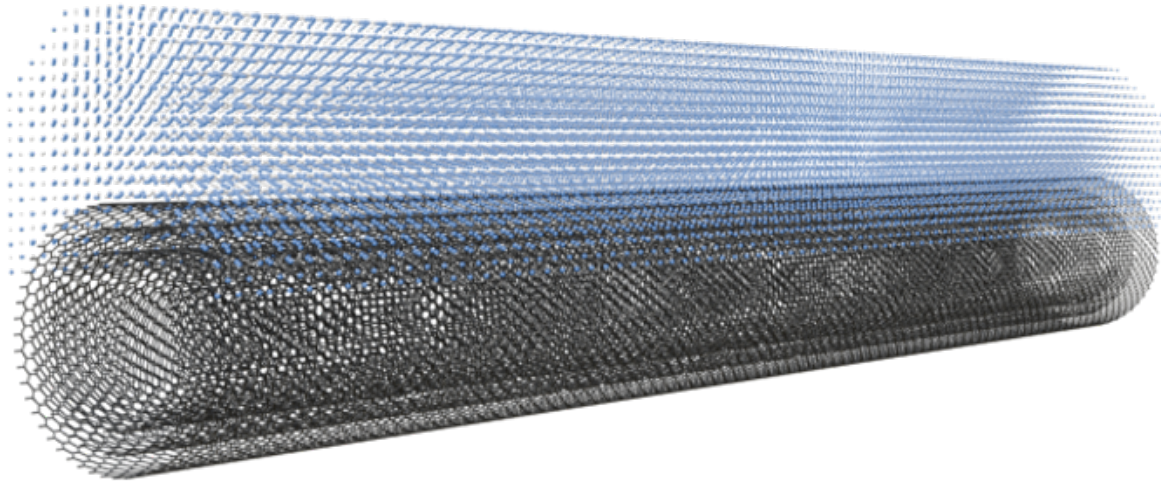




**CHALMERS**  
UNIVERSITY OF TECHNOLOGY



# **Sputtered Titanium Nitride Catalysts on Sulfur Hosts and Current Collectors for Lithium–Sulfur Batteries**

Master's thesis in Materials Chemistry

**HUGO ROSVALL**

**DEPARTMENT OF MECHANICAL ENGINEERING**

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CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2026  
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MASTER'S THESIS 2026

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Sputtered Titanium Nitride Catalysts on Sulfur Hosts and Current Collectors for  
Lithium-Sulfur Batteries  
Hugo Rosvall

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Cover: Three-dimensional rendering of a TiN-coated MWCNT, created in Blender  
and modeled to scale.

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## Abstract

Lithium-sulfur batteries (LSBs) offer high theoretical capacities ( $1675 \text{ mAh g}^{-1}$ ) and are a strong prospect for next-generation energy storage, but their performance is heavily limited by the polysulfide shuttle effect and slow redox kinetics. In this study, ultrathin layers of titanium nitride (TiN) were deposited by physical vapor deposition (PVD) onto multi-walled carbon nanotubes (MWCNTs) and aluminum current collectors to evaluate their effectiveness as a catalytic coating. The cells fabricated with TiN-coated current collectors delivered superior discharge capacities of  $1261.8$  and  $920.3 \text{ mAh g}^{-1}$  at  $0.1$  and  $0.5 \text{ C}$ , respectively, significantly outperforming the reference cells ( $1010.1$  and  $770.8 \text{ mAh g}^{-1}$ ), indicating enhanced interfacial conductivity and sulfur utilization. Modification of the MWCNT sulfur host material with TiN coatings also improved electrochemical performance, with TiN@MWCNT cathodes showing increased initial discharge capacities of  $1088.9 \text{ mAh g}^{-1}$  for a  $\sim 3 \text{ nm}$  TiN layer and  $1183.1 \text{ mAh g}^{-1}$  for a  $\sim 6 \text{ nm}$  layer at  $0.1 \text{ C}$ , compared to the uncoated MWCNT reference ( $1010.1 \text{ mAh g}^{-1}$ ), and consistently delivering higher capacities throughout extended cycling. An initial voltage decay was observed only in the TiN-modified MWCNT electrodes, after which the voltage profiles gradually stabilized over subsequent cycles, indicating an activation period associated with the TiN@MWCNT architecture. While PVD proved effective for both the planar aluminum current collector and the nanoscale MWCNT host, the fabrication of uniform TiN coatings was considerably more straightforward on the flat current collector surface, suggesting that nanotube-based architectures warrant further study using PVD-optimized or alternative coating strategies. Overall, the results highlight TiN as a promising interfacial modifier for LSBs.

Keywords: Lithium-sulfur, LSBs, MWCNTs, PVD, TiN coatings, current collector modification, catalysis



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Hugo Rosvall, Gothenburg, June 2026



# List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

|       |                                      |
|-------|--------------------------------------|
| ALD   | Atomic layer deposition              |
| CNT   | Carbon nanotubes                     |
| CV    | Cyclic voltammetry                   |
| CVD   | Chemical vapor deposition            |
| CrN   | Chromium nitride                     |
| DFT   | Density functional theory            |
| DME   | Dimethoxyethane                      |
| DOL   | 1,3-dioxolane                        |
| EDS   | Energy-dispersive X-ray spectroscopy |
| GO    | Graphene oxide                       |
| LiPS  | Lithium-polysulfides                 |
| LSBs  | Lithium-sulfur batteries             |
| MWCNT | Multi-walled carbon nanotubes        |
| NMP   | 1-methyl-2-pyrrolidinone             |
| PAA   | Poly(acrylic acid)                   |
| PVD   | Physical vapor deposition            |
| PVDF  | Poly(vinylidene fluoride)            |
| rGO   | Reduced graphene oxide               |
| SDBS  | Sodium dodecylbenzene sulfonate      |
| SEM   | Scanning electron microscope         |
| SWCNT | Single-walled carbon nanotubes       |
| TiN   | Titanium nitride                     |
| TMN   | Transition metal nitride             |



# Nomenclature

## Notations

|          |                                                         |
|----------|---------------------------------------------------------|
| C        | C-rate ( $\text{h}^{-1}$ )                              |
| I        | Current (A)                                             |
| $Q_n$    | Discharge capacity at cycle $n$ ( $\text{mAh g}^{-1}$ ) |
| R        | Electrical resistance ( $\Omega$ )                      |
| V        | Cell potential (V)                                      |
| n        | Cycle number (dimensionless)                            |
| $\eta_C$ | Coulombic efficiency (%)                                |

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# 1

## Introduction

### 1.1 Context

The increasing demand for high-performance energy storage in transportation, portable electronics, and grid-scale systems has intensified global interest in next-generation battery chemistries. Among these, LSBs stand out due to their exceptionally high theoretical specific energy of approximately  $2600 \text{ Wh kg}^{-1}$ , low material cost, and reliance on abundant sulfur [1, 2]. These characteristics make LSBs a promising candidate for applications requiring lightweight, high-energy-density storage [3].

### 1.2 Background

Despite their advantages, LSBs face several intrinsic challenges, primarily the shuttle effect, volume expansion during discharge, and the low intrinsic conductivity of sulfur and its final discharge product  $\text{Li}_2\text{S}$  [2]. Carbon-based host materials are commonly used for sulfur cathodes [2]. Among these, MWCNTs provide a high surface area and a conductive scaffold capable of accommodating sulfur while reducing mechanical stresses during cycling [1]. However, unmodified MWCNTs are non-polar and inert; they therefore interact weakly with lithium polysulfides (LiPS), allowing them to dissolve into the electrolyte and migrate to the anode, causing the well-known shuttle effect [1, 4].

To address this issue, recent research has focused on incorporating polar, catalytically active materials capable of chemically anchoring LiPS and accelerating their conversion kinetics. TiN has emerged as a prominent transition metal nitride (TMN) candidate due to its high electrical conductivity, spanning  $4 \times 10^3$  to  $5.55 \times 10^5 \text{ S cm}^{-1}$  [5], strong chemical affinity for LiPS, catalytic activity toward sulfur redox reactions, and excellent mechanical stability [5–9]. Consequently, TiN has been integrated into LSB architectures in various configurations. For instance, TiN-modified separators effectively suppress the shuttle effect and enhance sulfur utilization [10], while TiN-based interlayers placed between the cathode and separator yield significant performance improvements [11]. Furthermore, TiN coatings deposited via atomic layer deposition (ALD) or solution-based methods have demonstrated robust performance on porous carbon matrices [5], and magnetron sputtering has been utilized to apply these catalytic layers with high efficiency [12]. These collective findings highlight the potential of TiN-based modifications in mitigating the shuttle effect and improving electrochemical stability. Similarly, alternative TMNs, such as chromium nitride

(CrN), have demonstrated enhanced interfacial kinetics when applied directly to the current collector surface [13].

### 1.3 Gap in the literature

Although TiN has shown great promise across multiple configurations and composite host designs, studies on ultrathin TiN coatings deposited by PVD onto MWCNT scaffolds and current collectors specifically in LSBs remain limited. Most reported strategies for incorporating TiN as a catalyst rely on solution-based synthesis, high-temperature nitridation, or ALD, all of which pose challenges for industrial scalability. Furthermore, a direct comparative evaluation isolating the individual influences of an ultrathin PVD-coated TiN layer, applied separately to either the active MWCNT host or the aluminum current collector interface, has not yet been thoroughly established within the same testing framework.

### 1.4 Problem statement

LSBs suffer from the poor intrinsic conductivity of sulfur and severe LiPS shuttling, which together cause rapid capacity fade and low Coulombic efficiency. Although carbon substrates such as MWCNTs provide an effective conductive framework, they lack the chemical functionality needed to immobilize LiPS. This creates a clear need for scalable catalyst coatings that are both conductive, can inhibit the shuttle effect, and that are compatible with the host material and the current collector to enhance electrochemical performance.

### 1.5 Research question

How does the integration of ultrathin TiN coatings, applied separately to either the MWCNT hosts or the current collectors, impact the electrochemical performance and sulfur utilization of LSB cells?

### 1.6 Scope and limitations

This thesis investigates the PVD deposition of approximately 3 nm and 6 nm TiN coatings on MWCNT scaffolds, as well as TiN coatings applied directly to aluminum current collectors. Cathodes were fabricated utilizing either poly(vinylidene fluoride) (PVDF) with 1-methyl-2-pyrrolidinone (NMP) or poly(acrylic acid) (PAA) with deionized water, with sulfur mass loadings evaluated between approximately 0.8 and 2.5 mg cm<sup>-2</sup>. The cells were evaluated in Li-S half-cell configurations using metallic lithium metal chips as counter electrodes and a fixed electrolyte volume of 50  $\mu$ L per cell to ensure uniform wetting. Material properties and electrochemical responses were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA),

cyclic voltammetry (CV), and galvanostatic charge–discharge (GCD) cycling. Preliminary electrochemical impedance spectroscopy (EIS) was conducted but was not investigated exhaustively due to project constraints.

Due to project time constraints, cells were run for the maximum possible duration within the experimental window, meaning that not all tests completed identical cycle numbers. The scope of this study does not include full-cell configurations, high-sulfur-loading cathodes ( $> 3 \text{ mg cm}^{-2}$ ), mechanical adhesion testing, or alternative deposition techniques. Furthermore, detailed chemical oxidation or surface binding characterization of the catalyst layer, such as via X-ray photoelectron spectroscopy (XPS), was not performed.

## 1.7 Use of AI tools

Blender was used to generate 3D chemical structures. Rather than manual modeling, ChatGPT was used to generate the custom Python code used to build these chemical structures, and also to modify some of the figures in the thesis. Additionally, Microsoft Copilot was used for language polishing and grammar correction in some sections of the thesis.

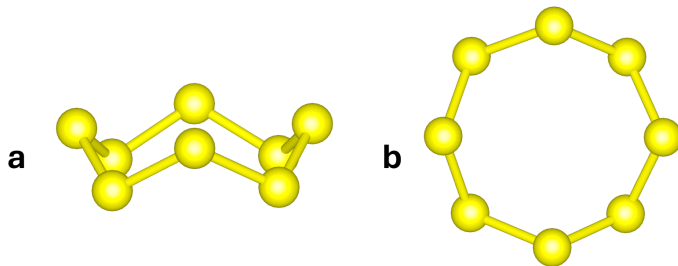


# 2

## Theory

### 2.1 Electrochemistry of sulfur

Sulfur (S) is a nonmetal that commonly exists as cyclooctasulfur ( $S_8$ ), as shown in Fig. 2.1. It is a stable, ring-shaped allotrope under ambient conditions and is nonpolar due to its symmetric, crown-like geometry. In this molecular form, S has an extremely low electronic conductivity of approximately  $5 \times 10^{-30} \text{ S cm}^{-1}$  and only weak intermolecular interactions, which severely limit charge transport in LSB cathodes [14]. The  $S_8$  ring is held together by covalent S–S bonds with a bond dissociation energy of approximately  $226\text{--}251 \text{ kJ mol}^{-1}$  [15], making the molecular architecture highly stable thermodynamically. Consequently, this closed structure must undergo ring opening before electrochemical reduction can proceed. These intrinsic properties govern the complex reaction pathway during discharge and play a central role in the downstream formation of LiPS.

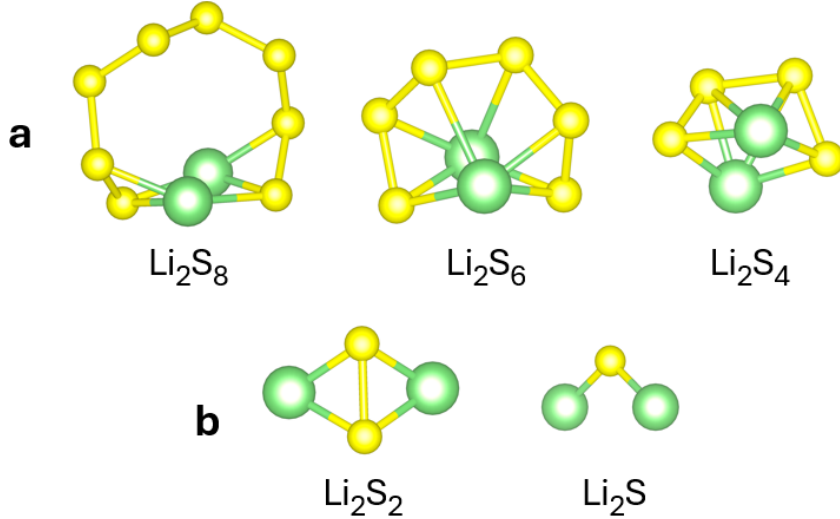


**Figure 2.1:** The molecular structure of  $S_8$  (a) Side view. (b) Top view.

Sulfur serves as the active redox material of the battery and typically constitutes 60–80% of the total cathode mass [2]. To overcome the low intrinsic conductivity of sulfur, the remaining mass is mostly filled by a conductive carbon host, which provides effective electron pathways [1, 8]. Maintaining high sulfur loading while keeping good transport properties is a major challenge in this field [2]. Increasing the sulfur loading per unit area and total sulfur content, while also lowering the electrolyte-to-sulfur (E/S) ratio, is crucial for commercial LSB applications. However, reaching these conditions is difficult because of the poor conductivity of sulfur and the complex way LiPS dissolves in the cell.

### 2.1.1 The lithium–polysulfides

During discharge, solid  $S_8$  undergoes a multi-step conversion reaction. It is first reduced to soluble, long-chain LiPS ( $Li_2S_x$ ,  $4 \leq x \leq 8$ ). As shown in Fig. 2.2(a), these long-chain species contain 4–8 S atoms coordinated to 2 Li atoms. As discharge continues, these soluble intermediates are further reduced into short-chain species ( $Li_2S_x$ ,  $1 \leq x < 4$ ), which end as the insoluble solid products  $Li_2S_2$  and  $Li_2S$ , with structures shown in Fig. 2.2(b).



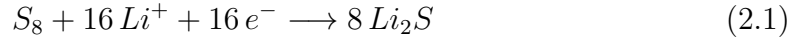
**Figure 2.2:** The LiPS species: (a) soluble long-chain LiPS and (b) insoluble short-chain LiPS.

The inherent solubility of long-chain LiPS causes the well-known shuttle effect. In this process, the long-chain LiPS species dissolve in the electrolyte, migrate to the anode, undergo unwanted reduction reactions, and move back toward the cathode. This continuous back-and-forth transport wastes active material, deposits insulating layers ( $Li_2S_2$  and  $Li_2S$ ) that passivate the lithium metal anode, and disrupts the structural stability of the cathode. As a result, the cell suffers from rapid capacity decay, poor Coulombic efficiency, and accelerated self-discharge [2, 14]. To effectively contain LiPS, a strategy combining physical trapping within the host to restrict diffusion with chemical anchoring onto polar or catalytic surfaces is required [8].

### 2.1.2 The conversion reaction

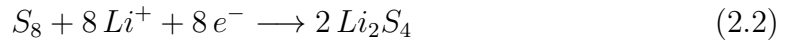
The reduction of elemental  $S_8$  to  $Li_2S$  is a multi-step conversion process involving a solid–liquid–solid transition and the transfer of 16 electrons per  $S_8$  molecule. The first part of the reaction converts solid  $S_8$  into dissolved  $Li_2S_4$  and delivers one quarter of the theoretical capacity ( $419 \text{ mAh g}^{-1}$ ). The remaining three quarters ( $1256 \text{ mAh g}^{-1}$ ) come from the further reduction of  $Li_2S_4$  to solid  $Li_2S$ . Completing these steps is necessary to reach the full theoretical capacity of  $1675 \text{ mAh g}^{-1}$ .

The overall reaction in a lithium–sulfur cell is:

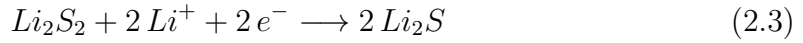


During discharge,  $S_8$  is not reduced directly to  $Li_2S$  but instead passes through a series of LiPS. This stepwise behavior produces the two characteristic voltage plateaus seen in GCD profiles (Fig. 2.3).

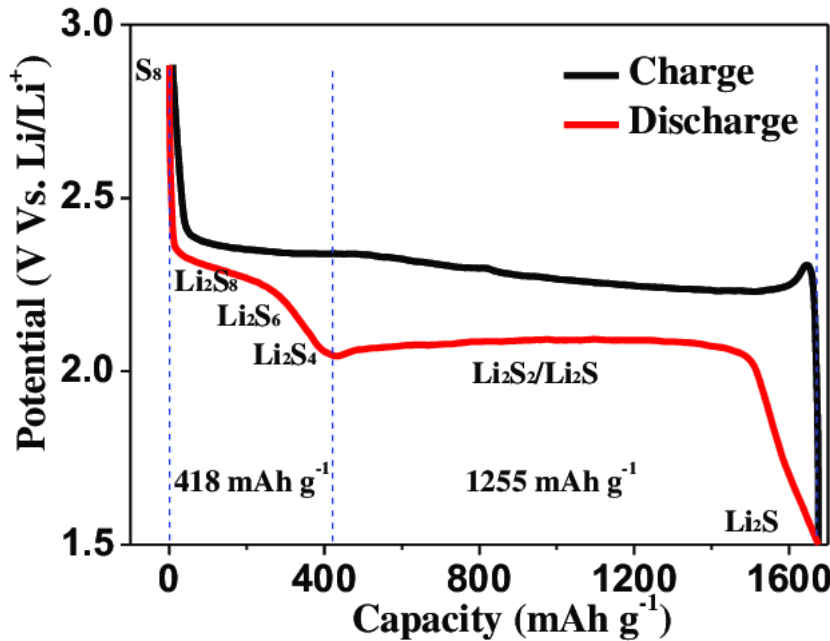
The high-voltage plateau ( $\sim 2.4$ – $2.1$  V) corresponds to the opening of the  $S_8$  ring and its reduction into long-chain polysulfides. This stage ends with the formation of  $Li_2S_4$ , described by:



The low-voltage plateau ( $\sim 2.1$  V) reflects the further reduction of these dissolved species into short-chain sulfides and, finally, solid  $Li_2S$ :



These sequential phase changes, especially the slow solid-state deposition in the second stage, strongly influence the electrochemical behavior and sulfur utilization of the cathode.



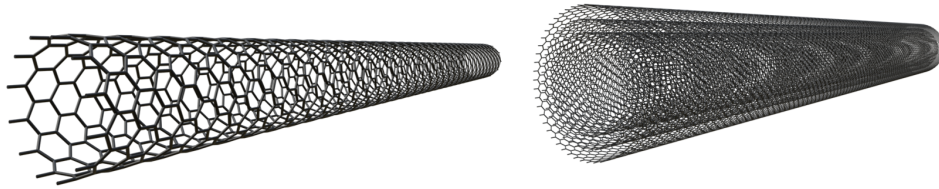
**Figure 2.3:** Representative GCD voltage profile of a Li–S cell under full sulfur utilization, highlighting the characteristic high- and low-voltage discharge plateaus and their corresponding polysulfide conversion stages [16].

## 2.2 Carbon host materials

Carbon nanomaterials such as carbon nanotubes (CNTs) and reduced graphene oxide (rGO) are widely used as sulfur hosts due to their large surface areas and high electrical conductivity [1]. Their conductivity and mechanical stability arise from networks of  $sp^2$ -bonded carbon atoms. However, because carbon is non-polar, its interaction with LiPS is inherently weak [17], often requiring additional functionalization or structural modification to improve LiPS anchoring.

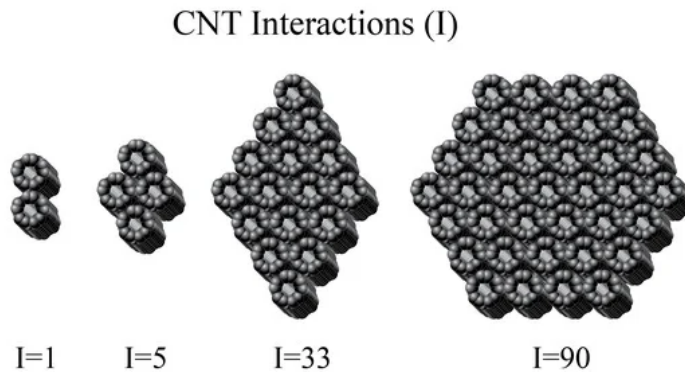
### 2.2.1 Carbon nanotubes

CNTs offer excellent mechanical and electrical properties, making them ideal for battery electrodes. They are divided into single-walled (SWCNTs) or MWCNTs, as shown in Fig. 2.4. In LSB cathodes, CNTs provide long, continuous conductive pathways that help maintain electronic connectivity [18].



**Figure 2.4:** Schematic models of a single-walled carbon nanotube (SWCNT, left) and a multi-walled carbon nanotube (MWCNT, right).

Pristine CNTs tend to form aggregates due to strong van der Waals interactions, which scale with their high aspect ratio [19]. This bundling complicates dispersion and slurry preparation (Fig. 2.5). To improve processability and enhance LiPS binding, CNTs can be functionalized with chemical groups such as nitrogen, carboxyl, or hydroxyl [18].



**Figure 2.5:** Schematic of CNT bundle sizes and their contact interactions ( $I$ ), illustrating how aggregate binding strength increases with bundle size [19].



### 2.2.1.1 Synthesis and characteristics of carbon nanotubes

Chemical vapor deposition (CVD) is commonly used to synthesize CNTs. Metal catalysts are deposited on a substrate, and at high temperatures a hydrocarbon feedstock decomposes on these sites, forming graphitic carbon structures. During growth, fragments of the substrate or catalyst can become encapsulated in the walls of the nanotubes [20]. Residual catalyst or substrate particles may remain if not fully removed during purification.

### 2.2.2 Graphene oxide

Graphene is a two-dimensional material with high conductivity and mechanical strength due to its  $sp^2$ -bonded carbon network. Graphene oxide (GO) contains oxygen functional groups that act as polar sites for LiPS interaction. Reducing GO to rGO increases conductivity but decreases the number of polar anchoring sites. Partial reduction can therefore be beneficial, balancing improved conductivity with sufficient residual functional groups for LiPS adsorption [21].

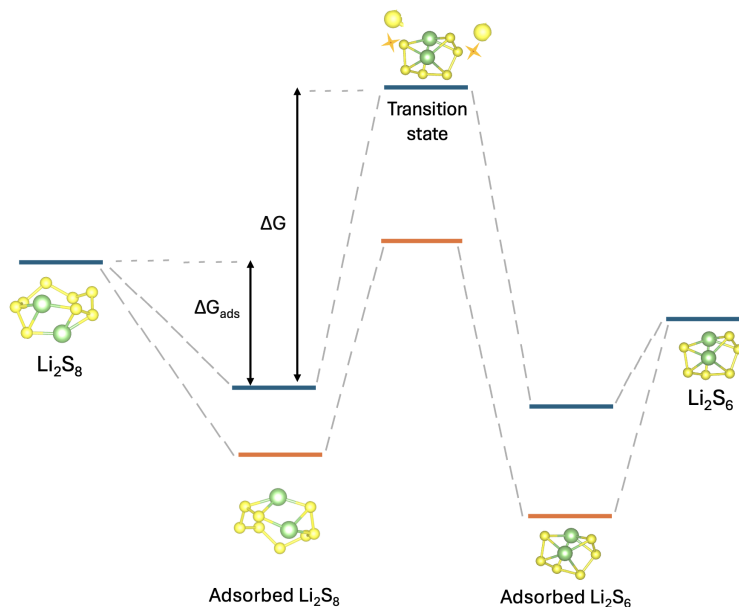
### 2.2.3 Conductive additives

Conductive additives typically make up around 10% of the total cathode mass and are included to ensure good electronic connectivity throughout the sulfur composite. Common options in LSBs include Super P, Ketjenblack, and acetylene black. Super P is a widely used carbon black powder consisting of small carbon nanoparticles. These particles fill the gaps between larger conductive structures like MWCNTs, providing short-range electronic contact points between sulfur particles and the carbon matrix while also improving binder distribution. When combined, Super P and MWCNTs form a complementary network: MWCNTs supply long-range conductive pathways, and Super P strengthens local connectivity, resulting in a robust overall conductive framework [22].

## 2.3 Catalysis in LSBs

Catalysis has been widely explored in LSBs to combat the challenges of these systems. In this context, a catalyst is a material that lowers the activation energy barrier for a reaction, enhancing kinetics without being consumed. Since the inherent nature of sulfur and its soluble intermediates is the root cause of these issues, the rational design of functional sulfur host materials featuring such catalysts is one of the most effective approaches to overcoming current performance limitations [1]. Catalysis has three main effects in combating the shuttle: (1) it provides polar or charged adsorption sites that chemically anchor LiPS; (2) it accelerates the conversion of soluble LiPS into solid species, reducing their diffusion time; and (3) it lowers the nucleation barrier for  $Li_2S$  formation, ensuring that discharge products deposit uniformly on the cathode host rather than migrating into the electrolyte.

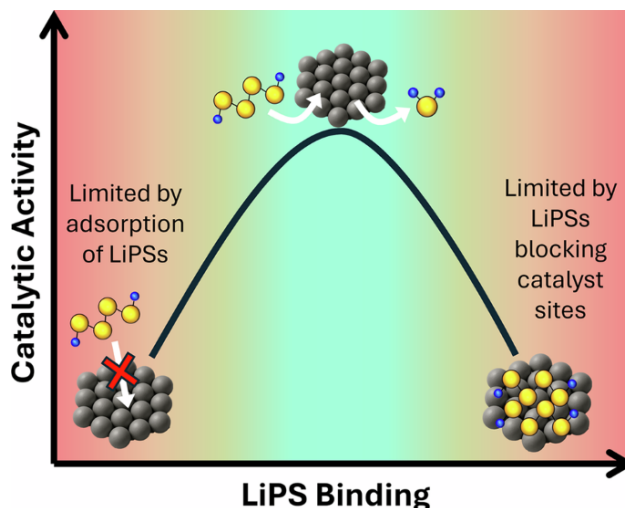
The basic principle is that both adsorption on the catalyst and the subsequent conversion reaction are energetically favored compared to the uncatalyzed pathway. This reduced activation energy barrier enhances conversion kinetics and enables faster reactions. See Fig. 2.6 for a simplified schematic of the  $\text{Li}_2\text{S}_8$  to  $\text{Li}_2\text{S}_6$  conversion process.



**Figure 2.6:** Simplified scheme of activation energies in the  $\text{Li}_2\text{S}_8$  to  $\text{Li}_2\text{S}_6$  conversion reaction. The orange plateaus show the catalyst-assisted pathway with a reduced activation energy barrier, while the blue plateaus represent the higher-energy pathway without the catalyst. Modified from [4].

Understanding the LiPS conversion mechanism is critical for catalyst design. During discharge, S is reduced through a sequence of soluble LiPS before forming insoluble  $\text{Li}_2\text{S}_2$  and eventually  $\text{Li}_2\text{S}$ . The conversion between  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  is widely regarded as one of the rate-limiting steps because it proceeds through sluggish solid-state phase transformation kinetics [4, 7]. As a result, catalyst selection should prioritize materials that can accelerate these final conversion reactions while still providing strong but reversible adsorption of LiPS.

For effective catalysis, LiPS binding strength must fall within a moderate range. As illustrated in Fig. 2.7, if the interaction is too weak, the LiPS molecules will not bind to the surface at all, preventing any catalytic activity. Conversely, if the interaction is too strong, the adsorbed species will fail to detach, thereby blocking the active catalyst sites and preventing other LiPS molecules from anchoring and reacting. Balancing this adsorption strength with catalytic turnover is therefore essential for designing high-performance sulfur cathode catalysts.



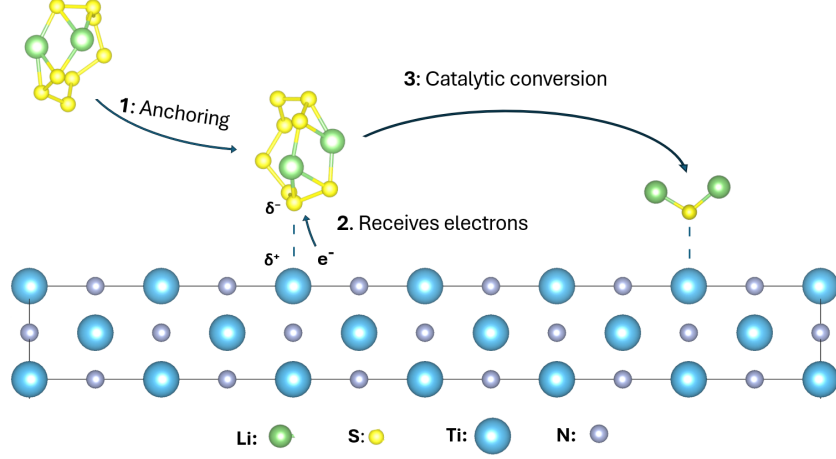
**Figure 2.7:** Relationship between binding strength and catalytic activity, highlighting the optimal intermediate binding regime [4].

Among the strategies used to improve sulfur cathode performance, heteroatom doping and catalytic surface modification are highly effective because they enhance LiPS adsorption, suppress shuttling, and accelerate redox kinetics [23]. Nitrogen doping introduces polar sites and defect structures that successfully strengthen LiPS adsorption and improve reaction kinetics. Oxygen-containing functional groups increase surface polarity, enhancing chemical binding with LiPS species while also improving electrolyte wettability. Additionally, the incorporation of transition metals introduces active catalytic centers that accelerate LiPS conversion and improve overall sulfur utilization. In particular, transition-metal compounds, such as transition-metal nitrides, have proven to be exceptionally effective because they uniquely combine this strong polysulfide affinity with high electrical conductivity, making them ideal hosts in LSB cathodes [5].

### 2.3.1 Titanium nitride as catalyst

Among these transition-metal compounds, TiN stands out as an effective host for LSB cathodes due to its unique combination of metallic conductivity, strong polysulfide affinity, and inherent catalytic activity. TiN exhibits high electrical conductivity, typically ranging from  $4 \times 10^3$  to  $5.5 \times 10^5 \text{ S cm}^{-1}$ , which enables rapid electron transport and significantly reduces charge-transfer resistance during sulfur redox reactions [5, 9]. This high electronic conductivity provides a distinct kinetic advantage over unmodified oxide or carbon hosts. Beyond electron transport, TiN also exhibits strong chemical interactions with LiPS. During cycling, the polar TiN surface forms chemical interactions where Ti sites bind with sulfur and N sites coordinate with lithium ions, as confirmed by XPS studies [5]. These interfacial interactions demonstrate that TiN chemically anchors LiPS rather than relying solely on physical confinement, which suppresses the shuttle effect and maintains high Coulombic efficiency. Furthermore, the nitrogen sites within the TiN lattice act as Lewis bases, promoting both the oxidation and reduction of polysulfides to acceler-

ate their conversion kinetics. This surface-mediated catalytic behavior is illustrated schematically in Fig. 2.8, where dissolved  $\text{Li}_2\text{S}_8$  approaching the polar TiN surface is efficiently converted into solid  $\text{Li}_2\text{S}$ .



**Figure 2.8:** Schematic illustration of  $\text{Li}_2\text{S}_8$  approaching a TiN surface, which catalyzes its conversion into solid  $\text{Li}_2\text{S}$ . The TiN surface provides both adsorption sites and catalytic centers that accelerate the polysulfide conversion pathway.

TiN crystallizes in the NaCl-type fcc lattice and is available in diverse morphologies, including hollow spheres, porous tubes, nanosheets, and mesoporous frameworks, each offering large surface areas and abundant active sites for LiPS capture and catalysis [5]. These structures also help accommodate the volume changes associated with sulfur conversion. For example, hollow TiN spheres and porous TiN tubes reported in [5] maintain their crystalline phase during cycling and support high sulfur loadings while preserving stable long-term performance.

### 2.3.1.1 Surface oxidation and its implications

Although TiN is deposited as a nitride, its outermost surface oxidizes rapidly under ambient conditions, leading to spontaneous dissociation of  $\text{O}_2$  and the formation of a thin  $\text{TiO}_x/\text{TiO}_2$  layer [24]. This oxidation is thermodynamically favorable and occurs even at room temperature, meaning that the electrochemically accessible surface in an LSB cathode is expected to be a  $\text{TiO}_2/\text{TiN}$  heterostructure.

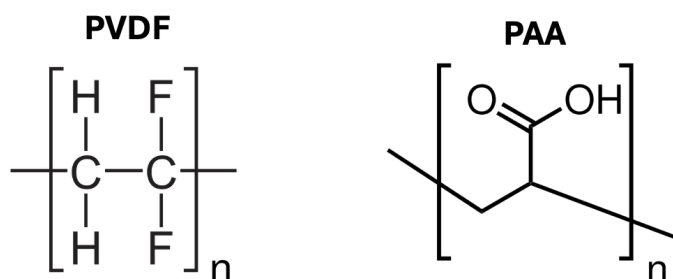
This surface structure is advantageous in several ways:  $\text{TiO}_2$  provides stronger adsorption toward polysulfides, while the underlying TiN maintains high electronic conductivity. As a result, the oxidized TiN coating simultaneously offers (i) strong LiPS anchoring through the  $\text{TiO}_2$  shell and (ii) rapid charge transport through the metallic TiN core. This dual functionality enhances both polysulfide confinement and redox kinetics, making TiN highly effective as a catalyst and conductive host material in LSBs. However, because detailed chemical state analysis falls outside the timeline of this thesis, the sputtered coatings are evaluated as pure TiN during subsequent electrochemical modeling.

Together, these properties (metallic conductivity, strong chemical anchoring of LiPS, catalytic acceleration of polysulfide conversion, and chemical robustness) make TiN one of the most promising host materials and catalytic modifiers for LSB cathodes, outperforming many traditional carbon, oxide, and sulfide hosts that lack this combination of characteristics [5].

A primary limitation of bulk TiN is its high density compared to carbon. Consequently, depositing only an ultrathin catalytic layer on a lightweight material such as MWCNTs keeps the total mass low. This approach enables the TiN layer to act as a highly effective surface modifier and catalyst while taking full advantage of the extraordinary length, mechanical strength, and excellent electrical conductivity of the underlying MWCNT scaffold.

## 2.4 Binders

Binders are an essential yet electrochemically inactive component of the cathode. They provide mechanical integrity, ensure adhesion between the sulfur composite and the current collector, and help maintain electrode cohesion during the large volume changes associated with the  $S_8 \leftrightarrow Li_2S$  conversion, which can reach up to  $\sim 80\%$  [25]. The most frequently used binders in LSBs include PVDF, PAA, carboxymethyl cellulose (CMC), styrene-butadiene rubber (SBR), and poly(vinyl alcohol) (PVA). PVDF is the traditional choice because it has good chemical stability and works well with standard ether-based electrolytes. However, PVDF is non-polar, so it cannot stop the polysulfide shuttle effect. In contrast, water-based binders such as PAA, CMC/SBR, and PVA are popular for their environmental benefits because they eliminate toxic solvents like NMP. Additionally, binders with polar functional groups, such as carboxyl ( $-COOH$ ) and hydroxyl ( $-OH$ ), can trap LiPS through strong polar interactions. Comparing a non-polar, organic binder like PVDF with a polar, water-based binder like PAA (see Fig. 2.9) shows how different binder properties affect LSB performance.



**Figure 2.9:** Chemical structures of organic-soluble PVDF and water-soluble PAA binders.

### 2.4.1 Poly(vinylidene fluoride)

PVDF is one of the most commonly used binders in lithium–sulfur cathodes due to its strong adhesion, high thermal stability, and wide electrochemical window [26]. As an electrochemically inactive and non-conductive polymer, PVDF does not participate in the sulfur redox reactions and does not chemically interact with LiPS, making it effectively an inert binder in LSB systems. This inertness allows PVDF to maintain structural integrity without interfering with LiPS conversion processes, which is useful when catalytically active hosts are employed. However, its weak affinity for polar sulfur species and its tendency to swell in organic electrolytes are known limitations that motivate the development of more functional binder systems.

### 2.4.2 Poly(acrylic acid)

PAA is a water-processable binder containing abundant -COOH groups, which provide strong hydrogen bonding and polar interactions with LiPS. These interactions improve electrode cohesion, enhance LiPS retention, and often lead to improved cycling stability compared to PVDF-based electrodes [25]. In LSB systems, the strong polarity of PAA enables more effective binding to sulfur species and conductive carbon surfaces, helping the cathode accommodate the large volume changes associated with sulfur conversion reactions [26].

## 2.5 Solvents

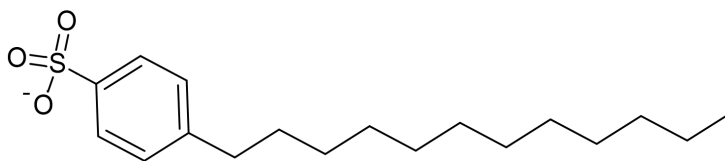
In slurry-based electrode fabrication, the primary function of the solvent is to suspend and uniformly distribute the solid components. Rather than achieving a molecular-level dissolution, the objective is to create a homogeneous, stable, and viscous suspension. Establishing a uniform macro-scale mixture prevents heavy particles from settling, allowing the slurry to be coated onto the current collector with a consistent thickness. The solvent provides this temporary fluidity during processing; upon evaporation, it leaves behind a interconnected solid network of active material, conductive carbon, and binder.

### 2.5.1 Deionized water as solvent

Water can be used as a solvent for processing battery slurries, offering clear environmental and practical advantages. However, most carbon materials like rGO and CNTs do not have polar groups on their surfaces, meaning they do not mix well in pure water. Only graphene oxide (GO) or functionalized CNTs with hydrophilic groups (such as -COOH and -OH) can form stable mixtures in deionized water, which is supported by both DFT calculations and experiments [27]. For non-functionalized carbons, additional mixing aids such as a surfactant may be used to get a smooth, coatable slurry texture.

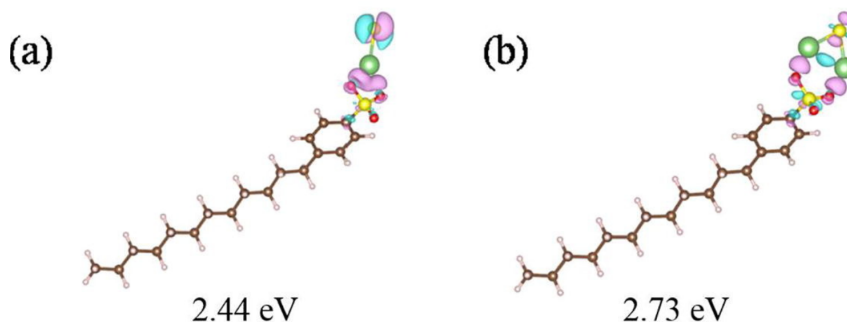
### 2.5.1.1 Surfactant: sodium dodecylbenzene sulfonate

Because water is polar, preparing uniform water-based mixtures with hydrophobic carbons like CNTs and rGO typically requires a surfactant. Surfactants possess both polar and nonpolar segments, allowing them to adsorb onto hydrophobic carbon surfaces while maintaining compatibility with the aqueous medium. Sodium dodecylbenzene sulfonate (SDBS), whose chemical structure is shown in Fig. 2.10, is used to stabilize the carbon components in water. Its aromatic ring and hydrophobic tail interact with the carbon surface, while the sulfonate headgroup keeps the mixture uniform and prevents particle agglomeration.



**Figure 2.10:** The chemical structure of SDBS.

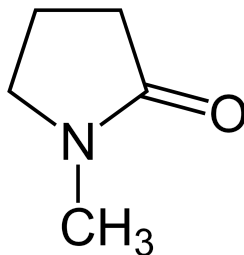
Although the total amount of surfactant in the final cathode is low, it is still considered dead mass that does not store energy. However, recent work shows that some ionic surfactants can actively help trap LiPS [28]. DFT calculations demonstrate strong binding between SDBS and  $\text{Li}_2\text{S}_x$  species, with binding energies of 2.44 eV for  $\text{Li}_2\text{S}_2$  and 2.73 eV for  $\text{Li}_2\text{S}$ . This suggests that SDBS might help anchor LiPS rather than just being an inactive additive, as illustrated by the binding models in Fig. 2.11.



**Figure 2.11:** Binding configurations and calculated energies of SDBS with  $\text{Li}_2\text{S}_2$  (left) and  $\text{Li}_2\text{S}$  (right). Adapted from [28].

## 2.5.2 NMP as solvent

NMP (Fig. 2.12) is a polar solvent widely used in battery manufacturing. Its high boiling point (202 °C), strong mixing ability, and excellent wetting of carbon surfaces make it very effective for processing graphene, CNTs, and other hydrophobic carbons into uniform slurries. The surface energy of NMP closely matches that of graphitic materials, leading to near-zero contact angles and stable mixtures that are easy to spread using a doctor blade.



**Figure 2.12:** The chemical structure of NMP.

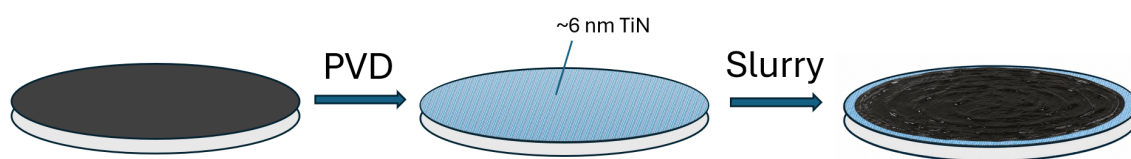
## 2.6 The current collector

The current collector in LSBs typically consists of aluminum foil, which can be coated with a thin carbon layer to improve slurry adhesion and prevent delamination during cycling. The electrode–current collector interface strongly governs contact resistance, charge-transfer resistance, reproducibility, and rate capability [29]. Specifically, direct contact between active sulfur and the metal surface leads to higher interfacial resistance and unstable voltage behavior, whereas carbon-mediated contact maintains low resistance and stable cycling. Furthermore,  $\text{Li}_2\text{S}$  preferentially precipitates near the current collector surface, forming a dense discharge layer that disrupts electronic percolation and triggers a premature end of discharge. Consequently, modifying the surface chemistry of the current collector directly influences adhesion, conductivity, and the extent of shuttle-related degradation [29].

PVD of TMNs serves as an effective method to strengthen this interface and improve LSB electrochemistry [13]. For instance, a CrN coating forms a tightly adhered, conductive layer on aluminum foil, where uniformly distributed CrN nanoparticles act as active sites for LiPS adsorption and catalysis. Density functional theory (DFT) calculations show that the CrN(111) surface binds  $\text{Li}_2\text{S}_x$  species more strongly than the native aluminum surface, suppressing LiPS diffusion and promoting faster interfacial redox kinetics. This modification accelerates both  $\text{Li}_2\text{S}$  deposition and dissolution, prevents the formation of dense insulating  $\text{Li}_2\text{S}$  layers, and lowers both interfacial and charge-transfer resistance. Experimentally, CrN-modified collectors deliver improved rate capability and long-term cycling stability, retaining 72.9% of their capacity after 500 cycles compared to 44.3% for unmodified aluminum [13]. PVD-based surface engineering of the current collector is therefore a powerful and scalable strategy for stabilizing the internal electrochemical interface.

Depositing an ultrathin TiN layer by PVD provides a uniform, conductive, and chemically stable interface that suppresses sulfur-rich contact formation and stabilizes  $\text{Li}_2\text{S}$  nucleation. Because the layer is extremely thin, it adds negligible mass to the electrode, thereby bypassing the disadvantage of the high gravimetric density of TiN. This modification layer alters the surface energy of the current collector prior to slurry casting, as shown schematically in Fig. 2.13, ensuring a more homogeneous interface.





**Figure 2.13:** Schematic of the current collector modification process, showing the bare current collector (left), the deposited TiN layer (center), and the final slurry coating applied onto the TiN layer (right).

## 2.7 Laboratory techniques

In this section, the theoretical principles behind the laboratory techniques used for LSB electrode fabrication and electrochemical evaluation are described.

### 2.7.1 Melt diffusion

Melt diffusion is a commonly applied technique for incorporating elemental sulfur into conductive carbon hosts for LSB cathodes. The method is based on the infiltration of molten sulfur into the porous structure and surface features of the carbon framework, resulting in improved sulfur distribution and enhanced sulfur–carbon contact.

Although sulfur melts at approximately 115 °C, elevated temperatures around 160 °C are utilized because molten sulfur exhibits its minimum viscosity within this regime. This low viscosity improves capillary-driven transport, allowing liquid sulfur to easily penetrate pores and irregularities within the carbon host. This confinement promotes intimate contact between the active material and the conductive network.

### 2.7.2 Doctor blade

Slurry coating using a doctor blade is a widely used method for producing uniform composite electrode layers. The technique enables controlled deposition of the cathode material onto a current collector, resulting in a consistent electrode morphology.

The resulting electrode structure is influenced by factors such as slurry composition, viscosity, and component dispersion. A uniform coating is important for achieving consistent sulfur loading, electrolyte accessibility, and efficient electron transport throughout the electrode. These properties directly influence the electrochemical performance and reproducibility of LSB cells.

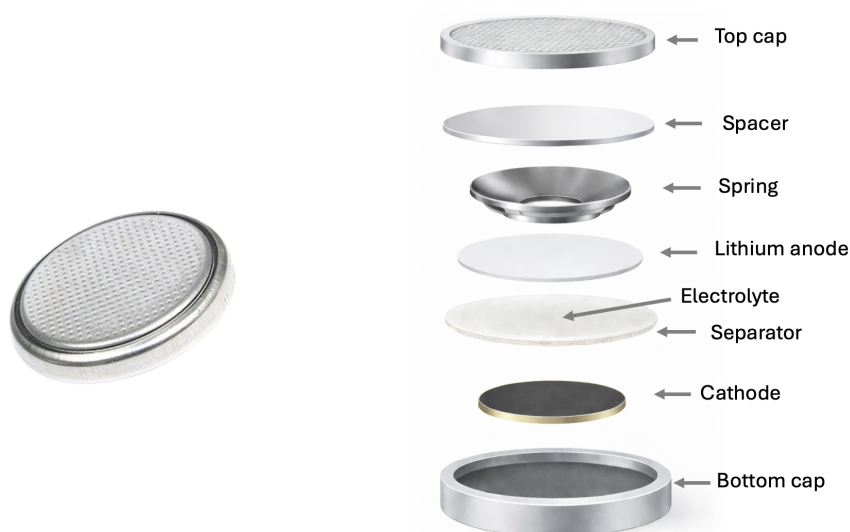
### 2.7.3 Vacuum oven

Drying is an important step in electrode preparation as it removes residual solvent from the composite electrode structure. Under reduced pressure, solvent evaporation is enhanced due to the lowered boiling point, allowing efficient removal while

minimizing potential changes to the electrode components. Complete solvent removal is necessary to achieve a stable electrode structure, as remaining solvent or moisture can influence binder distribution, electrode–electrolyte interactions, and electrochemical performance.

### 2.7.4 The coin cell

Coin cells are one of the most commonly used configurations for academic battery research due to their compact design, standardized geometry, and low material requirements. They enable controlled evaluation of electrode materials, electrolytes, and cell architectures. A schematic representation of a typical 2032 coin cell configuration is shown in Fig. 2.14.



**Figure 2.14:** The 2032 coin cell configuration with its main internal components.

**Top cap:** The top cap is typically made of stainless steel and provides mechanical support and electrical contact within the coin cell configuration. It contributes to maintaining a sealed environment and protects the internal components from external atmosphere.

**Spacer:** The spacer is a stainless-steel component that compensates for internal volume differences within the cell. It helps maintain appropriate mechanical contact between the different layers and contributes to stable cell operation.

**Spring:** The spring maintains continuous mechanical pressure inside the sealed coin cell. This pressure ensures uniform contact between the internal components, reducing contact resistance and supporting stable electrochemical cycling.

**Lithium anode:** In a lithium–sulfur cell, the negative electrode consists of metallic lithium chips, which act as the lithium ion source during electrochemical operation. During discharge, lithium is oxidized at this interface and transported through the

electrolyte toward the sulfur cathode, while charging reverses this process through lithium deposition.

**Electrolyte:** The electrolyte provides the ionic pathway required for lithium-ion transport between the electrodes. Ether-based electrolytes containing lithium salts are commonly used in LSBs due to their compatibility with sulfur conversion reactions. Additives such as  $\text{LiNO}_3$  are often introduced to improve the stability of the lithium metal interface by forming protective passivation layers.

**Separator:** The separator is a porous membrane that electrically isolates the two electrodes while allowing lithium-ion transport through its structure. In LSBs, the separator also influences the transport of dissolved lithium polysulfides ( $\text{Li}_2\text{S}_x$ ), which can contribute to the shuttle effect when migration is not controlled.

**Cathode:** The positive electrode acts as the host where sulfur reduction and oxidation reactions take place. It serves as the target for electron and lithium-ion collection during discharge and holds the active sulfur material within the cell assembly.

**Bottom cap:** The bottom cap is typically made of stainless steel and provides mechanical support for the base side of the cell, completing the sealed housing structure that encloses the internal components.

**Assembly and pressing:** The coin cell components must be assembled to ensure proper alignment, sealing, and mechanical contact between the individual layers. Maintaining a controlled internal environment is important for these systems because the metallic lithium and ether electrolyte components are highly sensitive to moisture and atmospheric contaminants.



# 3

## Methods and materials

### 3.1 Materials

All commercial reagents and components were used as received without further purification. Elemental sulfur ( $\geq 99.5\%$ , Sigma-Aldrich) was utilized as the active cathode material. For the conductive carbon additive, carbon black (Super P, Nanografi) was used. MWCNTs served as the primary carbon host for the sulfur, though SWCNTs and reduced rGO were also tested to a lesser extent. Both the MWCNTs and SWCNTs were obtained from Nanografi; their complete physical and structural specifications are detailed in Table A.1 in the Appendix.

PAA (25 wt% aqueous solution, Sigma-Aldrich) and PVDF served as the binder materials. The PAA was diluted in deionized water to a stock concentration of  $100 \text{ mg mL}^{-1}$ , while the PVDF was dissolved in anhydrous NMP (99.5%, extra dry, Thermo Scientific) to achieve a concentration of  $20 \text{ mg mL}^{-1}$ .

The electrolyte solution consisted of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 2 wt% lithium nitrate ( $\text{LiNO}_3$ ,  $\geq 99\%$ ) dissolved in a binary solvent mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 v/v). For electrochemical testing, standard CR2032 coin-cell assemblies were constructed using 19 mm diameter Celgard 2400 polypropylene (PP) sheets as the separator, 14 mm metallic lithium chips as the counter electrode, and stainless steel casings equipped with internal spacers and springs. Cathode slurries were coated onto either pristine carbon-coated aluminum foil or PVD-coated TiN modified aluminum foils.

### 3.2 Battery manufacturing

In this section, the experimental procedures for preparing the active material composites, formulation of the cathode slurries, and the final coin-cell assembly steps are detailed.

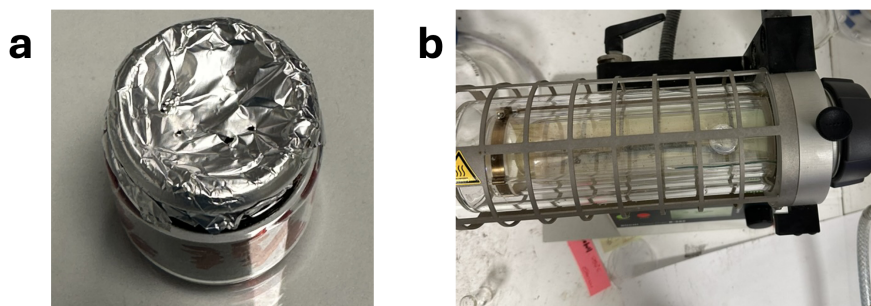
#### 3.2.1 Preparation of the active material powder

The sulfur-carbon (S/C) composite powder was prepared by melt diffusion. Elemental sulfur and the chosen carbon substrate (CNT, MWCNTs, or rGO) were mixed in a 75:25 mass ratio. The powders were weighed and lightly ground in a mortar and pestle for 5 minutes to ensure homogeneity and to break up sulfur agglomerates.

The mixture was transferred to a glass vial, and the combined mass of the vial and powders was recorded.

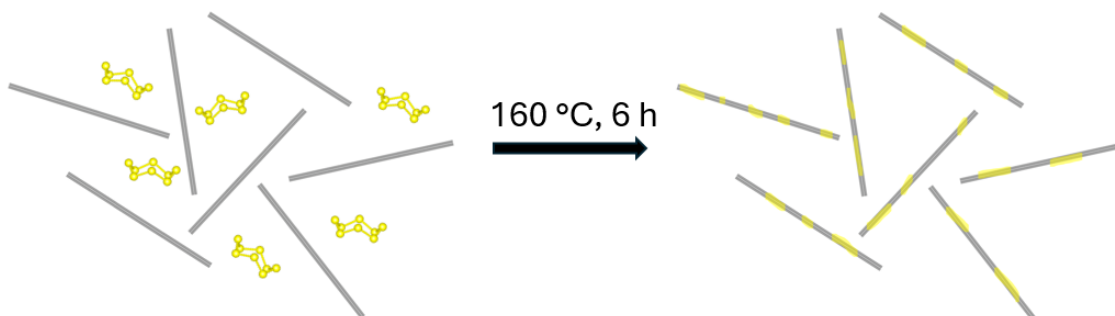
#### 3.2.2 Melt diffusion

Melt diffusion was used to incorporate sulfur into the carbon host. The powder mixture was placed in a glass vial sealed with aluminium foil perforated with five needle-sized holes to allow limited gas exchange while minimizing sulfur evaporation (Fig. 3.1). The vial was then heated at 160 °C for 6 h in a Büchi oven under N<sub>2</sub>, following three purge–vacuum cycles to remove residual air. After heating, the oven was allowed to cool to approximately 30 °C before opening.



**Figure 3.1:** (a) Glass vial sealed with aluminium foil punctured with needle-sized holes. (b) Büchi oven with the vial placed inside.

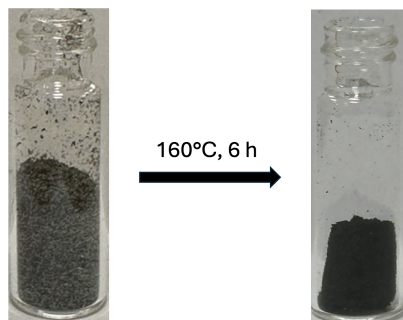
Heating the mixture to 160 °C melts the sulfur and lowers its viscosity. This allows the liquid sulfur to flow into the pores of the carbon structure through capillary forces, resulting in an intimate mixing of the materials. This improved contact between the sulfur and the carbon host is illustrated in Fig. 3.2.



**Figure 3.2:** Image showing improved sulfur–carbon contact after melt diffusion of sulfur into an MWCNT host, with 160 °C and 6 hours as example parameters.

For small batch sizes (around 200 mg), 1 ml vials were used instead of 5 ml vials to reduce internal surface area and prevent sulfur vapor from condensing on the vial walls. This setup consistently produced clean melt-diffused composites with negligible sulfur deposition on the walls of the vial, as shown in Fig. 3.3. A distinct decrease

in macroscopic powder volume is observed after processing. Because infiltration was conducted under an inert atmosphere, oxidation was prevented. The molten sulfur wets and flows into the interstitial voids of the fluffy MWCNT network, leading to a more compact composite structure without any loss of total mass.



**Figure 3.3:** 1 ml vial with S/MWCNT powder before and after melt diffusion.

### 3.2.3 Slurry preparation

Cathode slurries were formulated using an 8:1:1 mass ratio of S/C composite, binder, and Super P conductive carbon black. Two distinct binder systems were evaluated: PAA in deionized water and PVDF in NMP.

For PAA-based slurries, the stock solution was utilized to ensure a low-viscosity medium suitable for precise pipetting. Approximately 250  $\mu\text{L}$  of total deionized water, which includes the volume contributed by the binder solution, was added per 100 mg of total solid materials to achieve a workable consistency.

For PVDF-based slurries, a 20  $\text{mg mL}^{-1}$  PVDF solution in NMP was prepared by dissolving PVDF powder in a 10 mL glass vial equipped with a PTFE stir bar at room temperature for  $\sim 3$  h. A total of 1 mL NMP, including the volume from the PVDF binder solution, was added per 100 mg of solids to achieve the target slurry consistency.

The components were mixed manually using a mortar and pestle until a uniform slurry was obtained. While manual grinding served as the standard homogenization method, sonication was also evaluated as an alternative processing technique to help break up CNT bundles caused by strong van der Waals forces. In early trials, manual grinding was performed in conjunction with 10 minutes of bath sonication to improve component dispersion. However, this sonication step was completely omitted for the catalyst-coated electrodes, as well as for all reference cells used for direct comparison against those catalyst results, after initial tests yielded poor electrochemical performance with the sonicated catalyst-coated samples.

### 3.2.4 Electrode coating and drying

Slurries were coated onto aluminum foil current collectors using a doctor-blade technique. A blade height of 40  $\mu\text{m}$  was used for PAA-based slurries and 120  $\mu\text{m}$  for PVDF-based slurries. For substrates too small for the doctor blade (e.g., PVD-coated foils), the slurry was applied manually by spreading it with a spatula.

Coated electrodes were dried in a vacuum oven at 80  $^{\circ}\text{C}$  for 12 h. PVDF/NMP films were initially placed under a fume hood to prevent NMP contamination before vacuum drying. After drying, 12 mm circular electrodes were punched and weighed. The active sulfur mass loading ( $L_S$ ) was calculated using Equation 3.1:

$$L_S = \frac{(m_{\text{electrode}} - m_{\text{foil}}) \times 0.75 \times 0.8}{1.13} \quad (3.1)$$

where 0.75 is the sulfur mass fraction in the S/C composite, 0.8 is the target active-material fraction in the slurry solids, and 1.13  $\text{cm}^2$  is the geometric area of the 12 mm punched electrode. The target sulfur loading was approximately 2  $\text{mg cm}^{-2}$ . Separators (Celgard 2400) were punched using a precision disc cutter, with the PP sheet placed between two paper layers to ensure clean cuts.

## 3.3 Coin cell assembly

CR2032 coin cells were assembled inside an argon-filled glovebox ( $\text{O}_2$  and  $\text{H}_2\text{O} < 0.1$  ppm). The stacking architecture from top to bottom consisted of: the top cap, spacer, spring, lithium metal anode (14 mm), Celgard 2400 separator, cathode, and bottom cap. A total electrolyte volume of 50  $\mu\text{L}$  was used per cell, with 25  $\mu\text{L}$  applied directly to the cathode and 25  $\mu\text{L}$  to the separator to ensure uniform wetting. Cells were sealed using a coin-cell crimper at a pressure of 1000 psi.

## 3.4 Electrochemical testing

GCD cycling was performed within a voltage window of 1.7–2.8 V. The theoretical capacity of sulfur was defined as 1675  $\text{mAh g}^{-1}$ , and the calculated sulfur mass for each individual electrode was assigned accordingly. Newly assembled cells were rested for 6 h prior to cycling to allow full electrolyte equilibration and wetting. Cycling evaluation was primarily conducted at rates of 0.1 C and 0.5 C for up to 150 and 500 cycles, respectively.

To investigate internal cell kinetics, CV and EIS were performed. CV measurements were carried out at a scan rate of 0.1  $\text{mV s}^{-1}$  for a total of 10 cycles, and EIS spectra were collected both before and after the CV testing.



### 3.5 Physical vapor deposition

The TiN layer was deposited using an FHR MS 150x4-L magnetron sputtering tool [30], as shown in Fig. 3.4. This computer-controlled system features five magnetron cathodes and a load-lock chamber, allowing it to achieve a low base pressure below  $5 \times 10^{-7}$  mbar. Reactive sputtering of TiN was carried out in a mixed Ar/N<sub>2</sub> gas atmosphere utilizing a pure titanium target.

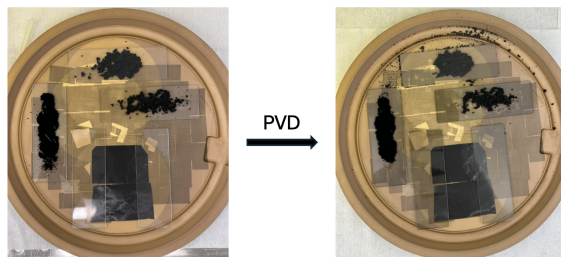


**Figure 3.4:** The FHR MS 150x4-L magnetron sputtering system used for TiN deposition.

#### 3.5.1 PVD processing and mass loss analysis

Two separate PVD runs were performed. The first trial targeted a uniform 6 nm TiN coating across MWCNT, SWCNT, and rGO powder samples. The second trial focused exclusively on MWCNTs to evaluate two different deposition times, corresponding to nominal TiN thicknesses of approximately 3 nm and 6 nm.

During both runs, several practical handling challenges arose due to the exceptionally low tap densities and fluffy nature of the carbon powders. When the chamber was evacuated during the initial pump-down stage, a significant portion of the loose powders was displaced or pulled toward the edges of the carrier plate by the gas flow. This physical displacement and the resulting material loss are shown in Fig. 3.5.



**Figure 3.5:** Glass substrate arrangement before and after PVD sputtering, showing powder around the edges of the plate caused by chamber evacuation.

In contrast, the aluminum foil current collectors remained firmly anchored in place between the glass mounting sheets. They did not experience any movement during pump-down, which makes this setup highly repeatable and scalable for larger foil sheets. The initial and final masses of the carbon powders for both PVD runs are summarized in Table 3.1.

**Table 3.1:** Summary of sample mass changes and material loss across the first and second PVD sessions.

| Sample                    | Thickness | Mass (Before → After) | Change |
|---------------------------|-----------|-----------------------|--------|
| <i>First PVD session</i>  |           |                       |        |
| MWCNT                     | ~6 nm     | 28.67 mg → 22.60 mg   | −21.2% |
| SWCNT                     | ~6 nm     | 49.84 mg → 36.84 mg   | −26.1% |
| rGO                       | ~6 nm     | 7.03 mg → 5.23 mg     | −25.6% |
| <i>Second PVD session</i> |           |                       |        |
| MWCNT                     | ~3 nm     | — → 46.60 mg          | —      |
| MWCNT                     | ~6 nm     | — → 85.20 mg          | —      |
| Total batch               | —         | 171.30 mg → 131.80 mg | −23.1% |

## 3.6 Thermogravimetric analysis

TGA was performed on the melt-diffused samples to determine the exact sulfur weight fraction. Approximately 2–3 mg of composite powder was loaded into a pre-weighed crucible and heated from room temperature to 900 °C at a constant heating rate of 10 °C min<sup>−1</sup> under a continuous nitrogen (N<sub>2</sub>) flow. Because sulfur evaporates while the carbon host remains thermally stable, the sulfur content was calculated directly from the resulting mass loss percentage.

## 3.7 SEM/EDS analysis

SEM and EDS were used to examine sample morphology and elemental distribution. For the powders, a small amount of sample was dispersed in ethanol via 5 seconds of sonication, drop-cast onto a silicon wafer substrate, and dried. For the cathode films, a small piece was cut and pressed firmly onto an SEM sample holder using double-sided carbon tape.

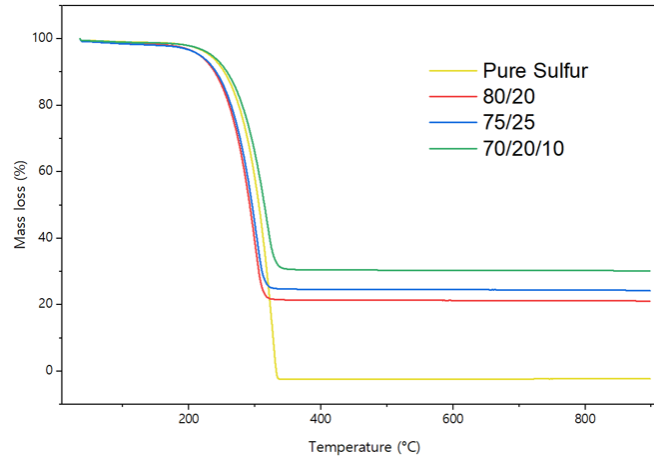
EDS analysis was conducted at accelerating voltages between 2 and 10 keV to locate the Ti peaks while minimizing beam-induced sulfur evaporation. However, detecting the Ti peaks proved highly challenging due to the low total Ti content. Additionally, higher electron beam penetration depths likely caused signals from the underlying carbon and aluminum substrate elements to overshadow the weak titanium signal response.

# 4

## Results and discussion

### 4.1 Sulfur content analysis

TGA was performed on the active-material powder mixtures to determine the actual sulfur weight fraction (Fig. 4.1). The resulting curves show that sulfur evaporates within the temperature range of 200 to 340 °C, with no further mass loss observed up to 900 °C, confirming the thermal stability of the carbon host materials.



**Figure 4.1:** TGA curves of the active material powder samples.

The measured sulfur contents align closely with the intended target compositions: target levels of 80%, 75%, and 70% correspond to measured values of 78.4%, 75.4%, and 69.7%, representing minimal deviations of  $-1.6\%$ ,  $+0.4\%$ , and  $-0.3\%$ , respectively. These minor differences are well within an acceptable range and likely originate from small weighing uncertainties or local sample inhomogeneity.

### 4.2 Electrochemical measurements

In this section, the electrochemical performance data is presented, comparing the coin cells fabricated with and without the TiN catalyst modifications.

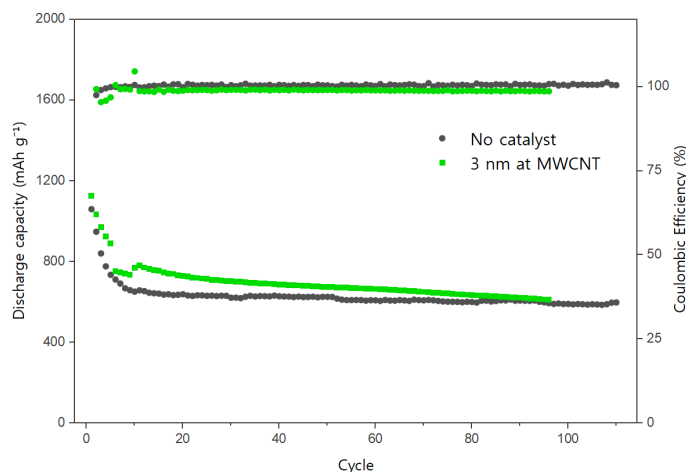
#### 4.2.1 TiN catalyst on MWCNT supports

This section evaluates the first configuration of catalyst deposition, which was applied directly onto the MWCNT host frameworks. Two different binders (PAA

and PVDF) were evaluated, as they were expected to exert distinct impacts on the cathode performance.

#### 4.2.1.1 With PAA as the binder

The first batch of cells was fabricated using PAA as the binder, as it had provided stable baseline results earlier in the project. This initial test compared a  $\sim 3$  nm TiN coating on MWCNTs with a no-catalyst reference, as shown in Fig. 4.2. The reference cathode delivered an initial discharge capacity of  $1060.1 \text{ mAh g}^{-1}$  at a sulfur mass loading of  $1.709 \text{ mg cm}^{-2}$  with an average Coulombic efficiency of 99.78%. The  $\sim 3$  nm TiN-coated sample reached  $1126.8 \text{ mAh g}^{-1}$  at  $1.84 \text{ mg cm}^{-2}$  and 98.90% efficiency, corresponding to a modest improvement of 6.29% in initial discharge capacity.



**Figure 4.2:** Comparison between the no-catalyst reference and the 3 nm TiN-coated MWCNT cathode using PAA as the binder.

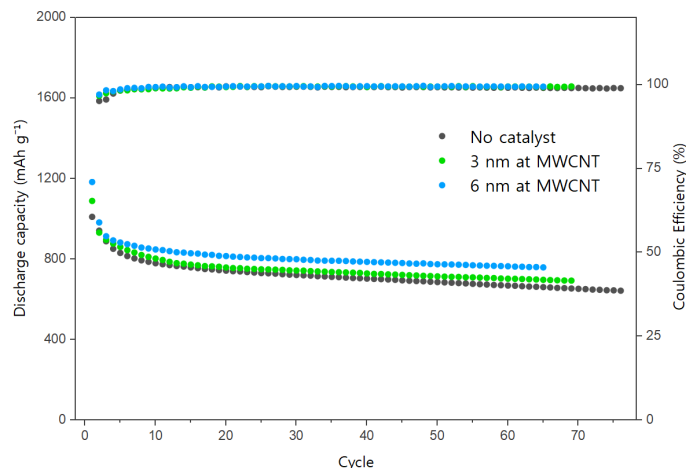
Although the increase in initial discharge capacity was positive, the gain was relatively small. Furthermore, the Coulombic efficiency was noticeably lower for the catalyst-coated sample, indicating that the PAA binder might interfere with the catalyst surface sites. This observation aligns with literature findings showing that carboxylic acid groups in PAA can adversely interact with titanium-based catalyst surfaces [31]. To avoid these binder-catalyst interactions and enable an unhindered evaluation of the TiN coating, PVDF was used in all subsequent experiments.

#### 4.2.1.2 With PVDF as the binder

PVDF is an electrochemically inert binder that does not interact with the TiN catalyst. The cycling behavior of the TiN-coated MWCNT electrodes using PVDF was evaluated at a  $0.1 \text{ C}$  rate over 65 cycles and compared directly to a reference electrode without a catalyst, as shown in Fig. 4.3. All electrodes showed stable cycling behavior at  $0.1 \text{ C}$ , with high Coulombic efficiencies after the initial formation cycles.

The reference electrode without a catalyst showed the lowest initial discharge capacity of  $1010.1 \text{ mAh g}^{-1}$  while maintaining a Coulombic efficiency of 99.04%. In

comparison, the catalyst-coated MWCNT electrodes showed enhanced initial capacities of 1088.9 and 1183.1 mAh g<sup>-1</sup> for the 3 and 6 nm TiN coatings, representing improvements of 7.8% and 17.1% in initial discharge capacities, respectively. Furthermore, these catalyst-coated MWCNT samples achieved high average Coulombic efficiencies of 99.15% for the 3 nm layer and 99.35% for the 6 nm layer.



**Figure 4.3:** Cycling performance at a 0.1 C rate over 65 cycles, comparing the reference electrode without a catalyst to the  $\sim 3$  and  $\sim 6$  nm TiN-coated MWCNT electrodes.

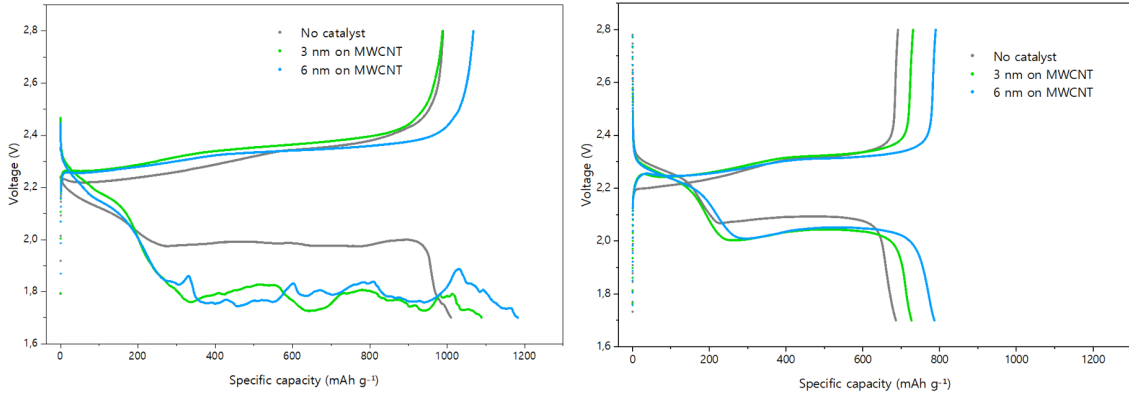
Fig. 4.4 compares the discharge voltage profiles for cycles 1 and 50. The first cycle shows some initial instability, which could be related to the activation of the catalyst. However, this effect may also be influenced by the higher sulfur mass loadings of 2.49 and 2.41 mg cm<sup>-2</sup> for the 3 and 6 nm TiN-MWCNT electrodes, respectively, compared to 2.12 mg cm<sup>-2</sup> for the reference.

All electrodes were coated using the doctor-blade technique with a set gap height of 40  $\mu$ m. The higher mass loadings observed for the catalyst-coated MWCNT electrodes are likely caused by the higher density of the TiN-modified powder, which allows a greater mass of solids to pack within the same wet film volume compared to the fluffy, low-density pristine MWCNTs. For a more direct comparison in future work, the doctor-blade height should be adjusted dynamically (e.g., 30 to 35  $\mu$ m) to normalize the final sulfur loading. Extending or intensifying the slurry mixing procedure should also be explored to ensure absolute component homogeneity.

#### 4.2.2 TiN catalyst on the current collector

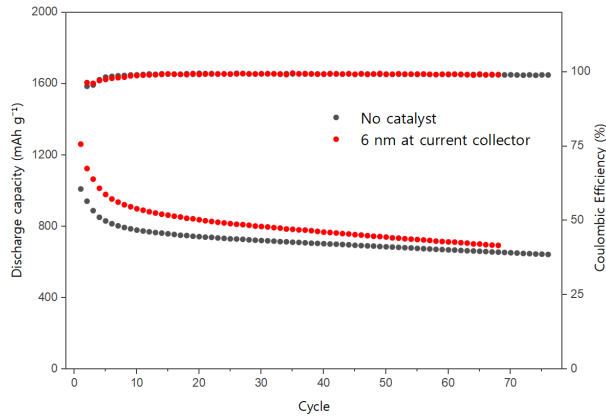
For these cells, PVDF was also used as the binder to allow for a fair comparison. The effect of depositing the TiN catalyst directly onto the aluminum current collector was evaluated at both low (0.1 C) and high (0.5 C) current rates and compared against the same no-catalyst reference electrode.

At a 0.1 C rate, the reference cell with a loading of 2.12 mg cm<sup>-2</sup> reached an initial capacity of 1010.1 mAh g<sup>-1</sup> and an average Coulombic efficiency of 99.04%.



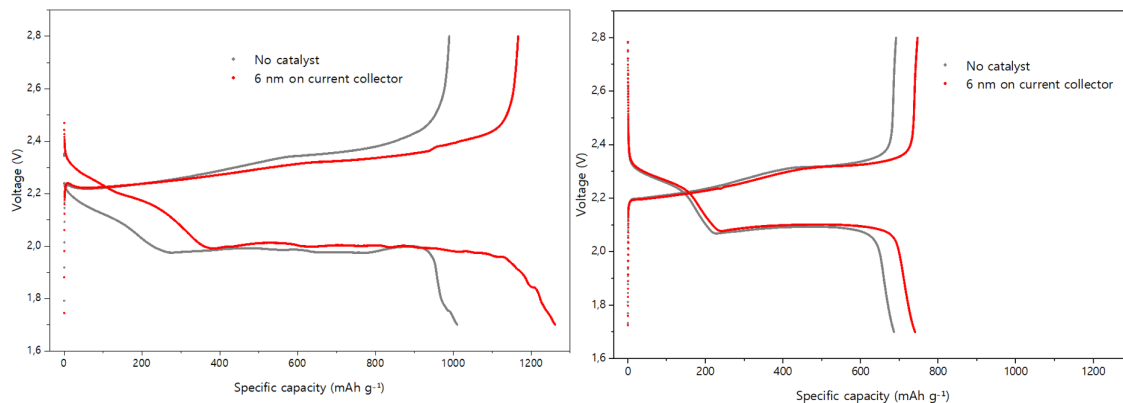
**Figure 4.4:** The PVDF electrode discharge profile comparison for the TiN-MWCNT cells compared with the no-catalyst reference, showing cycle 1 (left) and 50 (right).

In comparison, the electrode with a 6 nm catalyst coating on the current collector delivered a significantly higher initial discharge capacity of  $1261.8 \text{ mAh g}^{-1}$  with an average Coulombic efficiency of 98.90%, as shown in Fig. 4.5. This represents a 24.9% increase relative to the reference electrode despite a lower sulfur mass loading of  $1.77 \text{ mg cm}^{-2}$ . These results show that the greatest capacity enhancement at 0.1 C is obtained when the catalyst is deposited directly onto the current collector. This configuration does, however, exhibit a slightly lower Coulombic efficiency, indicating minor material degradation or polysulfide loss over cycling.



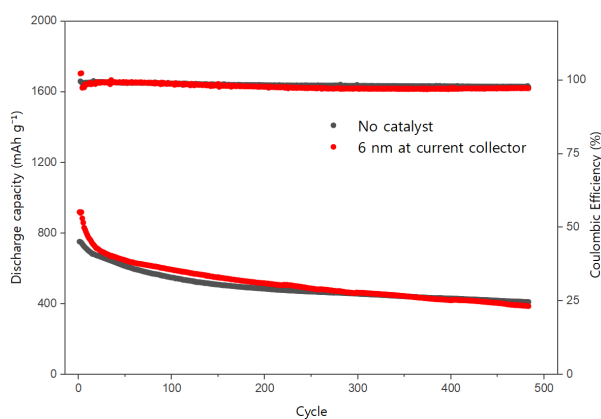
**Figure 4.5:** Cycling performance comparison at a 0.1 C rate between the no-catalyst reference and the  $\sim 6 \text{ nm}$  TiN-coated current collector.

Fig. 4.6 compares the discharge and charge voltage profiles for cycles 1 and 50. It is clear that the coated current collector provides better redox kinetics than the reference. This is demonstrated by the higher voltage during the discharge plateaus and the lower voltage during the charging plateaus, which corresponds to a significantly reduced cell overpotential. As noted above, the discharge capacity is also far greater, confirming more efficient active material utilization.



**Figure 4.6:** The PVDF electrode discharge profile comparison for the TiN-current collector cell compared with the no-catalyst reference, showing cycles 1 (left) and 50 (right).

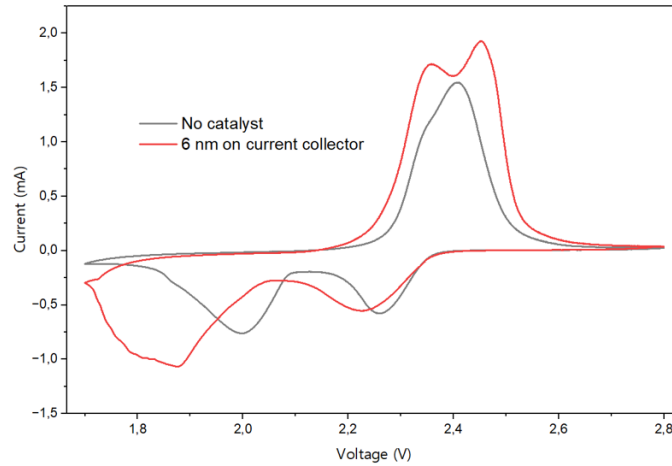
A higher current rate of 0.5 C was also tested to evaluate the rate capability of the cells, as shown in Fig. 4.7. At this higher rate, the reference cell had a sulfur loading of  $1.72 \text{ mg cm}^{-2}$  and delivered an initial discharge capacity of  $770.8 \text{ mAh g}^{-1}$  with an average Coulombic efficiency of 98.4%. With the 6 nm catalytic layer on the current collector, the cell delivered an initial discharge capacity of  $920.3 \text{ mAh g}^{-1}$  at a sulfur loading of  $1.87 \text{ mg cm}^{-2}$ . This represents a 19.4% improvement over the reference cell with a Coulombic efficiency of 98.0%, confirming enhanced kinetics. However, its slightly lower Coulombic efficiency compared to the reference led to faster capacity degradation. This behavior suggests potential catalyst delamination due to poor mechanical adhesion, which could be verified through post-mortem SEM characterization. While PVDF was used here, utilizing alternative binders like PAA could theoretically strengthen the current collector interface via polar functional group interactions and improve overall cycle life.



**Figure 4.7:** Cycling performance comparison at a 0.5 C rate highlighting the difference between the reference and the  $\sim 6 \text{ nm}$  TiN-coated current collector.

The enhanced conversion kinetics are also supported by the CV measurements shown in Fig. 4.8. The anodic peak positions indicate efficient re-oxidation of  $\text{Li}_2\text{S}$  and intermediate LiPS back to  $\text{S}_8$ , consistent with faster conversion kinetics. The second,

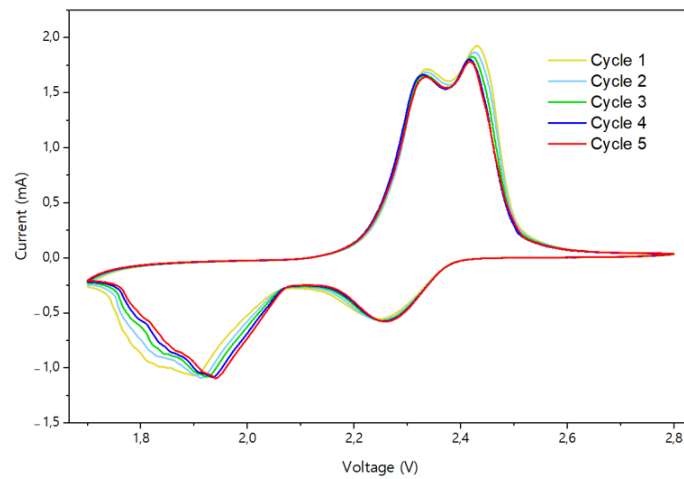
low-voltage reduction peak is highly pronounced, which aligns with the high discharge capacity observed in the galvanostatic testing. The reference sample without a catalyst also shows well-defined reduction peaks, confirming that it performs reasonably well, although the catalytic sample exhibits a more pronounced and sharper peak current response. The high capacity achieved by the coated current collector can be attributed to the interface processing conditions and liquid phase transport within the cell. Because this specific sample was hand-coated utilizing an NMP-based slurry, the manual spreading method using a spatula ensured intimate physical contact between the carbon-sulfur composite suspension and the underlying catalytic surface. During subsequent cell operation, the ether-based electrolyte dissolves the long-chain intermediates, allowing them to readily diffuse through the porous composite matrix to access these highly active catalytic sites at the modified current collector interface. Because the sputtered catalyst layer was thin and likely formed distributed surface features rather than a fully dense film, exploring a greater coating thickness by increasing deposition times could be beneficial to maximize active surface coverage, similar to related findings using CrN modifications [13].



**Figure 4.8:** The CV measurements of the modified current collector and the no-catalyst reference electrode.

The CVs in Fig. 4.9 also show a gradual positive shift of the low-voltage reduction peak over repeated cycles. This indicates decreasing polarization and faster reaction kinetics as the electrode wets fully and the internal interface stabilizes. In LSB systems, such a shift means the LiPS reduction step requires a less negative potential, reflecting an easier conversion process. This behavior is a clear sign of electrode electrochemical activation and aligns with the stable, high capacities seen in the cycling data.

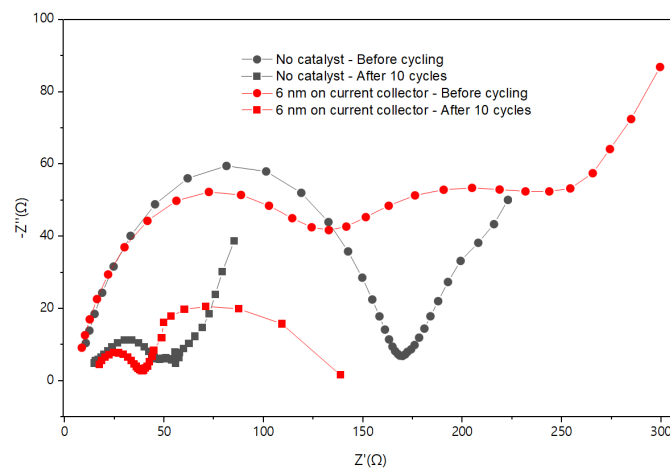




**Figure 4.9:** Cyclic voltammograms for the modified current collector over 5 repeated cycles.

#### 4.2.2.1 EIS comparison

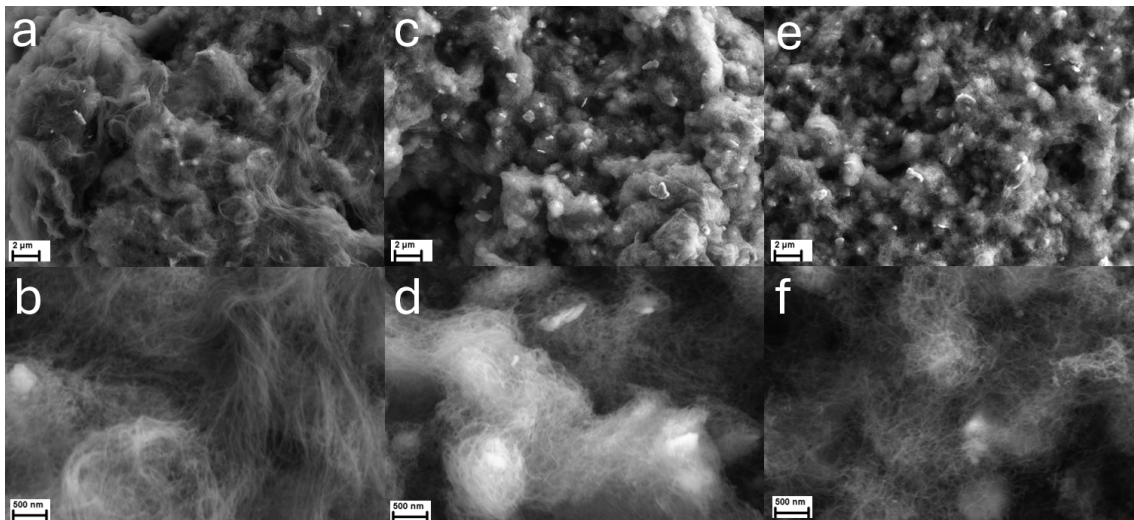
After ten CV cycles, both cells exhibit a clear reduction in impedance, evidenced by a leftward shift and a decreased semicircle diameter in the Nyquist plots (Fig. 4.10). The no-catalyst cell displays a single semicircle, where the reduced diameter after cycling suggests a decrease in interfacial resistance. In contrast, the current-collector-modified cell exhibits two distinct semicircles, indicating the presence of multiple interfacial processes. This behavior could indicate two separate resistive contributions: the first semicircle can likely be attributed to contact resistance or ion transport associated with the TiN catalyst layer, while the second potentially represents the charge-transfer resistance of the sulfur redox reactions. After cycling, both semicircles decrease substantially in size and the low-frequency tail disappears, suggesting that the TiN modification may accelerate interfacial kinetics and lower charge-transfer resistance more effectively than the reference cell.



**Figure 4.10:** Nyquist plots comparing the impedance profiles before and after 10 CV cycles for the no-catalyst reference and current-collector-modified cell.

### 4.3 SEM/EDS of the powders

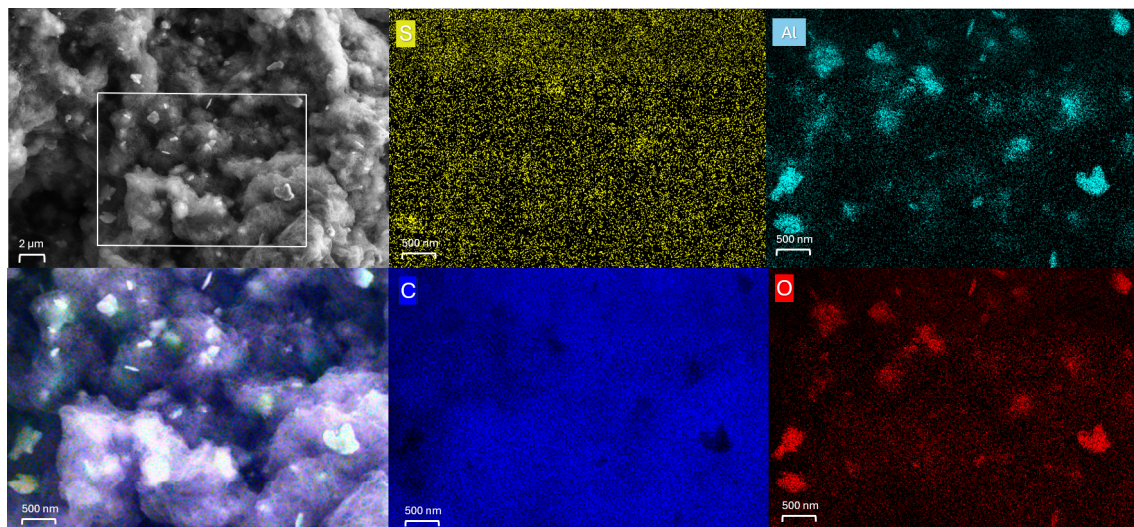
The SEM images of the melt-diffused sulfur on MWCNTs (Fig. 4.11) show no apparent morphological differences in the sulfur layer between the reference material and the TiN-coated samples. In the close-up view of the reference powder (b), the sulfur coverage appears similar to that of the catalyst-coated samples (d for  $\sim 3$  nm and f for  $\sim 6$  nm). Although micron-sized metallic-looking particles appear somewhat more frequent in the specific images of the catalyst-coated powders (c+d and e+f), these features are present in every specimen and likely reflect local heterogeneity. Because the SEM images were taken at a single spot on each sample, these observations may vary across other areas of the material. Furthermore, a general tendency for the MWCNT network to bundle and tangle around these particles is observed throughout the samples. The chemical identity of these particles, which originate from the residual Al substrate used during the manufacturer's CVD process for the 96% pure MWCNTs, is investigated and confirmed in the following section.



**Figure 4.11:** (a, b) Reference powder at 10k and 50k $\times$  magnification; (c, d)  $\sim 3$  nm catalyst-layered powder at 10k and 50k $\times$  magnification; (e, f)  $\sim 6$  nm catalyst-layered powder at 10k and 50k $\times$  magnification.

#### 4.3.1 Analysis and discussion of the Al-particles

The Al particles appear to possess a thin  $\text{Al}_2\text{O}_3$  layer, supported by the EDS maps showing that the O and Al signals overlap spatially in Fig. 4.12.  $\text{Al}_2\text{O}_3$ , like several other metal oxides, is known to bind LiPS strongly according to literature DFT calculations [32]. These high adsorption energies arise from the formation of Li–O and Al–S bonds, giving  $\text{Al}_2\text{O}_3$  a highly polar surface for LiPS anchoring. Such surfaces can therefore actively help trap polysulfides locally within the conductive carbon matrix. The relatively high performance of the baseline reference samples could partly be attributed to the unexpected presence of these catalytic particles.



**Figure 4.12:** SEM image at 10k $\times$  magnification of the  $\sim 3$  nm composite powder with corresponding EDS analysis, showing the elemental composition of the particles as Al and O.

In typical Li-S cathodes, the total amount of catalyst or polar additive is only a few weight percent (approximately 1–5 wt%), which is generally sufficient to influence LiPS anchoring and mitigate the shuttle effect. EDS analysis of the powders shows that the Al mass content in the present system falls within this range depending on the local site analyzed. The origin of these particles was confirmed by the manufacturer to be the substrate support material, which is typically alumina ( $\alpha$ - $\text{Al}_2\text{O}_3$  or alumina derived from  $\text{Al}(\text{OH})_3$ ).

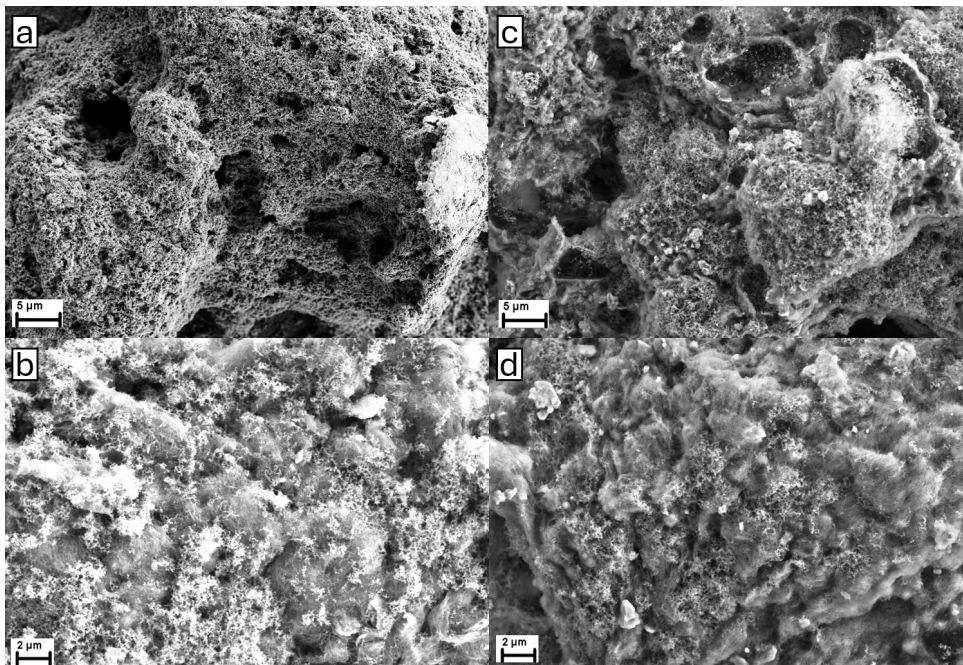
## 4.4 SEM/EDS comparison of binder systems

Fig. 4.13 displays SEM micrographs at 5k $\times$  and 10k $\times$  magnification for two LSB cathodes prepared with identical material ratios but different binder-solvent systems.

For the PAA/water system, high-magnification imaging reveals a rough, porous surface. Although individual particles appear less internally homogeneous due to the poor wetting of hydrophobic carbon in water, the PAA/water electrodes achieved a better overall macro-dispersion. Because water does not dissolve sulfur, the components remain strictly suspended rather than dissolved during slurry processing (see Appendix A.1).

In contrast, the PVDF/NMP system produced larger visible clumps. While NMP is initially an excellent dispersant for carbon, it also partly dissolves elemental sulfur. Upon drying, this dissolved sulfur recrystallizes, forcing the sulfur and MWCNTs to co-precipitate into agglomerates. This dissolution and subsequent recrystallization explain the formation of the larger macro-scale clumps observed visually in the PVDF/NMP electrodes (see Appendix A.2).

The PAA/water system prevents macro-agglomeration by keeping the sulfur insoluble and dispersed, whereas the PVDF/NMP system leads to structural agglomeration during drying due to sulfur phase changes.



**Figure 4.13:** (a, b) PAA/water: 5k $\times$  and 10k $\times$  magnification. (c, d) PVD-F/NMP: 5k $\times$  and 10k $\times$  magnification.

## 4.5 Observations of catalyst-coated samples

### 4.5.1 PAA-based cells

#### **SDBS interaction with catalyst-coated powders**

Initial electrode slurries were prepared using PAA as the binder. Upon introducing the 1 wt% SDBS aqueous solution, a strong affinity toward the powder mixture was observed. This behavior is highly plausible due to the amphiphilic nature of SDBS. The surfactant molecules likely engage in competitive adsorption on the polar TiN surfaces, which alters the local surface charge and dispersion dynamics within the aqueous medium. As illustrated by the DFT calculations in Fig. 2.11, the polar head group of SDBS is responsible for anchoring  $\text{Li}_2\text{S}_x$  species. Consequently, this competitive adsorption onto the TiN catalyst during processing may partially or entirely negate the beneficial LiPS-trapping effects of the surfactant after cell assembly, especially given the low initial concentration of SDBS. To clarify this phenomenon, the impact of varying SDBS-to-catalyst ratios should be explored in future work.

#### **Dispersion and mixing challenges**

The catalyst-coated powders exhibited increased resistance to dispersion during

slurry preparation, suggesting that the TiN deposition may have caused agglomeration of the MWCNTs. Because the MWCNT powder was distributed across a flat glass substrate during the PVD process, the TiN was deposited directionally over the exposed surface of the powder bed. The exact morphological consequences of this macroscopic deposition technique on the nanoscale structure remain to be fully elucidated.

#### 4.5.2 PVDF-based cells

Similar to the PAA system, the PVDF-based slurries suffered from poor dispersion, which was uniquely related to the presence of the catalyst. While NMP is highly effective at suspending pure MWCNTs and dissolving elemental sulfur into a homogeneous mixture [2], it struggled to properly disperse the TiN–MWCNT networks. This processing difficulty introduces a critical structural drawback during the film drying stage. Owing to its low volatility and high boiling point (202 °C), NMP evaporates negligibly at room temperature and remains largely present during the initial stages of vacuum drying at 80 °C, allowing continuous redistribution of the dissolved sulfur. As the solvent eventually evaporates, the sulfur recrystallizes into macro-sized agglomerates. This recrystallization causes a significant fraction of the active material to lose electrical and physical contact with both the conductive carbon network and the catalytic TiN interfaces. Furthermore, the growth of these large particles generates substantial internal stresses that manifest as visible cracks across the electrode film after drying. Consequently, these cells exhibit substandard electrochemical performance, aligning with previously reported detrimental effects of NMP-mediated sulfur redistribution on cathode morphology [2].



# 5

## Conclusion

This thesis evaluated ultrathin, PVD-deposited TiN coatings applied separately to MWCNT hosts and aluminum current collectors for LSBs. The experimental results confirm that TiN effectively enhances sulfur utilization, accelerates LiPS conversion kinetics, and reduces interfacial charge-transfer resistance.

For the powder-based configuration, the TiN-modified MWCNT electrodes exhibited higher initial discharge capacities and improved cycling performance compared to the reference cell, despite showing a brief initial activation period. However, structural characterization revealed no visible or continuous TiN layer on the nanotube surfaces, indicating that the line-of-sight PVD process likely resulted in highly dispersed, sub-nanoscale catalytic clusters below the detection limits of direct SEM/EDS imaging. Furthermore, residual aluminum-based impurities originating from the commercial carbon nanotube growth substrate provided an unexpected native oxide interface for LiPS anchoring, which partially masked the full isolated catalytic contribution of the intended TiN modification.

The most significant performance improvements were achieved by utilizing the flat, TiN-coated current collectors. This localized modification significantly lowered the cell overpotential and stabilized the electrode-collector interface. Consequently, the coated current collectors delivered superior discharge capacities at both low and high current rates compared to the reference samples. Furthermore, depositing onto a flat substrate completely avoided the vacuum-processing mass losses and powder fluidization challenges associated with processing lightweight carbon substrates. This makes the current collector modification highly reproducible and scalable for industrial roll-to-roll battery manufacturing.

Overall, these findings highlight PVD-sputtered TiN as a highly promising catalyst and interfacial modifier for high-performance LSBs. Future work should focus on optimizing the slurry formulation, specifically by quantifying the competitive adsorption between ionic surfactants and the catalyst surface, and exploring specialized fluidized-bed PVD systems to improve coating uniformity across loose three-dimensional carbon architectures.





# 6

## Future Outlook

Several directions for the continued development of TiN-based catalysts in LSBs have emerged from this work. First, extended cycling and rate-capability studies are required to evaluate long-term electrochemical stability and determine how the catalytic interfaces evolve under continuous operating conditions. Second, systematically varying the TiN layer thickness on both the MWCNT host and the current collector is essential to identify the optimal configuration and evaluate whether continuous films or nanoscale clusters provide the best balance between electronic conductivity and catalytic activity.

Furthermore, exploring alternative binder systems beyond PVDF and PAA could improve slurry homogeneity and prevent unwanted interactions with the active catalyst surfaces. Together, the use of doped CNTs with polar functional groups offers a promising route to enhance LiPS confinement, anchor solid  $\text{Li}_2\text{S}$  discharge products, and improve the mechanical adhesion of the TiN catalyst itself. Finally, expansion of the characterization toolbox with surface-sensitive techniques such as XRD and XPS is necessary to clarify the TiN phase stability and interfacial reactions, strengthening the mechanistic understanding to guide future PVD-based catalyst designs.



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# A

## Appendix 1

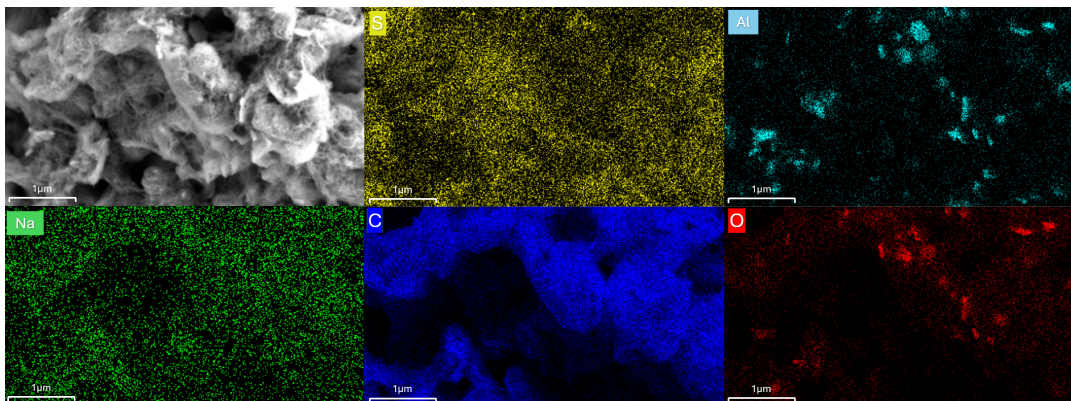
| Property                | MWCNT                     | SWCNT                  |
|-------------------------|---------------------------|------------------------|
| Purity                  | > 96%                     | > 96%                  |
| Color                   | Black                     | Black                  |
| Diameter                | < 8 nm                    | 1–2 nm                 |
| Inner Diameter          | 2–6 nm                    | 0.8–1.6 nm             |
| Length                  | 10–35 $\mu\text{m}$       | 20–55 $\mu\text{m}$    |
| Tap Density             | 0.3 g/cm <sup>3</sup>     | 0.15 g/cm <sup>3</sup> |
| True Density            | 2.4 g/cm <sup>3</sup>     | 2.4 g/cm <sup>3</sup>  |
| Specific Surface Area   | 300–550 m <sup>2</sup> /g | 570 m <sup>2</sup> /g  |
| Ash Content             | 1.5 wt%                   | 3.0 wt%                |
| Electrical Conductivity | 98 S/cm                   | 98 S/cm                |
| Manufacturing Method    | CVD                       | CVD                    |

**Table A.1:** Physicochemical and structural specifications of the commercial MWCNTs and SWCNTs investigated in this work, data acquired from the supplier’s website.

## A.1 SEM/EDS of the PAA electrodes

### PAA reference: without carbon black

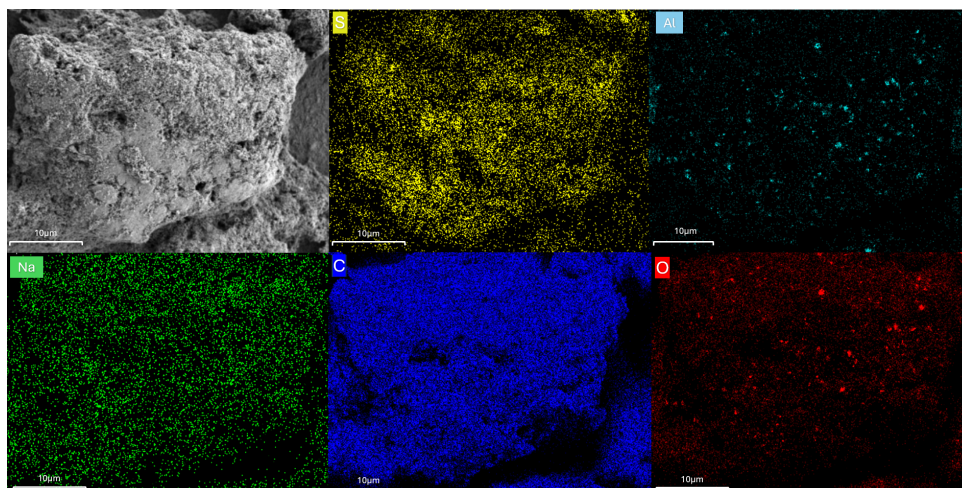
Fig. A.1 maps the elemental distribution (cycling in Fig. A.6). Isolated high-S regions indicate poor local electronic contact from incomplete mixing. Overlapping Al and O signals reveal residual native aluminum oxide particles (100–300 nm) from CNT synthesis. The Na signal tracks the carbon network, confirming successful adsorption of the SDBS surfactant onto the MWCNTs.



**Figure A.1:** SEM/EDS elemental mapping of a PAA electrode fabricated without carbon black conductive additives.

### PAA cathode reference

Fig. A.2 shows uniform elemental dispersion, confirming successful melt diffusion and matching the performance in Fig. A.7. As observed previously, the Na signal tracks the carbon framework due to the SDBS surfactant, while overlapping Al and O signals mark the remaining catalyst support particles.

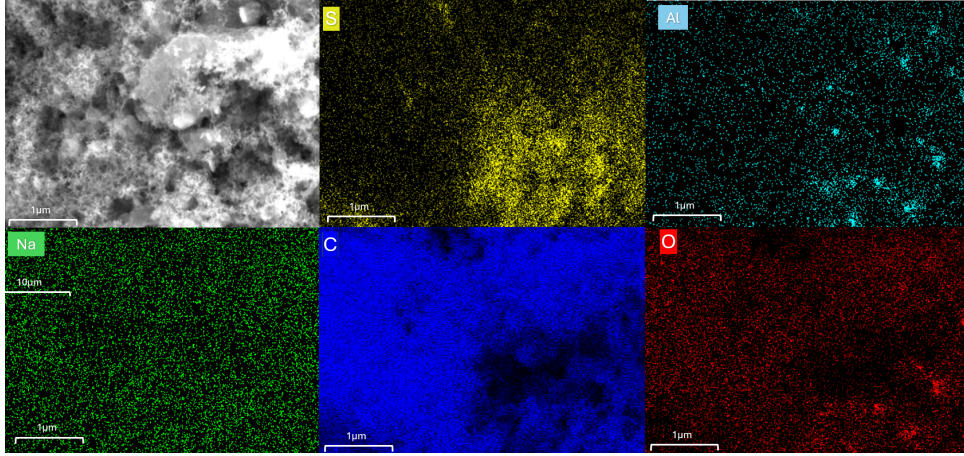


**Figure A.2:** SEM/EDS elemental mapping of the PAA cathode reference with a 75/25 active material to host ratio.



**PAA cathode reference with  $\sim 3$  nm TiN**

Fig. A.3 highlights a specific micro-region within the  $\sim 3$  nm TiN–PAA electrode where mixing was insufficient, resulting in an uneven distribution of S and the MWCNT network.

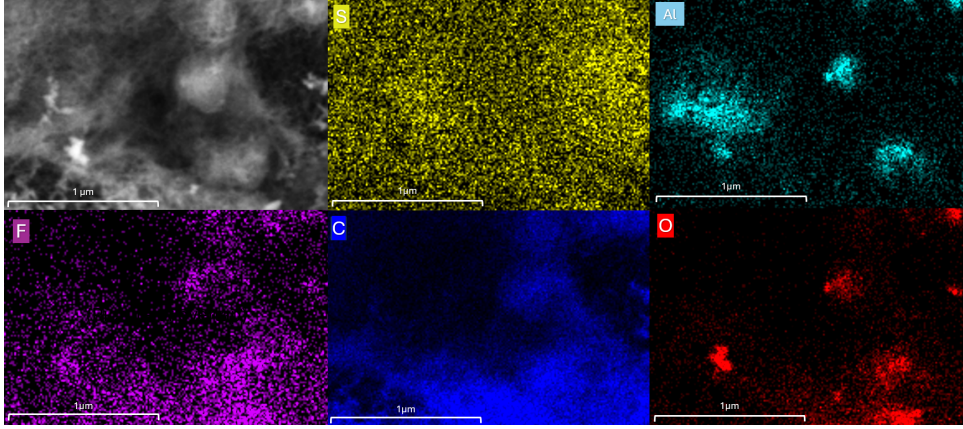


**Figure A.3:** SEM/EDS elemental mapping of the  $\sim 3$  nm TiN-modified cathode sample using PAA as the binder.

## A.2 SEM/EDS of the PVDF electrodes

### No-catalyst PVDF cathode

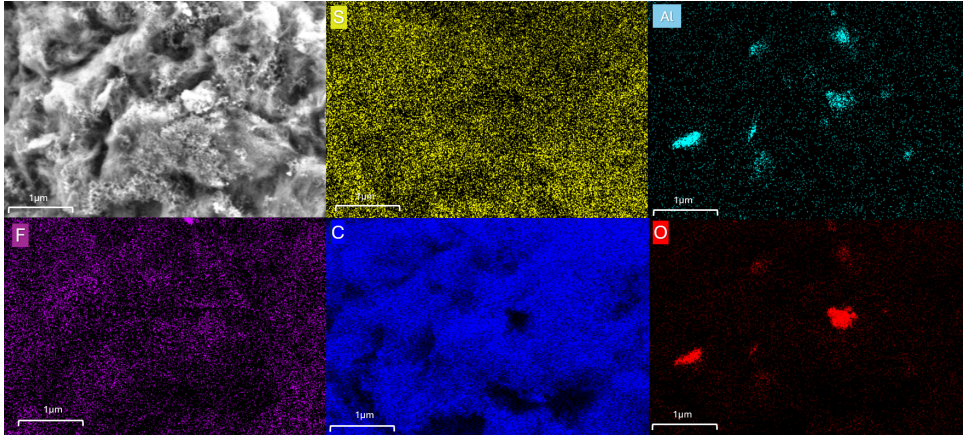
The PVDF reference electrode shows a homogeneous distribution of S, which is attributed to liquid NMP partially dissolving and redistributing elemental sulfur prior to drying. The binder is uniformly distributed, as evidenced by the F signal. Native aluminum oxide impurities are again present as larger clusters ( $\sim 600$  nm) and smaller features (100–200 nm).



**Figure A.4:** SEM micrograph and corresponding EDS elemental maps of the reference electrode fabricated with PVDF in NMP.

### PVDF cathode with $\sim 3$ nm TiN

The EDS mapping in Fig. A.5 confirms a homogeneous dispersion of both S and C across the film. Consistent with the other samples, sub-micron aluminum oxide particles remain locally visible.

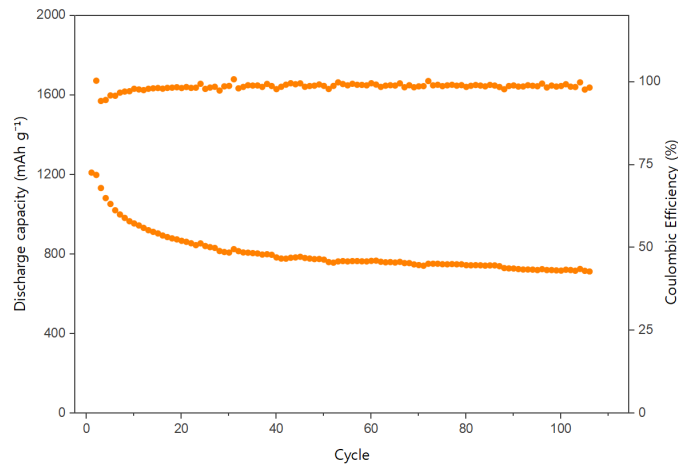


**Figure A.5:** SEM micrograph and corresponding EDS elemental maps of the  $\sim 3$  nm TiN-modified electrode using PVDF as the binder.

### A.3 More GCD measurements

#### PAA reference: without carbon black

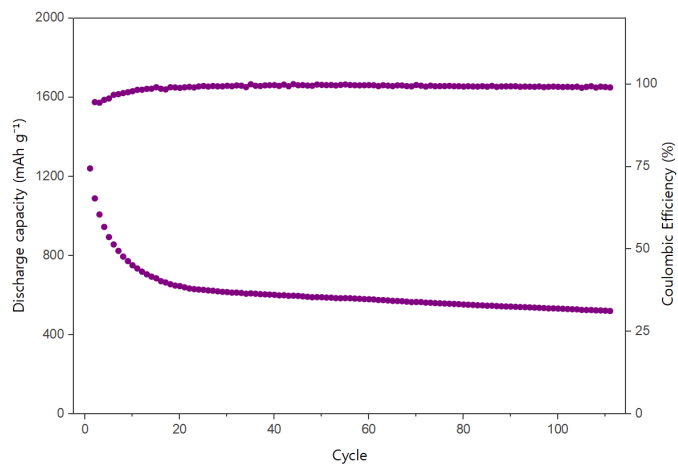
Fig. A.6 shows the performance at 0.1 C of a cell with a sulfur mass loading of  $1.95 \text{ mg cm}^{-2}$ . The cell delivered an initial capacity of  $1210.2 \text{ mAh g}^{-1}$  and stabilized at  $718 \text{ mAh g}^{-1}$  after 100 cycles (59.33% retention, 0.52% decay per cycle). However, consistently reproducing this high baseline performance proved challenging in subsequent trials.



**Figure A.6:** Galvanostatic cycling performance of the cell at 0.1 C without carbon black additives at a sulfur mass loading of  $1.95 \text{ mg cm}^{-2}$ .

#### PAA with low sulfur loading

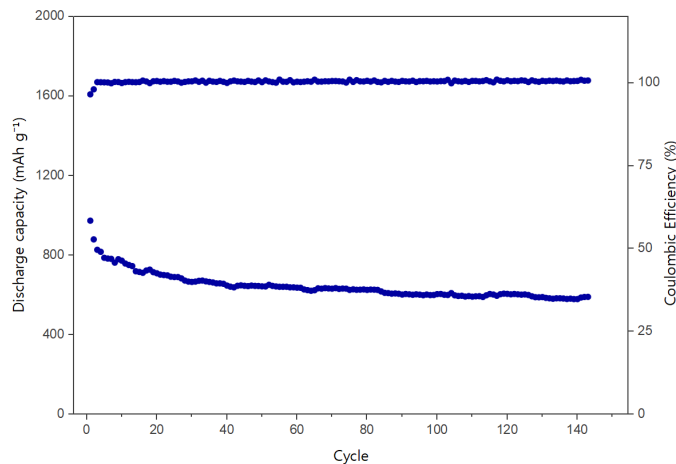
Fig. A.7 shows the performance of a cell with a lower sulfur loading of  $0.96 \text{ mg cm}^{-2}$ . The electrode delivered a high initial capacity of  $1217.3 \text{ mAh g}^{-1}$  but suffered rapid early capacity fading. The cell subsequently stabilized, maintaining a discharge capacity of  $550 \text{ mAh g}^{-1}$  after 120 cycles.



**Figure A.7:** Galvanostatic cycling performance of a PAA cell at 0.1 C with a lower sulfur mass loading of  $0.96 \text{ mg cm}^{-2}$ , showing a high initial discharge capacity followed by rapid early capacity fading.

### Experiment with higher MWCNT content

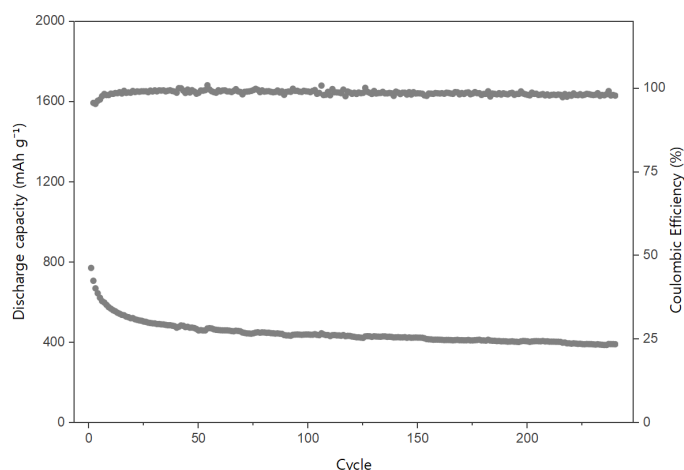
Fig. A.8 shows the performance of an electrode prepared with a lower S/MWCNT ratio of 65/35. At 0.1 C, the cell delivered an initial capacity of  $973.6 \text{ mAh g}^{-1}$  and maintained stable cycling at  $590 \text{ mAh g}^{-1}$  after 140 cycles (60.6% retention, 0.28% decay per cycle). An even lower carbon content (85/15) made slurry preparation and coating impossible, establishing the 75/25 ratio as the practical standard.



**Figure A.8:** Galvanostatic cycling performance of a cell utilizing a lower ratio of S/MWCNT (65/35 instead of the standard 75/25), yielding an initial discharge capacity of  $973.6 \text{ mAh g}^{-1}$  at 0.1 C.

### rGO-based electrode

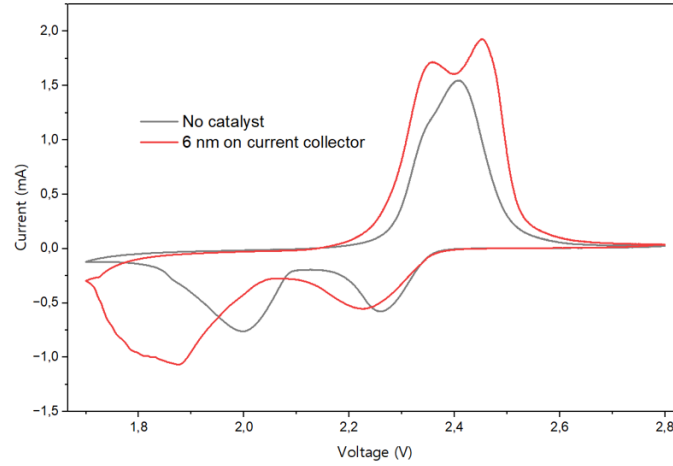
Fig. A.9 shows the performance of an rGO-based electrode at 0.1 C ( $1.94 \text{ mg cm}^{-2}$  sulfur loading). The cell delivered an initial capacity of  $772.5 \text{ mAh g}^{-1}$  and stabilized at  $390 \text{ mAh g}^{-1}$  after 240 cycles (50.49% retention, 0.21% decay per cycle). Because rGO performance was consistently lower than that of the MWCNT variants, it was not pursued further.



**Figure A.9:** The cycling profile of the rGO-based electrode, exhibiting a relatively low initial discharge capacity of  $772.5 \text{ mAh g}^{-1}$  at 0.1 C followed by stable long-term cycling.

**PAA reference CV: without carbon black**

Fig. A.10 shows the CV measurement of the no-catalyst baseline electrode without carbon black additives. The voltammogram displays well-defined peaks, confirming the baseline network supports charge transport, though it exhibits a larger peak separation than the catalyst-modified samples due to higher cell polarization.



**Figure A.10:** Cyclic voltammetry curve of the no-catalyst baseline PAA reference cell processed without extra carbon black additives.

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