

Incorporation of MoS_x/rGO electrocatalysts in sulfur cathode to reduce polysulfide
shuttling in Li-S battery

by

Zahirul Islam Saddam

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AN ABSTRACT OF A DISSERTATION

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Abstract

Lithium-sulfur batteries (LSB) have emerged as one of the most promising alternatives to Li-ion batteries due to their exceptionally high theoretical energy density, nearly an order of magnitude higher than that of Li-ion batteries. The sulfur cathode offers a theoretical specific capacity of 1,675 mAh/g. At the same time, the Li metal anode provides a theoretical capacity of 3,860 mAh/g, making LSBs attractive for high-energy applications such as EVs. However, the practical application of LSBs is hindered by several intrinsic challenges originating from the cathode, such as polysulfide shuttling and slow redox kinetics. This slow kinetics and polysulfide shuttling lead to sulfur loss, low coulombic efficiency, and rapid capacity fading. On the anode side, the Li metal anode undergoes dendritic growth during cycling, which causes the formation of electrically isolated dead Li, continuous consumption of electrolyte and active lithium, and ultimately short-circuits the cell.

To address polysulfide shuttling and sluggish redox kinetics, crystalline, multilayered 2D MoS₂ has been widely studied as an electrocatalyst that accelerates LPS adsorption and conversion. However, due to the limited number of active sites in micron-scale MoS₂ and the multi-step nature of sulfur redox chemistry, micron-scale MoS₂ is rarely capable of optimizing all reaction pathways simultaneously. This thesis, therefore, expands the design of MoS_x-based electrocatalysts into a tunable family of nanoscale molybdenum sulfide (MoS_x) materials anchored on reduced graphene oxide (rGO) sheets to enhance the active-site density.

MoS_x/rGO hybrids were synthesized through a rapid microwave-assisted reaction that initially forms 1D amorphous MoS₃. This precursor was subsequently annealed at 250, 325, and 600 °C under a 3% H₂/97% Ar atmosphere, enabling controlled structural transformation from amorphous 1D MoS₃ to few-layer 2D crystalline MoS₂ nano-patches approximately 5 nm in lateral

size. The amorphous MoS_3 exhibits a 1D chain-like structure with a high density of exposed Mo and S active sites, which enhances its ability to adsorb and catalytically convert LPS species. In contrast, the crystalline 2D MoS_2 shows catalytic activity concentrated at the edge sites rather than the basal plane. This work systematically investigates how structural evolution within the MoS_x family governs LPS adsorption capacity, polysulfide binding strength, catalytic activity, and overall battery performance.

In the first study, when MoS_x/rGO s were directly incorporated into sulfur cathodes, these structural differences led to distinct electrochemical behavior. The amorphous 1D MoS_3/rGO -250 catalyst delivers the highest specific capacity of $\sim 1277 \text{ mAh/g}$ at 0.1C due to its higher LPS adsorption capacity and abundant catalytic active sites. Meanwhile, the 2D MoS_2/rGO -600 catalyst provides superior electronic conductivity, faster charge-transfer kinetics, and excellent long-term cycling stability, achieving a coulombic efficiency of $\sim 97\%$ at 1C after 300 cycles.

Another independent study was conducted to develop a cathode electrolyte interphase (CEI), a protective thin layer on the cathode, using a rapid 10-second short-circuit method. The resulting CEI layer was selectively permeable, allowing Li^+ ions to pass through while effectively blocking LPS diffusion. This selective transport behavior significantly improved LPS confinement within the cathode region. When combined with the MoS_3/rGO -250-incorporated electrode, electrochemical testing revealed 25% higher capacity retention over 300 cycles, with a coulombic efficiency increase from 71% to 92%, demonstrating that a robust physical barrier on the cathode side can substantially mitigate LPS shuttling and enhance long-cycle performance.

Based on the first study's conclusion, where MoS_3 and MoS_2 show complementary behavior in delivering both capacity and reaction kinetics, and supported by the CEI findings that clarified how optimized interfaces minimize polysulfide diffusion, a new study was introduced

with the idea of using a dual-catalyst approach that brings together the strengths of both MoS_3 and MoS_2 catalysts to achieve cooperative polysulfide catalysis. In this configuration, 2D $\text{MoS}_2/\text{rGO-600}$ was integrated directly into the sulfur-carbon (S-C) cathode to enhance initial LPS adsorption, reaction kinetics, and reduce electron transfer resistance. At the same time, 1D $\text{MoS}_3/\text{rGO-250}$ was applied as a thin catalytic interlayer (denoted S-M6/M2) to enhance remaining LPS adsorption and complete the LPS conversion near the cathode–separator interface. This dual-catalyst architecture significantly improved LPS confinement and accelerated multi-step redox reactions. The S-M6/M2 system delivered an exceptional initial capacity of $\sim 1,417 \text{ mAh/g}$ at 0.1C and maintained $\sim 1,000 \text{ mAh/g}$ at 1C , with stable cycling over 500 cycles, demonstrating synergistic effects. The results of this dual-catalyst integrated cathode approach represent a substantial improvement over a mono-catalyst design.

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Major Professor
Dr. Jun Li

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Table 1: Glossary of frequently used abbreviations

ATM	Ammonium tetrathiomolybdate
CE	Coulombic efficiency
CEI	Cathode electrolyte interface
DM	Direct mixing of the catalyst with Sulfur
LCP	Long-chain polysulfide
LIB	Li-ion battery
LPS	Lithium polysulfides
LSB	Lithium sulfur battery
M2	MoS ₃ /rGO-250
M3	MoS _x /rGO-325
M6	MoS ₂ /rGO-600
OCV	Open circuit voltage
rGO	Reduced graphene oxide
SCP	Short-chain polysulfide
S-C	Sulfur in SuperP (C)
S-C\M	Catalyst interlayer followed by S-C cathode
SEI	Solid electrolyte interphase
THF	Tetrahydrofuran

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Dedication

I dedicate this work to my father, Kabir Bhuiyan, whose guidance from my earliest years shaped my values and taught me to become a good human being before anything else. His lessons on embracing failure gave me the courage to move forward even during the most challenging moments of my life. I also dedicate this work to my mother and my wife, whose sacrifices, love, and unwavering support have allowed me to grow and pursue my dreams. Finally, I extend this dedication to my sister and my entire family, who have stood beside me throughout this journey.

Preface

The dissertation comprises the following chapters,

Chapter 1: This chapter outlines the motivation and purpose of this dissertation by highlighting the importance of modern energy-storage systems and reviewing the working principles of various battery chemistries. Particular emphasis is placed on conversion-based batteries, specifically the lithium–sulfur battery (LSB), and their comparison to the current state-of-the-art lithium-ion battery (LIB). The chapter also discusses current strategies to improve LSB performance, and the materials used in these approaches, including the transition-metal sulfide materials that form the central focus of this dissertation.

Chapter 2: This chapter examines the material properties of 2D molybdenum sulfide and highlights the limitations of its bulk counterpart, particularly in its catalytic performance within the LSB cathode. It then outlines the synthesis protocol for MoS_x/rGO hybrids and discusses the drawbacks associated with micron-sized MoS_2 domains. In addition, this chapter presents the cathode-fabrication process parameters explored in this dissertation, including sulfur wt%, electrode thickness, compression, and heating methods, to optimize sulfur-cathode performance.

Chapter 3: This chapter presents the first published work from this dissertation ([*Chemical Engineering Journal*, 2025](#)). It details the synthesis routes for 1D MoS_3 chains and 2D MoS_2 nanopatches, emphasizing how increased active-site density enhances sulfur-cathode reaction kinetics. The chapter highlights the importance of selecting an appropriate catalyst to achieve the desired electrochemical performance. It also examines the role of the cathode-electrolyte interphase in improving cell stability and mitigating polysulfide shuttling.

Chapter 4: This chapter presents the second published paper from this dissertation (Materials Reports Energy, 2026). It demonstrates the interlayer-based mechanism used to enhance sulfur-cathode performance in terms of both capacity and cycling stability, while also providing additional protection to the lithium-metal anode. Furthermore, the chapter discusses the importance of selecting the appropriate catalyst for both the cathode and the interlayer, as well as the critical role of catalyst orientation in achieving optimal electrochemical performance.

Chapter 5: The final chapter of this dissertation presents the overall conclusions of these studies and offers perspectives on future research directions. It highlights how continued development of both the sulfur cathode and the lithium-metal anode is essential for advancing lithium-sulfur batteries toward commercial viability.

Chapter 1 - Introduction

1.1 Motivation

Global warming has become one of the most pressing challenges of the 21st century, driven largely by the continuous rise in atmospheric CO₂ concentrations from fossil-fuel combustion [1]. Automobile, particularly gasoline [2] and diesel-powered vehicles, remains a major contributor, as internal-combustion engines release significant amounts of CO₂ during fuel oxidation [3], as shown in Fig. 1.1. As global vehicle ownership increases, emissions from the transportation sector continue to accelerate climate change and worsen air quality. This challenge is amplified by the fact that the world's two largest economies, China and the United States, are also the largest CO₂

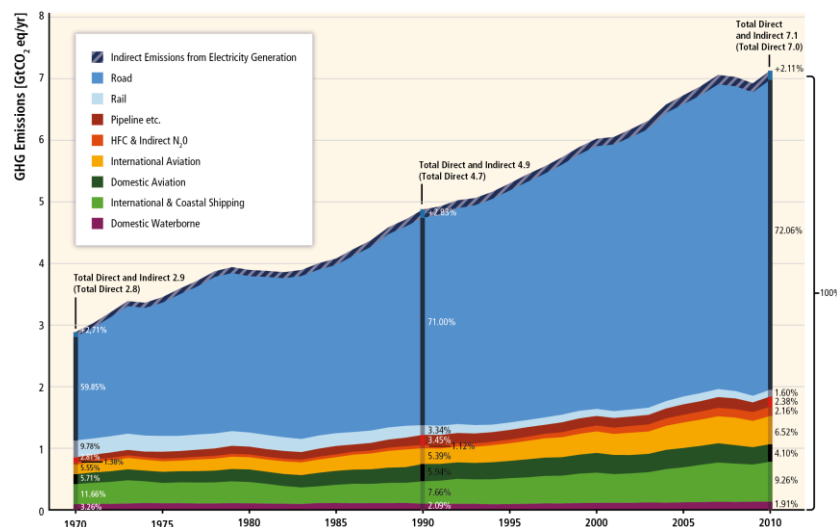


Figure 1.1. A statistic of the greenhouse gas emissions from the global transport sector using internal combustion engines. Reprinted from ‘Cars of the future that will help fight climate change–Imagine newsletter, (<https://theconversation.com/cars-of-the-future-that-will-help-fight-climate-change-imagine-newsletter-3-118289>)’.

emitters. China contributes roughly one-third of global CO₂ emissions, while the United States accounts for about 14-15%, together representing nearly half [4] of the world's annual carbon output. Reducing emissions from these regions is therefore essential for any meaningful global climate-mitigation strategy.

One of the most effective pathways to lowering transportation-related CO₂ emissions is the widespread adoption of electric vehicles (EVs) [5], which eliminates tailpipe emissions and can be powered by increasingly renewable electricity sources. However, the transition to EVs and renewable-energy-dominated grids requires energy-storage systems with far higher energy density, longer cycle life, and lower cost than conventional lithium-ion batteries (LIB) can provide. This creates a critical need for next-generation battery technologies, such as lithium-sulfur battery (LSB) systems [6, 7], that can support long-range EVs, stabilize intermittent renewable power, and enable large-scale decarbonization of the transportation sector.

1.2 Fundamentals of Battery Chemistry

Batteries operate by converting electrochemical energy into electrical energy through redox reactions occurring at two opposite electrodes [8], an anode and a cathode, separated by an ion-conducting electrolyte. Electron transfer in a battery originates from the intrinsic difference in electrochemical potential between the two electrode materials. Each material has a characteristic tendency to either lose electrons (oxidize) or gain electrons (reduce), determined by its internal energy state [9] and the stability of its ions. When two materials with different electrochemical potentials are paired in the same cell and connected through an external circuit, the system naturally moves toward a lower-energy, more thermodynamically stable state. This energy-lowering process drives electrons to flow spontaneously from the anode, where the electrons in the chemical species are at a higher free energy, to the cathode, where they reside at a lower free-energy state.

The electrolyte [10, 11] plays a crucial role by allowing ions to migrate between the electrodes while preventing electrons from crossing internally. This maintains charge neutrality as electrons travel through the external circuit to perform external work. During discharge, the anode

undergoes oxidation, releasing electrons, while the cathode undergoes reduction by accepting those electrons. Charging reverses these reactions by forcing electrons back toward the anode by applying an external voltage. The magnitude of the chemical driving force is reflected in the open-circuit voltage of the cell, and the total amount of charge corresponds to the specific capacity of the electrode materials.

Intercalation-based [12-15] systems, such as LIB, store energy by inserting and extracting ions into stable host structures without significantly altering the crystal framework. This mechanism provides excellent cyclability, but the capacity is limited because only a finite number of intercalation sites are available. In contrast, conversion-based systems, such as LSB [16, 17], Li-O₂ batteries [18-20] and Zn-O₂ batteries [21-23], rely on the full chemical transformation of the active materials. Instead of occupying interstitial sites, lithium reacts directly with the cathode active material to form a new chemical product that involves the transfer of multiple electrons during this process, enabling much higher theoretical capacities but introducing challenges related to reversibility, kinetics, and electrode stability associated with the chemical reaction. The following sections examine these two fundamental battery chemistries in detail, highlighting the mechanistic principles that govern their performance and limitations.

1.2.1 Intercalation-Chemistry Batteries

Intercalation batteries store energy through the reversible insertion and extraction of ions into layered or framework-type host structures without significantly altering the crystal framework and new chemical formation. In LIB, lithium ions shuttle between the anode [24] (typically

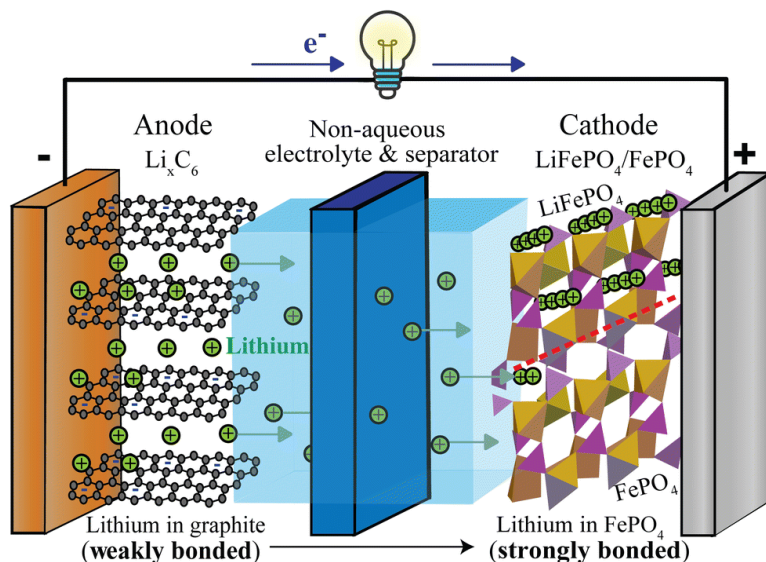


Figure 1.2. A schematic of the Li-ion battery describing the intercalation process, Reprinted with permission from Finkelstein et al., *Physical Chemistry Chemical Physics*, 2024, 26, 24157. Copyright 2024 Royal Society of Chemistry.

graphite) and the cathode (such as Lithium Cobalt Oxide, LiCoO_2 [25], Lithium Nickel Manganese Cobalt Oxide or NMC [26], or Lithium Iron Phosphate or LFP [27]) during cycling. The host materials maintain their structural integrity, serve as a host to store Li ions and release them to occupy interstitial sites in the anode [12, 28] during charging and to vacate them during discharge. Because the redox reactions occur on transition-metal centers within a stable lattice, the process is highly reversible and supports long cycle life. During discharge, lithium ions de-intercalate from the anode and migrate through the electrolyte toward the cathode, while electrons travel through the external circuit. Charging reverses this process, driving lithium ions back into the anode. The stability of the host structures enables excellent cyclability, but the finite number of available

intercalation sites limits the capacity. As a result, intercalation cathodes are fundamentally capped at capacities below ~ 200 mAh/g [29-32], which restricts the wide scale adoption of LIB for large energy need applications.

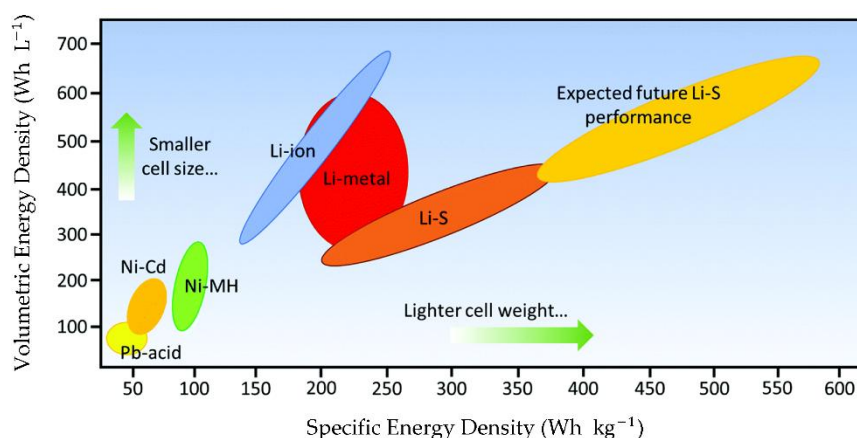


Figure 1.3. Ragone plot comparing different rechargeable battery technologies as a function of specific and volumetric energy densities. Reprinted with permission from E. Cha, et.al., Nanoengineering to achieve high efficiency practical lithium–sulfur batteries, Nanoscale Horizons 5(5) (2020) 808-831. Copyright 2020 Royal Society of Chemistry.

From the Ragone plot [33] in Fig. 1.3, it can be observed that the Li-ion battery has reached the theoretical capacity threshold, limiting further improvements in long-range, lightweight energy-storage systems. As shown here, early Ni-Cd and Pb-acid systems offered very low energy density, while modern LIB, based on intercalation chemistry, represent a major advancement with significantly higher energy density. However, even state-of-the-art LIB faces intrinsic limitations as discussed above. These constraints highlight the need to move toward next-generation chemistries such as LSB, which offer much higher theoretical energy density and the potential to meet modern energy-storage demands.

1.2.2 Conversion-Chemistry Batteries

Conversion-based batteries store energy through a full chemical transformation [34-36] of the active materials rather than simple ion insertion. LSB is a prime example in which sulfur undergoes multi-electron redox reactions to form a series of lithium polysulfides and ultimately Li_2S , as shown in Figure 1.4. Instead of occupying interstitial sites, lithium reacts directly with sulfur to form new chemical species, known as lithium polysulfides (Li_2S_n , $4 \leq n \leq 8$), which ultimately form lithium sulfide (Li_2S), enabling much higher specific capacities and energy density.

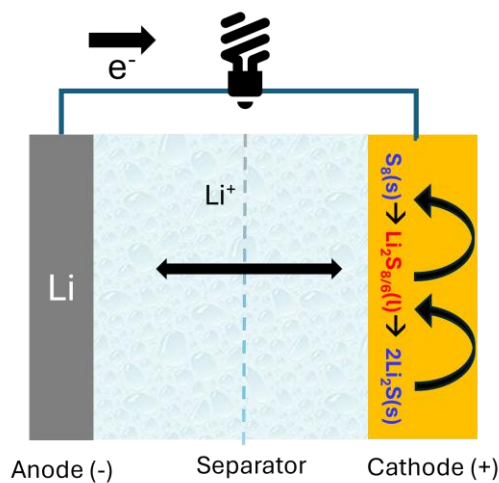


Figure 1.4. A schematic detailing the chemistry of the Li-S battery.

During discharge, sulfur (S_8) is reduced stepwise to long-chain and short-chain lithium polysulfides, and finally to insoluble solid Li_2S . The anode, typically lithium metal, undergoes oxidation to release Li^+ ions and electrons. Charging reverses these reactions, converting Li_2S back to elemental sulfur. Because each sulfur atom can accept two electrons, the theoretical capacity reaches 1,675 mAh/g [37-39], far exceeding intercalation-based systems. As a next-generation energy storage platform, LSB offers a compelling alternative because sulfur undergoes a multi-electron conversion reaction that delivers a much higher theoretical specific energy of

2600 Wh/kg and practical values potentially exceeding 500-600 Wh/kg. Beyond their superior energy density, LSBs rely on sulfur, an abundant, low-cost, and environmentally benign material, rather than the scarce and expensive transition-metal oxides used in LIB cathodes. This combination of higher energy density, lower material cost, and improved sustainability makes LSB a promising next-generation technology capable of meeting the increasing demands for long-range electric vehicles, grid-scale storage, and lightweight portable power.

However, since the conversion system produces new chemical species, the property of the intermediate species introduces challenges absent in intercalation batteries and limits the overall performance. For example, the intermediate polysulfides in the LSB system are soluble in common ether electrolytes and can migrate between electrodes, causing the well-known polysulfide shuttle effect [40-42]. Furthermore, the volume expands by almost 80% after full discharge, which creates severe mechanical stress on the cathode. Additionally, sulfur and Li_2S are electrically insulating, requiring conductive hosts and catalytic materials to facilitate efficient redox reactions. The lithium metal anode also suffers from dendrite [43-45] formation and instability during cycling.

1.3 History of LSB

The development of LSB can be traced back to the early exploration of high-energy electrochemical systems in the 1960s [46], when sulfur first attracted attention as a cathode material due to its exceptionally high theoretical specific capacity. Early research recognized sulfur's ability to undergo multi-electron redox reactions, offering far greater energy density than the intercalation-based cathodes used in lithium-ion batteries. However, practical progress was limited by the instability of lithium metal [47] and the solubility of intermediate lithium polysulfides (LPS) [48], which caused rapid capacity fading. Despite these challenges, the fundamental promise of the LSB chemistry motivated continued investigation.

The first wave of experimental LSB research began in the 1980s [49, 50], when researchers attempted to pair sulfur cathodes with lithium metal anodes in liquid electrolytes. These early prototypes demonstrated the feasibility of chemistry but suffered from severe polysulfide shuttling and poor cycle life. Intensified research efforts focused on understanding the electrochemical pathways of sulfur reduction and the formation of soluble lithium polysulfides, which were identified as the primary cause of self-discharge and rapid degradation. This decade marked the beginning of systematic attempts to control polysulfide dissolution through cathode confinement strategies and electrolyte optimization.

The early 2010s saw breakthroughs driven by advances in nanomaterials and carbon hosts by Linda Nazar [51, 52] to infuse sulfur inside the conductive carbon nano-channels to confine the polysulfide within the carbon matrix. Following on, researchers have begun incorporating sulfur into porous carbons [53-56], graphene [57-60] frameworks, and conductive polymers [61-63] to improve electrical conductivity and physically trap polysulfides. These innovations significantly improved sulfur utilization and cycle life, establishing LSB as a leading candidate for next-generation high-energy storage platforms. During this period, LSB gained attention for aerospace and defense applications due to its extremely low weight and high theoretical energy density, which can exceed 2,500 Wh/kg, nearly an order of magnitude higher than conventional LIB.

By the mid-2010s, LSB research expanded globally, with thousands of publications addressing challenges such as the shuttle effect, lithium-metal instability, and the insulating nature of sulfur and Li_2S [64-66]. Industrial interest also grew, with companies and research institutions exploring LSB prototypes for electric vehicles, drones, and grid storage. Reviews from this period emphasized that LSB could displace lithium-ion technology due to its higher energy density and

lower cost, particularly because sulfur is abundant and inexpensive compared to transition-metal-based cathodes.

In recent times, LSB development accelerated further as researchers introduced advanced catalysts, solid-state electrolytes [67-69], and protective interphases, such as CEI/SEI [70-72] to stabilize both the sulfur cathode and lithium metal anode. Modern studies highlight that LSB remains one of the most promising “beyond-LIB” chemistries, capable of meeting the energy demands of long-range electric vehicles and high-altitude aerospace systems. Recent analyses emphasize that LSBs are now approaching commercial viability, with ongoing efforts focused on improving cycle life and scaling manufacturing processes.

Overall, the history of LSB reflects steady progression from conceptual promise to practical feasibility. From early sulfur cathode experiments in the 1960s to today’s sophisticated nanostructured cathodes and engineered interfaces, LSB technology has evolved into a leading candidate for next-generation high-energy-density storage systems. Continued advances in materials design, electrolyte chemistry, and lithium-metal protection are expected to bring LSB closer to widespread commercialization in the coming decade.

1.4 Working Principle and Challenges of LSB

LSB represents one of the most promising next-generation electrochemical energy-storage systems due to its exceptionally high theoretical specific capacity and the natural abundance of sulfur. Unlike conventional LIB, which rely on the reversible intercalation of lithium ions into layered or framework-type host structures, LSB batteries operate through a multi-electron conversion reaction [9, 73, 74] between elemental sulfur and lithium metal, shown in Fig. 1.5(a).

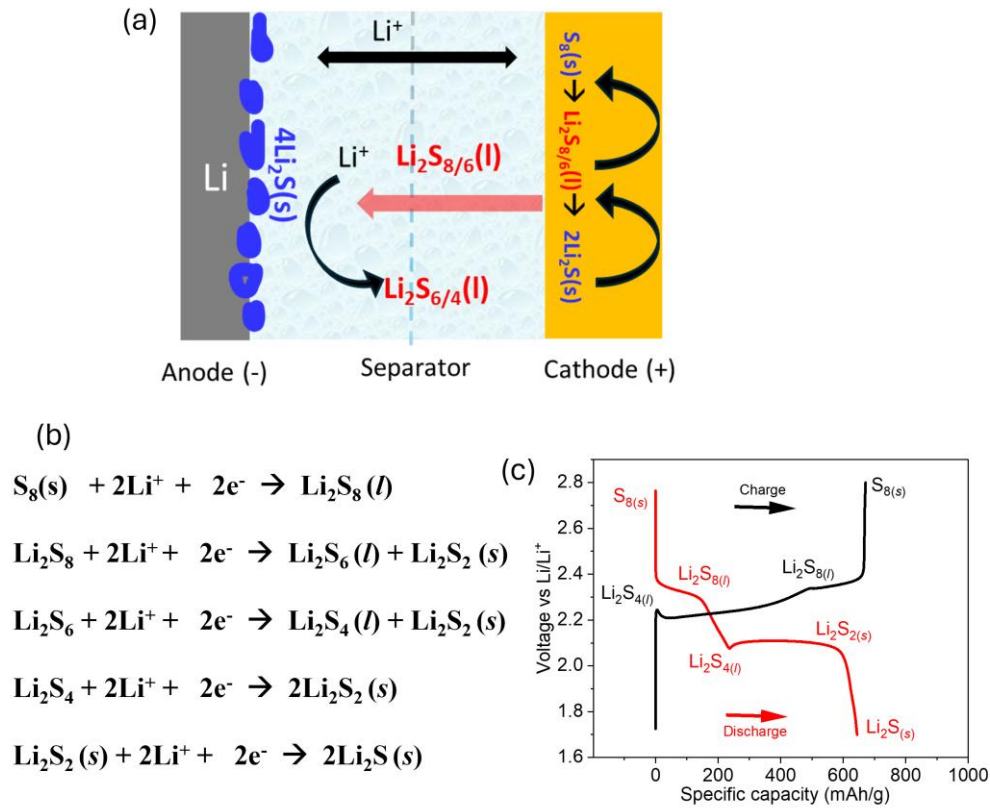


Figure 1.5. (a) Graphical illustration of the polysulfide shuttling process in LSB during charge-discharge operation. (b) Redox reactions of LSB, and (c) a typical charge–discharge profile in a traditional liquid Li–S cell.

A typical Li-S cell consists of a lithium metal anode, an ether electrolyte, and a sulfur-carbon composite cathode, as depicted below in Fig. 1.5(a). As sulfur exists in its fully oxidized

state (S_8), the cell is assembled in a 100% charged state, and operation begins with a discharge. During discharge, lithium metal at the anode side undergoes oxidation, releasing Li^+ ions and electrons. The Li^+ ions migrate through the electrolyte toward the cathode, while electrons travel through the external circuit to perform electrical work. On the other side at the cathode, sulfur undergoes a series of reduction reactions, forming soluble long-chain lithium polysulfides [74] or LCP (Li_2S_8 - Li_2S_6 - Li_2S_4). This first discharge reaction in LSB is often described in the literature as a three-step process, but there is no direct fundamental evidence confirming that this pathway is exclusive. A more realistic mechanism likely involves mixed reaction routes in which long-chain polysulfides (LCPs) can form through multiple but parallel steps. For example, S_8 can convert directly to Li_2S_4 through a four-electron transfer process, contributing roughly 25% of the theoretical capacity. From this point, the LCPs undergo further reduction through a twelve-electron transport sequence to generate short-chain polysulfides (Li_2S_4 to Li_2S_2) and ultimately the insoluble endproduct Li_2S . This multi-step redox pathway produces two characteristic discharge plateaus: the upper plateau near 2.3 V corresponds to the reduction of S_8 to long-chain polysulfides, LCP, as demonstrated in the charge discharge profile in Fig. 1.5(c), while the lower plateau near 2.1 V corresponds to the formation of short-chain polysulfides and Li_2S . Charging reverses this sequence, converting Li_2S back to sulfur through the oxidation of intermediate polysulfides. The theoretical capacity of sulfur (1,675 mAh/g) and the high capacity of lithium metal [75, 76] (3,860 mAh/g) together enable a theoretical gravimetric energy density exceeding 2,500 Wh/kg, far surpassing the limits of intercalation-based lithium-ion systems. However, the same conversion chemistry that provides this high energy density also introduces several intrinsic challenges that must be addressed for LSB to achieve practical viability.

One of the most critical challenges in LSB is the polysulfide shuttle effect [40, 41, 77, 78], which arises from the solubility and mobility of intermediate lithium polysulfides in ether DOL-DME electrolytes shown in Fig. 1.5 (a). This is the major focus of this dissertation to address and mitigate the polysulfide shuttling effect so that the LSB can be cycled with higher specific capacity and lifetime. During discharge, long-chain polysulfides dissolve into the electrolyte and diffuse away from the cathode. Driven by concentration gradients, these soluble species migrate toward the lithium metal anode. Upon reaching the anode, polysulfides undergo parasitic reduction reactions, forming SCP and Li_2S deposits on the anode surface. These reduced species, SCP, can then diffuse back toward the cathode, where they are re-oxidized, creating a continuous redox loop known as the shuttle mechanism. This phenomenon leads to several detrimental effects, including loss of active material, lithium metal corrosion, low coulombic efficiency, and severe self-discharge [79, 80]. Because polysulfides react chemically with lithium metal even when the cell is at rest, the open-circuit voltage gradually decreases, and the cell loses capacity without delivering useful work. The shuttle effect also increases charge overpotential, as additional energy is consumed in reversing parasitic reactions rather than restoring the active material. In severe cases, the shuttle mechanism can lead to infinite charging behavior [81], where the cell voltage fails to rise to the cutoff threshold because polysulfides are continuously consumed on the anode. There have been a few major methods to address and mitigate this polysulfide shuttle effect, such as physically confining sulfur within porous hosts, chemically [82-84] anchoring polysulfides using polar materials, catalytically accelerating polysulfide conversion, and utilizing interlayers [85-87] or modified separators [60, 88] to block polysulfide migration. Despite significant progress, eliminating the shuttle effect remains one of the most persistent obstacles to commercializing LSB.

Another fundamental challenge in LSB is the large volume change [89-91] associated with the conversion of sulfur to lithium sulfide. During full discharge, sulfur undergoes an approximate 80% volume expansion as it transforms into Li_2S . This dramatic structural change generates substantial mechanical stress within the cathode, leading to electrode pulverization, cracking, and loss of structural integrity. As sulfur particles expand and contract during cycling, they can detach from the conductive carbon matrix, disrupting the electron pathways and reducing the utilization of active material. The formation of isolated Li_2S regions, which are electrically disconnected from the conductive network, further contributes to irreversible capacity loss. These mechanical instabilities are particularly problematic at high sulfur loadings, where the electrode architecture must support large amounts of active material while maintaining mechanical resilience. Designing cathode structures that can accommodate volume changes, such as hollow carbon spheres, flexible graphene frameworks, and elastic polymer matrices, is therefore essential for achieving long cycle life in LSB.

Conductivity [92-94] limitations represent another major barrier where both sulfur and its discharge product, Li_2S , are electrical insulators, with conductivity many orders of magnitude lower than that of typical intercalation cathodes. This extremely low conductivity severely limits reaction kinetics and sulfur utilization. Without conductive carbon additives, such as carbon black (superP), sulfur cannot effectively participate in redox reactions, necessitating the incorporation of large amounts of conductive carbon. The insulating nature of Li_2S [95-97] also leads to high nucleation barriers during charging, requiring elevated overpotentials to initiate Li_2S oxidation. This increases energy loss, accelerates electrolyte decomposition, and contributes to capacity fading. To overcome conductivity limitations, researchers have developed conductive sulfur hosts such as carbon nanotubes, graphene, porous carbons, and metal sulfides. Catalytic materials,

including transition-metal sulfides, nitrides, and metal–nitrogen–carbon frameworks, have also been introduced to accelerate polysulfide conversion and reduce overpotential. Despite these advances, achieving uniform, low-resistance electron pathways throughout the cathode remains a key challenge.

Beyond the major issues of polysulfide shuttling, the lithium metal anode, while offering high capacity, suffers from dendrite formation, surface passivation, and continuous electrolyte consumption. Dendrites can penetrate the separator and cause short internal circuits, posing significant safety risks. The instability of the lithium metal surface also leads to the formation of a thick, resistive solid-electrolyte interphase (SEI), which increases impedance and accelerates capacity fading. Electrolyte consumption is another concern, as polysulfides react with the electrolyte, leading to solvent decomposition and increased viscosity. High electrolyte-to-sulfur ratios (E:S) are often required to achieve good performance, but these conditions reduce the practical energy density of the cell. Additionally, achieving high sulfur loading ($>5 \text{ mg/cm}^2$) and lean electrolyte conditions, both essential for commercial viability, remains difficult due to the combined effects of poor conductivity, slow kinetics, and mechanical instability. Rate capability is also limited by the multi-step redox reactions and slow solid-state diffusion processes inherent to the Li-S chemistry, making fast charging and high-power applications challenging.

1.5 Approaches to Solve LSB Problems

Any practical LSB architecture must incorporate strategies that either confine LPSs physically, chemically anchor them, or catalyze their rapid conversion of LCP to Li_2S to minimize their residence time in solution. In this context, multiple complementary approaches have been developed and should be treated methodologically in a thesis: porous nanostructured carbon hosts

such as CMK-3 [51] to physically confine sulfur and LPSs; ion-selective [98, 99] or functional membranes that regulate Li^+ /polysulfide transport; incorporation of catalysts into the cathode to accelerate sulfur redox; hybrid systems that combine conductive carbon frameworks with polar or catalytic components; and interlayers inserted between cathode and separator that serve as selective physical and chemical barriers. Each of these methods addresses a different step along the polysulfide migration pathway, and a detailed methodology section should specify not only the synthesis and cell fabrication steps but also how structural design, surface chemistry, and electrochemical testing are integrated to quantify and compare shuttle suppression.

1.5.1 Carbon Scaffold for Physisorption

Carbon materials are widely used as sulfur hosts in Li-S cathodes because they simultaneously address sulfur's poor conductivity, large volume change, physisorption of polysulfide, and electrochemical stability under the working potential window. Porous carbons (microporous, mesoporous, and hierarchical structures) provide high surface area and tunable pore networks that physically confine dissolved polysulfides inside the carbon framework, improving sulfur utilization and cycling stability. Classic examples include ordered mesoporous carbons such as CMK-3 [51] and hollow carbon spheres, where the internal cavities and mesopores store sulfur, buffer its volume expansion during lithiation, and slow the outward diffusion of lithium polysulfides into the bulk electrolyte, an approach pioneered by Nazar and coworkers using ordered mesoporous carbons such as CMK-3 to yield an ordered 2D hexagonal array of carbon rods with uniform mesopores (3-10 nm) and high surface area. Scientifically, the ordered mesopores and high conductivity of CMK-3 provide two key functions: physical confinement of sulfur/LPSs and continuous electron pathways. The pore size is tuned such that long-chain LPSs

are sterically confined, and their diffusion into the bulk electrolyte is restricted, while the interconnected carbon framework ensures that insulating S and $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ remain electronically wired during redox conversion. One and two-dimensional [100, 101] carbons, carbon nanotubes [82, 102-105], carbon nanofibers, and graphene build highly conductive percolation networks through the cathode, enabling fast electron transport while also forming flexible, mechanically robust scaffolds that help maintain electrode integrity at high sulfur loading. More recently, heteroatom-doped carbons [56, 106, 107] (e.g., N-doped nanospheres or sheets) and defect-rich carbon have been developed to add chemical affinity. Despite all of the efforts, Carbon materials provide high surface area and good conductivity, but their intrinsically nonpolar surfaces interact only weakly with polar lithium polysulfides that cannot be improved much even with polar heteroatom doping. As a result, polysulfide retention on carbon is dominated by physical adsorption, which offers limited binding strength and capacity. Once the carbon surface becomes saturated, it cannot effectively regenerate active sites, leading to rapid loss of adsorption capability and diminished electrochemical performance. These limitations have motivated the exploration of alternative strategies that incorporate polar or catalytic materials to achieve stronger chemical interactions and more efficient polysulfide conversion.

1.5.2 Ion-Selective Membrane

Ion-selective membranes [99, 108, 109] function by allowing the passage of desired ionic species, typically Li^+ , while blocking the transport of unwanted anions such as soluble lithium polysulfides (LPS), thereby mitigating the shuttle effect and improving cycling stability in LSB.

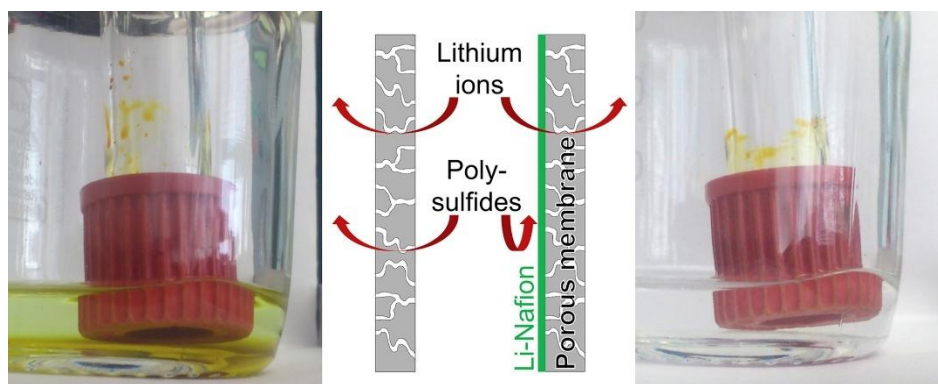


Figure 1.6. Graphical illustration of trapping polysulfides using ion selective membrane. (Reprinted with permission from ‘I. Bauer et al., Journal of Power Sources 251 (2014) 417-422). Copyright 2014 Elsevier Ltd.

These membranes operate through a combination of cation exchange, size exclusion, electrostatic repulsion, and chemical affinity, enabling selective ion transport while suppressing polysulfide crossover. Several classes of ion-selective membranes have been developed for LSB. Cation-selective polymer coatings, such as Nafion [108, 109], applied onto polypropylene separators (Celgard 2400) by a simple drop coating procedure, the ionomer electrolyte is composed of the lithiated-nafion ionomer film create a dense sulfonated layer that repels negatively charged polysulfides while maintaining high Li^+ conductivity; this approach significantly enhances charge efficiency and reduces active-material loss. Functionalized porous membranes, including covalent organic frameworks [110] (COF)-based hybrid separators, incorporate well-defined pore structures and heteroatom-rich frameworks that provide strong chemisorption sites for polysulfides while simultaneously catalyzing their conversion. When combined with conductive scaffolds such as graphene, these COF-based membranes further accelerate redox kinetics and improve rate

performance. In a different approach, a sub-nanoscale ion-sieving membrane [111] was developed to selectively regulate Li^+ transport by combining the angstrom-level channels of stacked graphene oxide with the negative charge of polydopamine (PDA). The ultra-narrow channels block bulky lithium polysulfide ion pairs, while PDA enhances Li^+ desolvation and raises the migration barrier for PS^- species, giving the membrane strong Li^+ selectivity. Covalent bonding between PDA and GO stabilizes the channel size and prevents swelling in organic electrolytes. With its ultrathin structure, the membrane adds almost no inactive mass yet effectively suppresses polysulfide shuttling and lithium dendrite growth, enabling long-term stability. Together, these ion-selective membrane strategies demonstrate how tailored chemical functionality, controlled porosity, and selective ion transport can be leveraged to suppress polysulfide migration, enhance catalytic activity, and enable high-performance LSB.

1.5.3 Catalyst Incorporation

A third route focuses on incorporating an electrocatalyst [112-114] within the sulfur cathode to accelerate the multi-electron sulfur redox reactions and shorten the residence time of soluble intermediates, thus electrochemically suppressing the shuttle effect. An electrocatalyst reduces polysulfide shuttling by accelerating the redox conversion of lithium polysulfides (LPS) at the cathode, preventing their accumulation and diffusion into the electrolyte. In an LSB, slow LPS conversion leaves long-chain species dissolved in the electrolyte, where they readily migrate to the lithium anode and trigger the shuttle effect. An effective electrocatalyst provides abundant active sites and fast charge-transfer pathways that promote higher adsorption with optimal binding energy, faster electron transfer, and stepwise conversion of LPS into shorter-chain intermediates and ultimately solid Li_2S . By lowering the activation energy and improving reaction kinetics, the

catalyst shortens the residence time of soluble LPS in the electrolyte, thereby reducing their concentration at the cathode and mobility toward the anode. This electrokinetic acceleration not only suppresses shuttling but also enhances sulfur utilization, decreases polarization, and stabilizes long-term cycling performance. The method consists of choosing catalytically active materials such as transition metal sulfides/oxides, metal–N–C sites, and single-atom catalysts, etc. Since most of the electrocatalysts are not good electrical conductors, an increasingly common approach is to construct hybrid cathodes [115] that couple a conductive carbon host to anchor these catalyst materials, thereby combining chemical anchoring and catalytic conversion in one integrated architecture. Here, carbon provides a high-surface-area, electrically continuous skeleton (e.g., carbon nanotubes, graphene, hollow carbon spheres), while a catalyst, such as metal sulfides/oxides, doped heterostructures, redox-active organics, or single-atom sites, anchors LPSs and catalyzes redox.

1.5.4 Interlayer Method

Finally, insertion of an interlayer [85, 116-120] as a physical and functional barrier between the sulfur cathode and the separator is a particularly versatile strategy that can be compared to an integrated method of the catalyst incorporation followed by the ion-selective membrane in a different way than we describe in the previous sections. Interlayers are typically thin, lightweight, and electronically conductive/catalytic films, often composed of porous carbon, conductive polymers, or carbon–catalyst hybrids, placed directly on the separator or on the cathode side to intercept migrating LPSs and catalyze them into insoluble Li_2S and prevent them from diffusing to the anode compartment. The method involves fabricating a free-standing or separator-supported

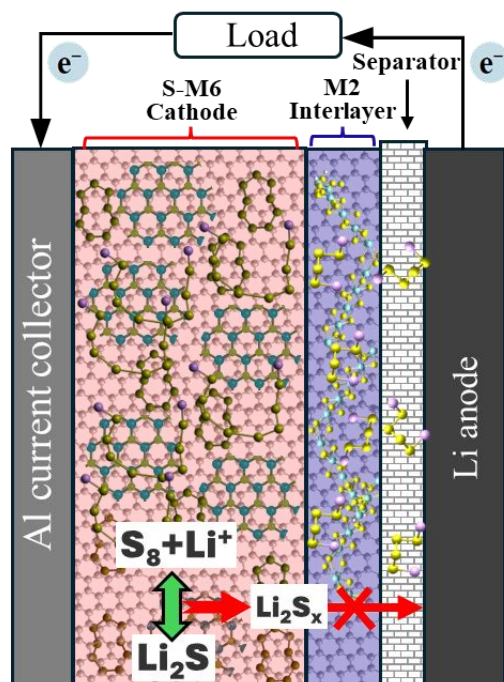


Figure 1.7. Graphical illustration of the interlayer thin film to improve Li-S battery performance.

interlayer by vacuum filtration, casting, or coating: for instance, dispersing carbon nanotubes or graphene with a polymer binder and optional catalyst in a solvent, filtering through a membrane to form a uniform film, peeling and drying to obtain a flexible interlayer of controlled thickness, and then stacking it between the separator and cathode during cell assembly. Alternatively, Janus-type interlayers can be prepared with two functional faces, for example, a conductive carbon side facing the cathode for physical confinement and electron transport, and a polar or catalytic side facing the separator to chemically adsorb and convert LPSs.

The functional role of interlayers is to physically/chemically confine the polysulfide within the cathode compartment and provide additional adsorption capacity and reaction sites along the LPS migration path, thereby promoting their reconversion to sulfur or Li_2S instead of allowing them to reach the lithium anode. Experimental protocols for evaluating interlayers include: (i) direct comparison of cells with and without interlayers under identical sulfur loading and

electrolyte/sulfur ratio; (ii) analysis of coulombic efficiency, capacity retention, and rate capability; and (iii) post-cycling characterization of the lithium anode surface (SEM, XPS) to quantify the extent of Li_2S /sulfur species deposition and surface roughening. Literature reports show that properly engineered interlayers, such as conductive polymer-based films or carbon interlayers, can significantly increase reversible capacity and preserve smooth lithium surfaces, confirming efficient suppression of the shuttle effect. When integrated into a comprehensive cell design that also employs optimized carbon hosts, catalysts, and membranes, interlayers can act as a final safeguard, ensuring that any LPSs that escape the cathode matrix are captured and reconverted before causing parasitic reactions. This work focused on developing a thin interlayer of carbon-supported catalyst and is discussed in Chapter 4 in detail. This thesis focuses on developing a hybrid catalyst/carbon electrocatalyst and incorporating it directly into the cathode as well as applying it onto the separator to improve LSB performance. It is therefore essential to examine the current status of materials being used to overcome these obstacles.

Before introducing specific catalyst materials, it is important to first outline how electrocatalysts function in mitigating the polysulfide shuttle in Li-S batteries. During cycling, sulfur undergoes a widely accepted multistep reduction sequence ($\text{Li}_2\text{S}_{8(l)} \rightarrow \text{Li}_2\text{S}_{6(l)} \rightarrow \text{Li}_2\text{S}_{4(l)} \rightarrow \text{Li}_2\text{S}_{2(s)} \rightarrow \text{Li}_2\text{S}_{(s)}$), producing intermediates with different solubilities and reactivities. The long-chain polysulfides, LCP, formed early in this pathway are highly soluble and liquid in normal conditions in the electrolyte and can diffuse away from the cathode, where they undergo unwanted redox reactions at the lithium metal surface. This continual migration and parasitic reaction, commonly known as the polysulfide shuttle, leads to loss of active material and poor reversibility. Electrocatalysis has emerged as a powerful strategy to address these intrinsic challenges by directly accelerating the sulfur redox reactions. Unlike approaches that rely solely on physical confinement

or chemical trapping, catalytic materials can lower kinetic barriers [121], improve the reversibility of the solid–liquid–solid transitions, and regulate the nucleation and growth of Li_2S [122] without being limited by the adsorption capacity. These catalytic effects become significant under practical conditions such as high sulfur loading and limited electrolyte volume, where sluggish intermediate conversion and insulating discharge products severely restrict performance.

1.6 Mechanistic Roles of Catalysts in LSB Chemistry

The sulfur reduction reaction governs the discharge process in Li-S cells. Elemental sulfur reacts with Li^+ to form a series of soluble and insoluble polysulfide intermediates, ultimately yielding solid Li_2S . This multistep reaction involves three fundamental processes: (i) adsorption of polysulfides onto the host surface [123], (ii) migration of adsorbed polysulfide to the catalytic site [124], and (iii) conversion of adsorbed intermediates into solid products [125].

During charging, these steps occur in reverse as Li_2S is oxidized back to sulfur. Each stage introduces kinetic barriers that can limit overall battery performance, and catalysts are designed to

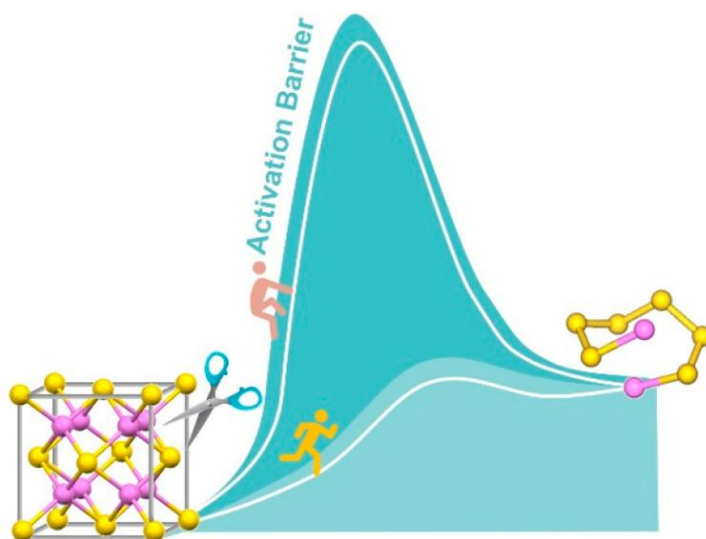


Figure 1.8. (a) Catalytic reduction of the energy barriers associated with LPS conversion. Reprinted with permission from Hualin Ye et al., ACS Energy Letters, 2020, 5 (7), 2165–2173. Copyright 2020 American Chemical Society.

modulate and reduce the energy barrier for these steps to accelerate the full redox sequence faster, as shown in Fig. 1.8. These sections discuss these processes in detail below.

1.6.1 Adsorption

The first prerequisite for a catalytic reaction is the capture of the analytes on the catalyst surface, which are the soluble polysulfides. Without proper interactions on the cathode surface, dissolved long-chain LPSs are introduced into the electrolyte and migrate toward the anode. Catalysts can immobilize these species through a variety of interactions, including chemical bonding [126] (e.g., Li–X or X–S bonds), Lewis’s acid–base interactions [127], or orbital coupling such as d–p hybridization between transition-metal sites and sulfur atoms [128]. Tailoring the electronic structure, by adjusting the band structure, introducing polar functional groups, or modifying the surface charge distribution, enables fine control over adsorption strength. Effective adsorption suppresses the shuttle effect and increases the local concentration of reactive intermediates, enabling faster downstream conversion. Both electronic structure tuning and surface polarity engineering are commonly used to optimize LPS binding.

However, adsorption must be balanced; this balance often follows a volcano-type trend, known as the Sabatier principle [129, 130]. The Sabatier principle applies directly to lithium polysulfide (LPS) conversion in LSB, where catalytic activity depends on achieving an optimal balance between adsorption strength and reaction kinetics. In this system, the catalyst must bind LPS intermediates strongly enough to anchor them at the cathode surface and suppress shuttling, yet not so strongly that the reduced species, such as Li_2S_4 or solid Li_2S_2 , become immobilized and unable to desorb or further convert. A Sabatier-type volcano relationship emerges as shown in Fig. 1.9, where weak adsorption leads to poor LPS capture, sluggish redox conversion, and severe shuttle effects, while excessively strong adsorption traps intermediates, blocks active sites, and promotes irreversible surface passivation. This behavior is often illustrated through a Sabatier plot, where catalytic performance peaks at intermediate binding energy and declines on either side due to insufficient or excessive adsorption strength. In Li-S electrochemistry, overly strong LPS binding can hinder Li_2S nucleation and decomposition, slow charge-transfer kinetics, and cause progressive capacity loss over cycling. Designing catalysts with adsorption energies near the

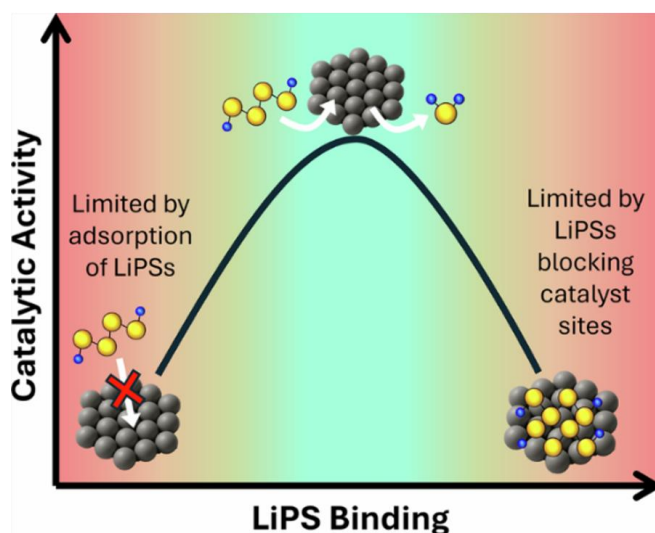


Figure 1.9. Volcano Plot demonstrates the binding energy and catalytic efficiency relationship, which can be explained by the well-known. Reprinted with permission from S. Lateef, et. al., Mechanistic roles and design criteria for catalysts in lithium–sulfur batteries, *Communications Materials* 6(1) (2025) 282. Copyright 2025 Nature.

Sabatier optimum is therefore essential for achieving fast LPS conversion, high sulfur utilization, and stable long-term cycling in LSB.

1.6.2 Diffusion

In sulfur cathode design, it is essential to distinguish simple polysulfide adsorption from true electrocatalytic conversion. Adsorption alone can immobilize lithium polysulfides (LPSs) and suppress their shuttle, but if the adsorption sites are not catalytically active or if the adsorbate cannot migrate to nearby active centers, the system remains limited by slow redox kinetics [124,

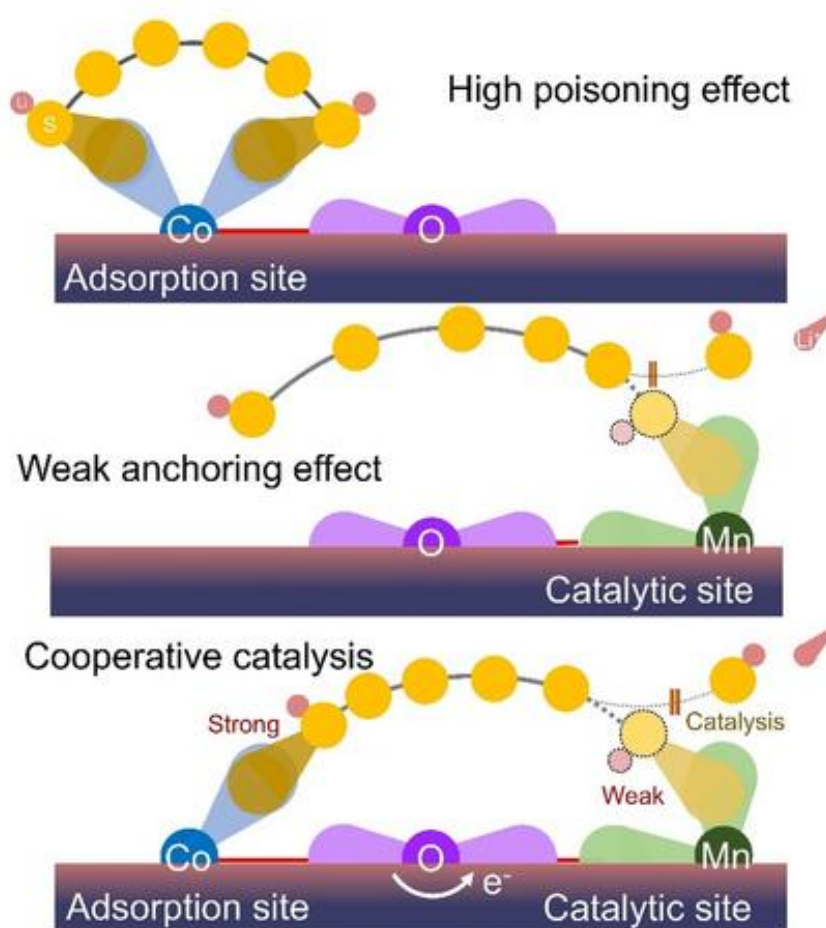


Figure 1.10. (a) Schematic illustration of the underlying mechanism for the consecutive “adsorption-conversion” process of LPSs on the surface of CoFeMnO YSNCs. Reprinted with permission from H. Li, et al., *Angewandte Chemie. International Edition*. 62(8) (2023) e202216286. Copyright 2022 John Wiley and Sons.

131, 132]. Mechanistic analyses of Li-S catalysts explicitly frame the LPS reaction pathway as a coupled “adsorption–diffusion–conversion” sequence: LPSs first adsorb on the host surface, LPS and the Li^+ both ions are transported to catalytically active sites, and only then do multi-step redox transformations proceed to form lower-order polysulfides and Li_2S . This implies that catalysis requires both appropriate binding and efficient relocation of adsorbed intermediates across the catalyst surface toward active centers, rather than mere static trapping.

The thermodynamic requirement for such “adsorption-enabled catalysis” is captured by the Sabatier principle: the interaction between LPSs and the catalyst must be neither too weak nor too strong. If binding is too weak, LPSs desorb and diffuse into the electrolyte before reaching active sites, perpetuating the shuttle effect and limiting catalytic turnover. Conversely, if binding is excessively strong, the LPSs (or Li_2S) become immobilized, leading to localized poisoning of surface sites, passivation layers, and large overpotentials for subsequent conversion or desorption; in this regime, adsorption suppresses the shuttle but effectively arrests catalysis because intermediates are locked at non-productive or blocked sites.

1.6.3 Conversion

The central catalytic role is to accelerate the transformation of polysulfides into Li_2S during discharge. These reactions involve multiple electron transfers and phase transitions that are inherently slow and spatially nonuniform. Catalysts reduce activation barriers, promote uniform Li_2S nucleation [133], and facilitate charge transfer at the triple-phase boundary where electrolyte, catalyst, and conductive support meet. Materials with high electronic conductivity and abundant redox-active sites enable rapid electron flow and localized conversion [134]. By guiding Li_2S deposition, catalysts prevent the formation of large insulating agglomerates that block active surfaces and hinder reversibility [135]. Catalysts that possess metallic or semi-metallic electronic

characteristics improve the overall conductivity of the cathode, allowing electrons to move more freely. This enhanced electron transport reduces the activation barriers associated with sulfur redox reactions, thereby promoting faster LPS reduction and facilitating the nucleation of Li_2S .

1.6.4 Decomposition

During charging, Li_2S must be oxidized back into soluble polysulfides [136, 137] and eventually sulfur. This decomposition step is widely considered the rate-limiting reaction for the charging step [38, 138] because Li_2S is electronically insulating and chemically stable. Catalysts lower the overpotential required for Li_2S oxidation by stabilizing transition states and providing active sites that facilitate bond breaking. The morphology of the Li_2S formed during discharge strongly influences its decomposition: finely dispersed Li_2S with abundant exposed surfaces decomposes more readily. Catalysts that promote uniform Li_2S growth, especially those rich in defects, grain boundaries, or heterointerfaces, therefore also enhance its subsequent removal. Because decomposition reverses the earlier steps, catalysts must also support efficient phase conversion and polysulfide diffusion during charging.

Taken together, these mechanisms show that effective electrocatalysis in LSB arises from the coordinated action of adsorption, ion and electron relocation and transport, and redox conversion processes. These functions are tightly coupled and depend on the catalyst's chemical composition, electronic structure, and physical architecture. The following sections highlight representative catalyst systems and illustrate how they contribute to each stage of the sulfur redox pathway.

1.7 Catalyst Materials for Sulfur Redox Reactions

Catalysts in sulfur cathodes are introduced to tackle two coupled problems: the polysulfide shuttling and slow sulfur/ Li_2S redox kinetics. Catalytic additives or hosts adsorb lithium

polysulfides (LPS) and lower the energy barriers for their stepwise conversion between S_8 , soluble Li_2S_n , and solid Li_2S/Li_2S_2 , thereby improving rate capability, coulombic efficiency, and cycling stability. This section summarizes the main classes of catalytic materials currently used in Li-S cathodes and explains why each is effective for sulfur electrochemistry.

1.7.1 Transition Metal Oxides

Transition metal oxides [139, 140] such as V_2O_3 [141], TiO_2 [142], MoO_2 [143], Co_3O_4 [144], and Fe_2O_3 [145] are among the earliest and most widely explored catalysts and hosts for Li-S cathodes. Their strong polarity and metal–oxygen bonds give high surface affinity for polar LPSs, enabling chemical anchoring that suppresses polysulfide dissolution and migration into the electrolyte. For example, MnO_2 [146] and TiO_2 surfaces can form Li-O and S-O interactions with LPS, which reduces their diffusion and keeps redox intermediates confined near the cathode, where they can be reconverted electrochemically. In addition to adsorption, many TMOs exhibit intrinsic catalytic activity for LPS conversion by providing redox-active metal centers that facilitate electron transfer and lower the activation energy for S-S bond cleavage and reformation. Defect-rich Nb_2O_5 [147] nanoclusters containing abundant oxygen vacancies have been shown to improve the exposure of active sites and accelerate LPS conversion, illustrating how defect engineering can further enhance TMO catalyst performance. However, the relatively low electronic conductivity of most TMOs hinders their use for high-loading sulfur applications, which means they are typically combined with conductive carbons to ensure efficient transport within the cathode.

1.7.2 Transition Metal Sulfides, Selenides, and Phosphides

Transition metal sulfides (TMSs) [148], selenides (TMSe) [149], and phosphides (TMPs) [150] have attracted growing interest because they are more electronically conductive than most oxides and often provide stronger, more specific interactions with LPSs. Compounds such as CoS_2 [151], Ni_3S_2 [152], MoS_2 [153], WS_2 [154], VS_2 [155], and CoSe_2 [156] can act as bifunctional materials that both adsorb LPSs and catalyze their redox, leading to higher capacities and improved rate performance. Du. et. al. [157] also studied the effect of the anions on the adsorption and catalytic effect of polysulfide redox chemistry through density-functional-theory, comparing FeCoNi-oxide, FeCoNi-sulfide, and FeCoNi-phosphide hosts, found that FeCoNiP offers superior electrical conductivity, stronger LPS adsorption, and faster conversion kinetics, resulting in the highest levels of polysulfide radicals and improved sulfur utilization during cycling. These results highlight that changing the anion (O vs S vs P) tunes the electronic structure, d-band position, and binding strength toward LPSs, which directly influences catalytic ability. For example, transition-metal sulfides exhibit strong catalytic behavior because their valence d orbitals hybridize with sulfur 3p orbitals to form surface states that interact effectively with reactants and intermediates. The position of the metal d band relative to the Fermi level determines the adsorption strength, and a partially filled, optimally aligned d band enables balanced adsorption and desorption, which is crucial for fast catalysis. Their partly covalent, directional metal–sulfur bonds create abundant under-coordinated sites at edges [158], and defects [159], which serve as highly active centers, as demonstrated in MoS_2 , where edge sites and sulfur vacancies [160, 161] show superior reactivity compared to the inert basal plane. Defects, vacancies, and dynamic surface reconstructions [162] further enhance activity by increasing the density of catalytic sites. Their surfaces provide multiple adsorption configurations (e.g., Li–S–M, Li–P–M) and redox-

active sites that facilitate the “adsorption–diffusion–conversion” of LPSs, thereby shortening the time LPSs spend in solution and mitigating the shuttle effect.

1.7.3 Metal–N–C

Metal–nitrogen–carbon (M–N–C) materials, often derived from pyrolysis of metal–organic frameworks [163] or polymer/metal salt precursors, combine high conductivity with an atomically dispersed single-atom catalyst [164, 165] or nanoclustered metal [166, 167] sites coordinated to nitrogen in a carbon matrix. Typical active motifs include MN_4 ($M = Fe, Co, Ni$, etc.) embedded in a graphitic carbon, which have been widely studied in oxygen reduction [168–170] but are now increasingly applied to Li–S chemistry. These materials bind LPSs through Lewis acid–base interactions at metal centers and nitrogen sites, while the conductive carbon framework ensures rapid electron transport to the catalytic sites.

Single-atom catalysts (SACs) [171–173] are a specific type where the metal center is a single metal atom, representing an emerging frontier in Li–S cathode design, in which isolated metal atoms are anchored on supports such as graphene, N-doped carbon, or covalent organic frameworks. Recent work on atomically dispersed Fe–N–C catalysts [112, 174, 175] shows that carefully tuned Fe–N coordination environments can promote both LPS adsorption and catalytic conversion, leading to higher sulfur utilization and improved rate performance at practical sulfur loadings. Because the metal loading is low and the active sites are highly dispersed, M–N–C catalysts typically exhibit high atom utilization efficiency and can be incorporated without greatly compromising the energy density of the cathode. The key advantages of SACs are maximized metal atom utilization and well-defined coordination environments that allow precise tuning of adsorption energies and reaction pathways. Theoretically and experimentally, SACs such as

MN₄@graphene (M = Fe, Co, Ni, etc.) have been shown to significantly reduce the energy barrier for Li₂S decomposition and oxidation, accelerating sulfur redox kinetics and mitigating LPS accumulation.

1.7.4 Defect Engineering

Creating and controlling defects, such as vacancies, dislocations, and grain boundaries, is another powerful strategy to enhance catalytic performance in Li–S cathodes. Vacancies in TMOs [176], TMSs [177], and related compounds (e.g., oxygen vacancies in Nb₂O₅ or Co₃O₄; sulfur vacancies in MoS₂) can increase the density of unsaturated metal sites, alter local electronic structures, and strengthen interactions with LPSs. For example, oxygen-vacancy-rich Nb₂O₅ quantum dots [178] have been reported to expose more active sites and accelerate the conversion of sulfur species, resulting in improved rate capability and capacity retention. Dual-defect engineering, combining vacancies with heteroatom doping [179-181], has been shown to produce synergistic effects: in Co₃O₄, introducing both oxygen vacancies and phosphorus dopants significantly enhanced LPS adsorption and conversion ability, enabling Li-S cells with high capacity and high areal capacity under lean electrolyte conditions.

In layered sulfide hosts such as MoS₂, defect engineering [182, 183] can convert otherwise inert basal planes into catalytically active regions. Creating sulfur vacancies and edge-like defects within the MoS₂ basal plane increases LPS adsorption and improves charge transfer, while also allowing heteroatom dopants to be incorporated at defect sites for additional tuning. From a mechanistic standpoint, defects introduce localized states near the Fermi level that can act as active centers for electron transfer and bond breaking/forming, thereby lowering kinetic barriers for LPS

conversion. Controlled defect creation (e.g., via plasma treatment, reductive annealing, or chemical etching) thus represents a key design principle for next-generation Li-S catalysts.

1.7.5 Metal-Organic Frameworks

Metal–organic frameworks (MOFs) [184, 185] are used in Li-S battery cathodes mainly as advanced sulfur hosts and electrocatalytic scaffolds that confine polysulfides and accelerate their conversion. Their metal center acts as a catalytic active site, a highly porous architecture provides a large internal surface area and tunable pore size structures, enabling physical confinement of sulfur and dissolved lithium polysulfides (LPS) inside the framework, which reduces active material loss and suppresses the shuttle. In hosts such as Fe-based MIL-88A [186] or Cu-based STAM-1 [187], open metal sites (Lewis acidic) and functional organic linkers (often Lewis basic or polar) offer abundant chemical adsorption sites that bind polysulfide anions and Li^+ , so LPS are both sterically trapped and chemically anchored in the MOF pores. More recently, electronically conductive MOFs and π –d conjugated [188] frameworks (e.g., Ni-MOF-1D, $\text{Ni}_3(\text{HITP})_2$) have been developed so that the host not only stores sulfur and traps LPS but also conducts electrons and catalyzes the bidirectional conversion between S_8 , soluble Li_2S_n , and solid Li_2S , leading to higher sulfur utilization (>80%), reduced polarization, and improved cycling at high sulfur loading. MOFs are also combined with conductive carbons (CNT@UiO-66/S, MOF–graphene aerogels) or used as precursors for MOF-derived [189] carbons/oxides [190] and even MOF-templated single-atom catalysts [191, 192], where the original ordered porosity and metal distribution are translated into hosts that couple strong polysulfide adsorption with fast redox kinetics for high-performance Li-S cathodes. MOFs themselves or their carbonized derivatives (MOF-derived carbons and MOF-derived metal compounds) are also widely used. Pyrolysis of MOFs can yield porous M–N–C

structures with atomically dispersed metal sites, combining high surface area, tunable porosity, and catalytically active centers. Such MOF-derived catalysts have been shown to enhance LPS adsorption and accelerate their conversion, improving both capacity and rate performance at high sulfur loading. By carefully selecting organic linkers and metal nodes, researchers can control the distribution of heteroatoms and metals in the final catalyst, making frameworks a crucial platform for rational catalyst design in Li-S systems.

1.8 Electrochemical Characterization of Batteries

1.8.1 Adsorption Capacity Assessment Using UV–Vis Experiment

The UV–Vis adsorption experiment for lithium polysulfides (LPS) of varying chain lengths was carried out by scanning the polysulfide solutions across a wavelength range of 800–300 nm. Among the characteristic absorption features, the dominant peak for the LPS species appeared at 411 nm, which is consistent with the strong visible-light absorption associated with the S_x^{2-} chromophore. Because LPS solutions are highly sensitive to air, moisture, and light exposure, all measurements were performed using tightly sealed quartz cuvettes. Each cuvette was capped immediately after sample preparation and kept sealed during transfer to the spectrophotometer to prevent oxidation or compositional changes that could alter the absorption profile.

The strong absorbance of LPS at 411 nm leads to rapid saturation of the detector when the concentration exceeds approximately 10 mM. To ensure that the Beer–Lambert law remained valid and to obtain a linear calibration curve between absorbance and concentration, all analyte solutions were therefore prepared at relatively low concentrations, with a maximum of 5 mM. This concentration range provided a reliable linear response while avoiding spectral distortion from excessive absorbance.

Another practical challenge arose from the physical properties of the LPS solutions and the MoS_x/rGO adsorbent. The polysulfide solutions are highly viscous, whereas the MoS_x/rGO catalyst is extremely lightweight and prone to floating or remaining suspended in the solution. To ensure uniform mixing and consistent interaction between the analyte and the adsorbent, each sample was stirred with a magnetic stir bar for 45 minutes before measurement. After stirring, the solution was allowed to rest for 15 minutes to allow the MoS_x/rGO particles to settle. This settling step was essential because floating rGO sheets can scatter the incident light beam, artificially increase the baseline, and interfere with accurate absorbance measurements.

A fixed amount of LPS analyte and a controlled mass of MoS_x/rGO adsorbent were used in each experiment to ensure reproducibility and to enable quantitative comparison of adsorption performance. By maintaining consistent analyte-to-adsorbent ratios, the specific adsorption capacity of the MoS_x/rGO materials could be accurately determined from the decrease in LPS absorbance at 411 nm. This methodological approach ensured reliable, interpretable UV–Vis data for evaluating the polysulfide adsorption behavior of the synthesized catalysts.

1.8.2 Symmetrical Cell

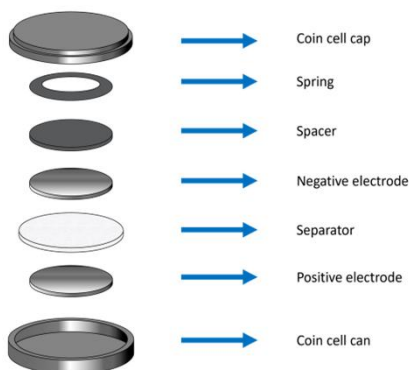


Figure 1.11. Schematic of the construction of a symmetric cell.

Symmetric cells were assembled and studied to evaluate the intrinsic catalytic activity of the electrode materials toward lithium polysulfide (LPS) redox reactions while eliminating complications associated with the lithium metal anode and solid sulfur. Two identical electrodes were prepared by coating the desired catalyst (e.g., MoS_x/rGO or control rGO) onto conductive Al foil using a 100 μ m thick slurry composed of active material, conductive carbon, and polymer binder dispersed in an NMP solvent.

The coated electrodes were dried under vacuum and punched into 15 mm circular disks of identical size and mass loading to ensure a symmetric configuration. An LPS-containing electrolyte was prepared by dissolving a pre-synthesized lithium polysulfide following its stoichiometric ratio in a mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) with a lithium salt, LiTFSI. The LPS concentration of 0.2M was chosen to provide a clear redox response without excessive viscosity or mass-transport limitations.

Coin-type symmetric cells CR2025 were assembled in an argon-filled glovebox with oxygen and moisture levels maintained below 0.5 ppm. The two identical catalyst-coated electrodes were placed on either side of a porous separator (e.g., Celgard 2400), and a fixed 60 μ L volume of LPS electrolyte was added to fully wet the separator and electrode surfaces.

No lithium metal was used in this configuration, ensuring that the electrochemical response originated solely from LPS redox processes at the catalyst interfaces. After sealing, the cells were rested for 12 hours, a defined equilibration period, to allow uniform LPS distribution and wetting.

Cyclic voltammetry (CV) was conducted in a potential window from -1.0 to $+1.0$ V (vs. the symmetric open-circuit potential of the cell) at selected scan rates (50 mV/s). This wide potential range ensured that both the reduction and oxidation of LPS species were fully probed on the catalyst surfaces. The resulting CV curves were analyzed for peak separation (voltage hysteresis), peak current density, and curve shape to assess the reversibility and kinetics of LPS conversion. Smaller potential differences between anodic and cathodic peaks and higher peak currents were interpreted as indicators of enhanced catalytic activity and faster charge transfer.

1.8.3 Full Cell

In LSB, the electrochemical testing of a cathode material is typically performed in a Li-S

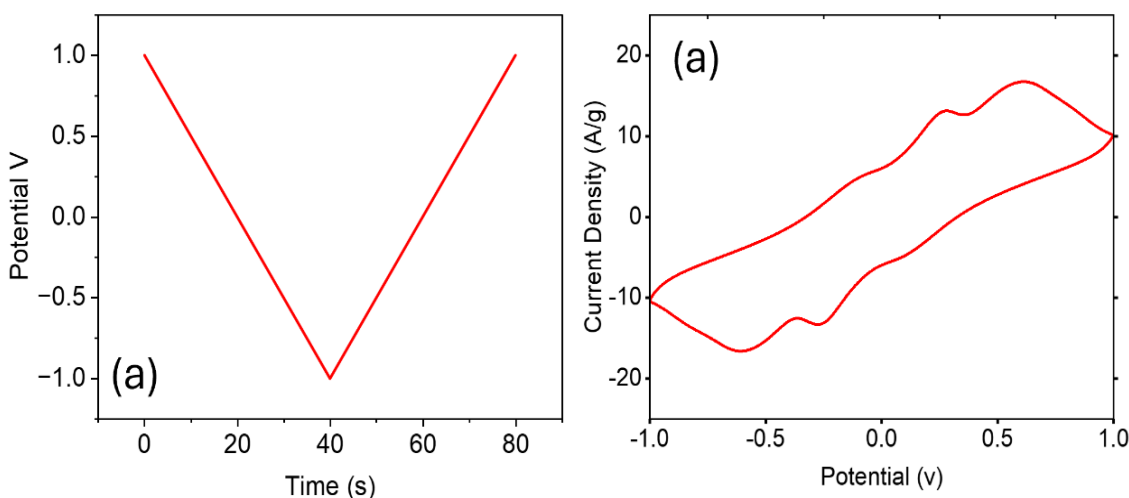


Figure 1.12. (a) Applied voltage profile of the symmetric cell CV, (b) current response received from the symmetric cell CV profile following the applied potential.

half-cell configuration with a two-electrode setup, where metallic lithium serves as both the counter and reference electrode. Because metallic Li is also the anode in a practical full cell, the

electrochemical environment experienced by the sulfur cathode is essentially identical in both cases. As a result, the voltage profile and redox behavior observed in a Li-S half-cell directly represent the full-cell operation, unlike intercalation systems (e.g., Li-ion), where half-cell and full-cell potentials differ due to the use of graphite or other insertion anodes. For Li-S chemistry, the characteristic operating window of 2.8–1.7 V vs. Li/Li⁺ corresponds to the thermodynamic and kinetic potentials of sulfur reduction and oxidation. During CV or galvanostatic cycling, scanning or cycling the cell between 2.8 V (upper cutoff) and 1.7 V (lower cutoff) captures the full sequence of sulfur conversion reactions, from S₈ to long-chain polysulfides and finally to Li₂S, while avoiding electrolyte decomposition and lithium corrosion at lower potentials. Thus, running CV within this 2.8–1.7 V range provides a complete picture of the redox processes relevant to practical LSB operation. The CV voltage profile is shown below in Fig. 1.13 (a-b), where the voltage profile starts from 2.8 to a negative scan with 0.1 mV/s to 1.7 V for the reduction. Since sulfur is already in its charge state. This reduction corresponds to two reduction peaks, R₁ and R₂, at ~2.35 V and ~2.05 V, respectively. This ensures the conversion of Sulfur to Li₂S. During the oxidation scan or scanning from 1.7V to 2.8V, the Li₂S oxidized to Sulfur in two steps, first it converts to LPS and then into sulfur solids with two oxidation peaks. Ideally, it is expected that the Oxidation and reduction peaks should appear much closer for a better catalyst.

1.8.4 Galvanostatic Charge Discharge

Opposite to the CV profile, in galvanostatic charge–discharge (GCD) measurements, the current is fixed, while the voltage is the response. In GCD for LSB are performed in a

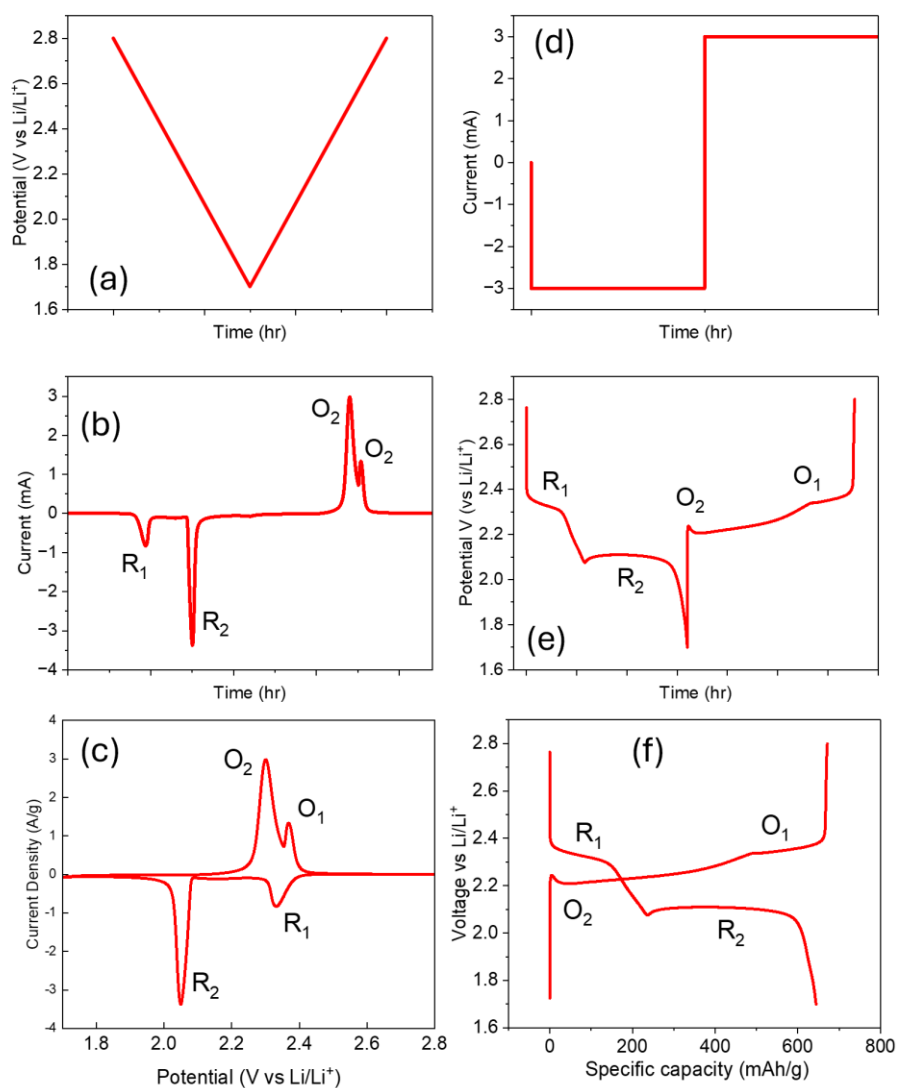


Figure 1.13. (a) Applied voltage profile of the full-cell cyclic voltammetry (CV) measurement in the Li–S configuration, (b) corresponding current response following the linear potential sweep, and (c) cyclic representation of the CV curve. (d) Applied current profile used for GCD testing of the Li–S full cell, (e) continuous charge–discharge behavior under the imposed current, and (f) individual charge–discharge curves extracted for presentation of the GCD data in this work.

two-electrode configuration as well using a sulfur composite cathode and metallic lithium foil as both the counter and reference electrode, allowing the cell to be cycled directly within the practical operating window of 2.8–1.7 V. After assembling the cell in an argon-filled glovebox, it is typically rested at open-circuit voltage to ensure complete electrolyte wetting and stabilization. The battery cycler is then programmed to apply a constant current corresponding to the desired rate, which is calculated based on the theoretical or practical sulfur loading of the cathode. During the discharge step, the instrument maintains a fixed current while the cell voltage decreases from its initial OCV to the lower cutoff of 1.7 V, capturing the full sequence of sulfur reduction reactions from S_8 to soluble polysulfides and finally to solid Li_2S , shown in Fig. 1.7 (c-d). Once the lower limit is reached, the current direction is reversed to charge the cell back to 2.8 V, enabling the oxidation of Li_2S and polysulfides back to elemental sulfur. This charge–discharge sequence is repeated for multiple cycles at various C-rates, typically starting from low rates such as 0.1C to evaluate intrinsic sulfur utilization and then increasing to higher rates to assess kinetic limitations, polarization, and rate capability. The resulting voltage profiles, plateau shifts, Coulombic efficiencies, and capacity retention trends provide comprehensive insight into the electrochemical behavior and reversibility of the Li–S redox processes under different current loads.

1.8.4.1 Determining the Applied Current for the GCD During Battery Testing

The C-rate is a standard measure used to describe the charge and discharge speed of a battery, analogous to how the scan rate defines the rate of potential change in cyclic voltammetry. A C-rate of 1C corresponds to the current setting to allow a full charge or discharge occurring within one hour, and the relationship between C-rate and cycling time is reciprocal. For example, a rate of 2C represents a 0.5-hour charge or discharge period, while 0.1C corresponds to a 10-hour process. Lower C-rates such as 0.1C and 0.2C (10 and 5 hours, respectively) are typically used to evaluate intrinsic capacity, sulfur utilization, and reaction completeness in Li-S cells. Moderate rates such as 0.5C (2 hours) provide insight into polarization and kinetic behavior, whereas higher rates such as 1C (1 hour) and 2C (0.5 hour) are used to assess high-rate capability, electron-transfer efficiency, and structural stability under fast cycling conditions. This reciprocal relationship between C-rate and time allows systematic evaluation of electrochemical performance across different kinetic regimes.

1.8.4.2 Sample Calculation of Charge–Discharge Current at 0.2C

To calculate the current for a given C-rate, the theoretical sulfur capacity is used. For a sulfur cathode containing 3.44 mg of sulfur and assuming the theoretical sulfur capacity of 1675 mAh/g, the theoretical capacity of the electrode is:

Theoretical Capacity,

$$\begin{aligned} &= 3.44 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times 1675 \text{ mAh/g} \\ &= 0.00344 \text{ g} \times 1675 \text{ mAh/g} \\ &= 5.76 \text{ mAh} \end{aligned}$$

Thus, the charge–discharge current for a 0.2C rate is,

$$= 0.2 \times 5.76 \text{ mAh}$$

$$= 1.152 \text{ mA}$$

Below is a detailed chart showing the calculated currents for the C-rates used in this thesis for a sulfur cathode with a mass of 3.44 mg. It should be noted that the applied GCD current depends entirely on the sulfur mass of each electrode, which must be calculated as described above. A sample calculation and the corresponding current values are provided in the table below.

Table 2: Calculated GCD currents for different C-rates of a 3.44 mg Sulfur cathode

C-Rate	Time Scale (h)	Current Calculation	Current (mA)
0.1 C	10 h	0.1×5.76	0.576
0.2 C	5 h	0.2×5.76	1.152
0.5 C	2 h	0.5×5.76	2.88
1 C	1 h	1.0×5.76	5.76
2 C	0.5 h	2.0×5.76	11.52

This measured current can be directly correlated with Fig. 1.13(d), where the current profile is presented, and with the corresponding voltage and capacity responses shown in Fig. 1.13(e–f).

1.8.4.3 Coulombic Efficiency Calculation From GCD:

The Coulombic efficiency (CE) is another important parameter that can be extracted from the charge–discharge profile. CE is defined as the ratio of the discharge capacity to the charge capacity within the same cycle and is expressed as follows:

$$CE = \frac{\text{Discharge Capacity}}{\text{Charge Capacity}} \times 100 \% \dots \dots \dots (1)$$

Since the Li–S cell is assembled in a fully charged state and the GCD measurement begins with the discharge step, the first discharge cycle is excluded from the Coulombic efficiency calculation.

Instead, CE is determined to use the first charge capacity and the subsequent discharge capacity, following the equation provided above.

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Chapter 2 - Material Development and Electrode Fabrication

2.1 Introduction to Transition Metal Sulfide Material

As outlined through the various methods and materials discussed in Chapter 1, the present work focuses on transition-metal sulfides, with particular emphasis on the synthesis, structure, and electrochemical behavior of molybdenum sulfide phases. Molybdenum disulfide, or MoS_2 , is a layered transition-metal dichalcogenide, and the stable 2H MoS_2 is composed of one molybdenum atom coordinated to two sulfur atoms in a trigonal-prismatic arrangement. Each structural unit

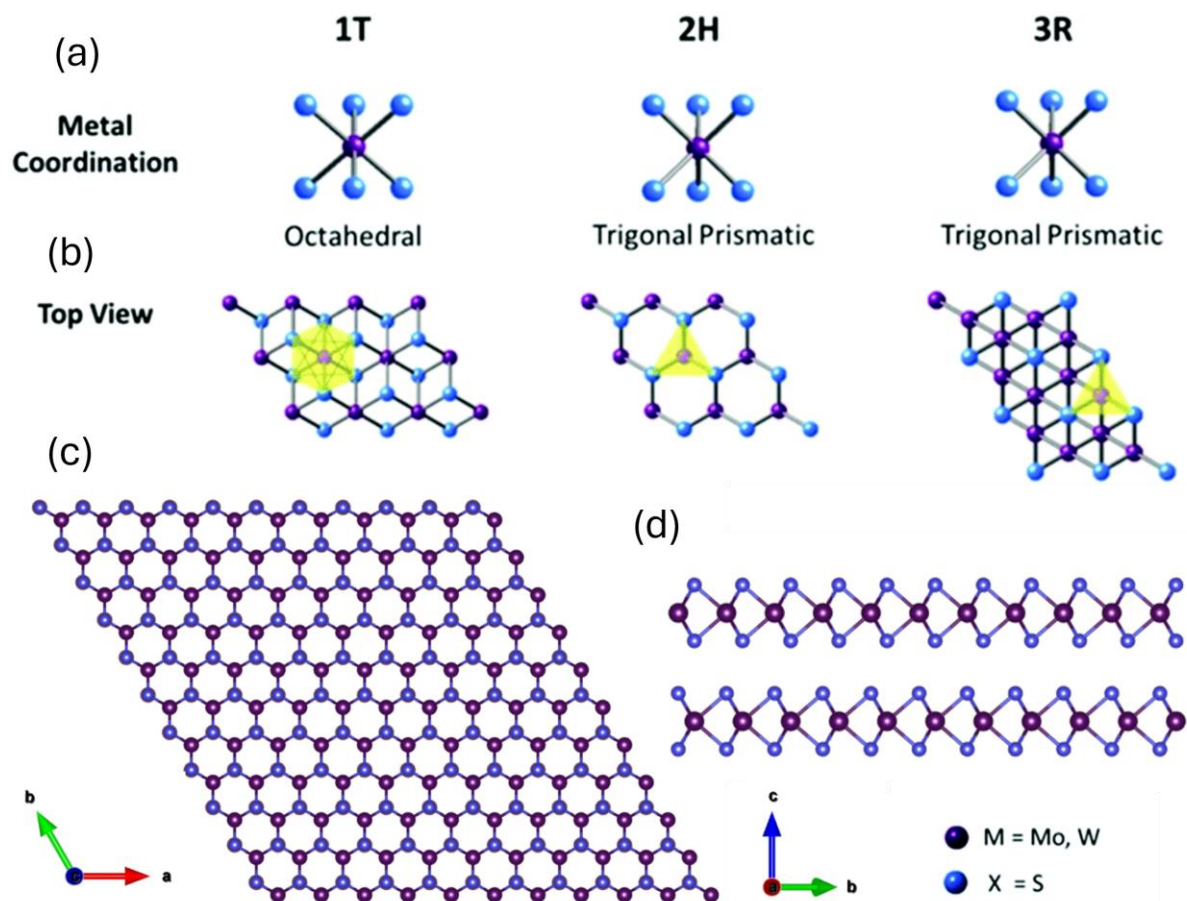


Figure 2.1. (a) Metal coordination and stacking sequences of TMD structural unit cells, tetragonal symmetry (1T), hexagonal symmetry (2H), and rhombohedral symmetry (3R). Reprinted with permission from Z. Li et al., *Chemical Communication*, 2017, 53, 3551–3554. Copyright 2017 Royal Society of Chemistry. (c) Top View and (d) Side view of 2H crystal structure of MoS_2 .

forms an S–Mo–S tri-layer [193], where strong in-plane covalent Mo–S bonds provide mechanical and chemical stability. These tri-layers stack along the c-axis through weak van der Waals interactions, enabling facile exfoliation into atomically thin sheets and giving MoS₂ its characteristic two-dimensional nature. The most common polytype [194], semiconducting 2H-MoS₂, exhibits hexagonal symmetry with two such layers per unit cell, although other stacking sequences, such as 3R and metastable and metallic 1T phases [195], can also occur. This combination of strong intralayer bonding and weak interlayer coupling underpins the unique electronic, mechanical, and electrochemical properties that make MoS₂ a versatile material for energy storage applications. Transition metal sulfides are effective catalysts because their partially filled metal d orbitals and relatively covalent metal–sulfur bonds generate surfaces that bind reactants strongly and present many sites where bonds can readily break and reform. Their electronic structure, especially the position of the metal d band, can be tuned by changing the metal, the sulfur-to-metal ratio, or introducing vacancies, thereby optimizing adsorption energies and accelerating surface reactions.

From an electronic perspective, transition metals possess valence d orbitals that combine in the solid to form a narrow d band. When these metals bond to sulfur, the metal d levels hybridize with sulfur 3p orbitals, yielding bonding and antibonding states at the surface. The energy of this d-band relative to the Fermi level determines the strength of adsorption [196] of reactants and intermediates: if adsorption is too weak, species do not stay on the surface long enough to react, while overly strong adsorption prevents products from desorbing, so an intermediate interaction, often associated with a suitably positioned, partially filled d-band, leads to high catalytic activity.

The character of the metal–sulfur bond and the resulting surface structure also play a central role in catalysis [197]. Metal–sulfur bonds are partly covalent and directional, causing real crystals to expose under-coordinated metal and sulfur atoms at edges, corners, steps, and defects [198], and these sites frequently serve as catalytically active centers, as seen in MoS₂, while the ideal basal plane remains comparatively inactive until defects are introduced. This will be discussed in more detail later in this chapter.

Defects, vacancies, and dynamic surface reconstructions further enhance the catalytic properties of transition metal sulfides. These materials readily form sulfur vacancies, grain boundaries, and reconstructed arrangements under reaction conditions, increasing the density and variety of active sites and often boosting turnover rates, with studies on MoS₂ and related sulfides revealing that an optimal concentration of sulfur vacancies maximizes hydrogen evolution kinetics, whereas too few or too many defects diminish performance. For these reasons, MoS₂ has been used in HER [199], Photocatalysis, and battery applications [200, 201]. However, the bulk MoS₂ is catalytically less active due to its semiconducting [194] nature, combined with the limited number of catalytically active edge sites [202], significantly restricts its electrochemical performance. Hence, it needs to be redesigned for the Li-S battery application that is discussed below. In the context of this study, commercial bulk MoS₂ was evaluated to understand its redox behavior, reaction kinetics, and capacity contribution within an LSB environment.

2.2 Electrochemical Behavior of MoS₂

2.2.1 Conductivity Limitations

An electrode was prepared to evaluate the catalytic performance of MoS₂ in sulfur cathodes, using a composite containing 60 wt% sulfur, 20 wt% commercial MoS₂, 10 wt% Super P, and 10% PVDF binder, mixed with NMP as the solvent and cast following a standard sulfur-cathode fabrication procedure. Similarly, a control sulfur cathode with the same ratio but 30% superP was added instead of any commercial MoS₂ and was run cyclic voltammetry (CV) in the LSB potential window with Lithium bis(trifluoromethanesulfonyl)imide known as LiTFSI in

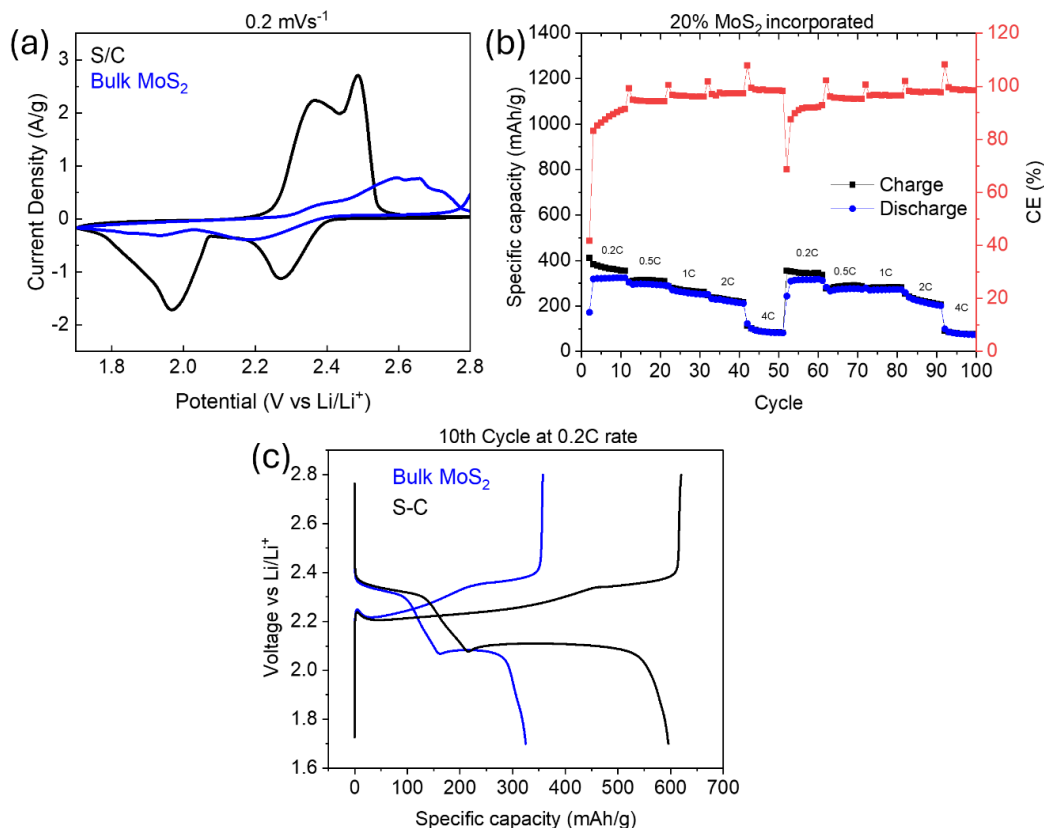


Figure 2.2. (a) CV profile of sulfur cathode with superP and 20 wt% commercial MoS₂ electrode. (b) The rate performance data of the sulfur cathode with 20 wt% commercial MoS₂. (c) Voltage profile comparison of the same cell from the 10th cycle at a 0.2C rate.

1,3-dioxolane and 1,2-dimethylethane solvent mixture (DOL/DME 1:1). As depicted in the CV profiles, bulk MoS₂ exhibits poor redox peaks, indicating sluggish reaction kinetics and limited electrochemical activity. The broad, low-intensity features in the CV suggest that electron transfer is hindered by the semiconducting nature of the material, preventing efficient participation in the multi-step polysulfide conversion reactions.

In contrast, control superP cathode (S-C) demonstrates markedly superior electrochemical behavior, with sharper redox features, higher current response, and lower overpotential. This difference arises from the high electrical conductivity and large surface area of carbon black, which facilitates rapid electron transport and provides abundant active sites for polysulfide adsorption and conversion. The disparity between the two materials is further reflected in the charge–discharge profiles and rate-performance data in Fig. 2.2 (c). When bulk MoS₂ is incorporated into the electrode, the delivered specific capacity remains significantly below the theoretical value of 1675 mAh/g for sulfur, and the capacity rapidly declines at higher current densities. The voltage profiles show pronounced polarization and incomplete plateau formation, both of which are signatures of slow reaction kinetics and poor catalytic activity.

These observations collectively confirm that the sluggish kinetics of bulk MoS₂ originate from its semiconducting behavior, which limits electron mobility, restricting the redox polysulfide conversion. As a result, bulk MoS₂ is unable to effectively catalyze the multi-electron redox processes required for efficient LSB operation. This highlights the need for structural modification, or hybridization with conductive carbon frameworks, to unlock the full catalytic potential of MoS₂ in sulfur-based electrochemical systems.

To overcome these limitations, MoS₂ is often hybridized with conductive graphene derivatives such as reduced graphene oxide (rGO), which provide rapid electron-transport pathways and improve the dispersion and accessibility of catalytic sites.

2.2.2 Conductive rGO Hosts Hybridization

To overcome the conductivity issue, this work focuses on rrGO as a substrate to hybridize with MoS₂ to compensate for the conductivity issue. The MoS₂/rGO hybrid investigated in this study was synthesized using a two-step microwave-assisted method, starting from 15.0 mM

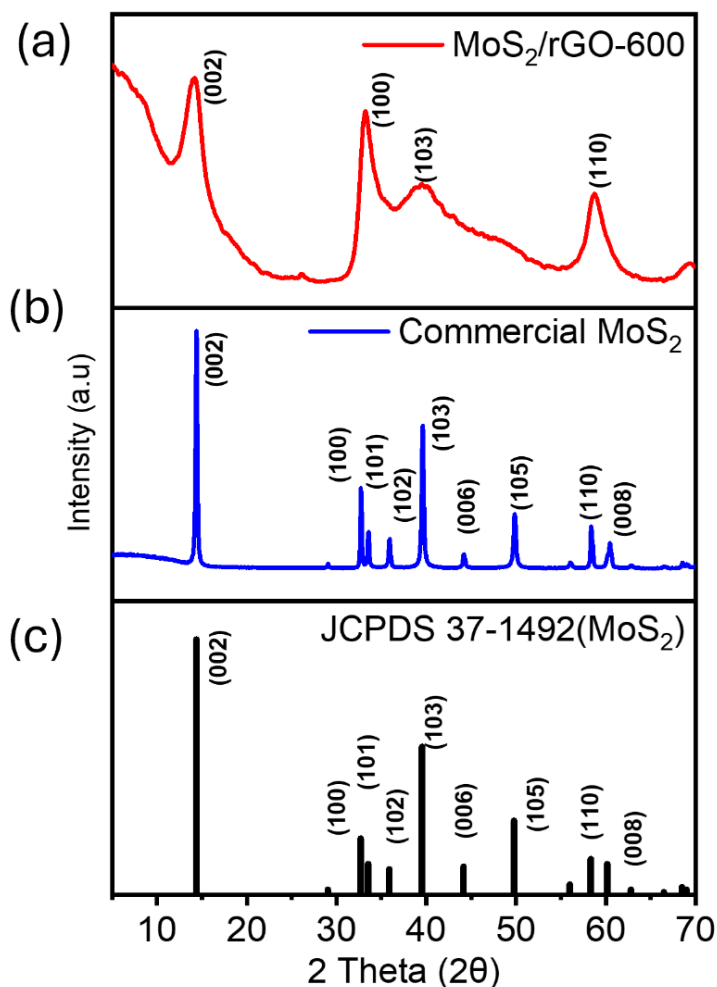


Figure 2.3. XRD of (a) MoS₂/rGO-600 with a higher MoS₂ composition (~80 wt%), (b) commercial MoS₂, and (c) JCPDS data of MoS₂.

ammonium tetrathiomolybdate (ATM) and graphene oxide (GO) as precursors. During the initial microwave reaction, ATM undergoes rapid decomposition and sulfurization, forming an amorphous MoS_3 phase uniformly anchored onto the rGO nanosheets. This intermediate product, denoted MoS_3/rGO -Intermediate. The MoS_3/rGO -Intermediate was subsequently annealed at 600°C , under a reducing atmosphere. These treatments yielded MoS_2/rGO -600, which is analogous to the commercial MoS_2 crystal anchored on rGO.

The XRD spectra of commercial bulk MoS_2 were compared with those of the synthesized MoS_2/rGO -600 hybrid to evaluate the structural evolution induced by the high-temperature annealing process. The MoS_2/rGO -600 sample exhibits well-defined diffraction peaks corresponding to the (002) and (100) planes of hexagonal 2H- MoS_2 , indicating the successful formation of layered MoS_2 nanosheets on the rGO scaffold. The pronounced intensity of the (002) reflection suggests improved crystallinity and stacking order along the c-axis, while the presence of the (100) peak confirms the development of in-plane Mo–S lattice ordering. These features collectively verify that the amorphous MoS_3 precursor underwent complete sulfur loss and structural rearrangement to form crystalline 2D MoS_2 during annealing at 600°C .

2.2.3 Optimization of MoS_2/rGO Hybrids Wt% in S-C Cathode

The electrochemical performance of the MoS_2/rGO -600 hybrid catalyst was first evaluated through CV)and charge–discharge testing, which required determining the appropriate wt% loading of the catalyst in the electrode. When the electrode was fabricated with 20 wt%

MoS₂/rGO-600, its catalytic activity was noticeably poorer than that of the control S-C electrode, as reflected in both the CV profiles and the rate performance shown in Fig. 2.4(a–b).

Despite achieving the desired structural conversion to crystalline MoS₂ anchored on conductive rGO, the 20 wt% hybrid exhibited significantly weaker catalytic behavior than expected, particularly when compared to carbon black. The multi-step sulfur redox reactions were

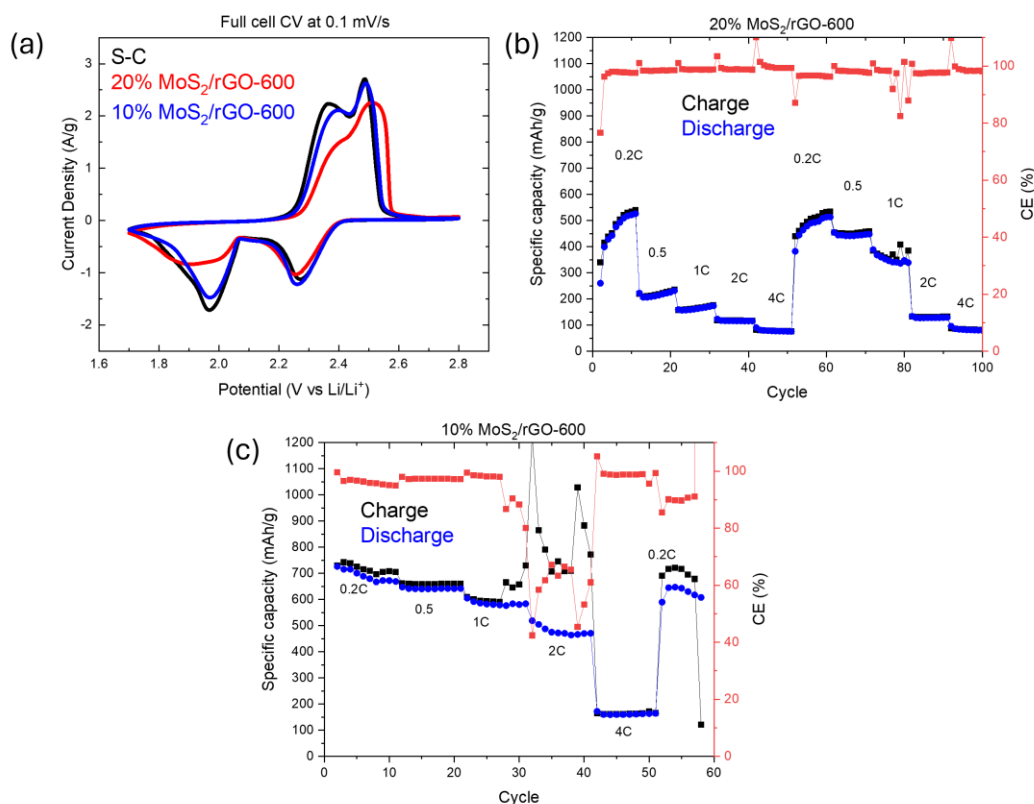


Figure 2.4. (a) CV of 60 wt% sulfur mixed with 20 wt% and 10% MoS₂/rGO hybrid and control S-C cathode, rate performance of (b) 20 wt% and (c) 10% MoS₂/rGO hybrid

insufficiently catalyzed, the second-reduction peak current was markedly lower than the control, and the discharge capacity decayed rapidly at 0.5 C and higher rates. Based on these observations, an initial hypothesis was made that the relatively low conductivity of the commercial MoS₂/rGO-600 might still be limiting the redox kinetics. To test this, a 10 wt% electrode was

fabricated and evaluated under identical conditions. Although the performance improved relative to the 20 wt% electrode, the S-C control still outperformed it in both CV and capacity testing, as shown in Fig. 2.4(a, c), indicating that conductivity alone could not explain the poor catalytic response.

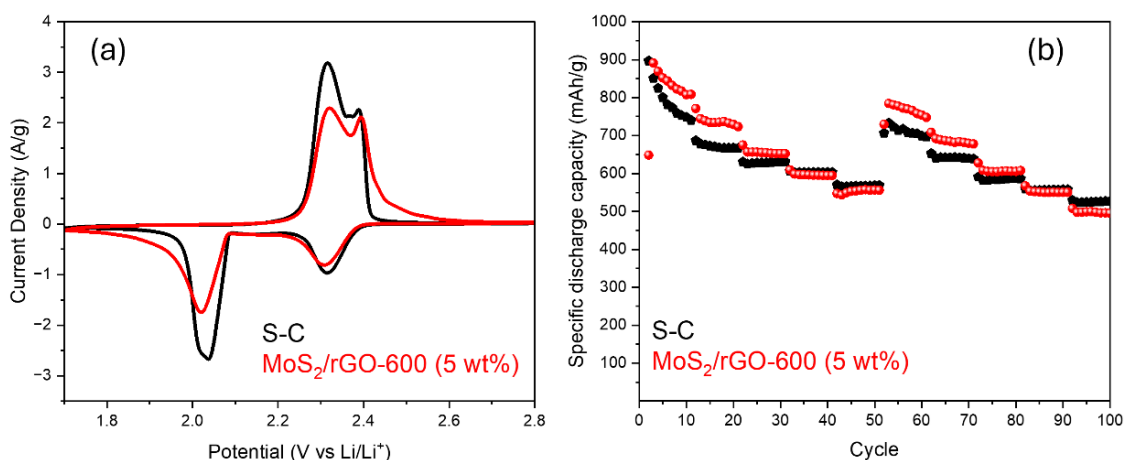


Figure 2.5. (a) CV and (b) rate performance data with 5 wt% of MoS₂/rGO-600 and 25 wt% of superP mixed electrode incorporated in the sulfur cathode compared with the 30% of super P electrode.

To further probe this behavior, the MoS₂/rGO-600 content was reduced to 5 wt% and re-evaluated. The CV profiles of the 5 wt% electrode displayed broad, low-intensity peaks characteristic of sluggish polysulfide conversion and weak catalytic participation, in stark contrast to the sharper and higher-current features of the carbon-based control. Charge–discharge testing similarly showed no meaningful improvement in specific capacity relative to the control electrode. Collectively, these results demonstrate that, besides the initial hypothesis, i.e., the conductivity limitation of MoS₂/rGO-600, a different intrinsic factor within the synthesized MoS₂/rGO-600 catalyst is also suppressing its redox activity, and this underlying limitation must be identified

before further optimization. A detailed and thorough literature review was performed and discussed below.

2.2.4 Limitation of Micron-Scale MoS₂ Patches

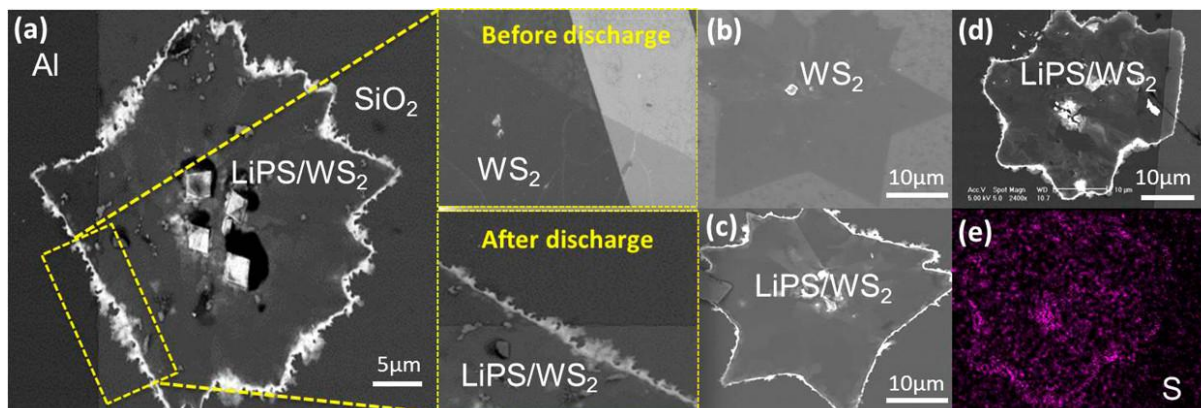


Figure 2.6. Exploration of preferential catalytic sites on XS₂ (X = W, Mo) nanosheets for LPS conversion. (a) SEM image showing LPS deposition at the catalytic edge sites of WS₂ nanosheets during discharge. (b,c) Comparison between pristine WS₂ nanosheets before discharge and controlled LPS adsorption after discharge. (d,e) Sulfur elemental mapping and corresponding SEM image of WS₂ nanosheets in the discharged state. Reproduced with permission from ‘G. Babu et al., *Journal of the American Chemical Society*. 139(1) (2017) 171-178. Copyright 2017 American Chemical Society.

Previous studies [203], including the work by Babu et al. [202], have also attempted to identify the intrinsic factors limiting the catalytic activity of MoS₂. Using CVD-grown MoS₂ and WS₂ thin flakes, they demonstrated that only the edge sites of these large 2D flakes actively adsorb lithium polysulfides (LPS) and facilitate their conversion to Li₂S, as shown in Fig. 2.6(a–e). In contrast, the extensive basal (100) planes of the MoS₂ and WS₂ flakes remained largely inert and did not participate in the LPS redox reactions.

From these observations, the authors concluded that the basal planes of 2D MoS₂ possess minimal catalytic activity, whereas the edge sites serve as the primary active regions responsible for polysulfide adsorption and conversion.

Now, in a typical large multilayer-stacked MoS₂ flake, most Mo and S atoms are fully coordinated within the interior S–Mo–S layers, and only a small perimeter of undercoordinated “edge” atoms can bind and activate reactants, which constrains the overall catalytic current, even if each edge site is individually very active.

This layered geometry means that increasing thickness mainly adds more stacked basal planes rather than creating new active edge sites, so the density of active edge sites does not scale with mass loading, and much of the material remains catalytically unused. As a result, strategies for high-performance MoS₂ catalysts focus on downsizing flakes, creating defects or porosity, or vertically aligning nanosheets [203] to expose more edge length per volume, all specifically aimed at overcoming the intrinsic shortage of edge sites in bulk-like 2D MoS₂. However, the synthesis of large MoS₂ patches by CVD is not scalable and yields structures with very low edge-site density, making them unsuitable for practical Li–S battery applications and useful primarily for fundamental mechanistic studies.

To overcome these limitations from a synthesis perspective, it is necessary to design alternative routes that can produce MoS₂ with higher edge exposure, tunable defect density, and morphology better aligned with catalytic requirements for polysulfide conversion. This limitation motivates the work presented in Chapter 3, where a new synthesis protocol for MoS₂ is developed specifically to enhance its catalytic suitability for Li–S battery applications. Before addressing this challenge, the latter section of this chapter examines the structural characteristics of the

MoS₂/rGO-600 system synthesized in this work, with particular attention to the relative contributions of basal-plane and edge-site activity.

2.2.5 Identification of the Limiting Factor of the Micron-Scale MoS₂/rGO

Increasing edge site density in bulk MoS₂ materials relies on restructuring the solid so that a larger fraction of atoms occupies edge-like environments rather than inert basal planes. One effective approach is nano-structuring, such as growing vertically aligned MoS₂ nanosheets or nano walls, which orient the layers perpendicular to the substrate and thereby expose a much greater edge length per geometric area.

When the synthesized material was characterized through TGA and TEM, it was found that several factors contribute to this low active site density that led to poor redox properties in LSB

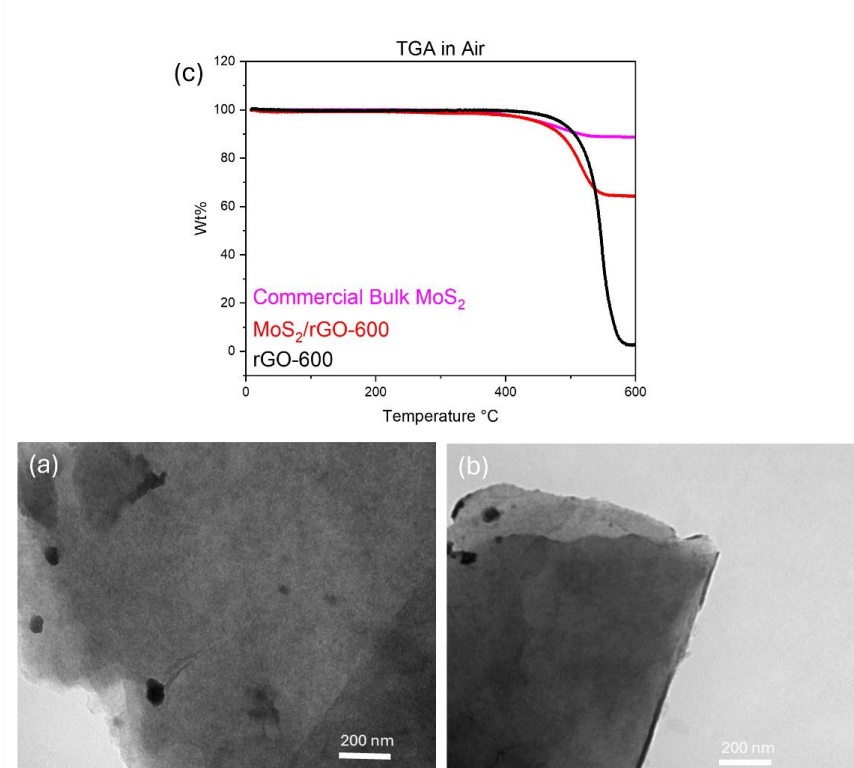


Figure 2.7. TGA curves measured in the air (b) Lower-magnification TEM images of the same MoS₂/rGO-600 sample with a higher MoS₂ composition (~70 wt%).

application. First, the high concentration of ATM promotes rapid nucleation and the following annealing crystallization into the growth of large multitasked MoS₂ domains very close to bulk MoS₂ as evident by the XRD in Fig. 2.3. The TGA shows that the hybrid contains 70% of MoS₂ in the MoS₂/rGO hybrids and covers the rGO substrate completely as a large micron-scale film, which reduces the density of catalytically active edge sites. Because MoS₂ is an intrinsic semiconductor with poor in-plane conductivity and catalytically inert basal planes, it is known that the catalytic activity is dominated by edge-exposed Mo and S sites. As the crystallite size increases, the edge-to-basal-plane ratio decreases, leading to fewer active sites available for polysulfide adsorption and conversion. Second, the formation of well-ordered multilayer MoS₂ reduces defect density and sulfur vacancies, both of which are known to enhance catalytic activity by facilitating electron transfer and improving polysulfide binding. Third, although rGO provides a conductive scaffold, the high wt% of semiconducting nature of MoS₂ still imposes a kinetic bottleneck, limiting charge transfer across the MoS₂-electrolyte interface.

Overall, the unexpectedly weak catalytic behavior of MoS₂/rGO-600 can be attributed to the combined effects of increased large MoS₂ patch size with a higher number of stacked, reduced defect density, limited edge-site exposure, and the intrinsic semiconducting nature of MoS₂. These findings highlight the importance of controlling structural disorder, defect engineering, and nanoscale morphology when designing MoS_x-based electrocatalysts for LSB. They also reinforce the conclusion that amorphous or partially sulfur-rich MoS_x phases, rather than fully crystalline MoS₂, are more effective for promoting fast polysulfide conversion and enhancing LSB performance.

2.3 1D MoS₃, an Alternative to 2D MoS₂

In conventional bulk MoS₂ catalysts, a fundamental limitation arises from their layered two-dimensional structure, in which only undercoordinated atoms located along the sheet edges function as intrinsically active sites, while the vast majority of Mo and S atoms within the extended basal planes remain catalytically inert. As the lateral size and thickness of MoS₂ flakes increase, most of the added material simply forms additional stacked basal layers without proportionally increasing edge length, so the density of active sites per unit mass or geometric area remains low, and a large fraction of the catalyst is effectively unused during reactions such as the hydrogen evolution reaction or hydrodesulfurization. Considerable research has therefore focused on strategies to “activate” MoS₂, for example, by downsizing flakes, introducing defects, or vertically aligning nanosheets, but these approaches still operate within the constraints of a fundamentally layered architecture, in which fully exposing all metal and chalcogen atoms as edge-like sites is structurally difficult and often compromises stability or conductivity.

In contrast, a one-dimensional chain-like MoS₃ structure that does not adopt a stacked layered arrangement offers a conceptual route to overcoming this limitation, because the extended 1D framework can, in principle, expose all Mo and S atoms directly to the surrounding environment so that every metal center and ligand participates as a potential active site rather than being buried in an inert interior. In such a 1D MoS₃ motif, the absence of van der Waals stacking and the higher structural openness would increase the surface-to-volume ratio and minimize the distinction between “edge” and “basal” positions; instead, the entire chain behaves as an extended active domain, thereby maximizing the utilization efficiency of the material. This structural paradigm addresses the central drawback of bulk MoS₂, its low fraction of catalytically accessible

atoms, by distributing active centers uniformly along the chain, which can translate into higher intrinsic turnover frequencies per mass and more effective catalyst design, provided that issues such as mechanical robustness, electronic conductivity, and long-term stability under operating conditions are simultaneously optimized. In Chapters 3 and 4, this amorphous MoS_3 will be discussed in detail.

2.4 Electrode Fabrication Protocol

Optimizing the sulfur-cathode preparation protocol is critical for achieving reliable and high-performance LSB because the electrochemical behavior of sulfur is extremely sensitive to electrode composition, microstructure, and processing conditions. Parameters such as sulfur-to-carbon ratio, mixing uniformity, conductive-network formation, and binder distribution directly determine sulfur utilization, reaction kinetics, and the extent of polysulfide dissolution. Even small deviations in preparation conditions can lead to poor conductivity, incomplete sulfur activation, excessive shuttling, or unstable electrode morphology. Therefore, systematic optimization of the cathode formulation and fabrication steps is necessary to balance active-material loading with electronic conductivity, ensure homogeneous dispersion, and create a mechanically robust structure capable of sustaining repeated volume changes during cycling. This optimization ultimately enables higher capacity, improved rate performance, and enhanced long-term stability in LSB.

2.4.1 Sulfur Weight Composition (wt%)

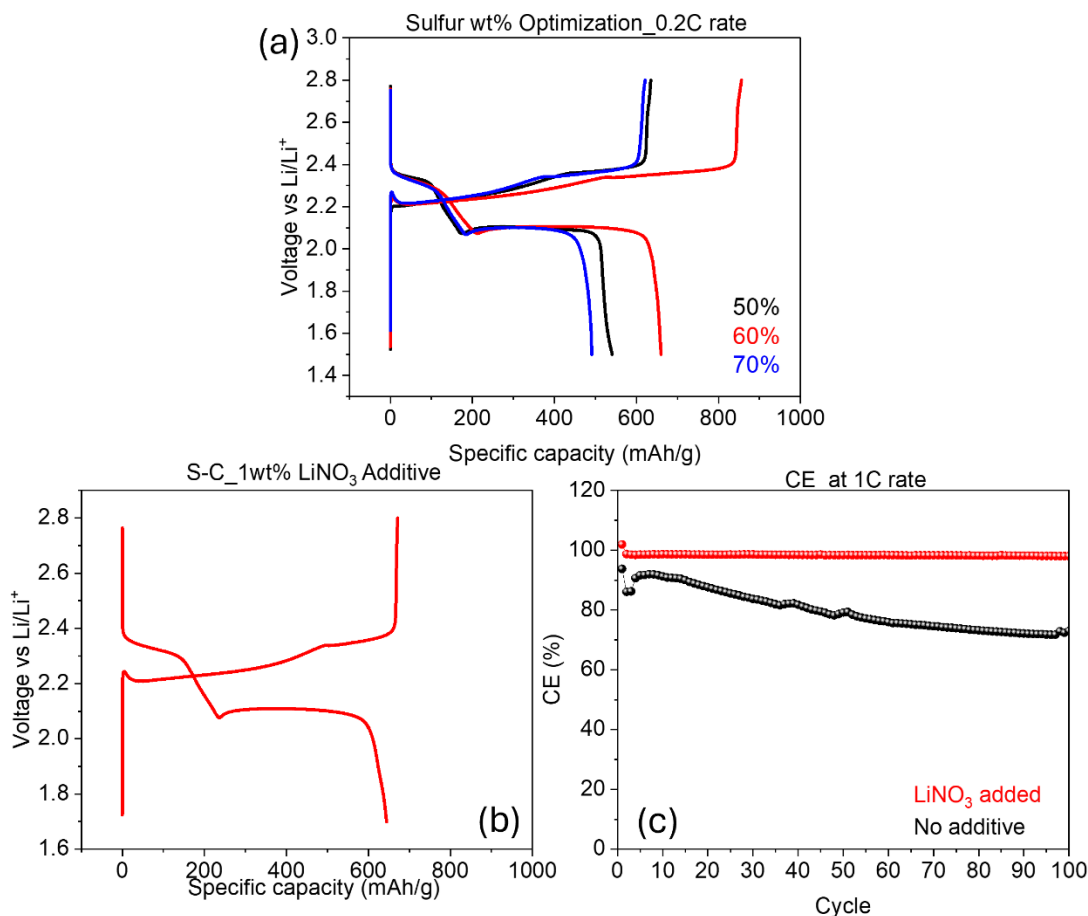


Figure 2.8. (a) Charge–discharge profiles of the S–C electrodes with varying sulfur compositions. (b) Effect of the LiNO₃ additive on extended charging behavior. (c) Cycling performance of cells with and without the LiNO₃ additive.

The sulfur–carbon composite with 50 wt% sulfur delivered lower capacity primarily because the active sulfur content was insufficient to provide a high theoretical charge storage. At this low sulfur loading, a significant fraction of the electrode mass is composed of carbon and binder, which, although beneficial for conductivity and structural support, does not contribute directly to capacity. As a result, the electrode becomes carbon-rich but sulfur-deficient, limiting the amount of electrochemically active material available for redox reactions and reducing the overall specific capacity.

In contrast, the 70 wt% sulfur electrode exhibited poor performance due to excessive sulfur content, which compromises electronic conductivity and reaction kinetics. At such high loading, the conductive carbon network becomes too sparse to effectively support electron transport throughout the electrode. The insulating nature of sulfur leads to sluggish charge transfer, incomplete sulfur utilization, and increased polarization. Additionally, high sulfur content can cause poor dispersion, agglomeration, and unstable electrode morphology, further hindering electrochemical activity. Therefore, 60 wt% sulfur represents an optimal balance: sufficient active material to deliver high capacity while maintaining an adequate conductive carbon framework to ensure efficient electron transport and uniform sulfur utilization.

2.4.2 Electrolyte Additive

At the beginning of this work, the role of LiNO_3 was not yet understood, and the cells were assembled using a standard DOL/DME electrolyte. As shown in Fig. 2.8(a), this electrolyte formulation led to pronounced side reactions during charging, resulting in poor Coulombic efficiency and unstable cycling. After introducing 1 wt% LiNO_3 salt as an electrolyte additive, a dramatic performance improvement was observed. Lithium nitrate forms a stable, inorganic-rich passivation layer on the lithium metal anode through controlled reduction during the initial cycles. This SEI, composed of species such as LiN_xO_y and Li_3N , effectively suppresses parasitic reactions between dissolved polysulfides and the reactive lithium surface. By preventing polysulfide reduction at the anode and stabilizing lithium plating/stripping, LiNO_3 minimizes shuttle-induced side reactions, reduces irreversible capacity loss, and significantly enhances Coulombic efficiency. Consequently, the addition of LiNO_3 leads to far more stable and efficient cycling behavior in Li–S cells.

2.4.3 Porosity and Thickness Optimization

After drying the coated sulfur electrodes, it became clear that the sulfur particles were not sufficiently integrated with the conductive carbon matrix, resulting in poor interfacial contact and limited electrochemical activation. To address this issue, a calendaring protocol was employed to systematically adjust electrode thickness and porosity, thereby improving the physical and electronic connectivity between sulfur and carbon. Moderate compression of approximately 20%

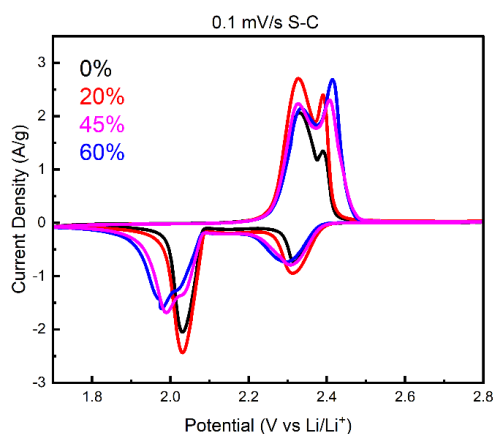


Figure 2.9. Effect of the compression by the calendaring machine on the cell current response, capacity, and overpotential.

proved to be the optimal condition: it reduced void spaces, increased particle–particle contact and strengthened the conductive network without compromising electrolyte accessibility. This balanced microstructure enhanced sulfur utilization, improved charge-transfer kinetics, and delivered higher discharge capacities. However, when the compression was increased to 45% or 60%, the electrode became overly dense, leading to significant pore collapse and restricted ion-transport pathways.

The reduced porosity hindered electrolyte infiltration and slowed Li⁺ diffusion, which in turn increased polarization and degraded overall performance. These observations highlight the

importance of carefully tuning electrode densification to achieve an optimal balance between mechanical integrity, electronic connectivity, and ionic transport, factors that collectively govern the electrochemical behavior of sulfur cathodes in LSB.

2.4.4 Flash Melting Method

The flash-melting method developed in this work provides a rapid and highly efficient alternative to the conventional melt-diffusion process previously performed at 155 °C for 12 hours before slurry coating. The cathode containing 60 wt% sulfur, 30 wt% Super P, and 10 wt% PVDF

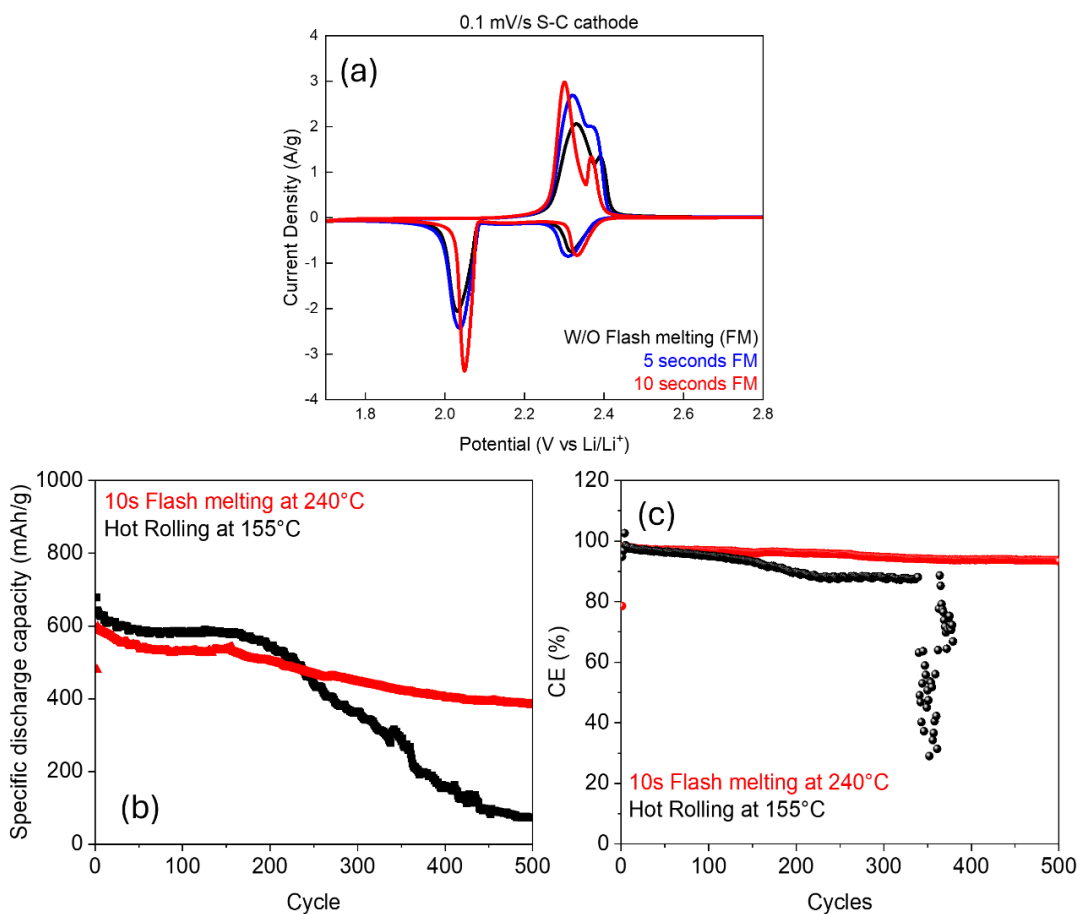


Figure 2.10. Effect of Flash melting and comparison without flash melting. (b-c) Comparison of the extended cycling performance, capacity, and CE on two cells with flash melting at 240°C and hot rolling at 155 °C.

binder was slurry-cast to a wet thickness of 200 μm and dried, yielding a final thickness of approximately 80 μm . The dried film was then punched into 15-mm discs and subsequently calendared to achieve $\sim 20\%$ compression relative to its initial thickness. In the optimized flash-melting procedure, this precoated, calendared flat sulfur–carbon cathode is briefly heated to 240 $^{\circ}\text{C}$ for 10 s on a glass Petri dish placed on a hotplate, with the temperature continuously monitored using a K-type thermocouple attached to the top surface of the Petri dish where the electrode rests to ensure precise thermal control.

Traditional melt diffusion relies on prolonged heating to gradually soften sulfur and allow it to infiltrate the carbon matrix; however, the extended processing time is inefficient and often results in incomplete infusion, leaving a significant fraction of sulfur loosely bound on the surface and poorly connected to the conductive network. In contrast, flash melting takes advantage of the sharp reduction in sulfur viscosity above $\sim 240^{\circ}\text{C}$, enabling sulfur to rapidly liquefy and diffuse into the porous catalyst or carbon support within seconds. This short, high-temperature exposure also removes weakly adsorbed or surface-residual sulfur through partial evaporation, resulting in more uniform sulfur distribution and fewer inactive sulfur domains. Experimentally, we observed a linear relationship between flash-melting duration and improved electrochemical kinetics, confirming that even brief heating substantially enhances S–C interfacial contact, charge-transfer pathways, and overall reaction uniformity. However, extended heating leads to measurable sulfur loss, introducing a trade-off between improved infusion and reduced active material; therefore, the process was carefully optimized to a short 10 s duration. Overall, flash melting achieves superior sulfur infusion, improved microstructural uniformity, and dramatically reduced processing time compared with conventional melt diffusion, making it a more effective, scalable, and energy-efficient strategy for preparing high-performance sulfur cathodes.

As a second approach, we evaluated a slow-heating process at 155 °C using a calendaring machine for approximately 80 s, which we refer to as the hot-roller method. However, this lower-temperature, gradual-heating strategy did not yield any improvement in cycling stability or Coulombic efficiency compared with the flash-melting method. The cathodes prepared by the hot-roller method exhibited rapid capacity fading, losing the majority of their capacity by around 300 cycles, and the Coulombic efficiency remained consistently poor throughout cycling. These results indicate that slow heating at 155 °C is insufficient to achieve effective sulfur infusion or stable interfacial contact. In contrast, the flash-melting method provides superior structural and electrochemical outcomes, further supporting its adoption as the standard protocol for enhancing both stability and Coulombic efficiency in sulfur cathodes.

2.5 Conclusion

The results of this chapter highlight how strongly the structural and compositional features of transition-metal sulfides and sulfur cathodes govern LSB performance. Although materials such as MoS₂ are widely used across energy and electronic applications, their effectiveness depends on how closely their physical properties match the functional demands of the system. The work here shows that large-flake 2D MoS₂, despite its advantages in intercalation-based batteries, performs poorly as a catalyst because its basal-plane-dominated morphology limits active sites and introduces conductivity bottlenecks when present at high loading. These findings establish that catalytic performance cannot be assumed from material popularity alone; it must be engineered through structural control.

At the same time, the sulfur cathode itself emerged as a critical determinant of overall cell behavior. Optimizing sulfur content to 60% enabled complete sulfur conversion and maximized

specific capacity, while higher sulfur fractions led to unreacted sulfur and diminished performance. Electrode compression was also shown to be a key processing variable, with 20 percent compression providing the best balance between mechanical integrity and Li-ion transport. Finally, the development of the flash-melting method demonstrated that rapid, high-temperature sulfur infusion can significantly enhance S–C interaction, improve reaction kinetics, and increase current response.

Together, these insights underscore the importance of coupling catalyst design with cathode-fabrication strategies to achieve high-performance LSB. The next chapter builds on these findings by demonstrating how tailored MoS₂/rGO hybrids can overcome the catalytic limitations identified here and enable more efficient polysulfide conversion.

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Chapter 3 - Improving Li-S Battery Performance by Tuning the Active Site of MoS_x/rGO Electrocatalysts in the S/C Cathode

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3.1 Introduction

Lithium-ion batteries (LIBs) have been commercially used for over three decades. However, the energy density of the state-of-the-art LIBs is limited by the low theoretical capacity of traditional intercalation-based cathode materials, typically less than 200 mAh/g [204, 205]. The Lithium-Sulfur battery (LSB) is considered one of the emerging batteries that may meet the future demand for higher energy-density storage systems due to the high theoretical sulfur (S) cathode capacity of 1,675 mAh/g and a theoretical cell-level energy density of 2,600 Wh/kg [51, 206]. The cathode material, sulfur is cheap and earth-abundant and matches well with the Li metal anode, which also has a very high theoretical capacity of 3,860 mAh/g in addition to the lowest standard reduction potential of -3.04 V vs. standard hydrogen electrode (SHE) [207, 208]. However, the Li-S battery is based on conversion reactions, which are much more complicated and have inherent limitations. The solid sulfur in the cathode produces intermediate species known as lithium polysulfides (LPSs) with the general chemical formula Li_2S_n ($n = 2-8$). These polysulfides are soluble in liquid electrolytes, such as 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME), and are able to diffuse from the cathode to the anode to form irreversible and nonconductive solid Li_2S . This unwanted side reaction is known as the polysulfide shuttling, which not only continuously consumes the active sulfur species in the cathode but also blocks the Li metal anode, leading to

low coulombic efficiency (CE), rapid capacity fading during repeated charge-discharge cycles, and a short cell life [46, 209-212].

To reduce polysulfide shuttling, Linda Nazar's group initiated an approach using mesoporous carbon CMK-3 to encapsulate the sulfur and confine the polysulfides [51]. Since then, various methods and strategies have been adopted to alleviate the limitations of LSBs. Carbon materials, such as activated carbon [213], carbon nanotubes (CNT) [105] and graphene and graphene-based materials [214], and metal oxides [215] have been extensively studied to retain soluble polysulfide species in the cathode matrices via physisorption onto the carbon surface. However, nonpolar carbon materials have a low adsorption capacity towards the polar LPSs and are quickly saturated, leading to rapid performance degradation during long cycling. Later, the incorporation of polar groups and heteroatoms into the carbon matrices significantly improved polysulfide adsorption and catalytic conversion by leveraging polar-polar interactions and providing active sites on the carbon surface [216-218]. Furthermore, a new concept based on the incorporation of metal sulfides [183, 219] and metal-nitrogen co-doped carbon [212] Electrocatalysts in S/C cathodes have emerged, which is very promising for further reducing polysulfide shuttling by accelerating their conversion inside the cathode.

2D transition metal dichalcogenides (TMD) have been used as electrode materials or catalysts in diverse fields, including batteries [220, 221], photocatalysis [222], and hydrogen evolution reaction (HER) [223-225]. 2D MoS₂ contains the empty d orbitals in Mo⁴⁺ and unsaturated S²⁻ as active sites, which is typically present as a stack of 2D sheets. In recent studies, 2D TMDs such as MoS₂ and WS₂ were found to be active for sulfur redox reactions [104, 183, 226-228] in LSBs. From then on, TMD materials were engineered in many ways to enhance

catalytic activity. Babu and Wang *et. al.* observed that the 2D TMD catalytic activity towards polysulfide chemistry is anisotropic, with the edge sites being catalytically more active than the (001) basal plane due to the presence of electronegative unsaturated S atoms [202, 229]. Thus, a chemical vapor deposition (CVD) method was used to fabricate triangular or star-like shapes of monolayer MoS₂ flakes to enhance the density of the unsaturated sulfur atoms in the edge site [202]. In a different approach, Lin and his coworkers later increased the active sites on the basal plane by removing the sulfur from the basal plane and found that a defective sulfur-deficient MoS₂ basal plane had higher activity than a pristine pure basal plane, which benefited LSB chemistry [183]. However, the available active sites are limited in the general multilayer-stacked crystalline 2D MoS₂ materials with a lateral size of over hundreds of nanometers. Most of the layers are buried inside the stack and are not involved in catalytic reactions. One approach to improving the LSB kinetics is to increase the edge sites of 2D crystalline MoS₂ catalysts by minimizing the number of stacks and reducing the lateral size.

In this study, we used a different approach by exploring a series of molybdenum sulfides (MoS_x) with tunable structures from MoS₃ to MoS₂. It has been reported that the amorphous MoS₃ is catalytically more active than the 2D MoS₂ and provides better performance for HER [225, 230-233] due to higher active sites available in the amorphous chain-like 1D MoS₃. However, the amorphous MoS₃ has rarely been explored in the LSB. The 1D amorphous MoS₃ could exist in different morphologies. Due to their amorphous nature and large variations depending on the synthesis conditions, it is extremely difficult to determine their molecular structures explicitly and correlate these with their catalytic properties. Ting and coworkers [234] have described that the MoS₃ structure could be in either a 1D chain-like structure consisting of uniform triangular dipyramidal units or a random polymeric chain consisting of larger polyatomic Mo and S clusters.

One of the most common types of 1D chain-like structure of the amorphous MoS₃ is the Hibble structure with a chemical formula Mo⁵⁺(S²⁻)₂(S₂²⁻)_{0.5} proposed by Hibble et al [235]. This Hibble structure consists of triangular bipyramidal units in which 3 sulfur atoms are bonded between two Mo atoms along the chain. Two sulfur atoms in every alternating MoS₃ unit form a bridging S₂²⁻ bond. The Weber model is another 1D chain-like structure [236] with a chemical formula of Mo⁴⁺(S²⁻)(S₂²⁻), where every MoS₃ unit contains two S atoms in a bridging S₂²⁻ bond and a S²⁻ atom. As these 1D amorphous MoS₃ chains do not form a close-packed structure like the stack of 2D crystalline MoS₂ basal planes, each atom of the MoS₃ unit is accessible by LPSs and is thus expected to provide a higher density of active sites that may act similarly to the edge sites of the 2D crystalline MoS₂.

Here, we report a two-step synthesis method that produces a set of MoS_x materials with tunable structures. It starts with a microwave-assisted synthesis to form 1D amorphous MoS₃, followed by a further thermal annealing process at different temperatures to gradually convert the 1D amorphous MoS₃ to nano-sized, few-layer crystalline 2D MoS₂ patches. A graphene oxide (GO) substrate was used to enhance the initial deposition of the amorphous MoS₃, which was converted into reduced graphene oxide (rGO) nanosheets during the microwave process and provided a better electrical connection to the small MoS_x nanomaterials. The as-prepared sample by microwave synthesis is denoted as MoS₃/rGO-Intermediate, which is dominated by a mixture of amorphous 1D Hibble and Weber structures with an S-to-Mo ratio of 2.7. During further thermal annealing at 250, 325, and 600 °C, respectively, in ultrapure Argon (Ar) gas containing 3% hydrogen, the Hibble structure was gradually converted into a Weber structure. Then, these amorphous MoS₃ structures were both converted into 2D crystalline MoS₂. The size of the crystalline MoS₂ nanopatches is less than ~10 nm, thus presenting a higher density of active edge

sites than the bulk crystalline MoS₂ reported in the literature. The advantage of this synthesis protocol over the traditional exfoliation [183] or CVD method [202] is that the lateral size is significantly smaller, and the average number of layers in the 2D stacks is only 3. We discovered that the 1D amorphous MoS₃/rGO annealed at 250 °C provided the highest specific capacity of 1,277 mAh/g at 0.1C rate, which is higher than the 2D crystalline MoS₂/rGO annealed at 600 °C. The capacity decay was only 0.04% per cycle at 1C rate in the 300 cycles of stability test for the amorphous 1D MoS₃/rGO-250 °C. On the other hand, the crystalline 2D MoS₂/rGO showed better redox kinetics and a higher CE of 97% at a 1C rate than the 1D MoS₃/rGO.

3.2 Materials and Methods

3.2.1 Chemicals

The precursor ammonium tetrathiomolybdate (ATM) (NH₄)₂MoS₄ was purchased from Millipore Sigma (Burlington, MA, USA), and the single-layer graphene oxide was purchased from ACS Materials (Pasadena, CA, USA). Lithium sulfide (battery grade) and solvents 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) were purchased from Sigma Aldrich (Sr. Louis, MO, USA). The electrolyte (1.0 M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in DOL/DME (1:1, v/v) with 1 wt% LiNO₃ additive) was purchased from Dodochem Limited (Suzhou, China). Li foil, polyvinylidene fluoride (PVDF) binder, CR2025 coin cell casings, spacers, and wave springs were purchased from MTI Corporation (Richmond, CA, USA). The Celgard 2400 separator was purchased from Celgard (Charlotte, NC, USA). The NMP solvent and solid sulfur powder (sublimed) were purchased from Fisher Scientific (Waltham, MA, USA).

3.2.2 Preparation of MoS_x/rGO Catalysts

In preparation for MoS_x/rGO catalysts, 17.5 mg of GO was dispersed in 3.5 mL of DI water and sonicated for 2 hours. After adding 21 mL of tetrahydrofuran (THF), 15.8 mg of ATM

precursor was added, which gives a concentration of 2.5 mM, and was further sonicated for 1 hour. The ATM concentration was deliberately set low so that the MoS_x deposited on rGO was limited to ~20 wt%, which provided a higher catalytic activity than those with higher MoS_x loadings of ~80% in our previous study [221, 225]. A microwave synthesis was used for 10 min at 170°C and 19 bar pressure. After the synthesis, the sample was washed with warm water (70°C) to remove impurities (such as ATM and MoO₃) and freeze-dried for 48 hours. This is also a critical improvement from our previous methods [221, 225], which enhances the electrocatalytic properties. The product is denoted as MoS₃/rGO-Intermediate. This material was further annealed in 3% H₂/97% Ar for 2 hours at 250, 325, and 600 °C. The resulting samples are denoted as MoS₃/rGO-250, MoS_x/rGO-325, and MoS₂/rGO-600, where the suffix refers to the annealing temperature.

3.2.3 Materials Characterization

The materials structure was analyzed by X-ray diffraction (XRD) using a D8 Advance diffractometer (Bruker Corporation, Karlsruhe, Germany) with a Cu K α radiation of wavelength 0.15418 nm and a detector slit width of 2 mm. The XRD spectra were smoothened with Origin Pro software using a 5-point adjacent average. The size and crystalline nature of MoS₂ nanopatches were studied using a Tecnai Osiris (Scanning) Transmission Electron Microscope (S/TEM) with a fully digital 200 kV system. The low-magnification images were taken with a PhiLPS CM 100 TEM with a tungsten source and a high tension of 100 kV. The material morphology was studied using field emission scanning electron microscopy (FESEM) with a Topcon/ISI/ABT DS 130F FESEM microscope (Akashi Beam Technology Corporation, Tokyo, Japan). The BET-SSA and pore-size distribution of the prepared samples were derived by N₂ adsorption at 77 K in a Quantichrome Autosorp IQ (Anton Paar, Ashland, VA) using N₂ as the analysis gas in a 9 mm

radius cell. The outgassing temperature was 100 °C for 12 hours. The Raman spectroscopy analysis was performed with a DXR™ Raman microscope (Thermo Fisher Scientific, Madison, WI) with a 532 nm laser at a power of 10 mW, using a 10× objective lens with a slit width of 50 μm. The surface composition and chemical environment of MoS_x/rGO hybrids were analyzed using a PHI 5000 Versa XPS system (Chanhassen, MN) with a monochromatic Al Kα source (1486.7 eV). The C 1s peak at 284.60 eV was used as the standard to calibrate the binding energy (BE) of all XPS spectra. The bulk mass ratio was analyzed by Thermogravimetric analysis (TGA) carried out with a TGA Q50 system (TA instruments-Waters LLC, New Castle, DE from room temperature to 800 °C in the air. The elemental analyses were taken using a PE 2100 Series II combustion analyzer (PerkinElmer Inc., Waltham, MA). The compounds were sampled using pressed tin capsules for CHNS analysis at the combustion and reduction temperatures of 975 °C using copper oxide wires and electrolytic copper, respectively. Silver capsules were used for O analysis with the oxygen reduction tube packed with nickel-plated carbon and quartz turnings. The precision and accuracy of the results were estimated to be about ± 0.3%.

3.2.4 Adsorption Capacity of Lithium Polysulfides on MoS_x/rGO Catalysts

The polysulfide solutions at a concentration of 5.0 mM in 1:1 DOL/DME (v/v) were prepared inside the glovebox with various stoichiometric ratios of Li₂S and sulfur for the respective chain length, i.e., Li₂S_n with n = 4, 6, and 8. For example, the ratio was 1:7 for Li₂S₈. The resulting solution was stirred for 5 days at 70 °C inside the glovebox. The 5.0 mM solution was diluted to 3.0 mM with DOL/DME solvents before the adsorption test. The adsorption of LPSs on the MoS_x/rGO catalysts was quantified by UV-Vis absorbance spectra by adding ~25 mg of MoS₂/rGO-600, ~26 mg of MoS₃/rGO-250, and ~30 mg of MoS₃/rGO-intermediate to keep the active MoS_x wt% similar among the experiments into 4.0 mL of 3.0 mM polysulfide solution in a

cuvette inside the glove box and tightly sealed before bringing it outside. A control experiment using 25 mg of rGOs was carried out in the same way. The adsorption capacity was normalized by the total mass of MoS_x/rGO or rGO added. The UV-Vis spectra were collected at the 1st, 2nd, 3rd, 4th, 6th, 8th, and 12th hours to study adsorption kinetics, and the saturated absorbance value at the 12th hour was used to calculate the specific adsorption capacity.

3.2.5 Preparation of Electrodes

The electrodes for symmetric cells were prepared by mixing 80 wt% active MoS_x/rGO catalysts (or rGO control), 10 wt% super P as conductive carbon, and 10 wt% PVDF binder. The slurry was prepared with NMP solvent until a uniform mixture was formed. The slurry was coated with a blade coater with a thickness of 100 μm on a 17 mm thick carbon-coated Aluminum foil. The coated foil was dried overnight in a vacuum oven at 90 °C. The S/C electrodes for full Li-S cells were prepared with 60% sulfur powder, 20% MoS_x/rGO (or rGO controls), 10% super P, and 10% PVDF binder. Similarly, the slurry was prepared with NMP solvent and coated as a 200 μm thick film on the Al foil. The coated foil was dried in a vacuum oven at 55 °C overnight. After drying, the electrodes in the form of disks with a diameter of 15 mm were punched out. The S/C electrode was then flash heated for 10 s at a 240 °C hot plate to allow S to infuse into the MoS_x/rGO before being used for electrochemical testing. The short flash heating ensured that negligible S was lost due to evaporation. The Sulfur loading was calculated to be 0.85 ± 0.05 mg/cm². The electrode thickness was precisely regulated to 70 ± 3 μm using a calendaring machine to ensure uniform thickness.

3.2.6 Cell Assembly and Electrochemical Measurements

All electrochemical measurements were taken in CR2025 coin cells. The symmetric cell was assembled with two identical MoS_x/rGO electrodes. The 1.0 M LPS solutions were prepared

inside the glovebox and diluted to 0.20 M with DOL/DME (1:1) solvent before using as an electrolyte. A 60 μL of 0.20 M LPS solution was used as an analyte. The full cell was assembled with a sulfur-mixed S/C electrode after flash melting of S as the cathode and a Li metal disk with a 0.6 mm thickness as the anode. A 60 μL 1.0 M LiTFSI with 1 wt% LiNO_3 additive was used as the electrolyte. For all the cell configurations, Celgard 2400 polypropylene was used as the separator, and cells were assembled inside the MBRAUN glove box in an ultrapure Argon atmosphere with O_2 and H_2O levels below 0.5 ppm.

3.2.7 Cell Charge-Discharge Evaluations

The performance of the assembled Li-S coin cells was evaluated by galvanostatic charge-discharge cycling in the potential range of 1.7 V to 2.8 V in two types of measurements using a battery testing system (Neware, Shenzhen, China) at room temperature. The first one involved changing the magnitude of the current corresponding to a series of C-rates (relative to theoretical S-specific capacity), while the second one, for long-term stability, was done at a fixed rate of 1C for continuous charge-discharge up to 1000 cycles. The chronoamperometric potentiostatic measurements were done by stepping the cell voltage of a pristine cell from ~ 2.37 V to 2.28 V to record the current vs. time until the current dropped to 10^{-5} A. After that, the cell was discharged to 2.2 V in a constant current of 1C to ensure that all the long-chain LPSs had been converted to Li_2S_4 . Then, the cell voltage was stepped to 1.90 V to record the current of further LPS reduction vs. time until the current dropped to 10^{-5} A. The same cell was further discharged to 1.70 V at a constant current at 1C rate to ensure that all LPSs were converted to Li_2S . The oxidation current was recorded similarly, while the cell voltage was stepped back to 2.4 V to study the kinetics of conversion of Li_2S into S_8 . Cyclic voltammetry (CV) measurements were taken from 2.8 to 1.7 V with a scan rate of 0.1 mV/s in a CHI 440a potentiostat (CHI instrument, Austin, TX, USA).

3.3 Results and Discussion

3.3.1 Synthesis Protocol

Fig. 3.1 schematically illustrates the routes to synthesize various MoS_x/rGO hybrid materials. Under ambient conditions, the ATM precursor is known to be converted into 1D amorphous MoS_3 as it is heated to 260-300 °C, and the amorphous MoS_3 starts to be converted into 2D crystalline MoS_2 above 310 °C [236]. An efficient microwave synthesis method was used in this study under solvothermal conditions (170°C and 19 bar), which quickly deposited the active material, i.e., amorphous MoS_3 , onto the rGO support. This forms the hybrid catalyst, i.e., amorphous MoS_3/rGO -Intermediate, which follows the nominal reaction equation [236]:

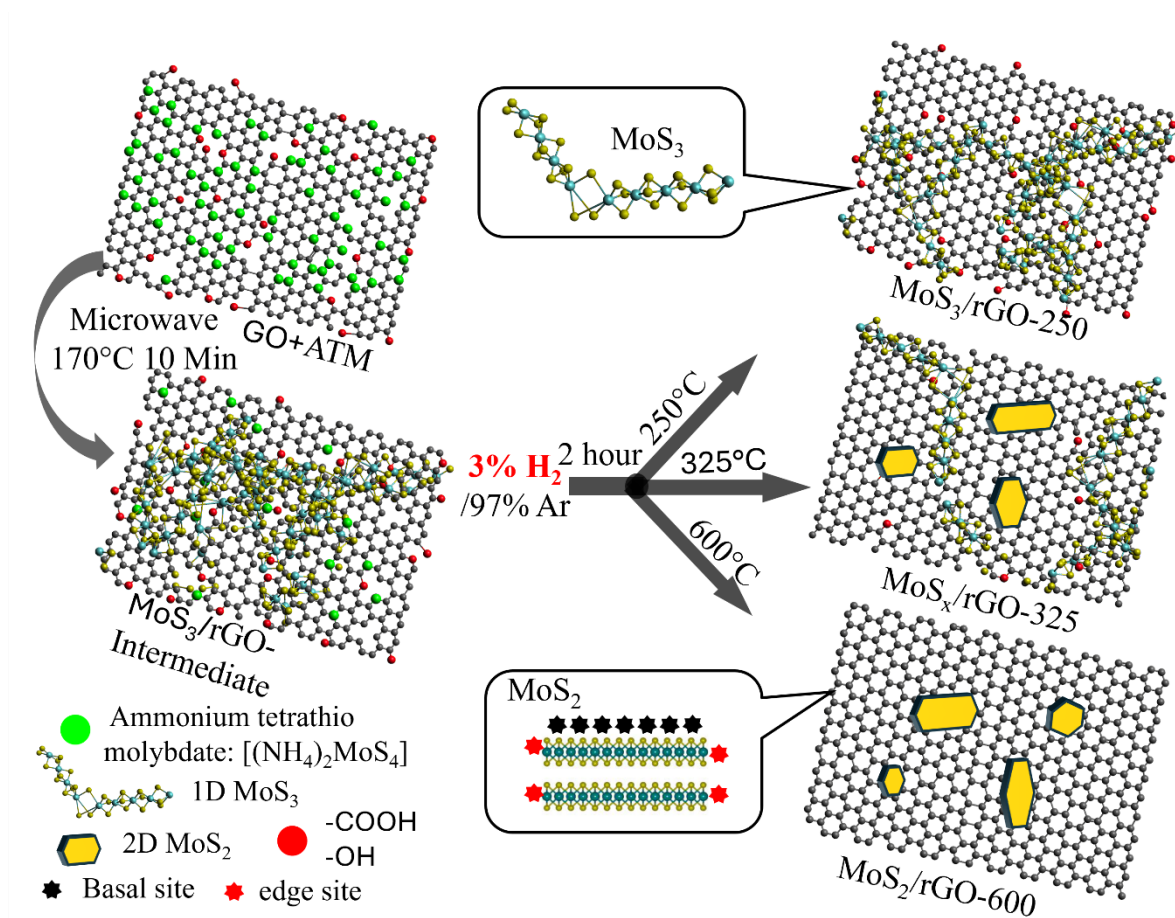
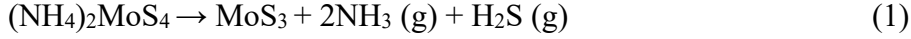


Figure 3.1. Schematic of MoS_x/rGO hybrids synthesis routes. Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.



THF was used as a solvent due to its low microwave absorptivity (loss tangent value, $\tan\delta = 0.042$) compared to the starting GO carbon support ($\tan\delta = 0.8\text{-}1.0$), which allowed the specific microwave heating of the carbon support instead of the whole reaction vessel due to the difference in their microwave absorptivity. This facilitates the selective deposition and growth of 1D chain-like amorphous MoS_3 on the GO substrate, which was converted into the more graphitized rGO. The 1D chain-like amorphous MoS_3 structure could exist in two forms, one being the Hibble structure [235] with a formula of $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{0.5}$ and the other one being the Weber structure with a formula of $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ [236]. The structure of the MoS_x/rGO hybrids can be tuned by further thermal annealing of the amorphous MoS_3/rGO -Intermediate at 250 °C, 325 °C, and 600°C, respectively, for 2 hours in a reducing atmosphere (3% H_2 balanced with 97% Ar). This provided a series of MoS_x/rGO materials from the starting 1D amorphous MoS_3 to the final few-layer stacked nano-size 2D crystalline MoS_2 patches, with a formula $\text{Mo}^{4+}(\text{S}^{2-})_2$, at 600°C, following the reaction:



The annealed hybrid catalysts are denoted as MoS_3/rGO -250, MoS_x/rGO -325 ($2 < x < 3$), and MoS_2/rGO -600, where the suffix represents the annealing temperature. This synthesis protocol provides a large structural variety at the molecular level, from 1D amorphous MoS_3 on defective rGO to 2D nanosized crystalline MoS_2 on a graphitic rGO carbon support.

3.3.2 Structural and Morphological Characterization

High-resolution TEM (HR-TEM) and XRD were used to study the deposition and growth of MoS_x on the rGO. The HR-TEM image in Fig. 3.2(a) and the low-magnification TEM image in Fig. A.1(c) show that the amorphous MoS_3 after the initial microwave synthesis at 170°C uniformly covered the rGO surface with no crystalline feature.

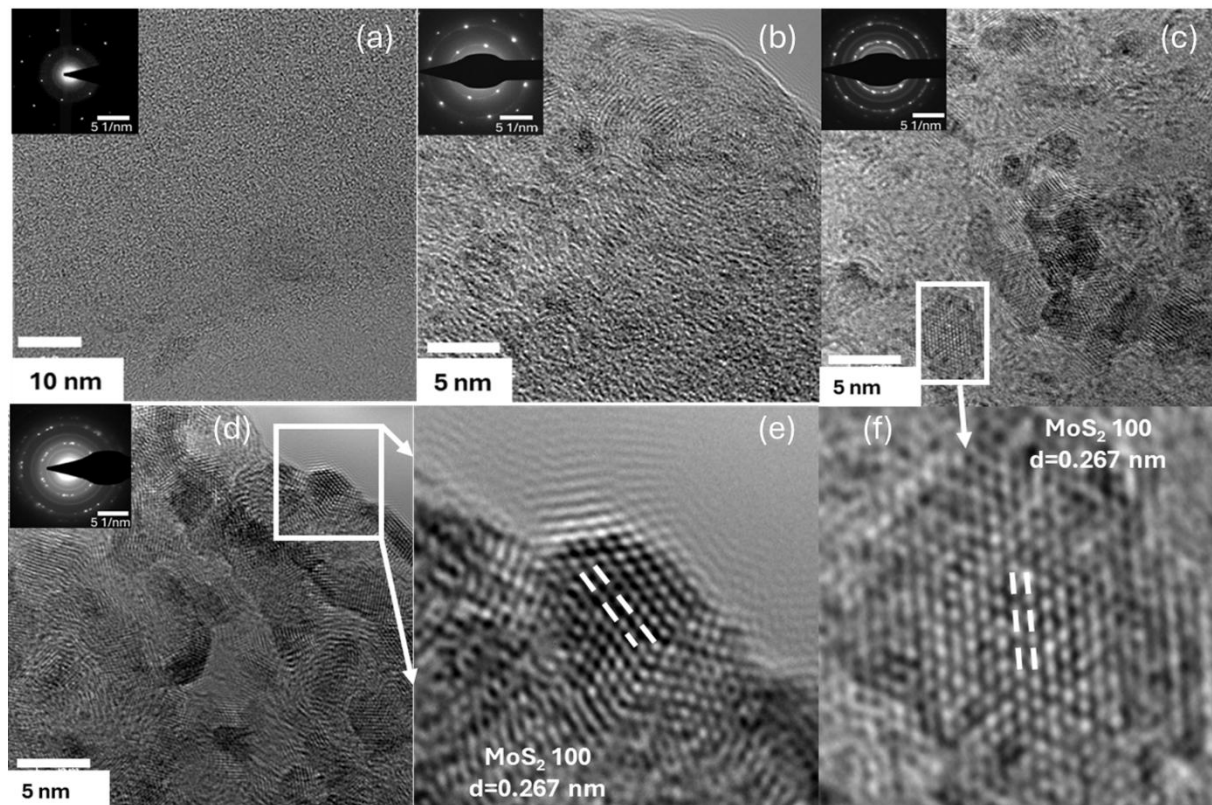


Figure 3.2. HR-TEM images with their respective SAED patterns in the insets: (a) MoS_3/rGO -Intermediate, (b) MoS_3/rGO -250, (c) MoS_x/rGO -325, and (d) MoS_2/rGO -600. Enlarged view of the lattice fringes are shown in (e) for MoS_2/rGO -600 and (f) for MoS_x/rGO -325. Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

The HR-TEM image of MoS_3/rGO -250 in Fig. 3.2(b) and the TEM image in Fig. A.1(d) are similar to those of MoS_3/rGO -Intermediate, though some lattice fringe patterns started to emerge in isolated local dark spots (< 4 nm in size). Since the annealing temperature was lower

than the MoS_3 to MoS_2 transition temperature of 310°C , the sample was still dominated by the 1D amorphous MoS_3 phase. Due to the low wt% and amorphous nature of the MoS_3 , it was difficult to observe the detailed structure of these low-temperature annealed samples by TEM. Interestingly, the selected area electron diffraction (SAED) patterns of these samples in the inset of Fig. 3.2(a) and 3.2(b) show sharp hexagonal diffraction spots attributed to the 2D crystalline structure of rGO with a unit cell lattice $a = 2.46 \text{ \AA}$. Clearly, the GO was effectively transformed into 2D crystalline rGO sheets during the microwave process.

Consistent with the TEM images, MoS_3/rGO -Intermediate and MoS_3/rGO -250 did not show any XRD peaks from MoS_x in Fig. 3.3(a). The two weak peaks at 2θ of $\sim 23.1^\circ$ and $\sim 43.3^\circ$ in MoS_3/rGO -Intermediate can be attributed to (001) and (100) diffraction from few-layer stacked rGO nanosheets. The d-spacing derived from the (001) diffraction peak was 0.39 nm, which was expanded from 0.34 nm in graphite, indicating that the stacking was disrupted by remaining oxygenated moieties in the rGO plane. In addition, two small humps were observed around the 2θ of $\sim 9^\circ$ - 12° , which can be attributed to a small amount of MoO_3 nanoparticles that formed along with MoS_3 during the microwave process. Most of this impurity was washed away using warm deionized water due to the relatively high solubility of MoO_3 (20.55 g/L at 70°C). The unreacted ATM and the remaining MoO_3 may have been converted into MoS_3 during thermal annealing at 250°C , which is indicated by the reduced MoO_3 humps in XRD of MoS_3/rGO -250 in Fig. 3.3(a). Interestingly, the (001) peak shifted to a higher 2θ value of 24.7° in MoS_3/rGO -250, indicating that thermal annealing removed more oxygenated moieties and further improved the graphitic crystallinity of rGO.

At a higher temperature of 325°C , the 1D amorphous MoS_3 started to be converted into 2D crystalline MoS_2 , and at 600°C , it was completely converted into MoS_2 , as shown in Fig. 3.2(c-

f). The low-magnification TEM images in Fig. A.1(e-f) show the formation of small, darker patches of crystalline MoS₂ in MoS_x/rGO-325 and MoS₂/rGO-600 materials. The HR-TEM images in Fig. 3.2(c-d) clearly show MoS₂ patches varying from 3 to 7 nm in size. The enlarged images in Fig. 3.2(e-f) show well-defined hexagonal lattice fringes with a d-spacing of 0.267 nm, matching that of the standard MoS₂ (100) lattice of 0.270 nm. The SAED patterns in the inset of Fig. 3.2(c-d) show the feature of polycrystalline rGO (i.e., a weak continuous diffuse ring superimposed with sharp brighter hexagonal spots from multiple rGO domains with different in-plane rotational orientations). Importantly, two additional uniform continuous rings with a radius smaller than those of rGO rings emerged, which nicely match the (100) and (110) diffraction of the 2D powder-like small MoS₂ nanopatches with a hexagonal unit cell lattice, $a = 3.18 \text{ \AA}$. The rotational orientation of these crystalline MoS₂ nanopatches was completely random, but they were apparently anchored flatly in the rGO plane.

The XRD spectra in Fig. 3.3(a) also show two weak peaks at 2θ of 33.1° and 58.9° , corresponding to (100) and (110) diffraction of crystalline MoS₂ in the MoS₂/rGO-600 sample. The low intensity of these MoS₂ peaks was due to the low MoS₂ loading ($\sim 20 \text{ wt\%}$) that was needed to obtain better performance in this work. For comparison, much stronger MoS₂ peaks were observed with the MoS₂/rGO-600 of $\sim 80 \text{ wt\%}$ MoS₂ loading (see Fig. 2.3) that was used in our previous studies [221, 225]. The rGO peak in the XRD spectra moved to a higher 2θ value of 26.0° , corresponding to a d-spacing of 0.34 nm. Clearly, while increasing the annealing temperature from 250°C to 600°C , the interlayer distance was reduced and became closer to 0.34 nm in graphite as more oxygenated groups were removed from rGO.

The FESEM images in Fig. A.2 show the wrinkled fluffy morphology of all the MoS_x/rGO hybrids. The BET surface analysis in Fig. A.3 shows that the MoS₃/rGO-Intermediate has a higher

specific surface area (SSA) of 123 m²/g than that of 92 m²/g in rGO control at similar conditions. The half-pore size distribution for these two samples is similar in the range of 3 to 30 Å. The

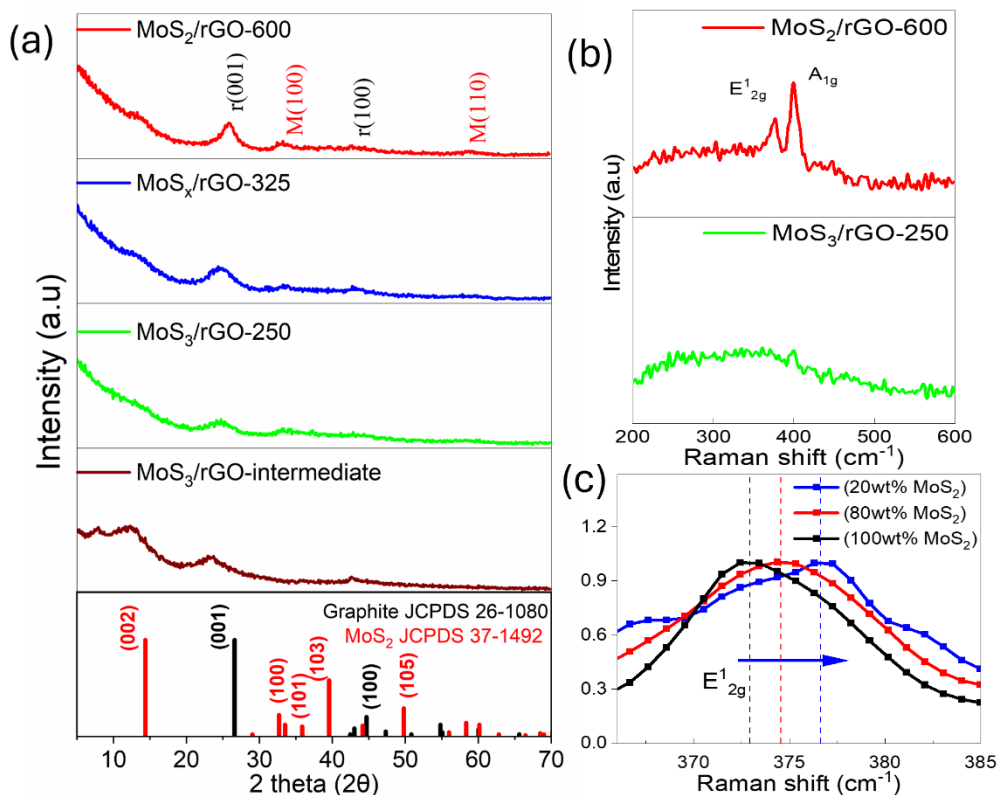


Figure 3.3. (a) XRD of MoS₂/rGO-600, MoS_x/rGO-325, MoS₃/rGO-250, and MoS₃/rGO-Intermediate compared with the JCPDS data of Graphite and MoS₂. (b) Raman spectra of MoS₂/rGO-600 and MoS₃/rGO-250 in the E_{2g}¹ and A_{1g} peak region. (c) The correlation of the E_{2g}¹ peak downshift with the thickness of 2D MoS₂ stacking. Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

deposited MoS₃ seemed to help suppress the rGO restacking but did not alter the pore structure.

The Raman spectra in Fig. 3.3(b) show the characteristic 2H-MoS₂ peaks, i.e., the E_{2g}¹ in-plane vibrational peak at 376 cm⁻¹ and the A_{1g} out-of-plane vibrational peak at 399 cm⁻¹, which only appeared in the MoS_x/rGO-325 and MoS₂/rGO-600 samples due to the formation of 2D crystalline MoS₂, but not in the amorphous MoS₃/rGO-250 and MoS₃/rGO-Intermediate. The full spectra of all four materials in Fig. A.4(c-d) further confirmed no characteristic Raman peaks in

1D amorphous MoS₃ in low-temperature annealed samples. It was also observed that the peak position of the E_{2g}¹ Raman peak depended on the MoS₂ stack thickness, which was tuned by the precursor concentration during the microwave synthesis. The Raman peak positions and peak separation are listed as a function of MoS₂ content in Table A.1. The E_{2g}¹ peak in Fig. 3.3(c) moves from 372.9 cm⁻¹ to 376.6 cm⁻¹ when the MoS₂ wt% is reduced. However, the A_{1g} in Fig. A.4(e) remains in nearly the same position. This leads to an overall peak separation of 22.9 cm⁻¹ in MoS₂/rGO-600, which suggests that the stacking in the 2D MoS₂ nanopatches could be at most 3 layers [237]. In recent years, there have been many efforts to synthesize nano-sized MoS₂ [183]. The synthesis route in this study can effectively control the size, thickness, and tunability from 1D amorphous MoS₃ to 2D crystalline MoS₂. The thinner stacking and smaller nano-size of crystalline MoS₂ help to increase the active edge sites.

The Raman spectra in Fig. A.4 also show the strong characteristic D and G bands at 1,341 cm⁻¹ and 1,583 cm⁻¹, representing the vibration from the sp³ carbon defects and sp² graphitic carbon of the rGO substrate. Weak 2D and S3 bands from the rGO were also observed at ~ 2700 and 2900 cm⁻¹. However, we did not observe any characteristic Raman signal in the range of ~ 320 to 550 cm⁻¹ from the cluster-like amorphous MoS₃ reported in the literature [238] or from ~200 to 400 cm⁻¹ of amorphous MoS₃ prepared by a different method [239]. This suggests that the MoS₃ synthesized with our protocol is different from the cluster-like morphology. However, with the typical spectroscopic and microscopic tools such as TEM and Raman spectra, it is impossible to derive a precise understanding of the molecular structure of the amorphous MoS₃.

3.3.3 Material Structure and Composition by XPS Analysis

XPS was used to quantify the chemical composition of different MoS_x/rGO hybrids and to understand the structure of the 1D amorphous MoS₃ and 2D crystalline MoS₂ at the atomic level. Fig. 3.4 shows the XPS spectra of the Mo 3d peaks in the BE range of 223 - 240 eV and S 2p peaks in 160 - 167 eV for all four catalysts. The Mo spectra of MoS₃/rGO-Intermediate can be deconvoluted into three doublets of Mo 3d_{5/2} and Mo 3d_{3/2} peaks at 229.46 and 232.49 eV, 230.18 and 233.06 eV, and 232.49 and 235.31 eV, respectively, corresponding to the three oxidation states

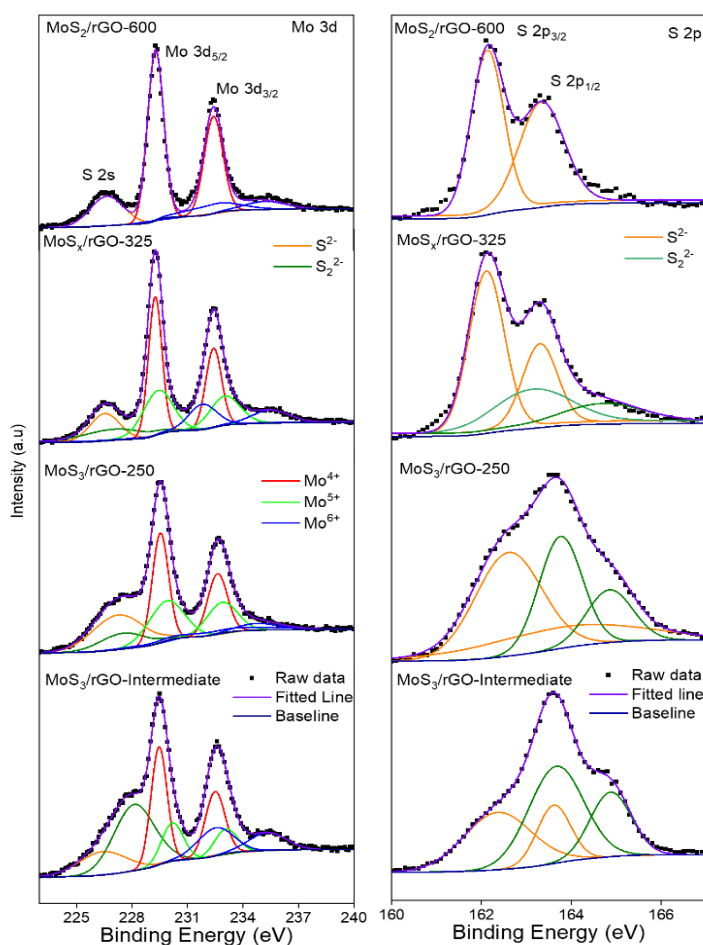


Figure 3.4. (a) High-resolution XPS spectra of Mo 3d (left) and S 2p (right) from MoS₂/rGO-600, MoS_x/rGO-325, MoS₃/rGO-250, and MoS₃/rGO-Intermediate, respectively. Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

of Mo^{4+} , Mo^{5+} , and Mo^{6+} . Mo^{4+} and Mo^{5+} are attributed to the amorphous MoS_3 , and Mo^{6+} is attributed to the unreacted ATM and some MoO_3 side products. The S 2p spectrum from the amorphous MoS_3 can be fitted with two sets of $2p_{3/2}$ and $2p_{1/2}$ doublets, with one set at a lower binding energy of 162.36 and 163.61 eV for unsaturated S^{2-} (shown with the orange color) and the other set at a higher BE of 163.66 and 164.84 eV for bridging S_2^{2-} (green color). As shown in Table A.2, there was 42.4% sulfur present as S^{2-} and 57.6% as S_2^{2-} in the MoS_3/rGO -Intermediate, with a ratio of S_2^{2-} to S^{2-} as 1.36:1. Mo was present as 34.8% of Mo^{4+} , 42.1% of Mo^{5+} , and the remaining 22.07% as Mo^{6+} that was attributed to impurities such as unreacted ATM and MoO_3 .

Due to the complicated amorphous nature, the material structure and composition of MoS_3 are ambiguous in literature. So far, it still lacks a convincing technique that can provide exact molecular information about the amorphous MoS_3 structure. To extract the structural information, we adopt a simplified model based on two proposed structures of a 1D chain-like MoS_3 . One is the Hibble structure $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{0.5}$ as shown in Fig. A.5(b), and the other one is the Weber structure $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ as shown in Fig. A.5(c). The atomic configurations and key bond lengths are also elucidated using DFT calculations in the later section. The MoS_3/rGO -Intermediate consists of 34.8% Mo^{4+} and 43.1% Mo^{5+} , where all Mo^{4+} is attributed to the Weber structure and Mo^{5+} is attributed to the Hibble structure. The Mo^{6+} species belongs to the unreacted ATM and MoO_3 as impurities. The temperature during the microwave synthesis was 170 °C, well below the temperature to form MoS_2 . Thus, we assume that no MoS_2 formed in this step, which was also supported by the HR-TEM and SAED observation in Fig. 3.2 and XRD/Raman data in Fig. 3.3.

While annealing the intermediate hybrid, it was found that the ratio of S_2^{2-} to S^{2-} and the Mo oxidation state changed significantly at higher temperatures. The high-resolution XPS spectra of the other three MoS_x/rGO catalysts were deconvoluted similarly. Table A.2 and Fig. A.6(a-c)

summarize the specific BE and the relative composition of all four catalyst materials. According to DFT calculations, the Webber $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ structure is energetically more favorable (by 0.08 eV per MoS_3 unit) than the Hibble $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{0.5}$ structure. For MoS_3/rGO -250, it was observed that the Mo^{4+} increased from 34.8% to 49.6%, attributed to the increase of Weber structure, whereas the Mo^{5+} decreased from 43.1% to 39.1%, associated with the decrease of Hibble structure. This indicates the conversion of the metastable Hibble structure to the more stable Weber structure at the annealing temperature of 250 °C. In a similar pattern, the bridging S_2^{2-} composition was reduced from 57.6% to 41.3%, whereas the S^{2-} composition increased from 42.4% to 58.7%, accompanying a decrease in the ratio of S_2^{2-} to S^{2-} from 1.36 to 0.70. Aside from this conversion, the unreacted ATM was converted to MoS_3 as reflected by the reduction of the Mo^{6+} from 26.1% to 11.3%. The composition of the Mo^{4+} and the S^{2-} monotonically increased as

Table 3. Summary of the XPS analysis of the Mo 3d and S 2p, and corresponding to their possible molecular structures.

Ox. state	Possible Structure	M-int	M-250	M-325	M-600
Mo^{4+}	1D Weber MoS_3 : $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$	34.80	49.61	4.49	0
	2D MoS_2 : $\text{Mo}^{4+}(\text{S}^{2-})_2$	0	0	55.14	81.72
Mo^{5+}	1D Hibble MoS_3 : $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{0.5}$	43.13	39.12	23.98	0
Mo^{6+}	$(\text{NH}_4)_2\text{MoS}_4^{\text{a}}$ or MoO_3^{b}	22.07 ^{a+b}	11.27 ^b	16.39 ^b	18.28 ^b

Note: a – unreacted ATM residue; b – MoO_3 impurity formed during the process.

the annealing temperature was raised to 325 °C and further to 600 °C, while the Mo^{5+} and S_2^{2-} followed the opposite trend. The typical threshold for the thermal conversion of MoS_3 to MoS_2 is ~ 310 °C. Hence, at 325°C, a partial conversion of 1D amorphous MoS_3 to crystalline MoS_2 was observed. Since all three phases were present at this condition, we refer to this sample as MoS_x/rGO -325 to reflect the complexity.

In MoS_x/rGO-325, it was found that 59.6% of Mo was in the Mo⁴⁺ state, where it can be present in either Weber 1D amorphous MoS₃ or 2D crystalline MoS₂. The composition was estimated to be 4.5% Weber amorphous MoS₃ and 55.1% 2D crystalline MoS₂, as described in Appendix A. All Mo⁵⁺ was attributed to the remaining 1D Hibble a-MoS₃. This caused the S₂²⁻ to S²⁻ ratio to further decrease from 0.70 to 0.49. Despite the difficulty in controlling the exact composition, this synthesis protocol provided the unique capability to tune the MoS_x structure at the molecular level, which offered the opportunity to study a set of materials with different active sites for electrocatalytic LPS conversion.

At the highest annealing temperature of 600 °C, all Mo⁵⁺ was converted to Mo⁴⁺, and all S₂²⁻ was converted to S²⁻, resulting in complete conversion to 2D crystalline MoS₂. At the same time, due to the high temperature, some Mo reacted with the residual oxygen in the tube furnace and oxygenated moieties in rGO to form a small amount of MoO₃, as represented by the 18.3% Mo⁶⁺ in Table 2. The overall transition of Mo and sulfur in various forms is presented in Fig. A.6(a-c). The atomic ratio of S to Mo in MoS_x decreases monotonically from 3.2 in MoS₃/rGO-Intermediate to 2.5, 2.3, and 2.1 when it was annealed at 250, 326, and 600°C, respectively. The S: Mo ratio in MoS₂/rGO-600 is close to the perfect 2D crystalline MoS₂ structure. The trend of the elemental composition derived from XPS agrees well with the CHNSO analysis shown in Fig. A.6(d-e) and Table S3, except for the MoS₂/rGO-600 sample. This is likely due to the difficulty of achieving the full oxidation of the highly stable crystalline MoS₂ phase during the CHNSO analysis. The overall hybrid material was further analyzed with TGA, shown in Fig. A.7. The weight ratio in the hybrid materials is given in Table A.4. It was found that the intermediate sample had the lowest stability and started to degrade around 250 °C. The three annealed samples had similar thermal stability, with MoS₂/rGO-600 being slightly more stable than the other two, as

indicated by the shift of the TGA curve to a higher temperature by ~ 15 °C and $\sim 1\%$ - 4% more weight remaining at 600 °C. All hybrid materials had fairly similar compositions, consisting of about 21 % to 29% MoS₂ and 79% to 71% rGO.

3.4 Electrocatalytic Activity Evaluation

In Li-S batteries, 75% of the theoretical capacity comes from the second discharge plateau, the limiting reaction [240] where the short-chain polysulfide (SCP; Li₂S₄) is converted into solid

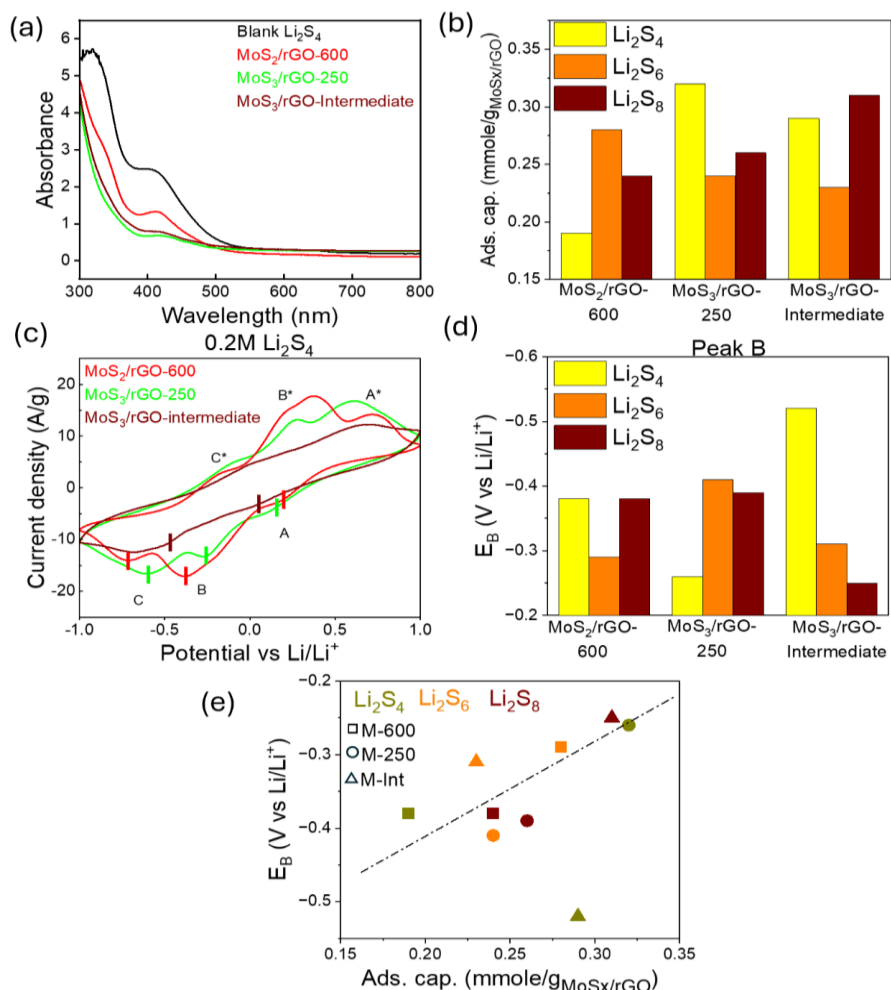


Figure 3.5. (a) Absorbance spectra of 3.0 mM Li₂S₄ with MoS₂/rGO-600, MoS₃/rGO-250, and MoS₃/rGO-Intermediate. (b) Bar chart of specific adsorption capacity of various materials in 3.0 mM Li₂S₄, Li₂S₆, and Li₂S₈. (c) Symmetric cell CV at 50 mV/s of MoS₂/rGO-600, MoS₃/rGO-250, and MoS₃/rGO-Intermediate electrodes in 0.20 M Li₂S₄. (d) Summary of the peak B potential (E_B) derived from the symmetric cell of different catalysts with 0.20 M Li₂S₄, Li₂S₆, and Li₂S₈ electrolyte, respectively. (e) The correlation of the LiPS adsorption capacity (in panel (b)) and E_B of the symmetric cell (in panel (d)). Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

nonconductive Li_2S . Hence, developing a catalyst with stronger interaction and higher adsorption capacity towards SCP is essential to reaching the theoretical capacity and improving the charge-discharge kinetics. The UV-Vis absorbance spectra were measured to assess the adsorption of various LPSs on MoS_x/rGO hybrids. Fig. 3.5(a) shows the absorbance spectra of 3.0 mM Li_2S_4 after incubating with three catalyst materials for 12 hours. The adsorption capacity was derived from the decrease of the absorbance at the peak wavelength of 411 nm and normalized to the total weight of the MoS_x/rGO hybrids, as shown in Fig. 3.5(b). The photos captured during the experiments and the calibration curves for all the materials are provided in Fig. A.8(a-b). The adsorption capacity was found to depend on the polysulfide chain length and the catalyst morphology. The SCP Li_2S_4 has a high adsorption capacity of 0.32 mmole/g and 0.29 mmole/g on the 1D MoS_3/rGO -250 and MoS_3/rGO -Intermediate, respectively, and a relatively lower adsorption capacity of 0.19 mmole/g on 2D MoS_2/rGO -600.

Traditional literature uses long-chain polysulfide (LCP) as an adsorbate since it is convenient to prepare because of its high solubility in ether solvents. In this study, we made more efforts to study Li_2S_4 as an adsorbate since this plays a more crucial role in the Li-ion storage capacity and energy density. We also measured the adsorption of LCPs, Li_2S_6 , and Li_2S_8 on various catalysts, as shown in Fig. A.9(a-b). Among the two LCPs, the adsorption capacity of Li_2S_8 on the MoS_2/rGO -600 is close to that of MoS_3/rGO -250. However, the MoS_3/rGO -intermediate has a slightly higher value than the other two, possibly attributed to the presence of more polar -OH and -COOH groups in the rGO, which generated the monotonically increasing adsorption capacity for all LPSs in the control rGO as the preparation temperature is lowered, as summarized in Fig. A.9(e). The adsorption capacity of Li_2S_6 has the opposite trend, with the highest adsorption on

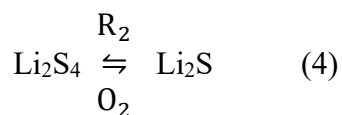
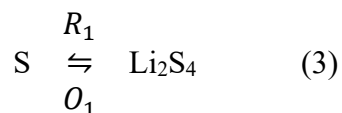
MoS₂/rGO-600. This further confirmed that using multiple catalysts with proper interactions with different LPSs may provide the ultimate performance.

To evaluate the catalytic activity of these MoS_x/rGO catalysts, the three LPSs with different chain lengths were used as electrolytes in the symmetric cell study in Fig. 3.5(c) and Fig. A.9(c). In 0.20 M Li₂S₄ as analytes, the CV curves show three pairs of redox waves marked in Fig. 3.5(c). Peaks A/A* represent the conversion between S₈ produced in the previous cycle and the Li₂S₆ and vice versa. Peaks B/B* represent the conversion between Li₂S₆ and Li₂S₄ from the bulk to Li₂S₂ and vice versa. The third pair of peaks, C/C*, represents the conversion between Li₂S₂ to the solid end-product Li₂S and vice versa [183, 241]. Similar CV measurements were made with symmetric cells filled with 0.20 M Li₂S₆ and 0.20 M Li₂S₈. In 0.20 M Li₂S₈ (Fig. A.9(c)), the third pair of peak C/C* was absent, leaving only two pairs of peaks. This is possibly due to the very low concentration of SCP produced, which is masked by the high concentration of 0.2 M Li₂S₈ in the bulk analytes.

Fig. 3.5(c) shows that MoS₃/rGO-Intermediate only produces weak redox waves over the background trace in 0.20 M Li₂S₄, while MoS₃/rGO-250 and MoS₂/rGO-600 exhibit higher redox peaks, indicating their higher catalytic activity. Further, during the reduction scan, MoS₃/rGO-250 provides a more positive potential for both B and C peaks than MoS₂/rGO-600, suggesting the easier conversion of SCP to the end product Li₂S due to the catalytic properties. The electrochemical results represented by the reduction potential of peak B (E_B) in the symmetric cell (Fig. 3.5(d)) are, in general, correlated well with the adsorption capacity in Fig. 3.5(b). Despite the complexity of multiple variables, the scattered plot in Fig. 3.5(e) shows a clear correlation between E_B in 0.20 M Li₂S₄ and its adsorption capacity on various catalysts. In general, a higher adsorption capacity leads to a higher E_B (i.e., higher electrocatalytic activity). The only outlier is MoS₃/rGO-

Intermediate, in which the abnormally high adsorption of Li_2S_4 can be attributed to the strong adsorption on rGO, which contained a high degree of oxygenated moieties. Overall, MoS_3/rGO -250 exhibited the highest activity for reduction peak B, while MoS_2/rGO -600 provided the highest activity for reduction peak A (Fig. A.9(d)).

Full Li-S coin cells with an S/C cathode vs. a Li anode were tested to assess whether incorporating MoS_x/rGO catalysts in the S/C cathode can enhance battery performance. Fig. 3.6(a) shows the CVs between 2.8 V and 1.7 V at a scan rate of 0.10 mV/s with MoS_2/rGO -600 and MoS_3/rGO -250 catalysts and the control rGO-250 in the cathode, respectively. More extensive CV curves are present in Fig. A.10. Four redox peaks denoted as R_1 , R_2 , O_2 , and O_1 represent the following reversible reactions:



The peak R_1 (at ~ 2.32 V) represents the reduction of S_8 up to SCP Li_2S_4 , and the peak R_2 (at ~ 2.03 V) represents the reduction of SCP Li_2S_4 to the end-product Li_2S . During the anodic scan, peak O_2 and O_1 are reverse processes of R_2 and R_1 . Ideally, all Li_2S and lithium polysulfides are expected to be converted to S_8 at 2.8 V. In the measured CVs, all catalysts showed higher peak current densities in both reduction and oxidation scans than the respective control rGO samples. In addition, the area under the CV peak reflects the capacity in the respective redox processes. The MoS_3/rGO -250 gave the largest peak areas, particularly in the oxidation process, which confirmed its superior catalytic property in delithiation. Fig. A11(a-c) shows the zoomed-in view of the reduction and oxidation peaks of the CVs in Fig. 3.6(a). In the R_1 region, the reduction peak

potential of the MoS₂/rGO-600 catalyst is ~8 mV higher than the other three catalysts. On the other hand, in the R₂ region, the onset potential of MoS₃/rGO-250 was the highest, followed by MoS_x/rGO-325, while MoS₂/rGO-600 showed a slightly higher peak current.

In the anodic scan, the conversion of the deposited solid Li₂S to S₈ shows similar trends. MoS₂/rGO-600 has the lowest oxidation peak potential, while the other three catalysts are comparable, as shown in Fig. A.11(c). Apparently, MoS₂/rGO-600 is most active in converting SCP to Li₂S and vice versa. However, the oxidation peak area is highest with 1D MoS₃/rGO-250, which is consistent with the higher adsorption capacity of the SCP on 1D MoS₃/rGO-250. To reveal the electrocatalytic properties, the Tafel slopes of the oxidation peak O₂ and the reduction peak R₂ were calculated from the CVs of all four catalyst materials, their respective rGO controls,

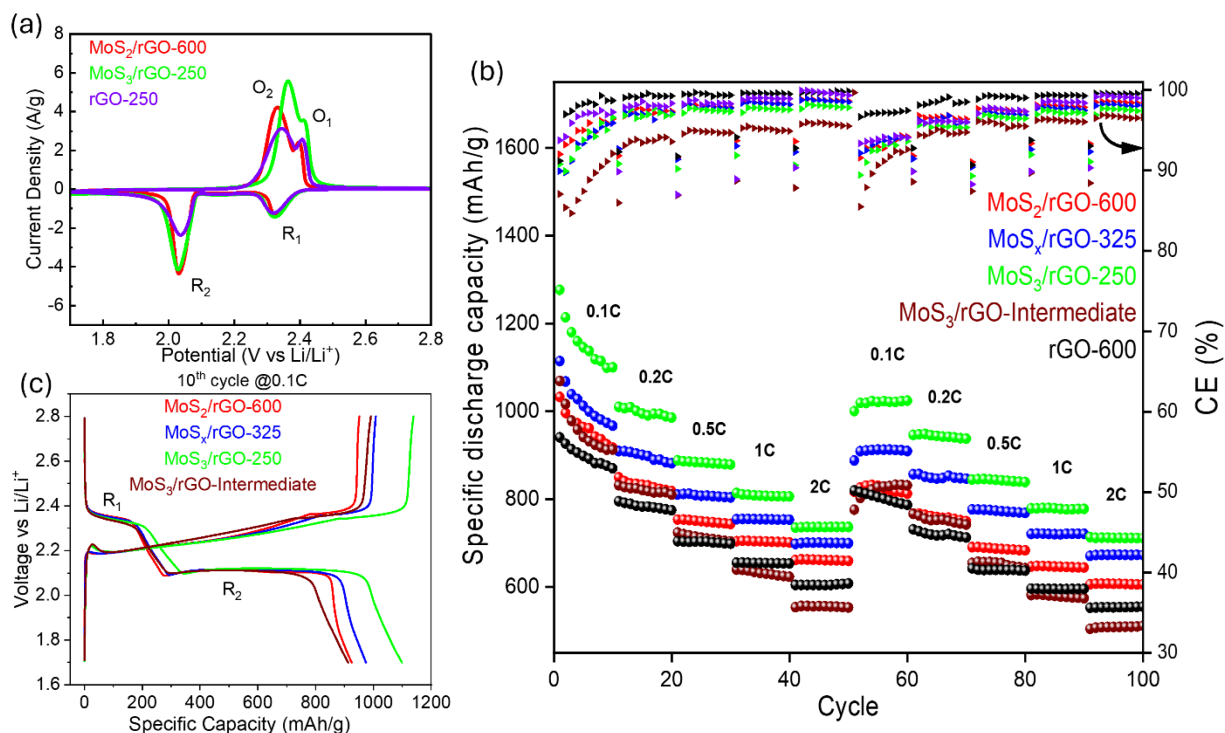


Figure 3.6. (a) CV at 0.1 mV/s, (b) rate performance test, (c) charge-discharge of 10th cycle at 0.1C rate of MoS₂/rGO-600, MoS_x/rGO-325, MoS₃/rGO-250, and MoS₃/rGO-Intermediate. Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

and the S/C cathode without adding any other materials. Fig. A.12(a) and A.12(b) represent the Tafel plots of the O_2 and R_2 peaks, respectively, which are summarized in Fig. A.12(c). The Tafel slopes in both oxidation and reduction are smaller in the three annealed MoS_x/rGO catalysts than their rGO controls. The smallest Tafel slope was obtained in $MoS_2/rGO-600$, shown as 24.7 mV/dec (for R_2) and 51.2 mV/dec (for O_2). Only the MoS_3/rGO -intermediate did not show improvement over the rGO -intermediate control. Again, it may be limited by the defects in rGO under these conditions.

Before the battery performance evaluation, material preparation was optimized by varying MoS_x wt% in the MoS_x/rGO hybrid. Fig. A.13(a) shows a significant increase in current response during CV with a low MoS_3 wt% ($\sim 20\%$) compared to a higher wt% ($\sim 80\%$, Fig. 2.6) under similar synthesis conditions. Washing the MoS_3/rGO -Intermediate sample before annealing to remove impurities (ATM and MoO_3) further enhanced the performance (Fig. A.13(a-c)). The discharge capacity increased from ~ 600 mAh/g to ~ 850 mAh/g at 1C, as shown in Fig. A.13 (b-c), highlighting the importance of precise control of MoS_x/rGO composition in the cell performance.

The MoS_3/rGO electrode, without any added sulfur, was evaluated to determine the capacity contribution of sulfur inherently present in MoS_3 . This experiment was conducted at a constant current of 0.2 mA, corresponding to the sulfur mass (1.3 mg) typically used in a standard MoS_3/rGO electrode with sulfur to maintain similar conditions. As shown in Fig. A.13(f), the capacity contribution from MoS_3 itself was negligible, yielding only ~ 10 mAh/g. These findings confirm that the sulfur in MoS_3 does not significantly impact the system's overall capacity, ensuring that the reported specific capacity values are predominantly attributed to the added sulfur powder.

3.4.1 Understanding the Catalytic Properties of LPS Conversion in Full Cell

Fig. 3.6(b) shows the rate-performance tests of the full Li-S coin cells by applying 10 discharge-charge cycles at each of the five discrete C-rates from 0.1C to 2C. The 1D amorphous MoS_3/rGO -250 catalyst provided the highest specific capacity of $\sim 1,277$ mAh/g in the discharge process of the first cycle at 0.1C rate, which was followed by the mix-phase MoS_x/rGO -325 at $\sim 1,118$ mAh/g, 1D amorphous MoS_3/rGO -Intermediate at $\sim 1,069$ mAh/g, and 2D crystalline MoS_2/rGO -600 at $\sim 1,033$ mAh/g, respectively. The control samples rGO-600 and rGO-250 provided much lower first specific discharge capacities of ~ 940 and ~ 908 mAh/g, respectively. The discharge capacity of all cells decreased rapidly during the first ten cycles at 0.1C. As the C-rate increased from 0.1C to 0.2C, 0.5C, 1C, and 2C, respectively, the cells became more stable, though the specific discharge capacity steadily decreased. The cells remained very stable and retained a large portion of the discharge-specific capacity at respective C-rates in the 2nd rate-performance testing sequence from cycle 51 to cycle 100. The MoS_3/rGO -250 catalyst gave the highest stable discharge specific capacity of $\sim 1,020$ mAh/g at 0.1C. Apparently, all electrodes need about 10–20 discharge-charge cycles to be activated and stabilized. The CE was $\sim 98\%$ at the highest 2C rate in cycles 41 to 50 and $> 95\%$ at 0.2C in cycles 61 to 71. The discharge-specific capacity trend among all catalysts and rGO controls was similar to that in cycle 1 at 0.1C rate, with MoS_3/rGO -250 maintaining the highest discharge-specific capacity of ~ 736 mAh/g at 2C. The only exception is MoS_3/rGO -Intermediate, which dropped more rapidly than other samples as the C-rate was raised, becoming even lower than that of the rGO-600 control. This is again attributed to the low electrical conductivity of the defective rGO in this unannealed sample.

In Fig. 3.6(c), the discharge voltage profiles in the 10th cycle at 0.1C rate show a short plateau at ~ 2.35 V in the R_1 region and a longer plateau at ~ 2.1 V in the R_2 region, correlated with

the reduction peaks in CVs shown in Fig. 3.6(a). The MoS₃/rGO-250 exhibits the highest charge and discharge capacities, consistent with Fig. 3.6(b).

The chronoamperometric curves during potentiometric charge and discharge tests for R₂ and O₂ reaction in Fig. A.14 provide additional information regarding the kinetics of these reactions catalyzed by MoS₂/rGO-600 and MoS₃/rGO-250, respectively. The rates of reducing Li₂S₄ to Li₂S were similar, reaching the peak current at 52 s with MoS₂/rGO-600 and 50 s with MoS₃/rGO-250. However, MoS₃/rGO-250 provided a higher specific capacity of 621 mAh/g than the 510 mAh/g offered by MoS₂/rGO-600. During the oxidation process to convert Li₂S to SCP, the peak current with MoS₂/rGO-600 appeared at 86 s with a specific capacity of 821 mAh/g. In contrast, the reaction was slower in MoS₃/rGO-250, with a peak showing at 208 s, but with a higher charge capacity of 1,001 mAh/g. From these observations, it can be concluded that the oxidation kinetics were faster in 2D MoS₂/rGO-600 than in 1D MoS₃/rGO-250. However, 1D MoS₃/rGO-250 had a higher SCP adsorption and thus provided a higher specific capacity.

The EIS data of the pristine cell (Fig. A.15(a)) demonstrate that MoS₂/rGO-600 exhibits inherently lower resistance, as evidenced by the smaller semicircle in the Nyquist plot, highlighting its superior conductivity compared to MoS₃/rGO-250 samples. The partially charged and discharged state shows significantly reduced resistance due to the formation of conductive LCP, and it increases slightly at the fully charged state (2.8 V), with the formation of S₈ [242]. Resistance changes are minimal at other charge and discharge states, except at the fully discharged state of 1.7 V, where MoS₂/rGO-600 exhibits significantly lower resistance compared to MoS₃/rGO-250, emphasizing its overall superior conductivity under these conditions.

The GITT test in Fig. A.16 shows that the internal resistance of the cell at different discharge and charge states, and it was calculated [243] using this equation (5), where OCV represents the

open circuit voltage, and the details of the data with Quasi OCV or QOCV and OCV are provided in Fig. A16(c-d).

$$(\Delta R) = \Delta(QOCV - OCV) / I_{\text{applied}} \quad (5)$$

Fig. A.16(e-f) shows a lower (ΔR) value for MoS₂/rGO-600 compared to MoS₃/rGO-250. This result reflects the superior electron transfer kinetics of MoS₂/rGO-600, which aligns with the findings from both electrochemical measurements and EIS data.

3.4.2 Improving the Long Cycling Stability of Li-S Full Cells

One of the major challenges for LSB is the short lifetime. To test stability, a continuous discharge-charge has been conducted for 300 cycles at 1C. Fig. 3.7(a) shows that 1D MoS₃/rGO-250 presented the highest specific discharge capacity of ~ 934 mAh/g, which was followed by MoS_x/rGO-325 (~ 868 mAh/g) and 2D MoS₂/rGO-600 (~ 819 mAh/g). The cells with these catalyst-incorporated cathodes all outperformed the control rGO-600 in terms of specific capacity. However, the cell with MoS₃/rGO-intermediate catalyst was inferior to the control rGO-600 in both specific capacity and stability. 2D MoS₂/rGO-600 exhibited the highest CE (~ 97%), which was maintained at ~ 90% even after 300 cycles, leading to a relatively high stability that maintained 80% of the initial specific capacity after 300 cycles. In contrast, the CE of all catalysts prepared at lower temperatures decayed much faster, particularly after 200 cycles.

The primary reason for the low CE of low-temperature annealed samples could be due to higher polysulfide shuttling from the cathode to the anode since the adsorption energy of LPSs on the Hibble structure is lower than that of MoS₂ (Fig. 3.8(d)). This may have caused the faster capacity to fade in long cycling. If this can be improved, 1D MoS₃/rGO could be a better candidate than 2D MoS₂/rGO due to the higher specific capacity.

To improve stability and CE for long cycling, we adopted a new method of creating a cathode-electrolyte interphase (CEI), reported in a recent study on lithium-ion batteries by Z. Zhang et. al. [244] with a thickness of $\sim 5\text{-}10$ nm. In this study, 10 seconds of short circuit was applied to the Li-S coin cell with a metal tweezer, which lowered the cathode potential below the

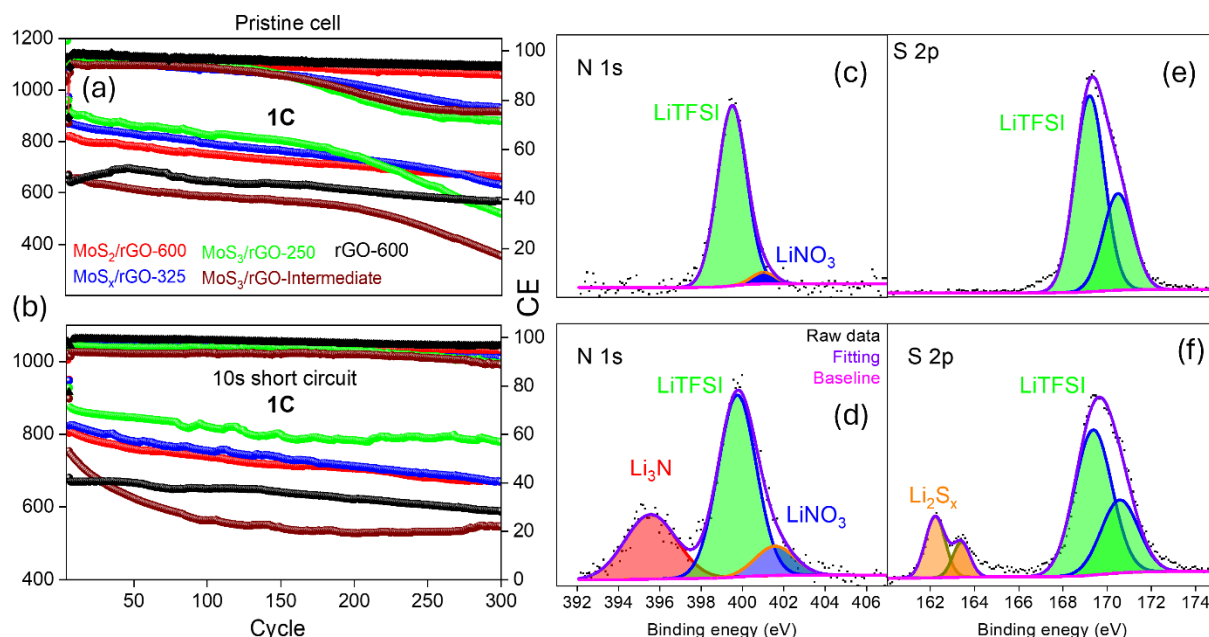


Figure 3.7. Stability test at 1C after 5 cycle activation at 0.1C (a) pristine cell, (b) after 10s short cycle of $\text{MoS}_2/\text{rGO-600}$, $\text{MoS}_x/\text{rGO-325}$, $\text{MoS}_3/\text{rGO-250}$, and $\text{MoS}_3/\text{rGO-Intermediate}$, and control rGO-600 . XPS data of the control rGO-600 electrode without sulfur, recorded after soaking in electrolyte, showing (c) N 1s and (e) S 2p spectra. After a 10-second short circuit, XPS data shows (d) N 1s and (f) S 2p spectra. Reprinted from *Chemical Engineering Journal*, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

stability window of the electrolyte to form a CEI that typically only forms at the Li anode (SEI).

This thin conformal in-situ formed CEI (Fig. A.18(a-b)) has been demonstrated to confine the soluble polysulfide with the cathode and the CEI protective layer, protecting the cathode material from side reactions with electrolytes while ensuring effective Li^+ diffusion. During the controlled short-circuiting process, the reduction current rose to a spike of -0.25 A in ~ 2 s and then exponentially dropped to ~ 0.08 A before switching back to the open circuit (Fig. A.17(a)). This

process caused the electrolyte and some soluble LCPs to form a Li^+ permeable solid interphase, corresponding to a discharge capacity of ~ 275 mAh/g. As shown in Fig. A17(b), after fully charging to 2.8 V, the cell was able to recover a specific discharge capacity of 1,263 mAh/g, close to $\sim 1,277$ mAh/g in a typical cell shown in Fig. 3.6(b). With the CEI layer formed by this short-circuiting method, the stability and CE were significantly improved for 1D MoS_3/rGO -250 and MoS_x/rGO -325 cathodes, as illustrated in Fig. 3.7(b). The specific capacity for the 1D MoS_3/rGO -250 remained the highest at $\sim 1,230$ mAh/g during the initial 5 activation cycles at 0.1C rate before switching to 1C for a long cycling test. The total capacity fading rate after 300 cycles at the 1C rate was reduced from 44% to 9.3% for 1D MoS_3/rGO -250. The short-circuited cell was able to maintain at 780 mAh/g after 300 cycles at a 1C rate. Corresponding to this, the CE of the pristine cell with MoS_3/rGO -250 dropped from 97% to 72% after 300 cycles, while that of the short-circuited cell slightly dropped from 97% to $\sim 90\%$ for the same conditions after 300 cycles. The short-circuited cell with MoS_x/rGO -325 showed a similar trend with slower capacity fading and improved CE in 300 discharge-charge cycles. The initial specific discharge capacity was comparable to that of the pristine cell. Overall, the short-circuiting method significantly enhanced the stability and CE of cells incorporating low-temperature catalysts but had a minimal effect on the stability of cells with 2D MoS_2/rGO -600. However, the CE improved from $\sim 90\%$ to $\sim 95\%$ after 300th cycles with 2D MoS_2/rGO -600.

To analyze the chemical composition of the short circuit-induced cathode electrolyte interphase (CEI) layer, the cathode surface was studied without sulfur using a control rGO electrode, ensuring no contributions from MoS_3 or sulfur active materials. XPS analysis (Fig. 3.7(c-f), and A.18(c-h)) revealed that the short circuit promotes the formation of Li_3N and increases the concentration of LiNO_3 , as observed in the N 1s spectra, while the S 2p spectra indicated the

formation of Li_2S_x , which could range from insoluble Li_2S_2 to SCP [245]. Unlike the control rGO electrode soaked in LiTFSI electrolyte, which showed no Li_3N and trace LiNO_3 , the CEI formed via the short circuit demonstrates a significant presence of these compounds. LiNO_3 , known for stabilizing the SEI on anodes [81] was found to provide similar benefits at the cathode, working alongside Li_3N [246, 247] to enhance cycle stability and Coulombic efficiency (CE). These findings underline the critical role of the short-circuit-induced CEI composition in improving battery performance.

3.4.3 Mechanistic Understanding Based on DFT Calculations

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna *ab initio* Simulation Package [248, 249]. Sahu and coworkers have systematically investigated the structural and energetic properties of MoS_3 polymorphs [250]. We adopted a similar computational approach to obtain optimized configurations for linear 1D MoS_3 . The project

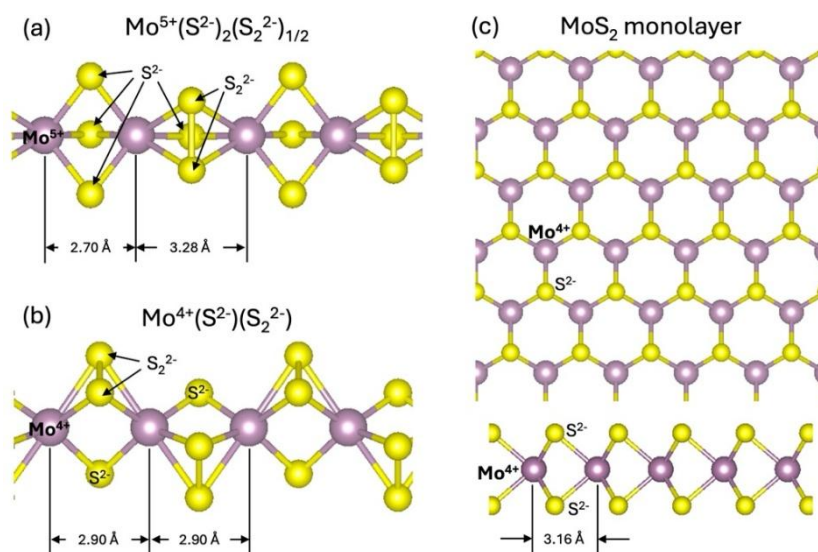


Figure 3.8. Optimized molecular structures of 1D MoS_3 in form of (a) Hibble structure $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$ and (b) Webber structure $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$. The elemental nominal charges and Mo–Mo separations are labeled. (c) A monolayer of MoS_2 in top and side views. The Mo and S atoms are shown in purple and yellow, respectively. Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

augmented wave (PAW) method [251] approximates the core electrons. The generalized gradient approximate Perdew-Burke-Ernzerhof (PBE) functional was used to account for the electronic exchange-correlation effects [252]. The density-dependent dispersion correction (dDsC) method [253, 254] was also used for long-range interactions. The kinetic energy cutoff for the plane-wave basis set is set to be 500 eV. The partial occupancy was treated using the Methfessel-Paxton method [255]. The break condition for electronic self-consistent iterations is set to be 1×10^{-6} . For structure relaxations, the ionic iteration is terminated when all the forces are smaller than 0.05 eV/Å.

Two 1D MoS₃ polymorphs, i.e., Mo⁵⁺(S²⁻)₂(S₂²⁻)_{1/2} (Hibble) and Mo⁴⁺(S²⁻)(S₂²⁻) (Webber), were considered to represent the active MoS_x catalysts for LPS conversions. A $6 \times 1 \times 1$ k-point mesh generated by the Monkhorst-Pack scheme was used [256]. Bader charge calculations were implemented using the algorithm introduced by Henkelmen *et al.* [257] to confirm the existence of the S₂²⁻ species and the corresponding charges on Mo.

As illustrated in Fig. 3.8(a-b), the Mo⁵⁺ species are connected by alternating S²⁻ and S₂²⁻ in Mo⁵⁺(S²⁻)₂(S₂²⁻)_{1/2}, with Mo–Mo interatomic distances of 2.70 Å and 3.28 Å. In Mo⁴⁺(S²⁻)(S₂²⁻), Mo atoms are separated equally at 2.90 Å. Both optimized structures are in excellent agreement with the values reported by Sahu *et al.* [250] using a similar set of parameters.

Moreover, a monolayer of MoS₂ (Fig. 3.8(c)) was adopted in DFT calculations to provide a reference for catalysis performance assessment. The monolayer was obtained from the relaxed MoS₂ structure bulk using a $10 \times 10 \times 3$ mesh. The optimized cell parameters are $a = b = 3.16$ Å, and $c = 12.33$ Å. A (4×4) supercell was created for the monolayer, with a vacuum of 25 Å separating the periodic images along the direction perpendicular to the basal plane.

The Li atoms attached to $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ and $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$ were relaxed using DFT (Fig. A.19a-b), which revealed that Li atoms favor the S^{2-} sites. However, the Weber structure $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ provides a more favorable configuration to bind Li atoms by 0.34 eV/Li, although

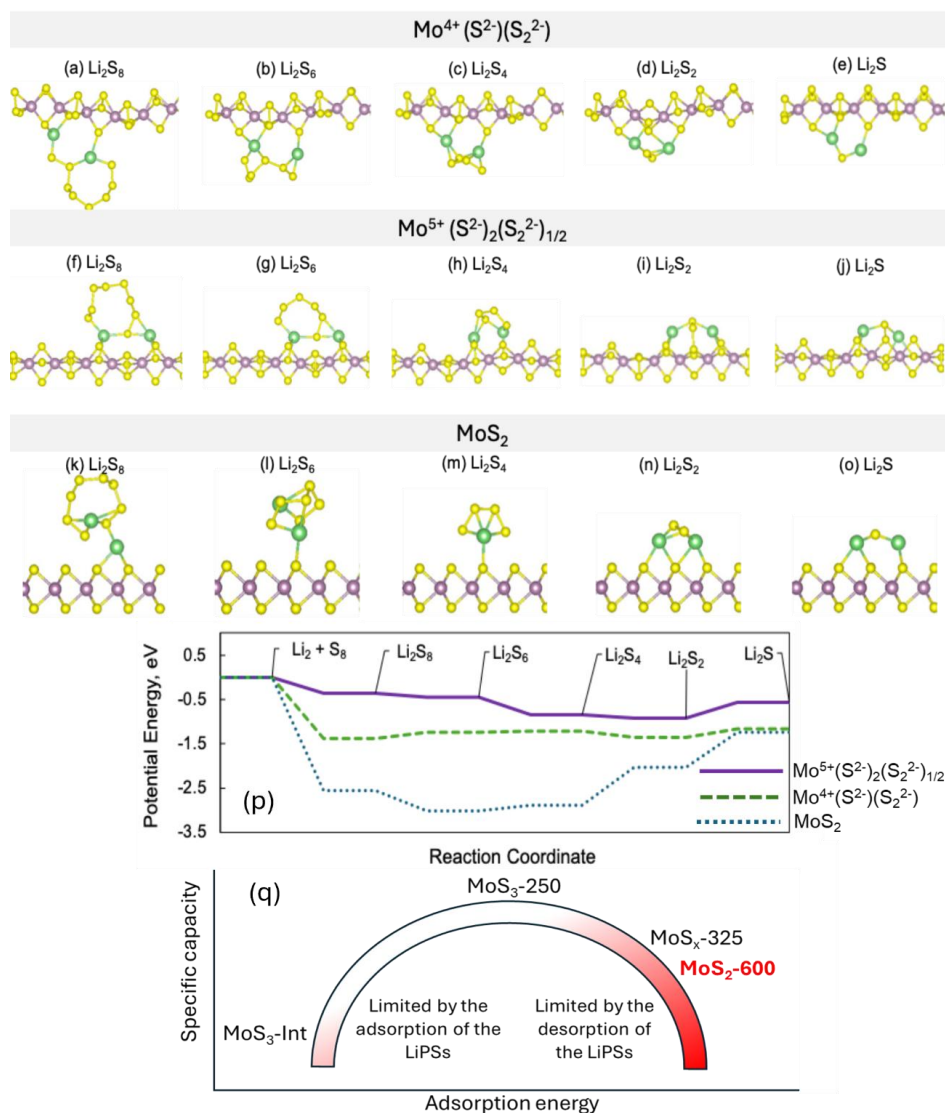


Figure 3.9. (a-e) LiPSs (Li_2S_x , $x = 8, 6, 4, 2$ and 1) bounded to $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$; (f-j) LiPSs bounded to $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$; (k-o) lithium sulfides bounded on the basal plane of 2D MoS_2 . The S, Li, and Mo atoms are depicted in yellow, green, and purple. (p) Potential energy profiles for the conversions of Li_2S_8 into Li_2S on $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ (green dashed line), $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$ (solid purple line), and 2D MoS_2 (blue dotted line). (q) A schematic representing the relationship between the adsorption energy of the LCP and the specific capacity. Reprinted from Chemical Engineering Journal, 519 (2025) 164963, Copyright 2025 Elsevier Ltd.

the Hibble structure $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$ consists of more S^{2-} species per unit cell. The adsorptions of LPSs at the active MoS_x sites were investigated using DFT calculations to reveal the preferred binding site and configurations on 1D $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ (Fig. 3.9a-e), $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$ (Fig. 3.9f-j), and 2D MoS_2 (Fig. 3.9k-o), respectively. Similarly, the Li atoms in LPS molecules also preferably bind at the S^{2-} sites. This consistent behavior explains why the LPSs bind more strongly to the Weber structure than to the corresponding Hibble structures.

The potential energy landscapes depicting the catalytic conversions between Li_2S_8 and Li_2S on the Hibble and Weber structures are shown in Fig. 3.9p. The conversions of LPS molecules on the 2D MoS_2 monolayer are included as a reference. The initial absorptions of the soluble long-chain Li_2S_8 on all catalyst models are energetically favored. The binding strengths of Li_2S_8 is the strongest on the MoS_2 basal plane, followed in a decreasing order of $\text{MoS}_2 > \text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-}) > \text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$. The stronger binding of Li_2S_8 , Li_2S_6 , and Li_2S_4 on MoS_2 is also consistent with the higher potential of the reduction peak A (E_A) with $\text{MoS}_2/\text{rGO-600}$ in the CV of symmetric cells (Fig. A.9(c-d)). Also, subsequent conversions into $\text{Li}_2\text{S}_6 \rightarrow \text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_2$ are facile on the 1D Hibble, suggesting that SCPs can be easily converted into the Li_2S end product. In particular, the energetic barrier to form Li_2S is the lowest for the Weber structure, in very good agreement with the reduction potential of peak B (E_B) on $\text{MoS}_3/\text{rGO-250}$ in Fig. 3.5(c), while conversions of Li_2S_4 into Li_2S will need to overcome a much steeper potential energy hill with the Hibble structure and MoS_2 .

Nevertheless, the large energy downslope suggests that the insoluble Li_2S is more likely converted back to the soluble short-chain LPSs such as Li_2S_2 and Li_2S_4 , during the charging process. This result successfully explains the experimentally observed lower potential of the O_2

peak in MoS₂/rGO-600 than other catalysts (Fig. 3.6(a) and Fig. A.11(c)) and the smaller voltage barrier at the beginning of the charging process (Fig. A.11(d)).

The potential energy profiles can also be used to understand the intricate relationship between molecular mechanisms and observable cell performance. Strong adsorption of soluble LPSs and the conversions into SCPs facilitate the discharge. However, the reverse charging process to regenerate the soluble long-chain LPS will be hindered due to strong binding. Experimentally, the specific capacities follow the order of MoS₃/rGO-250 > MoS_x/rGO-325 > MoS₂/rGO-600 > MoS₃/rGO-Intermediate. According to DFT calculations, MoS₂/rGO-600 has the highest adsorption energies, which favor both reduction and oxidation of LPSs, and are responsible for the smallest Tafel slope for R₂ and O₂ peaks in Fig. A.12(c). However, the binding is too strong and blocks further reactions, thus limiting the overall charge and discharge capacity. Hence, catalysts should enable moderate binding of long-chain LPS such as Li₂S₈ while simultaneously supporting the formation of Li₂S₂ and Li₂S₄, as demonstrated on the Hibble and Weber structures.

The schematic in Fig. 3.9(q) illustrates the complex and counterintuitive phenomena influencing the specific capacities of MoS₂/rGO-600 and MoS₃/rGO-250. The higher adsorption of liquid polysulfides (LCP) on MoS₂/rGO-600 is attributed to its stronger binding energy, which enables robust adhesion to the surface. However, this stronger binding can also lead to active site blocking, hindering subsequent reactions and limiting the material's capacity to facilitate further redox processes. In contrast, the binding energy on MoS₃/rGO-250 is more optimal, allowing reduced polysulfides with shorter chain lengths to desorb from the surface more easily. This desorption clears active sites, making them available for continued reactions, ultimately resulting

in a higher specific capacity for MoS₃/rGO-250. Conversely, the overly strong binding energy of MoS₂/rGO-600 restricts its specific capacity, despite its enhanced conductivity.

Finally, although the DFT findings provide critical insights into understanding the molecular mechanisms for the LPS conversions at the MoS_x active sites, the measured adsorption capacities of LPSs do not follow the predicted trend. One of the main factors is that the adsorption capacity is also proportional to the number of binding sites. Due to the crystalline structure, the soluble LPSs can only access the edges and the basal plane of the topmost layer in 2D MoS₂, while they can reach all amorphous 1D MoS₃ catalysts. Thus, the active site density of 1D MoS₃ is much higher than that of 2D MoS₂ catalysts, which is reflected in the specific capacitance derived by CVs in blank electrolytes in control half-cells. As illustrated in Fig. A.20, the MoS₃/rGO-250 catalyst exhibits the highest specific capacitance of 53 F/g, while the 2D MoS₂/rGO-600 only shows a specific capacitance of 16 F/g. The convoluted effects of binding energy and active site density determined the overall LPSs adsorption capacity, leading to the highest charge-discharge specific capacity in Li-S batteries.

In summary, the 1D MoS₃/rGO-250 achieved excellent stability after 300 cycles with a very low-capacity decay of 12% only from the initial cycle, with a ΔE_2 of only 0.33 V. This capacity retention is significantly lower than state-of-the-art literature compared to Table 3. The traditional 2D MoS₂ is in the Table. 3 showed a capacity decay of 45% after 300 cycles. Even the nano patches 2D MoS₂ used in this study have a capacity decay of 15.9% only with a ΔE_2 of only 0.30 V, which showcases the importance of using these few layers of nano-sized 2D MoS₂ rather than the bulk counterparts.

3.5 Conclusion

A set of MoS_x/rGO catalysts with tunable structures from the amorphous 1D MoS_3 to 2D crystalline MoS_2/rGO -600 was synthesized, which provides insights into the optimization of electrocatalytic properties for enhancing lithium polysulfide conversion in Li-S cathodes. Using a facile microwave-assisted synthesis, an amorphous 1D MoS_3 was successfully anchored on rGO nanosheets, forming the MoS_3/rGO -intermediate catalyst. Thermal annealing of this material at 250, 325, and 600 °C gradually tuned the dominant material from the initial amorphous 1D MoS_3 in Hibble form to Weber form and 2D crystalline MoS_2 nanosheets. During the full cell testing, MoS_3/rGO -250 provided the highest specific capacity of 1,277 mAh/g at 0.1C rates. The instability of the amorphous MoS_3 during long cycling can be mitigated with a 10 s short-circuiting method to form a conformal $\text{Li}_3\text{N}/\text{LiNO}_3$ CEI layer on the cathode, which significantly enhanced its stability and CE, able to retain 90.7% specific capacity after 300 continuous cycles at a 1C rate. The MoS_2/rGO -600, on the other hand, was found to be inherently more stable and relatively more conductive, which led to better kinetics during charging-discharging processes. It also provides higher CE compared to the MoS_3/rGO -250. The LPS adsorption capacity and redox properties on these MoS_x/rGO catalysts correlate well with their molecular structure models and the theoretical potential energy landscapes derived from DFT calculations. The tunability of the electrocatalytic properties provides insights into future catalysts to further optimize the Li-S battery performance.

Table 4: Comparison of this work with the literature on catalyst incorporation method

Material	Capacity mAh/g	Stability at 1 st /300 th cycles	Decay after 300 th cycles	S Loading ~mg/cm ²	ΔE_2 (V) @0.1 mV/s	Work
1D MoS ₃ /rGO-250	1277 @0.1C 735 @2C	896/781 @1C	12% @1C	0.80	0.33	This work
2D MoS ₂ /rGO-600	1033 @0.1C 665 @2C	800/673 @1C	15.9%		0.30	
2D MoS _{2-x} /rGO	1300 @0.2C 950 @2C	1190/700 @0.5C	45% @0.5C	1.5	0.35	[183]
3D MoS ₂ /rGO foam	1000 @0.2C 680 @2C	800/450 @1C	45% @1C	0.85	0.33	[227]
N doped-MoS ₂	1150 @0.1C 450 @2C	1030/900 @0.5C	12% @0.5C	5.0	0.34	[226]
3-amino-triazole on graphene	1300 @0.1C 1100 @2C	1300/1000 @1C	24% @1C	1.15	0.33	[78]
Ni _{0.1} Zn _{0.1} Co _{0.8} Se ₂	1200 @0.2C 630 @2C	690/510 @1C	27% @1C	1.0	0.22	[258]
NiMoO ₄ @NSCC/S	1300 @0.1C 650 @1C	800/600 @1C	24% @1C	2.0	0.36	[259]
NHCS-SnS ₂ /S	1200 @0.2C 790 @2C	900/600 (200 cycles) @1C	34% @1C for 200 cycles	0.8	0.40	[260]
Fe-PNC/S composites	1100 @0.1C 250 @ 2C	720/510 @0.5C	30% @0.5C	1.3	0.39	[210]
C/TiN	1500 @0.2C 900 @2C	1100/800 (50 cycles) @1C	27.5% @1C	1.2	0.43	[261]
WO _{3-x} nanoplates	1200 @0.2C 800 @2C	1000/600 @0.5	39% @0.5C	2.0	0.39	[262]

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Chapter 4 - Incorporating Different MoS_x/rGO Catalysts in Interlayer and Cathode to Enhance Li-S Battery Performance: a Dual-Catalyst Strategy

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4.1 Introduction

Li-ion batteries (LIBs) have dominated the energy storage market for the past four decades, enabling widespread use in portable electronics and electric vehicles (EVs). However, their energy density is below ~ 300 mAh/g, which drives up the cost, weight, and volume of EV battery packs [263]. This is largely limited by the cathode materials, nickel-manganese cobalt oxide (NMC) [264, 265], lithium cobalt oxide (LCO) [266], lithium iron phosphate (LFP) [267] or mixed materials[268-270], whose intrinsic specific capacities are below 200 mAh/g. In contrast, Li-S batteries (LSBs) offer a much higher theoretical capacity in the sulfur cathode (1,675 mAh/g) [271] and lithium metal anode (3,860 mAh/g) [207, 208], which have a theoretical energy density of $\sim 2,500$ Wh/kg [73, 272, 273]. This provides the potential to dramatically reduce the battery weight, size, and cost in EVs. However, the charge and discharge of LSBs involves electrochemical conversion of S₈ (the fully charged state) and Li₂S (the fully discharged state) through a series of highly soluble lithium polysulfides (LPSs). The poor electrical conductivity of sulfur and Li₂S, as well as the detrimental diffusion of LPSs from the cathode to the anode (*i.e.*, the shuttle effect), cause sluggish reaction kinetics, loss of active materials, and rapid capacity fading, which are currently limiting the LSB development [46, 209].

Researchers have employed various carbon-based materials, e.g., reduced graphene oxide (rGO), carbon nanotubes [105, 243], carbon nanofibers [119, 241], porous carbon [51], and amorphous carbon (carbon black/SuperP) to physically entrap the soluble LPSs to mitigate their shuttling. Yet simple physisorption is insufficient, due to the weak interaction between the ionic polysulfides and nonpolar carbon frameworks. Other strategies have been explored by introducing heteroatoms (e.g., nitrogen [217, 226]), metal oxide [274] and metal nitride [275] catalysts, single-atom catalysts [173] (e.g., Fe [210]), or molecular catalysts [276] into the carbon hosts to improve LPS binding and conversion. However, due to the high solubility of LPSs in the liquid electrolytes, fully confining them within the cathode remains challenging.

It is noteworthy that the redox kinetics of different polysulfide species vary significantly, as reported by Hualin *et al.* [212] and our own DFT calculation and experimental studies [271]. The electrochemical conversion between S_8 and Li_2S consists of a series of connected steps, governed by different kinetic barriers based on the LPS chain length and structure. Long-chain polysulfides (LCPs, e.g., Li_2S_8 and Li_2S_6) are highly soluble and exhibit relatively fast redox kinetics. In contrast, the short-chain polysulfides (SCPs, e.g., Li_2S_4 and Li_2S_2) are less soluble and require higher overpotentials for nucleation and conversion, rendering kinetically sluggish redox processes. Our recent investigation [271] of a series of molybdenum sulfide (MoS_x) electrocatalysts for LSB cathodes revealed that using a single catalyst alone, either the amorphous 1D chain-like MoS_3 or the crystalline 2D MoS_2 , was inadequate to catalyze the conversion of both LCPs and SCPs to deliver the desired high specific capacity and cycling stability. Specifically, MoS_3 exhibited a large adsorption and efficient catalytic activity for SCPs, yielding a higher specific capacity but a lower stability, whereas MoS_2 demonstrated enhanced kinetics for soluble

LCPs and demonstrated better stability in long cycling. These findings underscore the need for a dual-electrocatalyst system to facilitate the full LPS redox pathway from S_8 to Li_2S and vice versa.

In this context, we adopted a dual-catalyst approach, with one type of catalyst directly mixed in the sulfur-carbon (S-C) composite cathode while a second type of catalyst was applied as a thin-film interlayer between the cathode and the separator. This was found effective in confining LPSs at the cathode-interlayer interface and minimizing their diffusion toward the separator. The interlayer approach is a widely used strategy in the LSB by coating functional materials, typically tens of microns in thickness, on the separator (at the side facing the cathode) [116-118, 277]. Here, we implemented a different strategy by coating the catalytic interlayer directly onto the cathode surface. This configuration ensures intimate electrical contact and stronger adhesion to the S-C cathode compared to the conventional coatings on the polymer separator. This electrochemically active catalytic interlayer is expected to regenerate LPSs more rapidly than the traditional interlayer solely depending on physisorption.

To facilitate the dual catalyst design, we employed MoS_2 and MoS_3 from the transition metal chalcogenide family due to their distinct catalytic properties and stabilities across various redox platforms, including HER [223, 224, 278], batteries [183, 202], and photocatalysis. Particularly, crystalline 2D MoS_2 nanopatches (< 10 nm in size) consisting of only ~ 3 tri-atomic layers were synthesized on rGO nanosheets by a facile microwave-assisted synthesis followed by thermal annealing at 600 °C in our previous studies [221, 225, 271]. This material, referred to as M6 catalyst, consists of abundant edge sites, which are far more catalytically active than the basal plane that dominates the large crystalline MoS_2 materials prepared by mechanical exfoliation [183] and chemical vapor deposition [202]. On the other hand, amorphous 1D chain-like MoS_3 serves as a compelling alternative to the crystalline 2D MoS_2 . All Mo and S sites are accessible to redox

species, enabling a much higher density of active sites [230, 239, 250, 278]. In our previous studies [221, 225], the amorphous 1D MoS₃ was produced as an intermediate material on the rGO nanosheets during the microwave synthesis, which evolved into two types of MoS₃/rGO catalysts after thermal annealing at 250 and 325 °C, respectively, referred to as M2 and M3 catalysts. The M2 catalyst is dominated by the Hibble structure [235] that can be described with a chemical formula Mo⁵⁺(S²⁻)₂(S₂²⁻)_{0.5}, forming a chain of triangular bipyramidal MoS₃ units with a bridging S₂²⁻ bond appearing in every other unit (as illustrated in Fig. 1(a)). The M3 catalyst is dominated by the Weber structure [236], which is represented by a formula Mo⁴⁺(S²⁻)(S₂²⁻). It has a similar chain structure except that each triangular bipyramidal MoS₃ unit contains two S atoms in the form of S₂²⁻ and one S²⁻ atom bridging the two Mo⁴⁺ atoms (as illustrated in Fig. 4.1(a)). As we reported, these three types of materials exhibited different catalytic properties for LPS conversion when incorporated in the S-C cathode [271].

The present work focuses on two aspects: (1) evaluation of the above catalysts incorporated separately into a catalytic interlayer and (2) assessing the synergistic effect of incorporating two different MoS_x/rGO catalysts in the catalytic interlayer and the S-C cathode, respectively, in accelerating the overall LPS conversion and LPS confinement in the S-C cathode. The dual-catalyst LSB structure was found to effectively improve the overall redox kinetics and deliver a high specific capacity and long-term stability. Our findings show that the combination of M6 catalyst in the S-C cathode and M2 catalyst in the interlayer, referred to as S-M6\M2, yields the highest performance, with an initial specific capacity of ~ 1,417 mAh/g at the 0.1C rate. It is able to maintain a specific capacity from ~ 1,088 mAh/g to ~ 666 mAh/g during 500 continuous cycles at 1C. The capacity fading over 500 cycles was further lowered to ~ 26% by forming a protective cathode electrolyte interphase (CEI) via a simple short-circuiting procedure.

4.2 Materials and Methods

The materials, synthesis, characterization, and methodology for the MoS_x/rGO hybrids were previously discussed in detail in Chapter 3. This chapter, therefore, focuses solely on the interlayer electrode fabrication, their electrochemistry, and the resulting battery performance and their analysis.

4.2.1 Preparation of Electrodes

Method 1: **Mono-Catalyst** in interlayers. S-C composite electrodes were prepared by mixing 60 wt% sublimed sulfur powder, 30 wt% Super P, and 10 wt% PVDF binder. The slurry was dispersed in NMP and cast onto aluminum foil using a blade coater set at a thickness of 200 μm . The electrodes were dried overnight in a vacuum oven at 55 °C. After drying, an interlayer slurry consisting of 80% MoS_x/rGO, 10% Super P, and 10% PVDF binder (dispersed in NMP) was coated over the electrode at a wet thickness of 70 μm and dried under the same conditions, yielding a final dried thickness of $\sim 17 \pm 2$ μm .

Table 5: Notations used for the cathode\interlayer configurations

Notation (Cathode\Interlayer)	Method	Placement of Catalysts	
		S-C Cathode	Interlayer
M2_DM	Directly Mixed	MoS ₃ /rGO-250	None
M6_DM	Directly Mixed	MoS ₂ /rGO-600	None
S-C\M6	Interlayer	None	MoS ₂ /rGO-600
S-C\M2	Interlayer	None	MoS ₃ /rGO-250
* S-M6\M2	Dual-Catalyst	MoS₂/rGO-600	MoS₃/rGO-250
S-M2\M6	Dual-Catalyst	MoS ₃ /rGO-250	MoS ₂ /rGO-600
S-M2\M2	Dual-Catalyst	MoS ₃ /rGO-250	MoS ₃ /rGO-250
S-M6\M6	Dual-Catalyst	MoS ₂ /rGO-600	MoS ₂ /rGO-600
Note: * S-M6\M2 exhibited the best performance as the sulfur cathode			

This interlayer electrode is denoted S-C\M2, where S-C represents the sulfur mixed with Super P (carbon black) as the cathode, and M2 represents the interlayer consisting of MoS₃/rGO-250 applied on top of the S-C cathode. Table 4 illustrates the notation and composition of all used electrode configurations.

Method 2: **Dual-Catalysts** in both the cathode and interlayer. The S-MoS_x/rGO electrodes were first prepared by mixing 60 wt% sulfur, 20 wt% MoS_x/rGO (M2 or M6), 10 wt% Super P, and 10 wt% of PVDF binder in NMP solvent and cast at a thickness of 250 µm onto an aluminum foil with a sulfur loading similar to that in Method 1. For comparison, this was used as the directly mixed (DM) cathode, where no interlayer was used, denoted as M2_DM and M6_DM, respectively. In other experiments, an interlayer was coated over the S-MoS_x/rGO cathode, similar to Method 1. Various cathode\interlayer combinations are summarized in Table 4. As an example, the notation S-M6\M2 represents that a sulfur cathode containing MoS₂/rGO-600 catalyst (*i.e.*, S-M6) was coated with an interlayer consisting of MoS₃/rGO-250 catalyst (M2).

All electrodes were subjected to a flash-heating step at 240 °C for 10 seconds on a hot plate to promote sulfur infusion into the porous structure. This rapid thermal treatment ensured efficient sulfur infiltration with minimal mass loss due to sublimation. The final sulfur loading was calculated to be $0.85 \pm 0.05 \text{ mg/cm}^2$.

4.3 Evaluation of Mono-MoS_x/rGO Catalysts in Interlayers - Method 1

4.3.1 Electrochemical Characterization of Catalytic Interlayers

The catalytic properties of various MoS_x/rGO catalysts in accelerating LPS conversion were assessed in our previous study [271] by directly mixing them in the S-C cathodes. Here, we focus on incorporating the catalysts into a conductive interlayer between the S-C cathode and the polypropylene separator, as illustrated in Fig. B.1. The concept of using an interlayer to mitigate LPS shuttling in LSBs has been established in the literature [85, 119, 120, 212]. Our goal here is to understand the catalytic properties of different MoS_x/rGO catalysts in the interlayer and identify

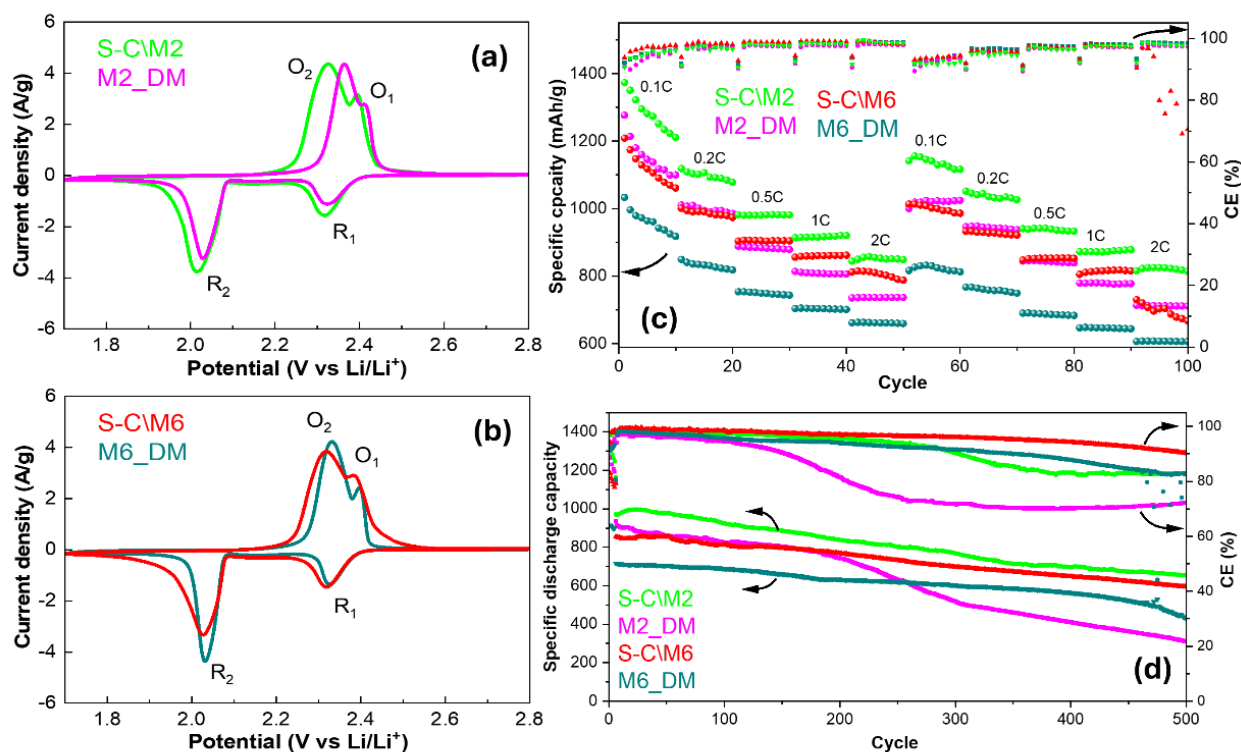


Figure 4.1. Comparison of the CV profiles of the cells with the catalyst directly mixed in the S-C cathode and in a catalytic interlayer, respectively, using (a) MoS₃/rGO-250 catalyst (M2) and (b) MoS₂/rGO-600 catalyst (M6). (c) The rate performance tests at varied C-rates and (d) stability tests at fixed 1C rate of M2 and M6 incorporated catalytic interlayers in comparison with the counterparts with catalysts directly mixed in the S-C cathodes. Reprinted from our accepted manuscript (Z. I. Saddam et al., Materials Report Energy, accepted).

the optimal one in suppressing LPS shuttling. Particularly, it would be interesting to know how the amorphous 1D MoS₃/rGO-250 catalyst (M2) and the crystalline 2D MoS₂/rGO-600 catalyst (M6) behave differently due to their distinct structures.

The M2 catalyst directly mixed in the S-C cathode (*i.e.*, M2_DM) provided the highest specific capacity up to ~ 1,300 mAh/g at 0.1 C in our previous study [271]. Here, a cell was first fabricated with a thin M2-incorporated interlayer coated on the bare S-C cathode, denoted as S-C\M2, as illustrated in Fig. B.1. The CVs in Fig. 4.1(a) show significant changes between S-C\M2 and the previously studied M2_DM cell. In the cathodic scan, the M2 catalytic interlayer clearly increased the current of the two reduction peaks marked as R₁ and R₂. More dramatic changes were observed in the anodic scan, with the oxidation peak O₂ shifted downward by ~ 40 mV and oxidation peak O₁ downshifted by ~ 17 mV, favoring faster oxidation reactions. The total integrated peak area in both cathodic and anodic scans increased by ~ 30 – 40%, indicating that a higher specific capacity can be obtained in the charge/discharge processes.

Incorporating the M6 catalyst into the interlayer exhibited similar changes in O₂ and O₁ peaks in the CV curves, *i.e.*, larger integrated areas and smaller overpotentials than those of M6 directly mixed in the S-C cathode. However, the R₁ and R₂ peaks showed longer tails toward the negative electrode potential. Particularly, the R₂ peak current was lower than that of the directly mixed S-C cathode, indicating a slower but elongated SCP conversion. Interestingly, while M6 directly mixed in the S-C cathode showed clearly smaller oxidation overpotentials than the corresponding M2 catalyst (Fig. B.2(a)), the M2 catalyst showed better performance than M6 as the catalytic interlayer, as indicated by the higher peak currents and comparable overpotentials in all four peaks in Fig. B2(b). The M3 (MoS_x/rGO-325) catalytic interlayer was inferior to those of both M2 and M6 (Fig. B2(c)).

In our previous study with the catalysts directly mixed in the S-C cathode [271], M2 showed the highest catalytic activity for SCPs, while M6 showed the strongest adsorption for LCPs. Mixing these two catalysts together in the S-C cathode was speculated to provide a better performance due to the possible concerted conversion of both SCPs and LCPs. Hence, a mixture comprising 10 wt% of M2 and 10 wt% of M6 was incorporated in the S-C cathode, denoted as M6+M2_DM. The rate-performance test in Fig. B2(d) revealed that the specific capacity of the mixed catalysts was superior to M6_DM but slightly inferior to that of M2_DM alone. Therefore, simply combining different catalysts in the cathode was not sufficient.

The battery rate-performance tests shown in Fig. 4.1(c) are consistent with the CV studies. The cell with S-C\M2 delivered a very high initial specific capacity of 1,376 mAh/g at the 0.1C rate and ~ 850 mAh/g at the 2C rate. S-C\M2 outperformed S-C\M6 at all C-rates, with the specific capacities increased by ~ 50 to 110 mAh/g. Importantly, cells with the catalytic interlayers (i.e., S-C\M2 and S-C\M6) showed significantly better performance at all C-rates than their counterparts with the catalysts directly mixed in the S-C cathodes (i.e., M2_DM and M6_DM). The specific capacities of S-C\M2 were about 90 to 140 mAh/g higher than those of M2_DM. The differences between S-C\M6 and M6_DM were even bigger, between 150 and 180 mAh/g. Even S-C\M6 showed slightly higher specific capacities than those of M2_DM. Using catalytic interlayers is clearly a better strategy than directly mixing catalysts in the S-C cathode. The coulombic efficiency (CE) varied from $\sim 94\%$ at 0.1C to $\sim 98\%$ at 2C.

The charge-discharge voltage profiles in Fig. B.3 show that the specific capacity follows the order of M2 > M3 > M6 > R6 (rGO control at 600 °C) as interlayers. All curves have a similar shape to that of blank S-C cathodes, with two well-defined plateaus at a relatively high voltage of ~ 2.3 V for the reduction of S₈ to LCPs and ~ 2.1 V for LCPs to SCPs. The capacity difference

among various MoS_x/rGO catalysts was larger at the lower C-rates (<0.5C) but became smaller at the high rate up to 2C. It is noteworthy that, although no catalysts were directly mixed in the S-C cathode in Fig. B.3, the overpotential for conversion of Li₂S to SCPs at the initial charging process was negligible at C-rates below 0.5C. Only a small hump showed up in the charging curve at the 2C rate. It is clear that the catalytic interlayer is sufficient to overcome this kinetic barrier in typical S-C cathodes [280].

While the rate-performance results are encouraging, the long-cycling stability tests at 1C rate revealed a different trend in the catalytic properties, which guided us for further improvement. As reported in our previous work [271], a major limitation of directly mixing the catalyst in the S-C cathode was the rapid decline in the capacity and CE after about 200 cycles. Fig. 4.1(d) shows that the CE of M2_DM cathode dropped from 96.6% in the 8th cycle to ~70% in cycles from 300 to 500. With a catalytic layer in S-C\M2, the CE not only increased to 98.8% at the 8th cycle, which slowly dropped to 92.5% in the 280th cycle, but also maintained a higher value of ~84% in cycles from 400 to 500. Interestingly, though the S-C\M6 catalytic layer showed lower specific capacity than the S-C\M2, it demonstrated the highest initial CE of ~99.6% at the 10th cycle and the highest stability (with a CE of ~90.8% in the 500th cycle and retained ~70% of the initial capacity after 500 cycles), which are attributed to its inherent structural stability and superior conductivity. The stability of the S-C\M6 catalytic layer was also substantially better than that of the directly mixed M6_DM cathode.

4.3.2 Materials Characterization of LSBs with Catalytic Interlayers

To understand the effect of the catalytic interlayers, we selected the M6-incorporated interlayer as a representative model for extensive materials characterizations. The LSB cell components were examined before coin cell assembly and after 100 charge-discharge cycles at a 1C rate. The surface of the lithium metal anode (LMA) facing the separator was analyzed first. As

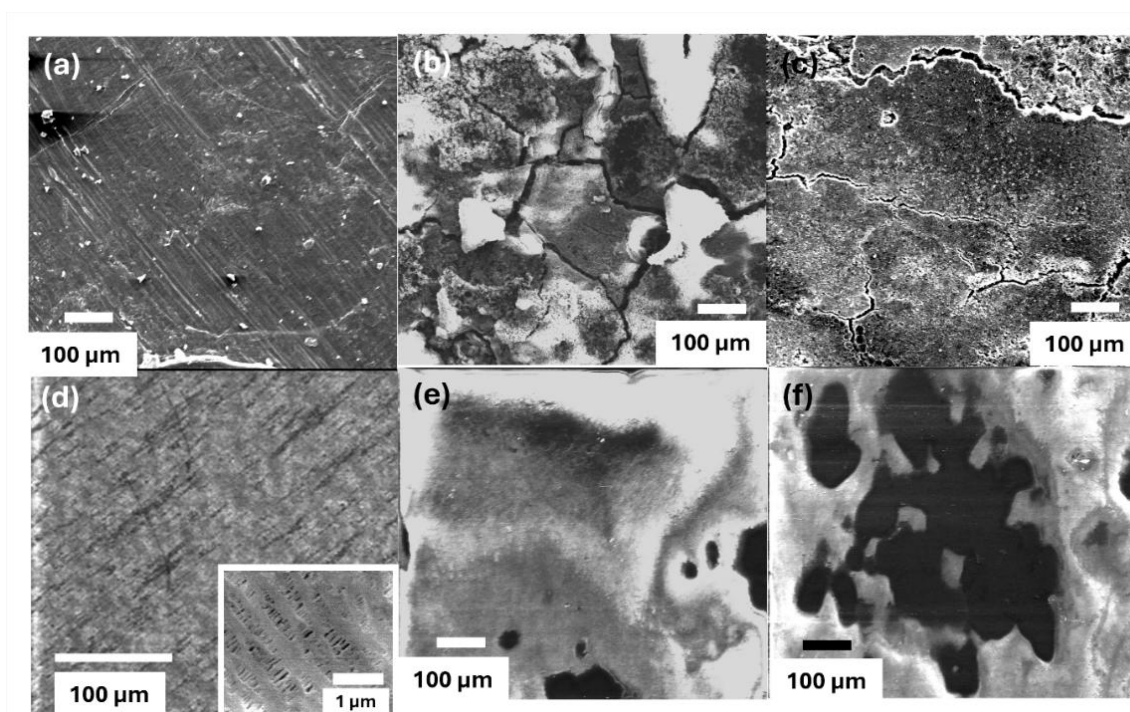


Figure 4.2. FE-SEM images of (a) a fresh LMA, and the LMA from an LSB cell after 100 cycles at 1C rate (b) without and (c) with a M6 interlayer (S-C\M6), respectively. FESEM images of the Celgard separator (d) in pristine condition and after 100 LSB cycles (e) without an interlayer and (f) with a M6 catalytic interlayer. Images in panels (e) and (f) were taken from the side facing the cathode. Reprinted from our accepted manuscript (Z. I. Saddam et al., Materials Report Energy, accepted).

shown in Fig. B.4(a-a'), the fresh LMA had a bright silver appearance. After 100 cycles, the LMA from a cell with a control S-C cathode without any interlayer became dull and nonuniform, with some particulate materials accumulating on the surface (Fig. B.4(b-b')). When the M6 interlayer was used, the LMA surface showed considerably less deposition, indicating reduced side reactions and less change on the surface (Fig. B.4(c)). The optical images of the Celgard 2400 separator

surface facing the cathode (Fig. B.4(a')-7(c')) also showed much less yellowish LPS deposits when an M6 catalytic interlayer was used.

SEM images in Fig. 4.2 showed microscopic information of these changes on the LMA and Celgard separator. The pristine LMA exhibited a smooth surface with a few dust particles, scratches, and cracks. In contrast, the cycled LMA without the interlayer displayed a thick overcoating with extensive cracking (Fig. 4.2(b)), which passivated the LMA, hindered lithium-ion transport, and increased overpotential during prolonged cycling. In the cell with M6 catalytic interlayer, the Li anode showed significantly less overlayer deposition, cracking, and corrosion (Fig. 4.2(c)). The interlayer effectively minimized the extent of surface damage and side reactions.

In the case of the separator, the cathode-facing side of the separator was analyzed to assess sulfur and LPS diffusion through the interlayer, as illustrated in Fig. B.5. The surface of the pristine Celgard separator is uniform with unilaterally stretched features containing well-defined nanoscale pores for Li^+ ion transport (Fig. 4.2(d)). In the cell without an interlayer, A thick layer of material was deposited during the 100 cycles, leaving only a small portion ($< \sim 10\%$) of the separator surface uncovered (Fig. 4.2(e)). With the M6 catalytic interlayer, the deposition on the separator was significantly reduced, leaving $\sim 40\%$ to 60% surface uncovered (Fig. 4.2(f)).

The chemical nature of the deposits on the Celgard polypropylene separator was revealed by XPS on the side facing the cathode (see Fig. B.4-5). The S2p spectrum from the cell using control rGO-600 directly mixed in the S-C cathode (denoted as R6_DM) is shown in Fig. 4.3(a). It can be deconvoluted into three pairs of peaks corresponding to the S2p_{3/2} and S2p_{1/2} doublets (at a ratio of 2:1) of different sulfur species. The pair of small peaks at BE of ~ 162.4 eV and ~ 163.3 eV (orange color), respectively, was attributed to the solid Li_2S_2 [245]. The dominant pair at BE of ~ 166.7 eV and ~ 168.8 eV (brown color) is attributed to the sulfur from the insoluble thiosulfate,

which formed through the redox reaction between soluble polysulfides and rGO [281], or S=O bonds in the decomposed products of LiTFSI salt [282]. The pair of peaks with the highest BE at ~ 167.9 eV and ~ 169.8 eV (green color), which are attributed to sulfonyl species from the condensed LiTFSI salt [282, 283]. Notably, when the M6 catalyst was directly mixed in the S-C cathode (without an interlayer) as shown in Fig. 4.3(b), the major peaks did not show significant

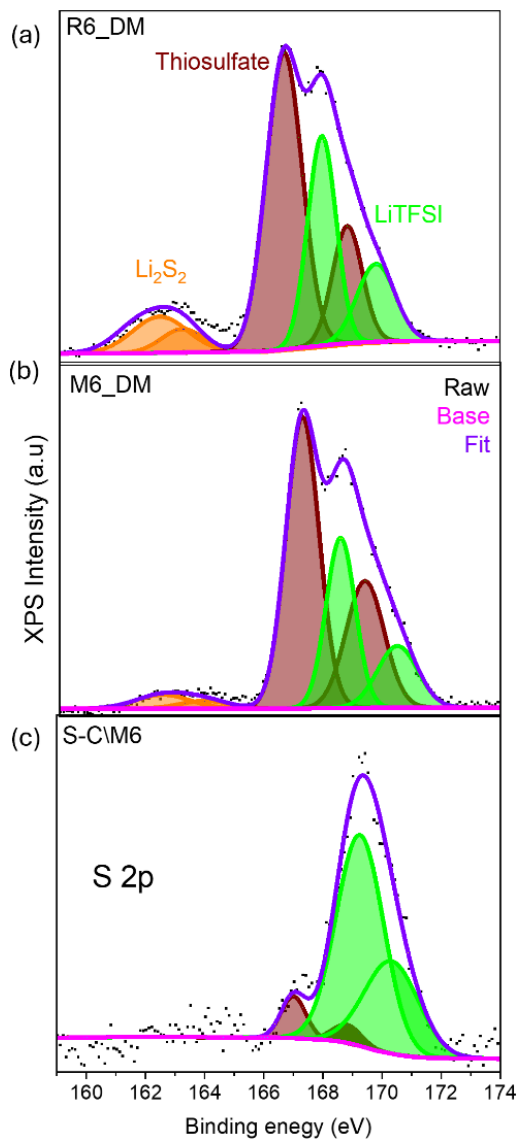


Figure 4.3. Sulfur 2p XPS spectra measured on the separator surface facing the cathode with the S-C cathode containing directly mixed (a) control rGO-600 (R6_DM) and (b) M6 catalyst (M6_DM), in comparison with (c) the S-C cathode covered with a M6 catalytic interlayer (S-C\M6). All cells were subjected to 100 charge-discharge cycles and stopped at 1.7 V after the last full discharge. Reprinted from our accepted manuscript (Z. I. Saddam et al., Materials Report Energy, accepted).

changes except that the Li_2S_2 peaks were reduced, indicating that the irreversible Li_2S_2 accumulation at the separator was suppressed. In contrast, when the M6 catalyst was applied in a catalytic interlayer on top of the S-C cathode in S-C\M6 (Fig. 4.3(c)), the signals of both Li_2S_2 and thiosulfate were significantly reduced. Only strong peaks attributed to the condensed LiTFSI salt remained. Clearly, the catalytic interlayer effectively collected the soluble LPSs that escaped from the cathode and retained them as active materials during the charge-discharge cycles. These helped to maintain the high specific capacity and prevent LPS shuttling.

4.4 Evaluation of Dual-MoS_x/rGO Catalysts in Both Interlayer and S-C

Cathode - Method 2

In the previous section, we demonstrated that using a single catalyst in the catalytic interlayer can substantially improve the LSB performance. It is interesting whether combining two types of catalysts that are effective for different LPSs would further enhance the performance. However, Fig. B.2(d) in the previous discussion showed that simply mixing M2 and M6 catalysts in the S-C cathode was not better than the mono-catalyst M2_DM. For that reason, cells were fabricated using one catalyst, MoS_x/rGO, directly mixed

in the S-C cathode and another MoS_x/rGO catalyst in the interlayer, referred to as ‘Method 2’. Four combinations of such cells with M2 and M6 catalysts were systematically studied and compared with the mono-catalyst approach by Method 1. Interestingly, the dual-catalyst approach indeed worked better, with the S-M6\M2 combination (*i.e.*, M6 directly mixed in the S-C cathode and M2 used in the catalytic interlayer) showing the highest performance.

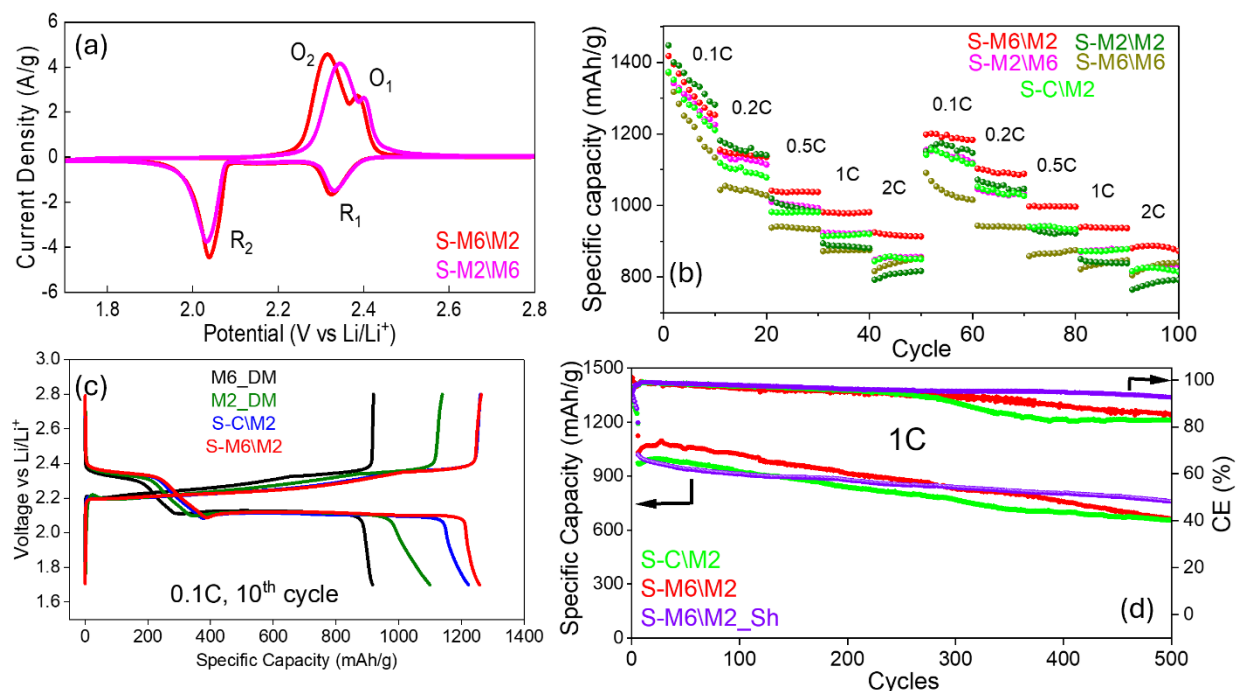


Figure 4.4. Comparison of the CV profiles of cells by Method 2 with (a) MoS₂/rGO-600 mixed in S-C cathode and MoS₃/rGO-250 in the interlayer (i.e., S-M6\M2) in comparison with MoS₃/rGO-250 mixed in S-C cathode and MoS₂/rGO-600 in the interlayer (i.e., S-M2\M6). (b) Comparison of the discharge capacity at varied C-rates. (c) Voltage profiles of the 10th charge-discharge cycle at 0.1C in panel (b). (d) Stability test at 1C of the best-performing cell with the dual catalyst S-M6\M2 with and without application of a 10-second short-circuiting in comparison to the best mono-catalyst interlayer (S-C\M2). Reprinted from our accepted manuscript (Z. I. Saddam et al., Materials Report Energy, accepted).

The CV profiles in Fig. 4.4(a) indicate that the S-M6\M2 combination exhibited lower overpotentials than the S-M2\M6 combination at the reduction peak R₂ and the oxidation peaks O₂ and O₁. The peak currents of R₂ and O₂ were clearly higher with the S-M6\M2 combination, reflecting superior redox kinetics for SCPs. The S-M6\M2 combination is superior to the best mono-catalytic interlayer S-C\M2 (Fig. B.6(a)) as well as the dual-catalytic approach using the same catalyst in cathode and an interlayer, i.e., S-M6\M6 and S-M2\M2 (see Fig. B.6(b)).

Consistent with the CV profiles, the S-M6\M2 combination showed the highest performance in the rate tests at 0.1C, 0.2C, 0.5C, 1C, and 2C rates (Fig. 4.4(b)). It exhibited an initial specific

capacity up to 1,417 mAh/g at a 0.1C rate, though it dropped quickly in the following 9 charge-discharge cycles. The capacity became more stable at 0.2C or higher rate. The CE of all cells was over 94% at the beginning at the low rate of 0.1C and increased as the C-rate was raised, reaching ~ 99% at 2C (see Fig. B.7(a)). The CE also increased over time at the low C-rates as the cells became stabilized. The cells were much more stable in the second rate-sequence, with the S-M6\M2 combination giving the highest specific capacity of 1,190 mAh/g at 0.1C and ~ 1,000 mAh/g at 1C. The charge-discharge voltage profiles of all cells in Fig. 4.4(c) showed the two characteristic plateaus corresponding to the LCP conversion around 2.35 V and the SCPs conversion at ~ 2.1 V, consistent with the CV features. Interestingly, no matter directly mixed in the S-C cathode or incorporated in the interlayer, the M6 catalyst showed a more rapid cell voltage drop from ~ 2.0 V to 1.7 V at the end of the discharge process than the M2 catalyst (Fig. 4.4(c)), indicating that M2 catalyst was more efficient in facilitating $\text{Li}_2\text{S}_2 \rightarrow \text{Li}_2\text{S}$ conversion, which helped to get higher specific capacity. The combination of S-M6\M2 seemed to best use their distinct catalytic properties. More extensive charge-discharge voltage profiles at other C-rates in Fig. B.7 showed similar features.

In terms of the long cycling stability, the dual-catalyst combination S-M6\M2 was higher than S-M2\M2, *i.e.*, using M2 catalyst in both cathode and interlayer (Fig. B.7(b)). The S-M6\M6 combination was able to retain the capacity better than S-M6\M2 but suffered from a lower specific capacity. Again, combining M6 in the S-C cathode and M2 in the interlayer provided the optimal performance with both high specific capacity and good stability. As shown in Fig. 4.4(d), the stability of S-M6\M2 can be further increased by applying a 10-second short-circuiting to the cell to form a cathode electrolyte interphase (CEI) following the procedure in our previous report [271]. Particularly, it showed nearly linear capacity, and CE changes over the continuous 500 cycles,

retaining a remarkable CE of 93.0% in the 500th cycle. The capacity fading at 1C rate from the 11th cycle to the 500th cycle was lowered to only ~ 26% (from 1,022 mAh/g to 757 mAh/g), ~ 0.06% per cycle, despite a small initial specific capacity loss (by ~ 150 mAh/g). The initial 10 cycles were excluded since it was the activation process at a lower 0.1C rate. Such performance is remarkable considering that the major components of the cathode were simply carbon black and grinded sulfur powders. The synergistic effect of the dual catalysts in the catalyst and interlayer was the key.

4.5 Discussion

The electrocatalytic properties of the ‘Dual-Catalysts’ configurations can be further analyzed. First, the CV profiles at varied scan rates in Fig. B.9 show that the current of all peaks (R_1 , R_2 , O_2 ,

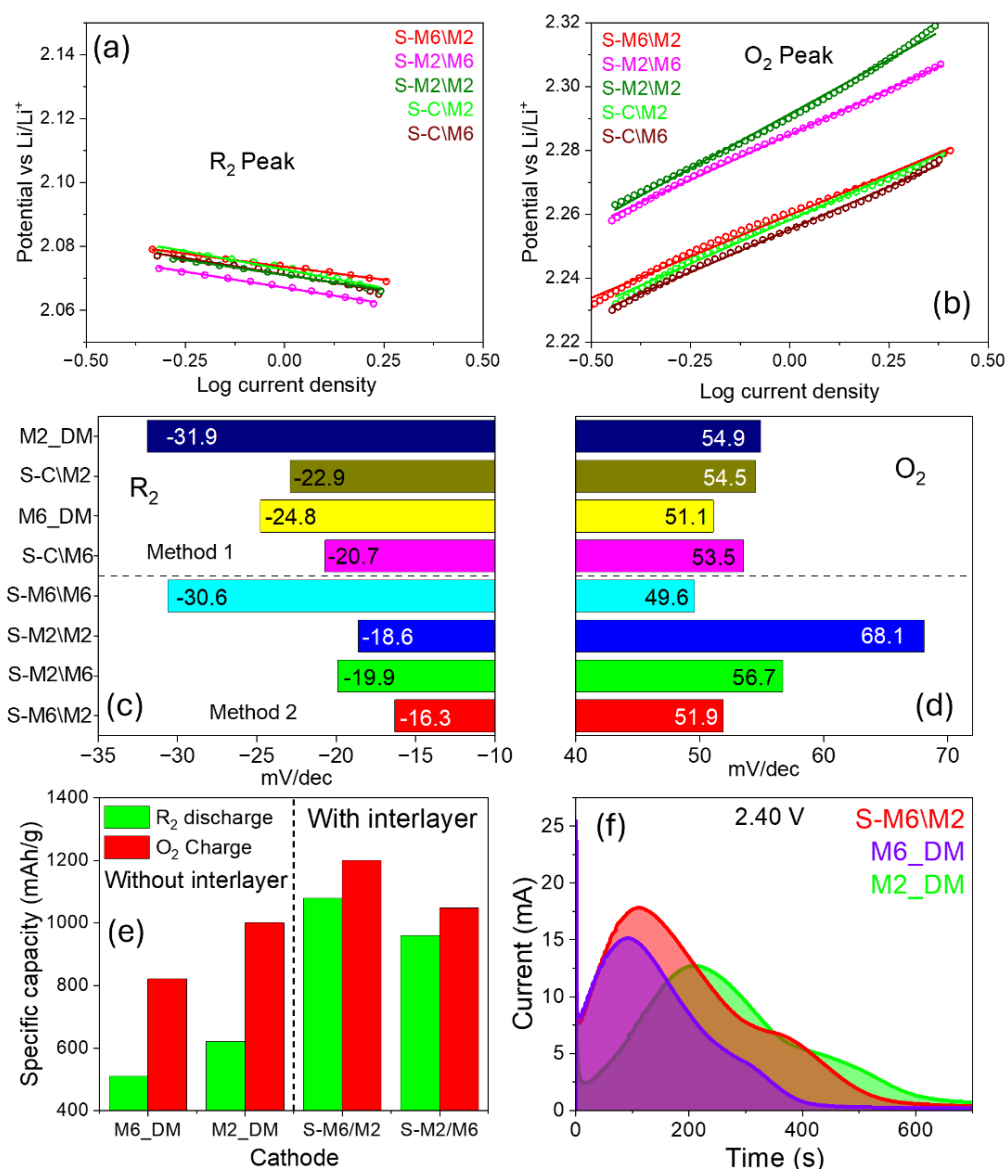


Figure 4.5. Tafel slope derived from the (a) reduction peak R_2 and (b) oxidation peak O_2 from the CV profiles. (c-d) Summary of the Tafel slopes for all the R_2 and O_2 peaks in CV at 0.1 mV/s. (e) The specific capacity derived from the chronoamperograms for R_2 and O_2 reactions. (f) Chronoamperograms of potentiostatic charging the Li-S coin cells of S-M6\M2 compared with the directly mixed $\text{MoS}_2/\text{rGO}-600$ (M6_DM) and $\text{MoS}_3/\text{rGO}-250$ (M2_DM) by stepping the cell voltage from ~ 2.10 V (OCV) to 2.4 V (*i.e.*, O_2 reaction). Reprinted from our accepted manuscript (Z. I. Saddam et al., Materials Report Energy, accepted).

and O_1) is a linear function vs. the square root of the scan rate. Hence, the CV features are all dominated by the diffusion of the soluble LPSs. The slopes of all curves are higher in C-M6\M2 than the control S-R6\R2 (with only control rGO but not catalyst in the S-C cathode), indicating a higher effective LPS concentration in the presence of the catalyst. Second, the Tafel plots in Fig. 4.5(a) and 4.5(b) can be derived from the initial region of the two major peaks R_2 and O_2 in the CV profiles (such as Fig. 4.4(a) and Fig. B.6), which provide kinetic information of the reactions. The smaller amplitude of the Tafel slope indicates the faster redox reaction. Two general observations can be quickly made from the summary in Fig. 4.5(c) and 4.5(d): (1) incorporating M2 or M6 in the interlayer worked better than directly mixing them in the S-C cathode, and (2) the O_2 reaction (converting Li_2S or Li_2S_2 to SCPs) is always slower than the R_2 reaction (converting SCPs to Li_2S_2 or Li_2S). This is consistent with the appearance of a hump (*i.e.*, an energy barrier) in the O_2 region in Fig. B.11(b2). The S-M6\M6 combination showed the smallest Tafel slope for the O_2 peak (49.6 mV/dec) but a large Tafel slope for the R_2 peak (-30.6 mV/dec). In contrast, the S-M2\M2 combination showed a small Tafel slope for the R_2 peak (-18.6 mV/dec) but the largest Tafel slope for the O_2 peak (68.1 mV/dec). As a result, using either of them alone was not sufficient. The dual-catalyst combination S-M6\M2 overcame this issue by providing the smallest R_2 Tafel slope (-16.3 mV/dec) and a relatively small O_2 Tafel slope (51.9 mV/dec), which explained why this combination provided the best overall performance.

A potentiostatic kinetics study was performed to further evaluate the electrochemical behavior to understand its synergistic effects. As shown in Fig. B.11(a) and Fig. 4.5(e), during the static discharge at 1.90 V (corresponding to R_2 reaction), the directly mixed M6 catalyst exhibited the lowest specific capacity of 510 mAh/g, whereas the M2 catalyst delivered a higher specific capacity of 621 mAh/g. When these two catalysts were combined in S-M6\M2, it provided the

highest specific discharge capacity of 1080 mAh/g. During the charging stage at 2.40 V (corresponding to O₂ reaction), as shown in Fig. 4.5(f), an oxidation peak appeared at 94 s with a specific capacity of 821 mAh/g for M6_DM, while a delayed peak appeared at 211 s with a specific capacity of 1,001 mAh/g for M2_DM. The dual catalyst S-M6\M2 demonstrated the highest oxidation peak at 110 s (close to M6_DM) with the highest specific capacity of 1,201 mAh/g (Fig. 4.5(e)), indicating the ability to combine the benefits of M6 and M2 catalysts. It is noteworthy that the sequence of the dual catalysts also has a minor effect on the performance. As shown in Fig. B.11(b), the potentiostatic peak current during charging at 2.40 V for S-M6\M2 is higher than that of S-M2\M6. Overall, the synergy of dual catalysts not only enhanced capacity but also improved overall reaction kinetics, underscoring the importance of designing dual catalysts to maximize the LSB performance.

To further unlock the full potential of the developed Cathode-Interlayer system, S-M6\M2, a

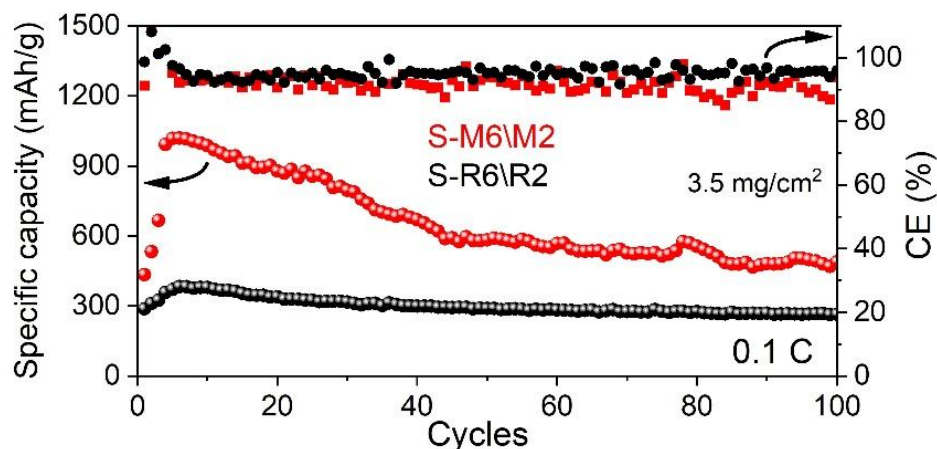


Figure 4.6. High sulfur loading cathode with the S-M2\M6 combination and the control with the similar rGO annealed samples.

higher sulfur loading cathode (3-4 mg/cm², ~200 μm thick) was fabricated and tested for practical Li-S battery applications, as shown in Fig. 4.6, as most prior studies used low sulfur mass loadings. The catalyst-loaded cathode-interlayer platform, S-M6\M2, delivered a specific capacity of ~950

mAh/g after a five-cycle activation period. This activation step facilitates deep electrolyte penetration into the cathode through the interlayer, promotes dissolution of LPSs, ensuring maximum redox activity, and enabling the catalyst to function effectively. In contrast, a similar interlayer fabricated cathode with bare rGO (S-R6\R2), without MoS₂ incorporation during synthesis, achieved only ~350 mAh/g in the first cycle and showed no improvement thereafter, like the S-M6\M2. This result underscores that the interlayer alone is insufficient; selecting the right catalyst material is essential. After 40 cycles, S-M6\M2 retained a stable specific capacity of ~600 mAh/g, nearly twice that of the control rGO cell, demonstrating that such high sulfur loading can be achieved without compromising stability, offering a promising route for practical Li-S battery fabrication.

In summary, the dual-catalyst interlayer (S-M6/M2) has shown a remarkable performance in specific capacity, CE, and long-cycling stability. The capacity drop after 500 cycles can be further reduced to ~ 26% after 500 cycles by forming a protective CEI with a simple 10-second short-circuiting protocol. Notably, similar studies using only interlayers reported in the literature (see Table 5) typically show a decay of ~30 - 40% after 500 cycles, underscoring the enhanced performance achieved in this work.

4.6 Conclusion

In this study, we systematically investigated the electrocatalytic properties of two distinct MoS_x/rGO hybrid materials, *i.e.*, the amorphous 1D MoS₃/rGO-250 (M2 catalyst) and crystalline 2D MoS₂/rGO-600 (M6 catalyst), in accelerating LPS conversion and suppressing polysulfide shuttling during Li-S battery charge-discharge processes. Incorporating these catalysts separately into a catalytic interlayer between the S-C cathode and the separator produced higher specific capacities and lower LPS redox overpotentials than directly mixing them in the S-C cathode. The M2 catalyst, in general, exhibited higher specific capacity than the M6 catalyst, while the latter showed higher CE and better stability. A dual-catalyst approach that incorporates them simultaneously in the S-C cathode and the interlayer showed much higher performance, which combines their distinct catalytic properties. Notably, incorporating M6 in the S-C cathode and M2 in the catalytic interlayer, *i.e.*, S-M6\M2, showed the highest performance, with an initial specific capacity of ~ 1,417 mAh/g at 0.1C rate, which stabilized at 1,190 mAh/g. The stability was much higher at a higher rate, such as 1C, which can be further improved by forming a CEI using a simple 10-second short-circuiting protocol. The capacity fading over 500 continuous cycles at 1C rate was lowered to only ~ 26% (from 1,022 mAh/g to 757 mAh/g), corresponding to only ~ 0.06% per cycle. This demonstrates that the dual-catalyst strategy is effective in optimizing the LSB performance by the synergy of distinct catalysts to overcome respective energy barriers in the complicated sequential processes to convert the series of LPSs.

Table 6: Comparison of this work with the literature on the interlayer method

Material	Specific Capacity (mAh/g)	Specific Capacity at 11 th /500 th Cycle	Specific Capacity Decay at 1C	S Mass Loading (mg/cm ²)	ΔE_2 (mV)	Work
S-M6/M2	1415 @0.1C 915 @2C	1098/670@1C	23%_300 th 39%_500 th	0.80	27	This work
S-M6/M2 Short-circuited	--	1031/773@1C	18%_300 th 25%_500 th	0.80	--	This work
SMG/PP	1370 @0.2C 850 @2C	955/640 (300 th) @1C	33%_300 th	1.5	30	[88]
CN/Mn-PDA	1360 @0.1C 680 @2C	800/600@1C	25%_500 th	1.25	37	[103]
2D MoS ₂ - _x /rGO	<u>1300 @0.2C</u> 950 @2C	1190/620@0.5C	48%_500 th	1.5	35	[183]
3D MoS ₂ /rGO	1000 @0.2C 680 @2C	800/450@1C	45%_300 th	0.85	33	[227]
Fe-PNC/S composites	1100 @0.1C 250@ 2C	720/510 @C	30% @0.5C(300 th)	1.3	39	[210]
MoP ₂ /CNT interlayer	1400 @0.2C 600 @2C	700/500 @1C	21%_500 th cycles	1.2	N/A	[102]
S/G-AT	1350 @0.1C 1100 @2C	1356/799 @1C	41% @1C(450 th)	1.15	33	[78]

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Chapter 5 - Conclusion and Future Perspectives

5.1 Conclusions

This thesis presents a comprehensive investigation into the structural tunability, electrocatalytic behavior, and functional integration of MoS_x/rGO hybrid catalysts for suppressing polysulfide shuttling and enhancing lithium polysulfide (LPS) conversion in lithium-sulfur (Li-S) batteries. A series of MoS_x/rGO catalysts with controllable architectures, ranging from amorphous 1D MoS₃ to 2D crystalline MoS₂/rGO-600, was synthesized to elucidate how molecular structure, active-site density, and electronic properties collectively influence Li-S electrochemistry. Using a rapid microwave-assisted synthesis, amorphous 1D MoS₃ was anchored onto rGO nanosheets to form the MoS₃/rGO intermediate catalyst. Subsequent thermal annealing at 250, 325, and 600 °C enabled a gradual structural transformation from amorphous MoS₃ in the Hibble form to the Weber form and ultimately to few-layer 2D crystalline MoS₂ nanosheets. These tunable structures provided critical insights into optimizing electrocatalytic properties for accelerating LPS adsorption and conversion.

Electrochemical testing revealed that MoS₃/rGO-250 delivered the highest initial specific capacity of 1277 mAh/g at 0.1C due to its abundant exposed active sites and higher LPS adsorption capability. However, the polysulfide shuttling effect could not be eliminated using amorphous MoS₃ during extended cycling and required additional improvement. This challenge was addressed using a rapid 10-second short-circuiting method to form a conformal cathode-electrolyte interphase (CEI) layer using an in-situ method of 10s short-circuiting. This short-circuiting process decomposes the LiTFSI salt in the electrolyte and LiNO₃ additive into solid stable Li₃N and Li₂S₂ thin film, which significantly reduces polysulfide diffusion further and enhances coulombic

efficiency, enabling the MoS₃/rGO-250 electrode to retain 90.7% of its capacity after 300 cycles at 1C. Even though the crystalline MoS₂/rGO-600 catalyst exhibits low catalytic activity and overly strong LPS binding energy, which together result in a lower specific capacity during battery operation, it still demonstrates inherently higher electronic conductivity, improved charge-transfer kinetics, and superior long-term stability, leading to a higher coulombic efficiency compared to MoS₃/rGO-250. Across the MoS_x series, LPS adsorption capacity and redox behavior correlated strongly with molecular structure models and theoretical potential-energy landscapes derived from DFT calculations, demonstrating that structural tunability directly governs catalytic performance.

Building on these complementary behaviors, a dual-catalyst strategy was developed, in an interlayer method, to combine their complementary strengths. In this configuration, MoS₂/rGO-600 was integrated into the S-C cathode to enhance conductivity and reaction kinetics, while MoS₃/rGO-250 was applied as a catalytic interlayer to maximize LPS adsorption and conversion near the cathode-separator interface. This synergistic S-M₆/M₂ architecture achieved exceptional performance, including an initial specific capacity of ~1417 mAh/g at 0.1C that stabilized at 1190 mAh/g. At higher rates, such as 1C, the system exhibited remarkable durability, which was further improved by CEI formation using the 10-second short-circuiting protocol. Over 500 continuous cycles at 1C, capacity fading was reduced to only ~26% (from 1022 mAh/g to 757 mAh/g), corresponding to ~0.06% per cycle.

Collectively, these results demonstrate that the dual-catalyst strategy effectively overcomes the sequential energy barriers associated with multi-step LPS conversion by leveraging the distinct catalytic functions of MoS₃ and MoS₂. The structural tunability of MoS_x, the ability to stabilize amorphous phases through CEI engineering, and the cooperative behavior achieved through

dual-catalyst integration provide a clear pathway for designing next-generation electrocatalysts for high-performance Li-S batteries. This thesis, therefore, establishes both a mechanistic foundation and a practical framework for advancing MoS_x-based catalytic systems, offering valuable insights for future optimization of Li-S battery technologies.

5.2 Future Research Directions

5.2.1 High Sulfur Loading

While this thesis has focused on understanding the mechanistic behavior of amorphous MoS₃ and crystalline MoS₂ anchored on rGO for Li-S battery cathodes, one of the primary limitations of the present work is the relatively low sulfur loading (~ 1.0 mg/cm²). Moving toward practical Li-S batteries requires developing cathodes capable of sustaining sulfur loadings of ≥ 4 mg/cm² while maintaining high sulfur utilization, fast reaction kinetics, and long-term cycling stability. Achieving this goal remains challenging because several interdependent limitations emerge as sulfur loading increases: sluggish ionic and electronic transport through a thick, less porous film, intensified polysulfide shuttle due to the larger active-material inventory, mechanical degradation from repeated volume changes, and lastly, the chronic acceleration of lithium dendrite formation caused by high local current densities during charging. Overcoming these limitations demands deliberate engineering of the cathode architecture and electrode formulation.

A key direction for future work is the design of a three-dimensional, porous, high SSA, and mechanically robust carbon framework that can uniformly host large amounts of sulfur. Simply increasing the thickness of a conventional slurry-cast carbon-sulfur film is insufficient, such as the MoS_x/rGO in this thesis work, due to transport limitations and sulfur-poor conductivity. Instead, the cathode should be constructed around an interconnected network of conductive carbon

materials, such as graphene, carbon nanotube, or templated porous carbons, that provide continuous electron pathways from the current collector throughout the entire electrode thickness. Within such scaffolds, macropores serve as ion-transport channels and buffer the ~80% volume expansion associated with sulfur conversion to Li_2S , mesopores provide accessible sites for sulfur and polysulfides while maintaining intimate contact with conductive surfaces, and micropores contribute to physical confinement and adsorption of smaller polysulfide species. This hierarchical pore structure enables high sulfur loading without severe pore blockage or transport bottlenecks and can be realized through freeze-casting, templating, 3D printing, or hybrid aerogels similar to those explored in this thesis.

In addition to the physical architecture of carbon, chemical functionality within the host becomes increasingly important at high sulfur loading because larger quantities of sulfur generate proportionally more polysulfides during cycling. Without adequate trapping and catalytic conversion, these polysulfides dissolve into the electrolyte, migrate to the lithium anode, and cause severe shuttle, self-discharge, and rapid capacity fading. Future cathode designs should therefore incorporate abundant polar or redox-active sites, such as transition-metal sulfides, metal–N–C motifs, or other catalytic species, uniformly distributed throughout the carbon scaffold. These components act as both chemical anchors and electrocatalysts, accelerating polysulfide conversion and maintaining fast redox kinetics across the entire electrode thickness.

Mechanical and chemical stability is another critical requirement for high-loading cathodes. At sulfur loadings of $\geq 4 \text{ mg/cm}^2$, the electrode undergoes substantial expansion and contraction during cycling, making it susceptible to cracking, delamination, and loss of electrical contact. To withstand these stresses, the host structure should possess sufficient elasticity or flexibility, and strong adhesion to the current collector. Networks of intertwined carbon nanotubes,

graphene sheets, or fibrous carbon frameworks can accommodate strain more effectively than rigid particulate films, while elastic binders and surface-modified current collectors can further enhance mechanical integrity. In some designs, the current collector itself may be replaced or supplemented by a 3D conductive scaffold, such as carbon cloth, metal foam, or etched metal mesh that provides both mechanical support and additional electron pathways.

Finally, achieving high sulfur loading requires precise control over sulfur distribution and morphology within the host. If sulfur forms dense agglomerates or thick surface coatings, only the outer regions of the electrode remain electrochemically active, while sulfur buried deep inside becomes isolated due to limited ion and electron access. Future work should therefore optimize sulfur incorporation methods, such as melt infiltration, solution impregnation, vapor deposition, or in situ precipitation, to ensure nanoscale sulfur dispersion throughout the porous framework. Uniformly distributed sulfur lowers local current densities, promotes homogeneous Li_2S nucleation, minimizes pore blockage, and improves reversibility under lean electrolyte conditions. Controlling sulfur morphology will be especially important in thick electrodes, where any kinetic limitation is magnified across the entire electrode thickness.

5.2.2 Li-Metal Anode

A durable lithium–sulfur battery ultimately depends on stabilizing the lithium metal anode, and the future direction of this work centers on engineering a host that enables uniform lithium deposition, suppresses dendrites, and maintains reversibility over hundreds of cycles. Lithium metal offers unmatched theoretical capacity and energy density, but its practical use is limited by dendritic growth, unstable SEI formation, and severe volume fluctuations during plating and stripping. In Li-S systems, these challenges are intensified by polysulfide shuttling, which

accelerates parasitic reactions and rapidly degrades the anode. Even when the sulfur cathode is highly optimized, the lithium metal surface remains the dominant failure point during long-term cycling. Achieving a stable lithium interface is therefore essential for translating Li-S chemistry into a commercially viable high-energy battery.

A promising path forward is the development of structured carbon hosts that regulate lithium nucleation and guide uniform deposition. Vertically aligned carbon nanofibers have demonstrated the value of a conductive, porous scaffold that accommodates lithium and mitigates dendrite formation. However, their reliance on PECVD limits scalability and restricts the incorporation of heteroatoms or metallic dopants that could further enhance lithiophilicity. Future progress requires a host architecture that preserves the advantages of VACNFs while enabling low-cost, large-scale fabrication and tunable surface chemistry.

A scalable electrospinning-derived carbon framework offers a practical solution. Electrospinning enables precise control over fiber morphology, porosity, and composition, and it readily accommodates heteroatom or metal doping. Incorporating lithiophilic metals such as silver into hollow carbon nanotube structures creates abundant nucleation sites that lower the energy barrier for lithium plating and promote uniform deposition throughout the 3D network. This Ag-CNT composite combines mechanical robustness, high conductivity, and strong interfacial affinity for lithium, reducing dendrite formation and stabilizing the SEI. Such a host can accommodate volume changes, maintain structural integrity, and support high-rate cycling with improved Coulombic efficiency.

Integrating this engineered lithium metal anode with a high-performance MoS_x/rGO sulfur cathode provides a complete strategy for advancing Li-S batteries. The MoS_x/rGO hybrid

suppresses polysulfide dissolution and accelerates redox conversion, while the Ag-CNT anode host protects the lithium surface from polysulfide-induced corrosion and guides uniform lithium cycling. Together, these components address the two fundamental bottlenecks of Li-S chemistry: sulfur utilization and lithium stability. This combined approach has the potential to deliver high energy density, long cycle life, and improved safety, moving Li-S batteries closer to practical deployment.

Developing such scalable, dopant-engineered carbon hosts represents a critical step toward next-generation lithium metal batteries. The insights gained here can extend beyond Li-S systems to other lithium metal chemistries, contributing to the broader goal of enabling high-energy, long-life rechargeable batteries for electric vehicles, grid storage, and emerging technologies.

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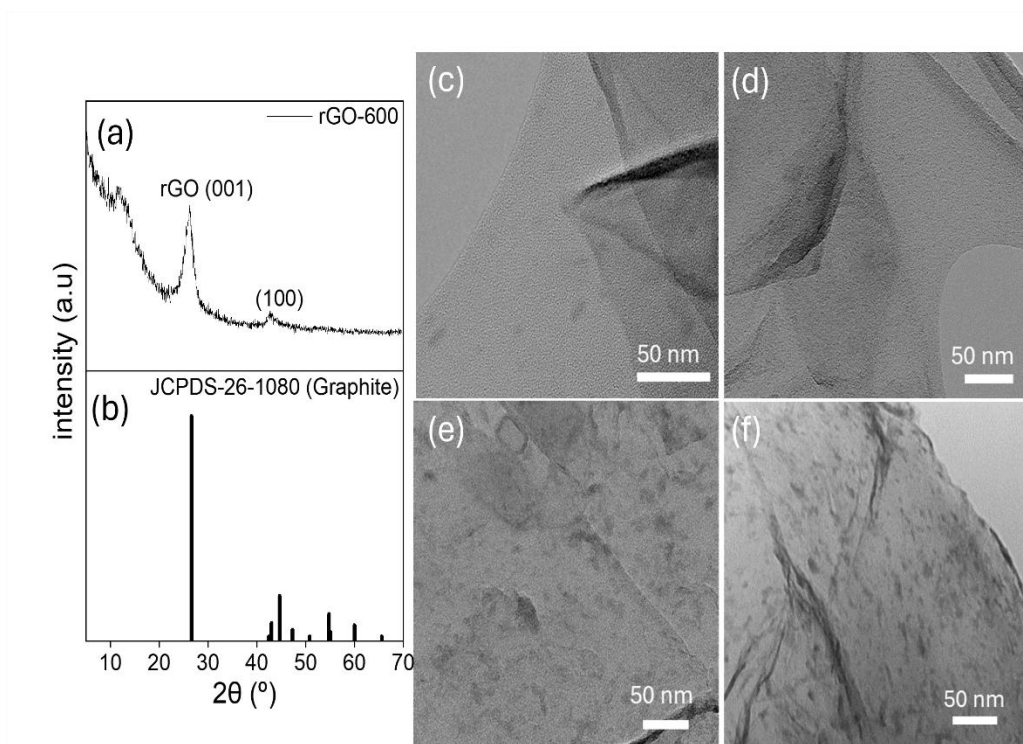
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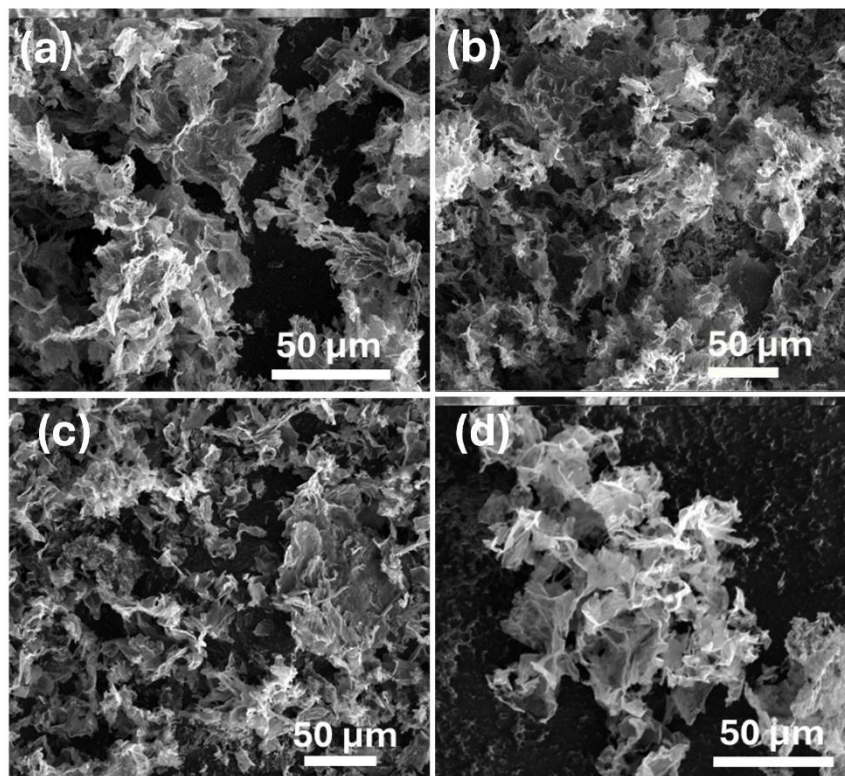
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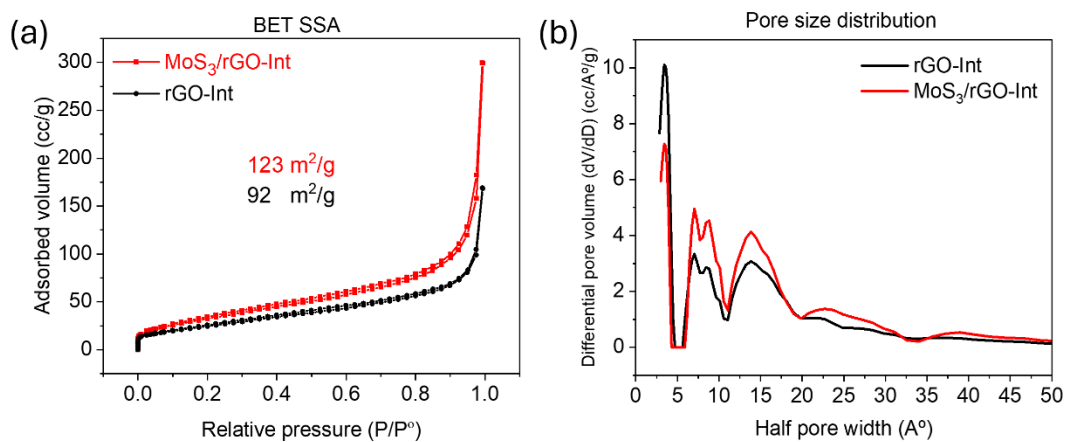
Appendix A - Supplementary Information for Chapter 3



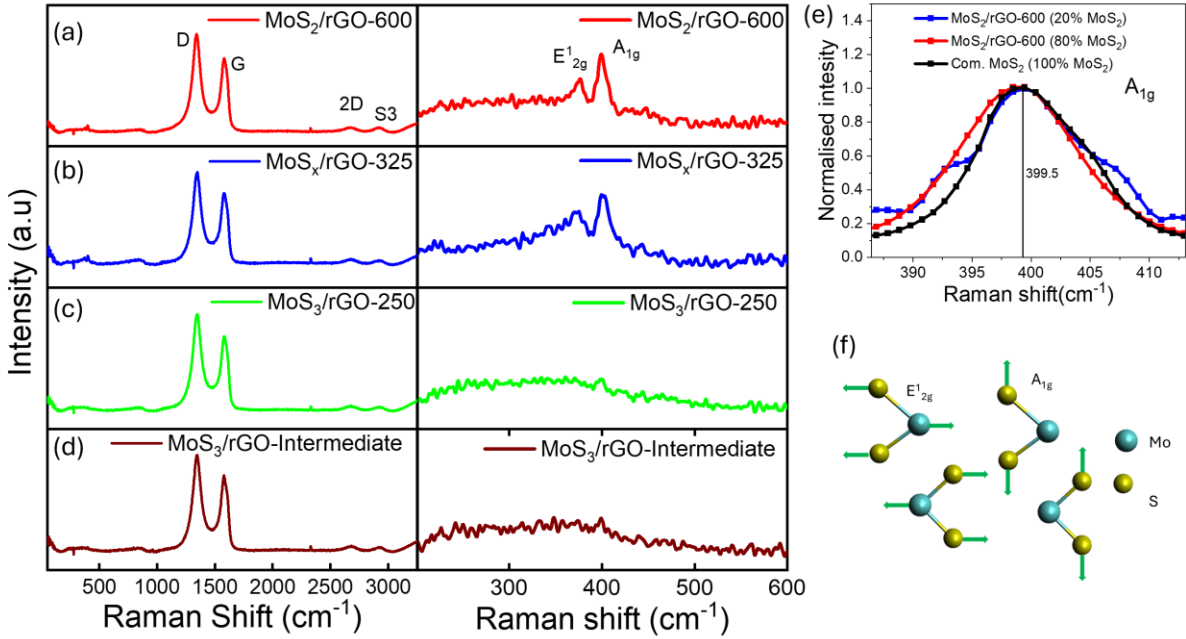
Appendix Figure A.1. XRD spectra of (a) rGO-600 control and (b) JCPDS data of graphite. Low-magnification TEM images of (c) MoS₃/rGO-Intermediate, (d) MoS₃/rGO-250, (e) MoS_x/rGO-325, and (f) MoS₂/rGO-600.



Appendix Figure A.2. SEM images of (a) MoS_3/rGO -Intermediate, (b) MoS_3/rGO -250, (c) MoS_x/rGO -325, and (d) MoS_2/rGO -600.



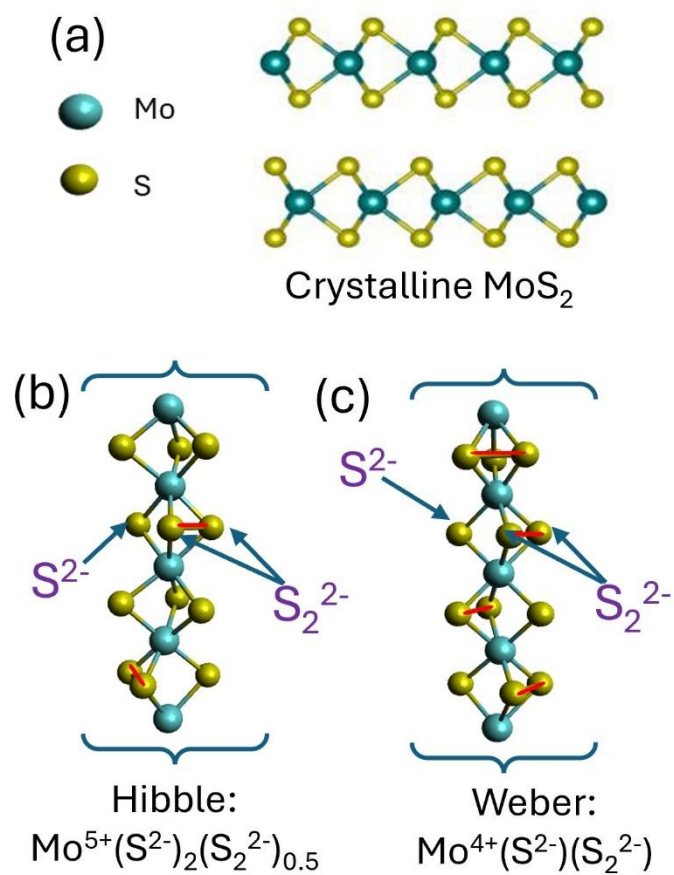
Appendix Figure A.3. (a) BET and (b) pore size distribution of MoS_3/rGO -Intermediate and rGO-Intermediate.



Appendix Figure A.4. The full (Left) and zoomed view (right) of Raman spectra of (a) MoS₂/rGO-600, (b) MoS₂/rGO-325, (c) MoS₃/rGO-250, and (d) MoS₃/rGO-Intermediate. (e) The peak position of A_{1g} out-of-plane vibrational mode of MoS₂. (f) Schematic illustration of the in-plane E¹_{2g} and out-of-plane A_{1g} vibration modes of crystalline MoS₂.

Appendix Table A.1. Peak position of Raman A_{1g} and E_{2g} and their difference

Material	$\sim A_{1g} \text{ cm}^{-1}$	$\sim E_{2g}^1 \text{ cm}^{-1}$	Δcm^{-1}	#layers
Commercial MoS ₂ (100% MoS ₂)	399.5	372.9	26.6	Bulk
MoS ₂ /rGO-600 (80 wt% MoS ₂ in the hybrid)	399.5	374.5	25.0	5-6
MoS ₂ /rGO-600 (20 wt% MoS ₂ in the hybrid)	399.5	376.6	22.9	≤ 3



Appendix Figure A.5. (a) Schematic of 2D crystalline MoS₂, 1D (b) Hibble MoS₃, and (c) Weber MoS₃ structure.

Appendix Table A.2. XPS peaks binding energy and relative at% of Mo and S species at different valence states in each MoS_x/rGO-xxx hybrid and the atomic ratio of total Mo atoms to total S atoms:

Oxidation state and peak assignment		MoS ₃ /rGO int		MoS ₃ /rGO-250		MoS _x /rGO-325		MoS ₂ /rGO-600	
		B.E. (eV)	Relative at%	BE. (eV)	Relative at%	B.E. (eV)	Relative at%	B.E. (eV)	Relative at%
Mo ⁴⁺	3d _{5/2}	229.46	34.80	229.53	49.61	229.25	59.63	229.30	81.72
	3d _{3/2}	232.49		232.62		232.41		232.43	
Mo ⁵⁺	3d _{5/2}	230.18	43.13	229.85	39.12	229.40	23.98	N/A	0
	3d _{3/2}	233.06		232.86		233.02		N/A	
Mo ⁶⁺	3d _{5/2}	232.49	22.07	232.62	11.27	231.80	16.39	232.43	18.28
	3d _{3/2}	235.31		234.80		235.47		235.20	
S ²⁻	2p _{3/2}	162.36	42.40	162.60	58.72	162.11	67.04	162.13	100
	2p _{1/2}	163.61		163.75		163.30		163.33	
S ₂ ²⁻	2p _{3/2}	163.66	57.60	163.76	41.28	163.14	32.96	N/A	0
	2p _{1/2}	164.87		164.85		164.71		N/A	
Atomic ratio of S in S ₂ ²⁻ : S ²⁻		1.36:1		0.70:1		0.49:1		0:1	
The total atomic ratio of Mo: S		3.24		2.44		2.27		2.05	

Calculation of the composition of Weber, Hibble, and 2D MoS₂ in MoS_x/rGO-325:

From the XPS measurements summary in Table S2:

Mo species are present as: 59.63% Mo⁺⁴; 23.98% Mo⁺⁵; 16.39% Mo⁺⁶

S species are present as: 32.96% S atoms are at S₂²⁻; 67.04% S atoms are at S²⁻

Assume the molybdenum species have the following fractional composition:

Weber MoS₃ structure: Mo⁺⁴(S²⁻)(S₂²⁻)=X

Hibble MoS₃ structure: Mo⁺⁵(S²⁻)₂(S₂²⁻)_{0.5}= Y

2D Mo⁺⁴S₂=Z

$$\text{For Mo}^{+4}: \quad X + Z = 59.63 \quad (3)$$

$$\text{For Mo}^{+5}: \quad Y = 23.98 \quad (4)$$

For S²⁻ (67.04%), it is proportional to the stoichiometric calculation from Mo species following:

$$X + 2Y + 2Z = 67.04 \quad (5)$$

$$\text{Inputting (4) to (5) gives:} \quad X + 2Z + 2 \times 23.98 = 67.04 \quad (6)$$

For S₂²⁻ (32.96%), it is proportional to the stoichiometric calculation from Mo species following:

$$2X + Y = 32.96 \quad (7)$$

$$\text{Inputting (4) to (7) gives:} \quad 2X + 23.98 = 32.96 \quad (8)$$

Solving these gives,

$$X (\text{Weber structure}) = 4.49\%$$

$$Y (\text{Hibble structure}) = 23.98\%$$

$$Z (2D \text{ MoS}_2) = 55.14\%$$

Appendix Table A.3. Summary of CHNSO elemental analysis

Samples	Wt% of N	Wt% of C	Wt% of H	Wt% of S	1.Wt% of total Mo
MoS ₂ /rGO-600	0.52	63.69	0.51	12.01	18.74
MoS _x /rGO-325	0.71	60.62	0.56	11.58	19.69
MoS ₃ /rGO-250	0.87	59.03	0.50	13.64	18.72
MoS ₃ /rGO-Int	0.96	54.12	0.78	15.36	19.91

5. At% of Mo	At% of S	6. S: Mo
2.12	5.59	2.35
2.58	5.43	2.10
2.65	6.50	2.46
2.45	7.27	2.96

Note:

Elements: N -

Nitrogen; C - Carbon;

H - Hydrogen; O - Oxygen; S - Sulfur; Mo - Molybdenum.

- Weight percentage of Mo = 100 % - (wt% of C + wt% of N + wt% of H + wt% of O + wt% of S)
- Weight percentage of Mo in form of Mo⁺⁴ and Mo⁺⁵ = a* the purity from XPS (Fig. S6)
- The weight percentage of MoS_x = c.wt% of Mo + wt% of S
- Weight percentage of rGO = wt% of C + wt% of O
At% = wt% /AW.....(a)
- At% of Mo = [wt% of Mo (1)/AW of Mo]/ [sum of the at% of all elements by equation (a)] * the purity from XPS (Fig. S6)
- Atomic ratio of Mo:S = at% of S/at% of Mo
AW = atomic weight

❖ **Sample calculation for the average S mass before and after flash melting:**

The S electrode before flash melting = 2.22 mg

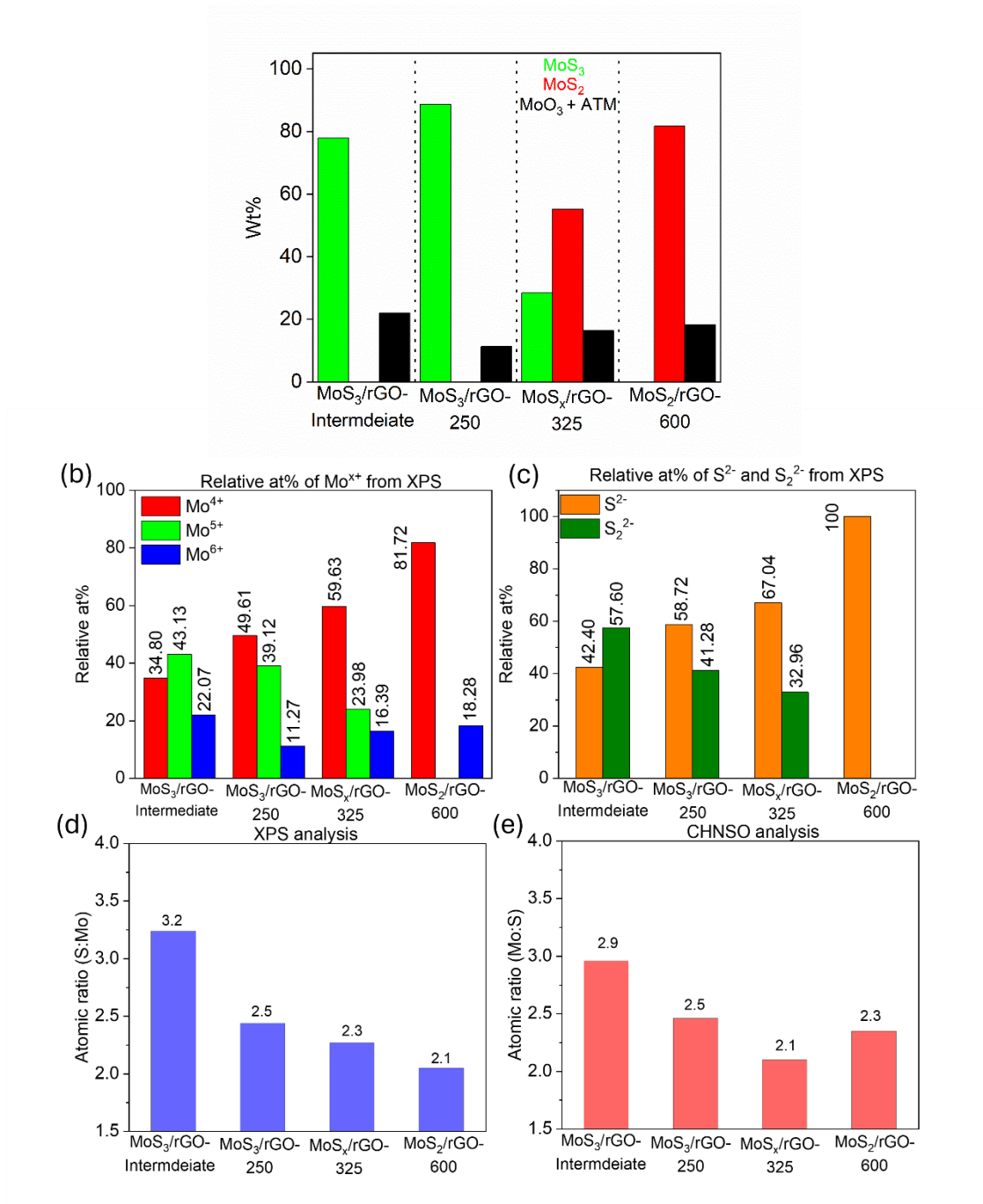
Sulfur loss during the flash heating = 0.80 mg

Sulfur mass retained = 1.42 mg

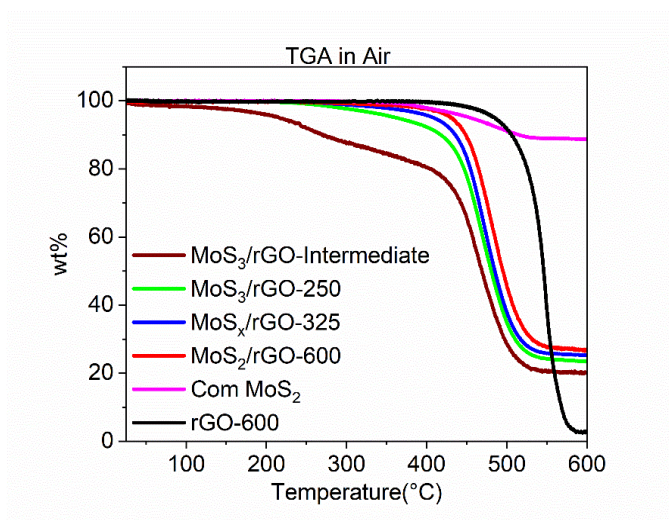
Electrode area = 1.767 cm² (15 mm in diameter)

Sulfur mass loading = 1.42 mg/1.767 cm² = **0.80 mg/cm²**.

The average final sulfur loading used in cell fabrication is 0.80 ± 0.11 mg/cm².



Appendix Figure A.6. (a) Summary total MoS₃, MoS₂, and impurity (MoO₃+ATM) composition derived from XPS analysis. Summary of (b) Mo 3d oxidation states, (c) S 2p oxidation states. (d) Mo: S ratio from XPS, and (e) CHNSO analysis.



Appendix Figure A.7. TGA curves measured

Calculation of wight composition of hybrids:

in MoS₂/rGO-600 by TGA:

Fraction of MoS₂ in MoS₂/rGO-600 = A

Fraction of rGO in MoS₂/rGO-600 = B

Fraction of commercial MoS₂ left at 600 °C
= 88.5%

Fraction of rGO left after 600 °C = 2.5%

Material balance at 600 °C,

$$88.5A + 2.5B = 27.2 \text{-----(9)}$$

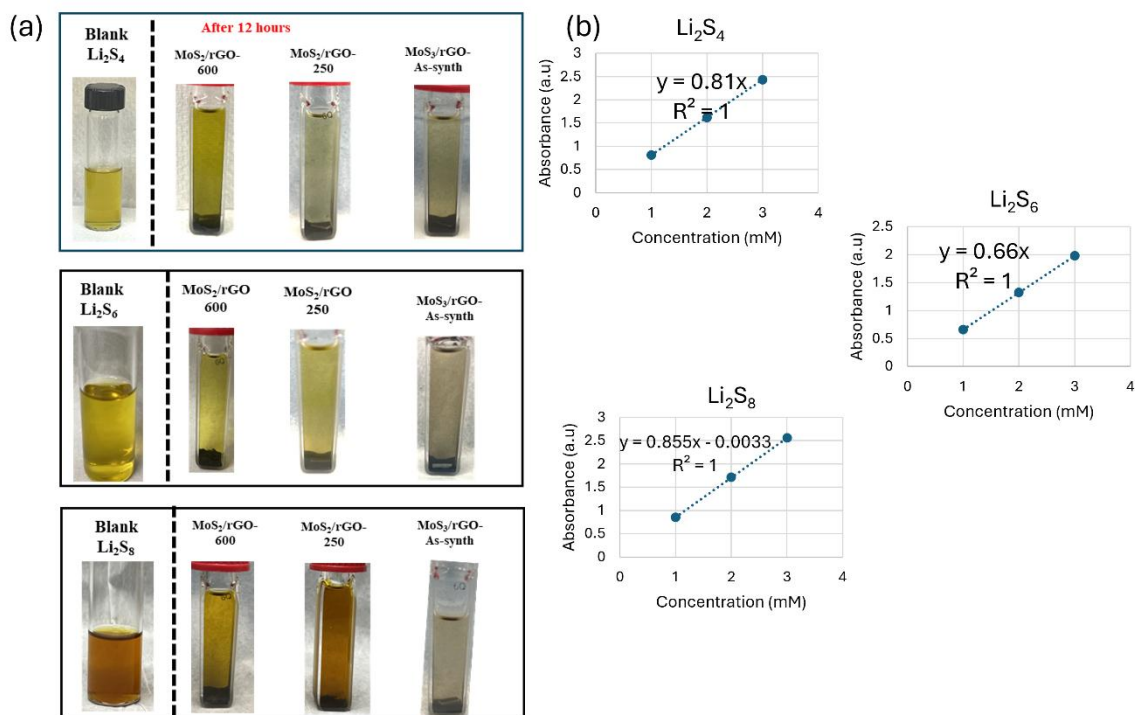
$$100A + 100B = 100 \text{-----(10)}$$

By solving the equations:

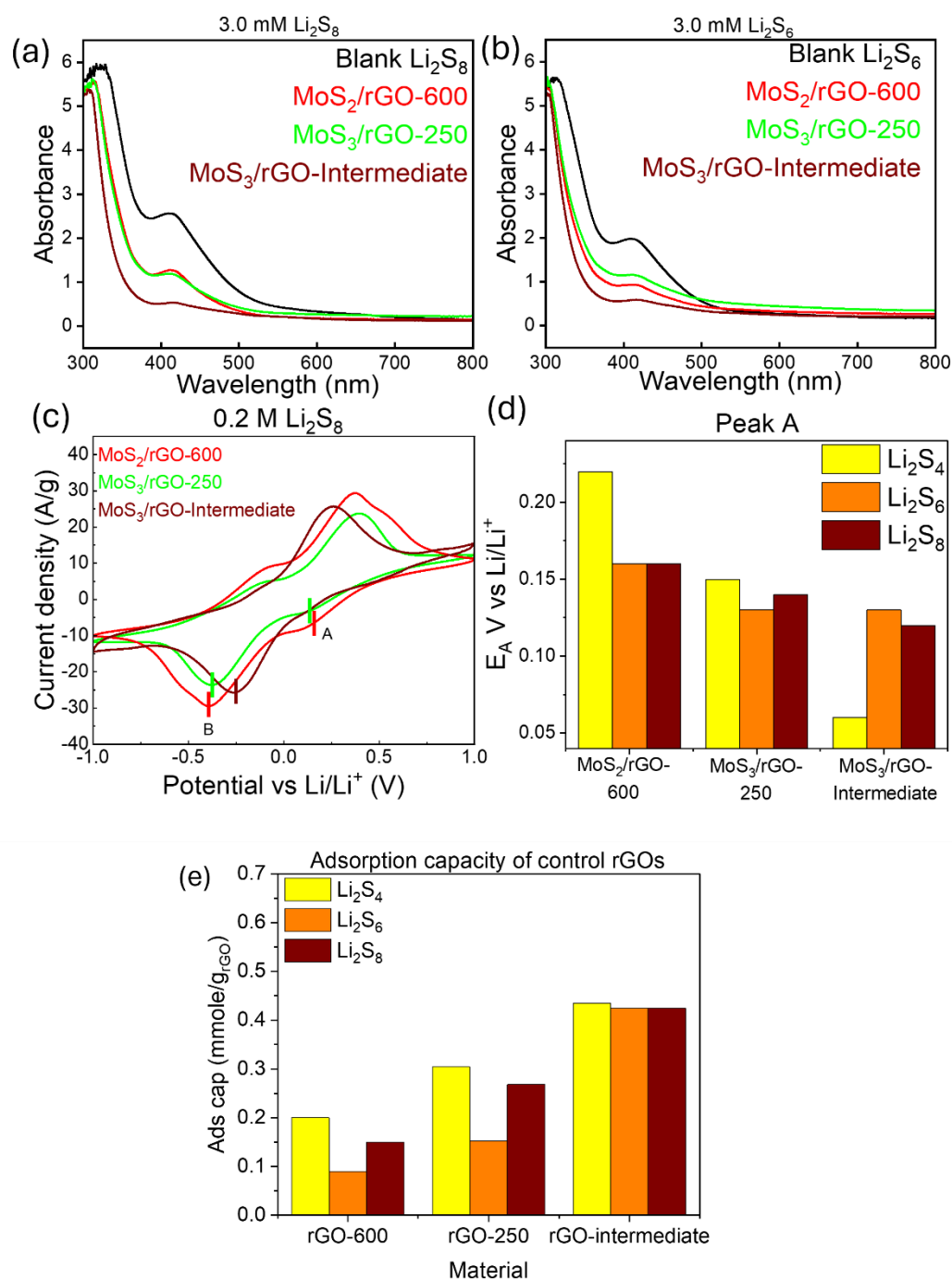
wight% of MoS₂ in the hybrid= 28.7% and
rGO=71.3%

Appendix Table A.4. Weight composition by TGA

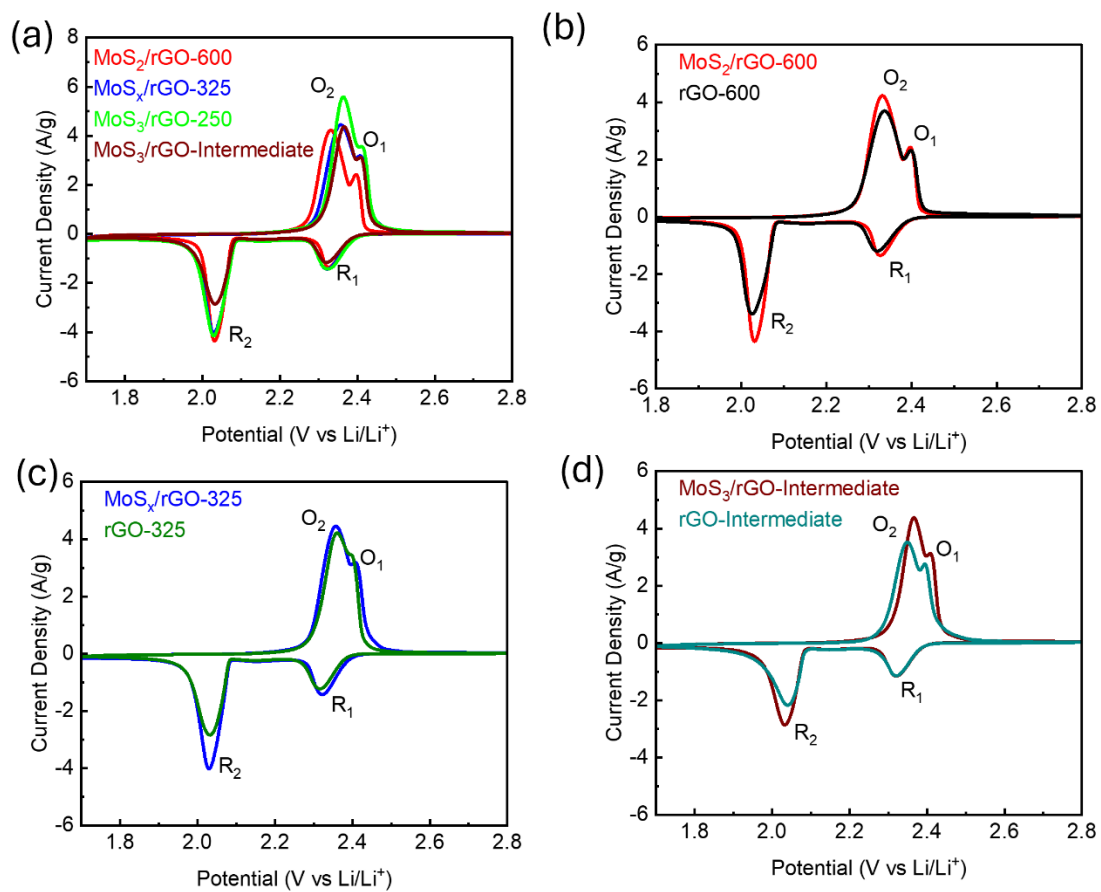
Material	Wt%MoS _x	Wt%rGO
MoS ₂ /rGO-600	28.7	71.3
MoS _x /rGO-325	26.7	73.2
MoS ₃ /rGO-250	24.7	75.3
MoS ₃ /rGO-int	20.8	79.2



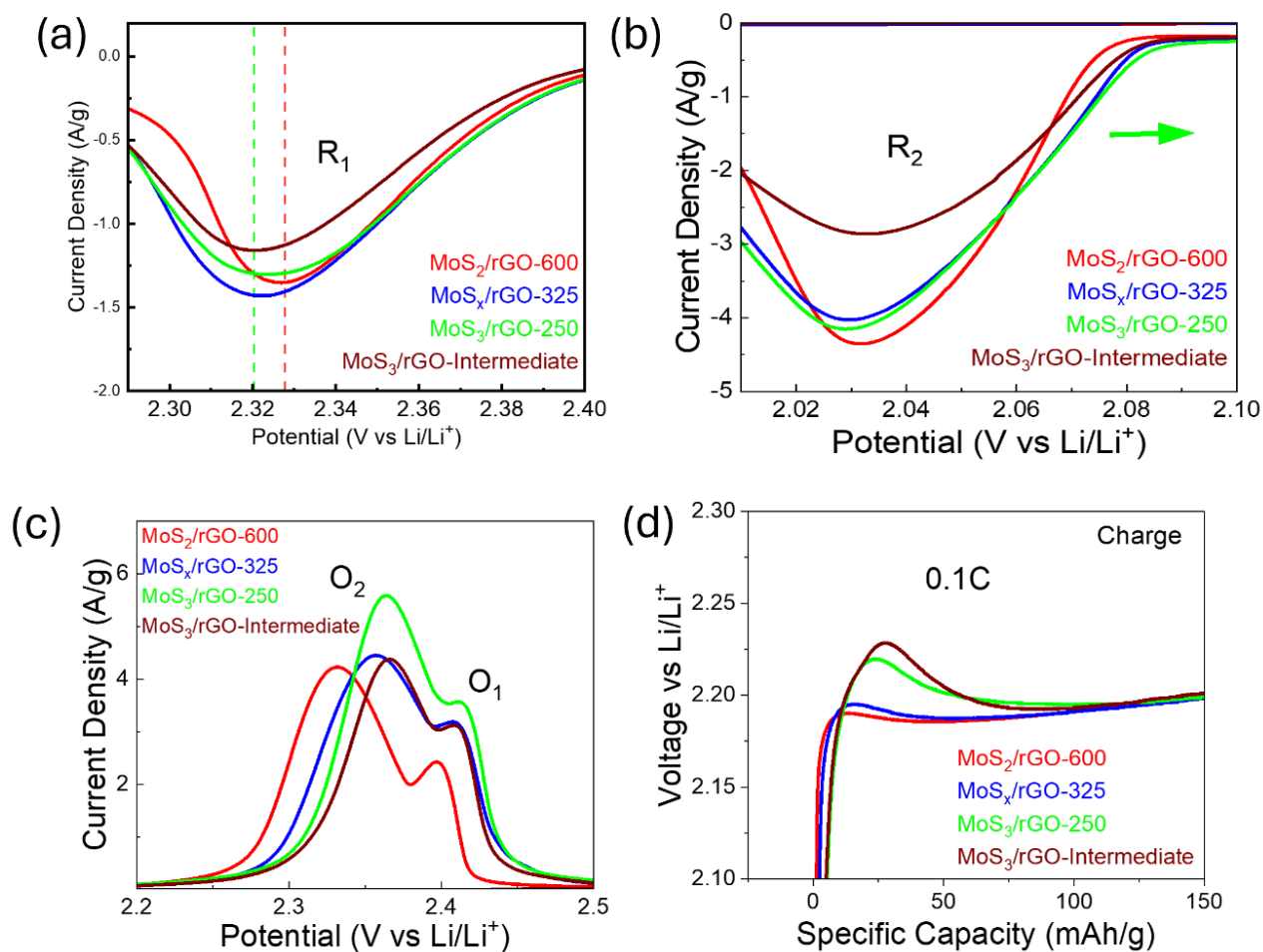
Appendix Figure A.8. (a) Photos captured during the polysulfide adsorption measurements monitored by UV-Vis absorbance spectra. (b) The calibration curves of the absorbance at 411 nm wavelength which were used for calculating the specific adsorption capacity.



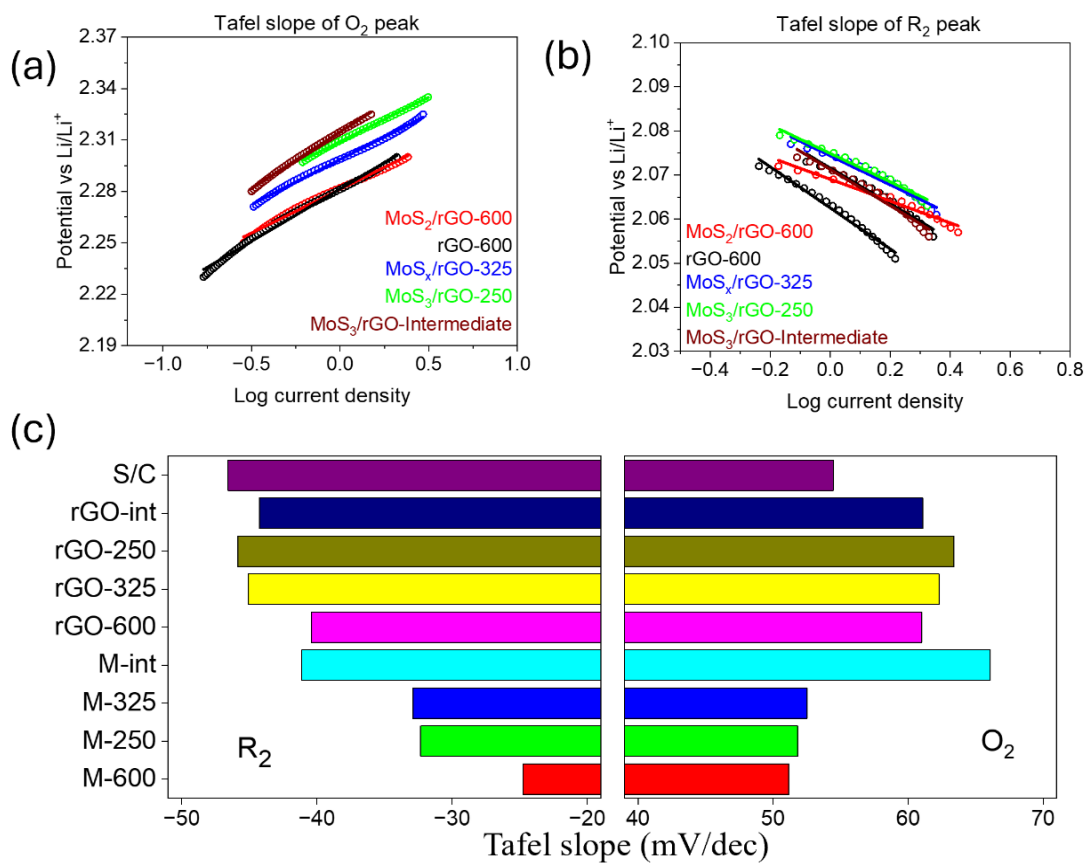
Appendix Figure A.9. Absorbance spectra in (a) 3.0 mM Li_2S_8 analyte and (b) 3.0 mM Li_2S_6 analytes. (c) CV curves in the symmetric cell filled with 0.2 M Li_2S_8 at 50 mV/s with different catalysts. (d) Summary of the electrode potential of peak A in the symmetric cell of different catalysts with 0.2 M Li_2S_4 , Li_2S_6 , and Li_2S_8 , respectively. (e) Summary of the adsorption capacity of the rGO control samples of rGO-600, rGO-250, and rGO-intermediate in 3.0 mM LiPSs solutions.



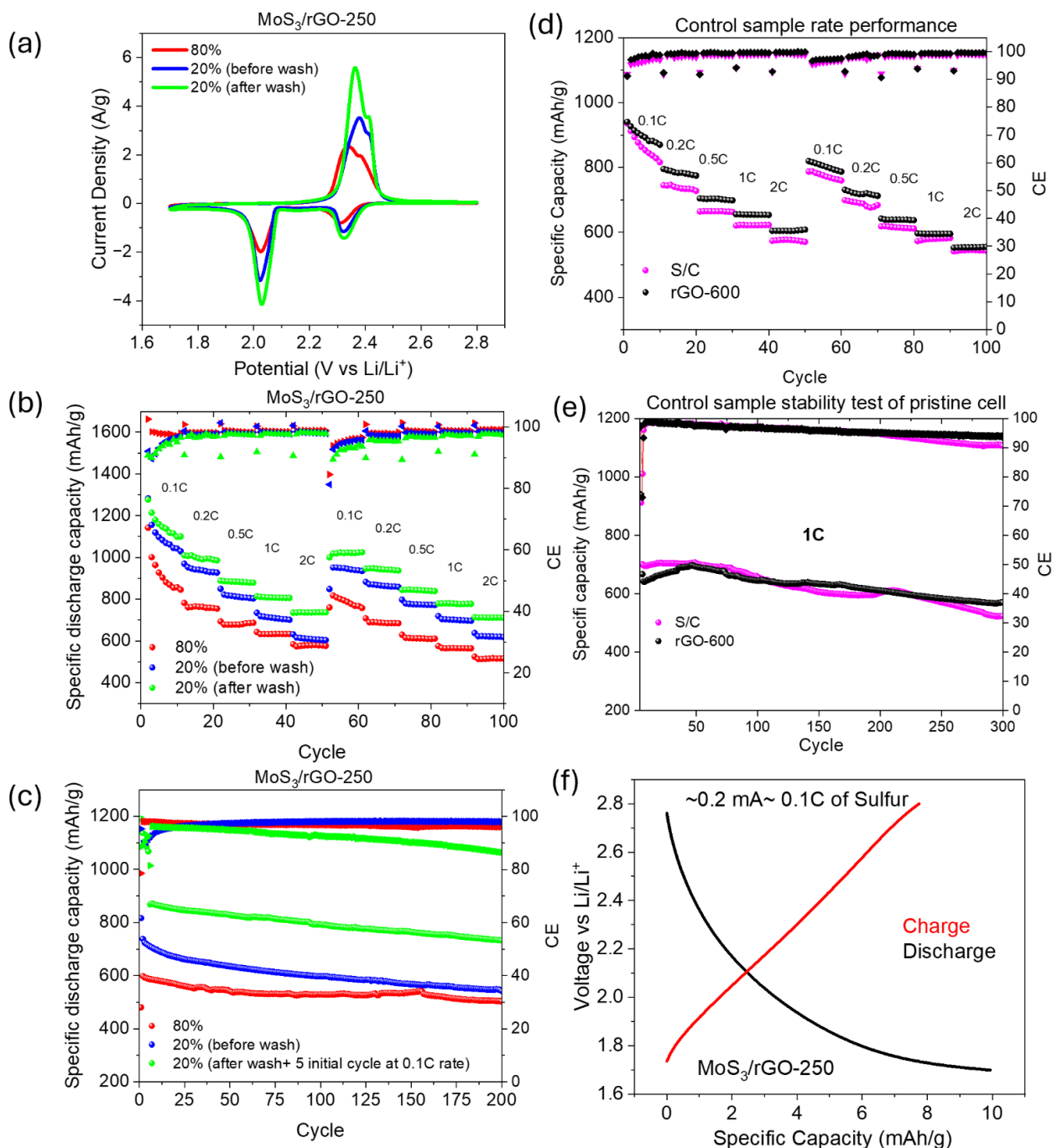
Appendix Figure A.10. CV of 20% (a) all four catalysts, (b) MoS₂/rGO-600, (c) MoS_x/rGO-325, and (d) MoS₃/rGO-250 compared with their respective rGO controls.



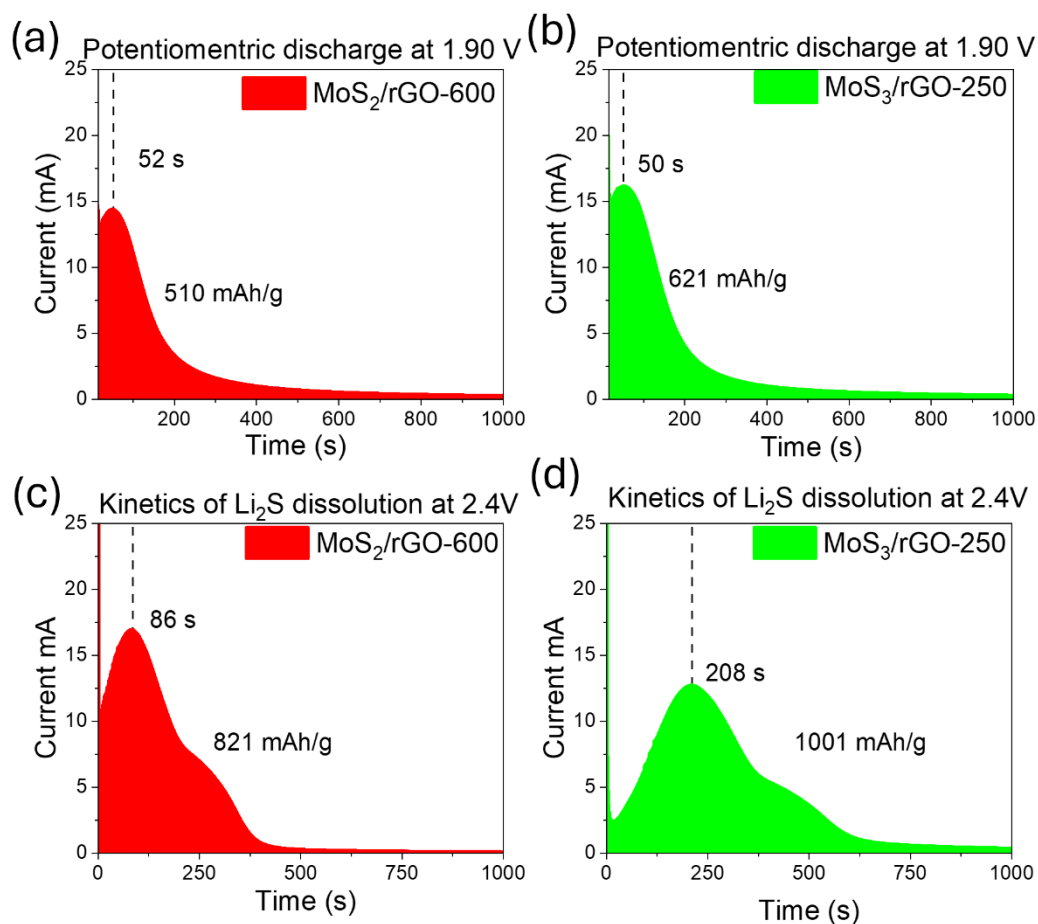
Appendix Figure A.11. Zoomed view of CV data [refers to figure 3.6(a)] at (a) R_1 , (b) R_2 , (c) O_1 and O_2 , and (d) Li_2S oxidation peak during charging for all four catalysts.



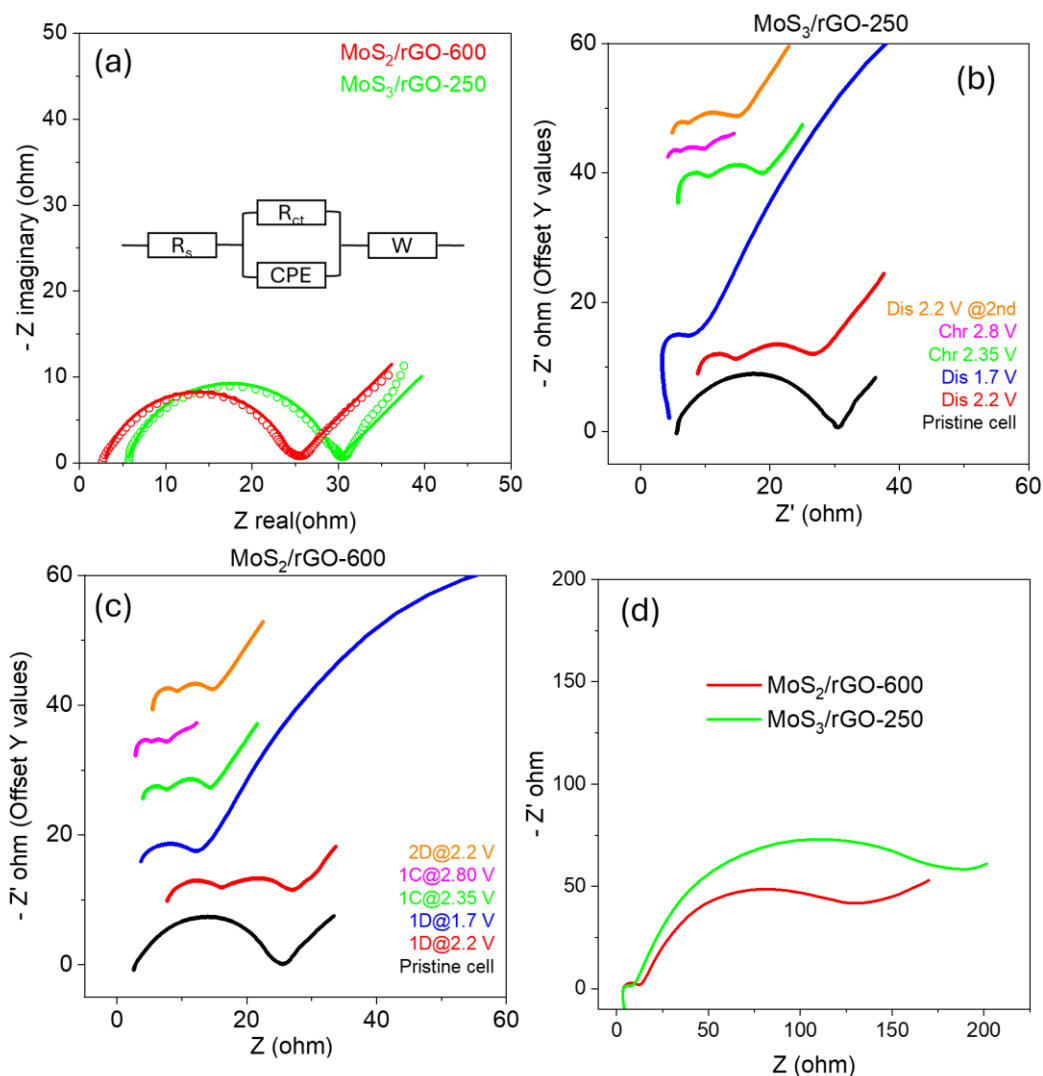
Appendix Figure A.12. The Tafel slope fitting curves of all four catalysts and their respective control rGOs from the rising of (a) the oxidation peak O₂ and (b) the reduction peak of R₂. (c) Summary of the Tafel slope values derived from panels (a) and (b).



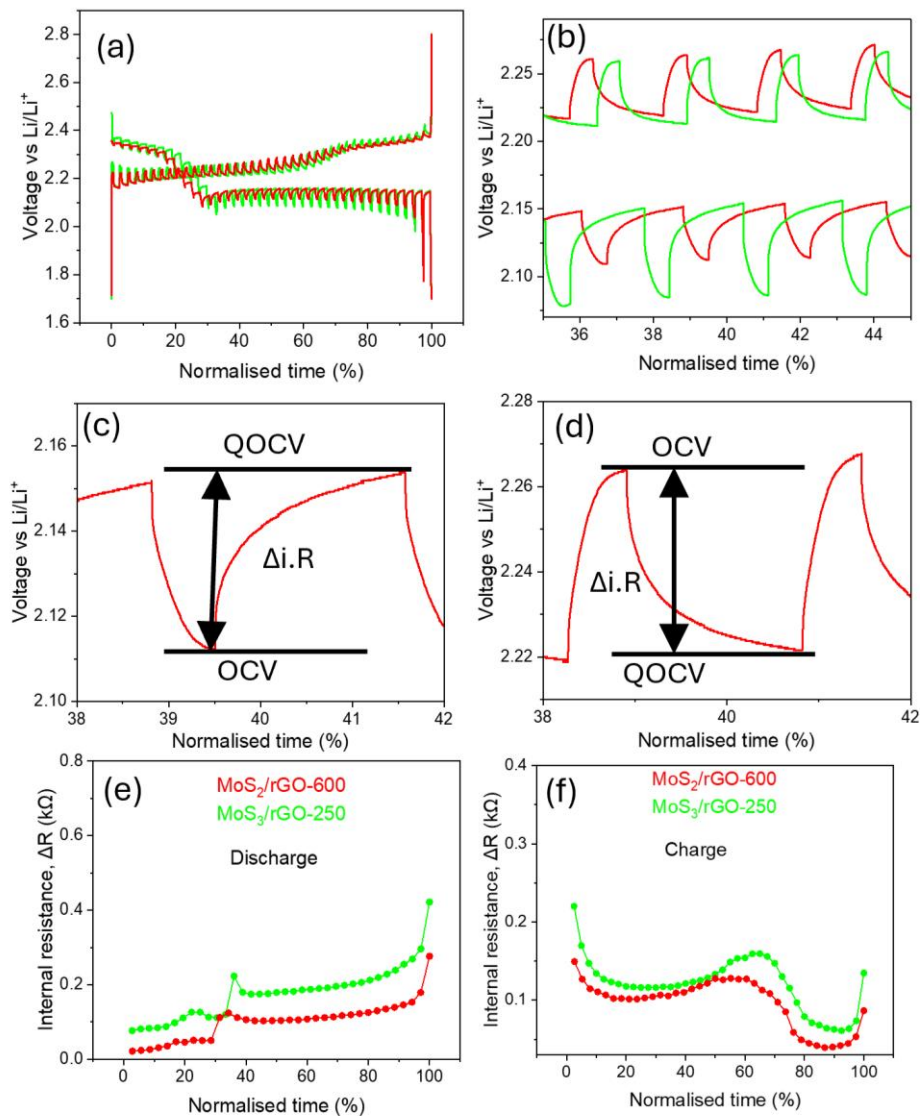
Appendix Figure A.13. Comparison of (a) CV at 0.1 mV/s, (b) rate performance and (c) cycle life stability test at 1C for Li-S full cells with the incorporated $\text{MoS}_3/\text{rGO}-250$ catalyst prepared at different conditions, including different MoS_3 loading (80% used in previous studies vs. 20% in this study) and removing MoO_3 impurities by washing with warm water. Comparison of the control rGO-600 and superP sample (d) rate performance, and (e) Cycle stability test. (f) A control test of $\text{MoS}_3/\text{rGO}-250$ cathode at a constant charge-discharge current of 0.2 mA, corresponding to a 0.1C rate for a typical cathode loaded with 1.3 mg sulfur. The specific capacity is converted to the equivalent value for a S-loaded cathode.



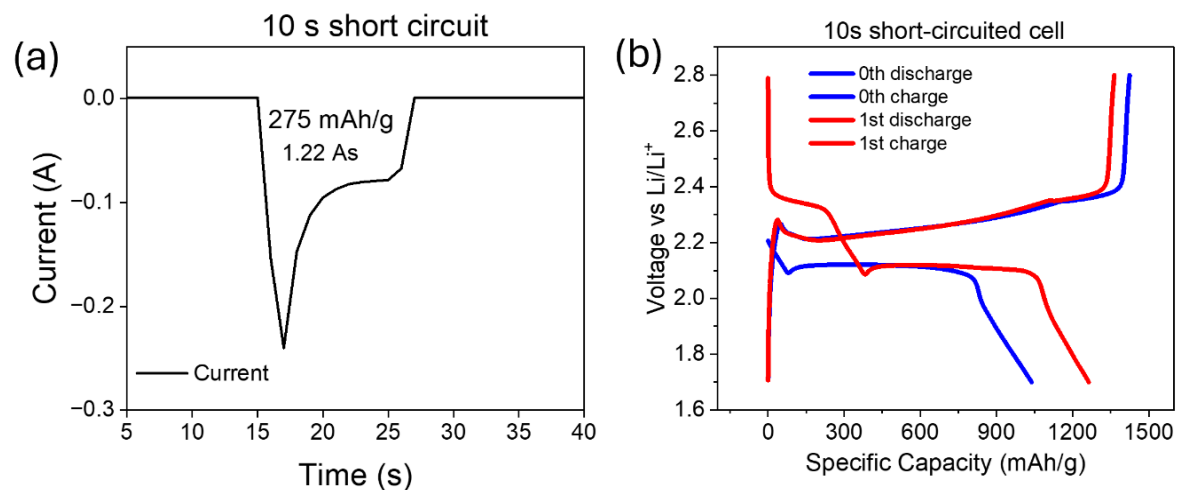
Appendix Figure A.14. Chronoamperograms of potentiostatic discharging the Li-S coin cells incorporated with (a) $\text{MoS}_2/\text{rGO-600}$ and (b) $\text{MoS}_3/\text{rGO-250}$ in the S/C cathode by stepping the cell voltage from 2.20 V to 1.90 V (corresponding to R_2 reaction), and (c) and (d) charging the respective cells by stepping the cell voltage from ~2.10 V (OCV) V to 2.4 V (i.e., O_2 reaction)



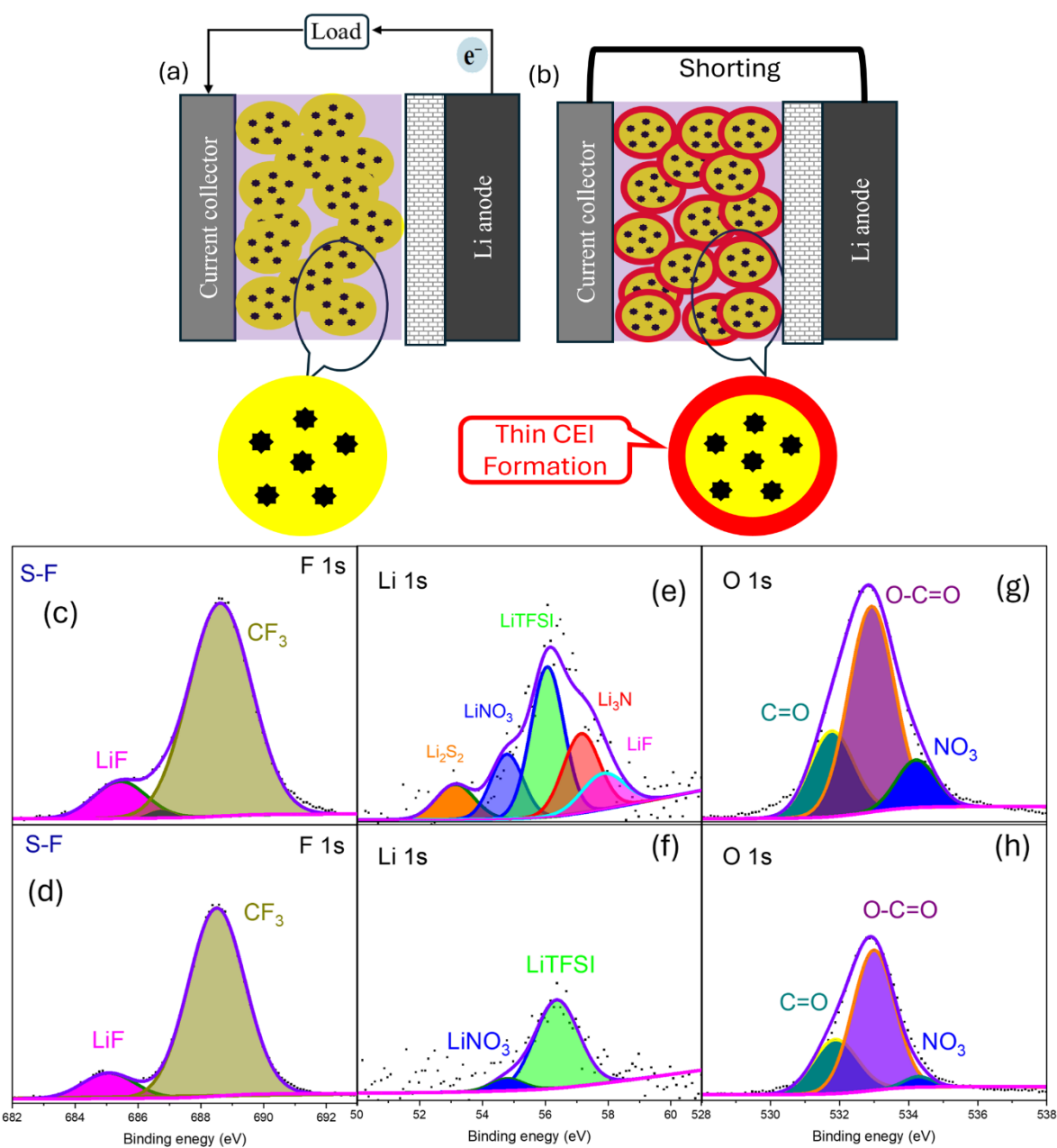
Appendix Figure A.15. (a) Raw and Fitted EIS data of the pristine Li-S cells consisting of $\text{MoS}_2/\text{rGO-600}$, and $\text{MoS}_3/\text{rGO-250}$ incorporated cathodes at OCV (~ 2.37 V to 2.28 V). EIS spectra at different states when the cell is discharged from the pristine condition (~ 2.37 V to 2.28 V) to a fully discharged state (1.7 V), recharged to 2.8 V, and then goes through the 2nd discharge to 2.2 V for (b) $\text{MoS}_3/\text{rGO-250}$ and (c) $\text{MoS}_2/\text{rGO-600}$ incorporated cathodes. (d) The full-scale EIS spectra of the two cells after fully discharged to 1.7 V, which are only partially shown in panels (b) and (c).



Appendix Figure A.16. (a) The galvanostatic intermittent titration technique (GITT) tests for MoS₃/rGO-250 and MoS₂/rGO-600, (b) expanded view of (a), Voltage profile reading method at discharge (c) and (d) charge state. The transfer internal resistance profile during (e) discharge and (f) charge processes, calculated by $\Delta R \text{ (Ohm)} = |\Delta V_{\text{QOCV-OCV}}| / I_{\text{applied}}$.

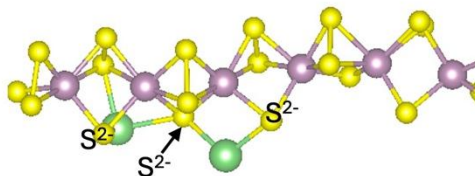


Appendix Figure A.17. (a) The current profile during the 10 s period of short-circuiting, and (b) the discharge-charge voltage profiles before and after the 10 s short-circuiting. The notation 0th represents the discharge right after short-circuiting). It was then followed by the 1st cycle of full charge and discharge to assess the specific capacities.

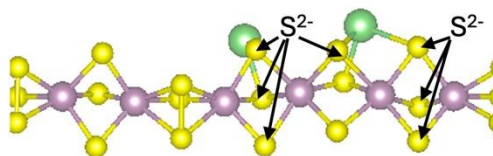


Appendix Figure A.18. (a) Schematic of the pristine cell without short circuiting. (b) A thin CEI layer formation (in red) and wrapping the sulfur particle around the cathode particles after a 10-s short circuit. XPS data of the control rGO-600 electrode without sulfur, recorded after a 10-second short circuit, showing (c) F 1s, (d) Li 1s, and (g) O1s spectra. Additionally, XPS data of the soaked sample without a short circuit are presented for (d) F 1s, (f) Li 1s, and (h) O1s spectra.

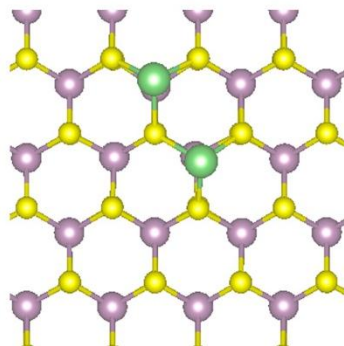
(a) $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$



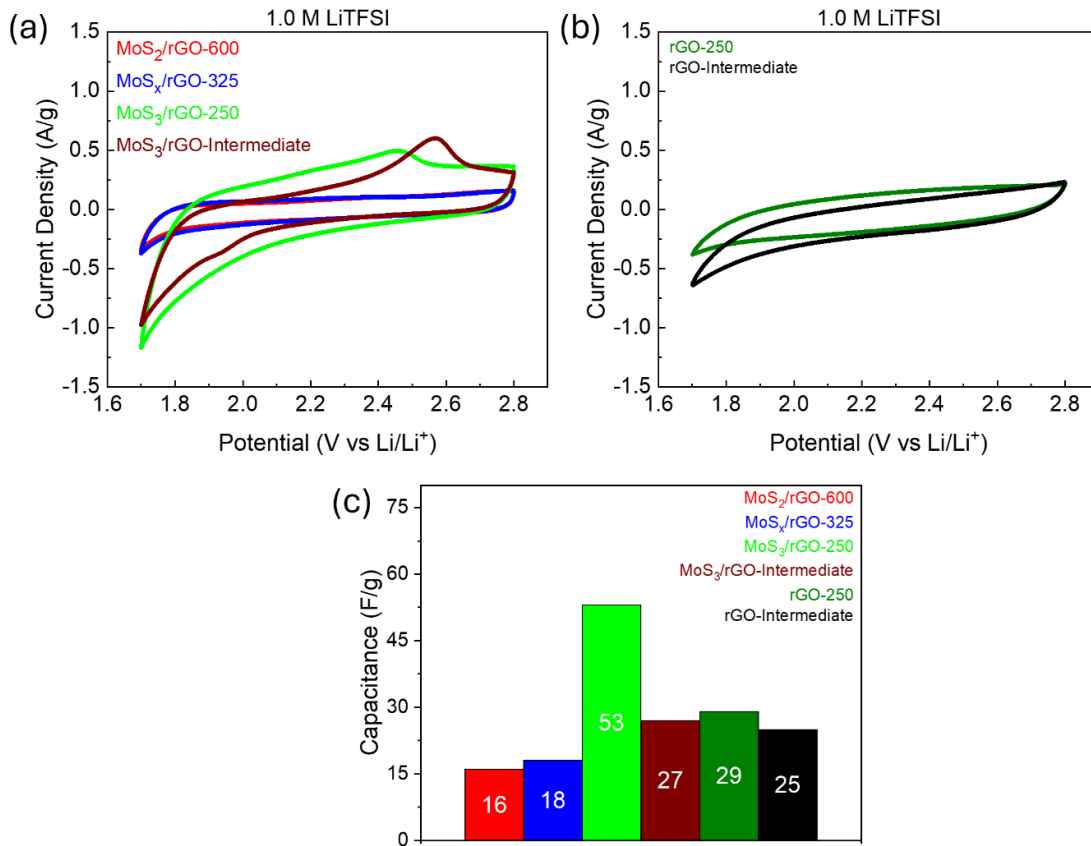
(b) $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$



(c) MoS_2 monolayer



Appendix Figure A.19. The optimized Li_2 binding configurations on (a) $\text{Mo}^{4+}(\text{S}^{2-})(\text{S}_2^{2-})$ (Weber structure) and (b) $\text{Mo}^{5+}(\text{S}^{2-})_2(\text{S}_2^{2-})_{1/2}$ (Hibble structure), and (c) MoS_2 monolayer, respectively.



Appendix Figure A.20. CV in 1.0 M LiTFSI electrolyte filled in symmetric cells made of carbon electrodes incorporated with 20 wt% of (a) MoS₂/rGO-600, MoS_x/rGO-325, MoS₃/rGO-250 and MoS₃/rGO-intermediate, and (b) compared with rGO controls. The scan rate is 5.0 mV/s. (c) Specific Capacitance derived from the CV for the above materials in the blank 1.0 M LiTFSI electrolyte.

Formula used:

The current density difference between the forward and reverse scan at the center of the potential window (2.25 V):

$$\Delta i \text{ (A/g)} = [2 \times \text{capacitance } C_0 \text{ (F/g)} \times \text{scan rate } \nu \text{ (V/s)}]$$

$$C_0 = (\Delta i / 2\nu) = (\Delta i \text{ A/g}) / (2 \times 0.005 \text{ V/s}) = (\Delta i / 0.01) \text{ F/g}$$

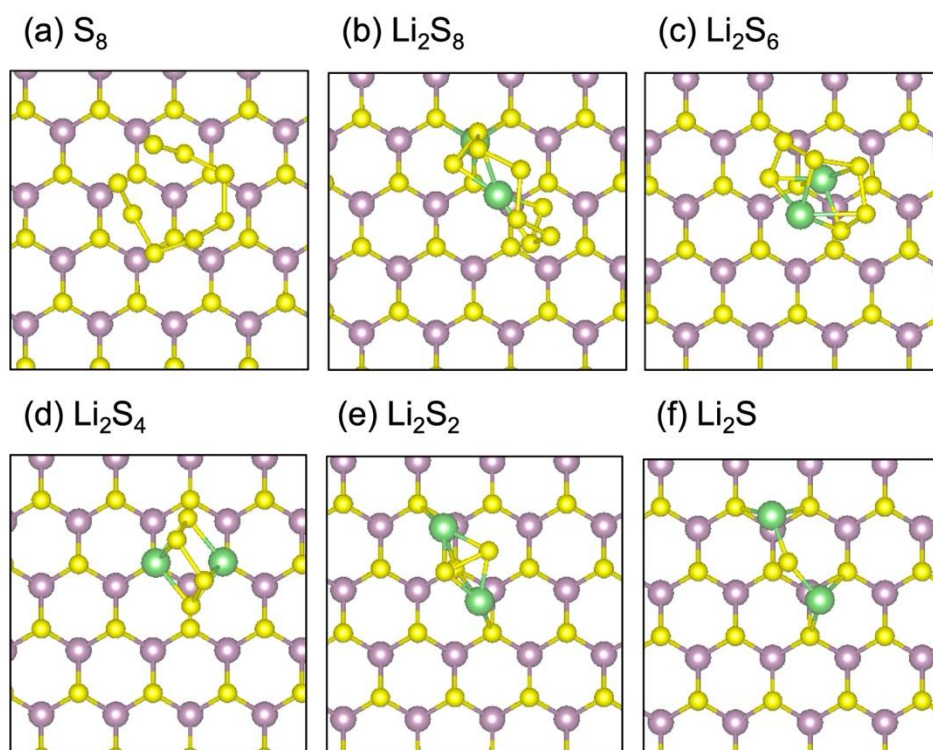
Example calculation:

For MoS₃/rGO-250,

$$\Delta i = 0.36 - (-0.17) = 0.53 \text{ A/g}$$

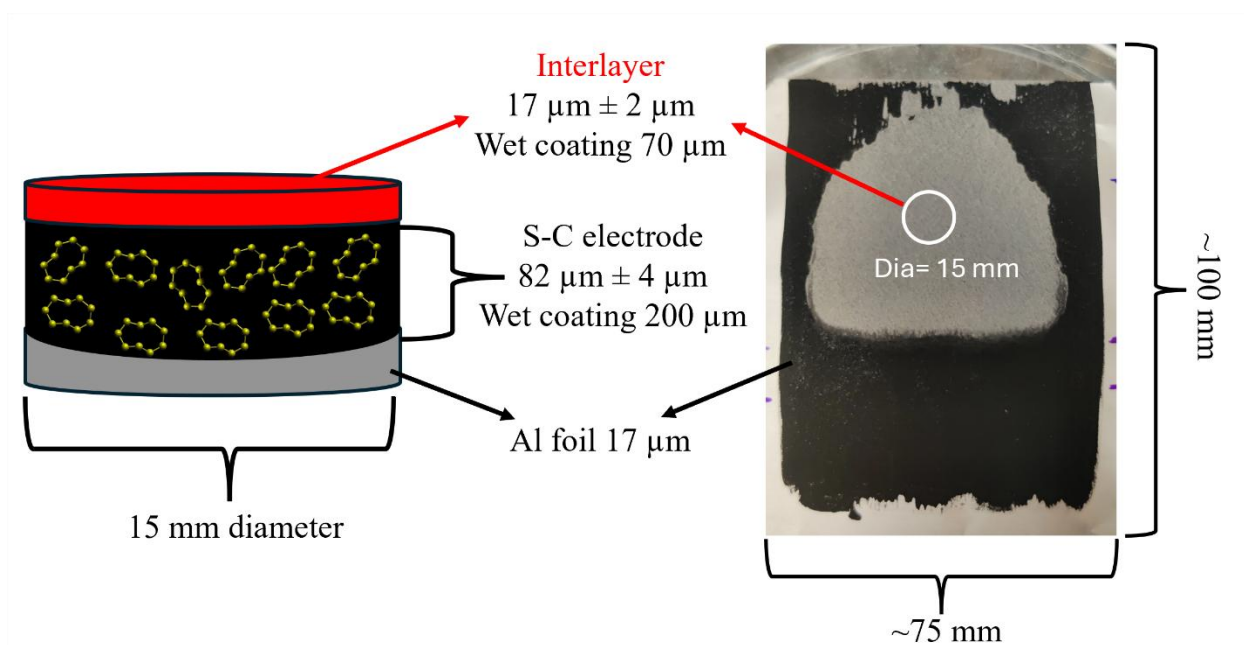
$$C_0 = 53 \text{ F/g}$$

Since C_0 is proportional to the Electrochemical Surface Area (ECSA), MoS₃/rGO-250, which presents the highest C_0 , also poses the highest ECSA.

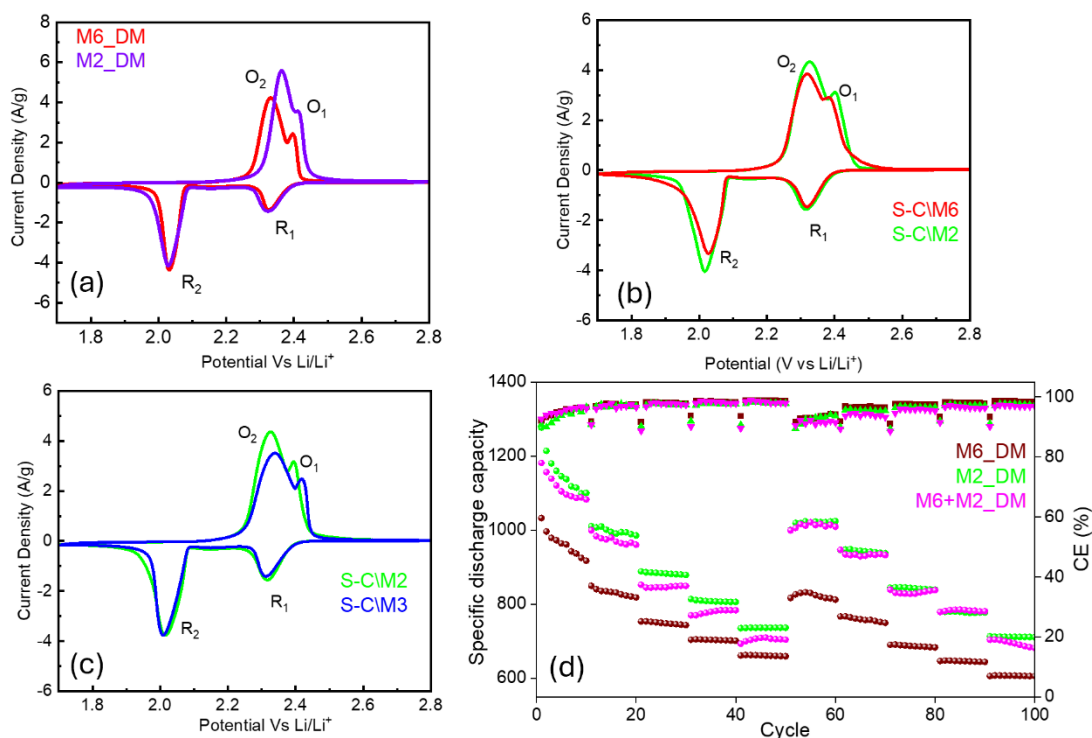


Appendix Figure A.21. Top views of the adsorption of (a) S_8 , (b) Li_2S_8 , (c) Li_2S_6 , (d) Li_2S_4 , (e) Li_2S_2 , (f) Li_2S on the basal plane of MoS_2 . The S, Li, and Mo atoms are displayed in yellow, green, and purple, respectively.

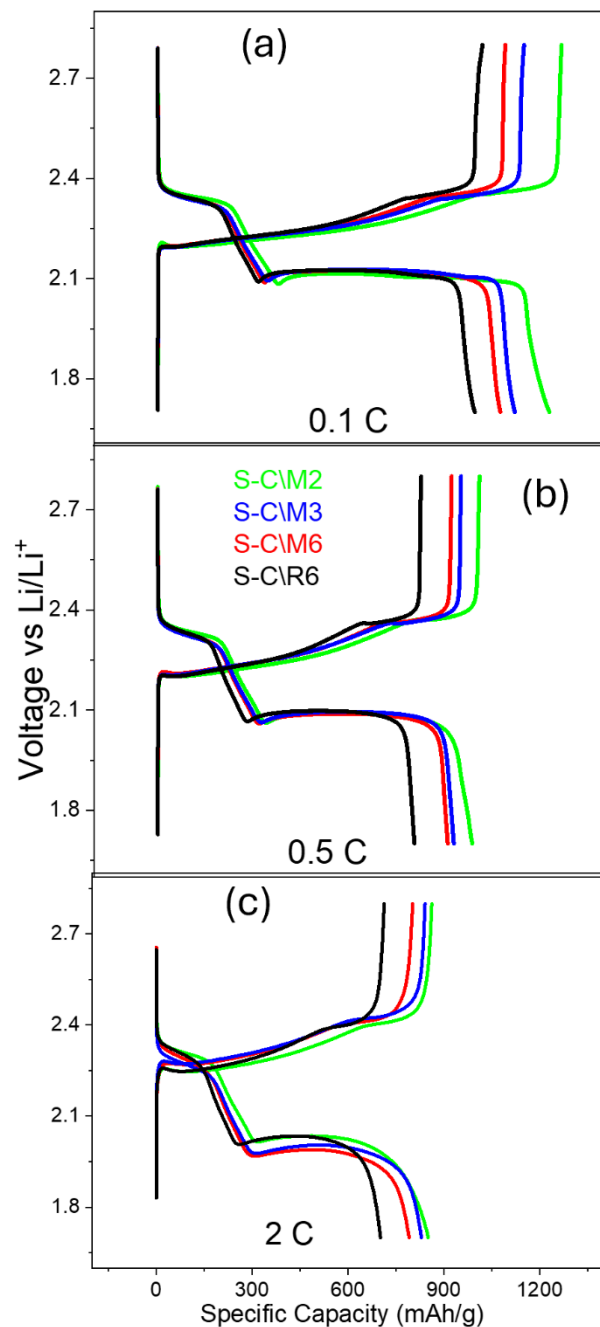
Appendix B - Supplementary Information for Chapter 4



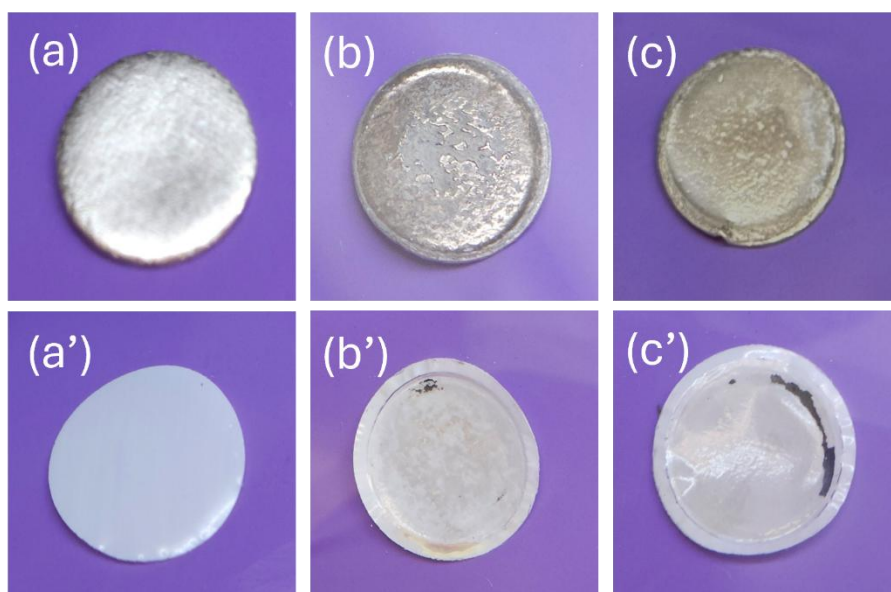
Appendix Figure B.1. Schematic representation (left) and optical photo (right) of the interlayer coated on the S-C cathode. A 15 mm diameter disk was cut out and used for coin cell assembly.



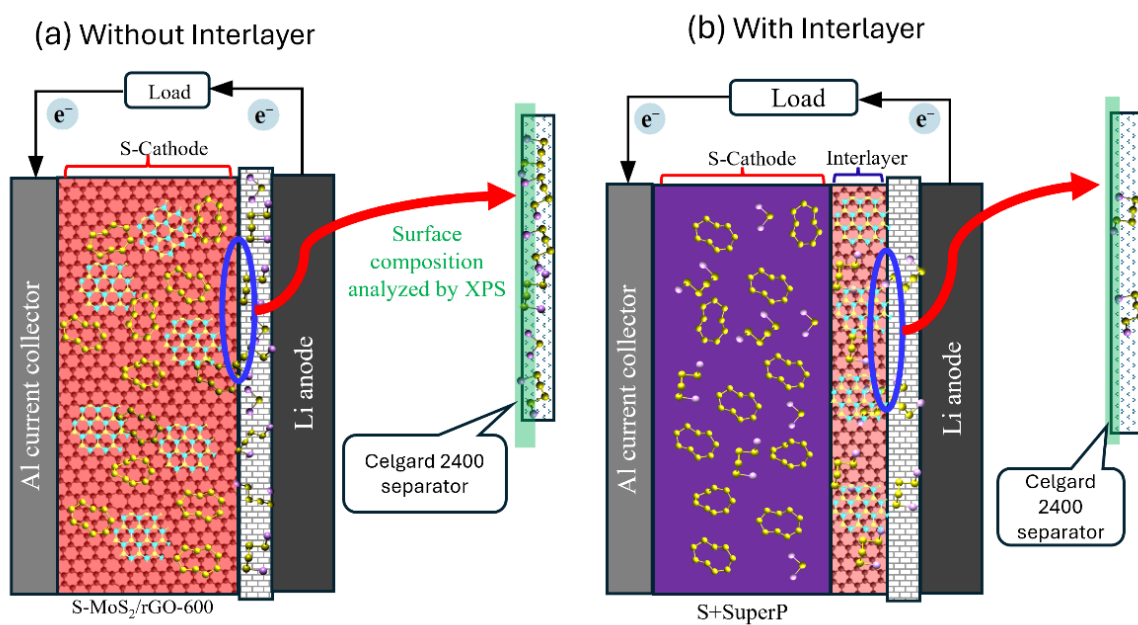
Appendix Figure B.2. Comparison of the CV profile of (a) MoS₃/rGO-250 (M2) and MoS₂/rGO-600 (M6) directly mixed in the S-C cathode without an interlayer, (b) MoS₂/rGO-600 (M6) and MoS₃/rGO-250 (M2) incorporated in the interlayer over the S-C cathode, and (c) MoS₃/rGO-250 (M2) and MoS_x/rGO-325 (M3) incorporated in the interlayer over the S-C cathode. (d) Capacity and CE comparison of MoS₂/rGO-600 (M6) and MoS₃/rGO-250 (M2) separately mixed and co-mixed in the S-C cathode. The total catalyst was controlled at 20 wt% in all three cases.



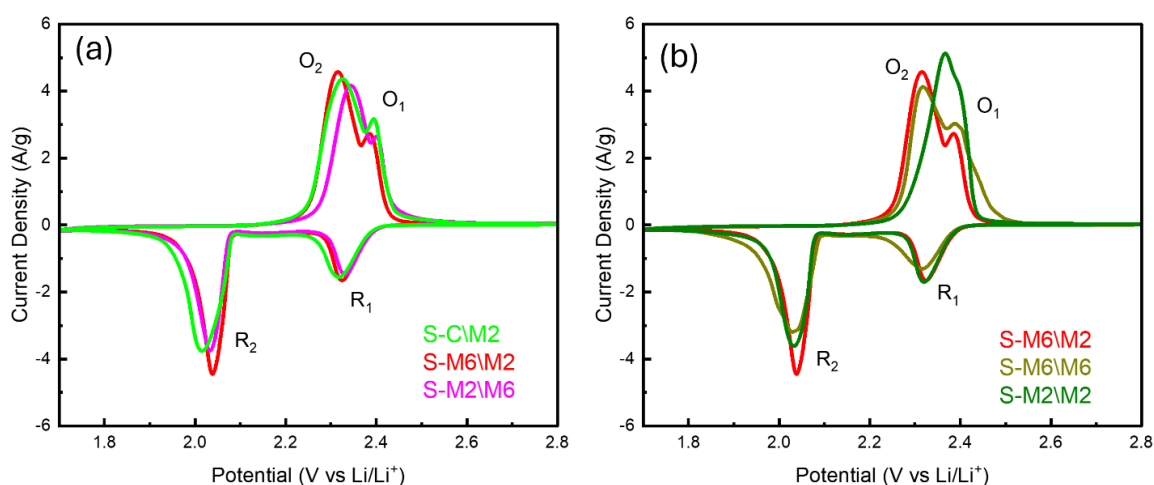
Appendix Figure B.3. Charge discharge voltage profiles from the rate-performance tests shown in Fig. 2(c) from cells consisting of a S-C cathode covered with an interlayer incorporated with M2, M3, and M6 catalysts in comparison with an interlayer containing only the control rGO gone through the same process as M6 but without the addition of MoS_x precursor. All fabrication and measurements follow the procedure of method 1 at 0.1C, 0.5C, and 2C.



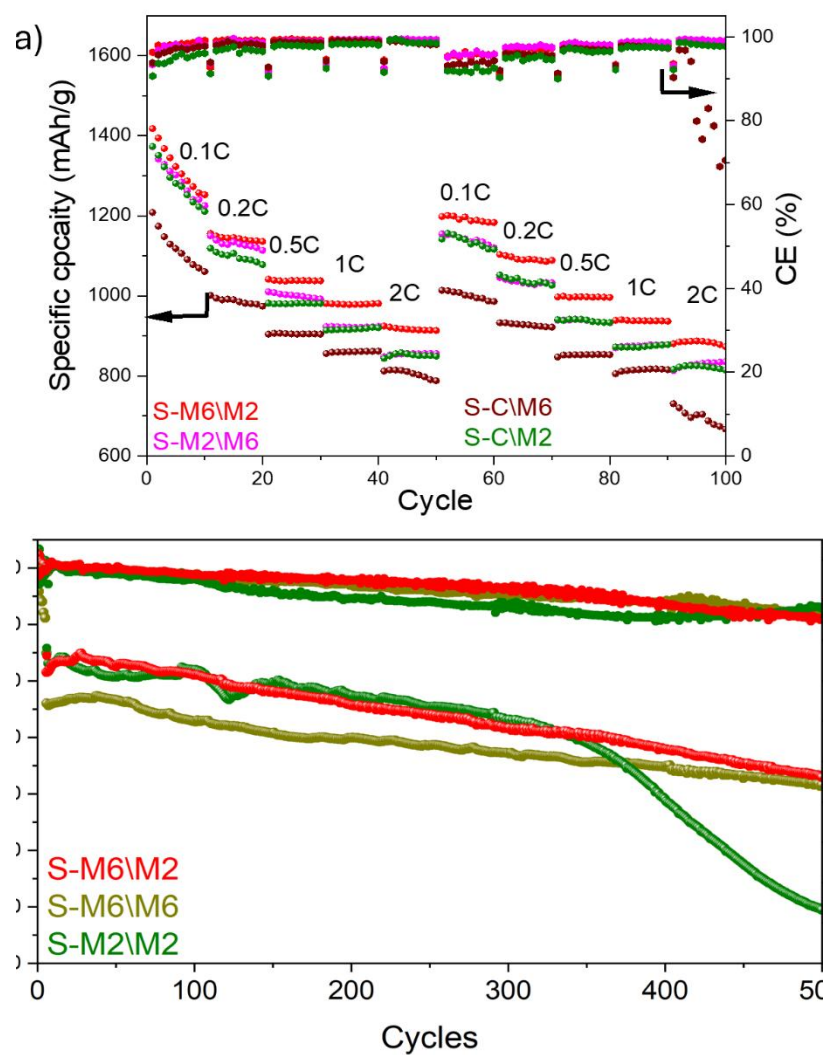
Appendix Figure B.4. Optical photos of (a) the fresh LMA before cell assembly and (a') a fresh Celgard 2400 separator. Similar photos from disassembled Li-S batteries after 100 cycles with (b) and (b') from cells using an S-C cathode without an interlayer, and (c) and (c') from cells using a S-C cathode with a M6 interlayer. The separator images in (b') and (c') were taken from the side facing the cathode.



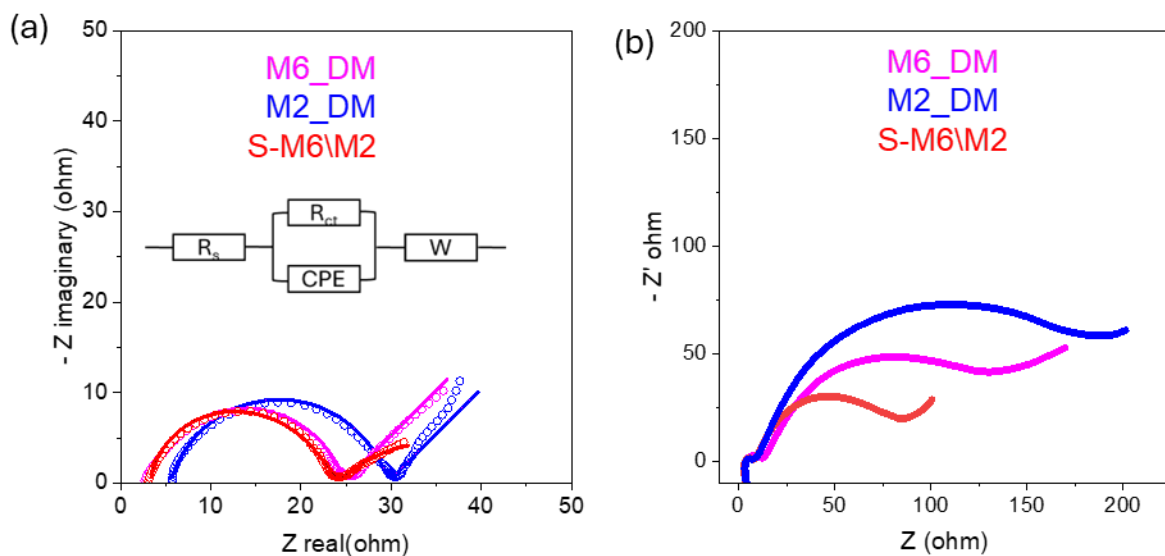
Appendix Figure B.5. Schematic illustration of the location on the Celgard separator where the XPS analysis was conducted from the cells (a) without and (b) with an interlayer.



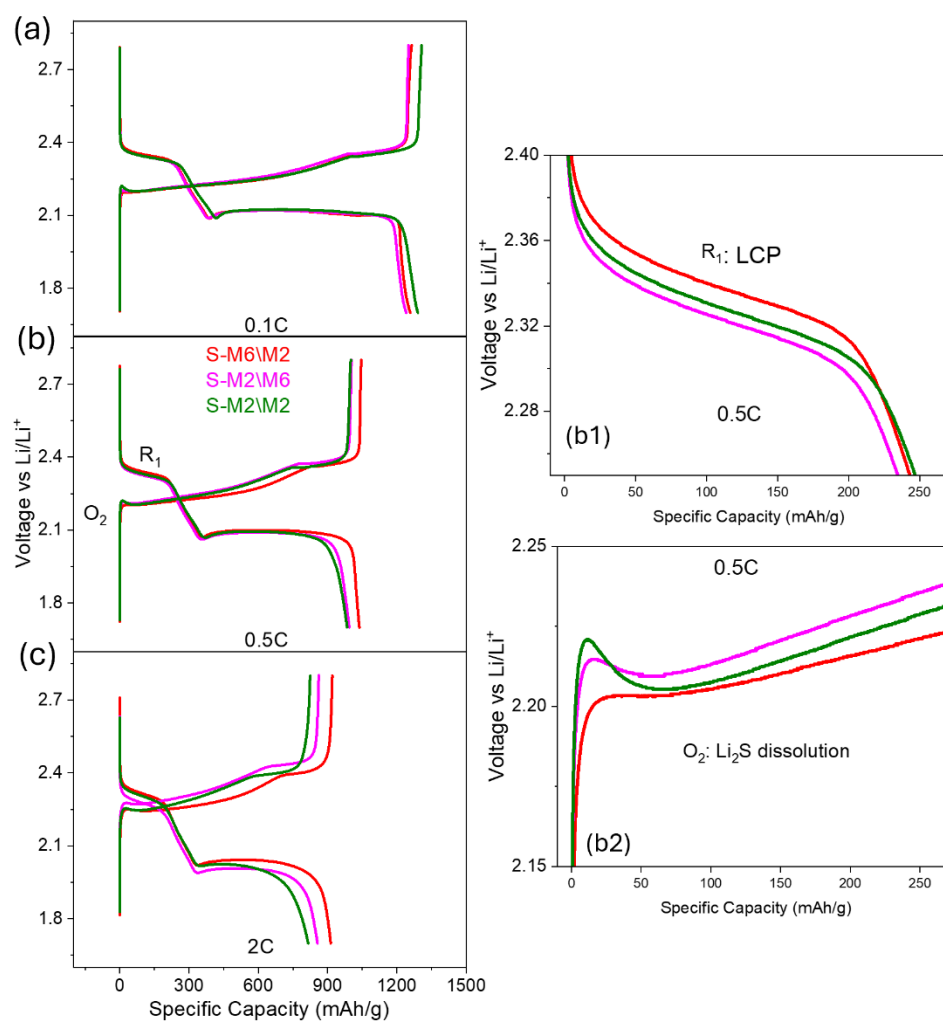
Appendix Figure B.6. Comparison of the CV profiles (a) with dual catalysts in S-M6\M2 (with MoS₂/rGO-600 in the cathode and MoS₃/rGO-250 in the interlayer), and S-M2\M6 (with MoS₃/rGO-250 in the cathode and MoS₂/rGO-600 in the interlayer) in comparison to the best performance by Method 1 with MoS₃/rGO-250 only incorporated in the interlayer (S-C\M2). (b) Comparison of three dual-catalyst combinations by Method 2 including S-M6\M2, S-M6\M6 and S-M2\M2.



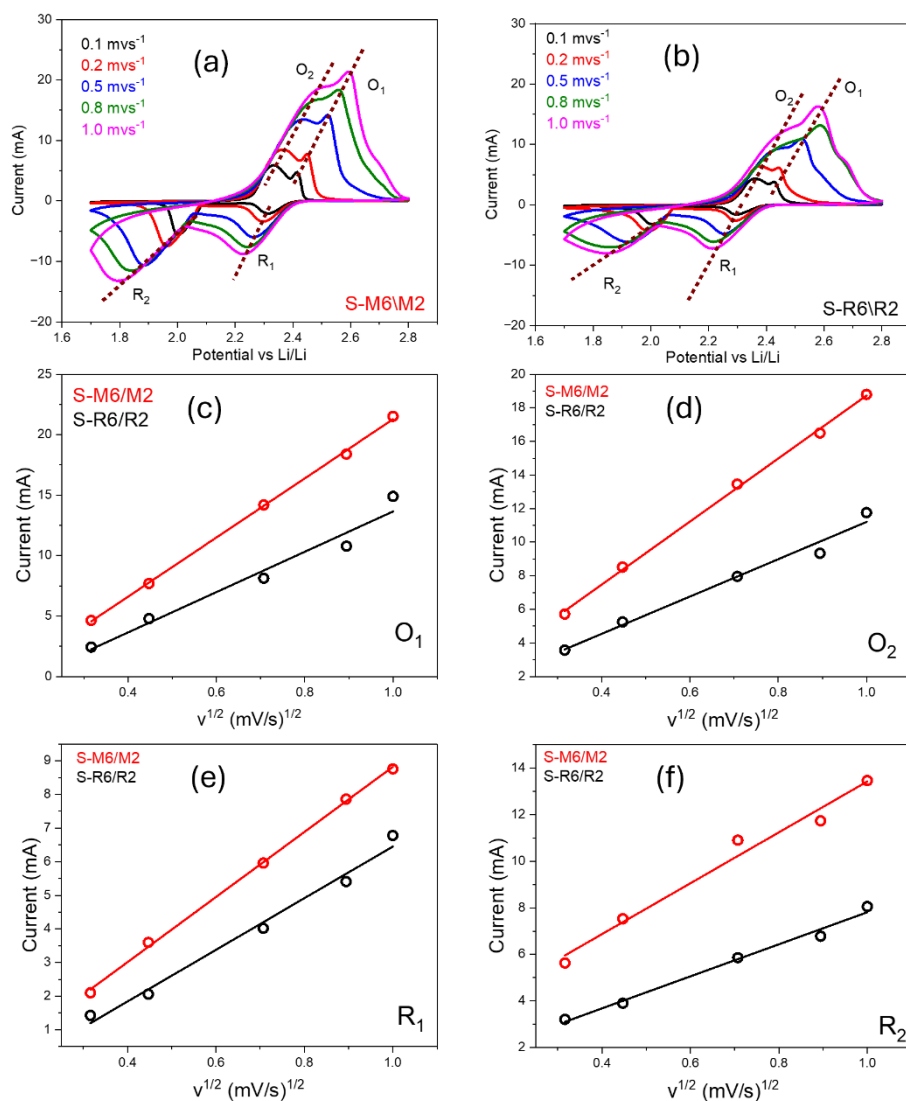
Appendix Figure B.7. Discharge capacity and CE during the rate-performance tests of (a) two dual-catalyst combinations: (S-M6\M2 and S-M2\M6) in comparison with two mono-catalyst interlayer cells (S-C\M2 and S-C\M6). (b) The stability test at 1C of S-M6\M2, S-M6\M6, and S-M2\M2.



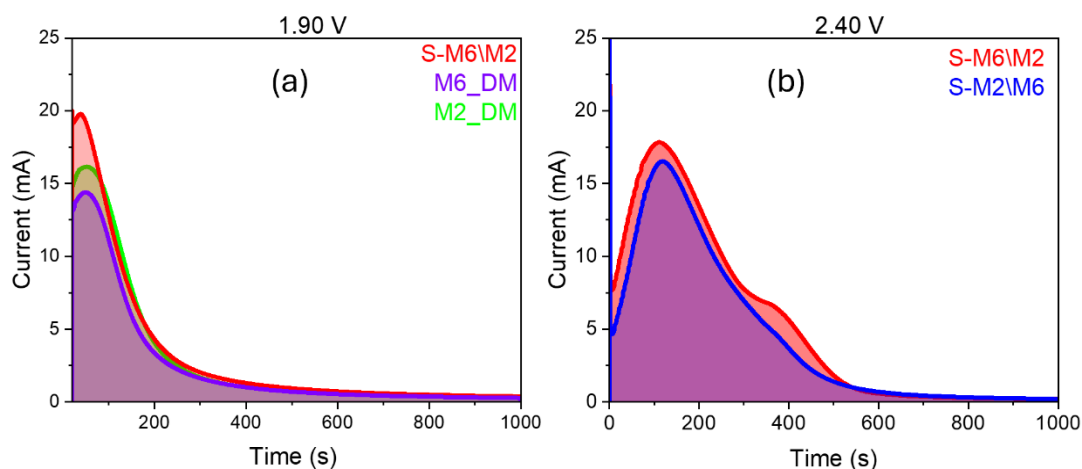
Appendix Figure B.8. EIS profile of the directly mixed MoS_2/rGO -600 and 250 with comparison of the interlayer with MoS_2/rGO -600 as cathode and MoS_3/rGO -250 as interlayer.



Appendix Figure B.9. The charge-discharge voltage profiles of various cells at the rate of (a) 0.1C, (b) 0.5C, and (c) 2C. (b1-b2) The expanded views of the R_1 and O_2 region in panel (b).



Appendix Figure B.10. (a) CV profiles at different scan rates of (a) S-M6/M2 and (b) S-R6/R2. The peak current vs the square root of scan rate for (c) O_1 peak, (d) O_2 peak, (e) R_1 peak, and (f) R_2 peak.



Appendix Figure B.11. (a) Potentiostatic discharge profiles of the dual catalyst S-M6\M2 (MoS₂/rGO-600 in the cathode with MoS₃/rGO-250 in the interlayer) in comparison to MoS₃/rGO-250 and MoS₂/rGO-600 directly mixed in the S-C cathode, i.e., M2_DM and M6_DM respectively. (c) Comparison of potentiostatic charge profiles of two dual-catalyst combinations, S-M6\M2 and S-M2\M6.

Appendix C - Portfolio

Publication:

1. Z.I. Saddam et al., Improving Li-S battery performance by tuning the active sites of MoS_x/rGO electrocatalysts in the S/C cathode, [Chem. Eng. J. 519 \(2025\) 164963](#).
2. Z.I. Saddam, and J. Li, Incorporating Different MoS_x/rGO Catalysts in Interlayer and Cathode to Enhance Li-S Battery Performance: a Dual-Catalyst Strategy; Mat. Rep. Energy (Accepted/ In press).

Patent:

1. Submitted US provisional patent application (KSURF Disc. Nos. 2026-009, 2026-011; titled “Use of Hybrids of Molybdenum Sulfide on Reduced Graphene Oxide in Lithium–Sulfur Batteries” (Patent Application No. 63/971,048).

Conference:

1. “Advancing Li-S Battery Performance with Tuned MoS_x/rGO Electrocatalysts: Insights from Cathode Hosts and Interlayer Designs,” **Zahirul Islam Saddam** et al.; American Chemical Society, Midwest regional meeting, Columbia, Missouri, USA, 2025.
2. “Enhancing Li-S battery performance with active sites controlled MoS₂ Nanopatches anchored on rGO nanosheets” **Zahirul Islam Saddam** et al.; American Chemical Society, Midwest regional meeting, Omaha, Nebraska, USA, 2024.

Award:

1. Awarded Meloyan Graduate Fellowship, Chemistry Department Awards: Summer 2025.
2. Winner, Capitol Graduate Research Summit 2025. Selected to present research at the Kansas State Capitol, Topeka, to Kansas legislators.