural changes. This method resulted in a high specific discharge capacity of 1300 mAhg\(^{-1}\) at 0.2 C, an outstanding rate performance (846 mAhg\(^{-1}\) at 2 C) and an areal capacity of up to 3.352 mAhcm\(^{-2}\) with a sulfur loading mass of 3.8 mg. Increasing the sulfur loading mass to 7 mg (areal capacity of up to 4.24 mAhcm\(^{-2}\)) still resulted in a desirable discharge capacity of 928 mAhg\(^{-1}\). In addition, an in situ TEM experiment was performed to directly
observe the reaction process and confirmed the fast lithiation of the polysulfide and the ability of the porous host to accommodate the volume changes of sulfur.

For the second strategy (chemical confinement), a novel sulfur composite was developed with Ga-based liquid metal (LM) nanoparticles and reduced graphene oxide (rGO) dispensed on a carbon cloth electrode (Chapter 4). Using a function of Ga as an electrocatalyst as described in Chapter 2, In and Sn were added to reduce the melting temperature and maintain its liquid state at the operating condition of LSB. This design provided a strong anchoring with sulfur inhibiting the polysulfide shuttle effect, and at the same time the LM acted as a self-healing binder to maintain electrical conduction paths to the sulfur active materials during the large volume changes in the charge/discharge process. This innovative composite resulted in a high discharge capacity, an outstanding capacity retention, and a high coulombic efficiency. First principles analysis supported the ability of the LM to anchor the polysulfides (particularly the long-chain lithium polysulfides). The results demonstrate an effective method to suppress the polysulfide shuttle effect by using multifunctional LM nanoparticle composites.

The two strategies successfully improved the performance of the lithium sulfur battery by enhancing the cycle lifetime, rate performance, and the capacity. The use of LM as an electrocatalyst set a new research direction towards multifunctional additives with abilities to enhance the electrochemical reactivity and polysulfide adsorption, and maintain electrical conduction paths utilizing its liquid characteristics. In situ TEM and ab initio simulation are useful tools to evaluate the functions and the underlying physics for developing new materials. The simulation also revealed the potential to tune the binding strengths for each polysulfide species to optimize the catalytic activities by combining different additives in the cathode composites. The combination of the physical and chemical confinement will be a key for
preventing the polysulfide dissolution and the shuttle effect to lead to the practical applications of LSBs. The scientific findings from this work not only provide intellectual merits to further advance the technology, but also contributes to developing advanced energy storage technologies essential for achieving a sustainable society utilizing renewable energy sources.
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A Liquid-Metal Electrocatalyst as a Self-Healing Anchor to Suppress Polysulfide Shutting in Lithium-Sulfur Batteries

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REFERENCES


