

Imperial College London

A Model Based Approach to Identifying
Performance Limitations in Lithium-Sulfur
Batteries: From Coin to Pouch-Cells

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PhD Thesis

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Statement of Originality

I declare that the work discussed throughout this thesis is my work, completed over a four-year period. Where the work has been completed in collaboration with other groups or researchers, this is clearly referenced at the beginning, or throughout the relevant Chapter.

Elizabeth Chinue Olisa

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Abstract

Lithium-sulfur (Li-S) batteries offer a promising alternative to current lithium-ion (Li-ion) batteries, with a high theoretical energy density, improved safety and high abundance of low cost materials. To be used commercially, it is essential to understand how the behaviour scales between cell formats. Physical differences contribute to the behavioural differences, in terms of achievable capacity, cyclability and potential degradation mechanisms.

To improve understanding of the causes of the observed behaviour changes, both experimental and modelling work is required. This work focuses on the steps required to capture and test coin-cell behaviour, building upon the existing pouch-cell models within the literature. The 0D model first tests the experimental hypotheses proposed, before implementing upgrades to improve the capability in terms of scaling and causality of predictions. The first upgrade to the model is the removal of the assumption of total active material utilisation, and the introduction of pore volume directly. This creates separate regions inside the cell which are later used in a simplified transport mechanism; the location of species within each region enables the 0D model to capture C-rate dependence. The following upgrade is to the porosity and area equations, creating separate dependencies on the influence of electrolyte volume and wetting, and precipitation leading to pore blocking. The model then separates the precipitation mechanism, accounting for both nucleation and particle growth, rather than assuming one mechanism occurs consistently throughout cycling.

The final model makes significant improvements to the capability and applicability of existing models; it captures many experimentally observed features that vary when scaling between cell formats, confirming the upgraded mechanisms are at least one explanation for the behaviour. Further work focusing on cell chemistry and degradation mechanisms is required for the model to be used alongside experimental testing to help determine the optimum conditions during cell manufacture.

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List of Acronyms

BMS	Battery Management System
BP	BuckyPaper Electrode
CNT	Carbon Nanotubes
DoD	Depth of discharge
DOL/DME	1,3-dioxolane/1,2-dimethoxyethane
DMF	Dimethylformamide
DryFilm	Powder-based Dry Transfer Electrode
ECM	Equivalent Circuit Network Model
E/S	Electrolyte to Sulfur Ratio
GO	Graphene Oxide
ICF	Innventia Carbon Fibres
LFP	Lithium Iron Phosphate
Li-ion	Lithium-Ion
LiNO ₃	Lithium Nitrate
Li-S	Lithium-Sulfur
LiSTAR	Lithium Sulfur Technology Accelerator Research
LiTFSI	Lithium Bis(trifluoromethane)sulfonimide
NaOH	Sodium Hydroxide
Na-ion	Sodium-Ion
NMC	Nickel Magnesium Cobalt
OCV	Open Circuit Voltage
ODEs	Ordinary Differential Equations
SEM	Scanning Electron Microscopy
SoC	State of Charge
S/C	Sulfur to Carbon Ratio
Wt%	Weight Percent
X-ray CT	X-ray Computed Tomography
0D	Zero-dimensional
1D	One-dimensional
3D	Three-dimensional

List of Symbols

Nomenclature	Description	Units
i	<i>Subscript representing S_8, S_4, S_L, S_p, $S_{p(growth)}$, $S_{p(nuc)}$</i>	-
H, M, L	<i>Subscripts representing high, medium, low</i>	-
A	Avogadro's constant	mol^{-1}
a_r	Positive electrode surface area	m^2
a_{r0}	Initial positive electrode surface area	m^2
a_{coin}	Coin-cell area	m^2
a_{geom}	Geometric surface area	m^2
a_{growth}	Particle growth surface area	m^2
a_{spec}	Specific area	$\text{m}^2 \text{g}^{-1}$
b	Conductivity fitting parameter	$\text{S m}^2 \text{mol}^{-1}$
β	Beta (fitting parameter)	-
CLi	Concentration of lithium	mol L^{-1}
CLi_0	Initial concentration of lithium	mol L^{-1}
CS^*	Saturation concentration	mol L^{-1}
CS_i	Concentration of sulfur species in the electrode	mol L^{-1}
$CS_{i\text{cathres}}$	Concentration of species in the positive electrode (cathode) reservoir	mol L^{-1}
$CS_{i\text{res}}$	Concentration of species in the reservoir (<i>when assuming two regions within cell</i>)	mol L^{-1}
$CS_{i\text{sep}}$	Concentration of species in the separator	mol L^{-1}
$CS_{i\text{sepres}}$	Concentration of species in the separator reservoir	mol L^{-1}
$\frac{dCS_i}{dt}$	Rate of change of concentration of species in positive electrode	$\text{mol L}^{-1} \text{s}^{-1}$
$\frac{dCS_{i\text{cathres}}}{dt}$	Rate of change of concentration of species in the positive electrode (cathode) reservoir	$\text{mol L}^{-1} \text{s}^{-1}$
$\frac{dCS_{i\text{sep}}}{dt}$	Rate of change of concentration of species in separator	$\text{mol L}^{-1} \text{s}^{-1}$
$\frac{dCS_{i\text{sepres}}}{dt}$	Rate of change of concentration of species in the separator reservoir	$\text{mol L}^{-1} \text{s}^{-1}$
$\frac{dS_i}{dt}$	Rate of change of mass of species	g s^{-1}
DS_i	Transport coefficient (<i>when assuming two regions within cell</i>)	s^{-1}
$DS_{i\text{cathres}}$	Positive electrode (cathode) reservoir transport coefficient	s^{-1}
$DS_{i\text{sep}}$	Separator transport coefficient	s^{-1}
$DS_{i\text{sepres}}$	Separator reservoir transport coefficient	s^{-1}
$DS_{i\text{res}}$	Positive electrode (cathode) and separator reservoir transport coefficient	s^{-1}
ε	Porosity	-
ε_0	Initial porosity	-
$\frac{E}{S}\text{ratio}$	Electrolyte to sulfur ratio	$\mu\text{l mg}^{-1}$
E_H, E_M, E_L	Nernst potentials	V
E_H^0, E_M^0, E_L^0	Standard potentials	V
E_{nuc}	Nucleation potential	V
F	Faraday's constant	C mol^{-1}

f_H, f_M, f_L	Dimensionality constants	-
i_H, i_M, i_L	Partial currents	A
i_H^0, i_M^0, i_L^0	Exchange current density	A m ⁻²
I	Current	A
I_{coin}	Coin-cell current	A
I_{pouch}	Pouch-cell current	A
j	Current density	A m ⁻²
$k_{p/d}$	Precipitation / dissolution rate	(m ² s) ⁻¹
k_s	Shuttle rate	s ⁻¹
K_{Sp}	Solubility product	mol ³ m ⁻⁹
l	Positive electrode thickness	m
$\text{mass}_{\text{electrode}}$	Electrode mass	g
$\text{mass}_{\text{sulfur}}$	Sulfur mass	g
$\text{mass}_{\text{sulfur}_{\text{coin}}}$	Coin-cell sulfur mass	g
$\text{mass}_{\text{sulfur}_{\text{pouch}}}$	Pouch-cell sulfur mass	g
$\text{mass}_{\text{sulfur}_{\text{usable}}}$	Usable sulfur mass	g
M_S	Molar mass of S ₈	g mol ⁻¹
n	Fitting parameter (within β equation)	-
n_H, n_M, n_L	Number of electrons per reactions	-
η_H, η_M, η_L	Overpotentials	V
ns_i	Number of sulfur atoms	-
nuc_{var}	Nucleation rate	L mol ⁻¹ s ⁻¹ m ⁻²
σ	Conductivity	S m ⁻¹
σ_0	Initial conductivity	S m ⁻¹
$\rho_{\text{CNT}_{\text{sheet}}}$	Density of CNT sheets (<i>assuming no loaded sulfur</i>)	g cm ⁻³
ρ_s	Density of sulfur	g L ⁻¹
$\rho_{\text{single}_{\text{CNT}}}$	Density single CNT (<i>before formed into a sheet</i>)	g cm ⁻³
r	Radius of precipitation sulfur atom	m
R	Gas constant	J mol ⁻¹
R_{ohm}	Resistance	Ω
r_p	Precipitation rate of Li ₂ S ₁	s ⁻¹
S^*	Saturation mass	g
S_i	Mass of sulfur species	g
$S_{i_{\text{res}}}$	Mass of sulfur species in the reservoir	g
T	Temperature	K
v	Usable electrolyte volume	L
V or V_{cell}	Cell voltage	V
$v_{\text{cath}_{\text{res}}}$	Volume in the positive electrode (cathode) reservoir	L
v_{CNT}	CNT volume	L
$V_{\text{electrode}}$	Electrode voltage	V
$v_{\text{electrolyte}}$	Electrolyte volume	L
v_{excess}	Excess volume	L
$v_{\text{Li}_2\text{S}}$	Volume fraction of Li ₂ S ₁ with respect to cell voltage	-
$V_{\text{Li}_2\text{S}_1}$	Molar volume of Li ₂ S ₁	m ³ mol ⁻¹
V_{losses}	Voltage losses	V
V_{neg}	Negative electrode voltage	V
V_{Nernst}	Nernst voltage	V

vol_{Li_2S}	Volume of Li_2S_1	L
$vol_{semisphere}$	Volume of semi-sphere	L
V_{pore}	Pore volume	L
$V_{pore/gram}$	Pore volume per gram	$cm^3\ g^{-1}$
V_{pos}	Positive electrode voltage	V
V_r	Reservoir volume	L
V_{sep}	Separator volume (total)	L
$V_{sep\ pore}$	Separator pore volume	L
$V_{sep\ res}$	Volume in the separator reservoir	L
V_{Sp}	Volume of precipitated sulfur	L
V_{sulfur}	Sulfur volume	L
$V_{terminal}$	Terminal voltage	V
$V_{tot\ electrode}$	Total electrode volume	L
V_{usable}	Usable volume	L
x	Number of positive electrode layers	-
x_{nuc}	Number of nucleation layers	-
γ	Gamma (area fitting parameter)	$m^2\ g^{-1}$
Y	Area fitting parameter (Zhang et al. [1])	-
Z	Fitting parameter	-

Introduction

Context

With the global aim towards reducing reliance on fossil fuels, the focus has shifted towards renewable energy generation methods and the use of batteries for energy storage. Currently, lithium-ion (Li-ion) is the dominating chemistry, for all applications from mobile phones to electric cars. To meet the growing demand, other cell chemistries are required. Lithium-sulfur (Li-S) batteries are one of the alternative options.

Significant testing is required to fully understand the mechanisms occurring inside a cell, under all conditions it is likely to be exposed to. To do this, varying cell formats are used, for reasons discussed in detail throughout this thesis. These formats include coin-cell, pouch-cell, prismatic-cell and cylindrical-cell [2]. For material development, coin-cells are predominately used, whilst commercial applications are likely to require pouch-cell or larger formats. However, each format has been found to behave differently, and investigation is required to understand why and how to mitigate these changes. Without this capability, successful developmental work at coin-cell level may not translate to a successful commercial pouch-cell.

Research Objectives

The research discussed throughout this thesis works towards understanding the mechanistic differences between coin and pouch-cells, and the reasons why these lead to behavioural differences. To do this, both experimental and modelling work was completed; the experimental work was required to obtain data for use to parameterise the model. The model was then be used to test the hypothesised mechanisms against both coin and pouch-cell behaviour. The knowledge gained through both processes became essential when making decisions relating to the model development, parameterisation and analysis.

The following questions will be answered to reach this aim:

- 1) How do the physical differences between coin and pouch-cells result in mechanistic differences?
- 2) To what extent do the existing models capture coin-cell behaviour?
- 3) What changes are required to the existing models to capture these mechanistic differences?

Structure

Introduction: This provides general context to the project, summarising the Research Questions this work is aiming to answer.

Chapter 1 (Literature Review): This Chapter provides an overview of Li-S cell chemistry, including the capabilities, limitations and applications. A review of the modelling and experimental work currently being completed created the overall plan for this project.

Chapter 2 (Experimental Positive Electrode Development): This Chapter provides details of the experimental work completed using coin-cells, working towards developing a data set to use to parameterise a later model.

Chapter 3 (Re-parameterising and Testing Existing Coin-Cell Models): This Chapter reviews the existing Li-S models in more detail, selecting Cornish et al. [3] for use preliminarily to adapt and test coin-cell behaviour.

Chapter 4 (Coin-Cell Model Development): This Chapter builds upon the areas of further work recognised through testing the Cornish et al. [3] model, discussing each model upgrade, why it was required and the impact it had.

Chapter 5 (Final Coin-Cell Model): This Chapter summarises all the model upgrades, testing the capability of the model when all are implemented together. The extent to which the model captures physical and mechanistic differences when scaling between cell formats is investigated.

Chapter 6 (Improving Model Predictions): This Chapter provides an overview of further work, some of which has begun, to improve the capability of the model.

1 Chapter 1: Literature Review

Some of the work within the Literature Review was part of work submitted for the internal Early Stage Assessment (ESA) at Imperial College London.

1.1 Introduction to Batteries

A battery, or collection of cells, is a system that converts chemical energy into electrical energy, and is often rechargeable, dependent on the components, allowing continuous charging and discharging [4]. The use of batteries as an energy storage system is essential to meet the increasingly large demand and growing range of applications. For example, with the shift towards renewable energy sources, the maximum energy generation through solar or wind sources may not align with the peak in energy demand, which can be addressed using batteries to provide the correct amount of energy as and when needed. Alternatively, within electric vehicles, a battery replaces an internal combustion engine and the dependence on fossil fuels.

There are many applications for batteries, including stationary storage such as homes and buildings, and mobile storage such as vehicles. The requirements for each vary significantly; for example, the volumetric energy density of a battery used for stationary storage is less critical than for mobile storage, where space and mass are the most important factors to consider [5]. The use of a high power or high energy battery also varies dependent on the application; a high energy battery provides energy over a long period of time, whilst a high-power battery provides a large amount of energy quickly, over a short period of time [6]. Li-S are considered high energy.

1.1.1 How Does a Cell Work?

A cell consists of a positive electrode and a negative electrode [4]. Each electrode produces electrically charged ions, which can travel between the electrodes dependent on their charge and the cycling conditions. The charged ions travel between the electrodes inside the cell, whilst electrons flow between electrodes in the outer circuit, generating a current [4]. Between these two electrodes is a separator, which prevents direct contact [6]. To allow ions to move around within the cell, a liquid electrolyte is typically used.

1.1.2 Li-ion Cells

Li-ion is the most common cell chemistry, with varying positive electrode materials, such as lithium iron phosphate (LFP) or nickel magnesium cobalt (NMC) [7]. The negative electrode is typically graphite. Li-ion works through an intercalation mechanism, whereby the electrodes allow reversible insertion and extraction of lithium cations (Li^+) [7]. Li-ion have a long lifecycle, a high energy density and a high operating voltage [7]. Dependent on the material, they can be used for both high power and high energy applications. Although Li-ion cells are used commercially over a wide range of applications, there are remaining problems including a protection requirement to prevent overcharging, calendar aging [8] and the ethics associated with sourcing the materials [9]. In addition, the availability and associated costs of the materials has led to the research and development of new cell chemistries, including Li-S and sodium-ion (Na-ion).

1.1.3 Li-S Cells

A Li-S cell is similar to a Li-ion cell, replacing the positive electrode material with a carbon host and using sulfur as the active material. As sulfur is insulating [10], the carbon host is required as the conductive element within the electrode [6]. The negative electrode is typically pure lithium [10]. The reaction mechanisms differ in a Li-S cell compared to Li-ion; a conversion mechanism occurs, meaning reactants form entirely new products [11] rather than forming reversible products by insertion of ions into the host material [12]. The conversion-type reactions enable Li-S cells to be stored and transported in a fully discharged state, improving the overall safety in comparison to Li-ion cells [13]. However,

the conversion mechanisms can result in a significant change in structure of the positive electrode, meaning the properties of the carbon host become very important.

Li-S is a likely alternative chemistry to the current Li-ion cells for high energy density applications [6]. They offer a significantly higher theoretical energy density compared to Li-ion, at 2,700Wh/kg [14] compared to 300Wh/kg [15] respectively, where kg refers to the mass of the cell. Although the practical energy density is reduced, at 450Wh/kg [16] for Li-S compared to 210Wh/kg [17] for Li-ion, it remains higher. This is important for many applications, including those within the defence and aerospace sectors that prefer high energy density over high power density chemistries [6]. The improved safety in comparison to Li-ion and higher tolerance to extreme temperatures [18] also makes Li-S competitive for aerospace applications, such as unmanned air vehicles (UAVs) and pseudo satellites [18].

The active material, sulfur, is low in toxicity and high in abundance [6]. The sulfur mining process is also considered more ethical than for other materials, such as cobalt [19]; the availability and accessibility to high quality and ethically sourced materials is an important consideration for future development. Separately, the nature and composition of Li-S cells means materials can easily be separated during cell disassembly, improving the ability to recycle the components at the end of life [20]. With legislation being introduced to reduce the amount of waste products within the lifecycle [20], this is critical for new cell development.

Figure 1 is a Ragone plot created by Cha et al. [21] showing the capability of cell chemistries based on the specific and volumetric energy density. Further development is expected to increase both the specific and volumetric energy density of Li-S. To do this, several key challenges must first be overcome, to reach commercial application. Firstly, as one of the largest degradation mechanisms occurring, polysulfide shuttle causes infinite charging and leads to irreversible capacity fade [22].

Secondly, due to the conversion mechanism, precipitation occurs on the electrode surface, leading to a reduction in surface area and limiting the cycling performance [22]. Thirdly, side reactions between highly reactive lithium and other components within the cell, including the electrolyte, consume active material, and can lead to degradation mechanisms such as uneven plating and stripping, and undesired SEI formation [6]. Whilst there are other mechanisms that impact the behaviour, collectively these mechanisms significantly reduce the cycle life of Li-S, which is a key criterion for commercial application. In comparison, a Li-S cell will run for approximately 300 cycles [23] while a Li-ion cell will run for 2000 cycles [24]. Although work is underway to improve the cycle life, it is unlikely to match that of Li-ion [25] without significant improvements to these mechanisms.

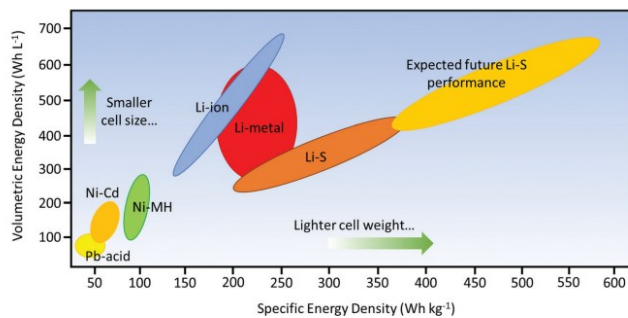


Figure 1: Ragone plot of various cell chemistries, taken from Cha et al. [21]

1.2 Structure of a Li-S Cell

As previously discussed, a Li-S cell comprises two electrodes, a separator and electrolyte. The schematic of these components in a coin-cell is shown in Figure 2.

1.2.1 Positive Electrode (Cathode)

The positive electrode, or cathode, is made of sulfur and a carbon host. The carbon scaffolding acts as a conductive host material and enables electrochemical reactions to occur through the creation of electronic pathways [6]. The electrochemical conversion reactions within a Li-S cell occur on the surface of the positive electrode, within the pores [6], also known as reaction sites. A porous carbon structure that can be highly wet by the electrolyte is ideal [18], as it improves ionic transport [6] and enables more reaction sites to be utilised. As sulfur is insulating, it must be in contact with the carbon for electrons to be removed and electrochemical reactions to take place [4].



Figure 2: Coin-cell schematic diagram, taken from [37]

A compromise between the ratio of insulating sulfur and conductive carbon is required. An ideal cell has a high proportion of active material, achieved through increasing the sulfur loading or weight percent (wt%), with minimal but sufficient carbon for electrochemical reactions to occur. As carbon is not an active material, it is considered as dead mass within the cell and reduces the energy density; dead mass contributes to the mass of the cell but is not directly involved in electrochemical reactions. The sulfur to carbon (S/C) ratio is optimised during manufacture.

The structure of the carbon host plays a significant role in the performance; for example, the mechanical stability is an important requirement to withstand the associated volumetric changes when conversion reactions occur inside the pores [6], particularly evident in pouch-cells. Significant advances in the performance have been made using nanocarbon materials [23], based on the high electrical conductivity and variable surface area [26]. Dependent on the formation of the electrode, a current collector may be required and is typically made of aluminium [27]. An electrode without a current collector is considered freestanding. Where a current collector is used, a binder is required to attach the electrode to the current collector [28]; a binder with a high degree of elasticity is required to accommodate for the volumetric changes [6] [29]. The cause and impact of volumetric changes is discussed in detail in Section 1.3.2.

1.2.2 Negative Electrode (Anode)

The negative electrode, or anode, is a pure lithium metal foil. Lithium metal is electronically conductive and highly reactive [30], which contributes to the relatively high voltage of the cell [31]. It is the lightest metal [30], a desired characteristic for commercial cells where a low mass is required. Typically, the lithium is included in excess to the sulfur; due to the high reactivity, it is common for side reactions to occur, depleting the total lithium available for electrochemical reactions [10].

Due to the conversion mechanism for Li-S, Li^+ do not interpolate inside the lithium metal of the negative electrode as the cell cycles [10], meaning there is no change to the internal structure. Instead, Li^+ precipitate on top, leading to the plating and stripping mechanism during cycling. This is explained in detail in Section 1.3.2.

1.2.3 Electrolyte

The electrolyte comprises an electrolyte salt and a solvent [32]. Throughout the thesis, the reference to electrolyte implies both the salt and the solvent combined.

All reactions in the cell occur in the electrolyte within the positive electrode pores [6]. Lithium polysulfides of varying chain length are produced from the reaction between sulfur and lithium [33], as the cell charges and discharges. The reactants and products of these reactions are contained and move around the cell within the electrolyte. When precipitation of lithium polysulfides on the surface of the positive electrode occurs at the end of discharge [6], the species are no longer contained within the electrolyte. The precipitation of species can lead to pore blocking, reducing the available area and number of reaction sites for electrochemical reactions [22].

For Li-S, the electrolyte solvent is usually ether-based due to the high solubility of lithium polysulfides [34]. The salt is typically lithium bis(trifluoromethane)sulfonimide (LiTFSI). The ratio of solvent volume and salt mass within the electrolyte influences the concentration of the solution and the behaviour of the cell. Additives can also be added to the electrolyte to influence the behaviour; for example, lithium nitrate (LiNO_3) is used to suppress polysulfide shuttle by reacting with lithium and building a robust SEI layer on the surface of the negative electrode to prevent further reactions [6], [35].

The electrolyte volume is one of the largest components within the cell, contributing most significantly to the mass. Typically, it is included in excess to other components, particularly for coin-cells when used for new material testing [18]. For commercial use, a low electrolyte volume is required to achieve a high gravimetric energy density [18]. The volume of electrolyte is determined by the electrolyte to sulfur (E/S) ratio; this ratio varies between cell formats, typically being much lower for larger cell formats.

1.2.4 Separator

The separator is located between the positive and negative electrodes, as shown in Figure 2. Similarly to the positive electrode, the separator is porous, meaning it is wetted by the electrolyte. During cycling, Li^+ travel through the separator between the electrodes [6]. After reacting with sulfur, the lithium polysulfides formed should be contained between the positive electrode and separator; however, it is possible for the species to travel back through the separator towards the negative electrode, which can lead to the degradation mechanisms such as polysulfide shuttle [10], [18]. Along with travelling through, the species can also be trapped within the pores of the separator [6]; an ideal separator would block the species travelling through, and experimental work is underway to determine how to achieve this [18].

1.2.5 Scaling: Differences in Cell Formats

There are various sizes of cells, predominately coin, pouch and cylindrical [2]. The components remain relatively similar for each, with the addition of tabs in larger cell formats, and varying casing. Bridgewater et al. [2] discusses the main differences between coin-cells, single-layer pouch-cells and multi-layer pouch-cells for Li-ion. The majority of these differences are applicable to Li-S, including the geometric size and manufacturing methods [2]. Separately, Dörfler et al. [36] investigated the differences in scaling for Li-S, with respect to the challenges and key parameters.

One of the key differences when manufacturing the varying size cells is the casing. The casing is used to house the components within the cell and is classed as dead mass. For a coin-cell, the casing is metal and rigid and is crimped together at the end of manufacture [37]. To maintain constant pressure and contact between the electrodes, internal springs and spacers are also used. In pouch-cells, the casing is plastic and is vacuum sealed at the end of manufacture [38]. External pressure is typically applied to ensure contact between the electrodes, but this can allow for more significant volumetric changes within a pouch-cell. In addition to the differences in casing, pouch-cells or larger cell formats require tabs to

connect to the external circuit, which contribute to the resistance within the cell, along with additional dead mass [36].

For Li-S, cylindrical cells often experience failure, explained by the inhomogeneous compression when the materials are rolled into a tight cylindrical configuration, leading to uneven degradation and utilisation of material [2]. For this reason, pouch-cells are typically considered and used for commercial application. This thesis will focus on coin and pouch-cells, and the main differences are summarised in Table 1.

Component	Coin-Cell	Pouch-Cell
Positive Electrode	Small, circular, single-sided	Large, rectangular, double-sided
Layers	Single	Multiple
Mass	Excess electrolyte contributing to dead mass (low energy density)	Less excess of materials (high energy density)
Packaging	Consistent, uniform internal pressure (hard casing, spacers, spring)	Variable, external pressure (soft casing)
E/S Ratio	High: large electrolyte excess ensuring full positive electrode utilisation, and preventing electrolyte as limiting factor	Low: minimal electrolyte to achieve high energy density

Table 1: Summary of the physical differences between coin and pouch-cells

1.3 Li-S Mechanisms

1.3.1 Charge and Discharge Mechanism

The positive electrode is the electrode with higher potential with respect to the reaction, and the negative electrode with lower with respect to the reaction [6]. These are also described as the cathode and anode, relating to the redox reaction, and whether charging or discharging [6]. The reduction or oxidation of species only occurs at the carbon/sulfur electrode. In discharge, carbon/sulfur is the positive electrode or cathode, and the lithium is the negative electrode or anode. For simplicity, the carbon/sulfur is referred to as the positive electrode, and the lithium as the negative electrode throughout the thesis.

Many reactions occur within a Li-S cell [10]. Some are essential for successful cell function, others are detrimental, and some are not yet fully understood. To develop a commercially viable cell, all mechanisms that impact the cell performance need to be accounted for. The overall reaction between sulfur and lithium [6] is shown in Equation [1].



The respective half-reactions at are shown in Equations [2] and [3].



During discharge, lithium on the surface of the negative electrode is oxidised, forming lithium cations, Li^+ , and providing electrons into the outer circuit [10]. Sulfur on the surface of the positive electrode is reduced, consuming the electrons that have travelled from the negative electrode in the outer circuit, and forming sulfur anions, S^{2-} . Li^+ travel from the negative electrode, through the electrolyte to the positive electrode. Li^+ reacts with the S^{2-} to form long chain polysulfides, for example Li_2S_8 . The reactions to form lithium polysulfides only occur on the surface, at the interface between the positive electrode and electrolyte, and require electrons from the outer circuit [6]. As the cell continues to discharge, Li^+ continues to react with S^{2-} and these long chain lithium polysulfides, breaking them down

to form intermediate and short chain lithium polysulfides. The chain length species can vary between Li_2S_8 and Li_2S_1 [6], dependent on the cell materials and cycling conditions. The shorter chain length species, typically Li_2S_1 and Li_2S_2 , then precipitate via a chemical reaction onto the positive electrode surface. The cell reaches full discharge when all the lithium polysulfides reach the shortest chain length. Within a real cell, there are various reasons why the end of discharge may be reached before this, for example due to time or voltage limits.

The opposite process takes place during charge; oxidation occurs at the positive electrode, providing electrons that travel to the negative electrode in the outer circuit [10]. As these electrons are pulled from the positive electrode, a Li^+ is released from the lithium polysulfides, leading to the formation of longer chain lithium polysulfides. The Li^+ travel from the positive electrode, through the electrolyte to the negative electrode, where they gain an electron and are deposited as metallic lithium onto the negative electrode surface [6]. Theoretical full charge is reached when all the Li^+ have travelled back to the negative electrode, leaving only sulfur on the surface of the positive electrode [33]. Similarly to during discharge, the end of charge may be reached before this occurs for several reasons. During either charge or discharge, the flow of negative ions in the electrolyte and electrons in the outer circuit needs to match the flow of positive ions.

At the beginning of charge, a larger amount of energy is required to dissolve the precipitated lithium polysulfides [6], before further reactions to form longer chain species can occur. This also applies at the beginning of discharge, if the long-chain species, Li_2S_8 , have precipitated in the previous charge [6].

The voltage curves associated with charge and discharge have two distinct plateaus, an upper and a lower plateau, as shown in Figure 3. The upper plateau relates to the reactions forming longer to intermediate chain lithium polysulfides: for example, Li_2S_8 , Li_2S_6 and Li_2S_4 [39]. The lower plateau relates to short chain lithium polysulfides: for example, Li_2S_2 and Li_2S_1 [40]. The exact number and order in which the lithium polysulfides form has not yet been confirmed within the research community [6], however, the existence of some species is more agreed upon than others. It is possible for different chain lengths to appear simultaneously [6].

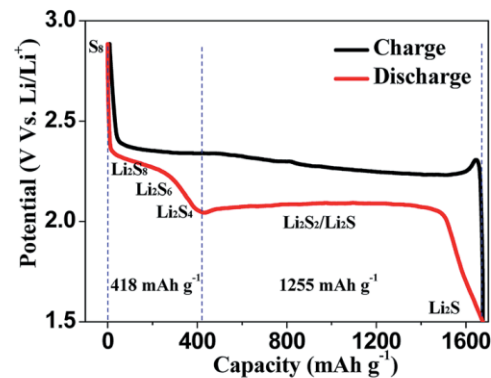


Figure 3: Li-S voltage capacity graph, taken from J. Guo and L. Liu [123]

1.3.1.1 Precipitation Dynamics

At the beginning of charge, a large amount of energy is required to dissolve the precipitates, corresponding to the jump in voltage that appears [17], as shown in Figure 3. A dissolution bottleneck is more likely following a discharge with high depth-of-discharge (DoD), where more precipitates have formed. The bottleneck can result in a lower achieved capacity as the species remaining in precipitated form cannot contribute to further electrochemical reactions [41].

During discharge, a voltage kink can be observed at the transition from high to low plateau, relating to the point at which species begin precipitating [17]. A slow precipitation reaction results in an accumulation of short chain species before they can precipitate, resulting in a larger kink. Precipitation can only occur once the saturation concentration has been reached [6]. The precipitation of species leads to blocking of available pores on the electrode surface, reducing the active surface area and limiting performance in terms of achieved capacity and cyclability [22]. Precipitation also limits the reaction pathways, increasing the tortuosity throughout the electrode, and potentially leaving regions inaccessible for reactions [6].

1.3.1.2 Voltage

The terminal voltage is the potential difference between the positive and negative electrodes [6], as shown in Equation [4], and is equivalent to the half-cell reactions at each electrode. It is also equivalent to the open-circuit voltage (OCV), measured when there is no current flowing [6] and assuming no losses. At equilibrium, the positive and negative electrode voltages are equal [6].

The internal resistance works against the direction of reactions. There are various sources of internal resistance within a cell, including electrolyte and charge-transfer resistance [1]. Measurements during experimental work by Zhang et al. [1] found that the electrolyte resistance was dominant in the high plateau region, and charge-transfer resistance was associated with the low plateau region. The external resistance within the outer circuit that the electrons flow through is calculated separately. Resistances contribute to various losses, including the Ohmic change [6]. The cell voltage is the measured output voltage, and is calculated from the terminal voltage, along with mechanisms that contribute to losses, including this Ohmic change, as shown in Equation [5]. During charge, the current is typically negative, and during discharge, it is typically positive. With increasing current, the cell voltage increases during charge and decreases during discharge, based on the Ohmic change.

During reactions, a reactant becomes a product. To reach the final product, there may be transition species that the reactant must overcome, some of which may be unstable configurations [6]. These transition state unstable species have higher energies and electrochemical potentials, meaning they require a higher activation energy [6]. To overcome the associated voltage, an overpotential is required, calculated as the difference between the equilibrium potential and potential required to form the species [42]. The electrode voltage is calculated with respect to this overpotential and the Nernst potential, as shown in Equation [6].

$$V_{\text{terminal}} = V_{\text{pos}} - V_{\text{neg}} \quad [4]$$

$$V_{\text{cell}} = V_{\text{terminal}} - V_{\text{losses}} = V_{\text{terminal}} + IR \quad [5]$$

$$V_{\text{electrode}} = \eta + V_{\text{Nernst}} \quad [6]$$

The change in cell voltage, as observed in Figure 3, occurs during cycling due to the change in number and distribution of species. Each chain length species is associated with a different voltage; longer chain species have a higher voltage, whilst shorter chain species have a lower voltage [10].

1.3.1.3 Current, and C-rate

Typically, the cell is cycled under constant current. A higher current increases the rate of reactions, both electrochemical and degradation [6]. As there is faster transport of the species at higher currents, for example diffusion, the limitations of these mechanisms also increase, and is typically observed with a reduced capacity [6].

1.3.2 Degradation

The theoretical performance of Li-S is calculated at the beginning life, without accounting for degradation mechanisms or losses. The actual performance, for example in terms of capacity and cyclability, is significantly lower. There are various degradation mechanisms that influence the cell behaviour differently during cycling [10], or dependent on manufacturing conditions. The largest degradation mechanism is polysulfide shuttle, which contributes to infinite, or incomplete charging [43]. Volumetric expansion [44] to both the positive and negative electrode can contribute to a loss in active material and area, and changes in electrode structure, including potential rupture [6]. Dendrite formation due to continuous uneven lithium plating and stripping on the negative electrode can cause cell short-circuiting and a loss of active material [10]. Side reactions between components, consuming active material but not contributing to electrochemical reactions, also results in a loss of active material, reducing the achievable capacity [10]. Taken from Wild et al. [10], Figure 4 summarises the degradation mechanisms occurring within a Li-S cell.

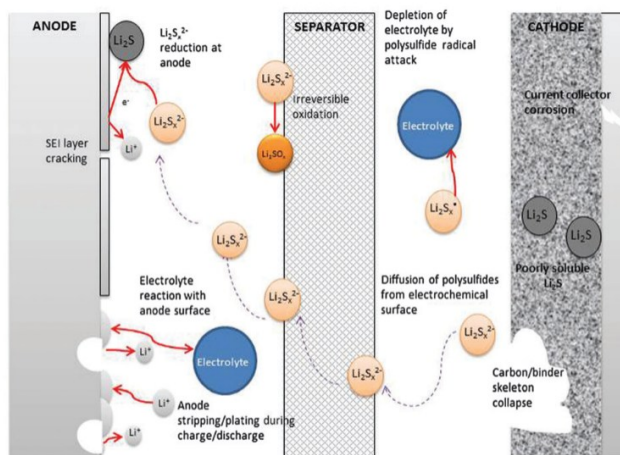


Figure 4: Schematic diagram of degradation mechanisms occurring, taken from Wild et al. [10]

1.3.2.1 Polysulfide Shuttle

Under ideal conditions, the dissolved lithium polysulfides would stay within or nearby to the positive electrode, in the region between the positive electrode and the separator; only Li^+ should travel back to the negative electrode during charge [6]. At the end of charge, the lithium polysulfides are fully oxidised to the longest chain species, which are highly soluble and highly mobile [6]. If they travel to the negative electrode, rather than remaining within the positive electrode region, they can consume an electron and be reduced to shorter-chain species; the electron bonds with the lithium polysulfides rather than Li^+ to form metallic lithium [10]. This reaction increases the concentration of intermediate lithium polysulfides at the negative electrode, creating a concentration gradient. This causes the species to travel back to the positive electrode through diffusion, creating a parasitic current opposing the charging current [6]. At the positive electrode, the intermediate lithium polysulfides are re-oxidised, forming longer chain lithium polysulfides, and then travelling back to the negative electrode [10]. Without change to the conditions, this continues and results in infinite charging, shown as a flat upper voltage plateau rather than a spike towards the maximum voltage [43], as full charging conditions are never reached. The shuttling current can also lead to internal self-heating of the cell [6].

To make Li-S cells a viable option with a competitive cycle life, work is underway to minimise the effect of polysulfide shuttle. The influence of shuttle is reduced at higher current rates as there is less time for the species to be reduced at the negative electrode [6]. Early research by Mikhaylik et al. [43] found that increasing the salt concentration within the electrolyte reduced the shuttle reaction. Other chemistry-based changes such as incorporating additives into the electrolyte, for example LiNO_3 [18], have been found to reduce shuttle through the impact on the SEI layer on the negative electrode surface [45]. LiNO_3 is also hypothesised to help convert lithium polysulfides to elemental sulfur towards the end of charge [6]. However, this method is unlikely for commercial use as LiNO_3 is depleted during cycling due to side reactions, contributing to capacity fade [6], along with swelling at temperatures over 40°C [46]. Another method to suppress shuttle involves creating protection layers on the electrodes to trap the lithium polysulfides, such as a free standing multi-walled carbon nanotube (MWCNT) on the positive electrode [47]. Modified separators are also being investigated [18], which work to physically

obstruct lithium polysulfides from travelling through. Further work is required to understand the influence modified separators and other shuttle-prevention layers have on the mass of the cell, cyclability and related costs if manufactured on a large scale [18].

Alternatively, without modifying the cell chemistry, it is common to set upper and lower voltage limits. The value varies based on several factors, including the aim of experimental testing, or the materials within the cell [6]. An upper voltage limit is used to reduce the likelihood of polysulfide shuttle occurring towards the end of charge, by preventing it reaching the shuttling region. A lower voltage limit reduces possible degradation of specific components, such as the additive LiNO_3 [18]. By limiting the voltage range, the cell is only operating in a portion of the total range; whilst this can reduce the achievable capacity, it also reduces potential degradation mechanisms occurring, which works towards increasing the cycle life.

1.3.2.2 Volumetric Expansion

Volumetric expansion is caused by precipitation and dissolution of lithium polysulfides on the positive electrode, and plating and stripping of lithium on the negative electrode [44]. The volumetric expansion of the negative electrode is more significant than the positive electrode [44].

1.3.2.2.1 Precipitation

Lithium polysulfides precipitate onto the positive electrode surface at the end of each discharge, and dissolve at the start of each charge [6]. The precipitation increases the volume of the positive electrode during discharge, whilst dissolution decreases the volume during charge. The location at which the species precipitate may differ from the location they were present in the previous cycle [6], [48]. Preferential precipitation across the electrode surface can cause uneven pore blocking, influencing the availability and accessibility of reaction sites for electrochemical reactions through the impact on transport pathways [6]. The size, distribution and location of pores also influences pore blocking.

1.3.2.2.2 Plating and Stripping

Stripping occurs during discharge when the lithium in the negative electrode provides an electron to the outer circuit and becomes a charged ion, Li^+ , removing it from the electrode and travelling towards the positive electrode through the cell. Plating occurs during charge, when Li^+ travels back to the negative electrode and precipitates, or plates, onto the surface [10]. Plating contributes to volumetric expansion of the negative electrode and stripping contributes to volumetric contraction of the electrode. Similarly to precipitation on the positive electrode, the lithium may precipitate in varying locations, different to their original location, leading to uneven plating [10].

1.3.2.3 Growth, Dendrite Formation and SEI Layer

In addition to volumetric expansion, the deposition and removal of lithium through uneven plating and stripping can lead to mossy growth [6]. Uneven plating, along with side reactions between the lithium and the electrolyte leads to the formation of an SEI layer on the surface of the negative electrode [49]. If uneven plating continues due to preferential plating onto existing precipitates, dendrites can form [50]. These are protrusions that form from the electrode surface, and under certain conditions, can grow long enough to perforate through the separator, allowing contact between positive and negative electrodes and short-circuiting the cell [6] [51]. Dendrites are more likely to occur if there are deformities, or non-uniformity on the electrode surface [6]. Other than potentially short-circuiting the cell, which is more likely to occur at higher currents, the dendrites can break off, creating dead lithium that contributes to a loss of active material, reducing capacity [6]. At higher current rates, which are required for commercial applications [18], the formation of dendrites is more significant and introduces potential safety concerns [6].

Activation cycles are implemented with the aim of obtaining an optimum SEI layer, which works as a physical barrier to overcome uneven plating and stripping and the formation of dendrites [6]. Cell manufacturers run the activation cycles under specific conditions, including very low C-rates, to create

an SEI layer that is stable, uniform and can accommodate volume changes [6]; the exact conditions to achieve this remains unknown within the research community. A smooth surface has been seen to promote even deposition [6], [52], and a thin SEI layer minimises the associated charge-transfer resistance [6]; electrochemical reactions take place through the SEI layer to reach the lithium underneath, adding transport limitations and lowering the cell voltage by increasing the resistance [1]. The SEI should also be elastic, with high mechanical strength to account for large strain without cracking [51]. In a real cell, without this optimisation, SEI layers are typically fragile and inhomogeneous, following the uniformness of the electrode surface underneath. These properties can lead to cracking, side reactions and possible corrosion of the electrode [50].

1.3.2.4 Sulfur Utilisation

Sulfur utilisation is the amount of sulfur that contributes towards reactions when the cell is cycling, relative to the total input amount of sulfur [6]. There are various causes of poor sulfur utilisation that result in a reduction in capacity [18], such as the method of sulfur loading [53], inaccessible material due to insufficient wetting of electrode pores, or blocked pores due to precipitation. It is possible to have a high sulfur mass but low sulfur utilisation.

1.4 Current Research: Modelling and Experimental

Experimental work is required to test new materials, different hypotheses and behaviour under varying conditions. It is currently being carried out across all areas, and for each component within the cell. Each different area of experimental research has a different aim, which can vary from improving the efficiency or performance of a material, finding a commercially viable manufacturing method for specific components, or testing completely new materials to overcome degradation mechanisms. It is essential that there is collaboration of work within all areas, as it is currently unclear the extent to which research developing new components will work successfully when combined with other research.

Alongside experimental work, models are an important tool for understanding what is happening inside the cell. There are a wide range of modelling tools, but the majority aim to capture or predict the behaviour based on a mathematical system of equations. The ability to analyse what is happening inside the cell, beyond what can be done during experiments, is essential to overcome the key challenges and reach commercial application.

A model can be used to test various hypotheses and assumptions, along with the impact of changing individual parameters, such as electrode thickness or porosity. By comparing the results against experimental findings, a model can be used to understand the most likely mechanisms. When scaling between cell formats and working to understand the behavioural differences, a model to test each mechanism becomes vital. A trustworthy model can also accelerate the experimental testing process; for example, running simulations to determine optimum cell parameters would be significantly faster and cheaper than designing, building and testing various cells. It also removes the influence of human error when experimentally testing cells. In addition, models can be used to obtain data not yet possible via experimental methods, for example, low E/S ratios in coin-cells.

Whilst experimental work in a laboratory is informative for the fundamental mechanisms occurring and how the behaviour varies, it is unlikely to match real-world behaviour. For example, a drive-cycle for a UAV is unlikely to experience continuous and complete charge and discharge cycles. The use of a model can help to test under more realistic conditions, rather than optimised and controlled laboratory set ups.

The variations in mechanisms between Li-S and Li-ion mean understanding and modelling the observed Li-S behaviour is different to the heavily researched and developed Li-ion models. For this reason, separate models have been developed to explain Li-S behaviour. There are a variety of model types that can be used. They vary in function, for example physics-based or equivalent circuit network models (ECM), along with complexity, for example from zero-dimensional (0D) to three-dimensional (3D). There are many highly regarded published models within Li-S literature, most of which are physics-

based. They vary in type and complexity, for example from 0D, cell-level models, to 3D positive electrode models. Based on both the input and output results, it is assumed most have been developed for pouch-cells. There are several hypothesised reasons for model development based on pouch-cells, including the availability of published pouch-cell data, or the use of pouch-cells for commercial applications, making these models more applicable.

1.5 Scaling: Cell-Format

As previously discussed, there are various formats for cells. Material development is predominately completed at coin-cell level for Li-S; manufacturing of coin-cells requires less material, lower current rates and moderate cycling conditions, along with simpler test equipment, reducing the overall experimental time and cost to investigate each new material [37], [38]. For commercial applications, pouch-cells are likely to be used due to their ability to achieve higher performance in terms of capacity, energy density and cyclability [36].

It is hypothesised the physical differences, as summarised in Table 1, result in mechanistic differences between the cell formats; whilst new materials tested at coin-cell level may produce promising results, the success is not guaranteed to scale to larger cell formats. As most experimental work focuses on one cell format only, it has not yet been fully understood how, why, and the extent to which these mechanisms differ. For the new materials tested to be considered for commercial application, it is vital the causes of these differences are fully understood. Several parameters to consider when scaling between cell formats are the sulfur mass and electrolyte volume, or E/S ratio, electrode surface area, cycling current based on current density, and casing [54] influencing pressure. These will influence mechanisms such as charging and discharging, precipitation dynamics and degradation mechanisms, including polysulfide shuttle and dendrite formation, as found by in work by Cheng et al. [55]. For example, lean electrolyte systems, or reduced E/S ratios in pouch-cells can result in incomplete positive electrode utilisation, leading to lower cell capacity and poor cyclability [6]. In terms of degradation, scaling may also influence the volumetric expansion to both electrodes, and potential inhomogeneities across the cell, based on the geometric size.

To bridge the gap between cell formats, there is the possibility of optimising the performance of coin-cells experimentally; once successful testing has been completed under standard coin-cell conditions, these can be varied towards pouch-cell conditions. For example, after preliminary testing at a high E/S ratio, the ratio could be reduced towards more applicable values for pouch-cells, with the aim of testing the behaviour at higher energy densities required for commercial application. Whilst these changes will not align exactly with a pouch-cell, they can work as a step towards improving the understanding and potentially save time and cost from scaling without prior knowledge or predictions. The hypotheses for the changes could then be tested within a model.

1.6 Summary: Project Plan and Methodology

Given the physical differences between coin and pouch-cells and the hypothesised impact on the mechanisms occurring, observed through behavioural changes when scaling, the aim of this project is to investigate what these are, and which have the most significant impact. This will be done both experimentally and through modelling. The aim is to create a model capable of predicting both coin and pouch-cell behaviour. To do this, a reliable experimental data set is required to parameterise and test the model. By completing the experimental work as part of the project, raw data can be obtained, with tests varied as required to obtain the correct information, rather than extrapolating from published work. To achieve this, the first part of the experimental work will involve understanding the process of manufacturing coin-cells, including potential associated challenges. Various material types will be tested, although the overall aim of the project is not to develop or improve new materials, but instead to obtain this reproducible data set. Ideally, this will come from a material that can be scaled between cell formats, accounting for the differences in the manufacturing processes that may apply, along with consideration of the requirements for commercial applications. In the scenario that a reproducible data

set could not be obtained within a realistic timeframe, an alternative source of data would be required. The knowledge gained from experimental work would help to determine the most appropriate data set.

Separately, analysis of existing models will be required to determine whether these can be modified and scaled down to accurately predict coin-cell behaviour, or whether a completely new model is required; this will work towards understanding the extent to which existing models capture coin-cell behaviour. Although the experimental data is first required to parameterise these models, an initial awareness of the capabilities of existing models will be required in parallel to determine the variety of data that would need to be obtained. For example, what manufacturing conditions or measurements would be required to be able to test a model against experimental results under varying condition, to determine the most dominant mechanisms occurring.

A significant period of time is likely to be required to investigate and understand the capability of the current models, of various types and complexity. From here, a constructive decision can be made as to the best type to use for the purpose of understanding mechanistic differences when scaling between cell formats. Building upon existing models is hypothesised to be the most reliable route, although derivation of new features or mechanisms may be required to capture all the experimental results. A consideration into the application of the model will also be required; for example, the time and computational cost to run, in comparison to accuracy, or quantitative fit of predictions.

Combining experimental work and model development in parallel will help to develop a better understanding of how cell features impact the behaviour, and the extent to which these can be included within the model. As there are a high number of unknown or unconfirmed mechanisms occurring, the experimental work will help to inform the model and modelling decisions, highlighting the areas that lack information or hypotheses, and filling those gaps. Undertaking experimental work also ensures that the assumptions made within the model are realistic, and any fitting parameters used are, to some degree, accurate and reasonable. A circular dependency between experimental work and modelling work would be the ideal outcome; using knowledge from the manufacturing of coin-cells to inform the model development, alongside the changes required when scaling up to pouch-cell experimental work. The modelling results can then be implemented into further experimental work, to validate whether the predicted mechanisms are correct, and what further changes are required to reach optimum performance.

A successful model will include the fundamental mechanisms required to capture standard cycling behaviour for varying cell formats but is unlikely to include every single mechanism. It will be able to test which hypotheses correspond to the observed behaviour and which may be dominant under specific conditions; several mechanisms could contribute towards an observed behaviour, each of which may be equally justifiable. The initial purpose of model is not to quantitatively reproduce experimental results, but to confirm whether the hypotheses are valid and realistic. The inputs for the mechanisms included must be obtainable and measurable via experimental work, or existing characterisation methods. The initial iteration of the model is likely to focus on beginning of life, but investigation into degradation mechanisms would be required to capture real cell behaviour.

The final model will be published open source, with full disclosure of the information used to design and validate it. This will allow comparisons to be made and further model testing by others in the community, working to improve the capability and enhance collaborative work. The collective use of models alongside experimental work may increase the likelihood of conclusions about behaviour being agreed upon within the research community, accelerating the process to find solutions to the current Li-S problems. The development of a coin-cell model will fill the gap within the literature, providing a standardised model that can be used to aid the development of commercially viable materials.

2 Chapter 2: Experimental Positive Electrode Development

This Chapter will summarise the experimental work completed as part of this project. After discussing the importance and reviewing the current state of experimental research for Li-S, the focus and aims of this experimental work will be determined. The selection of materials, the manufacturing and testing processes will be explained, along with the obtained results. With the overall project aim of developing a model to predict coin-cell behaviour, the experimental results will be reviewed to determine whether the requirements to use for model parametrisation are met.

The experimental within this project was completed within the Titirici group, in the Chemical Engineering Department at Imperial College London, under the supervision of Dr. Heather Au.

2.1 Research Objectives

The research aim within this Chapter was separated into two areas. Firstly, the experimental work focused on understanding the manufacturing process, the influence properties had on performance and the impact of cycling conditions. This included investigation into the experimental work currently being undertaken, focusing specifically on positive electrode materials. Other considerations needed to be accounted for during the process to ensure the materials and processes selected were viable for scaling up to larger quantities or larger cell formats, for example, in terms of cost and time. The work then focused on obtaining the required parameters for optimum coin-cell performance.

Separately, once testing procedures had been trialled, a reliable data set to use to parameterise a coin-cell model was required. This needed to include the fundamental cycling regimes, such as charge and discharge at varying C-rates. Measurements beyond those that could be directly measured during cycling, for example characterisation to determine the porosity of the electrode material, were taken from the literature or from work by colleagues. For use to parameterise a model, the final data set obtained had to be reproducible, reliable and based on a material that could be scaled.

Whilst the work aimed to achieve both, they were not dependent on one another; a reliable data set may not be obtained from a cell with optimum parameters. The extent to which each was achieved is discussed throughout this Chapter.

2.2 Introduction to Experimental Work and Cell Manufacturing

As previously discussed, experimental research focusing on new material development in Li-S is predominantly completed at coin-cell level, for several reasons. As coin-cells are significantly smaller than other cell formats, a smaller amount of material is required, corresponding to a lower cost [2]. Once materials for each component have been manufactured, full coin-cell assembly requires significantly less steps [37], meaning they can be made in larger batches at a much higher throughput rate than pouch-cells, or larger cell formats. Under ideal conditions, this also improves the reliability and reproducibility of cells, if all made under the same conditions. Due to the lower capacity of coin-cells, if run under the same current compared to larger cell formats, a shorter cycling period is required during testing.

An unintended consequence of creating cells at different scales is the ratio of components; this varies considerably between cell-formats. In coin-cells, there is typically an excess of lithium at the negative electrode, and an excess of electrolyte [6]. When focusing on material development of one component within the cell, an excess of all other components ensures the observed behaviour is due to the investigated component only. It has also been found that high, or optimised E/S ratios work towards obtaining more reproducible results [56]. On the contrary, commercial scale pouch-cells aim for higher energy density, meaning much leaner quantities of each component are used [6]. The variation in the ratio and magnitude of the excess between cell formats contributes to differences in the observed behaviour; for example, limiting the lithium available to react with the sulfur can contribute to a reduced achievable capacity due to incomplete reactions and lower utilisation [10]. In addition, the differences

in physical shape and geometry, the manufacturing processes and the structure, including casing and tabs [36], are also expected to contribute to the observed differences. The exact impact of each feature is unclear, which justifies why both experimental and modelling work is required when investigating new materials; models can make predictions about the mechanisms, whilst experimental work is required to verify which of these mechanisms are dominant. To help improve understanding of how a cell performs under varying conditions, it is essential to understand the exact reasons these variations occur, and how these differ between cell formats. It is unlikely Li-S will successfully reach commercial application without this capability.

Within experimental work, there are many variations, beyond the material manufacturing or cell assembly process, that need be accounted for, such as equipment calibration, the quality of the raw materials and the time and conditions under which materials are stored before use. For the manufacturing process itself, changes to the required equipment for different cell-formats adds to the complexity when accounting for experimental variations. In addition, human error is likely to impact both manufacturing and testing, and the effects are complex to quantify. To use experimental data for modelling work, it is essential to understand how these factors impact the results, and the extent to which they can be predicted, quantified or mitigated.

2.3 Essential Considerations in Developing Individual Components within a Li-S Cell

The aim of experimental work is to improve the cell performance, quantified by varying metrics, and overcome the problems with Li-S chemistry, as discussed in Section 1.3.2, whilst achieving the requirements for commercial application. Within the Faraday Institution LiSTAR (Lithium Sulfur Technology Accelerator Research) project, experimental research focuses on each component separately, including both electrodes, the electrolyte and separator, alongside collective work undertaking characterisation, full cell diagnostics and modelling of the cell [57].

Whilst the focus must be on commercial viability, in terms of scaling-up the manufacturing processes at low cost and with simple workflows, there are also other areas to consider when developing the next generation Li-S cells. For example, materials would ideally be environmentally friendly, such as low toxicity to the environment, along with being ethically sourced and highly abundant [6]. Laws and regulations between countries also play a role into the viability of materials, with the entire supply chain, manufacturing process, application and disposal after use needing to be considered [6]. This requires a large amount of collaborative work between researchers, manufacturers and industrial partners.

2.3.1 Positive Electrode

A heavy focus is placed on researching the positive electrode, predominantly the conductive host and the structure [6], [46]. As previously discussed, sulfur is the active material but it is insulating, meaning it requires a conductive host for electrochemical reactions to take place. This host can be free-standing, or the active material can be coated onto a current collector directly [6]. The structure and requirements of the host influence the manufacturing methods; for example, a free-standing electrode structure needs to be sufficiently flexible to allow for volumetric expansion caused by precipitation and dissolution of species, without suffering from irreversible mechanical damage [6]. If the active material is coated onto a current collector, properties such as the viscosity of the solution are important to ensure a smooth coating, which is required for optimal performance [6]. The mass of the host also needs to be considered; as the host is not the active material, it contributes to dead mass in the cell, reducing the energy density.

As the electrochemical reactions take place within the pores of the electrode, known as reaction sites, the structure of the host plays a significant role in terms of the porosity, with regards to the pore size and pore distribution [58]. Generally, a higher porosity correlates to a larger available surface area for reactions to occur and allows reactions to take place with a lower overpotential cost [6]. More reaction sites enable more reactions to occur, correlating to increased sulfur utilisation [59]. In addition, tuning

the porosity of the electrode can improve energy density, based on the amount of electrolyte required to fill the pores, working towards the commercially desired lean conditions [60]. The size of the reaction sites can also determine which reactions occur during cycling [6]. Whilst high porosity is optimal, the ideal size of pores varies dependent on the chemistry of the electrolyte and chain length of lithium polysulfides; the pores must be sufficiently large for reactions to occur within [61] [6]. Various techniques can be used to optimise the porosity of the positive electrode, for example, chemical or physical activation. These are discussed in more detail in Section 2.5. Further work into how material selection can impact degradation mechanisms is also underway; for example, an ideal positive electrode material would trap lithium polysulfides, preventing them from diffusing through the cell to the negative electrode and leading to polysulfide shuttle [10].

2.3.2 Electrolyte (Solvent and Salt)

As previously discussed, the electrolyte comprises a salt and a solvent. The sulfur is dissolved within the electrolyte, and electrochemical reactions occur in the electrolyte, within the pores of the positive electrode [6]. To maximise the achievable capacity, there must be sufficient electrolyte volume to fill all the pores and fully wet the positive electrode; insufficient wetting causes inaccessible, or non-utilised reaction sites. However, for commercial applications, a low volume of electrolyte is required to ensure a high gravimetric energy density [6], and to reduce the cost of materials required within the cell [6].

The volume of electrolyte also influences the behaviour within the cell. For example, a lower volume increases the concentration of lithium polysulfides, influencing the ionic conductivity and increasing the internal cell resistance [1]. In addition, a larger volume of electrolyte can mask the effect of otherwise limiting mechanisms, including degradation such as side reactions or solvent depletion, which contribute to a reduction of active material [10]. Currently, it is unclear which of these factors most significantly influence cell performance, especially when scaling between cell formats.

As previously discussed, coin-cells have a higher volume of electrolyte compared to pouch-cells. When the electrode pores are fully wetted with electrolyte, any remaining volume is considered excess [6]. The assumption is typically made that the lithium polysulfides are evenly distributed within the electrolyte, and the electrolyte is evenly distributed throughout the cell. However, it can be expected that the lithium polysulfides within the excess electrolyte are less immediately available for electrochemical reactions, and that the longer diffusion times for the transport of these species between the excess electrolyte and within the electrode reaction sites influences the cell performance [6].

The chemistry of the electrolyte also impacts the performance of the cell. Ether-based solvents have a high solubility, improving the transport mechanisms of the lithium polysulfides within the cell [6]. Changing the chemistry using additives influences which mechanisms occur; for example, LiNO_3 is used to prevent polysulfide shuttle from occurring through the creation of a passivation, or SEI layer [45], although this material has several safety concerns [46]. This highlights the importance of considerations beyond cell performance when selecting materials; it is likely solving one problem may lead to the creation of another, which can only be prevented by a holistic approach.

2.3.3 Negative Electrode

As previously discussed, the negative electrode in a Li-S cell is typically pure lithium foil, achieving a high energy density [6]. The lithium is typically included in excess compared to the sulfur in the positive electrode, ensuring sufficient Li^+ are available to react with the S^{2-} . To achieve the lean quantity required for commercial application, the mechanical properties of lithium need to be considered; for example, it may not be viable to roll the lithium thin enough without compromising the structure. Separately, the viability of using pure lithium for commercial application is currently unclear, due to the associated degradation mechanisms, including dendrite formation [10]. As discussed, during cycling, as Li^+ diffuses between electrodes, a plating and stripping mechanism occurs on the surface of the negative electrode [52]. It is essential that this mechanism occurs uniformly across the entire surface to prevent

uneven growth and pitting; any non-uniformity can lead to potential dendrite formation, and eventual short-circuiting of the cell [52]. The plating and stripping mechanisms have been identified to contribute to volumetric expansion of the negative electrode; the variation in thickness is larger than the expansion and contraction caused by precipitation and dissolution of lithium polysulfides on the positive electrode [44].

To minimise the influence of degradation mechanisms, activation cycles are used to optimise the SEI layer that forms on the negative electrode surface [6]. The aim is to create a protection layer, promoting more uniform plating and stripping, and minimising corrosion or cracking that would hinder the performance of the cell [10]. Beyond optimising this layer, further work into combining other materials into the negative electrode, such as graphite or silicon as included in Li-ion chemistries, may be required [6].

2.3.4 Separator

The separator creates a physical barrier between the positive and negative electrodes, preventing direct contact between them [6]. It is typically larger in size than both to ensure no contact between the electrodes occurs due to potential movement or misalignment within the cell during manufacturing [37].

The use of bespoke separators is common within Li-S, rather than using those optimised for Li-ion solvents, to improve performance in terms of capacity and cyclability, or minimise the effect of degradation mechanisms [6]. Further work is being carried out to investigate how separators can be used to control the transport of species in the cell. For example, a modified separator with the ability to physically block lithium polysulfides from diffusing towards the negative electrode during charge provides an alternative solution to address polysulfide shuttle, rather than through chemical additives in the electrolyte [18].

2.3.5 Cell Casing

Beyond the components required to form the cell itself, the casing of the cell, along with the internal components that vary between cell formats also impact the performance. For coin-cells, the outer casing comprises a metal lid and base and is filled with springs and spacers [37]. The use for spacers is dependent on the properties of the electrode, and the number or thickness is varied to ensure contact between components. Springs are used within coin-cells to apply and maintain a constant pressure, also ensuring constant contact between components [37]. The use of springs allows for changes in thickness or volume of components during cycling, such as by precipitation and plating [10]. To close the cell, a crimping tool is used, ensuring consistency across each manufactured cell [37].

For pouch-cells, soft plastic casing is used, which allows for variations to the thickness and number of layers within the pouch-cell. A vacuum sealing process is used instead of crimping [38]. Whilst this applies some pressure to the cell, it is usually lower than in a coin-cell with rigid casing. Instead, external pressure can be applied when cycling the cell to ensure contact between the components is maintained [62]. In addition, the alignment of components and the sealing edge around these to close a pouch-cell is significantly more difficult to accurately and consistently achieve, compared to in a coin-cell [38]; alignment and even sealing is essential for optimum performance.

2.4 Expansion of Positive Electrode Development

Whilst further work is required for all components, the experimental work completed as part of this project focused on the positive electrode. The cell behaviour relating to the positive electrode, including the precipitation dynamics, volumetric expansion and accessibility of active material, is one of the fundamental areas of focus if Li-S is to be considered for commercial application [18]. Whilst progress is being achieved in all areas, the optimum solution for Li-S is likely to be related to the positive electrode, as the host for electrochemical reactions to occur. This will then impact decisions relating to the separator and electrolyte, including the wetting of the electrode and transport of species, along with the ratio between the positive and negative electrodes. Solutions from other cell chemistries, such as Li-ion work on the negative electrode, can be tested within a Li-S system once the positive electrode challenges have been resolved.

There are many factors contributing to the viability of a material for the positive electrode, and a compromise between these must be found for the material to be successful for commercial application. The criterion for success includes low cost and high abundance, to minimise the risk of bottlenecks due to limited availability [6]. At the same time, the materials must be ethically sourced and environmentally friendly, along the entire supply chain [6]. The manufacturing process should be low in complexity and relatively quick, with a tendency towards fewer pieces of equipment required. The material must be scalable, both chemically and physically.

However, with the fundamental aim of new material development to improve the performance of coin-cells, ensuring the materials or processes meet these success criteria is often not the highest priority. The focus typically begins with achieving the highest capacity or cyclability, with further work then completed on the scalability of the manufacturing processes and the supply chain. The experimental work within this Chapter discusses the currently available materials which work towards the latter goal of high capacity and cyclability. The work then moves onto an alternative material, assessing the viability to meet both sets of criteria.

2.5 Initial Testing of Positive Electrode Materials

As previously discussed, the aims of the experimental testing were to obtain a reliable data set to use for model parameterisation, along with finding an optimum material for the positive electrode. This also required finding manufacturing and cycling conditions that resulted in high performance. With the plan to move to modelling work later, followed by further experimental work on pouch-cells, the process of achieving these aims needed to be relatively fast. In addition, the data collected for model parameterisation and validation needed to be reliable and repeatable, and contain results linked to mechanisms expected to change when scaling between cell formats.

To obtain an experimental data set to use for model parameterisation, all components within the cell, other than the positive electrode, were set to standard, following the LiSTAR guidelines [37]. The process of manufacturing the materials, and assembling the cell is discussed in Appendix, Section 9.1.1, irrespective of the positive electrode material, which is discussed in Section 2.5. Appendix, Section 9.1.1 also includes detailed information about the coin-cell assembly process and cycling of the cells; the impact of these on the observed behaviour are discussed throughout this Chapter.

2.5.1 Summary of All Materials

Experimental work developing new materials involves trialling new methods and processes, which can contribute to inconsistent results or unexpected behaviour. To quantify these as best as possible, the first step of experimental work was to ensure reproducible results could be obtained using standard materials. One method of doing this is attempting to reproduce published work and comparing the results. Alternatively, commercial positive electrode materials can be used, which would remove any variations caused during the electrode manufacturing process. Understanding the techniques and developing the skills to produce coin-cells with reproducible results was essential before positive

electrode material development and testing could begin. The positive electrode materials tested as part of this project are summarised in Table 2.

Material	Commercial / Handmade	Tested?	Purpose
NEI Nanomyte	Commercial	No	Benchmark
Innventia Carbon Fibre (ICF)	Commercial	Yes	Benchmark and testing
Organosolv Lignin	Handmade	Yes	Development and testing

Table 2: Summary of the positive electrode materials investigated within the project

2.5.2 NEI Nanomyte

The standard positive electrode material selected for the LiSTAR project was Nanomyte BE-70 by NEI Corporation Ltd [63]. It is made of 70% sublimed sulfur, 10% binder, CMC-SBR, and 20% conductive carbon host known as carbon black [63]. The mixture is coated onto an aluminium current collector [63]. It has an area capacity of 3.0 mAh/cm², and a sulfur loading of 3.75mg/cm² [63]. It is 55µm thick, which includes the thickness of the current collector [63]. As a commercial material, high reproducibility and homogeneity across the electrode is expected; any results that differ from expectation are assumed to be due to other components, or human error during manufacturing, as discussed in Section 2.9.1.1. As Nanomyte already includes sulfur, it removes the requirement for additional sulfur loading methods, which further add to potential inconsistencies and uncertainty. The sulfur content of 70wt% is higher than most laboratory methods can successfully achieve with relatively good capacity and cyclability [18].

This material would have been ideal to test and use as a benchmark for further coin-cell build protocols. Unfortunately, at the time of experimental testing, this material was unavailable due to Covid-19 and therefore was not tested as part of this project.

The manufacturer published details that this material achieved a capacity of 700mAh/g [S] for the first discharge, with voltage upper and lower limits of 2.7V and 1.9V respectively [63]. The theoretical specific capacity of a Li-S cell is significantly higher, at 1,675mAh/g [S]. For commercial application, a compromise between consistent results and high performance in terms of achievable capacity is required; 700mAh/g [S] is likely too low to be viable. However, work by others within the LiSTAR project using Nanomyte confirmed this achievable capacity and were able to obtain relatively reproducible results when testing, as shown in [64], [65], [66]. This confirmed it was possible to minimise the influence of human and manufacturing errors when using commercial materials.

2.5.3 Innventia Carbon Fibres (ICF)

As Nanomyte could not be used, the project relied on internally made or already available materials within the laboratory. An alternative and available commercial material to use as a benchmark that could be tested was Innventia Carbon Fibres (ICF). The ICFs did not contain sulfur, so sulfur loading was required. As Nanomyte was already loaded with sulfur and did not require this process, investigation was required into which sulfur loading method was best, and whether any methods introduced potential errors or variations. Several of the results, with variation to the electrolyte and catholyte volumes, and treatment including activation, are include in Figure 5. The reasons for each are summarised in the following subsections.

ICF		
A) ICF 800	B) ICF 800 AA 300	C) ICF 800 AA 300 Na ₂ S ₂ O ₃ H ₂ SO ₄
Carbonisation: 800°C Electrolyte: 100μL Catholyte: 20μL Electrode mass: 1.32g	Carbonisation: 800°C Air activation: 300°C Electrolyte: 100μL Catholyte: 20μL Electrode mass: 1.34g	Carbonisation: 800°C Air activation: 300°C Acid: Na ₂ S ₂ O ₃ H ₂ SO ₄ (<i>chemical activation</i>) Electrolyte: 50μL Catholyte: 20μL Electrode mass: 1.34g
Rest, 0.05C Discharge, 0.05C Charge, 0.1C Discharge, 0.1C Charge (Loop 0.1C 100 times)		

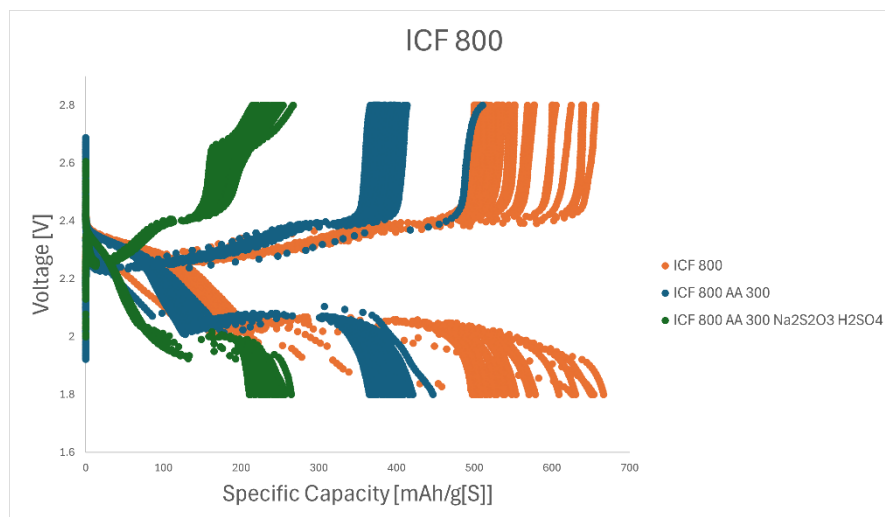


Figure 5: Experimental voltage-capacity graph for three ICF materials, with variations to the manufacturing methods

2.5.3.1 Sulfur Loading and Content

There are various methods of loading the sulfur onto the positive electrode, including incorporating it into the electrode structure during manufacturing, melting the sulfur onto the electrode surface, or dissolving sulfur into a solution, known as a catholyte [18]. The state of the sulfur at the beginning of cycling can influence the behaviour during later cycles. For example, if solid elemental sulfur is incorporated, a higher energy is required to dissolve the species [6]. The chain length of the polysulfides also influences the behaviour, as well as the initial state of charge of the cell [6]. Dependent on the cycling conditions or the aim of testing, the cell may be charged or discharged first.

Alongside the sulfur loading, the total sulfur content is important to consider. With a higher sulfur content, the ratio of insulating sulfur to conductive carbon is higher [25], along with the ratio of sulfur to lithium, which can influence the type and number of reactions occurring. A higher sulfur content could also increase the likelihood of pore blocking, through a larger amount of precipitation on the positive electrode surface, reducing the surface area available for reactions during cycling [28]. A higher sulfur content does not guarantee a higher proportion of sulfur is utilised for electrochemical reactions; this is an important consideration when determining the optimum manufacturing conditions.

After preliminary testing, a catholyte solution was selected for ICF testing. In comparison to sulfur melting, it was a relatively easy process to control, and the quantity of sulfur could be more accurately measured, with the assumption that all sulfur was accessible for use. This method also reduced the possibility of sublimation of sulfur and had a lower risk of altering the properties of the electrode. The amount of sulfur incorporated was changed through varying the concentration of the catholyte.

2.5.3.2 Treatment of Electrode Materials

Materials made in a laboratory are typically designed or manufactured to be porous, to some degree. Most commercial fibres are non-porous [6], making it difficult to make comparisons, if aiming to use as a benchmark for further material testing. There are various methods of treating a material to include or enhance the porosity. This is known as the activation process [67], and can be done chemically or physically, as shown in Figure 6. The method works through the creation of polygroups [67]. Hérou et al. [26] investigated the influence of activation methods and agents on the morphology of materials and found chemical activation to be one of the “most effective ways to enhance microporosity in a short time” [26].

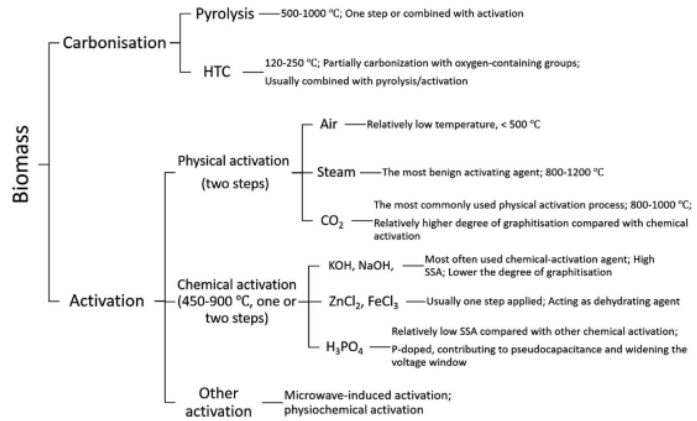


Figure 6: Diagram of the various activation methods, taken from H. Lu and X. Zhao [67]

In addition to activation, heat treatment such as carbonisation, as shown in Figure 6, can be used during the manufacturing process. This converts the material, or parts of it, to conductive carbon through heating [67]. Variations to the process and temperature influence the properties of the material, and therefore the final selection varies dependent on the aim of testing. To understand the influence, characterisation of the material is then required.

For ICF testing, the material was carbonised under varying temperatures but shown at 800°C in Figure 5. The process is described in detail in Section 9.1.2.3. Both air and chemical activation of the material were trialled. Air activation was completed during the carbonisation process and tested at varying temperatures but shown at 300°C in Figure 5. Chemical activation using acids Na₂S₂O₃ and H₂SO₄ [67] aimed to draw out the sulfur already existing within the electrode. Following this, the material was then washed with water, either tap or distilled H₂O, and dried before use.

The selection of these specific conditions was based on previous experimental work and testing by Dr. Heather Au.

2.5.3.3 ICF Results

Figure 5 shows results with both physical and chemical activation. It was found that air activation reduced the achievable capacity, from approximately 650 to 450mAh/g [S], which differed from expectation, as discussed in detail in Section 2.5.3.2. There was also a large drop in capacity between the initial cycle and further cycles, for both charge and discharge with air activation. Air activation reduced the magnitude of capacity fade, hypothesised to correspond to a higher porosity, therefore more available pores and a smaller impact of bottlenecks associated with inaccessible reaction sites. The increased number of reaction sites and number of reactions occurring was likely to correspond to more species dissolving and available for reactions, therefore a smaller loss in capacity. This also aligns with the lower voltage peak at the beginning of charge, associated with the dissolution bottleneck, at 2.3V compared to 2.35V without air activation; species dissolved more easily upon charge. The trends in capacity and voltage remained unchanged beyond this. Further work and repeated tests are required to investigate the reasoning for the lower capacity with air activation, and whether this could be due to human or testing errors.

Separately, the results shown with chemical activation also involved reducing the electrolyte volume; these initial tests were part of separate testing batches. The cell with chemical activation achieved significantly lower capacity, and experienced a second upper plateau in charging, which differed from the two cells without chemical activation. The high plateau in discharge was also considerably shorter. It was hypothesised this was due to the chemical activation changing the properties of the electrode. However, based on the difference in electrolyte volume and without repeated tests, further conclusions cannot be confidently made. These results are included for reference to further testing that was completed.

To summarise, the testing of ICF provided preliminary results for the extent to which sulfur loading and content, and chemical and physical treatment, impacted the behaviour of a cell. The results for the cell without chemical or physical activation after carbonisation, as shown in Figure 5, were confirmed with repeated testing, with minimal variations to the performance or reproducibility, beyond capacity fade. The assumption was therefore made that the sulfur loading method using catholyte had relatively high reproducibility. Dependent on the conditions of activation, this confirmed that further treatment of materials, beyond commercial manufacturing, contributed to behavioural differences. Further investigation would be required to understand the extent of this variation.

Whilst the results from ICF confirm this material could have been tested further and used to obtain a reproducible data set for model parametrisation, the additional aim of the project was to achieve high performance; the reproducibility of ICF was high, but the achievable capacity was low, with a maximum of approximately 700 mAh/g [S]. Alongside Nanomyte, the results prove that focus is required on the manufacturing method of the positive electrode specifically, if all other materials are standard, to reach the maximum theoretical capacity.

2.6 New Material Development: Organosolv Lignin

The testing on commercial materials improved understanding of the manufacturing and optimisation process for the positive electrode. To achieve the aims of the project and obtain a high performance cell, testing for a new electrode material then begun. As previously discussed, an ideal material would be scalable, environmentally friendly and easy to manufacture, along with achieving high performance in terms of capacity and cyclability. Thinking in terms of the application, it was important to try to consider the materials and processes in terms of commercial viability; the simplest and cheapest method is often preferred when considering manufacturing at large scales. Although performance is the overall aim, a compromise between viability is always sought. The selected material for use that met these requirements was Organosolv lignin.

Earlier work investigating materials and identifying Organosolv lignin occurred before this project, by other colleagues within the Titirici group at Imperial College London.

2.6.1 Introduction to Organosolv Lignin

Organosolv lignin is a raw material and a by-product of the paper-making industry, with approximately 50 million tonnes produced each year [68]. The type of lignin varies dependent on the extraction method [68]. Lignin has been investigated within Li-ion and other energy storage research for the negative electrode and as a binder material [69]. Within Li-S research, lignin has been studied for various components, including the positive electrode [70], the separator [71] and as a protection layer to prevent degradation due to polysulfide shuttle [47]. Meeting the criterion for low cost and high abundance, lignin is an ideal option for use in a Li-S cell due to the high carbon content and high porosity [69]. Lignin electrodes can be manufactured thinner and more porous than commercial materials [70]. These features make it a good electronic conductor, with an abundance of reaction sites without adding significant mass or volume, increasing the likelihood of high cycling performance. In addition, it has been found that lignin fibres show good performance through the provision of “adsorption sites for trapping or anchoring polysulfides” [70]. Most of the testing within the literature focuses on coin-cell

performance; further investigation is required into the performance of lignin and the manufacturing process required when scaling, in terms of cell format and quantity.

2.6.2 Organosolv Lignin Manufacturing

There are various methods of manufacturing lignin to create a carbon host for electrodes, including electrospinning [69] or a coating process [71], both of which have shown good performance in Li-S cells. The manufacturing method used in this project was the electrospinning process. Electrospinning is a process driven by voltage, using an electrohydrodynamic phenomenon, where a fibre mat is fabricated through a solution being deposited onto a host material or plate [72]. The material was unavailable for use at the time of testing, but RISE (Research Institutes of Sweden) [73] were already electrospinning lignin on a commercial scale [73].

The details relating to the manufacturing of organosolv lignin electrodes for this project, including the electrospinning, carbonisation and sulfur loading methods are summarised in Appendix, Section 9.1.2.

2.7 Property Characterisation of the Lignin Mats

2.7.1 Controlling Parameters

During the process of electrode development, cell build and cycling, only specific parameters were measured or controlled; these are summarised in Table 3.

	Electrode Development	Cell Build	Cell Cycling
Measured or controlled	Volume of solution Concentration of solution Humidity Flow speed Voltage Sulfur loading (if applicable)	Electrode size Electrode mass Electrolyte volume Electrolyte concentration Catholyte volume and concentration (if applicable) Rest periods (if applicable, during manufacture or before cycling)	Voltage (limits) Current magnitude Capacity throughput (time-limited constant current)
Minimal control	Activation (chemical and/or physical) Washing, heating and/or drying process		
Not measured or controlled	Ambient temperature (during electrospinning)	Material thickness	Ambient temperature

Table 3: Summary of the measured and controlled parameters during the electrode manufacturing process

Ideally, all parameters would be measured to ensure consistency and easily highlight any sources of error. Based on the methods or equipment used, this was not always possible. Where there was no information, assumptions were made. As characterisation of the material was not included within this project, all information relating to the results obtained from characterisation methods was taken from work completed by colleagues, or within the literature.

2.7.2 Testing Conditions

To test the behaviour under different conditions, various cycling regimes were trialled, including variations to the charge and discharge rates throughout cycling, and the upper and lower voltage limits. Dependent on the state-of-charge (SoC) of the cell when setting up for cycling, which varies dependent on the sulfur loading method or conditions, an initial charge or discharge were both trialled as the initial current profile. For final testing, the cell was first discharged.

LAND software was used to capture all the experimental data. When first connected to the cycler, the voltage (OCV) (V) of the cell was measured. The capacity (mAh) of the cell was estimated, based on the input mass of active material, sulfur, and the nominal specific capacity of 1,675mAh/g [S]. A maximum capacity limit prevented the cell from being overcharged above the rated or achievable capacity. Voltage and time limits were also applied when cycling. An example of a cycling regime used included one 0.05C activation discharge and charge, followed by a 0.1C discharge and 0.1C charge, looped for 100 cycles, or until the cycling cut-offs were reached.

2.8 Initial Testing

2.8.1 Cycling

As previously discussed, various cycling regimes, carbonisation temperatures, activation processes, both physical and chemical, volumes and concentrations of electrolyte and catholyte, if used, and

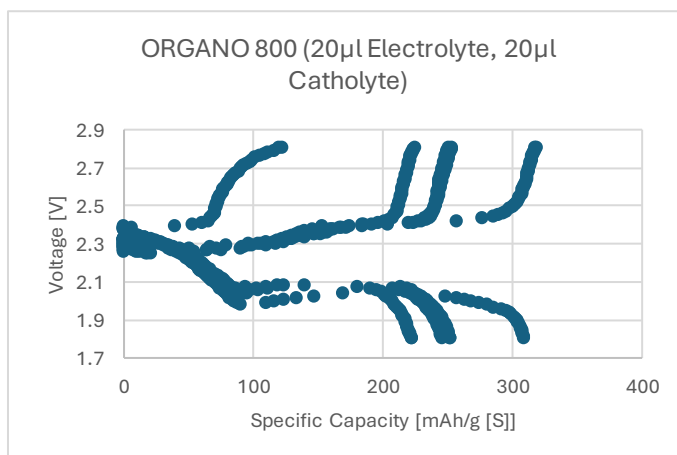
sulfur loading methods were trialled. The lignin fibre was already porous and therefore did not require physical activation. However, further activation at this stage, to enhance or tune the porosity, was tested to investigate the impact. The variations for each are summarised in Table 4, and an example of three variations is included in Figure 7.

Parameter		Values
Electrolyte	Volume	20 μ L – 100 μ L
	Concentration	0.1M – 0.8M
Catholyte	Volume	20 μ L - 40 μ L
	Concentration	0.6M
Carbonisation Temperature		800°C 1,000°C
Activation	Physical	Air 300°C
	Chemical	Na ₂ S ₂ O ₃ Na ₂ S ₂ O ₃ H ₂ SO ₄ 5wt% GO
Sulfur Loading		Sulfur Melting Catholyte

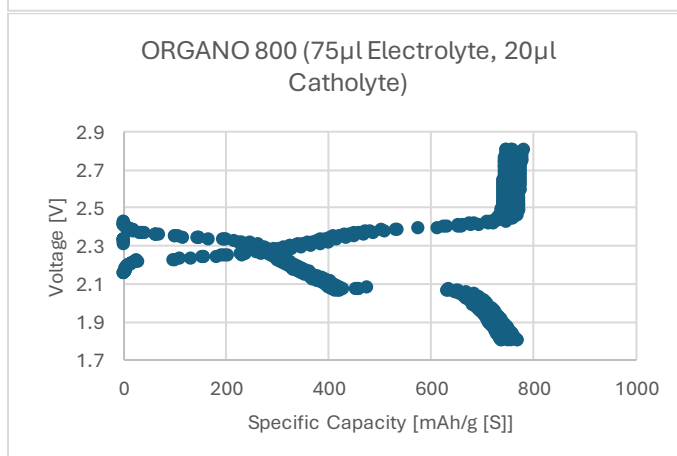
Table 4: Summary of the manufacturing variations

ORGANOSOLV LIGNIN
Rest, 0.05C Discharge, 0.05C Charge, 0.1C Discharge, 0.1C Charge (Loop 0.1C 100 times)

Carbonisation: 800°C
Electrolyte: 20µL
Catholyte: 20µL



Carbonisation: 800°C
Electrolyte: 75µL
Catholyte: 20µL



Carbonisation: 800°C
Activation/treatment:
5wt% GO
Acid: Na₂S₂O₃ H₂SO₄
Electrolyte: 100µL
Catholyte: 20µL

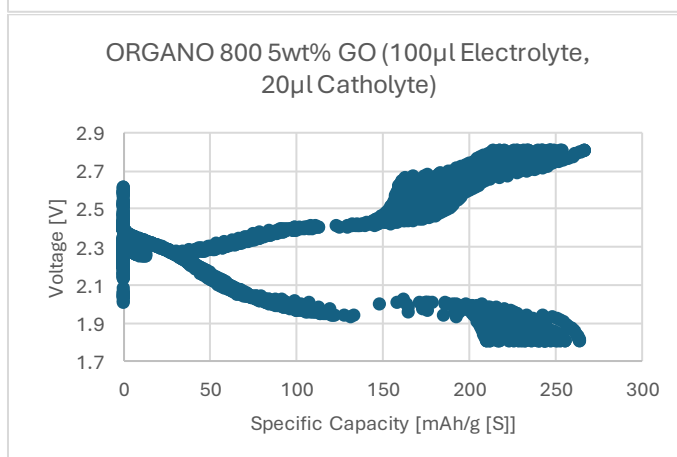


Figure 7: Experimental voltage-capacity graphs for three lignin positive electrode materials, with variations to manufacturing methods

Based on the examples shown in Figure 7, when comparing 75µl and 20µl of electrolyte, along with the other variations of lignin tested, it was found that increasing the electrolyte volume increased the achieved capacity. A larger capacity fade was also observed for lower electrolytes volumes. This aligns with the hypotheses that a larger volume corresponds to complete wetting of the electrode, a reduced concentration of species, reducing the transport limitations, and a smaller impact of potential degradation mechanisms depleting the electrolyte volume. Separately, physical and chemical activation both reduced the achievable capacity of the cell, although the opposite impact was expected based on

the increase in porosity. This was also found in ICF testing, and further work is required to investigate the cause, along with the influence on the voltage plateaus, as observed in Figure 7.

Beyond the results shown, a lower concentration of electrolyte or catholyte was found to reduce the achievable capacity, hypothesised due to less active material for reactions, and changes to the transport of species. A higher carbonisation temperature resulted in higher achieved capacity, hypothesised to be correlated to a more conductive carbon host, therefore more electrochemical reactions occurring. Separately, a lower OCV was found when using catholyte as the sulfur loading method, corresponding to the species already in a dissolved form.

2.8.2 Electrode Mass Variation

As discussed in Section 9.1.2, it was observed visually that the thickness of the fibre mat varied based on the location, with the greatest thickness at the location closest to the needle, in the centre of the mat. Characterisation techniques, such as X-ray CT or SEM, would have been required to measure the thickness of the mat accurately and without causing any damage, in comparison to a physical measurement via contact with the mat. Based on the time constraints, of both learning the skills required and access to the equipment, characterisation was beyond the scope of this project, and therefore not completed. Instead, for simplicity and time efficiency, the electrode mass was measured. These measurements

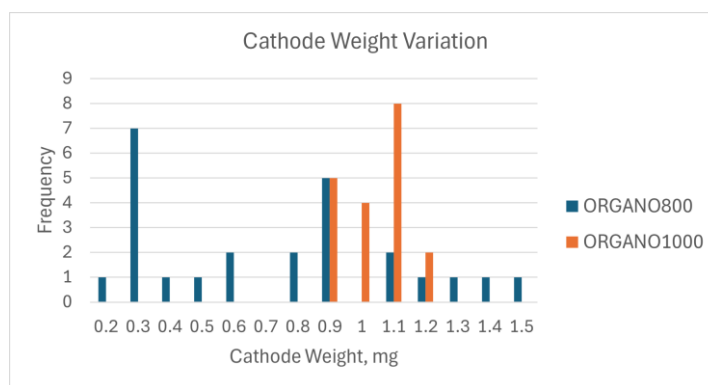


Figure 8: Variation in mass of the lignin positive electrodes

were taken before assembly into the cell, therefore before sulfur was loaded when using a catholyte solution. A lower mass was assumed to correspond to a thinner electrode, based on the assumption that each electrode was the same geometry, and had the same porous structure. Further work was being completed by other colleagues within the Titirici group to investigate the potential causes for variations between thickness and structure.

During initial testing, although the electrode masses were recorded, they were not directly considered when manufacturing cells in batches; consistent electrode masses were not always selected, based on the assumption that the quantities of most other components were always in excess, including the electrolyte and catholyte. The aim of initial testing was to investigate the performance, predominantly in terms of voltage plateaus and achievable capacity. For further testing, which required manufacturing repeated cells to test the reproducibility, significant variations were found when comparing the recorded masses, as shown in Figure 8. The varying electrode thicknesses, assumed through varying electrode masses, were expected to impact the amount of active material contained within the electrode through the sulfur loading process. For a larger electrode mass, therefore a thicker electrode, a larger mass of sulfur was required to achieve the same sulfur loading. If the same E/S ratio was to be achieved, a larger electrolyte volume was also required to account for the thicker electrode. A larger electrolyte volume influences the concentration of species within the cell, and in turn the transport mechanisms, along with increasing the pressure, all of which could impact the performance [6].

2.9 Attempted Solution to Irreproducible Results: Fibre Grid Method

Testing by colleague Dr. Julien Roman within the Titirici group using lignin for supercapacitors, where symmetric electrodes were required, found that matching the electrode mass was sufficient for reproducible results. These results justified the assumption that electrodes of the same mass had similar morphology and were sufficient for achieving reproducible results based on the positive electrode scaffolding.

To test this hypothesis, electrodes with similar masses needed to be harvested from the larger lignin mat. For this purpose, a grid was created, sectioning the mat based on the expected thickest and thinnest areas, as shown on the left in Figure 9. Based on the needle location, Section 1 was expected to be the thickest, Section 2 thinner, and Section 3 the thinnest. The exact size and locations of these sections needed to be determined for each mat, as these were likely to vary based on manufacturing conditions.

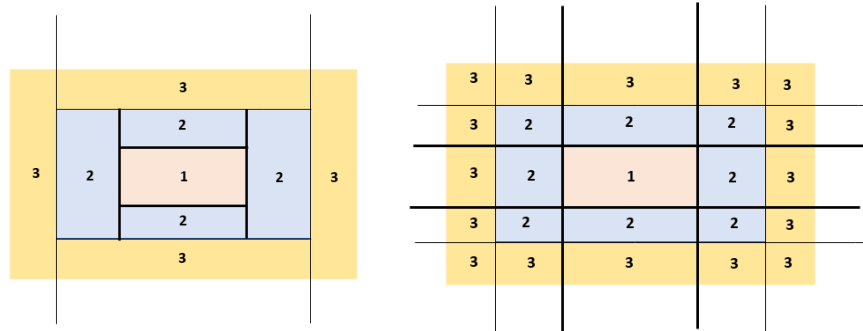


Figure 9: Proposed grid method for selecting similar mass electrodes from the lignin mat

Smaller sections could be formed, if needed, as shown on the right in Figure 9, to obtain more consistent electrode masses. The aim was to find multiple electrode samples of the same, or very similar mass, to use for repeated cells to test the performance and reproducibility. The electrodes were cut from symmetrically located sections, weighed and stored together. The electrode masses varied from Section 1, with an average of 1.5mg, to Section 3, with an average of 0.5mg, proving significant changes based on the location. Based on the gradual change in assumed thickness across the mat, there was a large spread across the regions; for example, the edge of Section 2 and 3 each had similar masses, whilst the mass of electrodes taken from the centre were significantly different. When using the smaller sections, this grid method was sufficient for the purpose of obtaining lignin electrodes of similar and repeatable masses. The process was also considerably simpler and more time efficient compared to further characterising the physical properties.

2.9.1 Cell Cycling Performance: Reproducibility with Equal Mass Electrodes

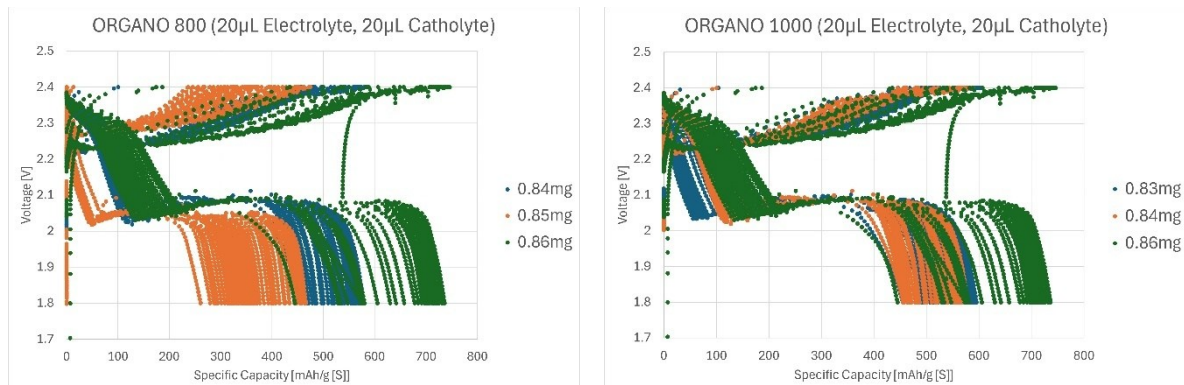


Figure 10: Experimental voltage-capacity graphs using lignin electrodes of similar masses

To test the reproducibility of cells using electrodes of similar masses, a median value of electrode mass was selected, taken from Section 2. An example of the results using electrodes with masses between 0.83mg and 0.86mg is shown in Figure 10. When cycling three coin-cells manufactured in the same way, from the same section of the lignin mat with masses within 0.03mg tolerance, the general trend in voltage and capacity performance were similar: two voltage plateaus were visible in discharge and charge, both decreasing in capacity with further cycling, as shown in Figure 10. However, despite significant improvements to the reproducibility of the electrode mass being achieved with the grid method, the quantitative measure of cycling performance was found to be highly irreproducible, exhibiting up to approximately a 50% variation in the achieved specific capacity. This is significantly more than would be expected for almost identical electrodes, manufactured from the same batch of material under the same conditions.

Whilst the assumption was made that similar masses corresponded to similar thicknesses and morphology, the mass may not be a sufficient metric correlated to coin-cell performance. Beyond the thickness of the electrode mat, there were several other factors that could impact the behaviour of the cell, as briefly described below.

2.9.1.1 Human Error

As previously discussed, due to the nature of new material testing, there are many variables that could cause inconsistencies, leading to irreproducibility of results between samples. One contributor is human error. The impact is difficult to quantify, as it can vary between stages during manufacturing. To ensure the error was consistent, cells were manufactured in large batches, with several sets of repeated cells cycled at a time. Based on this, the variation of human error was assumed to be minimal.

2.9.1.2 Positive Electrode: Mat Preparation

Results using commercial material Nanomyte obtained reproducible results, as previously discussed in Section 2.5.2. This indicated the manufacture and preparation of the positive electrode as the likely source of error during testing.

Beyond the variations during formation of the lignin fibre mat, as previously discussed, the carbonisation process introduced potential variations. To be carbonised, the mat was placed between two carbon fibre sheets, to prevent damage during the process inside the furnace. The mat remained in the same location for the duration of the carbonisation process. It was assumed that the temperature was homogeneous throughout the tube. However, the nitrogen flowed into the tube from one side, introducing the possibility of a gradient of carbonisation from one end of the mat to the other. This could have led to differences in conductivity across the length of the mat that would not necessarily correlate to differences in mat thickness, and which could have influenced the observed behaviour. To investigate whether this contributed to the lack of reproducibility, characterisation of the mat before and after carbonisation would be required, to confirm changes in structure and properties. After carbonisation, when cutting the electrodes from the fibre mat, each electrode was cut to the same size, leaving the thickness or mass as the only other likely variation.

2.9.1.3 Components

All components other than the positive electrode were assumed to be identical from cell to cell. This was justified from testing in the literature, following the same methodology but using Nanomyte for the positive electrode, which found consistent and reproducible results, as discussed in Section 2.5.2. The lithium electrode and the separator were both commercially available materials and assumed reproducible. However, imperfections such as impurities, marks or damage could contribute to behavioural differences. The addition of a cleaning step during manufacture could be included to minimise this.

The electrolyte and catholyte solutions, if used, were made in batches. Dependent on the time since manufacture, changes could occur, such as precipitation of the salts, which would influence the concentration. To overcome this, the solutions could be mixed during storage, or before each use. For the testing completed, materials from the same batches were used when repeating cells, to minimise any differences.

2.9.1.4 Cell Build

When assembling the cell, there were various steps that could cause changes or inconsistencies. Firstly, dependent on the porosity of the positive electrode, the time given for absorption of the electrolyte or catholyte, and any potential heating, variations to the electrode wetting and amount of utilised sulfur could occur. To overcome this, the temperature and time periods for absorption for each repeated cell should be measured and matched. In addition, an unmeasured volume of electrolyte is squeezed from the cell when it is crimped, further influencing the behaviour with regards to the internal pressure.

Secondly, the exact alignment of the electrodes within the cell would influence the available area and materials for reactions; based on the difference in shapes, with a square positive electrode and circular negative electrode, movement during manufacture could influence this degree of alignment. Electrodes are manufactured as large as possible, whilst remaining smaller than the separator diameter, to minimise this effect. Extra care should be taken when closing the cell, to ensure minimal disruption to the electrode locations. Whilst misalignment and contact between the electrodes would be observable as a short-circuited cell, which would not cycle or have unexpected voltage variations, a slight misalignment between electrodes would be less apparent, likely as a reduction in achievable capacity. As there are many factors contributing to the performance, it would be unclear, without cell disassembly, if this was the cause.

In addition, incorrect or different cycling regimes could influence the observed behaviour. However, this was clearly indicated in the output LAND results, along with the same regimes being set and run simultaneously for each cell. Whilst it is important to consider, this is an unlikely cause to the observed inconsistencies.

Beyond this, a summary of factors that could contribute to inconsistent results is included in Table 5.

Impact	Lignin Solution	Electrospinning	Mat Preparation	Cell Build
High	• Volume • Concentration of solvent	• Flow rate	• Activation • Nitrogen flow • Location of electrode from mat	• Rest time (absorption, before cycling)
Medium	• Ratio of PEO, lignin and solvent • Addition of salts • Length of dissolution time	• Voltage • Current • Distance needle to Al foil • Humidity • Temperature	• Temperature • Time • Porosity (volume, size, distribution)	• Pressure (spacers, electrolyte volume) • Cell cycling (C-rate, voltage limits)
Low	• Type of lignin			

Table 5: Summary of possible causes of inconsistencies when manufacturing cells using a lignin positive electrode

2.9.1.5 Summary of Inconsistencies

Based on the number of possible inconsistencies, a large amount of investigation would be required to mitigate each. Based on Nanomyte results in the literature, and initial testing using ICF, it was highly likely that the cause was related to the manufacturing of the positive electrode, if reproducible results could be obtained using commercial materials and following the LiSTAR guidelines.

It is hypothesised that further investigation into the properties of the lignin electrode, and how these vary across the mat would have the most significant findings. To test these inconsistencies, further stages would be required during the experimental process, including either characterisation or disassembly of the cell. For example, characterisation would provide clear information about the structure of the electrode, and the extent to which wetting could occur, impacting the behaviour, based on the pore size and distribution. Based on the use of the equipment for other types of material or cell chemistry testing, it is unlikely the extent of the irreproducibility observed would be caused by equipment variations, for example, due to uneven carbonisation. Results using lignin for supercapacitors found reproducible results, confirming it is likely the post-manufacturing processes

causing the most significant inconsistencies. In addition, later work by RISE found no correlation between the lignin fibre mat thickness and morphology, through SEM testing [73].

Whilst the experimental work aimed towards consistent masses, assuming this would correlate to consistent thicknesses, the cycling results proved an additional step to test the morphology was required before use in the cell. Although there was insufficient time to investigate this further within this project, to resolve the issue, alternative methods to manufacture lignin were trialled by other colleagues within the Titirici group, working towards obtaining a more uniform morphology. This work was based on findings from work with electrospinning, prior to and as part of this project. These methods are discussed in Section 2.9.1.6.

2.9.1.6 Alternative Manufacturing Methods (Lignin)

One method to produce a positive electrode using the lignin solution but removing the variations caused by electrospinning a fibre mat, is through a coating or casting process [71]. The lignin solution is created using the same method as previously described and then formed into a powder [26]. This was investigated by a colleague within the Titirici group, published by Hérou et al. [26], where the solution was cast onto a petri dish, dried in a forced air circulation oven to create a film, before being ground down to form the powder. Alternatively, the powder could be formed from electrospinning the mat and then sonicating or grinding down. A binder is then added to the powder before carbonisation and washing. The ground material from either method can be used for a slurry coating, onto foil or a current collector [26]. Coating onto a Celgard separator has also been trialled to improve performance by hindering shuttle [71]. It is hypothesised more control over the morphology homogeneity would be achieved with this method. The drawback to this process is the requirement for a current collector, contributing to the dead mass within the cell, and reducing the likelihood of viability for commercial applications. In addition, powders have been found to be less effective, with a lower capacitance than electrospun fibres [26].

Another attempt to resolve the issue of inconsistent electrode thicknesses used a drum collector, rather than a flat target plate for electrospinning, as shown in [72]. This method involved a constantly rotating drum with the target plate attached, in which the lignin solution was deposited onto throughout the electrospinning process. A moving target results in the deposition location consistently changing, increasing the likelihood of a more even distribution. This is hypothesised to result in a more consistent morphology across the central section of the mat. Further work to increase the consistency across the entire mat could include varying the location of the needle, perpendicular to the direction of drum rotation; this would require further equipment to achieve.

It is also important to note that whilst improvements could be made with lignin development, further issues may arise when scaling between cell formats. For example, the increased geometric size, or reduced E/S ratio in pouch-cells could influence the concentration of species and transport through the cell. This may result in further inconsistencies, despite potential improvements to the material itself.

2.10 Summary and Conclusions

The aim of new material development is to improve performance based on a change in properties, known or hypothesised to influence specific mechanisms. Due to the novelty of Li-S chemistry, there are still many unknowns that have not yet been agreed upon within the literature, including the exact mechanisms occurring and how they influence one another. The addition of experimental work with a high number of steps in the process, and therefore many factors contributing to potential inconsistencies, further adds to the complexity of aligning the observed cell performance with specific mechanisms. It is therefore essential that the experimental results are as accurate and reproducible as possible, so that the hypotheses made can be trusted. When considering data to parameterise a model, if a material and process exhibit irreproducibility with an unknown cause, they are unsuitable for use for model development to study the mechanisms.

2.10.1 Organosolv Lignin Summary

At the time of writing, further work developing lignin is still required to obtain results reproducible enough for model parameterisation.

To note for use for further experimental work, testing under the variety of conditions found that carbonisation at 800°C or 1,000°C, with no physical or chemical activation, with 50µl of electrolyte and 20µl of catholyte (0.6M (Li₂S₈ in DOL/DME (1:1)) obtained the highest capacity. One activation cycle was used, at 0.05C for both discharge and charge, followed by 100 cycles at 0.1C discharge and charge, with voltage limits of 1.8V and 2.4V.

Once the reproducibility issues are overcome, the use of lignin as an electrode material meets the criterion previously discussed for scale-up to commercial application. All materials involved in the process are abundant and non-toxic. The electrospinning and manufacturing process requires moderate equipment use, each of which could be mechanised or automated to further minimise potential variations, if required. Large quantities can be produced at a time, with variations to the process easily implemented, such as the sulfur loading method or carbonisation temperatures.

2.10.2 Experimental Work Summary

This experimental work testing a variety of materials and investigating coin-cell behaviour gave significant insight into the experimental development and testing procedure. Practice of the steps required and the process to take each measurement enabled understanding in greater detail. It also provided a better perspective when analysing and investigating other experimental work within the literature or by colleagues within the Titirici group.

The first aim of the experimental work was to understand how materials and their properties influenced the observed cell behaviour, and how these could be used to determine optimum conditions. These needed to be considered when accounting for changes that occur when scaling from coin to pouch-cell. As such, new material development was not itself central to the success of the project. Following this, the data collected for model parameterisation and validation from this work needed to be reliable and repeatable, along with containing results from mechanisms expected to change between coin to pouch-cells.

The initial timeline of the project involved experimental work developing coin-cells, followed by the development of a coin-cell model, based on the experimental results. This aim was then repeated for pouch-cells. As an initial proposal for time, each stage of the project should take approximately one year to complete. As the designated time for this stage of the project was coming to an end, and with the significant quantity of possible sources of error, it was unrealistic that a data set, even with reverting to commercial materials, would have been sufficiently reproducible to use for model parameterisation. The associated problem with using data from elsewhere in the project, including the discussed coin-cell results using Nanomyte, was the lack of data for larger cell formats, specifically pouch-cells. With the aim to scale, this information was essential.

Despite the data from experimental testing being non-viable for parameterisation for a model, the knowledge gained from experimental work would significantly help to understand how to select model parameters. This includes which parameters could be taken directly from experimental work, and which must be fitted, including what realistic values for the fitting parameters would be. For example, changes to the electrode properties, such as porosity, can be measured through characterisation, but the values that change through cycling, such as precipitation or dissolution rates, cannot be measured. The experimental knowledge gained helps to ensure model predictions are based on values accurately representing what would be expected experimentally; adjustments to fitting parameters must be done in a realistic manner, to ensure an accurate and trustworthy model. It also helps to determine, when comparing experimental data sets, what information is required to investigate the observed behaviour. For example, if investigating the impact of polysulfide shuttle, variation to the charging C-rate is likely

required to analyse the opposing currents and the magnitude of degradation. The success criteria for a data set required for parametrisation is discussed in the following Chapter. Finally, the knowledge obtained from experimental work will help to make informed decisions during the design and application process. For example, understanding how reproducible the published results are likely to be, or whether they are likely based on best case performance. Regardless of the data set, it is important to note that most are likely to contain a level of inconsistency, whether or not discussed in a publication.

The focus of this project therefore shifted towards modelling. In parallel, colleagues within the Titirici group continued work developing the lignin electrodes, using the various methods discussed. Once the cause of the reproducibility has been found, the developed model could later be used to test against experimental work.

2.10.3 Achievement of Research Objectives

The work in this section of the project helped develop an understanding of the experimental work being carried out, with the focus on new positive electrode materials. It enabled critical analysis and development of a set of criteria for an optimum material, including high porosity, a highly conductivity carbon host and free-standing electrode to minimise dead mass. The criteria for scaling and commercial application was also considered. An understanding of the impact of manufacturing methods on performance and reproducibility, including activation and carbonisation steps, was obtained.

Although the aim of obtaining a data set to use for parametrisation was not achieved, a clear understanding of the measured and assumed parameters was obtained. For some, this requires characterisation, for example the porosity or electrode thickness, whilst others could be measured in-situ or in-operando, including the sulfur content and voltage variations. The ease of collecting this data, along with the reliability of measurements, is an essential aspect to consider when using the data within a model, and the impact on trustworthiness of predictions.

Collectively, this information helped to understand the important considerations when creating an electrode with high performance, which would also scale to larger quantities or cell formats. This applies to the material itself, along with the manufacturing processes involved. Whilst the focus has moved away from experimental work using lignin, this knowledge will be important when analysing results through the remainder of the project. This also becomes useful when determining how a model can help improve experimental work, alongside experimental work improving model capability and predictions.

3 Chapter 3: Re-parameterising and Testing Existing Coin-Cell Models

This Chapter will introduce the concept of modelling and why it is required as part of the project. The different types of models will be discussed, analysing the existing Li-S models within the literature. To capture scaling between cell-formats, the differences between coin and pouch-cells must be included within a model. Combining all this information and selecting published experimental work to use to parametrise the model, an existing model will be re-parameterised to test the capability. The results will be analysed to determine what further work is required.

The nomenclature is included in List of Symbols.

The modelling work within this project was completed within the ESE group, in the Mechanical Engineering Department at Imperial College London, under the supervision of Dr. Michael Cornish and Dr. Monica Marinescu.

3.1 Research Objectives

The overarching aim of the project is to develop a model with the capability of predicting coin-cell behaviour, which can be used to investigate the changes when scaling between cell formats. To achieve this, the physical and mechanistic differences between cell formats, focusing specifically on coin and pouch-cells, will be investigated. A clear understanding of what changes occur and why they occur will become essential to develop a model that includes the correct mechanisms to capture the observed behaviour. This works towards new materials tested at coin-cell level being successfully scaled up to commercial application.

There are many published Li-S models within the literature, of varying types. This Chapter will investigate the extent to which existing models, primarily designed for pouch-cells, can predict coin-cell behaviour. This will test the prediction power of the models beyond the original data set used for parameterisation.

With the non-viability of experimental results collected within this project to use as parametrisation data for the model, an alternative source is required. However, the knowledge gained from the experimental work will help to ensure the model is derived realistically, and the causality of the model and experimental behaviour aligns.

3.2 Introduction to Modelling

Models are a mathematical tool used to predict the behaviour of a cell, computationally rather than experimentally. There are various types, each with different functions and requirements. The two most common types of models are physics-based and equivalent circuit network (ECM), both of which are discussed throughout this Chapter.

The development of a trustworthy model can accelerate the experimental testing process. For example, running simulations to determine optimum cell parameters would be significantly faster than designing, building and testing various cells. A model also reduces the cost of various iterations of experimental testing. Where there are multiple hypotheses for observed behaviour, a model becomes a useful tool to test these efficiently, determining which is most likely, or contributes most significantly, and mitigate the least likely. Where model results do not align, or disprove the hypotheses, further work can be undertaken to determine the reasoning and investigate alternative mechanisms contributing to the behaviour. A model can also be used to test a cell under conditions not yet achievable via experimental methods, such as low E/S ratios, or high C-rates.

3.2.1 Physics-based Models

A physics-based model works to analyse what is happening inside a cell by focusing on the mathematics defining the mechanisms. By implementing a system of equations that physically describe the behaviour, the model captures how changes occur during cycling [6]. Physics-based models vary in complexity, from zero-dimensional (0D) up to three-dimensional (3D) [6]. Lower order models are simpler to develop and require a low-computational cost to run. Higher order models have a much higher computational cost but produce more comprehensive results; they include a larger number, and more complex mechanisms to capture the behaviour within the cell. The complexity used depends on the aim of the model. Physics-based models work well alongside experimental work, as the mechanisms hypothesised to occur can be tested directly. However, they require a large data set to parameterise.

3.2.2 Equivalent Circuit Network Models (ECM)

Equivalent circuit network models (ECM) attempt to model behaviour through an electrical circuit [74]. This is useful when investigating the behaviour and interactions between the cells and the battery management system (BMS). The system is interpreted, using simplified equations to capture behaviour, rather than explaining each mechanism with a physical equation [6]. ECMs are simpler to develop and require for a much smaller data set to parameterise. However, the information provided differs from physics-based models, for example by providing SoC estimation [74]. These models cannot be used alongside experimental work as easily; they do not directly include or test the mechanisms occurring within the cell but instead predict the output results based on an assumed representation with electrical components within a circuit.

3.3 Experimental Considerations within the Model

There are many mechanisms hypothesised to occur within a Li-S cell. The causality for some has been agreed upon within the community, and others require further work. A model works to test and explain which mechanisms are likely to cause observed behaviours. By testing multiple hypotheses within a model, results can be proved or disproved, with alternatives provided for the latter. As previously discussed, using a model to do this saves experimental time adjusting and re-running experiments.

To compare a model to experimental results, both the charge and discharge mechanisms need to be captured. Variations to the cycling parameters are required to capture C-rate dependency, such as voltage limits and charging and discharging currents. Based on the cell manufacturing, the sulfur content and loading method must be variable. A constant E/S ratio results in a varying electrolyte volume with sulfur mass, which can influence conditions such as the concentration [1]. As experimental work can be carried out for extended cycling periods, long-term cycling capability is required. Further analysis is required to determine the exact cause of longer-term cycling effects relating to degradation, such as the loss of active material or potential electrolyte dry-out, leading to capacity fade across cycles [10]; these are likely to vary dependent on several conditions.

Based on experimental work and focusing on more detailed aspects, variations occur both across and through the cell; for example, diffusion between the electrodes [6] and temperature gradients across the electrodes [62]. Dependent on the type and dimensionality of a model, it may be important to account for these changes; as dimensionality is not included in low order models, they may be unable to capture this, which could contribute to differences between model predictions and experimental results. For example, high order models with spatial variations use transport mechanisms and the limitations to capture C-rate dependence [75].

When using a model in comparison to experimental work, predictions for the sulfur content and loading methods may be required to investigate the impact on behaviour. If the initial state of sulfur is in solid form, a higher energy barrier is required to dissolve the species at the beginning of discharge [6]. If included in a catholyte solution, the concentration or chain length of the sulfur species would influence the SoC and initial reactions occurring [6]. Similarly, the number of precipitating species at the end of

discharge could then cause a bottleneck at the beginning of the following charge, where further reactions depend on the rate at which species are dissolving [6]. Assumptions may need to be made about the number and type of reactions that occur within the cell. Beyond this, variations to the electrode also need to be considered, for example, in terms of porosity, geometry or homogeneity.

3.4 Selected Model Type

The overall aim of the project is to improve understanding when scaling between cell formats, through both experimental and modelling work, and to develop a model to predict coin-cell behaviour. To improve understanding of how the cell behaviour changes based on the format, it is essential to understand the fundamental mechanisms occurring inside. As previously discussed, a physics-based model can capture and test these mechanisms at varying levels. This includes the charging and discharging behaviour, along with the precipitation and dissolution dynamics, and can be expanded to capture degradation or rate dependencies during cycling, as required. A physics-based model, where mechanisms can be turned on and off, allows the cause and effect of each observed behaviour to be tested.

Beyond the specific aims of this project, the goal for a coin-cell model is to inform experimental decisions, and vice versa. For example, running various cycling regimes through a model to determine the conditions for the best performance, before trialling on experimental cells. This end goal of circular dependency enables both modellers and experimentalists to work together, encouraging collaboration within the community. It also accelerates research, with experimental work also being used to update the model and improve the capability.

To achieve this, based on the requirement to predict full cell behaviour, a physics-based, cell-level model will be used. Physics-based models vary in type and complexity, with many high order models focusing on one component, for example, a 3D model investigating the positive electrode properties [76]. A cell-level model only requires top-level details about how the full cell behaves, which can be achieved through low order models. Beyond the fundamental mechanisms, specific details of interactions within components may not be required.

3.5 Existing Physics-Based Models

Rather than developing a new model from scratch, there are many existing physics-based models within the literature. Most of the existing models are built using the same methods and fundamental physics, with additional features and variations dependent on the complexity and aim of the model. Collectively, the fundamental features required to capture coin-cell behaviour are included within these models; thorough analysis would determine which models, or model features would be viable to capture the required behaviour. Changes and further model iterations could then be made to improve the prediction accuracy, or to capture new behaviour. A selection of the existing models analysed is including in Table 6.

Author	Dimension	No. of Species	Discharge / Charge	Key Features	Weaknesses
<i>Mikhaylik and Akridge [43]</i>	1D	4	Both	One of the first models developed	Only simulated charge profiles shown
<i>Kumaresan et al. [77]</i>	1D	5	Discharge	General baseline model that further models have built upon	Discharge only
<i>Zhang et al. [1]</i>	0D	5	Discharge	Corrected resistance predictions	Discharge results only (but capable of charge)
<i>Zhang et al. [75]</i>	1D	5	Both	Focused on impact of transport	Discharge only
<i>Marinescu et al. [78]</i>	0D	4	Both	Predicts both charge and discharge, and includes detailed list of model parameters	Minimal comparison to experimental data
<i>Ren et al. [79]</i>	1D	4	Discharge	Effect of C-rate on precipitation	Discharge only
<i>Marinescu et al. [17]</i>	0D	4	Both	Contributions to both capacity fade and capacity loss Loss of sulfur due to polysulfide shuttle	Unable to capture C-rate dependence (no capacity change with varying discharge C-rate)
<i>Zhang et al. [80]</i>	0D	5	Both	Investigates contributors to rate capability, with detailed study into resistance	No new model developed (expansion upon existing model)
<i>Danner et al. [81]</i>	1D	5	Both	Focuses on precipitation	High complexity, high number of species
<i>Cornish et al. [3]</i>	0D	4	Both	Published open access Critical analysis of other available models	Constant area assumed, no inclusion of porosity

Table 6: Selection of existing physics-based Li-S models

Most available models are designed specifically for pouch-cells or using pouch-cell data for parametrisation. The existing coin-cell models available tend to focus on specific components within the cell, or work under specific conditions, such as Barai et al. [82] looking at the lateral expansion of the positive electrode in coin-cells. A model of this type is not useful for the purpose of full cell testing. Using a model to predict the behaviour of a different cell format, without first thoroughly testing, is likely to produce inaccurate results.

Despite many of the available models producing similar outputs, most models are only validated for the input parameters, meaning the accuracy to simulate results beyond this remains unknown. Further analysis also shows the input parameters used to obtain these outputs often vary. For example, Mikhaylik et al. [43], Hofmann et al. [83] and Marinescu et al. [17] models all predict the charge voltage. Mikhaylik et al. [43] used pouch-cells with ~1g of sulfur and ~4mL of electrolyte, which produced a high E/S ratio compared to the other models. Hofmann et al. [83] used Cheon et al. [84] data, which varied the positive electrode thickness. Marinescu et al. [17] used experimental data on partially cycled commercial pouch-cells by OXIS Energy Ltd. [85], with higher sulfur loading and lower electrolyte loading compared to other published results. Varying the input parameters makes it difficult to accurately compare models and make conclusions.

Whilst details of each of these models are included within the publication, very few are available open source. Cornish et al. [3] collated and published those that were, for reference, which included Marinescu et al. [78], Marinescu et al. [17] and Hua et al. [86]. The lack of access to the other models makes it difficult to investigate or test the capability beyond the initial data set used to parameterise or validate the model. For example, as Zhang et al. [1] only published discharge results, the capability of the model during charge cannot be tested. In addition, publishing a model open source improves the accessibility, and likely the reliability of the model via vigorous testing by others within the community. It can enable modifications and improvements to be made based on these findings, rather than based solely on hypotheses about the equations. It is therefore assumed further work based on open source models is likely to be more trustworthy, based on this additional level of testing.

3.5.1 Number of Species

The number of species within the reaction pathway varies between models and is dependent on several factors. The chain length of lithium polysulfides varies between Li_2S_8 and Li_2S_1 , and typically includes: $\text{Li}_2\text{S}_8, \text{Li}_2\text{S}_6, \text{Li}_2\text{S}_4, \text{Li}_2\text{S}_2, \text{Li}_2\text{S}_1$ [6]. Additional chain lengths may also be present, but some chain lengths are more common, or likely to occur, based their stability [6].

Experimental work observes a relatively gradual transition from high to low voltage plateau during discharge, hypothesised to be due to many chain length species present within the cell. Most models typically include a small number of chain lengths, which corresponds to a sharper drop at the transition between plateaus. This can be seen when comparing the 1D models by Hofmann et al. [83], which includes three species plus precipitates, and Andrei et al. [41], which includes five species plus precipitates. It is therefore hypothesised that the more species included in the model, the more accurately it can fit to the experimental voltage curve, and the transition from high to low plateau [82].

A larger number of species requires a larger number of equations to solve, increasing the computational power required. For example, with three species, one high and one low plateau reaction is required. Three species is the minimum number required to capture the two voltage plateaus observed experimentally. With four species, high, medium and low plateau reactions are required. The higher the number of species, the higher the number of intermediate plateaus introduced. Typically, the number is selected based on what the model is aiming to achieve, but there should be sufficient species to capture the fundamental behaviour. For the purpose of modelling coin-cell behaviour, this is assumed to include charge and discharge, and the precipitation dynamics, as discussed in Sections 3.5.2 and 3.5.2.1, along with the polysulfide shuttle, as the largest degradation mechanism [6]. Further experimental work is required to confirm the exact number present, and under which conditions.

3.5.1.1 Lithium

The amount of lithium, in relation to sulfur, varies between cells based on manufacturing decisions, and when scaling to larger cell formats. In a coin-cell, lithium is included in excess, typically with a thicker negative electrode [55]. An excess supply removes the possibility of incomplete reactions due to the unavailability or depletion of active lithium. In pouch-cells for commercial applications, a lower amount is used, as an excess of lithium would contribute more significantly to the mass of the cell, lowering the energy density [55].

Within a model, lithium can be calculated in several ways, including mass balancing with the sulfur, charge or concentration balancing, or as a separate variable to sulfur. Within low order models, lithium is typically assumed to balance the charge of sulfur, and therefore is not directly included as a variable.

3.5.2 Charging and Discharging Mechanism

One of the fundamental requirements to make comparisons to the experimental results is the inclusion of both the charge and discharge mechanisms within the model. This is achieved through reversible electrochemical and chemical reactions. It is common for models to focus on only one direction of

reaction, hypothesised to be due to the varying mechanisms that occur in each direction, and the complexity of capturing both accurately. For example, in discharge, precipitation and pore blocking occurs, whilst in charge, dissolution of the precipitates is required, along with the polysulfide shuttle mechanism occurring at the end of charge [6]. Typically, models predict the discharge reaction, as shown in the review by Cornish et al. [3], with 19 of the 26 models analysed capturing discharge, 11 capturing charge and only 6 capturing both. As previously discussed, with only a few models available open source to analyse, it is unclear whether these models do not include the capability to predict charge or simply do not include charge simulations in the published work.

The inclusion of both directions influences which mechanisms are included in the model. For example, precipitation on the positive electrode and stripping of the negative electrode occurs during discharge, whilst dissolution of species on the positive electrode and plating on the negative electrode occurs during charge, influencing the volumetric change of the cell [6]. As previously discussed, the model must include the minimum required number of lithium polysulfides to capture the fundamental mechanisms hypothesised to occur in each direction of reaction within a coin-cell.

3.5.2.1 Voltage Kinks and Jumps

During discharge a voltage kink occurs at the transition from high to low plateau, due to an accumulation of S_1 before precipitation begins [6]. The magnitude of the kink is dependent on the concentration of species, the rate of reactions and the point at which precipitation occurs, known as the saturation concentration [6]. This voltage kink also corresponds to a peak in electrolyte resistance, as observed and predicted by Zhang et al. [1]. This resistance is hypothesised to be influenced by various factors, including the electrolyte viscosity and conductivity, and the concentration and solubility of species [10]. The resistance is also related to the discharge rate; at higher rates of electrochemical reactions, but a constant rate of precipitation, the concentration of species is higher as less species precipitate, instead remaining within the electrolyte and increasing the resistance [1].

At the beginning of charge a spike, or jump, in voltage occurs, associated with a dissolution bottleneck of precipitated species attempting to be dissolved [78]. The DoD of the previous discharge influences the magnitude of the jump [6]; at a higher DoD, as more species are in precipitated form, a larger amount of energy is required to dissolve these species upon charge. Dependent on cycling conditions, a voltage jump can also occur at the end of charge due to the overpotential [6]; all species have been converted to the longest chain length, but charging current still flows into the cell. This is the opposite effect to polysulfide shuttle, which results in a plateau in voltage as the shuttling current exceeds the charging current [43], meaning species cannot be fully converted to the longest chain length, preventing complete charging [6].

A successful model must be capable of predicting all these features. Within existing models, this is achieved through the polysulfide shuttle mechanism and precipitation dynamics, with changes to fitting parameters, such as precipitation or dissolution rates, often required to capture under varying conditions. It may also be important to consider that despite physics-based models capturing the mechanisms directly, these features have also been captured in other model types including ECM, as found by Knap et al. [87] and Propp et al. [88]. This was due to the formulation of the equations and the associated resistance within the electrical circuit, rather than the precipitation dynamics, which is not typically included in ECMs. This is further evidence that the output results can be obtained from varying mechanisms or derivations, and from various types of models.

3.5.3 Rate Capability

Both reversible and irreversible changes occur in Li-S cells [17]. Reversible changes are linked to C-rate dependence; at higher currents, the rate of each reaction increases, but sluggish transport can lead to fewer, or incomplete reactions occurring [6]. The precipitated species at the end of discharge are insulating and contribute to pore blocking, reducing the number of available reaction sites and further

limiting the rate capability [6]. Lower C-rates have been found to correspond to fewer side reactions at the negative electrode, as a passivating layer can form [79]. Other mechanisms, such as polysulfide shuttle, are influenced by C-rate differently; the effect of shuttle is reduced at higher currents as there is less time for the S_8 species to be reduced at the negative electrode and travel back to the positive electrode [6]. These types of C-rate dependencies are reversible.

Irreversible changes that occur due to degradation mechanisms, such as side reactions, deplete the available active material and permanently contribute towards a reduction in performance and achievable capacity [10]. Within a coin-cell where most components are included in excess, these mechanisms are likely to be masked, making it unclear the extent to which irreversible changes are occurring.

Some mechanisms can fall into both categories. For example, the magnitude of shuttle varies with C-rate, influencing the reversible capacity change, but the shuttled sulfur species can contribute to a permanent loss of active material, contributing to irreversible capacity loss [17]. A clear understanding of the exact causes, and therefore distinction between the two types is required in a model to accurately capture experimental behaviour.

3.5.4 Chemistry Variations

As the aim of a coin-cell model is to help with testing of new materials, the model is required to capture variations in chemistry. Despite the experimental work within this project focusing on the positive electrode, the chemistry of all components must be considered. A clear understanding of the influence of each chemistry-based variation must be known, to be implemented into the model. For example, the composition of the electrolyte influences the transport of species, which influences the number and rate of reactions [18]. The structure of the positive electrode, including the size, number and distribution of pores influences the wetting by the electrolyte, and the available area for reactions to occur [89]. The level of inclusion of chemistry-based changes will vary dependent on the complexity of the model. To achieve these chemistry variations, it is likely separate components will be required in the model.

3.6 Scaling: Testing Models with Coin-Cell Data

As previously discussed, most of the available models are designed and parameterised for pouch-cells. Coin-cells differ from pouch-cells significantly, both physically and mechanistically. Without thorough testing, it is unclear the extent to which these pouch-cells models will predict coin-cell behaviour. To do this, the models must first be able to capture the areas discussed in Section 3.3, and include the capability to scale between cell-formats. This includes the geometric size, electrolyte volume, E/S ratio, and packaging. The key differences are summarised in Table 1.

3.6.1 Geometric Size

As the format of the cell changes, the geometric size also changes. From coin to pouch-cell, the size of the positive electrode increases significantly [2], influencing the active area available for reactions to occur. The electrolyte volume also needs to be considered when scaling, to ensure the electrode is fully wetted. When scaling to larger cell formats, the number of layers may increase, along with the use of double-sided electrodes, for example in multi-layer pouch-cells [36]. This further influences the wetting, along with the quantity and availability of active material. These changes may influence other mechanisms, such as the precipitation dynamics and the impact on available area due to pore blocking of the electrode.

3.6.2 Electrolyte Volume and E/S Ratio

The E/S ratio varies when scaling between formats and is typically lower for pouch-cells [2], [36], due to the requirement for a higher gravimetric energy density for commercial applications. To capture variations to the E/S ratio, separate parameters for sulfur mass, electrolyte volume and the E/S ratio are required. Changes to these parameters will impact the behaviour; for example, varying the concentration of species will influence the rate of reactions, resistance and viscosity of the electrolyte [3]. Whilst there

are various other types of resistance, the electrolyte resistance is hypothesised to be the largest [1]. Resistance is also influenced by the rate at which reactions occur, and when accounting for the Ohmic change within the cell, the resistance influences the cell voltage. Dependent on the saturation concentration, changes to the electrolyte volume or E/S ratio could also influence the precipitation dynamics.

3.6.3 Packaging

The variation in packaging between cell formats influences the pressure within the cell. It could also influence the extent to which the cell experiences volumetric expansion [44], [6]. Most existing models do not account for this; it is likely to require higher dimensionality to capture but is an important area to consider.

3.7 Existing Model Capability

The physical differences when scaling between cell formats are hypothesised to correlate to differences in the mechanisms occurring within the cell. The mechanistic differences will influence how the cell behaves, even if using the same materials or manufacturing processes, meaning the behaviour observed in coin-cells is unlikely to directly translate to pouch-cells, or vice versa. Investigation is required to understand the extent of this change, which first requires the model to be able to capture these variations, as discussed in Section 3.6. To the best of our knowledge, there are currently no available coin-cell, cell-level physics-based models.

This Section discusses the work to understand the extent to which current models include the required features and capability to scale. As previously discussed, building upon existing work increases the trust in the modelling decisions and provides more opportunities to analyse and critique each element. From the available physics-based models, as discussed in Section 3.5, it is likely features from several models will need to be combined.

3.7.1 Selected Models for Further Development

For simplicity, the initial iteration of the developed model will be 0D. As it remains unconfirmed within the literature which mechanisms occur and which are only hypothesised to occur, the philosophy of starting with the simplest method and building up from here, as required, ensures the correct causality of model predictions. By including only the fundamental mechanisms, each can be tested, with further mechanisms added incrementally as needed, enabling a clear understanding of the influence each has on the behaviour of the cell. This can then be compared to hypotheses to confirm the cause and effect align. A 0D model also reduces the number of assumptions and fitting parameters that are required in the model, increasing the reliability and trustworthiness when used in real-life applications. The number of experimental parameters required as inputs for the model is significantly reduced compared to higher dimensionality models [6]. The low computational time and cost associated with a 0D model is an important consideration for model development and application.

A 0D model calculates the behaviour of the cell without accounting for spatial variations, such as the transport of species. 0D models are not expected to match the experimental results perfectly; an exact match would imply the model captures all mechanisms occurring within the cell. Although this results in less accurate predictions in comparison to successfully validated higher order models, 0D models are the simplest to develop. The qualitative trends captured by an accurate low order model are sufficient to improve understanding of which mechanisms are occurring, and under which conditions within the cell. From the available 0D models within the literature, and from those summarised in Table 6, there were several that were focused upon more heavily.

3.7.1.1 Zhang et al. [1]

This paper focused on the precipitation dynamics and investigated how the electrolyte resistance influenced behaviour. The model addressed the issue of incorrect predictions and contradicting features within existing models with regards to “the evolution of cell resistance during discharge” [1]. It accounted for electrolyte resistance contributing more significantly to the high plateau, and charge-transfer resistance more significantly to the low plateau behaviour [1]. A new equation predicted the correct shape and magnitude of electrolyte resistance for the first time. This equation calculated resistance based on the geometric area and thickness of the positive electrode, along with the conductivity, which was based on the porosity of the positive electrode and the concentration of lithium.

3.7.1.2 Marinescu et al. [78]

This model was proposed as a simpler alternative to existing higher order models that captured the fundamental behaviour in charge and discharge. This included precipitation and dissolution, including nucleation, along with capacity fade relating to the current and precipitation dynamics. The model included four species, one of which precipitated, corresponding to three reactions. It captured both voltage and C-rate dependence, based on the electrolyte resistance and reversible precipitation.

3.7.1.3 Marinescu et al. [17]

This model investigated the differences between irreversible and reversible capacity fade, relating to the precipitation dynamics and polysulfide shuttle. Building upon the previously published model [78], the inclusion of a shuttled sulfur term contributed to a permanent loss of material, relating to capacity change during cycling. The rate at which species were lost due to shuttle was directly proportional to the number of species already precipitated. This additional mechanism enabled C-rate dependence within the model. The influence of shuttle during charge also contributed to infinite charging, where the voltage plateaued rather than spiking at the end of charge as the full reactions could not be achieved.

3.7.1.4 Cornish et al. [3]

This publication provided a “rigorously validated” 0D model, including detailed analysis of many other available models and their capability against the “minimum set of tests for cell-level Li-S battery models” [3]. Alongside the analysis of other existing models and the data used for validation, this publication offered a simple, clear model that captured all the stated requirements. When considering a model for coin-cell development, this was essential, in comparison to other models that focused on specific areas or mechanisms, which were often too niche for general application. This model was one of the few available open source, via GitHub and PyBaMM [90].

3.7.1.5 Summary

A combination of features from each of these models was then trialled. To begin, as Cornish et al. [3] was available open source, this was used as the base model. The development of this model was based on previously published models, and reference to the original models was required to understand the derivation and implementation. The parameterisation is discussed in Section 3.8. The influence of degradation was not directly accounted for at this stage.

3.8 Parameterisation

As discussed, experimental data is required for model parametrisation. The experimental work completed as part of this project, discussed in Chapter 2, found the irreproducibility of the data collected prevented use for parameterisation. Alternative raw data from experiments was sought. As observed from experimental work using Nanomylite [63], data from a commercial material is significantly higher in reproducibility than laboratory developed materials. The use of Nanomylite within the publications discussed focused on coin-cell testing; to understand scaling, testing within both coin and pouch-cell formats was required. Other work within the LiSTAR project commonly used commercial cell data from OXIS Energy Ltd. [85]. As pouch-cells are used for commercial application, OXIS predominately

developed this format, rather than coin-cells. The subsequent bankruptcy of the company removed the possibility of the development and publication of coin-cell experimental results.

As an alternative to commercial materials or commercially available cells, work at Cambridge University as part of the LiSTAR project focused on developing high quality positive electrode materials. The resulting company, Molyon [91], is now working to commercialise this material. However, similarly to OXIS Energy Ltd., the focus is on pouch-cell format for commercial applications. At the time of the initial coin-cell model development, data was unavailable for use.

A final option to obtain raw experimental data was from the team working at Coventry University, also as part of the LiSTAR project, to develop both coin and pouch-cells. The manufacturing process began obtaining reproducible results in both cell formats in early 2024, which similarly meant that usable data was unavailable at the time of initial coin-cell model development. Work is now underway to improve the performance of both coin and pouch-cells; for further work, this data could be used to validate or test the developed model.

As raw experimental data was unavailable for use, a list of requirements for data from existing publications was created. The publication must include coin-cell cycling, and ideally also include pouch-cell cycling with the same materials, for comparison. If pouch-cell data was unavailable, the materials used in the coin-cells must be relatively standard, to ensure separate pouch-cell data from another source could be obtained. The minimum testing matrix included standard cycling under relative C-rate and temperature conditions, for example 0.1C charging and discharging at ambient temperature. The cycling limits must be reasonable, to prevent degradation mechanisms significantly impacting the behaviour. Varying the C-rate was required to test the rate capability, in terms of capacity and voltage. Long term cycling would be required to investigate potential capacity fade.

When selecting and using published data rather than raw experimental data, several assumptions must be made. Firstly, the published data is reproducible, with multiple test sets confirming the same results are achieved every time. In reality, this may not be correct; the 'best' performance may be published, even if it is not reproducible. Separately, if inputs required for the model are not included in the published data, standard inputs can be taken from other experimental data, or fitting parameters can be derived. As the full data set is unlikely to be published, unless granted access from the authors, the extrapolated data from the publication will be assumed as sufficient for model parameterisation. It will be assumed that all published data will be correct, with no missing information.

Whilst the experimental data collected in this project could not be used, the knowledge obtained from the experimental work was important when deciding on parameterisation data and understanding how each input was calculated or measured. It helped determine which parameters were likely to change when scaling, and whether the values used within the model were realistic. If fitting parameters needed to be derived, as they could not directly be measured, these could be based on informed decisions, rather than trial and error values. For example, the rates of reactions were likely to change when varying cell format and with changes to concentration, electrolyte properties and current. The trustworthiness of parameter selection increased with the experimental knowledge obtained.

The essential and desirable input parameters needed for a coin-cell model are summarised in Table 7. Based on these, a selection of published work was investigated, with the focus on finding a publication that included all essential, and as many desirable parameters as possible. These publications are summarised in Table 8.

	Parameters
Essential	• Current • Voltage (if raw data unavailable, voltage-capacity plots required) • Sulfur mass • E/S ratio, or electrolyte volume • Electrode dimensions
Desirable	• Electrode properties (density, pore volume, porosity, thickness etc.) • Cycling limits (time, voltage, capacity) • Sulfur loading method • Number of layers • Electrode mass • Lithium mass • Total cell mass

Table 7: Summary of the essential and desired experimental parameters required when selecting data from the literature for parameterisation

	C-rate	Sulfur Mass (g)	Electrolyte (μl), E/S Ratio	P. Electrode diameter (mm)	P. Electrode surface area (cm ²)	Sulfur loading (mg/cm ²)	Sulfur wt%	P. Electrode mass (g)	Voltage cut-offs (V)
<i>Bruckner et al. 2014 [92]</i>	0.1 – 0.5	1.70	20 E/S: 12-14	12	1.131	1.5	53.3	-	1.5 – 2.6
<i>Wang et al. 2016[93]</i>	0.05, 0.1, 0.2, 1.0	4.62	100 E/S: 21.7	14	1.539	3.0	60	7.70	1.7 – 2.7 1.5 – 3.0
<i>Chen et al. 2017 [94]</i>	0.1	4.52	10 E/S: 5, 10	12	1.131	4.0	40, 50, 70	11.31	1.6 – 2.6
<i>Weller C et al. 2019[95]</i>	0.05, 0.1, 0.2, 0.5, 1.0	4.41	19.4 E/S: 5	15	1.767	2.2	60	6.48	1.0 – 3.0 1.5 – 2.5
<i>Boenke et al. 2021 [28]</i>	0.1, 0.2, 0.5, 1.0	3.53	24.74 E/S: 7	15	1.767	2.0	50	7.07	1.8 – 2.6
<i>Schmidt et al. 2022 [96]</i>	0.05, 0.1	4.41	22.09 E/S: 5	15	1.767	2.5	60	7.36	1.8 – 2.6

Table 8: Summary of the papers from which experimental data was analysed for use to parameterise the model

3.8.1 Selected Data

Due to the nature of coin-cells used for testing new materials, many of the papers that investigated coin-cell behaviour focused on specific areas or components, rather than general testing. For example, Chen et al. [94] focused on low E/S ratios, Wang et al. [93] focused on the electrolyte composition to mitigate self-discharge and Weller et al. [95] focused on polysulfide shuttle suppression. The type of testing was not initially considered when selecting possible data sets, but it would significantly influence the observed behaviour.

As experimental work completed as part of this project focused on the positive electrode development, it was useful to consider selecting a paper that also focused on this electrode. Whilst the results obtained experimentally were irreproducible, they could be used to as baseline to the published work to help make informed decision about assumptions, and how realistic the parameters would be. This narrowed down the pool of possible papers.

Based on these considerations, Boenke et al. [28] fit the largest number of criteria. It included both coin and pouch-cell results using the same material, built and tested under the same conditions, enabling comparisons as shown in Figure 11. The experimental study included detailed information regarding the manufacturing and characterisation of materials within the cell, which was sufficient to parameterise the model with minimal assumptions. In addition, the materials and techniques used were common within the field, meaning when used for parameterisation, the model predictions would likely be applicable to a large range of other experimental work. The inclusion of constant C-rate cycling at coin-cell level provided a baseline to make comparisons when investigating the rate dependence.

The differences between coin and pouch-cell experimental results can be used to investigate which predicted mechanisms give rise to observed behaviours and help understand the extent to which a coin-cell model would vary from a pouch-cell model. For example, the study found coin-cells achieved higher capacity at all C-rates, a higher voltage in discharge and a lower voltage in charge, which could relate to the transport mechanisms and internal resistance. The key findings are discussed in Section 3.8.3.

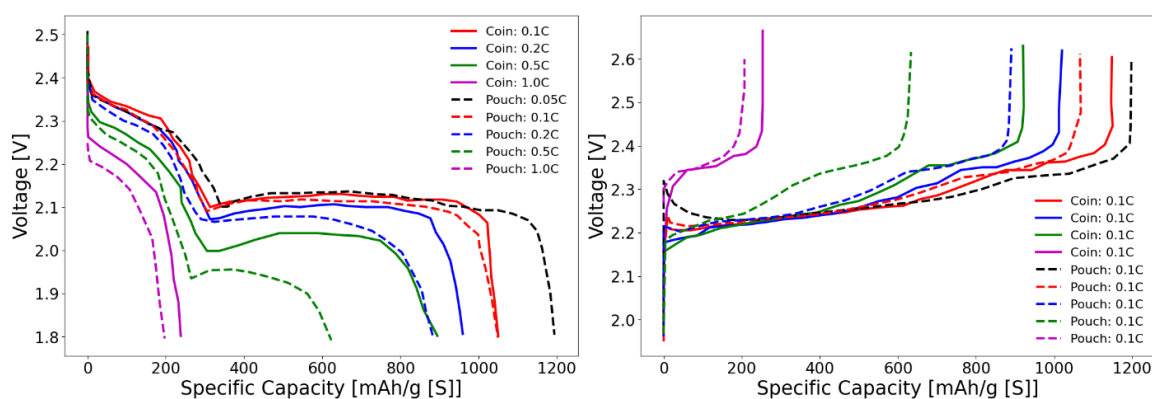


Figure 11: Experimental voltage-capacity graphs from Boenke et al. [28] for a coin-cell during discharge (left) and charge (right)

3.8.2 Overview of Boenke et al. [28]

The aim of the work by Boenke et al. [28] was to develop a positive electrode that was “scalable, non-toxic, with tailorable sulfur areal loading” [28]. The study attempted to improve the power density by using a low-porosity CNT material and varying the sulfur loading [28]. The experimental study focused on two different positive electrode materials, CNT BuckyPaper (BP) and CNT powder-based dry transfer electrodes (DryFilm). For coin-cell testing, both materials were used. For pouch-cell testing, only CNT BP was used as it provided a “free-standing CNT/sulfur composite” [28]. The pouch-cells

were multi-layer and the E/S ratio was varied. All other components remained consistent between coin and pouch-cells.

The study saw variations in sulfur loading and sulfur weight percent (wt%), along with circular perforations made to the current collector to test the influence of reduced mass on performance in pouch-cells. The fundamental aim of the work was to understand the most important factors for high power density, ensuring the cells were also lightweight [28]. It was hypothesised factors impacting power density included electrode thickness and porosity, electrolyte volume and viscosity, and mass/charge transfer [28].

The process of manufacturing the electrodes included a well-dispersed sulfur slurry cast onto aluminium transfer foils, before being dried, stacked together with carbon electrodes and sulfur-melt infiltration applied [28]. This contributed to variations in sulfur loading and sulfur wt%. Three double-sided positive electrodes of CNT BP were used for pouch-cell variation, and sulfur loadings of 2.0, 1.5 and 1.0mg/cm² were combined with sulfur wt% of 50% and 33%. The sulfur wt% was referred to as the sulfur in comparison to the total electrode mass, and sulfur loading was referred to as the amount of sulfur on the surface area of the positive electrode. Variations to the sulfur wt% and loading simultaneously were achieved as shown in Figure 12. This interpretation was confirmed from discussion with the author, Tom Boenke [97]. When varying the sulfur mass, the electrolyte volume was also assumed to vary to maintain the E/S ratio.

	Constant Sulfur Loading	Constant Sulfur Wt%
Reducing Sulfur Loading		Reduce sulfur mass Reduce electrode thickness
Reducing Sulfur Wt%	Reduce electrode thickness (only)	

Figure 12: Summary of how Boenke et al. [28] achieved varying sulfur loading and wt% simultaneously

From discussion with Tom Boenke throughout the project, further information including the order of charge and discharge cycling, the density values for the materials used, and several other parameters and calculations were provided [97]. These were essential when ensuring the assumptions made within the model were correct and realistic.

3.8.3 Boenke et al. [28] Results

3.8.3.1 C-rate

Boenke et al. [28] ran a variety of tests, looking into both constant and varying C-rate. The charging C-rate remained constant to reduce negative electrode degradation, hypothesised to occur due to lithium plating [28]. The discharge C-rate was varied at increments between 0.05C and 1C. An activation cycle at 0.05C was completed before cycling. Experimentally, an activation cycle is designed to optimise cell conditions and works to minimise the effect of degradation mechanisms through the formation of an ideal SEI layer on the negative electrode [10].

At the constant C-rate for coin-cells, Boenke et al. [28] found a high initial discharge capacity, approximately 1,200mAh/g [S], dropping to approximately 800mAh/g [S] after 100 cycles. Upon analysis, this capacity loss could have been caused by several mechanisms, including polysulfide shuttle or side reactions, contributing to a loss of active material. As observed in the Supplementary Documents [98], if shuttle was the cause of the capacity loss, the rate of shuttle was sufficient to contribute to a loss of material, but insufficient to contribute to infinite charging.

When varying the discharge C-rate, at the highest C-rate of 1C, a drastic drop in discharge capacity was observed [28]. This was hypothesised to be largely due to transport limitations and the temporary unavailability of species for electrochemical reactions. The capacity was regained upon lower C-rate cycling, as found in Figure 5D for coin-cells and 7E for pouch-cells in [28], confirming reversible

dependence. A small amount of irreversible capacity loss occurred between the initial 0.1C cycling and the final 0.1C cycling, although this may have been due to the initial cycling and stabilisation of the cell.

When testing the lowest current rates for pouch-cells, 0.05C and 0.1C, a sub-plateau was observed between 2.1V and 2.0V in discharge, as shown in Figure 7 in [28]. The cause was hypothesised to be due to the “electrocatalytic effect” of the electrode structure, and chemical conversion of lithium polysulfides [28].

For both cell formats, a larger voltage change was also observed at higher C-rates due to the Ohmic change. A larger current and resistance contributed to a larger voltage decrease in discharge, and voltage increase in charge, as shown in Figure 11.

3.8.3.2 Sulfur Content (for Pouch-Cells)

The sulfur content remained constant for coin-cells. For pouch-cells, Boenke et al. [28] varied the sulfur within the cell in terms of sulfur loading and sulfur wt%. Variations to the sulfur content were likely to contribute to changes in the precipitation dynamics and resistances within the cell. Boenke et al. [28] hypothesised a higher capacity was achieved with lower wt% due to the reduced mass and therefore reduced surface area coverage when species precipitate. As previously discussed, as the sulfur mass varied, the electrolyte volume also varied to maintain the E/S ratio. Whilst the concentration of species therefore remained constant, the influence of increased mass and therefore increased volume may influence the cell, for example, due to increased pressure.

Boenke et al. [28] hypothesised that lower sulfur loading resulted in an increase in capacity due to the reduced mass and charge-transfer resistance. A higher rate capability was found with lower sulfur areal loading, whilst the impact of sulfur loading was hypothesised to be minimal and therefore neglected at lower C-rates [28]. When decreasing the sulfur loading, the mass of all other components remained the same, influencing the ratio of active material to dead mass from passive components, and therefore altering the energy density of the cell. In addition, as the sulfur loading decreased, sulfur utilisation was found to increase, hypothesised to be linked to the increase in available area for reactions, along with the reduced internal resistance.

The trend in capacity change with increasing C-rate was found to vary with sulfur content; at high loadings, larger increments of capacity change were observed at higher C-rates, but at low loadings, larger increments of capacity change were observed at lower C-rates. A hypothesis was not given, and from further analysis, the reason remained unclear; further work is required to investigate this.

3.8.3.3 Degradation

One of the hypothesised reasons for higher capacity at lower current densities, achieved with lower sulfur content, was due to reduced degradation of the electrolyte and negative electrode [28]. A higher charging C-rate was also hypothesised to contribute to negative electrode degradation, relating to lithium plating [28]. Based on the reduction in usable materials for electrochemical reactions, degradation mechanisms contribute to the reduction in cell performance.

As different mechanisms occur in charge and discharge, such as precipitation compared to dissolution, or polysulfide shuttle in charge, the Coulombic efficiency could be used to calculate the performance of each cycling direction. A high Coulombic efficiency implies similar capacity in charge and discharge and is hypothesised to be linked to fewer degradation mechanisms or side reactions [28]. Boenke et al. [28] observed a drop in Coulombic efficiency in coin-cells from 98% to 60% at higher cycle numbers and hypothesised it was due to polysulfide shuttle. The magnitude of shuttle is likely to vary between cell formats, based on the increased current and varying rates of reactions.

3.8.3.4 Electrolyte (and Volume)

The electrolyte volume was calculated in relation to the sulfur mass, based on the E/S ratio. Boenke et al. [28] found the electrolyte volume influenced the dissolution of species, and a larger volume corresponded to a lower electrolyte viscosity and lower internal resistance [28]. The volume also influences the utilisation of active material [28], for example, a lower volume could lead to insufficient electrode wetting. A larger E/S ratio, and therefore a larger volume of electrolyte, is found in coin-cells. As the electrolyte is one of the largest components within the cell, a larger volume contributes to a lower energy density.

The electrolyte composition used in the study was standard: DME/DOL (1:1, v/v), 1M LiTFSI and 0.25M LiNO₃. As discussed in Chapter 1, lithium polysulfides are highly soluble in ether solvents, and the additive LiNO₃ works to minimise the influence of shuttle through improvements to the formation of the SEI layer [28]. However, shuttle was observed in the coin-cell results; this may be due to the reduced C-rates when cycling coin-cells compared to pouch-cells, allowing sufficient time for species to reduce at the negative electrode.

3.8.3.5 Positive Electrode Material

There are various features of the positive electrode that influence the behaviour. For example, the specific surface area and the pore size and distribution influence the uniformness of sulfur precipitation, along with the utilisation [28]. Electrodes of “CNTs with thinner diameters” were found to have more conductive pathways, increasing the sulfur utilisation [28]. Investigation into perforations in the pouch-cell positive electrode found that reducing the mass and therefore altering the ratio of insulating sulfur to conductive carbon did not compromise the cell performance [28].

3.8.3.6 Scaling

When comparing the results, the general trends in behaviour such as voltage kinks and jumps, and capacity C-rate dependence, were similar for both cell formats [28]. Some changes or tests were only completed on one cell format, such as constant C-rate testing on coin-cells to investigate irreversible capacity change, and sulfur content variation on pouch-cells only. From the results, and based on other experimental work, hypotheses could be made about the results in alternative cell formats when scaling.

In terms of capacity when scaling between cell formats, coin-cells achieved higher capacity at the same C-rate, in both charge and discharge. Boenke et al. [28] found pouch-cells showed poorer performance at higher C-rates due to increased electrolyte resistance and viscosity, based on the reduced electrolyte volume [28].

3.9 Setting up the Models to Test

Whilst features from the four models discussed in Section 3.7.1 could be combined and used to test the capability to predict coin-cell behaviour, the initial stage of testing used the Cornish et al. [3] model only. This model was available open source, along with a clearly defined data set from Hunt et al. [78]. By using this model as a baseline, the selected parameters from Boenke et al. [28] could be implemented and tested to investigate the capability when scaling a pouch-cell model to predict coin-cell behaviour, through changes to the input parameters only.

3.9.1 Modelling Software: PyBaMM

The tool used for the development of the battery model was Python Battery Mathematical Modelling (PyBaMM) [90]. PyBaMM uses Python but is designed specifically for battery testing. It is open source and allows access to up-to-date models that have already been developed by others within the research community. These models can be tested and adapted, saving time creating a new model from scratch. PyBaMM is considered highly efficient in comparison to others programmes due to the “state of the art automatic differentiation and numerical solvers” [99], meaning models can be run with lower computational cost than bespoke code. PyBaMM attempts to solve problems related to data

parameterisation by providing clear disclosure of the input data used and enabling model outputs to easily be reproduced and re-tested, if required.

To access PyBaMM, along with the Cornish et al. [3] model and data set, GitHub was used. This software enables creation, storage and sharing of code, along with clear versioning control. It also allows integration between projects and users. *Other modelling tools include MATLAB and COMSOL, although these were not used for predictive modelling in the project.*

3.9.1.1 Difficulties: PyBaMM Versioning

These findings became apparent throughout various stages of the model development, including during the work in Chapter 4, but are summarised and discussed here.

PyBaMM as a modelling tool is heavily used within the ESE research group at Imperial College London. Whilst the models included in PyBaMM are primarily designed for Li-ion chemistry, the capability is applicable to other cell chemistries.

PyBaMM is regularly updated to fix bugs and to include ongoing work and additional features that have been developed and tested to improve the capability. These updates are run and tested against the core Li-ion models within PyBaMM, before being published publicly. There is currently no official branch of work for Li-S model development in PyBaMM. Cornish et al. [3] found adjustments to the base model used were required to run a Li-S model, due to the differences in chemistry and interactions within the cell, making it incompatible with implementation of a Li-ion base model. In general, the Li-S models within PyBaMM are predominately 0D and 1D and do not use the sub-models.

Based on the heavy focus towards Li-ion, difficulties occurred when running the model after PyBaMM version updates. The bug fixes were designed to resolve or improve capability for Li-ion modelling; without an official branch for Li-S, these were not tested on Li-S models before being published, meaning errors were likely to occur. Updates to Python, separately to PyBaMM, further added to the potential errors caused. A separate issue arose when running the models on different operating systems; using the same model, different results could be obtained when using Mac, Windows or Linux. This was hypothesised to be due to PyBaMM being installed and working in a slightly different way on each system.

After significant investigation into the cause, to resolve both issues, a virtual environment was introduced. Due to the novelty of using Li-S in PyBaMM, and the two separate issues to resolve, a trial-and-error method was required to find the version that was able to run the model correctly, without any errors. Once found, this was set within the virtual environment, ensuring any further updates to PyBaMM or Python would not impact the code. This also worked to minimise potential differences across operating systems if the version remained consistent.

Details relating to setting up the virtual environments are included in Appendix: Section 9.2.

3.10 Implementation of a 0D, Physics-Based, Cell-Level Model in PyBaMM

The model developed in Cornish et al. [3] is discussed in detail in this Section. It also includes the changes required to capture coin-cell behaviour, based on Boenke et al. [28] experimental results.

3.10.1 Electrochemical Reactions

As discussed, the requirement for both the charge and discharge dynamics influences several model decisions, including the number of species, which species precipitate, and which species are required to capture mechanisms such as polysulfide shuttle. Based on the voltage-capacity curve from results by Boenke et al. [28], focusing on the transition from high to low plateau in discharge, it is likely many chain length species are present. Although a high number of species within the model would capture this gradual transition [82], with the aim of simplicity, the number of species remained unchanged for initial testing. Cornish et al. [3] included 4 species, with only S_1 precipitating and dissolving. Although

S₈ has also been found to precipitate at the end of charge [6], the inclusion into the model would add further complexity, and may not be required to capture the observed coin-cell behaviour. If necessary, it can be added during further testing.

The reactions included in the model shown in Equations [7] – [9] and correspond to the high, medium and low plateaus respectively. During charge, only S₈ shuttles to S₄.



3.10.2 Species Masses

The distribution of species is discussed throughout the thesis with respect to how the sulfur is divided into each chain length species, S₈, S₄, S₂ and S₁ in this iteration of the model. It does not relate to the spatial distribution of sulfur species around the cell.

The mass of sulfur was an input into the model, and the mass of each sulfur species was calculated as a portion of the total sulfur mass. Mass is always conserved during cycling; the total mass of each species cannot exceed the total input sulfur mass. When running a constant current cycle, the distribution of species within the cell influences the cell voltage, the Nernst potentials and in turn the overpotential, as discussed in Section 3.10.6. The distribution of species also influences rate of reactions, as discussed in Section 3.10.7.

A larger mass of sulfur correlates to a larger cycling current, when calculated based on the current density. Adjustments to the total mass, or distribution of species influences the capacity of each plateau. For example, at the start of discharge, if a small portion of sulfur species are in the longest chain length, S₈, a shorter high plateau will be observed. This capacity change is temporary and reversible, dependent on conditions of the cycle.

3.10.3 Electrolyte Volume and Pore Volume

The electrolyte volume is the total volume of electrolyte added to the cell during manufacture. It is determined by the mass of sulfur, based on the E/S ratio, as shown in Equation [10]. However, Cornish et al. [3] included the electrolyte volume as a separate input value, with no relation to the E/S ratio.

$$V_{\text{electrolyte}} = \frac{E}{S} \text{ratio} \cdot \text{mass}_{\text{sulfur}} \quad [10]$$

The E/S ratio given by Boenke et al. [28] was 7μl/mg for coin-cells and 4μl/mg for pouch-cells. The electrolyte volume was assumed constant during cycling, with no losses due to degradation. The model also assumed no change in behaviour due to the increased pressure with larger volumes of electrolyte. The total electrolyte volume was assumed to be used for electrochemical reactions, with full wetting and utilisation of the positive electrode. Within a real cell, this is not always true; an excess of electrolyte is present if the total electrolyte volume exceeds the volume required to wet all the pores. Coin-cells have a larger excess quantity than pouch-cells. In addition, the increased positive electrode surface area in a pouch-cell increases the likelihood of insufficient electrolyte to fully wet the electrode, reducing the number of reaction sites available, resulting in lower achievable capacity. The model also does not account for the electrolyte volume contained within the separator.

3.10.4 Porosity and Positive Electrode Surface Area

The model by Cornish et al. [3] did not account for the influence of porosity but suggested it could be incorporated into the Butler-Volmer dynamics. The model assumed a constant positive electrode surface area, with no change during cycling due to precipitation or electrolyte wetting; the total area was always available for reactions during cycling. An area value was taken from Boenke et al. [28] experimental results of 1.8cm² for the coin-cell electrode and 33.6cm² for the pouch-cell electrode. In addition, the model did not account for layers or thickness of the electrode, which are likely to vary when scaling between cell formats, for example in a multi-layer pouch-cell.

A reduction in available area towards the end of discharge is likely to occur due to precipitation and pore blocking of the positive electrode surface; Boenke et al. [28] found a correlation between higher sulfur content and a larger area coverage, resulting in a greater influence on performance. Based on the various factors likely to influence area, the decision was made to first test the predicted behaviour using a constant area value, before investigating the influence of electrode wetting and precipitation separately. As coin-cells are significantly smaller in geometric size, the influence of area may be reduced in comparison to pouch-cells.

3.10.5 Resistance and Conductivity

The study by Zhang et al. [1] found that the cell resistance had been incorrectly predicted in previous models and changed the formulation to predict the correct shape and magnitude for the first time, based on the electrolyte conductivity [1]. The resistance was found to peak at the transition between high to low plateau, corresponding to the onset of precipitation [1]. It was found that electrolyte resistance contributed most significantly to the high plateau, and charge-transfer resistance contributed to the low plateau during cycling [1]. The formulation of the equation was based on the most realistic assumptions without accounting for transport or the related properties. Cornish et al. [3] used this electrolyte resistance equation proposed by Zhang et al. [1], as shown in Equations [11] and [12]. As Cornish et al. [3] did not include porosity, this term was removed. Adjustments to the fitting parameters within the equation were likely required to match the experimental data.

Boenke et al. [28] did not provide measurements for the resistance of either coin or pouch-cells. Due to the lack of experimental data for coin-cell resistance within the literature, the resistance was assumed to be similar in order of magnitude to a pouch-cell, if derived in the same way. In a real cell, the format is likely to influence the magnitude of resistance more significantly; a lower volume of electrolyte corresponds to a higher concentration and increased internal resistance [28]. Further work is required to obtain realistic values of resistance for coin-cells, to remove this assumption.

$$\sigma = \varepsilon^Z (\sigma_0 - (b |C_{Li} - C_{Li0}|)) \quad [11]$$

$$R_{ohm} = \frac{1}{ar \sigma} \quad [12]$$

3.10.6 Butler-Volmer Dynamics (Voltage and Current)

For this model, the Butler-Volmer dynamics [77] contribute towards defining the voltage of the cell, based on the species distribution, the overpotential, calculated based on the Nernst potential, and the partial currents, as shown in Equations [13] – [15]. As the exchange current densities could not be measured, they were assumed fitting parameters within the model. The cell voltage accounts for losses due to internal resistance, referred to as the Ohmic change, as shown in Equation [16]. The sum of the partial currents equals the total applied current through the cell, as shown in Equation [17]; when the cell is cycling within a specific plateau, the partial current of that plateau is equal to the total current, and the other partial currents are equal to zero. The transition is almost instantaneous when the cell reaches the next plateau, with the partial current of the next plateau becoming equal to the total current,

and the previous plateau equal to zero. Only around the transition between plateaus do the partial currents vary between zero and the total applied current. The model testing was done under constant current conditions. A C-rate of 1C was equivalent to the total current, and lower C-rates were calculated from this.

$$i_H = -2i_H^0 \operatorname{ar sinh} \left(\frac{n_H F}{2RT} \eta_H \right) \quad [13]$$

$$i_M = -2i_M^0 \operatorname{ar sinh} \left(\frac{n_M F}{2RT} \eta_M \right) \quad [14]$$

$$i_L = -2i_L^0 \operatorname{ar sinh} \left(\frac{n_L F}{2RT} \eta_L \right) \quad [15]$$

$$V = V_{\text{terminal}} - IR_{\text{ohm}} \quad [16]$$

$$I = i_H + i_M + i_L \quad [17]$$

The overpotentials within the Butler-Volmer were calculated with respect to the Nernst potential and the cell voltage, as shown by Equation [24], where $i = H, M, L$ plateau. The Nernst potentials were calculated based on several constant parameters, the standard potentials, and the variation in mass of species, as shown in Equations [18] – [23]. The standard potentials were fitting parameters in the model. The voltage limits during cycling were set to 1.8 – 2.8V, to align with Boenke et al. [28] experimental testing. These values were hypothesised to be selected due to the degradation mechanisms, or unwanted behaviour that occurs outside of these limits, which contribute to a reduction in cycle life [18].

$$E_H = E_H^0 + \frac{RT}{n_H F} \ln \left(f_H \frac{S_8^0}{(S_4^{2-})^2} \right) \quad [18]$$

$$E_M = E_M^0 + \frac{RT}{n_M F} \ln \left(f_M \frac{S_4^{2-}}{(S_2^{2-})^2} \right) \quad [19]$$

$$E_L = E_L^0 + \frac{RT}{n_L F} \ln \left(f_L \frac{S_2^{2-}}{(S^{2-})^2} \right) \quad [20]$$

$$f_H = \frac{(n_{S_4^{2-}})^2 Ms v}{n_{S_8^0}} \quad [21]$$

$$f_M = \frac{(n_{S_2^{2-}})^2 Ms v}{n_{S_4^{2-}}} \quad [22]$$

$$f_L = \frac{(n_{S^{2-}})^2 Ms v}{n_{S_2^{2-}}} \quad [23]$$

$$\eta_i = V - E_{\text{nuc}} \quad [24]$$

3.10.7 Ordinary Differential Equations (ODEs)

Within a 0D model, the rates of reactions are calculated using an algebraic system of equations involving ordinary differential equations (ODEs) based on a single independent variable, here the species mass. The equations also include several fitting parameters: the shuttle rate and the precipitation and dissolution rates. As the cell cycles, electrochemical reactions occur, changing the distribution and quantity of each chain length species. The equations govern the rate at which these changes occur, as shown in Equations [25] – [28]. During discharge, the model predicts S_8 will reduce to S_4 , to S_2 , to S_1 . The amount of S_4 present at any time, for example, is determined by the amount being gained from S_8 reduction, and the amount being lost from the reduction to S_2 . As the species distribution changes, the

voltage also changes. As the current increases, the net rate of reactions increases, based on the inclusion of the partial currents.

$$\frac{dS_8^0}{dt} = -\frac{n_{S_8^0} Ms}{n_H F} i_H - k_s S_8^0 \quad [25]$$

$$\frac{dS_4^{2-}}{dt} = \frac{n_{S_8^0} Ms}{n_H F} i_H + k_s S_8^0 - \frac{n_{S_4^{2-}} Ms}{n_M F} i_M \quad [26]$$

$$\frac{dS_2^{2-}}{dt} = \frac{n_{S_4^{2-}} Ms}{n_M F} i_M - \frac{n_{S_2^{2-}} Ms}{n_L F} i_L \quad [27]$$

$$\frac{dS_1^{2-}}{dt} = \frac{n_{S_2^{2-}} Ms}{n_L F} i_L - \frac{k_p}{v \rho_s} S_p (S_1^{2-} - S^*) \quad [28]$$

$$\frac{dS_p}{dt} = \frac{k_p}{v \rho_s} S_p (S_1^{2-} - S^*) \quad [29]$$

3.10.7.1 Precipitation Dynamics

The model assumes the cell is influenced consistently by one precipitation mechanism throughout cycling. The precipitation occurs via particle growth only and is determined based on the precipitation rate and the saturation concentration, both of which are fitting parameters. Despite experimental findings observing the opposite, the area has no influence on the precipitation dynamics.

The mass of S_1 , in relation to the saturation concentration, determines the point at which species begin precipitating or dissolving. When the S_1 mass is below the saturation mass, the system is undersaturated, meaning precipitation does not occur. When the mass of S_1 exceeds the saturation mass, the system is considered oversaturated and precipitation occurs, until the mass of S_1 falls below the saturation mass again. Whilst various factors may influence the saturation mass, such as the electrolyte chemistry, and it is likely to change when scaling between cell formats, the saturation mass was assumed constant within the model. As this was a fitting parameter and could not be measured experimentally, the saturation mass value was taken from Marinescu et al. [78]. Whilst this value is based on a pouch-cell, it was assumed to be the same for a coin-cell.

The mass of S_p also influences the reaction. Marinescu et al. [78] found that species already precipitated on the electrode surface provided a nucleation site for further precipitation reactions to occur, given the system was oversaturated. With the inclusion of S_p within the ODE, the model assumed that number of species precipitating was proportional to the number that had already precipitated [78]. This worked to include the influence of nucleation, without a separate equation. The influences of nucleation and particle growth are discussed in more detail in Section 4.7.1.

The precipitation and dissolution rates were fitting parameters, and determined the rate at which these mechanisms occurred once all other conditions were satisfied. It was unclear whether the precipitation and dissolution rates should be constant and equal, or able to vary during cycling. It was likely if the precipitation rate exceeded the dissolution rate, the sulfur would not be fully utilised, as a portion would remain undissolved at the end of charge. If the dissolution rate exceeded the precipitation rate, it was hypothesised all species would dissolve during charge, enabling complete reactions and tending towards maximum achievable capacity.

3.10.7.2 Polysulfide Shuttle

Shuttle occurs when the longest chain lithium polysulfides are reduced during charge, creating a shuttling current that opposes the charging current [6]. Dependent on the magnitude of the current in each direction, along with the distribution of species, shuttle can lead to infinite charging. To capture this in the model, a shuttle term was included within the ODEs, as shown in Equations [25] and [26]. This term, which included a shuttle rate and the mass of S_8 , accounted for the loss of S_8 and the corresponding gain of S_4 due to shuttle. The shuttle rate included in the model was a constant fitting parameter, calculated dependent on other conditions within the model. Further work is required to determine how this may change with cycling, for example, based on the C-rate. The shuttle mechanism was included to investigate the movement of species during charge; no species were irreversibly lost due to this mechanism. No other degradation mechanisms were included in Cornish et al. [3].

3.10.8 What assumptions did Cornish et al. [3] make?

3.10.8.1 Resistance

The same formulation of the resistance equation derived by Zhang et al. [1] was used, with adjustments to the fitting parameters. Whilst the total internal resistance is the sum of all resistance sources, the assumption was made that the magnitude of electrolyte resistance was significantly larger than any other resistance, and therefore the only type considered. When implemented, the assumption was made that the magnitude of coin-cell resistance was the same as that for pouch-cells; further work to investigate and obtain coin-cell experimental results is required to update this.

3.10.8.2 Electrolyte Distribution between Components

The total active material was assumed to be contained within the positive electrode. The species were assumed to be homogeneously distributed within the electrolyte and across the electrode, contributing to each electrochemical and chemical reaction as expected. The volume of the electrolyte and species dissolved within the separator were not accounted for within this model.

3.10.8.3 Transport

As the model was only 0D, no transport effects were included. Along with the justification of selecting the simplest model for initial development, the assumption was made that based on the coin-cell size, transport effects could be neglected. Whilst this is an unrealistic assumption for larger cell formats, for consistency, the same assumption remained.

3.10.8.4 Lithium

The model did not account for the negative electrode, including the mass of lithium or the geometry of the electrode. It was assumed that there was sufficient lithium for all reactions with sulfur, without creating a bottleneck. Further development to include lithium as a separate component may be required at a later stage to investigate this.

3.11 Model Testing

3.11.1 Full Parameter Set

The data from Boenke et al. [28] used to parametrise the model is summarised in Table 9, along with the required fitting parameters.

Parameter	Unit	Value	Source
Sulfur Mass	G	0.003534	Given in Boenke et al. [28]
Electrolyte Volume	L	0.00002474	Calculated from Boenke et al. [28]
Exchange Current Densities (i_H^0, i_M^0, i_L^0)	A m ⁻²	Varied	Fitted
Standard Potentials (E_H^0, E_M^0, E_L^0)	V	Varied (between 2.4 – 2.0)	Fitted
Voltage Cut-offs (high, low)	V	2.6 1.6	Based on experimental work
Geometric Area	m ²	0.0001767	Given in Boenke et al. [28]
Electrode Thickness	m	80e-6	Given in Boenke et al. [28]
Electrode Density	g cm ⁻³	0.5	Given in Boenke et al. [28]
Precipitation Rate	s ⁻¹	1e2	Fitted
Dissolution Rate	s ⁻¹	1e3	Fitted
Shuttle Rate	s ⁻¹	0	Fitted
Saturation Mass	g	0.0001	Given in Marinescu et al. [78]

Table 9: Summary of all the input parameters to test coin-cell capability in the model

3.11.2 Cycling Capacity

Boenke et al. [28] ran an activation cycle of 0.05C, followed by incrementally increasing the discharge C-rate from 0.1C to 1C, and then decreasing down to 0.1C by the same increments. To compare C-rate variation with the experimental data and investigate C-rate dependency, only the discharge current was varied in the model; the charging C-rate was kept constant at 0.1C. No activation cycling was completed before standard cycling as Cornish et al. [3] did not include this capability. To match the experimental process used in Boenke et al. [28], the cell was first discharged. The initial conditions for discharge, where S₈ was not in precipitated form, were also easier to obtain stable values for within the model, compared to charge conditions.

The achievable capacity varied based on several conditions, including the current and mass of sulfur available within the cell. The maximum theoretical specific capacity of a Li-S cell is 1,675mAh/g [S]. As the model did not account for degradation or transport limitations, and assumed full material utilisation, including the electrolyte and sulfur, the model tended towards the maximum capacity at all C-rates. This was significantly higher than the experimental capacity achieved by Boenke et al. [28], where these assumptions were likely to be untrue. Other factors such as the rate of precipitation or dissolution would also impact the behaviour, in terms of reactions and sulfur utilisation [6], as discussed in Section 0. These could work towards capturing the change in capacity observed when cycling at a constant C-rate, as shown in Supplementary Documents by Boenke et al. [98], without the inclusion of degradation mechanisms. However, whilst adjustments to fitting parameters could capture the correct capacity value to match experimental results, there would be no related mechanisms to describe why, or what causes the incomplete reactions, and the assumption of full material utilisation would remain. Other parameters within the cell, including the pore volume and porosity of the electrode, could be optimised to capture how the materials are utilised and the impact on achieved capacity.

At higher C-rates, Boenke et al. [28] observed a larger capacity loss. The influence on the high and low plateaus were different, with a larger magnitude of change within the low plateau. There are several hypotheses for this, including the charge-transfer resistance [1] in the low plateau, the impact of the

precipitation dynamics, or cycling limits being reached earlier at higher C-rates. As previously discussed, higher order models capture capacity C-rate dependence through transport limitations. Without spatial variations, further investigation is required to understand how to implement mechanisms to capture C-rate dependence into a 0D model.

3.11.2.1 Mass Variation

The total mass of active material within the cell, dependent on other conditions, influences the behaviour of the cell. For example, a higher sulfur content, or higher areal loading corresponds to a higher internal resistance [6], influencing the transport within the cell [28]. Based on the E/S ratio, increasing the sulfur mass also increases the electrolyte volume. The influence of an increased electrolyte volume, for example increasing the internal pressure, is not considered within the model. The mass of sulfur in relation to the mass of carbon, known as the S/C ratio, is also not considered within the model. A higher ratio corresponds to a larger mass of insulating sulfur in relation to the conductive carbon host, which influences the number and type of reactions occurring [6].

3.11.2.2 History Effect

The history effect is related to the conditions from the previous cycle(s) and the influence these have on subsequent cycles. Within the model, this was largely due to the distribution of species at the end of each cycle; this distribution determined the SoC and voltage of the cell, both of which impact the performance of the following cycle(s). Boenke et al. [28] observed this experimentally to some extent, as shown in Figure 5D in [28] with variations to C-rate; occasionally, the capacity of the first cycle after the C-rate had been changed did not align with the capacity of the following cycles. This was hypothesised to be due to the history effect from the previous cycle having a larger impact on the performance than the change in C-rate.

Within the model, only the discharge current was changed to match Boenke et al. [28] experimental data. Based on the history effect, the charge behaviour also varied, as observed experimentally. The model captured the history effect with the species distribution at the end of a cycle becoming the initial conditions for the following cycle. Neither discharge or charge experienced C-rate dependence.

3.11.3 Resistance

As the negative electrode was not included as a separate component within the model, Cornish et al. [3] calculated the mass of lithium to match the mass of charged species, S_4 , S_2 and S_1 . When using the equation derived by Zhang et al. [1], the predicted resistance spiked at the transition between high and low plateau, in both charge and discharge. The magnitude of resistance increased with C-rate, hypothesised experimentally to be due to an increased rate of all reactions, therefore increased movement of species, with more collisions occurring. Experimentally, at higher currents, if the precipitation rate remains the same, higher rates of reaction result in less S_1 precipitating, a higher mass of dissolved species within the electrolyte, increasing the viscosity, decreasing ionic mobility and increasing the resistance [6].

Beyond the inclusion of charged species within the conductivity equation, as shown in Equation [11], the model does not directly account for precipitation, which influences the concentration of species and the available surface area of the electrode, reduced due to pore blocking. Experimentally, ionic resistance increases with increasing electrode thickness [6]; this is incorporated in the model within the numerator of the resistance equation, although variations to the electrode thickness were not tested.

3.11.3.1 Voltage

The resistance contributes to the Ohmic change, which influences the cell voltage, as shown in Equation [16]. A larger current corresponds to a larger resistance, both of which contribute to a larger Ohmic change, observed as a larger voltage drop during discharge. As the charging C-rate remained constant, an Ohmic change was not observed during charge.

The standard potentials of the medium and high plateau were set to very similar values, meaning there was not a clear distinction between the two upper plateaus; the aim was to match the voltage plateaus observed by Boenke et al. [28].

3.11.3.2 Conductivity

As previously discussed, the electrolyte conductivity was formulated as stated by Zhang et al. [1] and used to calculate the electrolyte resistance. The fitting parameters within the conductivity equation were selected to obtain the correct magnitude of resistance, and therefore Ohmic change with C-rate variation to match experimental results. The values used in this model are described in Section 3.11.1. These fitting parameters were carefully selected to ensure numerical errors did not occur based on the initial and varying value of lithium within the exponential term in the model. Errors resulted in significant jumps in resistance, corresponding to spikes in the voltage plateau during cycling.

3.11.4 Polysulfide Shuttle (Degradation)

The model by Cornish et al. [3] included no degradation mechanisms. Polysulfide shuttle was formulated to create infinite charging through the reduction of S₈ during charge, preventing the upper voltage limit being reached. The shuttle mechanism did not contribute to an irreversible loss of material or capacity, as tested by Marinescu et al. [17] with the inclusion of shuttled sulfur losses. For further work, this may become an important area of focus when analysing long-term cycling and the observed capacity fade.

Alongside transport limitations, the larger capacity change at higher C-rates is hypothesised to be due to higher rates of the degradation mechanisms occurring. For polysulfide shuttle, the shorter time for species to reduce during charge, competing against the increased rates of reaction at higher C-rates results in a smaller parasitic current and therefore a smaller impact of shuttle on performance. At a lower C-rate, the impact of shuttle is increased. With the presence of shuttle, cycling will continue until a cut-off limit is reached, likely capacity or time. As S₈ does not accumulate, the voltage does not spike, resulting in a high apparent capacity being achieved. The flattening of the curve occurs due to the competition between shuttling and charging current; if the shuttle current exceeds the charging current, the rate at which species are reduced from S₈ to S₄ is faster than the rate at which S₄ is oxidised to S₈ during charge. The apparent capacity differs to the actual achieved capacity, which is calculated based on the electrochemical reactions. Despite the high apparent charging capacity, the following discharge capacity will be reduced, based on the incomplete reactions during charge. This results in a low Coulombic efficiency, as described in Section 3.11.4.1. To some extent, this links the current to the achieved capacity without the requirement for transport mechanisms within the model.

3.11.4.1 Coulombic Efficiency

Coulombic efficiency is one method of calculating the efficiency of the cell during cycling. It is typically related to polysulfide shuttle when discussed for Li-S. It is a measure of the charge throughout via coulomb counting [6], and is calculated as shown in Equation [30]; 100% efficiency implies the coulombs in are equal to the coulombs out, or that the charge and discharge capacities are equal. An efficiency of 100% would imply no losses due to degradation, or polysulfide shuttle [28]. The Coulombic efficiency also varies with C-rate.

$$\text{Coulombic Efficiency (\%)} = \frac{\text{Discharge Capacity}}{\text{Charge Capacity}} \cdot 100 \quad [30]$$

3.11.5 Area and Precipitation Dynamics

Area is included in the model as a fixed parameter, calculated based on the details given by Boenke et al. [28], as included in Section 3.11.1. As previously discussed, experimental work has found changes during cycling, including precipitation onto the electrode surface, influences the available area for reactions [6]. Further model development requires an update to introduce variable area. This area variable may also need to be included within the precipitation dynamics; this is hypothesised to further improve the model predictions for the reduction in available surface area due to pore blocking.

With the inclusion of a constant area, based on the equations described in 3.10.7, variations to the precipitation and dissolution rate largely influence the behaviour of the cell. Increasing the precipitation rate was found to reduce the voltage kink observed at the transition from high to low plateau in discharge, as S_1 was unable to accumulate before precipitating. Increasing the dissolution rate was found to increase the capacity, ensuring all precipitated species dissolved and were available for further reactions during charge. It was found that the dissolution rate needed to be higher than the precipitation rate to obtain results similar to those by Boenke et al. [28].

3.12 Summary and Further Model Development

The model derived by Cornish et al. [3] was re-parametrised and tested against Boenke et al. [28] experimental data. For the fundamental mechanisms included, it was found the model behaved as expected. A larger electrolyte volume was found to increase the achievable capacity and reduce the resistance within the cell. An increase in the sulfur mass was also found to increase the achievable capacity, as it did not directly influence a change in area due to pore blocking. A relationship between the sulfur mass and electrolyte volume is required in the model. C-rate dependence was not captured with increasing current due to the lack of transport mechanisms; however, a change in discharge voltage was observed due to the Ohmic change. A higher current correlated with a smaller influence of polysulfide shuttle. The precipitation dynamics captured changes to the voltage plateaus and capacity, although further work is required to correlate these to a change in area. Implementing voltage limits influenced the extent of polysulfide shuttle during charge and the DoD during discharge.

3.12.1 Scaling Parameters

Additional scaling parameters to capture the differences between coin and pouch-cells are required, including the geometric size, the E/S ratio, the number of layers and the current flowing through the cell, based on current density as given by Boenke et al. [28]. The inclusion of these parameters, along with the other mechanisms described, may influence existing parameters, such as the saturation mass; investigation into whether these require a dependence on other factors may be required.

3.12.2 Capacity Change

Without transport mechanisms within the model, and with the shuttle rate set to zero, the model results confirm that the precipitation dynamics alone were insufficient to capture a change in capacity due to increasing current. It is hypothesised that separate mechanisms to capture reversible and irreversible capacity change are required. To predict reversible capacity change, transport-related mechanisms are likely, or behaviour relating to the limitations, such as temporarily inaccessible active material, or incomplete reactions at higher currents. Degradation mechanisms would be required to capture irreversible dependence, such as side reactions leading to depletion, or a loss of shuttled sulfur, as achieved by Marinescu et al. [17]. A loss of material relating to the precipitation dynamics, such as a slow dissolution rate, could be captured in the existing model; modifications to make this a permanent loss could contribute to irreversible capacity change.

Calculating how species move around the cell within a 0D model that does not account for spatial variations is not strictly possible. However, the influence of this transport could be implemented in some way, for example, through the inclusion of a modified diffusion mechanism; diffusion occurs when species travel from a region of high concentration to a region of low concentration. This could be

captured in a 0D model through concentration gradients alone, without spatial variations, but would require a large number of assumptions. The inclusion of diffusion would also require regions, with varying concentration in each; this could link to the investigation into the presence of excess electrolyte.

3.12.3 Area Change

As previously discussed, a variable area is required, rather than a constant parameter, to account for the influence of precipitation and electrolyte wetting. To capture this, additional parameters such as porosity are required, along with parameters related to scaling, including the positive electrode thickness and number of layers, as discussed in Section 3.12.1. Further investigation is required into how each of these parameters may change or impact other mechanisms, such as the change in porosity due to geometric size, packaging or electrolyte volume variation. Alternatively, thicker electrodes in larger cell formats may have more pores and therefore require more electrolyte to sufficiently wet, but simultaneously have longer distances for species to diffuse through [6]. Additional details about the electrode structure would be required to capture this, and it further highlights the importance of obtaining experimental data that tests on both coin and pouch-cells under the same conditions, to capture realistic input values. To capture Boenke et al. [28] hypotheses when varying the sulfur content, a relationship between the available surface area of the electrode and the sulfur mass would be required; as previously discussed, pore blocking influences area, more significantly when the mass of sulfur is larger.

3.12.3.1 Electrolyte

The assumptions that the total area is utilised, and the total electrolyte volume always contributes to electrochemical reactions need to be removed. Within a real cell, it is likely an excess of electrolyte is present, beyond what is needed to fill the electrode pores. A mechanism or feature is required to capture the impact of the volume of electrolyte, whether in excess or insufficient to wet the pores, and the resulting change on the available area. Other components, including the porous separator, also impact the location and availability of species and need to be accounted for. The impact of these may vary further if the electrolyte volume becomes dynamic; in a real cell, depletion of the electrolyte can occur due to side reactions, or degradation of the solvent [10].

3.12.3.2 Precipitation Dynamics

Currently, there is no direct link between precipitation and area. The inclusion of area in the precipitation dynamics is one method to overcome this; area would influence the rate at which reactions occur, and a larger rate of precipitation or dissolution would result in a larger area change. It would also influence the number of reaction sites available for reactions and could contribute to C-rate dependency.

The uniformness of precipitation is another feature that may need to be accounted for. Uneven precipitation, and therefore uneven pore blocking, occurs due to preferential utilisation of reaction sites and can influence the reactions occurring, contributing to uneven degradation or volumetric expansion of the electrode [44]. Parameters such as surface area, pore size and distribution were all found to contribute to the uniformness of precipitation, influencing the utilisation of active material [28].

3.12.4 Chemistry

The model also does not account for variations to the cell chemistry, such as sulfur infiltration method or the use of additives in the electrolyte. If the model is to be used alongside experimental work, further work is required to add these features and the hypothesised impact on behaviour. This may also link to other mechanisms, such as transport or degradation; for example, how the pore volume and porosity relate to the tortuosity within the electrode could impact the transport of species during cycling. This would require detailed information about the positive electrode structure.

3.12.5 Other Considerations

Degradation mechanisms may not be required to capture the current experimental data, but the capability to predict behaviour due to these mechanisms is essential for realistic predictions. The type and magnitude will vary dependent on the type of testing.

The assumption is currently made that only S_1 precipitates in the model, but in a real cell, other chain length species could also precipitate [6]. Further investigation into the conditions under which each species precipitate may be required.

Other considerations for further model development include temperature changes, both internally and externally, and the impact on features such as resistance [62]. Boenke et al. [28] did not provide information relating to the temperature, so the cell temperature was assumed constant and ambient.

3.13 Achievement of Research Objectives

The work towards investigating how a model could capture coin-cell behaviour began with analysis of the existing Li-S models, varying in type and complexity. For development, a 0D model was selected due to the low computational time and cost. A physics-based model was the most applicable type as it could be parametrised directly from the experimental results obtained by Boenke et al. [28]. The use of a cell-level model rather than a model focusing on a specific component enabled predictions of the full cell behaviour, under varying conditions.

The re-parameterisation of the 0D model by Cornish et al. [3] tested the extent to which an existing pouch-cell model could predict coin-cell behaviour, by changing only the input parameters. As discussed throughout the Chapter, the model was able to capture the general trends but was not expected to quantitatively capture all the observed behaviour by Boenke et al. [28].

Based on the re-parameterisation with Boenke et al. [28] coin-cell data, several areas of further development were recognised. With the aim of the model to be used alongside experimental work, the inclusion of chemistry-based features was essential. The parameters that vary when scaling, including the geometric size, number of layers and current, must also be easily varied within the model. Updates to existing mechanisms or features, such as a variable area, or accounting for the distribution of electrolyte, were hypothesised to improve model predictions. New mechanisms, such as degradation, may be required to capture long-term cycling behaviour, although there is varying causality of the observed results. Transport was not included, and homogeneity was assumed within the model; further work would be required to capture these more accurately. To summarise, the additional features and mechanisms will all work to improve the model capability and test the extent to which model predictions align with the hypotheses made by Boenke et al. [28], for both coin and pouch-cells. This includes rate capability, sulfur content variations and utilisations of active material.

Based on the further work required to improve model predictions, further experimental work was not required at this stage; the improvements required were unrelated to the parameterisation, but instead the model capability based on the formulation and mechanisms included. Most of the proposed model changes would apply to both coin and pouch-cell predictions. The detailed information included in Boenke et al. [28], along with the information provided from further communication [97] was sufficient at this stage of development.

To summarise, the work throughout this Chapter discusses the importance of modelling and the contribution towards reaching commercial application. The use of a model alongside experimental work aims to significantly reduce the time and cost of manufacturing, along with improving the efficiency of selecting the best operating conditions. Through analysis of the available models, and the benefits and drawbacks of each, the most relevant model was selected for this purpose. The knowledge obtained from this, along the knowledge obtained from experimental work, helped to understand which mechanisms are established, and which are only hypothesised to occur and therefore require further

investigation to confirm. This worked towards obtaining a clear understanding of the capability of existing models. Alongside this, analysis of the differences between cell formats and the results obtained by Boenke et al. [28] was conducted; the extent to which these were included in the existing models was analysed, highlighting the areas of further work to capture scaling variations.

4 Chapter 4: Coin-Cell Model Development

This Chapter will begin with discussing the main objectives of the work to be completed. It will then highlight the capability of existing models, and the recognised areas that require further work, with the aim of improving predictions for coin-cells, although these are also likely to be applicable for pouch-cell predictions. Each model change, referred to as an upgrade, will be discussed in the chronological order in which they were carried out, with a summary of the impact of each. The Appendix, Section 9.2 discusses the installation and set up within PyBaMM in further detail.

The work contained within this Chapter contributes to the work within a paper, currently in the final stages of review before submission.

The nomenclature is included in List of Symbols.

4.1 Research Objectives

This Chapter continues to work towards understanding what changes are required to existing pouch-cell models to capture coin-cell behaviour. The work throughout investigates how the model can be improved, and how these changes can be implemented. The aim is to use the simplest and most efficient method, ensuring the model captures the correct causality of predictions when compared to experimental results. Whilst the work focuses on coin-cell behaviour, the applicability to pouch-cells is also considered, working towards understanding what the mechanistic differences between cell formats are. The changes, at this stage, are not hypothesised to require a change in type or complexity of the model; the further work will expand upon the model developed by Cornish et al. [3].

4.2 Further Requirements for the Model

This section expands upon the conclusions made in Chapter 3.

The model derived by Cornish et al. [3] and tested using Boenke et al. [28] experimental coin-cell data captured the fundamental features of Li-S behaviour, including charging and discharging, polysulfide shuttle and the precipitation dynamics. As previously discussed, further work building upon this baseline model is required to improve predictions and accurately capture experimental coin-cell results, focusing on the results from Boenke et al. [28]. A summary of the key features is included in Table 10, based on the discussion in Section 3.12.

As discussed throughout this Chapter, some of the features implemented were captured in other existing models; for example, Zhang et al. [1] included the influence of variable surface area on cell behaviour, and Marinescu et al. [17] investigated the influence of precipitation on the achieved capacity. Where the features aligned with requirements to capture the results from Boenke et al. [28], the mechanism was directly implemented and tested. Based on thorough testing at each stage to understand the influence of each additional mechanisms and any potential errors that may arise, several were combined into the model together. Some required a new derivation, for example, Ren et al. [79] investigated the influence of C-rate on precipitation within a 1D model, looking into nucleation and particle growth, but this could not directly be implemented into a 0D model. Instead, this was modified, removing the dependence on spatial variations. Each of these changes are discussed throughout the Chapter.

Model Features	Included in Cornish et al. [3]?	Notes
Charging and Discharging	Yes	4 species assumed
Voltage C-rate Dependence	Yes	Based on the Ohmic change
Capacity C-rate Dependence (Reversible)	No	Requires transport mechanisms
Capacity Fade (Irreversible)	No	Requires degradation
Precipitation Dynamics (and relating volage kinks/drops)	Yes	Assumes only particle growth Kinks and drops observed with adjusted fitting parameters
Variable Area	No	Relating to precipitation and electrode wetting
Degradation	No	Shuttle included, but does not contribute towards degradation
Material Utilisation	Assumed complete	No features to account for variations
Inclusion of all Components (Separator, Negative Electrode)	No	Predicted to be required to capture scaling variations
Cell Chemistry	No	Required to capture material variations
Scaling Parameters	No	E.g., the number of layers and geometric size

Table 10: Summary of the features required within the model

4.2.1 Capacity C-rate Dependence (Reversible)

Based on the features discussed in Table 10, a model update was required to capture reversible capacity C-rate dependence. As discussed, this is typically captured through transport mechanisms and the resulting limitations in higher order models that account for spatial variations [6]. With the aim of keeping the model at the lowest dimensionality, other than through manipulation of the precipitation dynamics, it was likely a modified transport mechanism would be required.

4.2.2 Capacity Fade (Irreversible) and Degradation

Irreversible capacity fade is typically captured by degradation mechanisms [6]; various degradation mechanisms occur within Li-S, each of which contribute to the behaviour in different quantities dependent on the cycling conditions. Further investigation is required to determine the mechanisms contributing to the observed changes in Boenke et al. [28]. With the aim of using the model across a range of applications, it would be ideal to include the capability of capturing variations due to multiple causes.

4.2.3 Precipitation Dynamics and Area

Under various experimental conditions, a voltage kink and jump can be observed [28]. The model achieved this through the precipitation dynamics, with variations to the precipitation and dissolution rates, and the saturation concentration which determines the point at which precipitation occurs. Beyond these, both the voltage kink and jump relate to the viscosity, conductivity and solubility of species in the electrolyte, all influencing the resistance [10]. Other factors, such as the overpotential and the DoD of the previous cycle, influence the precipitation dynamics in what has been denoted as the history effect [6].

The precipitation dynamics also influence the available positive electrode surface area; precipitation leads to pore blocking, influencing the number of available reaction sites, and the rate at which reactions can occur [6]. It has been found that the presence of precipitates within the cell influences the rate of further precipitation [78]. Cornish et al. [3] does not account for this, and instead includes area as a constant parameter.

4.2.4 Sulfur Utilisation

The model currently assumes complete utilisation of all materials, including the sulfur and electrolyte. It has been found experimentally that this is rarely achieved, with cells typically achieving less than maximum capacity [28]. Coin-cells have a significant excess of electrolyte, beyond the volume required for electrochemical reactions and to fully wet the electrode pores. As only the sulfur dissolved within the electrolyte in the pores of the electrode is available for electrochemical reactions, one method of calculating the sulfur utilisation within the model is by splitting the electrolyte volume into a usable volume and an excess volume. To do this, the pore volume within the positive electrode must be calculated; the volume required to fill the electrode pores is considered usable, and anything extra is assumed to be excess. The sulfur dissolved in the usable electrolyte is also usable and contributes to electrochemical reactions, whilst anything within the excess electrolyte is assumed to be unused. In a real cell, whilst the sulfur in the excess region may be accessible via transport mechanisms such as diffusion, the time scales are likely to be much longer. As the E/S ratio varies between cell formats, the usable active sulfur also varies. This highlights the requirement for the inclusion of the E/S ratio parameter, to ensure the correct mass and volume is calculated and maintained throughout cycling.

4.2.5 Cell Chemistry (and Separation of Components)

The structure of the positive electrode influences the behaviour; properties such as the pore size and distribution, along with the morphology of the carbon host influence the tortuosity and reaction pathways [6]. The precipitation mechanism, contributing to volumetric changes [44], also influences how the structure changes during cycling. In addition, the sulfur content and loading method, beyond the mass value, plays a role in the behaviour. For example, incorporating sulfur via melting onto the positive electrode compared to using a catholyte solution will impact the initial reaction rates and mechanisms, if dissolution of the sulfur is required. To use the model alongside experimental work to test new materials, the inclusion of chemistry-based features, including material properties and variables, is essential.

Beyond the positive electrode, the electrolyte properties influence behaviour, for example, the solubility of lithium polysulfides, or the presence of an additive to minimise polysulfide shuttle [18]. The availability of lithium is important, to ensure a sufficient quantity to react with the sulfur, accounting for potential side reactions due to the high reactivity of lithium [10]. To account for these, separate components are hypothesised to be required within the model.

4.2.6 Scaling Parameters

Testing the model by Cornish et al. [3] confirmed there were several areas that required further development, beyond what was required specifically to capture coin-cell behaviour. With the aim of understanding the changes when scaling between cell format, the model should include the capability to vary the input parameters that change between different formats, for example, the mass of sulfur, the E/S ratio and the number of electrode layers. As most existing models are not published open source, it is unclear the extent to which these parameters are included.

4.3 Overview of All Changes

The changes required to implement these features are summarised in Figure 13. The reasoning for each Iteration is discussed in detail throughout this Chapter, based on the findings and impact of the previous changes implemented. The details included in each Iteration, as shown in Figure 13, correspond to Sections 4.4, 4.5, 4.6 and 4.7 respectively. In Figure 13, they are separated into specific components or mechanisms, each of which was discussed as a requirement for further model development in Chapter 3.

The updates are made to the Cornish et al. [3] model in PyBaMM. Unless discussed, the equations remain the same as included previously in Chapter 3.

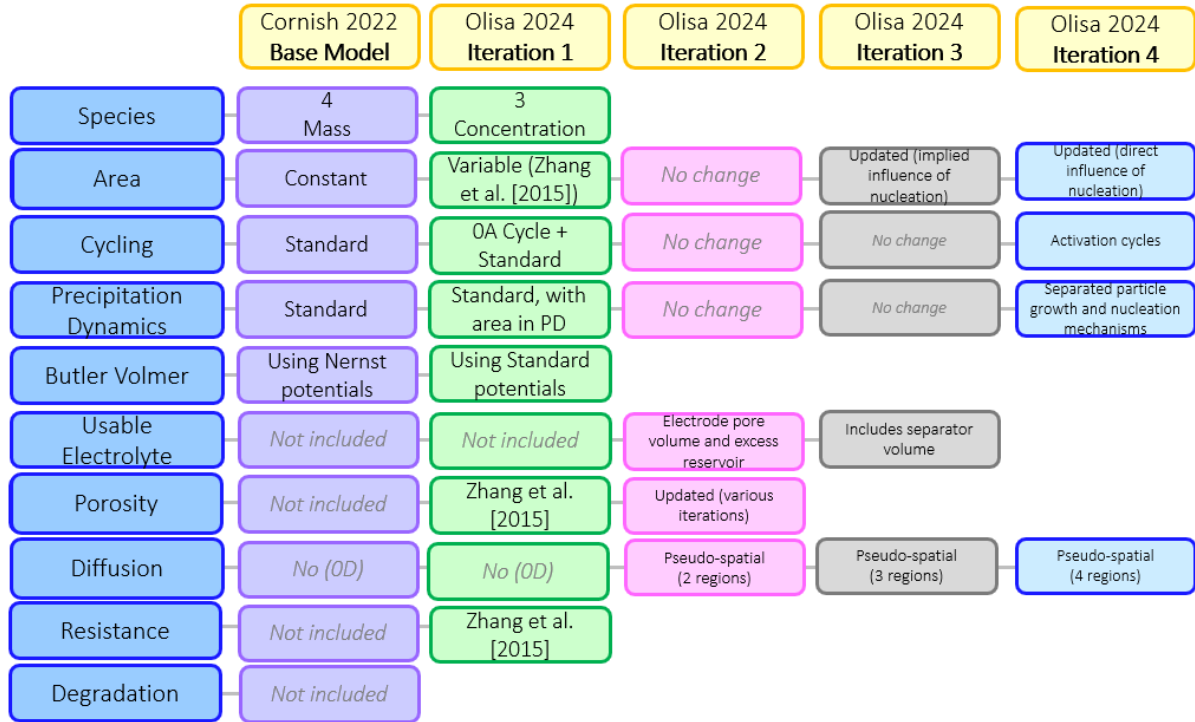


Figure 13: Summary of all changes to Cornish et al. [3] to reach final derivation of the model

4.4 Iteration 1

4.4.1 Dimensionality: 0D

The dimensionality of this model remained the same as Cornish et al. [3], at 0D. Once trustworthy results have been obtained and the causality of all observed behaviour has been confirmed within the literature, further mechanisms and higher dimensionality can be added, as required, to capture additional features.

4.4.2 Electrochemical Reactions and Number of Species

The total capacity is determined by the sulfur mass and sulfur utilisation; if all the sulfur is utilised and contributes to electrochemical reactions, the maximum capacity is achieved. The capacity of each plateau is determined by the reactions occurring within that region; for example, the high plateau in discharge is determined by the reduction of S_8 to S_4 . The distribution of species also influences the behaviour; if there are more S_8 species present, more high plateau reactions occur and the capacity of the high plateau increases. Changing the number of reactions, or the distribution of species changes the ratio of the plateaus.

In the model, the number of species was reduced from four to three, reducing the number of equations from three to two, as shown in Equations [31] and [32]. Three species enabled the correct ratio of capacity for high to low plateau, as found in Boenke et al. [28] experimental data: approximately one third high plateau and two thirds low plateau. With four species, Cornish et al. [3] captured one quarter of the capacity in the high and medium plateau, and three quarters in the low plateau, to match Hunt et al. [62] experimental data. Although four species correspond to three plateaus, based on parameter selection, there was minimal distinction between the medium and high plateau. The reduction in number of species in this model resulted in the medium plateau being removed. As in Cornish et al. [3], the assumption was made that only S_1 precipitated and dissolved, and during charge, only S_8 shuttled to S_4 .



The ODEs describing the species mass evolution with time as a result of the reactions considered are shown in Equations [33] - [36]. As previously discussed, with a low number of species, the gradual transition observed experimentally between high and low plateau cannot accurately be captured. Further experimental work to confirm the exact number of species would be needed to justify increasing the number present, although these types of experiments can be difficult and prone to errors. There is also disagreement within the literature, for example, Walus et al. [3], [100] found Li_2S_2 precipitates, whilst first principles work predicts lithium polysulfides are unstable in this form [101].

$$\frac{dS_8^0}{dt} = -\frac{n_{S_8^0} Ms}{n_H F} i_H - k_s S_8^0 \quad [33]$$

$$\frac{dS_4^{2-}}{dt} = \frac{n_{S_8^0} Ms}{n_H F} i_H + k_s S_8^0 - \frac{n_{S_4^{2-}} Ms}{n_L F} i_L \quad [34]$$

$$\frac{dS_1^{2-}}{dt} = \frac{n_{S_4^{2-}} Ms}{n_L F} i_L - \frac{k_{p/d}}{v \rho_s} S_p (S_1^{2-} - S^*) \quad [35]$$

$$\frac{dS_p}{dt} = \frac{k_{p/d}}{v \rho_s} S_p (S_1^{2-} - S^*) \quad [36]$$

The Nernst potentials corresponding to the high and low plateaus are shown in Equations [37] - [40], remaining unchanged from Cornish et al. [3] other than the number of reactions.

$$E_H = E_H^0 + \frac{RT}{n_H F} \ln \left(f_H \frac{S_8^0}{(S_4^{2-})^2} \right) \quad [37]$$

$$E_L = E_L^0 + \frac{RT}{n_L F} \ln \left(f_L \frac{S_4^{2-}}{(S_1^{2-})^2} \right) \quad [38]$$

$$f_H = \frac{(n_{S_4^{2-}})^2 Ms v}{n_{S_8^0}} \quad [39]$$

$$f_L = \frac{(n_{S_1^{2-}})^2 Ms v}{n_{S_4^{2-}}} \quad [40]$$

4.4.2.1 Results: Electrochemical Reactions

As observed in Figure 14, the change in number of species and therefore the number of reactions improved the prediction of the plateau capacity in comparison to Boenke et al. [28] experimental data. A voltage jump at the start of discharge was observed due to inaccurate initial conditions. This is discussed and resolved in Section 4.4.3.

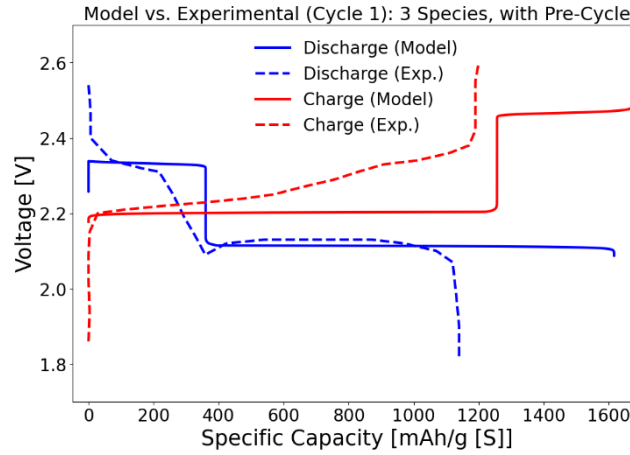


Figure 14: Model voltage-capacity predictions with three sulfur species, compared to Boenke et al. [28], capturing the correct ratio of plateaus

4.4.3 Pre-cycling Step

The cell was cycled under constant current, calculated from the current densities given by Boenke et al. [28] and the positive electrode area, as shown in Equation [41]. When calculating the current for a pouch-cell, the number of electrode layers needed to be accounted for, as shown in Equation [42].

$$I_{\text{coin}} = j \cdot a_{\text{rcoin}} \quad [41]$$

$$I_{\text{pouch}} = (j \cdot a_{\text{rcoin}}) \frac{x \cdot \text{mass}_{\text{sulfur pouch}}}{\text{mass}_{\text{sulfur coin}}} \quad [42]$$

Before standard cycling under these currents, a pre-cycle step was introduced. This was a 0A cycle that was designed to obtain stable initial conditions, allowing the model to run without numerical errors. Consistent initial conditions were required across all equations, which could be difficult to achieve based on the number of input parameters. The use of a 0A cycle saved significant time trying to find these consistent values, especially when testing the model for varying applications where other parameters, such as precipitation or dissolution rates, may also require variation. The 0A cycle ensured the modelled cell tended towards equilibrium conditions before cycling. This differed from an activation cycle which is introduced experimentally to optimise the cell through cycling at low C-rates and under controlled conditions, to increase the performance in terms of cyclability and cycle life.

During a 0A cycle in the model, only chemical reactions occurred that did not require the flow of electrons; this included polysulfide shuttle and the precipitation and dissolution reactions. Unchanged from Cornish et al [3], to mimic the history effect observed in real cells, the distribution of species at the end of the 0A cycle was used as the input for the following cycle.

Several trials were run to understand the required length of time for the 0A cycle. The aim was for the species to reach equilibrium, meaning the time varied dependent on how far the initial conditions were from the equilibrium conditions. A rest time of 2,000 seconds was found to be sufficient to ensure no further changes occurred.

Following the 0A cycle, the activation cycles included in the model worked to further stabilise the initial conditions, based on both electrochemical and chemical reactions. The cycles aimed to help remove any further errors caused due to sensitivity to parameters at the beginning of cycling. As Boenke et al. [28] first ran a discharge, the model began cycling with a discharge activation cycle, following the 0A cycle. Whilst the initial discharge was required to match experimental data, it was also optimal to run in the model; the dissolution of species required during the initial stages of charge is much more complex to accurately predict initial conditions for, as the dissolution can occur simultaneously to the oxidation of S_1 to longer chain length species.

Increasing the number of activation cycles was found not to significantly change the performance of the cell. However, to account for possible variations under all conditions and potential parameter values, three activation cycles were implemented into the model. The aim of the activation cycles in the model were to obtain stable conditions, whilst experimentally, the aim is to create a stable SEI layer. This capability has not yet been achieved, and would require a separate negative electrode component, a plating and stripping mechanism, and potentially degradation relating to C-rate.

4.4.3.1 Results: Pre-Cycling Step

The initial conditions for S_8 , S_4 and S_1 were set values, and S_p was considered a ‘free’ parameter which varied dependent on the values of all other species, calculated based on the total input sulfur mass. When running a 0A cycle, based on the formulation of the equations, no electrochemical reactions were allowed; the species reached equilibrium via chemical reactions only. During the subsequent activation cycles, stable conditions were reached through electrochemical reactions at slow C-rates.

The inclusion of a pre-cycle step, including a 0A cycle and activation cycles, enabled the model to obtain more accurate initial conditions. This removed the voltage jump observed at the beginning of discharge, as shown in Figure 15.

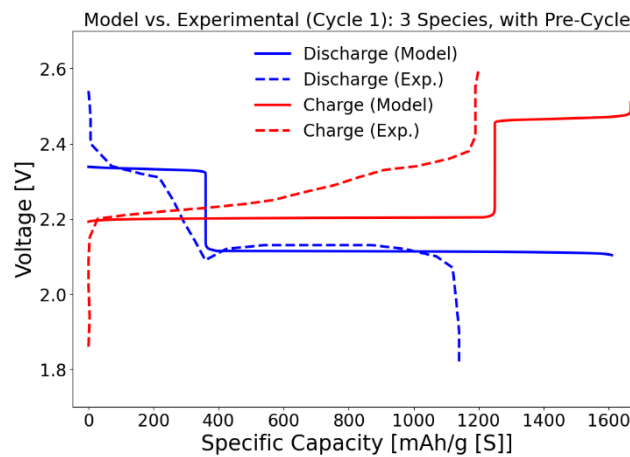


Figure 15: Model voltage-capacity predictions with a pre-cycle step, in comparison to Boenke et al. [28]

4.4.4 Converting Masses to Concentrations (Including the Updated Reactions and Pre-cycling Step)

Whilst Cornish et al. [3] used the mass of species, the model was updated to use the concentration instead. The use of concentration improved the ease of several calculations, such as the resistance based on a concentration dependent conductivity [1], and removing the requirement for a conversion factor when calculating the Nernst potentials. The concentration of species was calculated based on the electrolyte volume, the molar mass of sulfur and the number of sulfur atoms in each polysulfide, as shown by Equation [43]. This allowed the electrolyte volume to have a larger influence on the behaviour of the cell during cycling; previously, the volume only directly influenced the Nernst potentials.

$$CS_x = \frac{S_x}{Ms \cdot v \cdot ns_x} \quad [43]$$

In the 0D model, the concentration was derived with respect to time, rather than location. Without accounting for dimensionality, the species were assumed to be included at one point in the cell; in a coin-cell, the species were assumed to be at one point on the single-sided positive electrode, and in a pouch-cell, at a single point between the required number of layers of double-sided positive electrodes. The distinction between the number of layers became important when investigating the influence of the total sulfur mass and electrolyte volume on electrode wetting, as discussed in Section 4.5.1.

The concentration represented a real variable for all species other than precipitated sulfur, S_p . As sulfur precipitates out of the electrolyte, a concentration of S_p based on the relationship with electrolyte volume has no physical meaning. However, S_p was included as a concentration to ensure the variables were consistent across the model, and the assumption was made that the S_p concentration was equivalent to a physically meaningful variable. The model did not include the capability to predict a change in the electrolyte properties during cycling when species precipitated out of the electrolyte, for example, a reduction in concentration and resistance. It also did not account for a change in electrolyte volume during cycling, for example, due to depletion from side reactions [10]. Therefore, it was assumed that the difference was minimal whether S_p was included as a concentration, or as a separate and more realistic term. It is important to note that while the conservation of mass ensures the maximum mass of each sulfur species never exceeds the input sulfur mass, the total concentration of species is not conserved.

With the update to use concentrations rather than masses, several other equations needed to be updated, including the Butler-Volmer, as shown in Equations [44] and [45], and the ODEs, as shown in Table 11. The Butler-Volmer equations were updated to account for concentration rather than mass, and were rewritten with respect to the exponential terms, equivalent to the hyperbolic sine function, as included in Cornish et al. [3]. The change to concentration also influenced the ratios in the ODEs; for example, when using masses, the same term for the loss of shuttled S_8 was included in S_8 and S_4 equations, whilst with concentrations, the term was doubled for S_4 as it was equivalent to half the concentration of S_8 . The electrolyte volume and density were removed from the precipitation dynamics, and the molar volume introduced to balance the units within the equation.

$$i_H = (-i_H^0 \ar) \left(CS_4^2 e^{\frac{n_H F}{2RT} (V-E_H)} \right) - \left(\frac{CS_8}{e^{\frac{n_H F}{2RT} (V-E_H)}} \right) \quad [44]$$

$$i_L = (-i_L^0 \ar) \left(CS_1^4 e^{\frac{n_H F}{2RT} (V-E_L)} \right) - \left(\frac{CS_4}{e^{\frac{n_H F}{2RT} (V-E_L)}} \right) \quad [45]$$

ODEs	Masses	Concentration
S_8	$\frac{dCS_8^0}{dt} = -\left(\frac{n_{S_8^0} Ms}{n_H F} i_H\right) - ks S_8$	$\frac{dCS_8^0}{dt} = -\left(\frac{i_H}{n_H F v}\right) - ks CS_8^0$
S_4	$\frac{dCS_4^{2-}}{dt} = \left(\frac{n_{S_8^0} Ms}{n_H F} i_H\right) + ks S_8 - \left(\frac{n_{S_4^{2-}} Ms}{n_M F} i_M\right)$	$\frac{dCS_4^{2-}}{dt} = \left(\frac{2 i_H}{n_H F v}\right) + 2 ks CS_8^0 - \left(\frac{i_L}{n_L F v}\right)$
S_2	$\frac{dCS_2^{2-}}{dt} = \left(\frac{n_{S_4^{2-}} Ms}{n_M F} i_M\right) - \left(\frac{n_{S_2^{2-}} Ms}{n_L F} i_L\right)$	<i>Not included</i>
S_1	$\frac{dCS_1^{2-}}{dt} = \left(\frac{n_{S_2^{2-}} Ms}{n_L F} i_L\right) - \left(\frac{k_{p/d}}{v \rho_s} S_p (S^{2-} - S^*)\right)$	$\frac{dCS_1^{2-}}{dt} = \left(\frac{4 i_L}{n_L F v}\right) - \left(\frac{Ms}{\rho_s} k_{p/d} CS_p (CS_1^{2-} - CS^*)\right)$
S_p	$\frac{dCS_p}{dt} = \left(\frac{k_{p/d}}{v \rho_s} S_p (S^{2-} - S^*)\right)$	$\frac{dCS_p}{dt} = \frac{Ms}{\rho_s} k_{p/d} CS_p (CS_1^{2-} - CS^*)$

Table 11: Changes to the ODEs when using concentrations rather than masses, alongside the updated number of species

4.4.4.1 Results: Converting Masses to Concentrations

The change from mass to concentration required adjustments to the fitting parameters and their units to ensure the equations remained balanced. These changes resulted in a difference in the observed voltage and capacity, as shown in Figure 16. With concentration, a larger transition between the high to low plateau was observed in discharge due to S_1 accumulating before precipitating. A smoother and more gradual transition between plateaus in both charge and discharge was also observed, corresponding to more species being present simultaneously throughout cycling. These observed behavioural differences were based on both the use of concentration and the variation of selected parameters, such as the exchange current density and standard potentials; the conversion from mass to concentration alone, without changes to other parameters, would not result such a significant change.

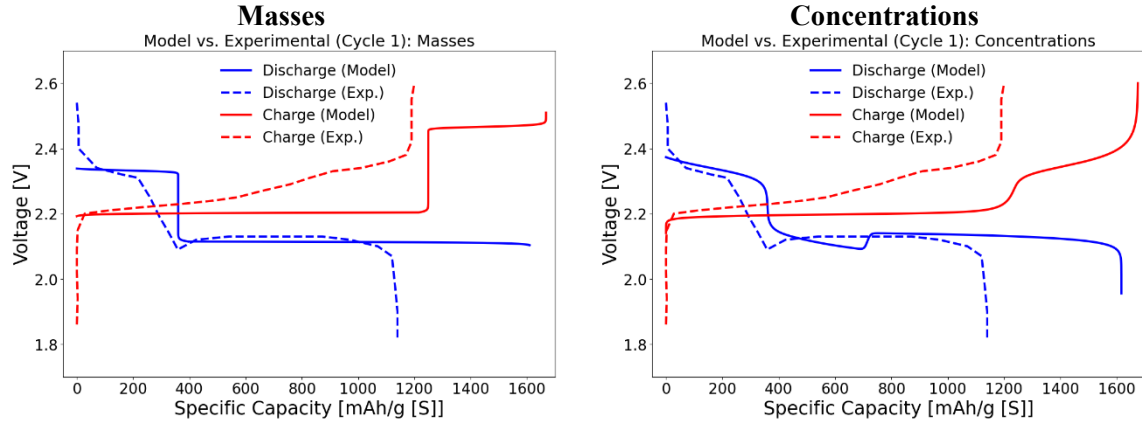


Figure 16: Model voltage-capacity predictions when using concentrations instead of masses

4.4.5 Updating to a Variable Area, and Inclusion of Porosity

Cornish et al. [3] assumed a constant area, with no change throughout cycling. As previously discussed, this does not align with experimental findings; towards the end of discharge, precipitation of species leads to surface coverage and pore blocking, reducing the number of active sites and therefore area available for reactions [10]. A larger mass of sulfur, as expected with larger cell formats, corresponds to a larger coverage of the electrode surface, and therefore a larger impact on the achievable capacity [28]. As Cornish et al. [3] assumed a constant area, even with the correct magnitude, minimal change to the capacity during cycling was observed.

To capture the experimentally observed behaviour, the variable area equation derived by Kumaresan et al. [77] was used, as shown in Equation [46]. This calculated area based on a ratio between the minimum porosity, if all the sulfur species were in precipitated form and blocking the available pores, and the

varying porosity, calculated as the distribution of species changed throughout cycling. A fitting parameter was required within the equation as the exponential, and a value of 6 was selected, taken from Zhang et al. [1]. This could be adjusted as necessary to improve the magnitude of area change. The value for the initial area was updated at the end of each cycle; the final area became the initial value for the next cycle.

$$ar = ar_0 \left(\frac{\varepsilon}{\varepsilon_0} \right)^Y \quad [46]$$

To implement this equation into the model, the addition of a porosity variable was also required, as it was not included in Cornish et al. [3]. The porosity equation from Zhang et al. [1] was used, similar to Kumaresan et al. [77], as shown in Equation [47]. The porosity equation was calculated based on the molar volume of Li_2S_1 and the precipitation rate of Li_2S_1 [1]. It did not directly account for the influence of precipitation. Similarly to Boenke et al. [28] findings, this relationship suggested that as the rate of precipitation increased, which had been linked to the presence of already precipitated species [78], both the porosity and the total available area decreased.

$$(-) \frac{d\varepsilon}{dt} = V_{\text{Li}_2\text{S}_1} r_p \quad [47]$$

4.4.5.1 Results: Updated Area and Porosity

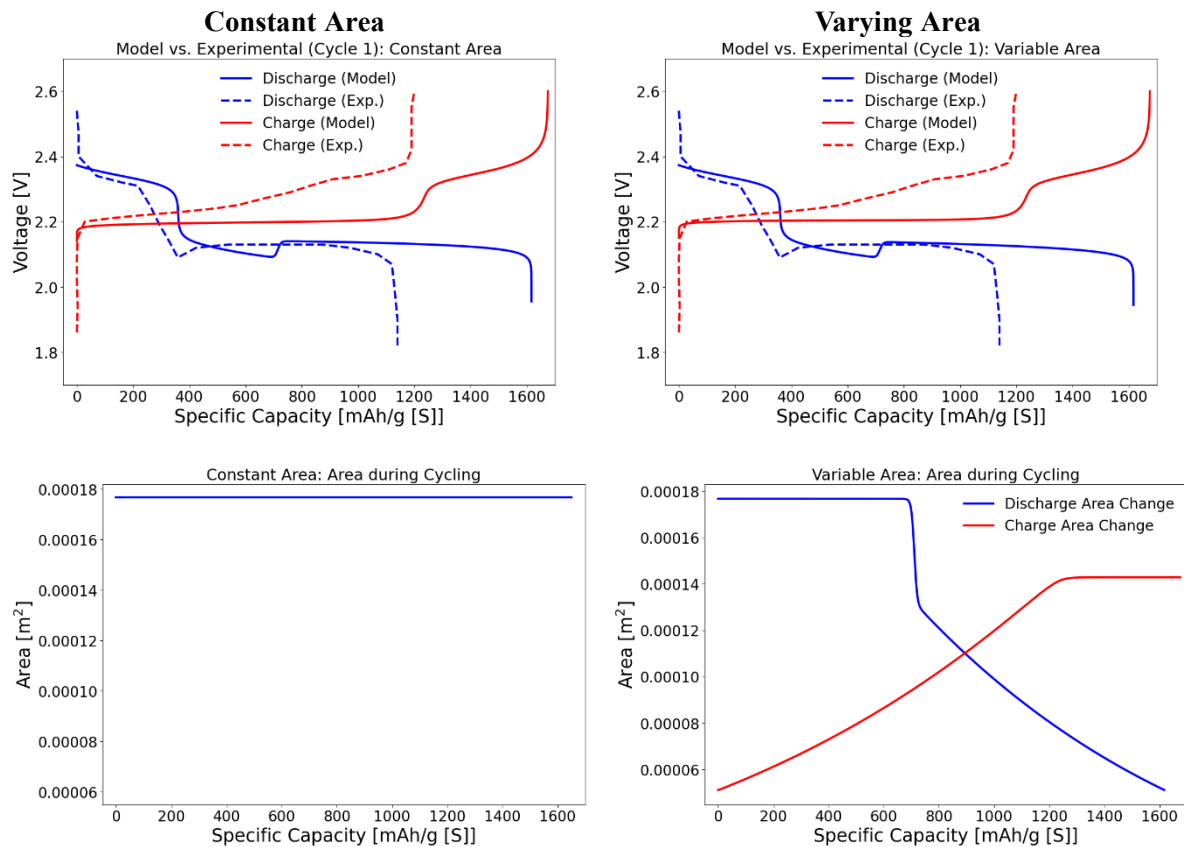


Figure 17: Model voltage-capacity and area predictions when calculating area as a variable rather than a constant parameter

Within the model, the area term was only included within the Butler-Volmer dynamics; with the update to a variable area, the voltage could experience a large change to ensure the partial currents, i_H and i_L , remained constant. However, the observed influence on the behaviour was minimal in comparison to the expected experimental influence, as shown in Figure 17. It was hypothesised this was due to the precipitation influencing the porosity, rather than directly influencing the area. It was also hypothesised

the magnitude of the area change was smaller than the magnitude of change in concentration of species, minimising the impact on behaviour. The fitting parameters within the equation could be adjusted to influence the area change during cycling, although this would have no direct link to experimental work. There was also no variation of area with C-rate; it was hypothesised that as the rate of reactions vary with current, the amount of precipitation, leading to surface coverage via pore blocking, would also change. Although this update to make area a variable improved the causality of model predictions in comparison to the experimental results, further work was required to capture the expected results.

4.4.6 Inclusion of Area into Precipitation Dynamics

As updating the area to a variable was insufficient to capture the observed experimental changes, and to capture the dependencies previously discussed, area was added into the precipitation dynamics. The inclusion of area in the precipitation dynamics was equivalent to varying the dissolution or precipitation rate; at the beginning of discharge, there would be a high rate of precipitation as all species are dissolved in the electrolyte, and therefore no surface coverage. As species begin to precipitate, covering the surface of the electrode, the available area reduces, equivalent to reducing the rate of precipitation. Surface coverage can prevent regions of the electrode being available to contribute towards electrochemical reactions and therefore capacity [6]. During charge, the precipitates dissolve, increasing the available surface area for reactions, equivalent to increasing the rate of dissolution.

Experimental work has found two types of precipitation occurs, nucleation and particle growth [102]. It was found that the formation of new nucleation sites requires a higher driving force to overcome the surface energy barriers, in comparison to particle growth which occurs on top of the existing nucleation sites [102]. The inclusion of area attempts to mimic this; a higher rate of reaction is associated with the beginning of discharge, when new nucleation sites are being formed on the fresh electrode surface, compared to towards the end of discharge when particle growth is more likely to occur, at a lower rate [102]. Other studies have captured the opposite effect, with the rate of precipitation increasing with a higher presence of existing precipitates [78]. This hypothesis was captured in the model with the inclusion of the concentration of precipitated species within the ODE, as proposed by Marinescu et al. [78]. As the concentration increases, so does the rate, relative to the magnitude of other parameters and variables in the equation, which now also includes area.

Without the inclusion of area in the precipitation dynamics, the model assumed surface area had no impact on the rate at which reactions occurred, which was physically incorrect. To account for the addition of area, the precipitation rate and dissolution rate, k_p and k_d respectively, were adjusted, with units as $s^{-1}m^{-2}$.

4.4.6.1 Results: Inclusion of Area in Precipitation Dynamics

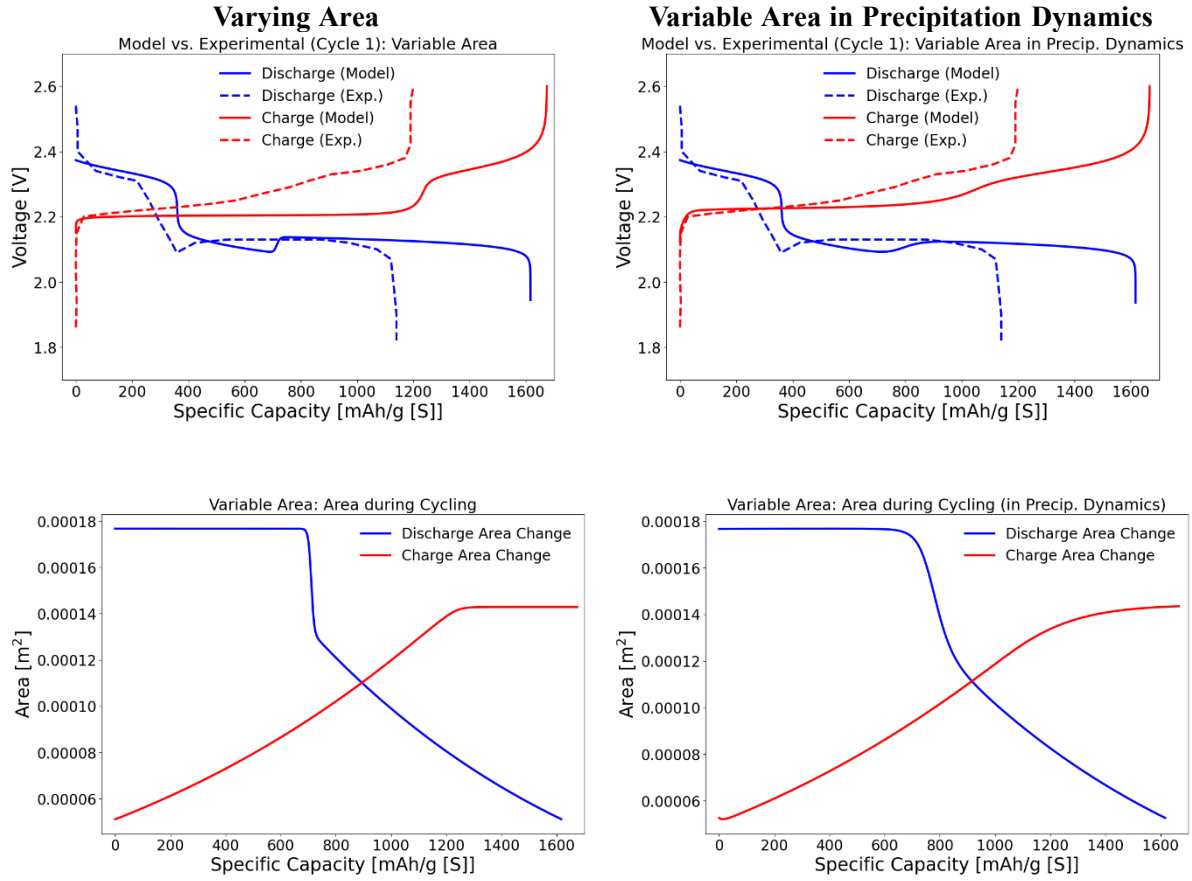


Figure 18: Model voltage-capacity and area predictions with the inclusion of area in the precipitation dynamics

As the precipitation and dissolution rates were fitting parameters that could not be directly measured from experimental results, they were adjusted as necessary to account for the inclusion of the area variable in the precipitation dynamics. Based on the magnitude of the area of a coin-cell, larger precipitation and dissolution rates were required when area was included. The rates were set at the beginning of cycling and had no influence on each other. The dissolution rate was set at a higher value than the precipitation rate to ensure all species dissolved upon charge, preventing any potential bottlenecks, or loss of material or surface area. Dependent on the rate of precipitation in comparison to the rate of electrochemical reactions, adjustments could result in a voltage kink at the transition from high to low plateau, if S_1 was able to accumulate before precipitating, as shown in Figure 18. The rates will vary when scaling between cell formats.

Within the precipitation dynamics, the saturation concentration was calculated based on Marinescu et al. [78] saturation mass. For simplicity within the model, the saturation concentration did not vary. Further investigation would be required to understand how the magnitude varies between cell-formats, and during cycling. As previously discussed, precipitation only occurred when the concentration of S_1 exceeded the saturation concentration.

Whilst it was hypothesised that the rate of precipitation would vary with current, based on the ODEs previously discussed, the magnitude of this change was insufficient to capture area C-rate dependence within a coin-cell, when tested at varying C-rates; further work was required to capture this. Despite this, the changes ensured the correct causality of model predictions, aligning with experimental findings. At larger cell formats, with a larger mass of sulfur or a larger total surface area, this update is likely to have a larger impact. In addition, this circular dependency between area and the precipitation

dynamics can work to capture a loss of active surface area or active species, leading to a loss in cell capacity [10].

4.4.7 Update to Fixed Standard Potentials (from Nernst Potentials)

As previously discussed, the partial currents were defined by the Butler-Volmer dynamics, calculated based on the overpotential, derived from the Nernst potential and the varying cell potential. For this model, with the use of concentration instead of mass and therefore a concentration dependent Butler-Volmer, the equation was calculated using the fixed standard potentials rather than the Nernst potentials, removing the variable overpotential, as shown in Equations [48] and [49].

$$i_H = (-i_H^0 \ar) \left(CS_4^2 e^{\frac{n_H F}{2RT} (V - E_H^0)} \right) - \left(\frac{CS_8}{e^{\frac{n_H F}{2RT} (V - E_H^0)}} \right) \quad [48]$$

$$i_L = (-i_L^0 \ar) \left(CS_1^4 e^{\frac{n_L F}{2RT} (V - E_L^0)} \right) - \left(\frac{CS_4}{e^{\frac{n_L F}{2RT} (V - E_L^0)}} \right) \quad [49]$$

There are various factors influencing the overpotential, including the potential required to overcome the activation energy of a reaction, and the Ohmic overpotential relating to the electrolyte resistance [6]. The simplicity of the model made it unable to capture all of these, and therefore the assumption that it could was removed by replacing the variable with a fixed, standard potential. In addition, the use of standard potentials increased the stability when running the model; the varying concentrations and area, also now included within the precipitation dynamics, impacted both the cell voltage and the Nernst potentials, which could lead to possible instability caused by varying magnitudes simultaneously.

4.4.7.1 Results: Updated to Fixed Standard Potentials

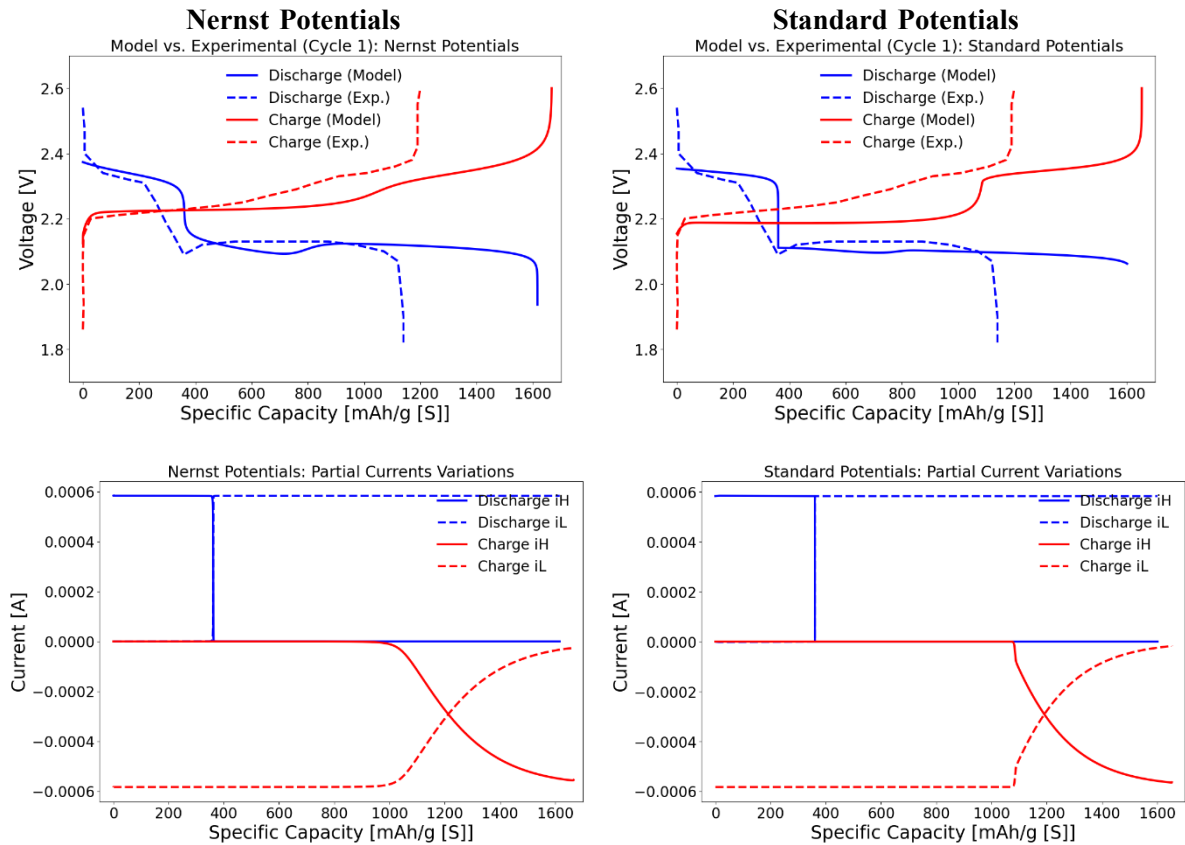


Figure 19: Model voltage-capacity and partial current predictions using standard potentials rather than Nernst potentials

As shown through the Butler-Volmer equations, as the cycling C-rate changes, the partial currents, voltage and concentration of species change. The cell voltage accounts for losses due to internal resistance, contributing to the Ohmic change. When the cell reaches the low plateau region and precipitation occurs, the area also changes. Based on the equations, it was predicted there would be a larger voltage change with the use of standard potentials, due to removing the variable overpotentials. In the model, the magnitude of change was too small to observe any significant change, beyond a change in transition between plateaus, as shown in Figure 19. This was also linked to adjustments to the fitting parameters, including the precipitation and dissolution rates.

4.4.8 Resistance (Ohmic Change)

Similarly to Cornish et al. [3], as the magnitude of electrolyte resistance is significantly larger than other types [1], the model assumed all others were negligible. In a real cell, the presence of precipitated species influences the electrolyte resistance within the cell; a larger portion of precipitates reduces the concentration of species in the electrolyte, reducing the electrolyte resistance [1]. In this model, the resistance equation, as previously described based on the Zhang et al. [1] derivation, was calculated based on the concentration of charged species, here S_4 and S_1 . These concentrations were used to calculate the concentration of lithium, as shown in Equation [50], as lithium was not included as a separate component within the model. Although S_8 was included as a charged species only within the model, it could also be considered as a precipitating species at the end of charge [6]. For simplicity, and to ensure the concentration of lithium was calculated correctly under all conditions, the concentration of S_8 was not included. The inclusion of porosity was also captured within the resistance equation, unlike for Cornish et al. [3].

$$CLi = 2 (CS_1 + CS_4) \quad [50]$$

If more species were in precipitated form, the concentration of the charged species, and therefore lithium, would decrease, resulting in a reduction in resistance, as hypothesised. Experimentally, the volume of electrolyte influences the concentration of species and therefore the electrolyte resistance, along with the viscosity and the available area, if there is an insufficient volume to fully wet the electrode pores. The influence of electrolyte viscosity was not included in the model.

The concentration of lithium was used to calculate the conductivity, using the same equation as Zhang et al. [1]. Conductivity decreases with increasing concentration of the electrolyte, which occurs at lower E/S ratios or a higher sulfur content [6]. The conductivity was then used to calculate resistance, as previously discussed and shown in Equation [12]. Within the conductivity equation, the fitting parameters, σ_0 and b , were varied to obtain the correct magnitude of resistance, and therefore Ohmic change with C-rate variation. Dependent on the values, as an exponential term was used within the conductivity equation, numerical errors could occur causing the voltage to spike. This predominately related to the variation in lithium concentration when it became close in value to the initial lithium concentration. All other fitting parameters, including the porosity exponential, remained the same as for Zhang et al. [1]. However, it is likely the magnitude of these fitting parameters will vary when scaling between formats.

4.4.8.1 Results: Testing Ohmic Change and Voltage C-rate Dependence

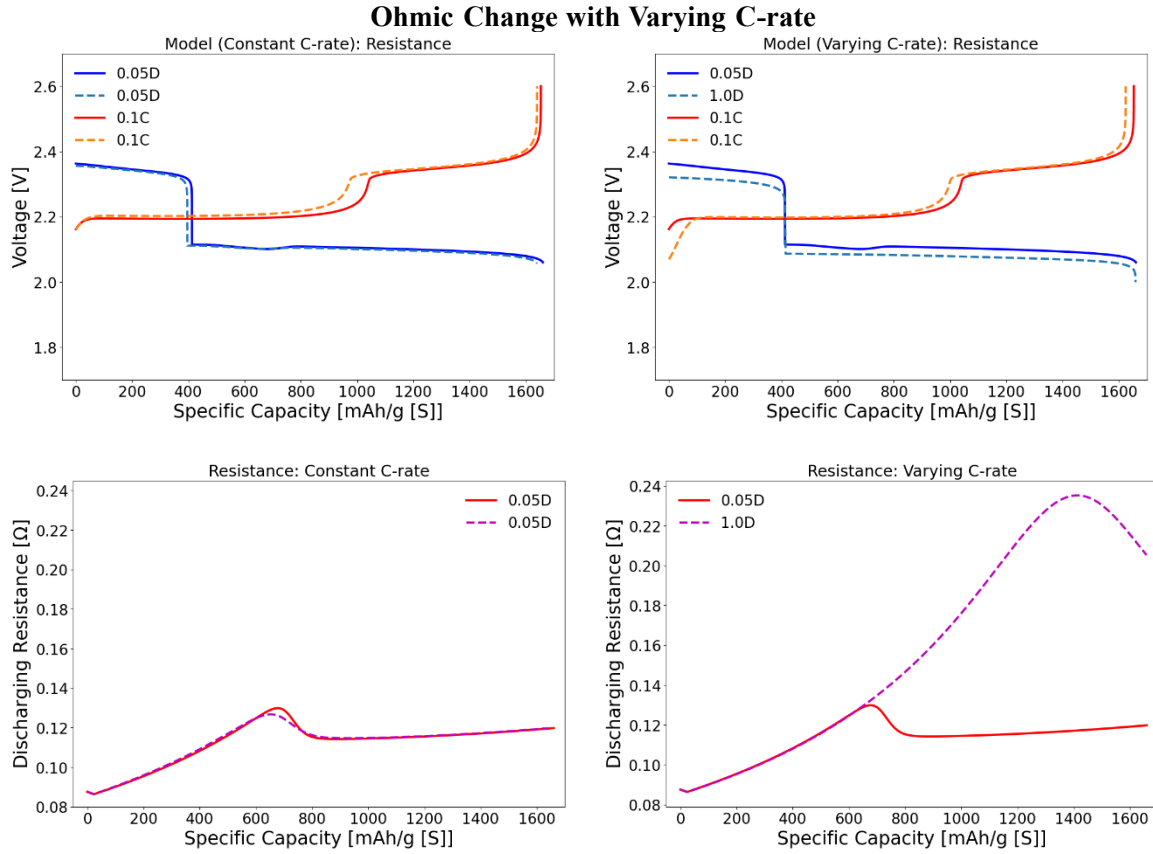


Figure 20: Model voltage-capacity and resistance predictions with varying C-rate when accounting for Ohmic change

As previously discussed, due to the lack of experimental data, the magnitude of coin-cell resistance was assumed similar in order of magnitude to a pouch-cell, with the values compared to those from Zhang et al. [1]. When varying the C-rate, a decrease in discharge voltage was observed at higher rates, as shown in Figure 20; the influence was similar in both high and low plateaus. As the charging current remained constant, minimal variation with C-rate was observed; any observed changes were due to the history effect from the previous discharge. The resistance change aligned with experimental findings of increased internal resistance at higher C-rates [28], as shown in Figure 20. However, the magnitude of the voltage change was smaller than the change observed experimentally by Boenke et al. [28]. As the model only considered electrolyte resistance, based on conductivity only, there are likely to be other sources that may need to be included to capture the correct magnitude. These may also vary between cell formats.

4.4.9 Summary

When running the model, various limits were added to prevent the model exceeding the expected conditions. Cornish et al. [3] only included voltage limits, but the additional limits included the minimum and maximum sulfur mass, and the minimum and maximum porosity. Whilst the equations were designed to ensure limits were not exceeded, they were included for reassurance and to account for any unexpected changes, for example caused by numerical errors.

Table 12 includes a summary of how the model compared to the original Cornish et al. [3] model, along with the Zhang et al. [1] model which several mechanisms had been implemented from. These include changes to the number of species and reactions, the use of concentrations rather than masses and the inclusion of variable area. These changes improved the capability of the model, and the causality of predictions in comparison to experimental results. The assumption of a constant area was removed, and

the model now included a dependency between the available surface area and precipitation leading to pore blocking. It also included a clear influence of the Ohmic change, calculated whilst accounting for porosity, with the ability to capture voltage C-rate dependence.

	Zhang et al. [1]	Cornish et al. [3]	Olisa 2024
Sulfur Reactions	$\frac{1}{2}S_8^0 + e^- \rightarrow 0.5 S_8^{2-}$ $\frac{3}{2}S_8^{2-} + e^- \rightarrow 2S_6^{2-}$ $S_6^{2-} + e^- \rightarrow \frac{3}{2}S_4^{2-}$ $\frac{1}{2}S_4^{2-} + e^- \rightarrow S_2^{2-}$ $\frac{1}{2}S_2^{2-} + e^- \rightarrow S_1^{2-}$	$S_8^0 + 4e^- \leftrightarrow 2S_4^{2-}$ $S_4^{2-} + 2e^- \leftrightarrow 2S_2^{2-}$ $S_2^{2-} + 2e^- \leftrightarrow 2S_1^{2-} \downarrow$	$S_8^0 + 4e^- \leftrightarrow 2S_4^{2-}$ $S_4^{2-} + 6e^- \leftrightarrow 4S_1^{2-}$
Lithium Reactions	$Li \rightarrow Li^+ + e^-$ $2Li^+ + S^{2-} \rightarrow Li_2S \downarrow$	<i>Not included</i>	
Porosity	$(-)\frac{d\varepsilon}{dt} = V_{Li_2S}r_p$ $ar = ar_0 \left(\frac{\varepsilon}{\varepsilon_0}\right)^Y$	<i>Not included</i>	$(-)\frac{d\varepsilon}{dt} = V_{Li_2S}r_p$ $ar = ar_0 \left(\frac{\varepsilon}{\varepsilon_0}\right)^Y$
Rate of Reactions	$r_p = k_p \cdot v_{Li_2S} (C_{Li}^2 + C_{S^{2-}} - K_{sp})$	$\frac{dS_8^0}{dt} = -\frac{n_{S_8}Ms}{n_H F} i_H - k_S S_8^0$ $\frac{dS_4^{2-}}{dt} = \frac{n_{S_8}Ms}{n_H F} i_H + k_S S_8^0 - \frac{n_{S_4}Ms}{n_M F} i_M$ $\frac{dS_2^{2-}}{dt} = \frac{n_{S_4}Ms}{n_M F} i_M - \frac{n_{S_2}Ms}{n_L F} i_L$ $\frac{dS^{2-}}{dt} = \frac{n_{S_2}Ms}{n_L F} i_L - \frac{k_{p/d}}{vp} S_p (S^{2-} - S^*)$ $\frac{dS_p}{dt} = \frac{k_{p/d}}{vp} S_p (S^{2-} - S^*)$	$\frac{dCS_8^0}{dt} = -\left(\frac{i_H}{n_H F v}\right) - k_S CS_8$ $\frac{dCS_4^{2-}}{dt} = \left(\frac{2 i_H}{n_H F v}\right) + 2 k_S CS_8 - \left(\frac{i_L}{n_L F v}\right)$ $\frac{dCS_2^{2-}}{dt} = \left(\frac{4 i_L}{n_L F v}\right) - \left(\frac{Ms}{\rho_s} k_{p/d} CS_p (CS_1^{2-} - CS^*)\right)$ $\frac{dCS_p}{dt} = \frac{Ms}{\rho_s} k_{p/d} CS_p (CS_1^{2-} - CS^*)$
Current	<i>Not included</i>	$I = i_H + i_M + i_L$	$I = i_H + i_L$

Table 12: Comparison of the model derivation for Zhang et al. [1], Cornish et al. [3] and the updated model

Further work is required to include a direct relationship between the mass of precipitated species and the available area; a larger mass correlates to more pore blocking, therefore a larger decrease in area. Currently, the area is calculated based on the rate of precipitation, rather than the mass or concentration of precipitates directly. This relationship is insufficient to capture the blocking of pores within the cell, without accounting for the influence of pore size and distribution. The positive electrode mass and thickness should also be considered when making assumptions, as this would likely influence the porosity and the movement of species within the cell. This is addressed through a change in porosity in Section 4.5.2, and the inclusion of a transport mechanism in Section 4.5.3.

The model should also be able to account for the influence of electrolyte volume. This will vary when scaling between cell formats, and with E/S ratios depending on the sulfur mass. Lower volumes, or lower E/S ratios, influence the wetting ability and result in a higher concentration of species, impacting the viscosity and kinetics within the electrolyte [6]. The wetting of all components, including the electrode and the separator, along with the distribution of dissolved sulfur species within, would need to be included. This would further influence the electrolyte behaviour and internal resistance within the cell, and could also address the issue of increasing sulfur mass not correlating to a decrease in capacity. This is addressed in Section 4.5.1.

4.5 Iteration 2

4.5.1 Electrolyte Solution Volume and Pore Volume

Currently, the model assumes that the total electrolyte volume input into the cell contributes to electrochemical reactions. The assumption is also made that the total sulfur mass dissolved within the electrolyte is utilised for reactions. In a real cell, this is not true. Only the electrolyte contained within the pores of the positive electrode is used for electrochemical reactions; anything outside of this volume is considered excess volume. Cornish et al. [3] did not account for the volume of the pores within the electrode, meaning the utilised electrolyte and dissolved sulfur species could not be predicted. Without the inclusion of degradation mechanisms, the assumption of total material utilisation results in the model aiming towards the maximum achievable capacity.

Within the model, the total volume of electrolyte put into the cell during manufacture was determined by the E/S ratio, which was maintained throughout cycling. The mass of sulfur was an input calculated from Boenke et al. [28] experimental parameters. The E/S ratio given was 7 μ l/mg for coin-cells, and 4 μ l/mg for pouch-cells [28]. The electrolyte volume was calculated as shown in Equation [51].

$$V_{\text{electrolyte}} = \frac{E}{S} \text{ratio} \cdot \text{mass}_{\text{sulfur}} \quad [51]$$

The electrolyte volume was considered the total volume of electrolyte solution added to the cell during manufacture. It was assumed constant, with no losses due to degradation. The model also assumed no change in behaviour due to increased pressure with larger volumes of electrolyte. The pore volume was the volume made up by all the pores within the positive electrode, irrespective of the size and distribution. Similarly to electrolyte volume, the pore volume was assumed to be a fixed volume and represented the volume of pores within the electrode structure at the time of manufacture. During cycling, the precipitation of sulfur leads to a change in available surface area, caused by pore blocking, resulting in a change in the pore volume available for reactions. This was captured by the variable porosity and area, as discussed in Section 4.4.5. To allow the model to account for material utilisation, the assumption was made that no other factors contributed to a change in available area other than precipitation and the electrolyte volume.

The total electrolyte volume was calculated from the input parameters, as shown in Equation [51]. The usable electrolyte volume required to fill the pores was calculated separately. Any volume remaining after the pores have been filled was referred to as the excess volume, or the reservoir of excess electrolyte. To calculate these respective volumes, the volume of the pores was first calculated. To do this, the total volume of the positive electrode, shown in Equation [52], was calculated assuming the positive electrode was completely solid, based on the area, thickness and number of layers, if accounting for multiple electrodes in a larger cell format. The volume of the electrode structure, or carbon host, shown in Equation [53], was calculated from the mass of carbon nanotubes (CNTs) before sulfur was loaded, based on the density of the CNT sheet (without any sulfur loaded), the density of single CNTs (before being formed into sheets), the area and the thickness. The density details were provided by Tom Boenke [97], and the values ignored any volume in the sheet that may have been empty pores. The number of layers was used to account for a multi-layer cell, or double-sided electrodes. The sulfur volume, shown in Equation [54], was calculated based on the mass and density of sulfur. The pore volume, shown in Equation [55], was then calculated by removing the CNT volume

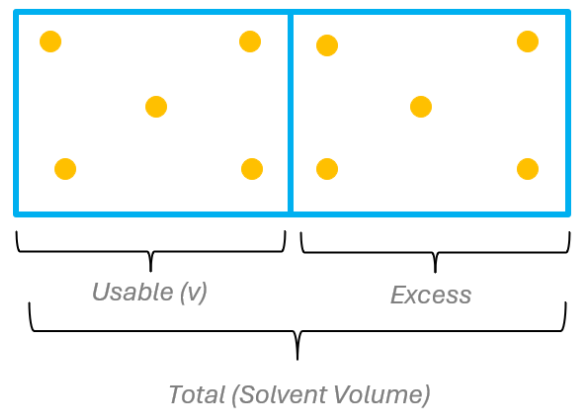


Figure 21: Schematic diagram of the total, usable and excess electrolyte volumes

and the sulfur volume from the total electrode volume. The excess volume of electrolyte, shown in Equation [56], was the pore volume subtracted from the total electrolyte volume.

$$V_{\text{tot_electrode}} = ar \times l \quad [52]$$

$$V_{\text{CNT}} = \frac{\rho_{\text{CNT_sheet}} ar \times l}{\rho_{\text{single_CNT}}} \quad [53]$$

$$V_{\text{sulfur}} = \frac{\text{mass}_{\text{sulfur}}}{\rho_s} \quad [54]$$

$$V_{\text{pore}} = V_{\text{tot_electrode}} - V_{\text{CNT}} - V_{\text{sulfur}} \quad [55]$$

$$V_{\text{excess}} = V_{\text{electrolyte}} - V_{\text{pore}} \quad [56]$$

$$\text{if } V_{\text{pore}} < V_{\text{electrolyte}}: \quad [57]$$

$$V_{\text{usable}} = V_{\text{pore}}, \quad [58]$$

$$ar_0 = ar_{\text{spec}} (\text{mass}_{\text{electrode}} - \text{mass}_{\text{sulfur}}) \quad [59]$$

$$\text{If } V_{\text{pore}} \geq V_{\text{electrolyte}}: \quad [60]$$

$$V_{\text{usable}} = V_{\text{electrolyte}}, \quad [61]$$

$$ar_0 = ar_{\text{spec}} (\text{mass}_{\text{electrode}} - \text{mass}_{\text{sulfur}}) \left(\frac{V_{\text{electrolyte}}}{V_{\text{pore}}} \right) \quad [62]$$

$$\text{if } V_{\text{pore}} < V_{\text{electrolyte}}: \quad [63]$$

$$\text{mass}_{\text{sulfur_usable}} = \text{mass}_{\text{sulfur}} \frac{V_{\text{usable}}}{V_{\text{excess}}}$$

$$\text{if } V_{\text{pore}} \geq V_{\text{electrolyte}}: \quad [64]$$

$$\text{mass}_{\text{sulfur_usable}} = \text{mass}_{\text{sulfur_global}}$$

$$\text{if } V_{\text{pore}} < V_{\text{electrolyte}}: \quad [65]$$

$$\text{excess}_{\text{sulfur}} = \text{mass}_{\text{sulfur_global}} - \text{mass}_{\text{sulfur_usable}}$$

$$\text{if } V_{\text{pore}} \geq V_{\text{electrolyte}}: \quad [66]$$

$$\text{excess}_{\text{sulfur}} = 0$$

If the total electrolyte volume exceeded the pore volume, as shown in Equations [57] – [59], the usable electrolyte volume was equal to the pore volume, and the model assumed the positive electrode was completely wetted. When the total electrolyte volume was less than the pore volume, as shown in Equations [60] – [62], the usable volume was equal to the total electrolyte volume, and the positive electrode was insufficiently wetted. This could occur in larger cell formats due to the increased sulfur mass, lower E/S ratios and larger surface area compared to coin-cells [2]. Insufficient wetting leads to a portion of the electrode being inaccessible, reducing the available surface area. This was captured in the model through recalculating the initial area based on the electrolyte to pore volume ratio, as shown in Equations [59] and [62]. To calculate the initial area, a specific area term was required. For the positive electrode materials tested by Boenke et al. [28], specific surface areas of $38\text{m}^2\text{g}^{-1}$ and $261\text{m}^2\text{g}^{-1}$ were given for CNT BP and CNT DryFilm respectively. These were calculated with respect to the total surface area of a material for a given mass.

When calculating the area, the model assumed a certain percentage of the electrode was utilised, with this section being completely wetted, rather than all pores across the electrode being partially wetted. The volume of excess electrolyte remained constant throughout cycling. The model also assumed that the electrolyte was either located in the positive electrode pores or in an excess region; no electrolyte

was included in other components such as the separator. The usable electrolyte volume was used throughout the model to calculate other variables, such as the species concentrations within the positive electrode. Based on the formulation in the model, the usable electrolyte volume could not exceed the pore volume. The model did not account for the displacement of electrolyte within the electrode pores when precipitation occurred.

The excess volume present when the electrolyte volume exceeded the pore volume did not contribute to electrochemical reactions. The sulfur species were assumed to be homogeneously distributed throughout the electrolyte; the species dissolved within the excess electrolyte volume also did not contribute to electrochemical reactions, leading to a reduction in available species and the achievable capacity of the cell. The usable sulfur mass was calculated as shown in Equations [63] and [64]. Equations [65] and [66] show the calculation for the mass of sulfur within the excess electrolyte, referred to as the excess sulfur mass.

Calculating the usable electrolyte volume and usable sulfur mass this way removed the assumption of total material utilisation. It also worked as an initial step towards resolving to physically unmeaningful S_p concentration term; the assumption was made that sulfur could only precipitate within the electrode region and was not included in the excess. The concentration of all other species was calculated based on the volume within the region they were in; the concentration of species within the excess electrolyte did not account for precipitation and was therefore correct and physically meaningful. For further model development, the removal of S_p from the usable electrolyte volume would allow more realistic concentrations to be calculated within this region, based on fewer species contained within the electrolyte.

4.5.1.1 Results: Usable and Excess Electrolyte

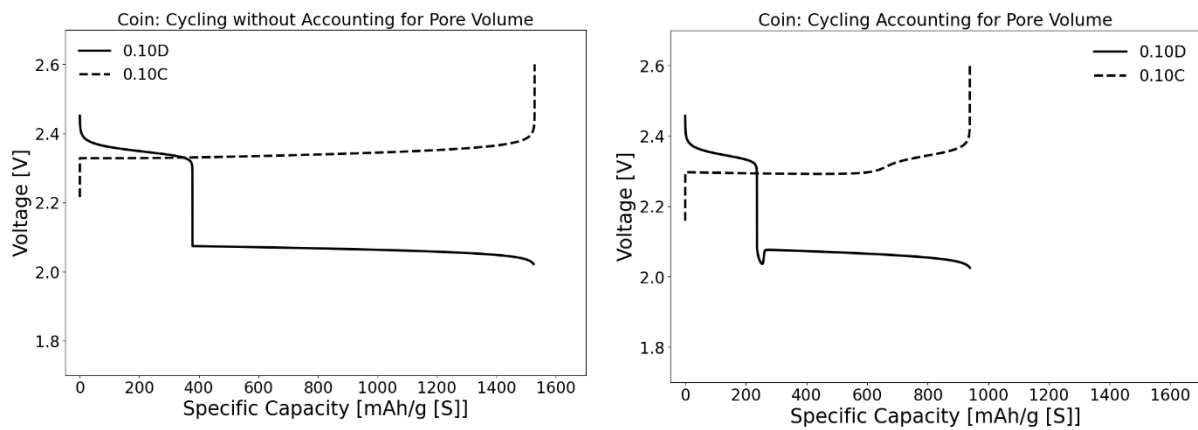


Figure 22: Model voltage-capacity predictions with and without accounting for electrolyte wetting

Boenke et al. [28] found that electrochemical performance was strongly dependent on the volume of electrolyte and the solubility of the lithium polysulfides. Assuming the sulfur mass remained constant, a lower electrolyte volume would result in higher viscosity and internal cell resistance [28]. It was also hypothesised that lower volumes reduced the utilisation of active material within the cell [3]; the utilisation was calculated by the achieved capacity in relation to the maximum theoretical capacity. Whilst the model did not account for viscosity, this update allowed utilisation of active material to be captured.

Without accounting for the positive electrode pore volume, the total electrolyte volume and sulfur mass were assumed to contribute towards electrochemical reactions, and the model achieved the maximum capacity of 1,675mAh/g [S] [28], as shown in Figure 22. When the pore volume was accounted for, the usable volume was calculated dependent on whether the electrolyte volume was in excess, matched or

was insufficient to fill the pore volume. As previously discussed, as the sulfur species were homogeneously distributed throughout the electrolyte, those dissolved within the excess electrolyte did not contribute to electrochemical reactions and were permanently lost, resulting in reduced capacity as shown in Figure 22. In a coin-cell, a larger E/S ratio results in a larger volume of excess, corresponding to a larger proportion of sulfur species not available for electrochemical reactions, and therefore a lower achievable capacity compared to pouch-cells.

Further investigation found that if the electrolyte volume was similar or matched the positive electrode pore volume, the highest capacity was achieved, as shown in Figure 23. This applied to both high and low plateau capacity. This was due to no, or a minimal amount of excess electrolyte, meaning the total electrolyte volume and dissolved sulfur were contained within the positive electrode, contributing towards electrochemical reactions and allowing the model to reach maximum capacity. If the electrolyte volume was insufficient to fill all the positive electrode pores, the electrode was not fully utilised; the portion of the positive electrode that was filled by electrolyte was fully accessible, with the remaining unfilled portion inaccessible for reactions. This reduced both the usable pore volume and usable sulfur mass, resulting in a lower achieved capacity. This capacity change was irreversible, and although it does not capture degradation directly, it proved the influence of availability of active material on cell performance. Whilst similar capacities were achieved in both cases when the electrolyte volume did not match the pore volume, if in excess or when insufficient, as shown in Figure 23, the causality for the behaviour was different. This was an important consideration for further work into how species dissolved within the excess electrolyte change during cycling, as discussed in Section 4.5.3.

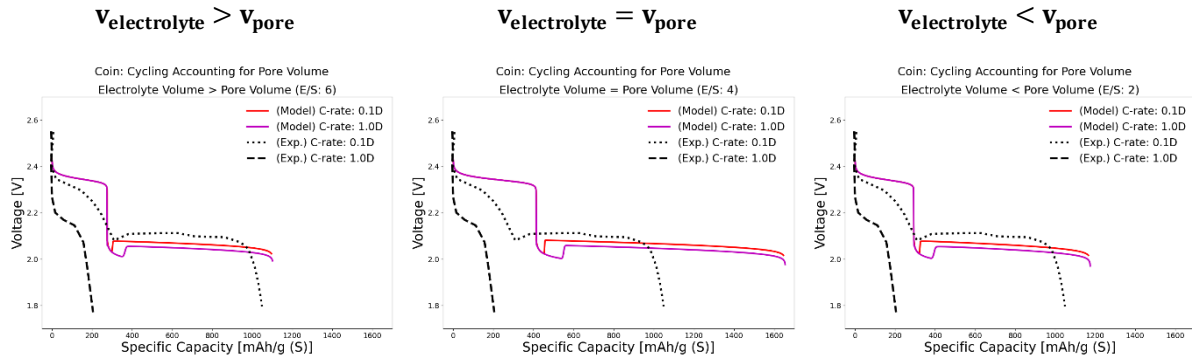


Figure 23: Model voltage-capacity predictions for varying electrolyte volumes, to exceed, match or fall below the pore volume

4.5.2 Updated Porosity

This work was completed alongside Section 4.5.1.

As discussed in Section 4.4.5, as Cornish et al. [3] did not include a positive electrode porosity variable, the equation given by Zhang et al. [1] was implemented. This equation calculated the porosity based on the molar volume of Li_2S_1 and the rate of precipitation, using the saturation concentration and the concentration of S_1 . The rate of precipitation did not account for the mass of precipitated species directly. The concentration of S_1 varied dependent a volume of electrolyte. As the assumption was made that the initial electrode porosity was measured at the time of manufacture, the electrolyte volume should have no influence. Instead, the electrolyte volume should influence the number of pores available for reactions directly, through the amount of wetting. This was captured as discussed in Section 4.5.1. The precipitation of species, leading to pore blocking, should be the only direct influence on the porosity. To capture a separate dependency, an update to the porosity equation was required to directly account for the variation of precipitates during cycling, in addition to the new pore volume equation.

The porosity value should always remain between zero and one, as it represents the ratio of available volume to total volume; zero porosity implies no available area due to complete electrode coverage from precipitates, and one implies full availability of area, for example at the end of charge when all

species have dissolved. To create a separate dependency between precipitation and the porosity of the electrode, several equation variations were tested. The derivation of the equations should ensure these conditions are always satisfied, but stopping conditions were added to the model as a backup, as previously discussed. These were also used to check the equations were implemented correctly, and all other conditions were satisfied during cycling. For simplicity within the model, the assumption was made that precipitation was homogenous across the electrode surface. All the precipitated species were assumed to be deposited onto the electrode surface, without floating in the electrolyte.

The electrodes used within the experimental work by Boenke et al. [28] had a maximum porosity of 70% at a fully charged state [97], equivalent to 30% of the electrode being solid; a high porosity corresponds to a larger number of reaction sites. The porosity equations aimed towards obtaining a similar value.

4.5.2.1 Iteration 1

As a very simple initial test, the first attempt to remove the dependency on electrolyte volume involved recalculating porosity as a ratio between pore volume and total volume, as shown in Equation [67]. This iteration was attempted before the final equation for pore volume was obtained, as discussed in Section 4.5.1. Instead, pore volume was calculated using the pore volume per gram value, as shown in Equation [68], given by Boenke et al. [28] as $0.08\text{cm}^3\text{mg}^{-1}$ for CNT BP and $0.83\text{cm}^3\text{g}^{-1}$ for CNT DryFilm. This pore volume per gram value was similar to those found in other experimental papers [26].

$$\varepsilon = \frac{V_{\text{pore}}}{V_{\text{tot_electrode}}} \quad [67]$$

$$V_{\text{pore}} = v_{\text{pore/gram}} (\text{mass}_{\text{electrode}} - \text{mass}_{\text{sulfur}}) \quad [68]$$

Boenke et al. [28] found a porosity of 70%, and other experimental porosity values usually vary between 45 – 70% [26], [58]. When implemented together, these equations resulted in a porosity value of approximately 2%; despite the simplicity and the removal of the dependence on electrolyte volume, this equation was insufficient to capture the correct magnitude.

4.5.2.2 Iteration 2

The second iteration of the porosity equation was adapted from Zhang et al. [1] to account for the concentration of precipitated species directly, as shown in Equation [69]. Instead of using the rate of precipitation and the concentration of S_1 , the difference between the initial and varying concentration of precipitates was included; as the number of precipitated species increased, this difference also increased. When multiplied with the negative molar volume term, this resulted in a reducing porosity value with increasing concentration of precipitates. Based on the ODEs previously discussed, the concentration also varied dependent on the rate of precipitation, which was a fitting parameter.

This update also accounted for the maximum porosity of the electrode, calculated if no species were in precipitated form; when the concentration of precipitates was at a minimum, for example at the beginning of discharge, the porosity value was at the maximum. This value could not be derived within the model, as numerical errors occurred when any species value equalled to zero. Instead, the value was obtained from experimental results, although it could also be implemented as a fitting parameter.

$$\varepsilon = -V_{\text{Li}_2\text{S}} (C_{\text{S}_p} - C_{\text{S}_{p_0}}) + \varepsilon_0 \quad [69]$$

This update to the equation captured the causality of precipitation leading to pore blocking through the inclusion of the concentration of precipitates directly. However, the inclusion of concentration terms meant it still directly relied on the volume of electrolyte; this dependence needed to be removed.

4.5.2.3 Iteration 3

This next equation was calculated similarly to the previous iteration but instead used the volume, rather than the concentration of precipitated sulfur, to obtain the varying electrode porosity. To remove the dependence on electrolyte volume, the volume was calculated by converting the concentration to a mass using density, as shown by Equation [70]. The density of sulfur was assumed to be the same for all sulfur species. The molar volume term was no longer required to balance the units of the equation. The change in porosity was then calculated based on the change in sulfur volume compared to the total electrode volume. These are summarised in Equations [71] - [73].

$$S_{p_{vol}} = \frac{S_p}{\rho_s} = \frac{CS_p (Ms \ v \ ns_1)}{\rho_s} \quad [70]$$

$$\Delta S_{p_{vol}} = (S_{p_{vol}(t)} - S_{p_{vol}(t=0)}) \quad [71]$$

$$\Delta \varepsilon = \frac{-\Delta S_{p_{vol}}}{V_{tot_{electrode}}} \quad [72]$$

$$\varepsilon = \Delta \varepsilon + \varepsilon_0 \quad [73]$$

With the aim of obtaining a porosity value between 45 and 70%, this derivation significantly improved upon the first iteration, with a maximum porosity of approximately 60%. However, to remove the requirement of the maximum porosity as a potential fitting parameter, a final iteration of the equation was required.

4.5.2.4 Iteration 4

Alongside the work in Section 4.5.1, an amended version of the pore volume equation was used to calculate the initial porosity. Taking the simplified porosity equation as derived in Iteration 1, the pore volume, as shown in Equation [55], was divided by the total electrode volume to obtain the porosity, as shown in Equation [74]. The total volume of sulfur was replaced with the volume of precipitated sulfur, as only this form should influence how the porosity changes during cycling. To calculate the maximum porosity, the volume of precipitated sulfur was set to zero, therefore removing the last term in the equation, as shown in Equation [75].

$$\varepsilon = \left(1 - \frac{V_{CNT}}{V_{tot_{electrode}}} - \frac{V_{S_p}}{V_{tot_{electrode}}} \right) = \Delta \varepsilon + \varepsilon_0 \quad [74]$$

$$\varepsilon_0 = \left(1 - \frac{V_{CNT}}{V_{tot_{electrode}}} \right) \quad [75]$$

This equation obtained a porosity value of approximately 71%, aligning with Boenke et al. [28] findings. It included the influence of precipitation directly and removed the dependence on electrolyte volume through the concentration of species term. Alongside the previous update to account for electrolyte wetting and material utilisation, the model now accurately accounts for separate influences on behaviour due to precipitation and electrolyte volume. In addition, the model can capture the impact of varying sulfur content or loading through the volume of precipitates, improving predictions when varying between cell formats. The drawback of this equation is the requirement for details relating to the volume of the electrode structure within published experimental results. Without this, fitting parameters or assumptions must be made. This equation also does not account for the influence of tortuosity, or the location at which species precipitate; this may be required for further work.

4.5.2.5 Results: Updated Porosity

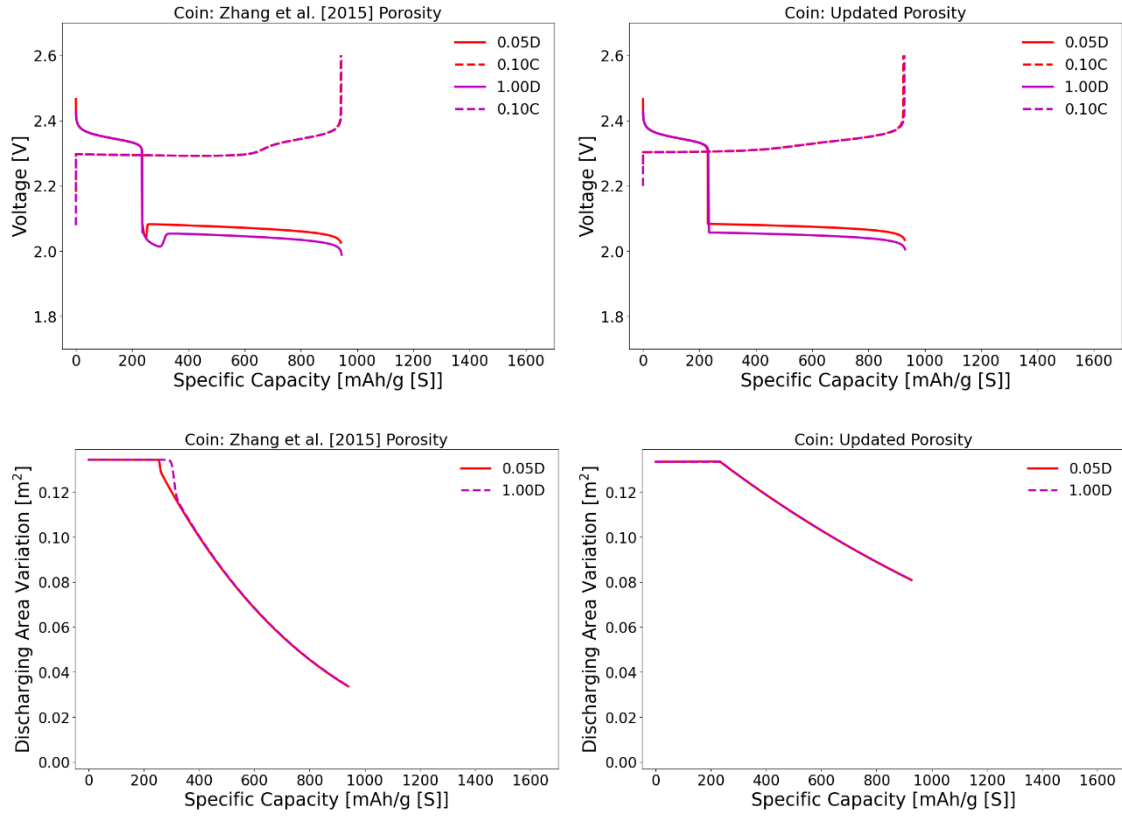


Figure 24: Model voltage-capacity predictions with Zhang et al. [1] porosity and the updated porosity equation

The aim of updating the porosity equation was to account for changes to the sulfur within the cell and the precipitation that occurred during cycling. The influence of variations to sulfur mass and the positive electrode thickness, both of which vary with cell format, can now easily be accounted for within the equation. Further to this, with the inclusion of porosity within the area equation, area now influences and is influenced by the change in precipitated sulfur.

Whilst capturing the correct dependencies and removing the requirement for fitting parameters such as the maximum porosity, the model was unable to capture significant area change with the updated formulation of porosity, as shown in Figure 24. Further changes to the area equation are required to improve the magnitude of predictions; this is discussed in Section 4.6.1. In addition, further work to understand the other factors that vary with porosity, or cause a variation to porosity, may be required. For example, porosity may vary between cell formats depending on the pressure applied to the cell [6]. Currently, the electrolyte volume and corresponding pressure is assumed to have no influence. The model also does not account for electrolyte displacement, or inaccessible electrolyte when precipitates form and block the pores. Separately, the size and distribution, or location of pores throughout the electrode would impact the transport within the cell. For example, reaction sites closer to the surface, or accessed through less tortuous pathways would be more favourable [6]. Dependent on the number and rates of reaction, variations to porosity due to pore blocking, leading to a change in available area, may influence the behaviour in different ways. For further model development, this may be considered.

4.5.3 Excess Electrolyte with Diffusion (Increased Dimensionality)

With the update to calculate the usable electrolyte volume within the model, the presence of an excess volume results in a lower achievable capacity; the dissolved sulfur within the excess volume becomes inaccessible for electrochemical reactions. This calculation assumes coin-cells will always have a lower achievable capacity than pouch-cells, based on the larger excess volume. Experimental results, including Boenke et al. [28], confirm this is not always true.

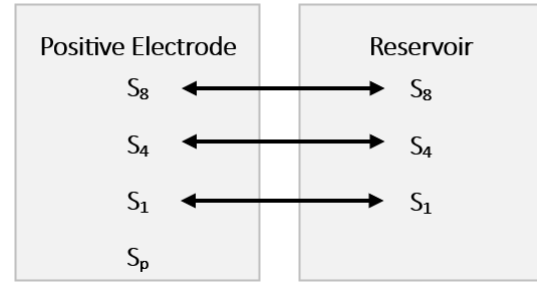


Figure 25: Schematic diagram of the diffusion pathways between the positive electrode and reservoir

Within higher order models, transport mechanisms would enable species to be regained from the excess electrolyte region into the positive electrode region. One of these mechanisms is diffusion, which enables transport around the cell based on the concentration gradients [6]. With the separation of the electrolyte in the electrode and excess region, a simplified diffusion mechanism can be implemented into this 0D model. If the species were all assumed to be at one point, either in the electrode or in the excess region, the concentration gradient between these two points would enable 'transport' between. This attempts to mimic behaviour achieved in higher order models, without the spatial variations.

The introduction of this mechanism was considered an intermediate step before increasing the dimensionality to 1D. To capture the behaviour in both regions, a pseudo-spatial 0D model was required, similar to the Cornish et al. [103] model. This assumed two separate systems were working in parallel, with variations in each region influencing the other; one region was the positive electrode, and the other was the reservoir of excess electrolyte, as shown in Figure 25. The difference in concentration between the regions, varying with time, was the only driving force, with species travelling from higher to lower concentration to reach an equilibrium [6]. This mechanism introduced the capability for species to be regained from the excess electrolyte, rather than being permanently lost, allowing a higher achievable capacity. For example, during discharge, as S_8 reduces to S_4 , the concentration of S_8 in the positive electrode decreases. As the S_8 in the excess reservoir does not contribute to electrochemical equations, it remains at the same value. A concentration gradient has now developed between the regions, causing S_8 to diffuse from higher to lower concentration, from the reservoir to electrode, increasing the concentration of S_8 species contributing to electrochemical reactions. A larger concentration gradient contributes to a larger rate of diffusion. As diffusion occurs in both directions between the regions, species could also be lost to the excess electrolyte region.

To account for diffusion, an additional term was added to each of the ODEs. The rate of change of species within the reservoir of excess electrolyte was calculated as shown in Equations [77], [78], [79]. As precipitated species were not present in the excess electrolyte, a diffusion equation was not required. The concentration of species within the excess electrolyte was calculated based on the volume of excess electrolyte within the reservoir, as shown in Equation [76]; V_r represents the reservoir volume, replacing v , which is the usable volume within the electrode. If the reservoir volume was larger than the usable volume in the positive electrode, the mass of species in the reservoir would also be larger, if the system was in equilibrium and the concentrations were balanced. For this reason, the ratio of volumes was included in the ODEs to ensure diffusion was balanced based the corresponding concentrations in each region, as shown in Equations [80] - [82]. The volume of electrolyte in each region remained constant throughout cycling.

$$CS_{i_{res}} = \frac{S_{i_{res}}}{Ms \text{ Vr } ns_i} \quad [76]$$

$$\frac{dCS_{8_{res}}^0}{dt} = -DS_8 (CS_{8_{res}} - CS_8) = DS_8 (CS_8 - CS_{8_{res}}) \quad [77]$$

$$\frac{dCS_{4_{res}}^{2-}}{dt} = -DS_4 (CS_{4_{res}} - CS_4) \quad [78]$$

$$\frac{dCS_{1_{res}}^{2-}}{dt} = -DS_1 (CS_{1_{res}} - CS_1) \quad [79]$$

$$\frac{dCS_8^0}{dt} = -\left(\frac{i_H}{n_H F v}\right) - k_s CS_8 + \left(DS_8 (CS_{8_{res}} - CS_8) \frac{Vr}{v}\right) \quad [80]$$

$$\frac{dCS_4^{2-}}{dt} = \left(\frac{2 i_H}{n_H F v}\right) + 2 k_s CS_8 - \left(\frac{i_L}{n_L F v}\right) - \left(DS_4 (CS_{4_{res}} - CS_4) \frac{Vr}{v}\right) \quad [81]$$

$$\frac{dCS_1^{2-}}{dt} = \left(\frac{4 i_L}{n_L F v}\right) - \frac{Ms}{\rho_s} \ar k_{p/d} CS_p (CS_1^{2-} - CS^*) - \left(DS_1 (CS_{1_{res}} - CS_1) \frac{Vr}{v}\right) \quad [82]$$

$$\frac{dCS_p}{dt} = \frac{Ms}{\rho_s} \ar k_{p/d} CS_p (CS_1^{2-} - CS^*) \quad [83]$$

The direction and rate of diffusion was determined by the concentration of species in each region. The term, D , related to a transport coefficient, with units m^2s^{-1} . A higher transport coefficient related to faster transport between regions; at the highest value, species always tended towards the equilibrium concentration between regions, meaning the maximum capacity may not be achieved as a portion of species would remain in the excess electrolyte. A lower value of the transport coefficient would mean a slow regain of species into the electrode, also reducing the maximum achievable capacity. Each species had a separate transport coefficient within the model, allowing variations to be captured. Experimentally, it has been found that higher chain length species are more mobile than lower chain length species, but are less soluble and therefore do not precipitate as easily [6]. Within the model, the transport coefficient was unaffected by this, or other factors such as current, mass, or E/S ratio. Further work to implement it as a variable may be required at a later stage.

4.5.3.1 Results: Diffusion between the Electrode and Excess Electrolyte Regions

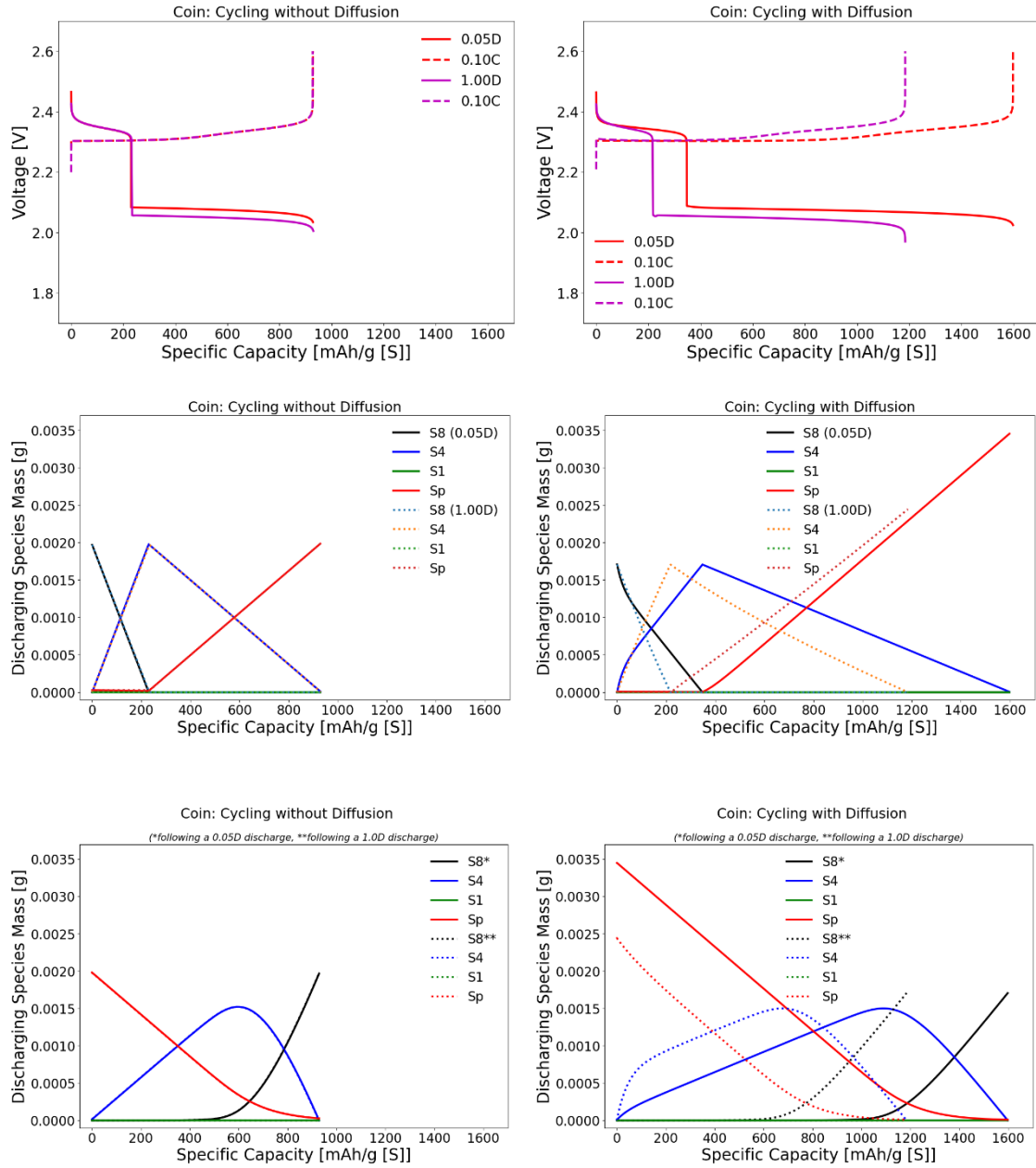


Figure 26: Model voltage-capacity predictions with and without the diffusion mechanism

The inclusion of diffusion enabled reversible C-rate dependence to be achieved, as shown in Figure 26, due to temporarily inaccessible material in the excess electrolyte region, which varied with C-rate. The relative rate of diffusion compared to the current and the precipitation dynamics contributed significantly to the dominating reactions. For example, with a larger excess of electrolyte (larger E/S ratio), or slower transport (lower D term), a larger proportion of species remained in the excess region, resulting in a larger C-rate dependence. This occurred at both high and low plateaus, although a larger change was observed in the low plateau; one hypothesis for this within the model was due to the cell reaching cut-off conditions earlier, for example the voltage limit. The observed behaviour during cycling was also linked to the history effect from the previous cycles.

From further testing, if the rate of diffusion was similar to the electrochemical rate of reaction, a high capacity was achieved as the model aimed towards utilising all the sulfur species by regaining them from the excess region. If the rate of diffusion was lower, fewer species were regained, resulting in lower achievable capacity. As the rate of reactions increased with increasing current, the rate of diffusion, which was set by the fixed transport coefficient, became smaller in comparison, further reducing the species regained and therefore the achievable capacity. Separately, as diffusion was a chemical reaction, the influence of the pre-cycle step became more prominent with the addition of the diffusion mechanism. A larger change in species was observed, to reach equilibrium between each region.

With the inclusion of diffusion, the model also achieved higher discharge capacity with lower sulfur content; a lower mass corresponded to a lower electrolyte volume, if the E/S ratio was maintained. Assuming there was still sufficient electrolyte to fill the pores, this resulted in a smaller volume of excess electrolyte, and a smaller portion of dissolved species that did not contribute to electrochemical reactions. The larger proportion within the positive electrode reduced the impact of bottlenecks due to diffusion, and a higher capacity was achieved. Under these conditions, the concentration in the electrode was also higher, resulting in a higher electrolyte resistance. Dependent on the magnitude of resistance in relation to the rate of diffusion, this could further impact the performance of the cell.

The use of diffusion to capture C-rate dependence relied on the assumption that a reservoir of excess electrolyte was present. In coin-cells, there is typically always an excess, however in pouch-cells, with larger geometric sizes and lower E/S ratios, it is possible the reservoir may be significantly smaller, or negligible. This would be exaggerated further with multi-layer pouch-cells, or larger cell formats. Without a reservoir, and therefore no separate region to compare concentrations, the impact on C-rate dependence cannot be captured. Further investigation would be required to understand the extent to which transport alone explains the differences in the observed behaviour between cell formats, and which other mechanisms that could also capture this behaviour.

In this iteration of the model, the impact was reversible, but the diffusion mechanism could also contribute to a permanent loss of active material that cannot be regained. This would remove the requirement for additional degradation mechanisms to capture capacity fade. Separately, whilst it is likely the separator will contain electrolyte and a portion of sulfur species, this region was not yet considered in the model. This is investigated in Section 4.6.2.

4.6 Iteration 3

4.6.1 Positive Electrode Surface Area

Boenke et al. [28] experimental work found the specific area and pore size influenced the utilisation of sulfur and the uniformness of precipitation [28]. Pore size and uniform precipitation were not accounted for in the model due to the dimensionality, but the influence of area on sulfur utilisation was investigated further. The initial hypothesis for the model was that a larger surface area would improve sulfur utilisation as more active sites would be available for reactions to take place. Other factors to consider were the electrolyte volume and sulfur mass; a larger electrolyte volume ensured all the pores were fully wet and could be utilised for reactions, along with lowering the concentrations of species and reducing the resistance. A smaller mass reduced the magnitude of pore blocking as there were fewer species to precipitate, resulting in a higher porosity and larger available area. To maximise the area, and therefore sulfur utilisation, the optimum cell required a low sulfur mass and high electrolyte volume.

The current model captured variations to the positive electrode surface area through the change in porosity, by updating the equation derived by Kumaresan et al. [77] to account for the influence of precipitation directly. However, this calculation did not obtain the correct magnitude of change. Whilst the fitting parameter in the equation could be adjusted to increase the magnitude, the causality would

not be captured. The model should also be able to capture variations to area with C-rate; this was currently not achievable.

To capture these requirements, a review of existing models and the area equations used was completed. The aim was to find an equation that directly captured the influence of precipitation, resulted in the correct magnitude of area change, and varied with C-rate. The equation would need to be implementable into a 0D model. Several of the findings from this review have been summarised below.

The first equation investigated was by Kang et al. [58], whose work focused on investigating the porosity to optimise the energy density. This model was 1D, and the total surface area was also calculated as the ratio of initial area and porosity, as shown in Equation [84].

$$A_{(p)} = \frac{A_0}{1 - p} \quad [84]$$

An effective area was also calculated to account for unutilised sulfur that remained in precipitated form, blocking the surface, as shown in Equation [85], where $P_{s(uti)}$ was the percentage of utilised sulfur and $m_{s(total)}$ was the total mass of sulfur. Whilst the effective area equation by Kang et al. [58] accounted for utilised sulfur, it was included as a percentage rather than a direct quantity of the sulfur precipitating and blocking the surface area; it was hypothesised the same issue surrounding magnitude and causality would apply.

$$A_{eff} = A - k m_s(total)(1 - P_s(uti)) \quad [85]$$

The original area equation by Kumaresan et al. [77], shown in Equation [46], was used in several other models. These included Zhang et al. 0D model [1], the upgrade of this model to 1D [75], along with investigation by Hofmann et al. [83] and Fronczek et al. [104] into performance at low C-rates. Whilst focusing on rate capability, another model by Zhang et al. [80] built upon this, adapting it to calculate the ratio based on the volume fraction of Li_2S , rather than porosity directly, as shown in Equation [86]. As with other iterations of this area equation, whilst thoroughly validated, this did not capture the influence of precipitated species directly.

$$a = a_0 \left(1 - \frac{V_{Li_2S}}{V_{Li_2S \max}} \right)^\theta \quad [86]$$

Following the review, including several other papers not discussed here, the decision was made to create a new area equation to meet the requirements. In addition to these, the type of precipitation mechanisms occurring would also need to be considered. The current model assumed species precipitate consistently throughout cycling, although experimental work has found separate precipitation mechanisms occur, nucleation and particle growth [102]. Nucleation occurs first onto a fresh surface, and creates new sites for further precipitation reactions [102]. This is followed by particle growth, which occurs on top of the nucleation sites, in a perpendicular direction to the surface [102]. Nucleation covers a significantly larger proportion of the electrode surface area than particle growth precipitation [102].

The effect of precipitation via nucleation was captured in the 0D model by Marinescu et al. [78], by assuming the presence of precipitated sulfur influenced further precipitation. This was implemented into the developed model, as shown in Equation [36]. However, this effect did not capture the impact of different precipitation mechanisms on area. For simplicity, further work to include the influence nucleation and particle growth on surface area was first attempted through modifications to the area equation, rather than the creation of two separate precipitation reactions. The species were assumed to dissolve by the same mechanism, regardless of whether they precipitated via nucleation or particle growth. Several iterations were trialled.

4.6.1.1 Iteration 1 (New Equation, Constant β)

To improve the magnitude of the model predictions for area change, the assumption was made that area varied based on nucleation only. To account for the influence of two precipitation mechanisms, the precipitating species needed to be split into a portion that were nucleating and a portion that were growing. As there were likely to be many influences, for simplicity, this was initially achieved through a fitting parameter, β . This parameter represented the percentage of precipitates that had nucleated, rather than grown. A larger β corresponded to more nucleation, meaning more blocked pores, therefore a larger area change. It was unclear what a realistic value for β would be, as it could not directly be measured from experiments. Various magnitudes were tested to understand the impact and obtain the correct magnitude of area change, corresponding to pore blocking due to nucleation.

The individual masses of particle growth and nucleated precipitates were calculated as shown in Equations [87] and [88] respectively. The area was then calculated from the proportion of precipitates that nucleated, multiplied by a fitting parameter, γ . This was first estimated, before being updated to a term representing the thickness of the nucleated precipitation layer, as shown in Equation [89]. The parameter for the number of nucleation layers was added to try to resolve potential magnitude issues; if it was assumed one layer was approximately one atom thick, with an atom radius of 10^{-10}m , 100 nucleation layers would be equivalent to 1% of the positive electrode thickness. As shown in Equation [90], a larger number of layers would increase the magnitude of area change due to nucleation.

$$S_{p_{\text{growth}}} = (1 - \beta) S_p \quad [87]$$

$$S_{p_{\text{nuc}}} = \beta S_p \quad [88]$$

$$\gamma = \frac{\pi r^2 A}{M_s} \frac{1}{x_{\text{nuc}}} \quad [89]$$

$$ar = ar_0 - (\gamma S_{p_{\text{nuc}}}) = ar_0 - (\gamma S_p \beta) \quad [90]$$

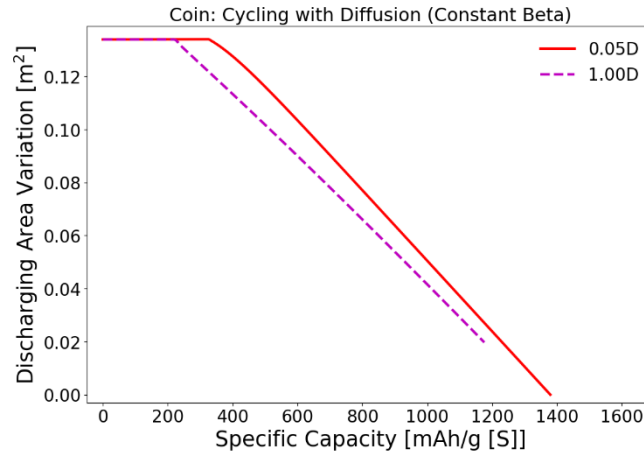


Figure 27: Model predictions for the area variation with constant β parameter

Whilst adjustments to both β and γ captured the required magnitude of area change to match experimental results, as shown in Figure 27, this was insufficient to capture significant C-rate dependence, beyond that obtained from diffusion. There was also no correlated causality to the behaviour with the use of fitting parameters. Further investigation was required to understand how β varied when scaling between cell formats, along with which features impacted the dominating precipitation mechanism. For example, at higher currents, faster reactions mean more nucleated precipitates form, dependent on other conditions, leading to a larger area change. To achieve this, a variable β was trialled.

4.6.1.2 Iteration 2 (Variable β)

By using a variable, the magnitude of β adjusted dependent on cycling conditions. A larger β corresponded to more nucleation, meaning a larger area change, for example at the beginning of the low plateau during discharge. A smaller β would be present towards the end of discharge when particle growth was dominant. For this reason, it was hypothesised a non-linear function would be required within the model. There were several dependencies that could have been implemented to capture this.

Firstly, β could have been dependent on the mass or concentration of S_1 and S_p , although these both vary linearly with time. Secondly, β could have been dependent on the partial current of the low plateau, however this would result in a minimum or maximum value, as no gradual change at the transition between plateaus occurs. Alternatively, a relationship with voltage could have been implemented; Fan et al. [102] found nucleation only occurred below a certain voltage or at a certain overpotential. A change in the cycling conditions or current would change the discharge voltage, varying the point at which nucleation began.

The aim of a variable β was to obtain a faster decrease in area as precipitation begun, to capture the hypothesis that species are more likely to nucleate onto a fresh surface where there are fewer existing nucleation sites. As the nucleated species accumulated, covering the surface, the number of species continuing to nucleate would then decrease, and the number particle growth precipitates would increase, having a smaller impact on the available area.

Starting with the simplest method, the first iteration of a variable β included the mass of precipitated species as the only variable, as shown in Equation [91]. This was selected over a voltage dependence, as voltage would require making the reaction electrochemical, rather than chemical. It is undecided within the literature what type of reactions the precipitation mechanisms should be; electrochemical would imply the precipitation reactions contribute towards achievable capacity. The use of an exponential function ensured the behaviour was non-linear, as shown in Figure 28. This equation for β was then implemented into Equation [90].

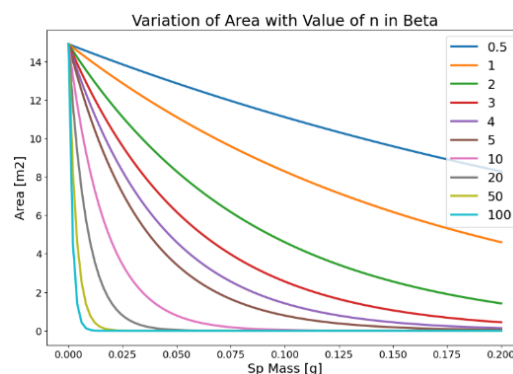


Figure 28: Variation in β with varying values of n in exponential function

$$\beta = e^{-S_p n \left(\frac{\ln(10)}{\text{mas}_{s_{\text{sulfur}}}} \right)} \quad [91]$$

The equation defined β as a scaling factor that varied with precipitated sulfur directly. The equation did not check if the area was fully covered when all the sulfur was in precipitated form, although the inclusion of the total sulfur mass in the denominator prevented the fraction exceeding a value of one. The use of the natural logarithmic term within the numerator ensured the correct magnitude of β was achieved, and the use of the exponential prevented the area falling below zero. The fitting parameter, n , was used to obtain the correct magnitude and trend of area change when cycling, as shown in Figure 28. With small values of n , the magnitude of area change was found to be smaller than when using a fixed β value, resulting in higher achievable capacity based on a larger available area remaining for electrochemical reactions. Whilst n was a fitting parameter, it could be linked to the current, for example, where increasing the value corresponded to faster reactions and therefore more area coverage.

4.6.1.3 Results: Variable β

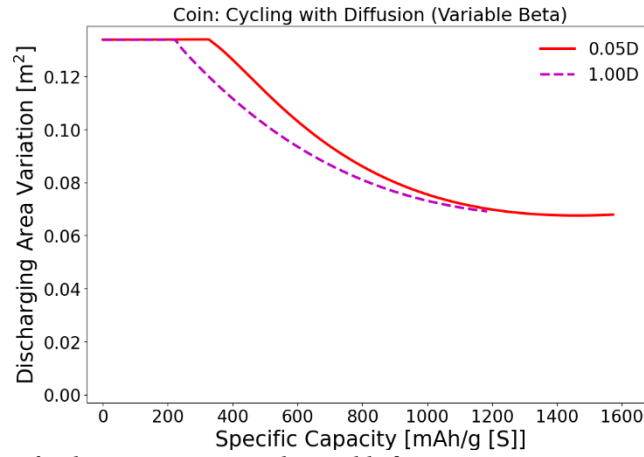


Figure 29: Model predictions for the area variation with variable β

This update to the area equation removed the dependence on the ratio of porosity. The porosity variable now only influenced the conductivity and electrolyte resistance. The area directly accounted for the influence of precipitated species and the proportion of those nucleating, based on the variable β and fitting parameter γ . However, as shown in Figure 29, the model predicted a smaller magnitude of area change using this equation, without significant variations to the fitting parameters.

Whilst the variable β worked to capture the influence of nucleation and particle growth without separate mechanisms, the equation required several assumptions and fitting parameters. It worked as a shortcut to understanding the influence, but it was likely complete separation of the precipitation mechanisms would be required to capture behaviour accurately. This is addressed in Section 4.7.1. In addition, further investigation was required to understand the extent to which the area was covered during cycling, and how easily full coverage could be achieved due to nucleation. In the current state, the model was unable to capture complete area coverage due to numerical errors. Further work may also be required to understand whether porosity needs to be updated based on nucleation and growth precipitation.

4.6.2 Inclusion of Separator (and Additional Diffusion)

With the update to account for the usable electrolyte volume, the model included a region of electrolyte in positive electrode and an excess electrolyte region. Within a real cell, the porous separator also consumes a portion of the electrolyte. With the aim of accurately capturing the usable active material within the cell, an update was required to account for the electrolyte volume within the pores of the separator.

Similarly to the reservoir, the model assumed the species within the separator did not contribute towards electrochemical reactions. Based on the location of the separator next to the negative electrode, only species within the separator would experience polysulfide shuttle, removing this term from the ODEs in the positive electrode. No precipitated species were contained within the separator, therefore no pore blocking of the separator pores occurred. The diffusion between the electrode and separator was assumed instantaneous, justified by the proximity between the regions. It was assumed that there were no transport limitations, other than the rate of diffusion.

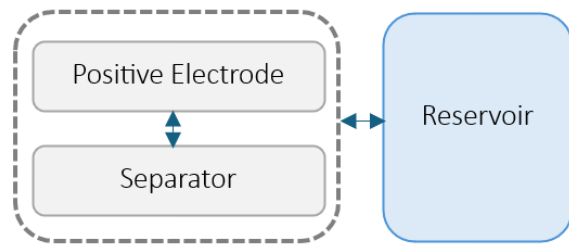


Figure 30: Schematic diagram of the positive electrode, separator and excess electrolyte regions

It was assumed that all species were contained within one of the three regions: the positive electrode, separator, or reservoir of excess electrolyte. To capture diffusion between the three regions, two pathways were assumed: between the reservoir and a lumped region containing the separator and positive electrode, and then between the separator and electrode, as shown in Figure 30. Similarly to the diffusion between the electrode and the reservoir, the equation required balancing with the volumes, based on the assumption that the volume within the electrode and the separator did not match; this is shown in the second term in Equation [92]. This also worked to overcome potential issues surrounding the splitting of species between the electrode and separator, based on what was being gained and lost to the reservoir. The volume averaging weighted the reactions inversely to the concentration, so that the region with a larger volume lost more and gained less until equilibrium was reached. The volume averaged concentration in the lumped region was then compared to the reservoir, as shown by the first term in Equation [92]. This based diffusion on the total concentration in both the electrode and separator, compared to the concentration in the reservoir. The diffusion between the reservoir and lumped electrode-separator region had to be faster than the diffusion between the electrode and separator; as the species will always take the path of least resistance, a slower diffusion would prevent species being regained from the reservoir. This equation was added onto each ODE for charged species: S₈, S₄ and S₁.

$$\frac{dCS_{i_{sep}}}{dt} = \left(\left(DS_i \left(CS_{i_{res}} - (CS_i + CS_{i_{sep}}) \right) \right) \frac{V_r}{v + v_{sep}} \right) + \left(\left(DS_{i_{sep}} \left(CS_{i_{sep}} - CS_i \right) \right) \frac{v_{sep}}{v} \right) \quad [92]$$

Similarly to the usable electrolyte volume, the separator volume used within the equation was based on the total separator volume and the volume of electrolyte available for wetting. If the electrolyte volume available exceeded the separator pore volume, the usable separator volume was equal to the pore volume, as shown in Equation [93]. If the electrolyte volume available was less than the pore volume, the separator volume was equal to the available volume of electrolyte, as shown in Equation [94]. This available volume was assumed to be the reservoir volume, or equivalent to the usable volume subtracted from the total input electrolyte volume. The magnitude of the reservoir volume decreased when accounting for separator wetting, and was recalculated as shown in Equation [95]. Assuming there was sufficient electrolyte to wet the separator, theoretically, this would help to achieve C-rate dependence without the presence of a reservoir.

$$\text{if } V_r > v_{sep_{pore}}: \quad [93]$$

$$v_{sep} = v_{sep_{pore}}$$

$$\text{if } V_r < v_{sep_{pore}}: \quad [94]$$

$$v_{sep} = V_r$$

$$V_{excess} = v_{electrolyte} - (v_{usable} + v_{sep}) \quad [95]$$

Dependent on the rates of reaction, and the precipitation, dissolution and diffusion rates, it was possible not all sulfur within the separator or reservoir of excess electrolyte would be regained into the electrode and contribute to electrochemical reactions. As discussed in Section 4.5.3, this could contribute to a reduction in achievable capacity. Whilst the inclusion of the separator improved the comparison between the components in the model and a real cell, further work was required to investigate how species diffuse both between regions, and within one region. This was likely to require further information relating the material properties, such as the porosity or the tortuosity of reaction pathways. Work towards this, in terms of the diffusion regions, is discussed in Section 4.7.2.

4.7 Iteration 4

4.7.1 Separated Particle Growth and Nucleation Mechanisms

As previously discussed, although the use of β within the area equation improved predictions, it was insufficient to capture the correct magnitude of area change, as observed experimentally, without significant fitting of parameters. Rather than assuming the split of precipitates into nucleation and particle growth using a fitting term, two separate equations were proposed. As previously assumed, the area should only be influenced by nucleation. Nucleation should occur first, followed by particle growth on top of the nucleation sites. For either precipitation mechanism to occur, the concentration of species must exceed the saturation concentration [78]. Based on the existing models, it remains undecided whether precipitation is chemical or electrochemical; the decision influences the driving force of the reaction within the model.

Based on experimental findings for the materials used by Fan et al. [102], an overpotential of 0.1V, equivalent to 2.05V, assuming 2.15V was equilibrium [102], was required for nucleation to begin. This occurred at the voltage dip at the transition from high to low plateau in discharge [102]. Particle growth then occurred at lower overpotentials [6]. At higher C-rates, the overpotential is higher, corresponding to a higher nucleation rate [102], resulting in a higher nuclei density and a continuous morphology of small crystals, increasing the cyclability and stability of the cell [6]. At a lower C-rate, the opposite occurs, with large particle depositions leading to faster capacity fade [6]. Ren et al. [79] was able to capture this phenomenon within a 1D model. For simplicity in this model, the input value for nucleation voltage remained constant, as chemistry and material variations were not included, and the morphology of precipitates was not considered. The same nucleation voltage as found by Fan et al. [102] was used, with voltage becoming the driving force of the nucleation reaction.

4.7.1.1 Nucleation and Particle Growth Rate Equations

To differentiate between nucleation and particle growth precipitation, separate differential equations were derived. By separating the equations this way, the assumption was made that there were 5 species: S_8 , S_4 , S_1 , S_p (nuc) and S_p (growth).

4.7.1.1.1 Derivation of Particle Growth

As shown in Equation [96], the initial derivation of the growth equation was similar to the existing precipitation equation, as shown in Equation [83]. The concentration of all precipitates was replaced with the concentration of particle growth precipitates only. As previously included, this term ensured the rate of reaction fell to zero when no growth precipitates remained.

$$\frac{dCS_{p_{\text{growth}}}}{dt} = \frac{MS}{\rho_s} CS_{p_{\text{growth}}} (ar_0 - ar) k_{p/d} (CS_1^{2-} - CS^*) \quad [96]$$

As discussed in Section 4.4.6, the area was now included in the rate equation. However, as the surface area was not directly influenced by particle growth precipitation, the area term within the equation was instead calculated by the amount of area covered by nucleated precipitates. To achieve this, a relationship between the varying area and the initial area was introduced. If implementing the difference between the two terms as $ar - ar_0$, the rate of change of particle growth precipitation would be negative whenever precipitation via nucleation occurred, as the area would fall below the maximum area, resulting in a negative concentration of growth precipitates. If implementing $ar_0 - ar$, the rate of reaction of particle growth would decrease as nucleates cover the surface. In a real cell, the opposite behaviour is expected.

An updated equation was required to capture how the change in area influenced the particle growth reaction; separate terms were proposed for the area covered by nucleation, and the area created due to particle growth precipitation. The aim of a separate area term was to ensure the rate of particle growth precipitation increased as nucleation rate slowed, due to the surface being covered; this was the opposite

to what the model currently achieved. In addition, particle growth precipitation should be able to occur when there is no change in the positive electrode surface area; the current equation could not capture this.

To account for the area created by the formation of particle growth precipitates, a separate equation was introduced. This term captured the area created on top of the nucleation sites, which did not directly contribute to coverage of the positive electrode surface area. The inclusion of this term within the ODE also worked towards ensuring that particle growth precipitates dissolved first upon charge, before nucleated precipitates.

The particle growth area was calculated by assuming all precipitates on top of the nucleation sites were semi-spheres, based on the investigation by Ren et al. [79] into the deposition. The volume of Li_2S_1 was assumed to match the volume of the semi-sphere, as shown in Equation [97], and the area assumed to match the area of a semi-sphere, as shown in Equation [98].

$$\text{vol}_{\text{semisphere}} = \text{vol}_{\text{Li}_2\text{S}_1} = \frac{2}{3} \pi r^3 \quad [97]$$

$$\text{ar}_{\text{semisphere}} = \text{ar}_{\text{growth}} = 2\pi r^2 \quad [98]$$

The radius was calculated by rearranging the volume equation, as shown in Equation [99].

$$r = \sqrt[3]{\frac{\text{vol}_{\text{Li}_2\text{S}_1}}{\frac{2}{3}\pi}} = \left(\frac{3 \text{ vol}_{\text{Li}_2\text{S}_1}}{2\pi}\right)^{\frac{1}{3}} \quad [99]$$

The radius equation was substituted into the area equation, as shown in Equation [98], to calculate the area of the Li_2S_1 species, as shown in Equation [100].

$$\text{ar}_{\text{growth}} = 2\pi \left(\left(\frac{3 \text{ vol}_{\text{Li}_2\text{S}_1}}{2\pi}\right)^{\frac{1}{3}}\right)^2 = 3 \text{ vol}_{\text{Li}_2\text{S}_1}^{\frac{2}{3}} \quad [100]$$

The volume of Li_2S_1 can also be calculated from the molar volume of Li_2S_1 , the concentration of particle growth precipitates and the usable electrolyte volume, as shown in Equation [101].

$$\text{vol}_{\text{Li}_2\text{S}_1} = \text{CS}_{\text{pgrowth}} v \text{VLi}_2\text{S}_1 \quad [101]$$

This volume was then substituted back into the growth area equation, as shown in Equation [102]. Whilst the assumption was made that particle growth precipitates were semi-spheres, a further update could include the use of multiple mini-spheres, or a varying volume, as likely to occur with varying C-rates [79].

$$\text{ar}_{\text{growth}} = (3 (\text{CS}_{\text{pgrowth}} v \text{VLi}_2\text{S}_1))^{\frac{2}{3}} \quad [102]$$

The growth area was then implemented into the particle growth precipitation equation, as shown in Equation [103]. The rate of change of precipitation due to particle growth was now calculated based on how saturated the system was, with relation to the concentration of S_1 , and two different area terms; $\text{ar}_0 - \text{ar}$ captured the area consumed due to nucleation, and $\text{ar}_{\text{growth}}$ was the area formed due to particle growth on top of the nucleation sites. The inclusion of the growth area term ensured that particle growth began when nucleation slowed and a larger portion of the surface area was covered. The term also worked to increase the rate of reaction as particle growth precipitates began forming.

$$\frac{d\text{CS}_{\text{pgrowth}}}{dt} = \frac{\text{Ms}}{\rho_s} \text{CS}_{\text{pgrowth}} (\text{ar}_{\text{growth}} + (\text{ar}_0 - \text{ar})) k_{\text{p/d}} (\text{CS}_1^{2-} - \text{CS}^*) \quad [103]$$

As particle growth was driven by the saturation concentration, it remained as a chemical equation. As previously discussed, the precipitation and dissolution rates remained as fitting parameters; the units were $\text{m}^{-2}\text{s}^{-1}$. As these cannot directly be measured when testing, there was no limit to the magnitude of these rates, nor the value in comparison to each other. Whilst it was realistic to assume the precipitation and dissolution rates would be similar, these could be varied to capture the required behaviour. For example, a higher dissolution rate would ensure all precipitated species were able to dissolve during charge, allowing the full capacity to be achieved, if no other mechanisms impacted the behaviour. Within a real cell, other properties such as electrolyte viscosity would impact behaviour and the rate of reactions, although these were not included within the model.

4.7.1.1.2 Derivation of Nucleation

The final iteration of the equation is shown in Equation [104]. The derivation is discussed below.

$$\frac{dCS_{p_{nuc}}}{dt} = CS_1 CS_{p_{nuc}} \text{ ar nuc}_{var} e^{-F \frac{V-E_{nuc}}{RT}} \quad [104]$$

4.7.1.1.2.1 Existing Nucleation Equations

To include voltage as a driving force for nucleation, as found by Fan et al. [102], the equation would become electrochemical rather than chemical. Investigation of published work that had included this mechanism was required to understand how a nucleation equation could be derived for a 0D model.

The Classic Nucleation Theory [105] assumed both nucleation and particle growth were chemical reactions. The rate of nucleation was calculated as shown in Equation [105], *where X is a fitting parameter; y is surface energy (J/cm^3), V is molecular volume, k is Boltzmann coefficient, T is temperature and S is the supersaturation ratio, $S = \frac{c-c_s}{c_s}$, or $\frac{c}{c_s}$ for larger equilibrium concentrations.*

The rate of reaction had units $\text{m}^{-3}\text{s}^{-1}$. This equation did not include voltage as a driving force for nucleation.

$$J = J_0 \exp\left(\frac{X \gamma^3 V^2}{3 k^3 T^3 (\ln S)^2}\right) \quad [105]$$

Ren et al. [79] predicted both the nucleation and particle growth equations were electrochemical. The rate of nucleation was calculated as shown in Equation [106], *where $1-\theta$ is the surface coverage, α is the charge transfer coefficient and η is the overpotential.* The rate of reaction had units $\text{mol L}^{-1}\text{s}^{-1}\text{m}^{-2}$. This equation was simpler than the Classic Nucleation Theory, although the model by Ren et al. [79] did not capture charging behaviour, so it was unclear how the equation would work when implemented into the current model. This equation also included the influence of lithium, which the current model did not account for.

$$P = P_0 C_{Li+}^{\frac{4}{3}} C_{S2-}^{\frac{1}{6}} (1 - \theta) \exp\left(\frac{\alpha \eta F}{R T}\right) \quad [106]$$

Danner et al. [81] predicted nucleation was electrochemical and growth was chemical. The rate of nucleation was calculated as shown in Equation [107], *where a is specific surface area, n is number of nucleation sites, k_f is frequency factor, Z is Zeldovich coefficient and ΔG is critical energy of formulation.* This equation was complex, with many fitting parameters, but included both charge and discharge behaviour. However, the equation did not account for area or voltage dependence.

$$\frac{d_{nuc}}{dt} = a n k_f Z \exp\left(\frac{-\Delta G}{k T}\right) \quad [107]$$

Whilst designed for Li-O₂ chemistry, Lau et al. [106] predicted both nucleation and particle growth were electrochemical. The rate of nucleation was calculated as shown in Equation [108], similar to both the Classic Nucleation Theory and Ren et al. [79] equations, with two exponential terms representing the reaction.

$$J = J_0 \exp\left(2 \frac{\alpha' \eta e_0}{k T}\right) \exp\left(\frac{\alpha \eta e_0}{k T}\right) (1 - \theta) \quad [108]$$

One of the key issues that arose when investigating whether these equations would be viable was the dimensionality of the models; as most were 1D, it was unclear how these would be fit to a 0D model. A higher dimensionality model requires a higher number of assumptions and fitting parameters. As 1D models such as those by Danner et al. [81] and Ren et al. [79] captured C-rate dependence, it was unclear whether this was due to the transport mechanisms, or the correct surface coverage due to nucleation. These models also included varying numbers of precipitating species, for example, Danner et al. predicted both S₈ and S₁ precipitated [81].

Instead of implementing one equation directly, variations of the existing equations discussed were tested, with the aim of capturing the required features.

4.7.1.1.2.2 Iteration 1

$$\frac{dCS_{p_{nuc}}}{dt} = A \exp\left(\frac{16 \pi \gamma^3 V^2}{3 k^3 T^3 (\ln S)^2 ar}\right) \quad [109]$$

An expanded version of the Classic Nucleation Theory equation was first implemented and modified, as shown in Equation [109]. The modification involved adding area to the denominator of the exponential, to capture the dependence previously discussed. The equation used the saturation concentration and temperature, if this varied, as driving forces. The temperature was used to calculate the energy, rather than voltage, meaning the equation remained chemical. The pre-exponential term, A, was considered a fitting parameter and was re-calculated to fit the 0D model, as shown in Equation [110]. The rate of nucleation was also a fitting parameter and replaced the dissolution and precipitation rates; separate dependencies were required between growth and nucleation equations, as it was likely different features would impact each precipitation mechanism differently. As a fitting parameter, the nucleation rate was not directly measured or calculated, and could be adjusted as required to capture the observed behaviour.

$$A = ar_{nuc_{var}} CS_{p_{nuc}} \quad [110]$$

The supersaturation was calculated based on the concentration of S₁ and S_p, and the saturation concentration term, as shown in Equation [111].

$$S = \frac{CS_1}{K_{Li_2S}} CS_p \quad [111]$$

When testing this equation, the model was found to be very sensitive to values within the supersaturation term; as the term was logarithmic, small variations could cause significantly large changes, causing the model to experience numerical errors. In addition, with saturation concentration and temperature as the driving forces, without the influence of voltage, this equation did not guarantee nucleation would occur before particle growth.

4.7.1.1.2.3 Iteration 2

$$\frac{dCS_{p_{nuc}}}{dt} = ar_{nuc_{var}} \left(CS_1 e^{-\frac{V-E_{nuc}}{RT}} - CS_{p_{nuc}} e^{\frac{V-E_{nuc}}{RT}} \right) \quad [112]$$

To include the influence of voltage and remove the sensitivity of the saturation term, the next iteration reverted back to the standard precipitation equation, as shown in Equation [83], combined with the Ren et al. [79] equation. It was calculated with the dependence on the available surface area; as nucleated precipitates form, the area reduces, decreasing the rate of nucleation. The nucleation mechanism was driven by voltage, with a threshold value at which nucleation began, making the reaction electrochemical and therefore contributing to capacity.

Although precipitation only occurs when the concentration of S_1 exceeds the saturation concentration, the inclusion of voltage as a driving force removed the requirement for saturation concentration as a second driving force within the equation. Instead, only the S_1 and S_p concentrations were required. The concentration of S_1 was required in both precipitation mechanisms to ensure it was split correctly between the two types of precipitates, conserving the total sulfur mass throughout cycling. Within the nucleation reaction, as more S_1 became available, the rate of reaction became faster. In particle growth, the amount of S_1 was required in relation to the saturation concentration, to determine whether the conditions were satisfied for particle growth to begin.

To include voltage as a driving force, an exponential term was selected and implemented, similar to Ren et al. [79] and Lau et al. [106]. The Arrhenius relationship related the energy to the cell voltage and nucleation voltage. The nucleation voltage subtracted from the cell voltage ensured nucleation only became significant below this expected voltage. The inclusion of S_1 and S_p terms, each with an exponential, followed the methodology of Lau et al. [106] accounting for separate rates. The exponential was negative for S_1 and positive for S_p to account for the losses and gains correctly.

One hypothesised problem with this equation was that when the area reached zero, equivalent to when the surface was fully covered, the rate of change of nucleation would also reach zero. Based on the formulation of the equation, adjustments to fitting parameters were unable to increase this rate. This would prevent nucleated species dissolving upon charge. The problem would be exacerbated at higher sulfur contents, with a higher likelihood of full coverage.

When testing this equation, it was found that only particle growth precipitation occurred, as the magnitude of the exponential powers were the same. As S_1 remained very small and S_p was negligible at the beginning of discharge, no significant changes could occur to enable nucleated precipitates to accumulate, resulting in particle growth dominating cycling. This was further tested and confirmed by setting the precipitation and dissolution rates to zero, ensuring particle growth could not occur.

4.7.1.1.2.4 Iteration 3

Assuming that the exponential equation was correct, one exponential term was then trialled, as shown in Equation [104], instead of separately for S_1 and S_p . It was initially unclear whether the exponential term should be positive or negative, however, numerical errors occurred when it was tested as positive and used alongside the growth equation. As discussed, the inclusion of the concentration of nucleated precipitates was required to ensure the mass did not fall below zero, and the rate of reaction fell to zero when all nucleates had dissolved. The concentration of S_1 was required to ensure conservation of mass between the two separate precipitation reactions. With the inclusion of both S_p and S_1 concentrations, the meaning and units of the nucleation rate changed to ensure balancing; the units became $L \text{ mol}^{-1} \text{ s}^{-1} \text{ m}^{-2}$, and the value corresponded to a rate constant per nucleation site.

4.7.1.2 Results

The results are shown in Figure 33. As the cell reaches low plateau, precipitation via nucleation begins, decreasing the electrode surface area. Dependent on other cycling conditions, when the electrode area becomes low enough, particle growth precipitation begins, causing the growth area to increase. As growth continues, the growth area also increases, causing the rate of change of particle growth to further increase towards the end of discharge.

During discharge, S_1 precipitates based on the rate with the highest driving force; at the beginning of the low plateau, this is predominately nucleation, and towards the end of discharge, this is predominately particle growth. The separate dependencies on voltage for nucleation and saturation concentration for particle growth, along with the area terms, ensure both mechanisms occur. During charge, the assumption is made that both nucleated and growth precipitates dissolve at the same rate, or dependent on the fitting parameters within the equation. In a real cell, it is expected that particle growth precipitates dissolve first as these are located on top of the nucleation sites, followed by nucleated precipitates, which are now no longer trapped. However, without significant fitting of the parameters, this was not always captured; this is discussed in more detail in Chapter 6.

In the model, there was no limit to the number of species that could dissolve. Within a real cell, it is likely that a portion will remain in precipitated form due to incomplete dissolution during cycling. This could be achieved in the model through reducing the dissolution, precipitation or nucleation rates. This would also result in reduced capacity.

4.7.1.3 Summary

The surface area calculation remained the same as shown in Equation [90], now calculated based on nucleated precipitates derived from the separate rate equation, replacing the β variable. Separate equations for nucleation and particle growth were required to improve predictions in comparison to experimental results, capturing the correct magnitude and causality of area change. Nucleation had a larger impact on available area, whilst growth occurred on top of the nucleation sites. The separation of the mechanisms worked towards capturing area C-rate dependence, along with capturing separate dependencies on behaviour, of nucleation on voltage and particle growth on saturation.

From each iteration, there were several criteria that had to be reached. The nucleation and particle growth equations could not be dependent on the same rates of reaction, leading to the introduction of the nucleation rate term. This differentiated between the separate mechanisms and factors impacting each. The nucleation rate needed to be negative during charge, to ensure the nucleated species dissolved. The rate also needed to be sufficiently large to ensure it exceeded the concentration value of nucleated species and enabled the precipitates to dissolve. The inclusion of separate area terms for particle growth and nucleation helped to ensure the precipitates accumulated. The inclusion of the available area term influenced the rate at which species formed on the nucleation sites; if there was a lower available electrode surface area, the rate of nucleation was lower. Variations to the fitting parameters further helped this, although it was unclear how realistic these values were. The S_1 term needed to be included in both mechanisms to dictate how the concentration varied, and the influence on each reaction. It also ensured mass conservation, and that the same amount of S_1 lost was gained as S_p . The inclusion of the concentration of each precipitated species in the corresponding equation acted as a self-limitation, preventing the reactions from continuing when the species became negative.

4.7.2 Reservoir Update (4 Regions)

The model predicted species travel from a lumped region made up of the positive electrode and separator, to the reservoir of excess electrolyte. Potential issues arose when attempting to understand how the species diffused between the positive electrode and separator, after travelling from the reservoir, under varying conditions. For example, if the concentrations in the positive electrode and separator were the same, it was unclear which region the species would diffuse into.

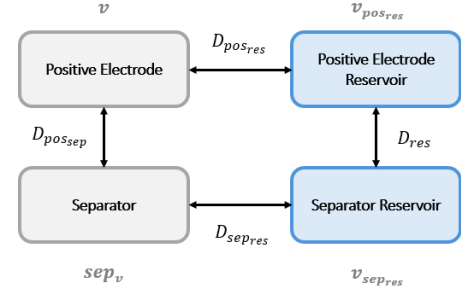


Figure 31: Schematic diagram of the diffusion pathways with four regions within the model

To overcome this, the reservoir was split into two regions: the positive electrode reservoir and the separator reservoir. Species within each region diffused between the two neighbouring regions only. For example, the positive electrode species diffused to the separator and the positive electrode reservoir, as shown in Figure 31. Similarly to previous equations, the diffusion between regions was balanced based on the volume within each region. The total reservoir volume was split equally between the positive electrode reservoir and the separator reservoir. The transport coefficient between the two reservoir regions was set very high, in comparison transport coefficients between other regions, to mimic one large region.

Several iterations were tested to determine how to balance the transport between regions. The first involved a simple ratio of the volume of each region, as implemented for diffusion between the positive electrode and separator. The volume of the reference region, which was the first term in subtraction equation, was the numerator of the ratio, as shown in Equation [113].

$$\frac{dCS_{i_{cathres}}}{dt} = - \left(DS_{i_{res}} \left(CS_{i_{cathres}} - CS_{i_{sepres}} \right) \frac{V_{cathres}}{V_{sepres}} \right) - \left(DS_{i_{cathres}} \left(CS_{i_{cathres}} - CS_i \right) \frac{V_{cathres}}{V} \right) \quad [113]$$

However, this equation did not balance the mass of species; the sum of the ratio when gaining species, added to the ratio when losing species did not always equal to zero, removing the conservation of mass. To resolve this, a summation of the total volume of the two regions was required as the denominator, as shown in Equation [114].

$$\frac{dCS_{i_{cathres}}}{dt} = - \left(DS_{i_{res}} \left(CS_{i_{cathres}} - CS_{i_{sepres}} \right) \frac{V_{sepres}}{V_{sepres} + V_{cathres}} \right) - \left(DS_{i_{cathres}} \left(CS_{i_{cathres}} - CS_i \right) \frac{V}{V + V_{cathres}} \right) \quad [114]$$

Along with a separate transport coefficient for each species, separate coefficients were introduced for each region. This worked towards accounting for differences in properties, for example the porosity of the separator and positive electrode, and therefore differences in transport likely to influence the diffusion mechanism. As previously discussed, higher rates of diffusion resulted in a larger proportion of species available for reactions, removing the likelihood for potential bottlenecks.

With the updated precipitation dynamics, particle growth remained as a chemical reaction, without requiring electron transfer and therefore not contributing to capacity, whilst the nucleation became electrochemical. Electrochemical reactions can only occur in the positive electrode, based on the requirement for the conductive carbon host to accept electrons [6]. As precipitation via nucleation occurred first, the requirement for current meant precipitation of both mechanisms only occurred within the positive electrode region.

4.7.2.1 Results

The initial conditions of species in each region were selected in similar quantities to the initial conditions in the positive electrode. With the inclusion of the 0A pre-cycle and the activation cycles, these were allowed to vary towards equilibrium, or towards more stable conditions before standard cycling.

The addition of two separate reservoirs improved the ease of predicting the movement of species during cycling, based on simple equations that clearly defined the direction and pathway of diffusion. It also created an area for further development of components within the model, such as the separator, to include more detailed mechanisms about how species would behave based on the properties.

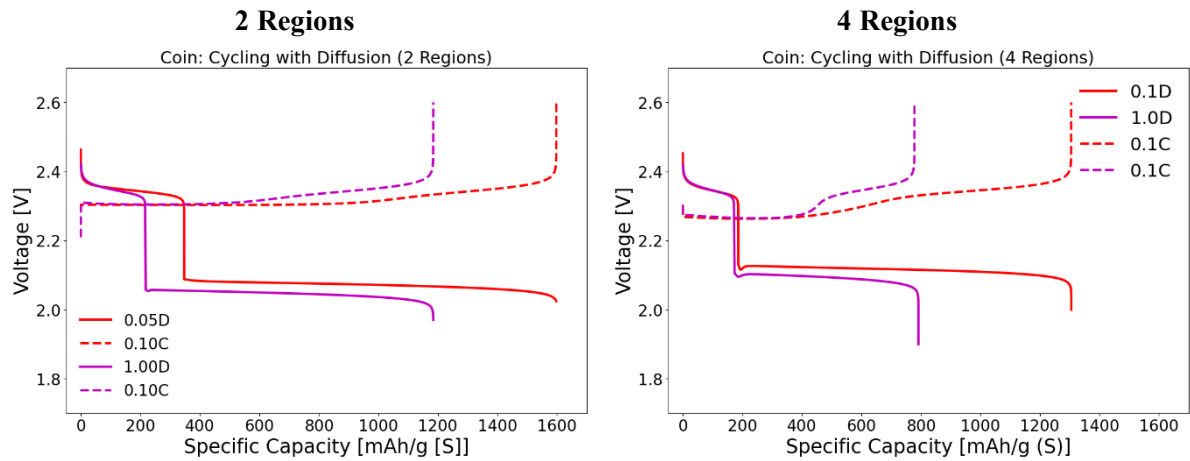


Figure 32: Model voltage-capacity predictions for a cell with two compared to four regions for diffusion

The results with four regions within the cell (positive electrode, separator, positive electrode reservoir and separator reservoir), in comparison to two regions (positive electrode and one excess electrolyte reservoir) are shown in Figure 32. The model with four regions accounts for all the additional changes and upgrades made, including the updated area equation and the separation of the precipitation mechanisms. The associated parameters also vary, including the precipitation and dissolution rates, along with the addition of new parameters, such as the nucleation rate, all of which contribute to the observed changes between two and four regions.

As shown in Figure 32, with only two regions, a larger high plateau C-rate variation is observed in discharge, with a higher capacity of the high plateau at high C-rates. It is hypothesised that with only one diffusion pathway, there are fewer potential bottlenecks preventing species being regained into the positive electrode, resulting in a higher achieved capacity. With four regions, the species are distributed between a higher number of regions, meaning a smaller proportion is available within the positive electrode due to the cell continuously aiming for equilibrium between regions. In the low plateau in discharge, a larger variation with C-rate is observed with four regions; this is hypothesised due to the bottleneck of slow diffusion against fast rates of reaction, resulting in a smaller quantity of species available within the positive electrode for electrochemical reactions. A more distinct transition between plateaus is observed in both charge and discharge with four regions, correlating to the adjustment of fitting parameters.

4.8 Achievement of Research Objectives

This Chapter has investigated the changes required to improve the model capability and predictions in comparison to the 0D model by Cornish et al. [3]. Through various iterations, focusing on different elements of the cell, the model can now capture realistic changes based on experimentally observed phenomenon.

Iteration 1 focused on the model upgrades discussed in Chapter 3, based on results from changing only the input parameters in Cornish et al. [3]. This first required the inclusion of scaling parameters, including the geometric size, E/S ratio and number of layers, allowing the model to directly capture the physical differences. From here, the number of species included in the model was varied to improve alignment with experimental results from Boenke et al. [28], in terms of the ratio between high and low plateau capacity. This was purely a fitting process, and further variation would be required for further

work dependent on the specific experimental data the model is aiming to capture. A pre-cycling step was introduced to improve model stability with relation to the initial conditions. The use of concentrations rather than masses improved the ease of several variable calculations and created a larger dependence on the electrolyte volume. The area was updated to a variable and then introduced into the precipitation dynamics to capture a circular dependency and improve alignment between the causality of model predictions and experimental behaviour; a fixed available area throughout cycling was an unrealistic assumption for a real cell. The impact of resistance, and Ohmic change when varying C-rate was also investigated. Whilst the model was now capable of capturing the physical differences between coin and pouch-cells, several areas of further development were highlighted, based on the causality and results of predictions.

Iteration 2 removed the assumption of complete material utilisation by accounting for the location of the electrolyte within the cell. To do this, the pore volume of the positive electrode was introduced, allowing the electrolyte volume required to wet these pores to be calculated; anything in addition to this volume was considered excess. Only the electrolyte and the sulfur homogeneously distributed within the pores of the positive electrode would contribute towards electrochemical reactions and therefore the achievable capacity. As coin-cells have a larger excess of electrolyte, and therefore a larger unutilised volume, a lower capacity was always achieved in comparison to pouch-cells. To regain some of this capacity, a diffusion mechanism, based purely on the concentration of species within the separate regions, was introduced, enabling C-rate dependence to be captured within a 0D model. In addition, the assumption was removed that the porosity, calculated initially at the time of manufacture, was influenced by the electrolyte volume. Instead, a sole dependency on precipitation was introduced, and the electrolyte influenced the usable pore volume separately. Despite these upgrades, the magnitude of area change was insufficient to capture the expected experimentally observed change.

Iteration 3 attempted to update the area equation to account for the influence of nucleation and particle growth precipitation separately. This was attempted as a simpler step than introducing two separate precipitation mechanisms, which would require additional parameters and variables to solve for. To further improve the causality of model predictions in comparison to experimental results, a separator region was introduced. Whilst both changes improved the model capability, a large number of assumptions and fitting parameters were required, which did not directly link, or could not directly be derived from experimental results, such as β .

Iteration 4 removed the assumption of one precipitation mechanism governed solely by the saturation concentration. Instead, separate differential equations were introduced for particle growth, driven by saturation concentration, and nucleation, driven by voltage. As captured previously, the area was only influenced by precipitation via nucleation, although a separate equation to account for the growth area was introduced. In addition, the diffusion pathways were updated by introducing a second reservoir region, improving the ease of calculating the transport route based on the concentration in each region.

Whilst the aim of the model development was to capture coin-cell behaviour, several of the changes discussed throughout the Chapter also impacted the magnitude and causality of predictions for pouch-cells. A full summary of all the changes and the impact when implemented together is discussed in Chapter 5.

5 Chapter 5: Final Coin-Cell Model

This Chapter summarises the upgrades to the model discussed in the previous Chapter. The final iteration of the model with all the upgrades included is reviewed, showing the difference to the initial version, and testing the capability to predict mechanistic differences between cell formats. The extent to which the model matches hypotheses by Boenke et al. [28] is also included.

The work contained within this Chapter contributes to the work within a paper, currently in the final stages of review before submission.

The nomenclature is included in List of Symbols.

5.1 Research Objectives

This Chapter concludes the work towards understanding the changes required to improve the capability of existing models to predict coin-cell behaviour. It summarises how well the model captures both coin and pouch-cell behaviour with the proposed upgrades to mechanisms and features. These are used to investigate how and why the behaviour differs between cell formats. Alongside highlighting the improvements, further work for the model to reach full capability and be used alongside experimental work is recognised, with consideration of the model complexity.

5.2 Final Model Iteration

The previous Chapter discussed a variety of model changes and upgrades that were implemented to improve predictions. Some were required to capture coin-cell behaviour, for example, accounting for the excess volume of electrolyte, and some were general improvements to the model, including a variable area, an updated porosity equation and separate precipitation mechanisms. The final iteration of each change is summarised below.

5.2.1 Electrochemical Reactions



5.2.2 Butler-Volmer Dynamics

$$i_H = -i_H^0 \ar \left(CS_4^2 e^{\frac{n_H F}{2RT}(V-E_H^0)} \right) - \left(\frac{CS_8}{e^{\frac{n_H F}{2RT}(V-E_H^0)}} \right) \quad [117]$$

$$i_L = -i_L^0 \ar \left(CS_1^4 e^{\frac{n_L F}{2RT}(V-E_L^0)} \right) - \left(\frac{CS_4}{e^{\frac{n_L F}{2RT}(V-E_L^0)}} \right) \quad [118]$$

$$I = i_H + i_L \quad [119]$$

$$V = V_{\text{terminal}} - (I R_{\text{ohm}}) \quad [120]$$

5.2.3 Porosity and Area Equations

$$\varepsilon = \left(1 - \frac{V_{CNT}}{V_{to\text{electrode}}} - \frac{V_{Sp}}{V_{to\text{electrode}}}\right) = \Delta\varepsilon + \varepsilon_0 \quad [121]$$

$$ar = ar_0 - (\gamma S_{p_{nuc}}) \quad [122]$$

Where $\gamma = \frac{\pi r^2 A}{Ms} \frac{1}{x_{nuc}}$ and ar_0 varies dependent on the electrolyte volume.

5.2.4 Ordinary Differential Equations (Positive Electrode)

$$\frac{dCS_8^0}{dt} = -\frac{i_H}{n_H F v} - \left(\left(DS_{8_{cathres}} (CS_8 - CS_{8_{cathres}}) \right) \frac{v_{cathres}}{v + v_{cathres}} \right) - \left(\left(DS_8 (CS_8 - CS_{8_{sep}}) \right) \frac{v_{sep}}{v + v_{sep}} \right) \quad [123]$$

$$\frac{dCS_4^{2-}}{dt} = \frac{2 i_H}{n_H F v} - \frac{i_L}{n_L F v} - \left(\left(DS_{4_{cathres}} (CS_4 - CS_{4_{cathres}}) \right) \frac{v_{cathres}}{v + v_{cathres}} \right) - \left(\left(DS_4 (CS_4 - CS_{4_{sep}}) \right) \frac{v_{sep}}{v + v_{sep}} \right) \quad [124]$$

$$\begin{aligned} \frac{dCS_1^{2-}}{dt} = & \frac{4 i_L}{n_L F v} - \left(CS_1 CS_{p_{nuc}} ar_{nuc_{var}} e^{-F \frac{V-E_{nuc}}{RT}} \right) - \left(\frac{Ms}{\rho_s} (ar_{growth} + (ar_0 - ar)) k_{p/d} (CS_1^{2-} - CS^*) C_{Sp_{growth}} \right) \\ & - \left(\left(DS_{1_{cathres}} (CS_1 - CS_{1_{cathres}}) \right) \frac{v_{cathres}}{v + v_{cathres}} \right) - \left(\left(DS_1 (CS_1 - CS_{1_{sep}}) \right) \frac{v_{sep}}{v + v_{sep}} \right) \end{aligned} \quad [125]$$

$$\frac{dCS_{p_{nuc}}}{dt} = CS_1 CS_{p_{nuc}} ar_{nuc_{var}} e^{-F \frac{V-E_{nuc}}{RT}} \quad [126]$$

$$\frac{dCS_{p_{growth}}}{dt} = \frac{Ms}{\rho_s} (ar_{growth} + (ar_0 - ar)) k_{p/d} (CS_1^{2-} - CS^*) C_{Sp_{growth}} \quad [127]$$

Where $ar_{growth} = (3 (C_{Sp(growth)} v V Li_2S))^{\frac{2}{3}}$

5.2.5 Ordinary Differential Equations (Separator)

$$\begin{aligned} \frac{dCS_{8_{sep}}}{dt} = & -k_s CS_{8_{sep}} + \left(\left(DS_{8_{sep_{res}}} (CS_{8_{sep_{res}}} - CS_{8_{sep}}) \right) \frac{v_{sep_{res}}}{v_{sep_{res}} + v_{sep}} \right) \\ & - \left(\left(DS_8 (CS_{8_{sep}} - CS_8) \right) \frac{v}{v + v_{sep}} \right) \end{aligned} \quad [128]$$

$$\begin{aligned} \frac{dCS_{4_{sep}}}{dt} = & -2 k_s CS_{8_{sep}} + \left(\left(DS_{4_{sep_{res}}} (CS_{4_{sep_{res}}} - CS_{4_{sep}}) \right) \frac{v_{sep_{res}}}{v_{sep_{res}} + v_{sep}} \right) \\ & - \left(\left(DS_4 (CS_{4_{sep}} - CS_4) \right) \frac{v}{v + v_{sep}} \right) \end{aligned} \quad [129]$$

$$\begin{aligned} \frac{dCS_{1_{sep}}}{dt} = & \left(\left(DS_{1_{sep_{res}}} (CS_{1_{sep_{res}}} - CS_{1_{sep}}) \right) \frac{v_{sep_{res}}}{v_{sep_{res}} + v_{sep}} \right) \\ & - \left(\left(DS_1 (CS_{1_{sep}} - CS_1) \right) \frac{v}{v + v_{sep}} \right) \end{aligned} \quad [130]$$

5.2.6 Ordinary Differential Equations (Electrode Reservoir, Separator Reservoir)

$$\frac{dCS_{i_{cath_{res}}}}{dt} = - \left(\left(DS_{i_{res}} (CS_{i_{cath_{res}}} - CS_{i_{sep_{res}}}) \right) \frac{v_{sep_{res}}}{v_{cath_{res}} + v_{sep_{res}}} \right) \quad [131]$$

$$\frac{dCS_{i_{sep_{res}}}}{dt} = \left(\left(DS_{i_{res}} (CS_{i_{cath_{res}}} - CS_{i_{sep_{res}}}) \right) \frac{v_{cath_{res}}}{v_{cath_{res}} + v_{sep_{res}}} \right) - \left(\left(DS_{i_{sep_{res}}} (CS_{i_{sep_{res}}} - CS_{i_{sep}}) \right) \frac{v_{sep}}{v + v_{sep}} \right) \quad [132]$$

5.3 Overview of Model Changes

As previously discussed, without rigorous testing, it was unclear the capability of existing pouch-cell models to predict coin-cell behaviour. Whilst this could be hypothesised based on the equations included, the lack of available open source models further contributed to the difficulty, as the capability could not be directly tested. Therefore, the initial aim was to investigate the predictive power of the pouch-cell model by Cornish et al. [3]. In the work investigating this model, several missing areas were highlighted, and through iterations of testing, changes were proposed to improve the model capability.

- The inclusion of the fundamental scaling parameters; existing models either did not include these or could not be tested as they were unavailable open source.
- The assumption that all active material was fully utilised was removed through the introduction of a pore volume parameter to account for the associated material within separate regions of the cell.
 - Further work investigating the behaviour associated with these regions led to the introduction of a diffusion mechanism, enabling the model to capture C-rate variations.
- The porosity equation was updated to solely be influenced by precipitation; the electrolyte volume and wetting influenced the available pore volume separately.
- Separate precipitation mechanisms were introduced, nucleation and particle growth, as observed experimentally [102].
- The area equation was updated based directly on precipitation, rather than a ratio of porosity change.

Along with capturing the behavioural differences between cell formats, as observed by Boenke et al. [28], the model was updated to ensure it met the success criteria and captured all features discussed in Table 10. The final results with all the model upgrades, for both coin and pouch-cells, are shown in Figure 33.

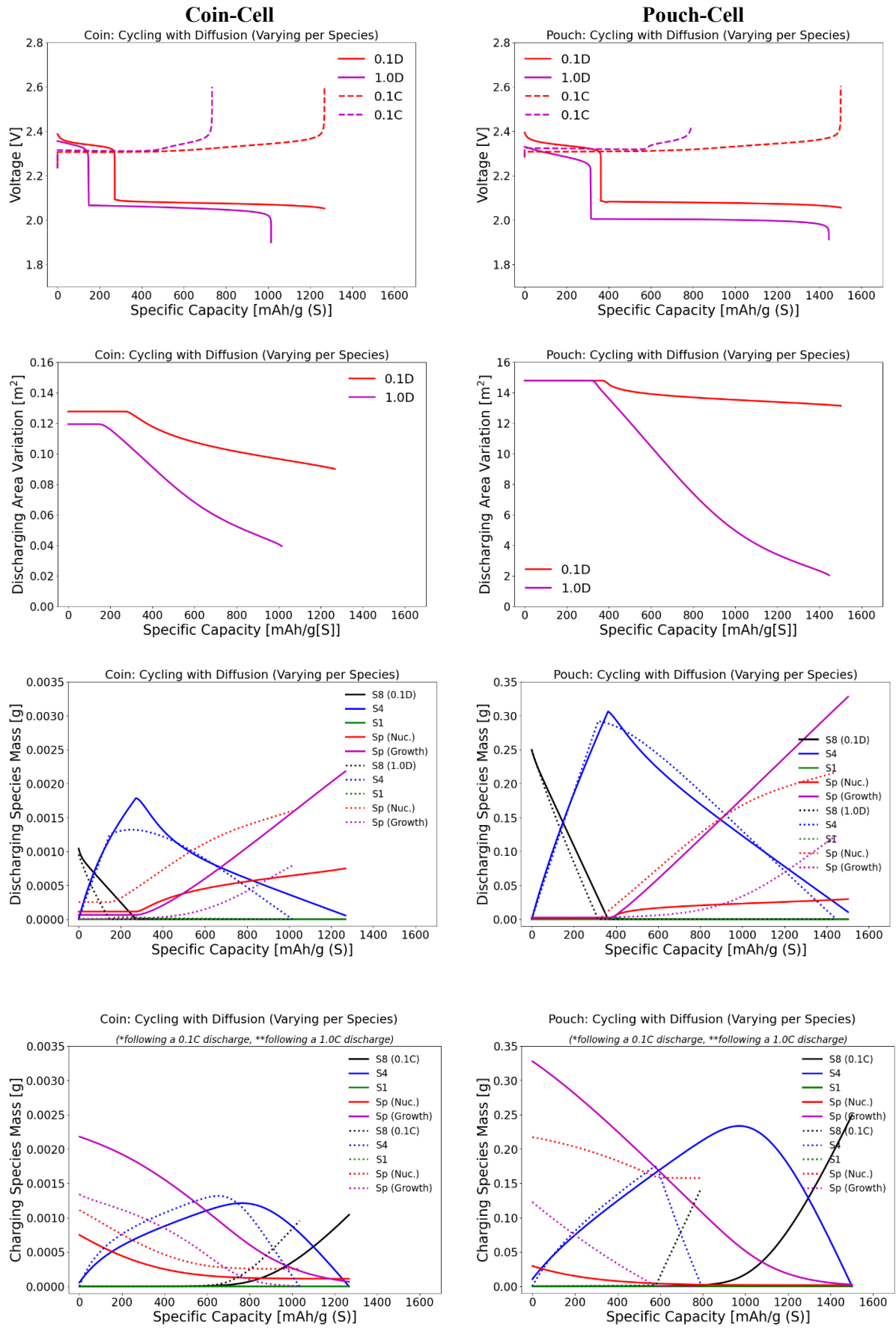


Figure 33: Final model predictions for a coin-cell compared to a pouch-cell, including voltage-capacity, area and variation in species distribution

5.3.1 Scaling between Cell Formats

As the aim of coin and pouch-cell testing is very different, the purpose of existing pouch-cell models varies to the requirements for coin-cell models. A coin-cell model should focus on material development and differences in parameters relating to specific components, whilst a pouch-cell model is more likely to test real-life conditions, including long-term or high C-rate cycling, and the associated mechanisms that occur. It may also aim to account for external influences such as temperature or pressure, based on the structure of the cell, or use within a battery pack.

For the existing pouch-cell models that were not available open source, most did not discuss scaling variations, therefore it was unknown whether the models included the capability to test coin-cell behaviour. For the models that were available open source, including Marinescu et al. [78], Marinescu et al. [17], Hua et al. [86] and Cornish et al. [3], as provided on GitHub [107], most lacked the inputs parameters that changed when scaling between cell format, such as electrode geometry or pore volume. To capture the changes associated with scaling, new parameters and variables were required. These included an E/S ratio to ensure the electrolyte volume and sulfur mass were correctly calculated and varied dependent on one another. The electrode dimensions were introduced, including the geometric area and thickness, along with accounting for single or double-sided electrode coating. These impacted the pore volume, which was also introduced as a separate parameter. The current was recalculated based on the current density, as provided in experimental work by Boenke et al. [28], based on the previously implemented electrode dimensions.

Based on the physical differences, many changes were hypothesised. For example, a larger geometric area increases the likelihood for inhomogeneities across a pouch-cell, in comparison to a coin-cell. This capability was not included in the model due to the requirement for spatial variations. Separately, coin-cells have a larger E/S ratio to ensure electrolyte is not the limiting factor when testing other materials; a lower volume in pouch-cells ensures the high energy density required for commercial applications [6]. The lower volume or E/S ratio in pouch-cells, along with the increased surface area, contributes to reduced wetting of the electrode or separator, likely to influence the utilisation of materials. A lower volume also increases the concentration within the electrolyte, influencing the transport mechanisms and increasing the impact of side reactions and potential electrolyte dry-out [6]. In the model, the wetting of components was captured through the newly introduced pore volume parameter, and the influence on transport was assumed through the diffusion mechanism based on the concentration gradients between regions. The electrolyte volume influenced the rate of reactions, along with resistance, but the model did not account for the influence on other features, such as electrolyte viscosity. Degradation mechanisms are discussed as part of further work in Chapter 6.

5.3.2 Positive Electrode Wetting and Porosity

The influence of the electrolyte wetting the positive electrode, or any other component, and the corresponding impact this has on cell behaviour is rarely discussed in existing models or publications. In a real cell, incomplete wetting can lead to poor sulfur utilisation or inaccessible regions, contributing to irreversible capacity loss [6]. This can occur alongside side reactions and degradation of the electrolyte [10], further contributing to poor performance. As previously discussed, many scaling parameters would influence the wetting, including geometric area, porosity, including the pore size and distribution, the number of layers and the E/S ratio. Without discussion in the publications, it was hypothesised existing models assumed full component wetting and accessibility.

Initial testing after re-parametrising the model by Cornish et al. [3] with Boenke et al. [28] experimental data, including the scaling parameters, confirmed maximum wetting and utilisation of material caused the model to tend towards the maximum capacity of 1,675mAh/g [S]. Therefore, the first change to the model was to remove the assumption of total material utilisation, including the electrolyte volume and sulfur mass. This was achieved through updating existing parameters, including the porosity, and introducing a pore volume parameter. The pore volume parameter represented the volume available in

the positive electrode for reactions to take place. The availability of this pore volume was dependent on electrolyte volume; only when the electrolyte completely filled all the pores was the total pore volume usable. Any volume remaining formed the reservoir of excess electrolyte. The ratio of electrolyte volumes, within the electrode pores or in excess, was used to update the calculation for the available surface area at the beginning of cycling.

This update then led to the removal of the dependence of porosity on the electrolyte volume. The porosity of the positive electrode was assumed to be measured before assembly into the cell, and therefore before electrolyte was added. The use of the porosity equation derived by Kumaresan et al. [77] and implemented in Zhang et al. [1] included a dependence on electrolyte volume through the concentration terms, for all species included precipitated sulfur. Only pore blocking, caused by precipitation, should influence the porosity. The porosity equation was therefore rederived to remove the electrolyte dependence and account for the mass of precipitated sulfur directly. This was separate to the available pore volume dependency on electrolyte volume. This update worked to improve the causality of model predictions against experimental results, with differentiation between the influence of electrolyte volume on pore volume, accounting for electrolyte wetting, and precipitation on porosity. Whilst the updated porosity equation did not account for the pore size or distribution, it accounted for the volume of the pores and the volume of the sulfur precipitating. With further work, detailed geometry could be implemented into the model to better account for how precipitates interact with the available pores.

5.3.2.1 Experimental Results

As previously shown in Figure 11, Boenke et al. [28] observed higher capacity in coin-cells, alongside higher rate capability in both discharge and charge. The influence of wetting cannot be directly measured or extrapolated from these experimental results. However, as it is known coin-cells have a significantly larger excess of electrolyte, it was assumed that the electrode was fully wetted. This worked as one hypothesis for the improved performance in coin-cells, aligning with a separate experimental hypothesis by Pan et al. [108] that the insulating nature of precipitates contributes to lower performance in lean electrolyte systems. It is also likely degradation mechanisms, such as depletion [10], have a larger impact on pouch-cells, further contributing to the reduced capacity observed. This hypothesis cannot be confirmed separately to the C-rate variations observed in the experimental data [28], as only coin-cells were tested at constant C-rate.

5.3.2.2 Model Results

The model predicts that if the electrolyte volume matches or exceeds the electrode pore volume, all pores are fully wetted and available for reactions. This is equivalent to the maximum available surface area. However, the excess electrolyte volume, along with the sulfur species dissolved inside, are assumed to be unavailable for electrochemical reactions, therefore reducing the maximum achievable capacity of the cell. The model predictions when the electrolyte volume exceeds, matches or falls below the pore volume are shown in Figure 23.

These updates allow the model to better capture sulfur utilisation based on the availability of active material and area, which links to the achievable capacity. The results from this change show that electrolyte wetting is one hypothesis to explain sulfur utilisation. It also confirms one explanation for the differences observed between coin and pouch-cells. Within a real cell, however, it is likely several other factors will impact the behaviour and utilisation, for example, transport mechanisms or electrolyte properties. These are currently not included in the model, but the implementation for further investigation is discussed in Chapter 6.

Whilst the updates captured electrolyte wetting, along with an improved porosity calculation and the addition of the pore volume parameter, they were unable to capture C-rate dependence. The differentiation between the usable electrolyte in the electrode and the reservoir of excess electrolyte

resulted in a permanent loss of capacity. This led to the addition of a diffusion mechanism, as discussed in Section 5.3.5. This mechanism enabled differentiation between species permanently lost due to insufficient wetting, and species temporarily inaccessible due to the location outside of the electrode pores.

5.3.3 Area Change

The area was updated in several stages. Firstly, it was converted from a constant parameter to a variable, calculated as derived by Kumaresan et al. [77]. The aim was to capture changes throughout cycling due to precipitation leading to pore blocking [6]. This led to the inclusion of the area term within the precipitation dynamics; as species precipitate, covering the surface area, the rate at which further precipitation occurs should change, based on the accessibility of available area to precipitate upon [102]. This addition created a circular dependency between the variables and aimed to improve surface coverage predictions.

With adjustments to the fitting parameters, this change improved the predicted behaviour with relation to the precipitation and dissolution of species during cycling, aligning with experimental work. However, without significant adjustments to these fitting parameters, the magnitude of area change remained significantly smaller than expected experimentally. Separately, experimental work had found separate precipitation mechanisms occurred within a Li-S cell [102], which impacted area differently during cycling; the model was unable to capture this. Another requirement for area change was C-rate dependence; with area included in the precipitation dynamics, the area influenced the rate of reaction, which also varied with current, which should then influence precipitation and further area coverage, creating a circular dependency. However, the magnitude of this influence was insufficient within the model. As discussed, variations to the fitting parameters could improve this, but would not capture the correct causality. Separately, it was hypothesised the area equation should be calculated based on the precipitation directly, rather than through the porosity ratio, despite the newly updated formulation of porosity.

Various stages of development took place to understand how area predictions could be improved to account for the influence of particle growth and nucleation separately. The final iteration predicted only nucleation influenced the positive electrode surface area through the formation of nucleation sites. Particle growth that occurred on top of the nucleation sites did not cover the surface area but was captured by the addition of a separate growth area term. The update to the electrode surface area equation removed the dependency on the porosity and created a direct dependence on precipitation, as the porosity value itself does not always provide sufficient information. For example, a material with a small number of large diameter pores, or a material with many small diameter pores could have the similar porosity values but very different surface areas; this would significantly impact the behaviour of the cell, but the previous area equation by Kumaresan et al. [77] would be unable to capture this.

The final iteration of the area equation capturing separate precipitation mechanisms improved the causality and magnitude of area predictions. The model predicted that a smaller area change, or higher available area resulted in a larger achieved capacity, during both charge and discharge, as more reactions were able to occur. Whilst various other factors contribute to the utilisation of sulfur, such as electrolyte volume, chemistry and C-rate, these results confirm that area was one feature positively influencing the electrochemical reactions and sulfur utilisation.

5.3.4 Updated Precipitation Dynamics

The initial iteration of the model assumed that precipitation occurred consistently and only via particle growth. Despite changes to incorporate the influence of area into the rate equation, precipitation alone could not capture the expected change in behaviour, especially with varying current. Whilst fitting parameters could be adjusted, for example to capture the observed dissolution bottleneck during initial charge or voltage kink in discharge, there was no associated causality. As previously discussed, experimental work had found two precipitation mechanisms occurred: nucleation and particle growth [102]. The nucleation mechanism is the formation of new nucleation sites and has the largest impact on available surface area during cycling [102]. The particle growth mechanism causes precipitation on top of existing nucleation sites, with minimal impact on available surface area [102]. The impact of these mechanisms was tested within the model.

There were several requirements for nucleation and particle growth. Nucleation occurs at higher overpotentials or lower voltages, below the nucleation voltage, as found by Fan et al. [102]. As overpotential was not included in the model, this was achieved through the inclusion of voltage within the exponential term, $V - E_{\text{nuc}}$; the rate of nucleation was negligible until the cell voltage fell below this nucleation voltage. Separately, nucleation must occur first, with particle growth on top [77], [102]. This was achieved with the inclusion of area in the equations; at the beginning of discharge, the growth area was equal to zero, making the rate of change of particle growth also equal to zero, ensuring nucleation occurred first. Both nucleation and particle growth only occurred when the system was oversaturated. Finally, the precipitation rate increases with C-rate, as found for nucleated species by Ren et al. [79]. As the cell cycles at higher currents, the discharge voltage is lower, based on Ohmic change, increasing the exponential term and increasing the rate of nucleation [102]. A higher rate was found to lead to more uniform and smaller precipitates [79], although the model was unable to capture this.

The precipitation, dissolution and nucleation rates were included as separate rates to be varied individually. As these were considered fitting parameters, not taken directly from experiments, they were varied as needed to match experimental results. Similarly to when assuming one precipitation mechanism occurred, if the rates were varied to allow precipitated species to remain at the end of charge, a temporary reduction in capacity was observed due to the reduction in available area and active material. Without the inclusion of degradation mechanisms within the model, this worked to test the impact of reducing the accessible material on cell performance. Further work is required to capture the correct order of nucleation and growth in charge; currently, the dissolution rate is varied to ensure dissolution of growth occurs first. Methods to overcome this error, without significant fitting of parameters, are discussed in Chapter 6.

5.3.5 Diffusion

C-rate dependence is captured in higher order models through transport mechanisms [6]. Low order models do not include these mechanisms, so are typically unable to capture this dependence. As previously discussed, variations to the precipitation dynamics, based on the rate at which reactions occur, can capture capacity changes based on a different causality, as also observed by Marinescu et al. [17].

By removing the assumption of total material utilisation and accounting for the usable portion of electrolyte within the cell, there became a volume of excess electrolyte that did not contribute to electrochemical reactions. This resulted in a reduction in achievable capacity through a loss of active material. To better capture what happens to the species dissolved in the excess electrolyte, a diffusion mechanism was introduced. This mechanism allowed species to be regained from the excess electrolyte into the positive electrode, based on the concentration gradients between regions, working to increase the achievable capacity. To accurately account for how species move around in a real cell, the separator region also needed to be considered; similarly to the positive electrode, this was porous, meaning

electrolyte and dissolved species could also be contained within. To improve the ease of calculating diffusion between the reservoir of excess electrolyte, the electrode and the separator, the excess electrolyte was split into two regions, with diffusion only occurring between the two neighbouring regions. Both reservoir regions behaved similarly, with very high diffusion between to mimic one large region. Only species in the separator region experienced polysulfide shuttle.

The inclusion of diffusion increased the dimensionality from 0D to a pseudo-spatial 0D model. The species were assumed to be located at one point within one of the four regions, and the concentration gradients were calculated with respect to time. The model did not account for other influences on transport, such as electrolyte viscosity or electrode tortuosity [6]. Separate diffusion rates for each species and between each region allowed the model to be manipulated to capture separate influences. It also allowed the model to capture the variations to mobility and solubility of different species [6].

5.3.5.1 Results

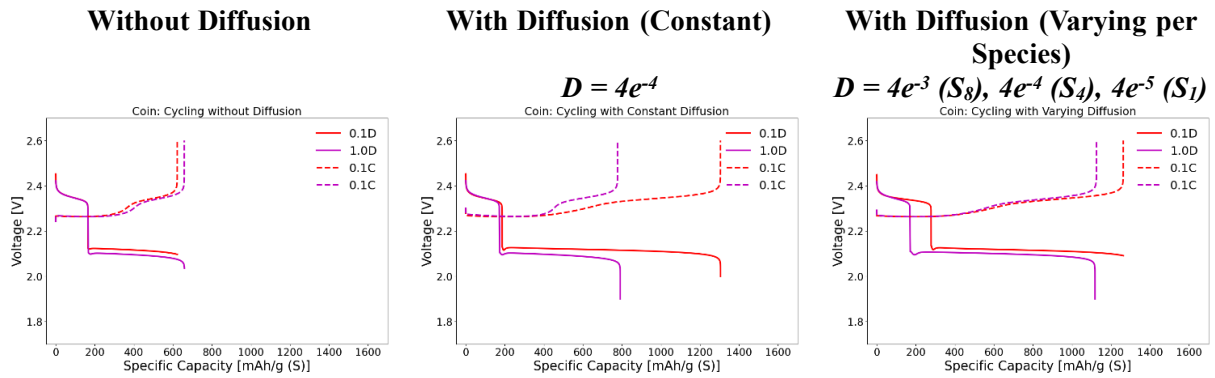


Figure 34: Model voltage-capacity predictions when varying the transport coefficient

As shown in Figure 34, a low capacity was achieved with no diffusion occurring; the sulfur contained within regions other than the positive electrode could not be utilised for electrochemical reactions. In addition, the model predicted a higher capacity at higher C-rates with no diffusion; whilst experimentally the opposite has been found, the precipitation dynamics and selected rates within the model caused this increase. At higher discharge C-rates, the rates of electrochemical reactions are faster, but the rate of precipitation and dissolution remains the same; as nucleation is also electrochemical, more nucleated precipitates form, resulting in a higher achieved capacity and a larger area coverage. The increase in charge capacity is due to the history effect from the previous discharge. Adjustments to the fitting parameters could enable the model to capture irreversible C-rate dependence due to species remaining in precipitated form during charge.

As shown in Figure 34, the inclusion of diffusion increased the achievable capacity at all C-rates, and enabled the model to capture reversible capacity C-rate dependence, at both high and low plateaus, through the loss and gain of species between all four regions. High diffusion rates, achieved through high transport coefficients, correspond to a higher achieved capacity; species are regained from other regions into the positive electrode faster, ensuring more are available for reactions, increasing the sulfur utilisation. The diffusion rate in relation to the rate of electrochemical or chemical reactions is also an important consideration; a decrease in capacity is observed when the rates are competing. This works to mimic transport limitations within a real cell.

With the same transport coefficient for all species, a small high plateau capacity variation and a large low plateau capacity variation was observed in discharge with varying C-rate. When varying the transport coefficient per species, a larger high plateau capacity variation and smaller low plateau capacity variation was observed in discharge, as shown in Figure 34. It was hypothesised that the high plateau capacity at 0.1D was higher for varying coefficients compared to constant, due to a faster rate of S_8 being regained into the positive electrode from other regions, meaning more active species

available for electrochemical reactions. This outweighed the influence of reduced coefficients for shorter chain length species, in comparison to the constant coefficient testing, resulting in higher low plateau capacity being observed.

The C-rate dependence achieved in the model was similar to the results achieved by Cornish et al. [103] with dynamic diffusion between the separator and electrode regions only. Four regions were implemented into this model, including the reservoir, to improve similarity to a real cell. Whilst the dynamic diffusion implemented by Cornish et al. [103] was not required to capture the desired coin-cell behaviour, further work could investigate the impact, improving alignment to experimental results where the diffusion varies based on the concentration.

5.4 Model Capability to Capture Boenke et al. [28] Hypotheses

Throughout the experimental study, Boenke et al. [28] made numerous hypotheses and conclusions. Following on from the summary of model changes, the extent to which the model captures, tests or aligns with these is discussed in this Section.

5.4.1 Electrolyte Volume

Boenke et al. [28] found that the performance of the cell was dependent on the volume of electrolyte and the dissolution of species within, both of which influenced the resistance and viscosity. A lower volume correlated with a higher resistance and viscosity, and a reduction of material utilisation [28].

Whilst the model did not account for electrolyte viscosity directly, the updates to account for pore volume and electrolyte wetting, resulting in a reservoir of excess electrolyte, enabled it to capture material utilisation. A larger volume resulted in fewer active species being contained within the electrode, meaning a lower achieved capacity or a larger dependence on diffusion; slow diffusion led to bottlenecks when attempting to regain species into the electrode. If the pores were fully wetted, a lower volume resulted in a higher achievable capacity as a larger portion of species were within the electrode. If the electrode was insufficiently wetted, there was an irreversible loss of capacity due to unutilised material. The volume of electrolyte also influenced the concentration of species, influencing the rate at which reactions took place.

This hypothesis, with relation to the electrolyte resistance, was qualitatively captured by the model.

5.4.2 Rate Dependence and Associated Impact (Shuttle, Resistance)

Within the model, the current was calculated from the current densities given by Boenke et al. [28], based on the geometry of the positive electrode. This was then scaled when calculating the current through a pouch-cell, as the current density values given were for a coin-cell, as shown in Equations [41] and [42].

5.4.2.1 Capacity Change

Boenke et al. [28] found a larger capacity change, or loss, at higher C-rates, for both coin and pouch-cells. This reduction could be regained upon reducing the discharge C-rate. The influence of irreversible capacity loss, as seen when cycling the coin-cells under constant C-rate, was not investigated or discussed in detail [28].

The model was able to achieve C-rate dependence through diffusion and updated precipitation dynamics. Based on the concentration gradients between regions and the corresponding transport coefficients, species could be regained into the electrode from other regions. At higher C-rates, the rates of reaction were faster, meaning fewer species were regained from other regions if the transport coefficient remained unchanged, resulting in a larger C-rate dependence. Separately, dependent on the rate of precipitation, dissolution or nucleation, the precipitation dynamics could result a temporary reduction in active material if species remained in precipitated form. This loss was more significant at higher C-rates, but was regained at lower C-rate, further capturing the C-rate dependence.

Specifically, whilst Boenke et al. [28] observed a higher capacity in coin-cells, as shown in Figure 11, the model predicted pouch-cells achieved a higher capacity. As discussed, the diffusion mechanism is based on the regions of electrolyte; pouch-cells have a smaller excess volume, meaning a larger proportion is contained within the electrode to contribute to electrochemical reactions. This also reduces the rate dependence in pouch-cells. For further work to capture all experimental changes between coin and pouch-cells, additional mechanisms are required, relating to transport or degradation.

This hypothesis was qualitatively captured by the model, although it is predicted the addition of further mechanisms would improve model predictions.

5.4.2.2 Polysulfide Shuttle

When cycling at lower currents, the rates of reaction are slower, allowing more time for all reactions to occur, including degradation mechanisms such as polysulfide shuttle. The parasitic shuttling current works against the electrochemical charging current, preventing species reaching the full charge state and resulting in infinite charging [6]. This occurs until one of the cycling cut-offs are reached, typically capacity or time. Due to the competing reactions, a flat upper voltage plateau appears, without spiking, corresponding to a high apparent capacity; this differs to the actual achieved capacity due to electrochemical reactions [6]. The current rate selected for experimental testing is typically a compromise between a relatively high and efficient rate of reaction, with minimal degradation.

Within the model, a higher shuttle rate means a larger proportion of long chain length species reducing to shorter chain length species, opposing those oxidising to a longer chain length during charge. Whilst the shuttle rate itself is a constant parameter within the model, the rate of shuttle increases with the concentration of long chain length species. The mechanism works to influence Coulombic efficiency only, with no direct losses due to shuttled material.

Boenke et al. [28] found shuttle occurred in coin-cells, observed through a reduction in the Coulombic efficiency to 60% after 80 cycles. Typically, coin-cells are cycled at a lower current than pouch-cells, based on the current density, aligning with the hypothesis that shuttle increases with decreasing C-rate. This was tested in the model, as shown in Figure 35, where shuttle occurred during charge when the previous discharge C-rate was lower, but was less prominent when the previous discharge C-rate was higher, linked to the history effect and distribution of species.

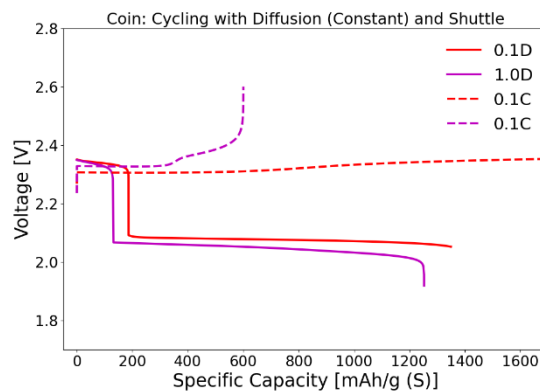


Figure 35: Model voltage-capacity prediction with shuttle ($k_s = 1e^{-3}$)

This hypothesis was qualitatively captured by the model.

5.4.3 Sulfur Content (Loading and Sulfur Wt%)

5.4.3.1 Experimental Variations

At pouch-cell level, the sulfur loading and sulfur wt% within the electrode were varied. Although the published experimental results cannot be compared to the coin-cell model results, to investigate the impact, the qualitative trends were assumed the same for both cell formats. To vary the sulfur loading, the sulfur mass incorporated in the positive electrode was varied, whilst the thickness of the electrode remained constant. Experimentally, this was done by combining CNT BP sheets and sulfur sheets, where the sulfur loading on the sulfur sheets was varied and the CNT BP loading was constant [97]. To vary sulfur wt%, the thickness of the positive electrode was varied, whilst the sulfur mass within the electrode remained constant. Experimentally, this was done by combining varying loadings of both the sulfur sheets and CNT BP sheets [97]. Boenke et al. [28] varied both together, to obtain sulfur loadings of 2.0, 1.5 and 1.0mg/cm², and sulfur wt% of 50% and 33%.

Within the model, whilst the inclusion of the geometric area and the thickness of the electrode were required to calculate the electrode wetting, they also became essential to calculate the sulfur content variation. The model formulation for sulfur content is shown in Equations [133] and [134]; sulfur wt% involved varying the electrode mass through varying the thickness, whilst the sulfur mass remained constant, and sulfur loading involved varying the sulfur mass whilst the geometric area remained constant.

$$\text{Sulfur Wt\%} = \frac{\text{mass}_{\text{sulfur}}}{\text{mass}_{\text{electrode}}} \quad [133]$$

$$\text{Sulfur Loading} = \frac{\text{mass}_{\text{sulfur}}}{\text{ar}_{\text{geom}}} \quad [134]$$

With the formulation in the model, varying the thickness of the electrode influenced how much electrolyte was required to fully wet the electrode. If the E/S ratio was maintained, and the sulfur mass remained unchanged, a thicker positive electrode related to an increased pore volume, leading to reduced wetting of the electrode, or a smaller reservoir of excess electrolyte. The proportion of species in the electrode, rather than in the other regions, further influenced behaviour; if the usable sulfur increased, but there was insufficient electrolyte to fill the pores, a lower capacity could be achieved due to a reduction in area. A smaller reservoir corresponded to a reduced C-rate dependence in the model.

5.4.3.2 Experimental Results

Boenke et al. [28] found that a lower sulfur mass corresponded with a larger active area available for reactions, as less precipitation and pore blocking occurred, increasing the achieved capacity. It was also hypothesised to be linked to the ratio with carbon; if the quantity of insulating sulfur in relation to conductive carbon was too high, a lower capacity was achieved [28]. Lowering the sulfur loading increased the capacity due to reduced internal resistance, relating to the mass and charge-transfer resistance [28]. It was found that the sulfur utilisation increased with decreasing sulfur mass [28], along with a reduced likelihood of lithium degradation in the negative electrode due to lower areal loading [1]. Boenke et al. [28] also found a lower sulfur content resulted in a higher rate capability.

5.4.3.3 Modelling Results

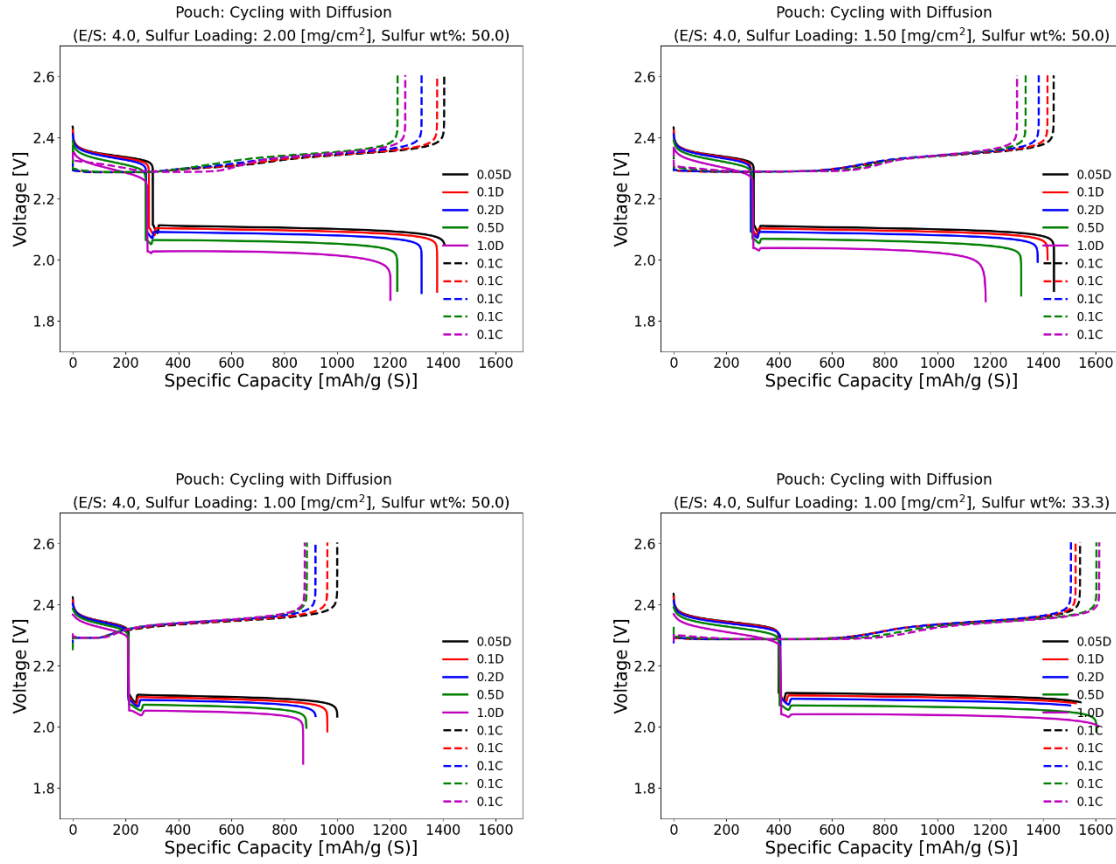


Figure 36: Model voltage-capacity predictions for varying sulfur content (loading and wt%) to match Boenke et al. [28]

Within the model, increasing the sulfur content increases the number of reactions that can take place, along with contributing to a higher internal resistance [28], which influences the cell voltage based on the Ohmic change. Aligning with experimental hypotheses, a higher sulfur content also corresponds to a larger electrode area coverage due to more species precipitating [28]. In theory, this would align with lower achieved capacity at higher sulfur content, however, the model did not directly capture this. As shown in Figure 36, the higher sulfur loadings of $2.0\text{mg}/\text{cm}^2$ and $1.5\text{mg}/\text{cm}^2$ achieved a similar capacity, approximately $1400\text{mAh}/\text{g}$ [S] at 0.05C . The high plateau C-rate variation was larger for $2.0\text{mg}/\text{cm}^2$; along with more S_8 species present at the beginning of discharge, a higher mass results in a higher electrolyte volume, based on a constant E/S ratio, therefore more species contained within the other regions of the cell, creating a larger influence of diffusion bottlenecks. Other than this, the trend in behaviour remained similar between both sulfur loadings, based on the majority of the sulfur being contained within the positive electrode region, excess regions being present in both, and the same transport coefficients, resulting in the high achievable capacity.

For $1.0\text{mg}/\text{cm}^2$ at $50\text{wt}\%$, the excess region was reduced but still present, but the impact of the precipitation dynamics became larger. Based on the fitted precipitation and dissolution rates, a large quantity of species remained in precipitated form, becoming unavailable for further reactions and reducing the capacity at all C-rates. For $1.0\text{mg}/\text{cm}^2$ at $33\text{wt}\%$, the increased thickness of the electrode resulted in most of the active material being contained within the positive electrode, removing the influence of diffusion bottlenecks and allowing the model to tend towards the highest achievable capacity. With reduced diffusion regions, minimal C-rate dependence was observed.

The trend in behaviour change within the model was not as significant and did not align exactly with Boenke et al. [28] predictions under all conditions. Within the model, as the capacity was calculated based directly on the sulfur mass, a reduction in mass corresponded to a reduction in achievable capacity, which outweighed the influence of resistance or area coverage. Whilst the precipitation dynamics and diffusion mechanism, based on concentration and time, captured capacity variation, these were only two hypothesised reasons; further work to investigate additional mechanisms, an update to the magnitude of resistance, or the inclusion of cell chemistry may improve the accuracy or causality of model predictions for varying sulfur content. In addition, whilst a thicker electrode provides more active sites for reactions to take place, the location and tortuosity of pathways to reach these sites influences the number and rate of reactions [6]. With a larger sulfur mass, or thicker electrode, the influence of inhomogeneities is likely to be increased. Currently, the model only accounts for changes relating to wetting or the quantity of precipitates, with no influence of spatial distribution; this may be required for further development. Separately, the ratio of insulating sulfur to conductive carbon host was not considered in the model but may also be required.

Overall, the hypothesis by Boenke et al. [28] was not fully captured and requires further work to achieve qualitatively.

5.4.4 Resistances

Boenke et al. [28] found a larger reduction in voltage during discharge at higher C-rates when cycling pouch-cells compared to coin-cells, hypothesised to be due to the increased electrolyte resistance contributing to Ohmic changes. When cycling at higher currents, the discharge voltage decreases, and charge voltage increases; the internal resistance is higher due to the increased transport of species and more frequent collisions [18].

Work by Zhang et al. [1] found that at higher C-rates, the lower plateau was strongly influenced by charge-transfer resistance. This type of resistance was not included within the model so could not be tested, nor did the model account for electrolyte viscosity. However, with only the electrolyte resistance and diffusion mechanism, the model was able to capture changes to both high and low plateaus, more significantly in the low, for both coin and pouch-cells. The magnitude of voltage change was larger in pouch-cells, aligning with a larger resistance due to reduced E/S ratios. However, the change remained smaller than observed by Boenke et al. [28], in both cell formats. Further work to account for the influence of charge-transfer resistance could improve the magnitude of model predictions.

This hypothesis was qualitatively captured by the model, although it is hypothesised the addition of further resistance mechanisms could improve the model predictions.

5.4.5 Additional Features Required to Capture

The additional features required to capture Boenke et al. [28] predictions are discussed briefly here, and in further detail in Chapter 6.

5.4.5.1 Degradation

Boenke et al. [28] did not vary the charging C-rate, with the aim of minimising degradation to the lithium metal due to plating. It was also hypothesised that reduced sulfur content, therefore reduced current densities, reduced the stress on the negative electrode, decreasing the dendrite formation [28]. Currently, the model does not include any degradation mechanisms. A separate negative electrode is likely required to capture these, along with the possibility of higher dimensionality, for example, to capture the formation of dendrites. In addition, various degradation mechanisms may occur to other components within the cell, such as electrolyte side reactions [10], contributing to the reduction in performance. The potential mechanisms added to the model would depend on the specific experimental behaviour being predicted, and under which conditions. To capture Boenke et al. [28] experimental results, the degradation mechanisms would need to capture a loss in capacity over long-term cycling,

as observed in the constant C-rate coin-cell testing. Similarly to the link between electrochemical reactions and current, the rates of degradation are likely to vary with current.

5.4.5.2 Chemistry

5.4.5.2.1 Electrolyte Chemistry

Boenke et al. [28] used an ether-based solvent with high polysulfide solubility and an additive in the electrolyte to help reduce the impact of shuttle. Details relating to the electrolyte chemistry and the inclusion of additives were not included in the model. As previously discussed, this may require modifications to the activation cycles incorporated into the model, to optimise the SEI layer along with finding stable initial conditions. In the current state, the model could capture an implied influence; for example, the extent to which LiNO_3 additive contributes to a reduction in polysulfide shuttle could be related to the shuttle rate, with a larger proportion of additive corresponding to a lower shuttle rate. Alternatively, as ether-based solvents improve solubility of lithium polysulfides, this could be captured through a larger dissolution rate. Further work would be required to understand what other information would be required to capture the correct magnitude of behaviour, and remove any unrealistic assumptions, such as homogenous dissolution of species.

5.4.5.2.2 Positive Electrode Chemistry

The model also does not account for all variations to the chemistry of the positive electrode. Whilst features such as the ratio of sulfur to carbon could be calculated, specific details such as the sulfur infiltration method, pore size or distribution were not included.

Boenke et al. [28] first tested positive electrode materials at coin-cell level, before scaling up and testing the CNT BP material in pouch-cells, as it provided a free-standing electrode option. It was found that CNTs with thinner diameters had a higher proportion of conductive pathways, increasing the sulfur utilisation within the cell [28]. The tortuosity of the electrode also influenced the behaviour, and how species travelled through the pathways. This level of causality cannot be achieved in the model as it is, but the thickness of the positive electrode could be tested to understand the effect on sulfur utilisation. An implied relationship between electrode thickness and number of pathways, ultimately affecting the rate at which these reactions occur, could be added to the model, for example, through the rates of precipitation, nucleation, dissolution, or through the transport coefficients. To capture the impact directly, higher dimensionality is likely required.

Separately, Boenke et al. [28] found that specific area and pore size influenced the uniformness of precipitation, along with the utilisation of active material. Whilst the pore geometry was not considered in the model, the updated area equation, accounting for electrode wetting, impacted sulfur utilisation; based on the assumption that precipitation was homogenous across the electrode within the model, the area influenced the rate of reactions and the precipitation dynamics. Separately, the electrode dimensions and structure, along with volume of electrolyte, influenced the available area for reactions. Further work to include the influence of pore size and distribution more accurately could further investigate the utilisation of sulfur. In summary, further work is required to add all these features and capture the impact on reactions, with the aim to use the model alongside experimental work.

5.5 Summary and Achievement of Research Objectives

To summarise, a physics-based model was developed as it directly includes varying mechanisms, each of which can be tested and manipulated to compare to experimental results. Whilst ECMs predict similar outputs, they cannot be used in the same way to investigate the mechanistic behaviour within the cell. The model was built based upon existing models, using Cornish et al. [3] as a baseline. Zero-dimensionality was selected to ensure minimal assumptions and fitting parameters within the model; only the fundamental mechanisms known to occur were included, most of which had been included and thoroughly validated in previous models, ensuring trust in the fundamental predictions. Whilst the accuracy of a 0D model is lower in comparison to higher order models, and fewer experimental features are typically captured, the additional mechanisms tested and implemented throughout this study could confidently be trusted as one of the potential mechanisms responsible for the observed behaviour. In a real cell, it is likely there may be several mechanisms simultaneously contributing to each of these. Further work, both experimentally and through modelling, is required to confirm this.

Alongside capturing the fundamental behaviour, the final version of the model included reversible C-rate dependence due to a simplified diffusion mechanism. This was captured through the removal of the assumption of total material utilisation, including the sulfur and electrolyte. This allowed for usable and unusable regions to be created within the cell, with behaviour in each affecting the other. To achieve this, a pore volume parameter was introduced, along with a clearer definition of how porosity varied during cycling; separate dependencies were created based on precipitation and the electrolyte volume. As C-rate variation is typically captured in higher order models through transport mechanisms related spatial variations, the inclusion within a 0D model showed the capability without significant computational cost. It also created the potential for further mechanism updates; for example, with the introduction of a negative electrode component, the shuttle mechanism could be captured through diffusion between the negative and positive electrodes, rather than through a fitted shuttle constant. This could also allow the model to capture self-discharge, during cycling or storage. For further model development, however, it is likely spatial variations would have a large impact on the behaviour; the current updates improve the model capability but may not be the final solution.

Alongside the diffusion mechanism, the model more accurately captured the influence of precipitation with separated nucleation and particle growth mechanisms; only nucleation led to pore blocking and a reduction in available area. A temporary loss of active material could be captured through adjustments to the fitting parameters within the precipitation dynamics, resulting in species remaining in precipitated form rather than dissolving, and therefore unable to contribute towards electrochemical reactions. Whilst earlier work in the project confirmed the precipitation dynamics alone could not capture the required C-rate dependence, this update worked towards improving the causality in comparison to experimental results, and provides one mechanism to explain irreversible capacity fade. However, further work should include mechanisms that are directly related to experimental results, rather than through fitting parameters; for example, the formation and impact of an SEI layer, which could be investigated through post-mortem analysis, and the link to loss of active material. Whilst most additional mechanisms would require some assumptions, these may be more reliable and provide alternative hypotheses to the observed behaviour.

Alongside implementing and testing all the model upgrades together, this Chapter also investigated the extent to which the model captured or tested Boenke et al. [28] hypotheses. With the updated parameters and mechanisms, the model included the capability to investigate varying C-rate, sulfur loading and sulfur wt%. The extent to which the model captures or aligns with hypotheses made by Boenke et al. [28] is discussed in Table 13.

Boenke et al. [28] Hypotheses	Captured in the model?
Discharge capacity increases with lower sulfur content - At lower sulfur wt%, more active surface area is available for reactions - At lower sulfur loading, the internal cell resistance is reduced <i>(Also observed higher rate capability at lower sulfur content)</i>	Yes (also requires further work): - Influence of area on behaviour based on inclusion in precipitation dynamics, and direct link to nucleation mechanism - Resistance calculated based on the mass of species within the cell, which decreases with sulfur content - Further work required to account for thickness and mass changes simultaneously, and potential inclusion of other resistance types
Larger capacity loss at higher C-rates, hypothesised to be due to transport limitations and degradation mechanisms	Yes (also requires further work): - Achieved through diffusion mechanism - Further work to account for capacity fade unrelated to C-rate (e.g. degradation)
Influence of electrolyte volume on electrochemical performance, in terms of dissolution, viscosity and resistance	Yes: - Usable and unusable electrolyte volumes with diffusion between regions, and only species within the positive electrode available for electrochemical reactions - Use of concentrations (instead of masses) accounts for impact of electrolyte volume
Larger capacity loss at higher C-rates. Regain capacity on reduction of discharge C-rate	Yes: Achieved through diffusion mechanism
Impact of surface area and pore size geometry on uniform sulfur precipitation and utilisation	Yes (also requires further work): - Variable area and inclusion within the precipitation dynamics - Further work to test pore size geometry and uniformity (likely requires higher dimensionality)
At higher masses, unfavourable ratio of sulfur to carbon, therefore lower capacity achieved	No: Mass included but influence of conductive carbon to insulating sulfur ratio not considered
Poorer performance of pouch-cells at higher C-rates (0.1C and above), caused by higher electrolyte viscosity and strengthened internal resistances	Yes (also requires further work): - Formulation results in higher resistance in pouch-cells - Additional mechanism required to account for viscosity and capture C-rate performance beyond diffusion and precipitation dynamics
Electrolyte chemistry influences solubility of species, SEI formation and mechanisms such as polysulfide shuttle. Positive electrode chemistry influences conductive pathways and sulfur utilisation	No (requires additional features): Component chemistry required

Table 13: Summary of Boenke et al. [28] hypotheses and the model capability to capture these

To summarise, of the success criteria discussed in Table 10, the model was able to capture all except degradation and chemistry-based features, although the preliminary methods to capture both were discussed. The inclusion each is required to ensure the model can be used alongside experimental work, to investigate the behaviour associated with each included mechanism; these are all discussed further in the following Chapter. The changes made to this model have improved the capability compared to previous 0D models and created a strong baseline for further work. Whilst the initial aim was to develop a coin-cell model, the changes have improved predictions for both coin and pouch-cells, capturing how the behaviour varies between cell formats, based on conditions such as the geometric size, area variation and component properties.

6 Chapter 6: Improving Model Predictions

This Chapter discusses the potential further work that was not fully completed as part of this project. It is discussed with respect to components within the cell, and includes the chemistry-based changes, the cycling behaviour and the degradation mechanisms that are recommended to improve the capability of the model. Some of these have been preliminarily tested to understand the potential impact.

The nomenclature is included in List of Symbols.

6.1 Research Objectives

Whilst the updates to the model have significantly improved the capability to predict experimental behaviour of both coin and pouch-cells, providing a foundation to test the mechanisms occurring in each, further work to the model is still required. The most predominant is the inclusion of chemistry-based features, to allow the model to be used alongside coin-cell experiments when testing new materials. Secondly, the inclusion of degradation mechanisms would enable the model to capture long-term cycling behaviour and the changes observed beyond C-rate dependency, such as uneven plating and stripping, or the loss of shuttled material. The process to implement these are considered within this Chapter, along with other areas such as cycling dependencies. Whilst there is a significant number of changes that could be applied to the model, the areas discussed are the most promising based on testing results, and work towards improving predictions for the observed experimental behaviour [28]. The focus will remain on capturing the scaling between formats and will require improvements to specific mechanisms within each component.

6.2 Recommended Further Work

The model used to fulfil the aim of predicting coin-cell behaviour was developed as physics-based, cell-level and 0D. Whilst this type of model includes the required capability to test hypotheses and the impact of the mechanisms occurring, it is unlikely to quantitatively predict behaviour changes during cycling and when scaling. However, the simplicity of the model ensures it has a low computational cost and is relatively easy to use and implement by other researchers when published open source. It also requires a low number of experimental parameters, fitting parameters and assumptions. Therefore, the further work discussed in this Chapter primarily focuses on improvements to the model whilst maintaining the low dimensionality. Features can be implemented, or relationships between variables introduced, working towards capturing all the observed behaviour without the requirement for higher order mechanisms. The areas are summarised into three categories.

6.2.1 Chemistry Changes

The first area of further work involves the implementation of chemistry-based features; this is essential for the model to be used alongside coin-cell experimental work. To include these features, clear differentiation between each component is required: the positive and negative electrode, the electrolyte and the separator. Within each individual component, the effect of changing chemistry-based parameters needs to be included either directly, or through assumed, fitted mechanisms. For example, the addition of LiNO_3 into the electrolyte to suppress polysulfide shuttle could be introduced through a fitted rate parameter which minimises the shuttle rate, or through a reaction with lithium from the negative electrode to reduce the availability to shuttle. For simplicity, other components such as the casing, tabs or current collectors will not be considered as part of the immediate further work. For later investigation, the inclusion of these would influence the behaviour when scaling between cell formats, for example the pressure within the cell, or the volumetric expansion, expanding the work towards determining all the mechanistic differences.

6.2.2 Cycling

Once chemistry-based changes have been accounted for, the model predictions during cycling can be improved. For example, once manufactured, the first step of any experimental testing, regardless of the cell format, is to run activation cycles. The conditions of these cycles are highly controlled, often at very low C-rates, with the aim of allowing the cell to reach stable conditions and creating a uniform SEI layer between the negative electrode and the electrolyte [6]. The exact conditions at which this is achieved are rarely provided by the manufacturer when the cells are supplied for use. Within the model, the 0A cycle followed by several activation cycles were introduced to ensure the species distribution reached equilibrium before cycling and achieved stable initial conditions, reducing the likelihood for numerical errors to occur. Further investigation is required to understand how to capture the experimental effect of an activation cycle, along with the influence of a stable SEI layer on performance during cycling.

Alongside the activation cycles, the transport of species also needs to be accounted for more accurately. As the model was 0D, a diffusion mechanism based on time and concentration gradients only was implemented; this was one mechanism to capture C-rate dependence, but there are likely several others. The transport of species impacts which reactions occur, how they occur and the rate at which they take place. Transport limitations are the cause of the observed C-rate dependence, for example, due to inaccessible species based on the tortuosity of the reaction pathway [6]. There are various factors that influence transport, such as the current and temperature of the cell, the solubility of species and the structure of the positive electrode. The type or chain length of the species also influence the kinetics [6]; for example, short-chain species have slower reaction kinetics and are less soluble, therefore more likely to precipitate [6]. Typically, higher dimensionality would be required to capture these mechanisms, however the influence could be assumed or implied within a lower order model, as discussed throughout this Chapter.

6.2.3 Degradation Mechanisms

When testing a cell, cycling beyond the limits specified by the manufacturer can cause or enhance the degradation mechanisms occurring. For new material testing in coin-cells, these are often exceeded to understand the behaviour of the materials at the limits of performance; for example, a higher upper voltage cut-off results in an initially higher achievable capacity as more species are allowed to form elemental sulfur at the end of charge [6], but it also increases the likelihood of polysulfide shuttle to occurring [10]. Therefore, when investigating degradation mechanisms within the model, it is also important to account for the conditions at which they occur or are enhanced, and whether this may vary when scaling between cell formats.

Whilst a successful model should include the majority of degradation mechanisms, as discussed in Section 1.3.2, all of which behave differently under different conditions, these can only be accurately included in a model with sufficient experimental data. Polysulfide shuttle was the only discussed and to some extent quantifiable mechanism that was hypothesised to occur within the parameterisation data set, and therefore the only degradation mechanism included in this model. The model only included the capability to reversibly influence behaviour based on the quantity of long chain species at the end of charge; further work is required to correlate shuttle to irreversible losses, for example as included in Marinescu et al. [17].

As previously discussed, as the model is 0D, the accuracy in terms of quantitatively matching the experimental data is low, but trust is high based on minimal fitting parameters and assumptions. The inclusion of degradation mechanisms without experimental data to validate would compromise this trust. Instead, to ensure the simplification and robustness remains, when applying the model in the current form, it is made clear it is not expected to capture behaviour relating to long term cycling, where degradation mechanism would occur. It is only able to capture reversible C-rate dependence with the inclusion of the diffusion mechanism, and temporarily irreversible capacity relating to the precipitation

dynamics. For further development, additional degradation mechanisms should only be implemented as required when the data is available. Details of several mechanisms, and how they could be implemented into the model to improve the capability are discussed throughout this Chapter, with relevance to a specific component.

6.3 Components

To capture the three areas of further work, separate components are required within the model; the impact is discussed with relation to each component. The inclusion of these will also work towards improving predictions when scaling between cell formats.

6.3.1 Positive Electrode

The sulfur positive electrode component is already included in the model. The model accounts for the porosity, with relation to the pore volume, area, thickness and density, and the amount of sulfur within. No other features are considered.

6.3.1.1 Chemistry (Positive Electrode)

6.3.1.1.1 Location

Based on the dimensionality of the model, all reactions are assumed to occur at one location in the positive electrode. In a real cell, reactions are likely to occur at different locations, with preference to reaction sites closer to the electrode-electrolyte interface, or with less tortuous pathways [109]. These are therefore depleted first. The further the distance into the electrode to reach the reaction site, or the more tortuous the pathway, the higher the reaction overpotential [6]. This can lead to variations across the electrode, with areas with a high level of precipitation and pore blocking, whilst others are fully available [102].

The inclusion of spatial inhomogeneity across the electrode surface would influence how and where reactions occur. It is hypothesised to be more influential within larger cell formats, such as pouch-cells, due to the increased geometric size. To capture this in a model, it is likely to require higher dimensionality, but the influence could be accounted for through other mechanisms. For example, higher tortuosity results in slower transport within the cell, [6], which could be achieved through manipulation of the transport coefficients. The tortuosity also lowers the cell voltage [6], which could be achieved through adjustments or addition of other resistances within in the model. Separately, similarly to the four regions to account for the distribution of the electrolyte, separate regions could be created for the positive electrode, for example one at the surface and one closer to the current collector, influencing where reactions occur.

6.3.1.1.2 Pore Size (Porosity)

Currently, the model includes porosity as the ratio of the pore volume to the total positive electrode volume. The variation in porosity is influenced by precipitation leading to pore blocking directly. The electrolyte volume influences the wetting, and therefore availability of electrode pores. The thickness and number of layers within the cell are also considered. This formulation ensures the porosity is scalable between cell formats, and captures the influence on available material, area and resistance, based on the equations discussed in Chapter 4.

For further model development, the size, location and distribution of the pores within the electrode would need to be considered, based on the impact on transport of species, and which reaction sites or pathways are utilised [58]. For example, mesopores have been found to enable diffusion of lithium ions but are small enough to trap intermediate lithium polysulfides [110]. The size of sulfur species and other active materials are also likely to be required in the model in relation to the pore size and distribution. For example, Boenke et al. [28] considered primary porosity as the space inside of the CNTs, and secondary porosity as the space between the CNTs [97]. Investigation into whether the size of the pores, primary or secondary, would be sufficient to incorporate the active material would be required when

using the model to investigate behaviour relating to different materials. Separately, the morphology of precipitates has been found to change with C-rate, as observed by Ren et al. [79]; at low C-rates, larger deposits form, and at high C-rates, smaller and more uniform deposits form [79], [111]. This morphology influences further precipitation, which may need to be accounted for in relation to the availability of reaction sites for further reactions after precipitation has occurred.

Within the existing model, without increasing the dimensionality, a mechanism could be added to confirm or deny viability of reaction sites for specific reactions, to mimic pore blocking. For example, introducing size parameters for each chain length species, and adding a relationship between the current and the precipitation or dissolution rate to capture varying morphology. As an initial step, this could provide insight into the utilisation of sulfur, but further work, likely requiring higher dimensionality, would be needed to accurately account for the relationship between pore and species size.

6.3.1.1.3 Material Properties

The positive electrodes created as part of this project were free-standing, removing the requirement for a current collector. However, real cell electrodes often use current collectors, which are attached to the electrode using a binder [6]; the properties of these components need to be considered. For example, the binder needs to be sufficiently elastic to accommodate volume changes within the electrode [6]. A loss of contact between the electrode and current collector due to binder breakdown can compromise the electronic reaction pathways, reducing the achievable capacity of the cell [6]. The carbon host itself also needs to be flexible to account for the conversion mechanisms occurring within the pores and the associated volumetric changes [44].

6.3.1.1.3.1 Electrode Mass

It is unclear the influence the positive electrode mass has on the behaviour of the cell, although a larger mass implies more scaffolding, resulting in a higher carbon to sulfur ratio if the sulfur mass remains the same, hypothesised to correspond to a higher conductivity [6]. It may also influence properties such as the pore size and distribution. These variations would be an important consideration when scaling between cell formats. To investigate, experimental characterisation of materials would be required, obtained through results from published work, or through direct experimental testing. This information could be implemented into the model with relation to the pore volume, porosity, or introduction of new parameters and variables to capture structural changes.

6.3.1.1.3.2 Packaging

Coin-cells have a hard casing, with constant and uniform pressure applied across the cell using springs and spacers [37]. The excess volume of electrolyte is also likely to contribute to increased pressure; the components and excess quantities all significantly contribute to the dead mass of the cell, reducing the energy density. To ensure higher energy density for commercial applications [6], pouch-cells have soft casing [38], which requires external pressure to ensure contact between the components. The impact of the casing and pressure is hypothesised to influence the wetting of the electrode, and therefore the availability of reaction sites for electrochemical reactions. To fully understand the influence of pressure, further experimental investigation into the impact on behaviour when scaling between formats and varying cycling conditions would be required.

6.3.1.1.4 Sulfur Content

The mass of sulfur influences the rate of reactions, the precipitation dynamics, the electrode porosity and available area within the model. As hypothesised by Boenke et al. [28], a lower sulfur loading achieves a higher capacity due to reduced internal resistance. If the areal loading is also reduced, the length and tortuosity of pathways are reduced, improving the transport mechanisms [6]. As discussed, tortuosity and reaction pathways are not currently included within the model. Only electrolyte resistance is accounted for based on the assumption that this is the most dominant type [1]. Separately, Boenke et al. [28] found that a lower sulfur wt% achieves higher capacity based on the reduced surface area

coverage due to precipitation [28]. This capability is included within the model based on the precipitation dynamics.

If the E/S ratio is maintained, a lower sulfur content relates to a smaller electrolyte volume, reducing the volume of excess. Within the model, if there is sufficient electrolyte to wet the pores of the electrode, a lower sulfur content can correlate to a larger proportion of species within the positive electrode region and therefore contributing to electrochemical reactions. This influences C-rate dependence with relation to the concentration in each region, and the transport coefficients. However, reducing the sulfur content does not always translate to a higher achieved capacity. Within the model, capacity is calculated based on the sulfur mass directly, with complete utilisation assumed if all conditions are optimum, as no degradation mechanisms are included. However, dependent on other cycling conditions, this could result in a lower achievable capacity, for example, if the electrode is insufficiently wetted, or if species remain in precipitated form, unavailable for further reactions. To capture experimental data more accurately, all factors contributing to the achievable capacity would need to be considered.

The current parameters and variables enable the model to capture variations to sulfur content, in terms of loading and weight percent (wt%). The method of sulfur incorporation is not included but is likely to influence behaviour. For example, sulfur melting of solid S₈, in comparison to dissolved S₈ being included within a catholyte solution, would impact the energy required at the beginning of cycling for electrochemical reactions [6]. This could be introduced into the model with the capability of longer-chain species to precipitate, alongside S₁, similarly to Danner et al. [81].

6.3.1.2 Cycling (Positive Electrode)

6.3.1.2.1 Mobility of Species

As previously discussed, the model does not account for specific details relating to the sulfur species, including the size and mobility, both of which would strongly influence behaviour. For example, smaller particles require less inertia when colliding with other particles and are less soluble than longer chain length species [102]. As diffusion is currently the only transport mechanism within the model, variations to the transport coefficients for each species, and within each region, could work as an initial step to investigate the influence. The impact of dynamic diffusion is discussed in Section 6.3.1.2.2.1.

6.3.1.2.2 Diffusion and C-rate Dependence

Within a real cell, the limited rate capability is largely due to the precipitating species being insulating and poor transport within the electrolyte [6]. Diffusion is the only transport mechanism included in the model, working towards capturing C-rate dependence. To achieve this, the electrolyte volume must exceed the pore volume, creating an excess electrolyte region, allowing concentration gradients to form and species to diffuse between the regions. The transport coefficients should only vary for mechanisms that could impact the movement of species: currently, they are fitting parameters.

The model assumes all the species are located at one point within each region. The diffusion mechanism does not account for transport distances, or diffusion within an electrode, which is influenced by properties such as tortuosity [6]. To directly account for these, higher dimensionality would be required. However, within this model, the influence of current or viscosity on diffusion could be implemented to investigate the behaviour. For example, a simplified relationship between diffusion and viscosity was proposed in [6], as shown in Equation [135], where K_B is the Boltzmann constant, T is temperature, r is the radius and η is the viscosity. Separately, this could be tested with dynamic diffusion, as discussed in Section 6.3.1.2.2.1.

$$D = \frac{k_B T}{8\pi\eta r^3} \quad [135]$$

When scaling between cell formats, it is also important to account for the associated differences to transport, in this case diffusion. For example, the increased geometric size in a pouch-cell would likely correlate to longer diffusion distances. This could be indirectly captured in the current model with changes to the transport coefficients. The lower E/S ratio, or higher number of layers, both of which are more likely at larger cell formats [36], would reduce the volume of excess electrolyte. Under these conditions, most or all the electrolyte and dissolved species would be contained within the positive electrode, leading to no transport mechanism or limitations, and therefore no C-rate dependence. An additional transport mechanism would be required to capture C-rate dependence under these conditions.

Further testing is required to investigate how diffusion interacts with the polysulfide shuttle mechanism. For model testing, the shuttle rate was typically set to zero to test the capability of the other mechanisms added or changed. It is likely shuttling and non-shuttling species would diffuse differently [83]. This could be captured in the model with a relationship between the shuttle rate and transport coefficients.

As diffusion is based on concentration gradients, with no direct relation to current, the mechanism could be used to investigate self-discharge of the cell when stored. Whilst it may only tend towards equilibrium, this would influence the SoC of the cell, impacting further reactions. In addition, whilst diffusion is the movement of species based on concentrations, a separate mechanism for migration, with movement based on electrostatic charge [6], could be implemented without increasing the dimensionality, to better account for how all species are influenced within the cell.

6.3.1.2.2.1 Testing Dynamic Diffusion

With the focus on temperature and current inhomogeneity, Cornish et al. [103] investigated the influence of concentration on diffusion by introducing a dynamic transport coefficient. The dynamic transport coefficient was calculated with respect to the concentration of all charged species, including lithium. When tested preliminarily, the C-rate dependence with dynamic coefficients was very similar in magnitude to when a constant rate of diffusion was tested. It was hypothesised that the inclusion of four regions, with species spread across all, captured C-rate dependence sufficiently without the requirement for variation to the transport coefficients; the impact of dynamic diffusion may be more significant with a lower number of regions, as tested in [103] with two. Further work into other dependencies may be required to confirm this hypothesis.

6.3.1.3 Degradation (Positive Electrode)

6.3.1.3.1 Capacity Fade

When testing under constant C-rate, Boenke et al. [28] found a loss in capacity, although it was less significant than when cycled under varying C-rates. This capacity change was irreversible and differed to the reversible loss at varying C-rates caused by temporarily inaccessible material, or surface area [17]. A separate mechanism is required to capture this, although there are several causalities of this behaviour relating to different components: for example, undissolved precipitates or incomplete reactions [22] in the positive electrode, or loss of active material in the electrolyte. The impact on the positive electrode could be captured within the current model due to slow dissolution, causing bottlenecks. Alternatively, irreversible losses due to undissolved species could be captured through an additional area term. Currently, the model assumes the entire pristine area is available after each charging cycle, which is unlikely to be realistic. The inclusion of permanently lost area, for example calculated as shown in Equation [136], alongside the inaccessible material, would work to capture capacity fade during cycling, if the losses were cumulative.

$$a_r = a_{r0} - a_{r_{irr}} - (\gamma S_{p_{nuc}}) \quad [136]$$

As there are many mechanisms that contribute to irreversible capacity loss, the type of mechanism included in the model would be highly dependent on the experimental data it is aiming to capture. For experimental use, it is likely the capability to predict various loss mechanisms within the model would be required, which could be manipulated as necessary.

6.3.1.3.2 Volumetric Expansion

Within the positive electrode, the precipitation and dissolution of sulfur species onto the carbon host structure causes a change in the volume [44]. Volumetric change occurs in both the positive and negative electrodes, although the impact in the positive electrode is less significant [44]. Overall, excessive volumetric expansion causes cell swelling, and potential rupture if the cell continues to cycle under these conditions [6]. Alongside precipitation, gas evolution can occur [6], further contributing to the total volumetric expansion. Within a pouch-cell, this is reduced by only partially sealing the cell, running the activation cycles to obtain the required conditions, de-gassing and then re-sealing the cell [38]. To capture volumetric expansion, along with the inclusion of separate components, it is likely higher dimensionality will be required. However, further investigation is required into other potential methods to capture the behaviour, as it is a fundamental degradation mechanism and is likely to occur differently dependent on cell formats.

6.3.1.3.3 Precipitation Dynamics

The precipitation dynamics have been updated to account for the differentiation between nucleation and particle growth, more accurately capturing the experimentally observed behaviour. Whilst nucleation contributes to a reduction in available surface area through pore blocking, particle growth results in overpotential changes [102], although this is not directly captured within the model. Under certain conditions, the derivation of these equations allows all the nucleated species to dissolve first during discharge, before the growth species dissolve. Based on the assumption that particle growth occurs on top of nucleation sites, this is not realistic. Adjustments to increase the dissolution rate to a high value prevented this, however, for further work and to ensure the correct causality of model predictions, this must be resolved more accurately. As many of the models that include separate precipitation equations did not include charging behaviour, such as Ren et al. [79], it was difficult to test whether these models also experienced similar issues.

6.3.1.3.3.1 Dissolution of Precipitates

Without changing the precipitation dynamics, one method to overcome this issue is creating a portion of the nucleated area that cannot dissolve, and growth occurring on top of this. For example, separating the available nucleation area and the unavailable nucleation area; this would justify the dissolution of nucleated species before particle growth species. A separate method would be to create different dependencies between variables and parameters to capture the correct order of precipitation and dissolution, for example, as shown in Equations [137] - [138]. The aim would be to create a relationship where nucleated precipitates only dissolved when the growth area, or the mass of particle growth precipitates equalled to zero.

$$k_d = k_{d_{rate}} \frac{1}{ar} \quad \text{or} \quad k_d = k_{d_{rate}} ar_{growth} \quad [137]$$

$$\begin{aligned} &\text{if } ar_{growth} \leq 0: & [138] \\ &\quad nuc_{var_{cha}} = nuc_{var} \\ &\text{elif } ar_{growth} > 0: \\ &\quad nuc_{var_{cha}} = 0 \end{aligned}$$

Equation [137] shows a variation in the dissolution rate for particle growth related to the surface area. At low surface area, or high coverage at the beginning of charge, the rate of dissolution of particle growth precipitates is very high. Alternatively, at high masses of particle growth precipitates, the growth area is also high, resulting in a high rate of dissolution. This changes the dissolution rate from a fixed parameter to a variable.

Equation [138] sets the charging nucleation rate based on the amount of growth area. In charge, only when the growth rate falls below zero does the nucleation rate equal to the fitted rate parameter; when growth area remains, the dissolution rate of nucleates is equal to zero, preventing any dissolution. This

equation still relies on a relatively high fixed dissolution rate for particle growth. The nucleation rate during discharge would remain as a fixed rate parameter throughout the discharge cycle.

6.3.1.3.4 Saturation Concentration

Beyond the precipitation mechanisms, the saturation concentration determines when precipitation and dissolution occur. It is likely the saturation concentration will vary based on several factors within the model, including the C-rate. Further work to calculate this concentration more accurately, rather than using a fixed parameter, may be required.

6.3.2 Electrolyte

The electrolyte is already included as a component within the model. The electrolyte resistance is assumed to be only type and is calculated based on conductivity and porosity. The electrolyte volume is accounted for with respect to the sulfur, through the E/S ratio. The model does not account for pressure; a higher volume has no influence on behaviour other than the wetting of the electrode. Within a coin-cell, with a solid casing that is crimped under a constant pressure, and a larger volume of electrolyte, the pressure is likely to be higher. As previously discussed, further investigation is required into the impact of pressure on component properties and cell behaviour; for example, a higher pressure could impact the morphology of the carbon host [82], influencing porosity and the available pore volume, or alter the precipitations of species [6], [52]. A separate mechanism to capture pressure would be required.

6.3.2.1 Chemistry (Electrolyte)

As previously discussed, to use the model alongside experimental work, chemistry-based features of all components are required. The electrolyte solvent influences the solubility, reaction kinetics and stability, along with any potential side reactions occurring [6]. For example, ether-based solvents have been found to improve the wetting of the electrode [112] and reduce the impact of dendrite formation [6]. The electrolyte salts also influence the behaviour and potential degradation mechanisms, including polysulfide shuttle and dendrite formation, based on the concentration [43]. The salt concentration needs to be considered in relation to the active material contributing to electrochemical relations, for example, to the lithium in LiTFSI [6]. The model does not currently account for this, but the capability is required to fulfil the aim of using the model alongside experimental work. It may also be important to include the impact of chemistry under varying conditions; for example, when the cell is cycled at voltages below 1.8V, the additive LiNO_3 degrades significantly [113].

6.3.2.2 Cycling (Electrolyte)

The model currently assumes the species are homogeneously distributed throughout the electrolyte. Whilst this is unrealistic within a real cell, higher dimensionality would likely be required to capture inhomogeneity within the model.

6.3.2.2.1 Concentration of Precipitates

Changes to calculate the concentrations of species during cycling, accounting for sulfur precipitating out of the electrolyte at the end of discharge, are required to improve model accuracy. The update to the precipitation dynamics, along with the inclusion of four regions within the cell, with only precipitated sulfur in the positive electrode, provides a first step towards this; the concentration in all other regions is based on the soluble species only. To account for the influence of precipitation on the electrolyte concentration, the total mass of species within the electrolyte should decrease when precipitation occurs, resulting in a reduction in concentration of all other species. In addition to this, the corresponding pore blocking when precipitation occurs can reduce the electrode pore volume available for the electrolyte to fill, which needs to be accounted for.

6.3.2.2.2 Resistance

Currently the model only considers electrolyte resistance based on conductivity, porosity and the concentration of lithium, calculated from balancing with the charged sulfur species. Beyond the conductivity, the electrolyte resistance is also influenced by the SoC of the cell, in relation to the number of dissolved lithium polysulfides, which would influence the viscosity and ionic mobility [114]. The diffusion attempts to capture the mobility of species within each region, influencing the corresponding concentrations. Based on a lack of experimental data, the model currently calculates the electrolyte resistance as a similar magnitude for coin and pouch-cells; in a real cell, it is likely to be very different, based on variations including the geometry and E/S ratio. An update to the model to account for this more accurately when scaling is required. Separately, in a real-life application, the temperature of operation is likely to influence the resistance, with a higher temperature typically correlating to a lower internal resistance [115]. With temperature included as an initial parameter in the current model, this could be investigated further without significant modifications.

Another type of resistance that could be implemented into the model is charge-transfer, predominant in the low plateau [1], which may improve predictions relating to the precipitation dynamics and reactions occurring within the low plateau. Zhang et al. [1] hypothesised this resistance was related to slow transport and trapping of species. The dissolution of precipitated species and the associated energy required, along with the changes due to the solubility of varying chain length species may also need to be considered.

6.3.2.3 Degradation (Electrolyte)

Electrolyte degradation has been found to contribute to the poor performance and instability of the cell, for example due to low conductivity [6]. Currently, the model assumes that the total electrolyte volume is always available for reactions and split across the four regions; no side reactions occur, depleting the volume or influencing the concentration. Within a real cell, it is likely the volume of electrolyte will reduce as the cell cycles, impacting both the excess and usable electrolyte volumes. Further work would be required to investigate this impact, and the correlation to observed behaviour such as capacity fade. There are several methods this could be achieved, for example, through implementing a similar mechanism to the loss of shuttled sulfur by Marinescu et al. [17], but applying it to the electrolyte volume to capture depletion.

Implementing a dynamic, or variable electrolyte volume would influence the available pore volume, impacting the available area based on the wetting of the electrode, along with the concentration of species throughout cycling. The overall influence of depletion would vary dependent on the initial quantity of excess electrolyte; in coin-cells, a much larger excess is included, so the impact of depletion is hypothesised to be smaller than in pouch-cells. The relationship between usable and excess electrolyte would need to be investigated and updated within the model as the cell cycles. An assumption would need to be made about the location of the depleted electrolyte, for example, whether the volume in the electrode, the separator or the excess region reduces, or whether all reduce by the same magnitude. Adjustments to the electrolyte volume and concentration within each region would impact the C-rate dependence.

6.3.3 Negative Electrode (Lithium)

The negative electrode is currently not considered within the model. The amount of lithium contained is calculated based on balancing with the charged sulfur species within the cell. It is assumed that the number of positive and negative electrode layers within the cell are equal when considering a pouch-cell or larger cell format, and therefore the quantity of lithium should match the quantity of sulfur. To capture experimental results accurately, the inclusion of a negative electrode, with separate lithium species is required. When added to the model, it is likely the lithium would be included in an excess quantity to ensure enough is available to react with the sulfur.

6.3.3.1 Chemistry (Negative Electrode)

The lithium added to the model within the negative electrode would be pure lithium, assumed pristine, with no imperfections or variations that would influence behaviour. It would include similar parameters to the positive electrode, such as geometric area and thickness.

6.3.3.2 Cycling (Negative Electrode)

With the addition of a separate component for the negative electrode, transport of lithium within the cell between the electrodes would need to be considered. This could be captured through the diffusion of lithium, similar to sulfur, which has been investigated in 1D by Zhang et al. [75]. Further work within the model may also need to account for diffusion within a solid, and the limitations as the slowest type [6], as this occurs to species inside the negative electrode to reach reaction sites. Whilst this would require higher dimensionality to capture accurately, it could be tested in the current model with variations to the transport coefficients, and corresponding relationships between location and the properties. Alongside diffusion, the reactions between the electrolyte and negative electrode, and the formation of an SEI layer will influence transport and the associated resistance for further reactions through this layer [6].

6.3.3.3 Degradation (Negative Electrode)

6.3.3.3.1 Plating and Stripping (leading to Volumetric Expansion and Dendrite Formation)

During cycling, an SEI layer forms on the surface of the negative electrode [6]. This is influenced by various features and mechanisms, alongside the reactivity of lithium [10]. The optimisation of this layer works to prevent uneven plating and stripping during charge and discharge respectively. Uneven plating occurs due to preferential deposition, based on several factors including the presence of already precipitated species, or deformities in the electrode surface [6]. The kinetics have also been found to be slower for nucleation, contributing towards species precipitating on top of existing sites, rather than consuming fresh surface [49]. The process of uneven plating and stripping causes capacity loss at higher rates [6], [44] and contributes to variations in volumetric changes of the negative electrode [44]. The influence on volume change is also likely to vary with cell format. If uneven plating and stripping is allowed to continue, it can lead to the formation of dendrites [10], [116]. If a dendrite grows long enough, it either breaks off, making the lithium inaccessible for reactions, or it perforates through the separator, creating contact between the electrodes and short-circuiting the cell [10], [117]. Dendrite formation, in all lithium metal systems, has been found to impact the safety of the cell [6], [44].

To capture the plating and stripping mechanism, along with volumetric changes, it is likely higher dimensionality is required, unless the causality could be captured through implied mechanisms. For example, to mimic the behaviour, smaller regions within the negative electrode could be considered, similar the four regions of electrolyte in the current model. If lithium precipitates in one of these regions, when the total mass exceeds a specified value, mimicking precipitation on top of existing nucleation sites to form a dendrite, a change in behaviour occurs. This could be stopping conditions for a mechanism taking place, equivalent to short-circuiting, or contribution to a loss of the precipitated material, equivalent to the dendrite breaking off.

6.3.3.3.2 Depletion

As lithium is highly reactive, it often reacts with other species in the cell, including the electrolyte, in side reactions that work towards depleting the active material for the electrochemical reactions contributing to the capacity of the cell [10]. Modelling results have found a reduction in side reactions on the negative electrode with lower C-rates [79]. This could be captured in the model, similarly to the loss of shuttled sulfur in Marinescu et al. [17], with a direct relation to current.

6.3.3.3.3 Polysulfide Shuttle

Polysulfide shuttle is the largest degradation mechanism, with a large amount of work towards investigating and mitigating the impact. This includes modified separators to block lithium polysulfides travelling between the electrodes [18], or the inclusion of LiNO_3 within the electrolyte [6]. The effect of shuttle is more detrimental at higher voltages within the shuttling region, above approximately 2.8V [6]. To mitigate this, voltage limits are set, both experimentally and within models.

Within the model, various mechanisms compete to determine the behaviour during charge, including the rate of S_8 diffusion, the current rate and the shuttle rate; the highest rate becomes the dominating mechanism. For example, the influence of shuttle is reduced at higher currents, as there is less time for species to react and concentration gradients to build across the cell, reducing the rate of shuttle in comparison to electrochemical reactions [6]. However, the reduction in performance at higher C-rates, along with the increased influence of other degradation mechanisms, such as uneven plating and stripping, also needs to be considered in comparison. Additionally, the impact of shuttle in varying cell formats must be accounted for; for example, as coin-cells include thicker lithium for the negative electrode to ensure an excess, the effect of shuttle is more significant in comparison to larger cell formats [6].

The results shown in this project do not include the influence of shuttle. It is included within the model as a constant value, set to zero, to focus on investigating the other mechanisms. When tested at a higher value, flattening of the upper voltage plateau occurred, and a varying influence at different C-rates was captured. For further testing and model development, the shuttle rate could be changed to a variable to capture the impact of other mechanisms in the model. Separately, the influence of losses of shuttle sulfur, as captured by Marinescu et al. [17] by assuming a fraction of shuttled material was rendered inactive, proportional to the amount already shuttled, could be added to investigate the influence on achievable capacity, alongside the other mechanism updates.

6.3.3.4 Testing Lithium within the Model

To test the influence of lithium on the behaviour, working towards capturing the associated mechanisms, a separate negative electrode component was implemented as part of the further work, based on findings from Cornish et al. [103]. Within the developed model, the lithium concentration was calculated based on the charged sulfur species, S_1 and S_4 . Based on the charge of sulfur anions (2-) and lithium cations (1+), the supply of lithium was calculated through balancing, resulting in double the quantity of lithium compared to sulfur. In a real cell, a significantly large supply of lithium can be assumed, based on the excess quantities typically included, predominately in a coin-cell. This lithium would be spread between the negative electrode, the lithium cations, the lithium polysulfides and any lithium contained within other components, such as the electrolyte.

With the update to include lithium directly in the model, the lithium was assumed to be spread throughout the four electrolyte regions in the cell, calculated based on charge balancing to form lithium polysulfides. It accounted for the available lithium cations for further reactions and the solid lithium in excess within the negative electrode separately. The total concentration of lithium did not account for any of the salts included in the electrolyte, but this would need to be considered for further work accounting for the chemistry. With the introduction of lithium, the Butler-Volmer equations were updated, as shown in Equations [139] and [140], with lithium included in electrochemical reactions. This followed work by Cornish et al. [103], who also tested the influence of lithium when it was excluded from the electrochemical reactions, or as a catalyst. This model update required a decrease in the magnitude of standard potentials and initial exchange current densities, each of which were fitting parameters, to account for the concentration of lithium term. The model was also very sensitive to values of the initial lithium concentration, similarly to sulfur species under certain conditions; the use of the pre-cycle and activation cycles helped to obtain stable conditions.

$$i_H = ar i_H^0 \left((CLi_+)^4 CS_8 e^{-\frac{n_H F}{2RT}(V-E_H^0)} - (CLi_2S_4)^2 e^{\frac{n_H F}{2RT}(V-E_H^0)} \right) \quad [139]$$

$$i_L = ar i_L^0 \left((CLi_+)^6 CLi_2S_8 e^{-\frac{n_L F}{2RT}(V-E_L^0)} - (CLi_2S_1)^4 e^{\frac{n_L F}{2RT}(V-E_L^0)} \right) \quad [140]$$

Lithium was included in the electrochemical equations based on lithium polysulfides, meaning no change was required to the existing ODEs. An additional ODE for Li^+ was added, as shown in Equation [141], including the diffusion similarly to the sulfur species. Further work is required to capture the precipitation relating to plating and stripping of lithium.

$$\frac{dCLi^+}{dt} = DLi_+ (CrLi_+ - CLi_+) - \frac{I}{v F} \quad [141]$$

The inclusion of lithium also meant the negative electrode voltage needed to be included. This was calculated as shown in Equation [142] [6].

$$V_{neg} = \frac{RT}{F} \log \left(\frac{C_{Li}}{1000} \right) \quad [142]$$

Within the model, the concentration of lithium was included in the conductivity equation, which was used to calculate electrolyte resistance. This was updated based on the concentration calculated accurately here; based on the magnitude of this value, variations to the fitting parameters were also required.

Based on the sensitivity of the model to parameters, and numerical errors occurring when implementing lithium alongside sulfur based on the equations discussed, reproducible results have not yet been obtained, beyond initial cycles. Work is being completed to resolve this and test the results in comparison to Cornish et al. [103]

6.4 Other Mechanisms: Temperature

Whilst temperature is a parameter in the model, variations were not considered in this study. Boenke et al. [28] did not state temperature was varied, so the cell temperature was assumed to be ambient.

In a real cell, temperature or temperature gradients across the cell can impact the behaviour, such as the component properties or the mobility of species. Polysulfide shuttle and internal cell resistance both contribute to heating of the cell during cycling, although it has been found resistance decreases at increased temperatures [6]. Hunt et al. [62] found both temperature and current inhomogeneity caused degradation. Within the model, temperature was included as a constant parameter. Further work to account for the impact of temperature could include relationships with the rate of reactions, including precipitation and nucleation, or alongside the updated dynamic diffusion transport coefficients. A relationship between temperature and the resistance could also be introduced, capturing a reduced internal resistance at higher temperatures. The variation in temperature across the cell to capture inhomogeneity would likely require higher dimensionality, although this could be tested with separate regions within the cell, similarly to the electrolyte regions.

6.5 Timeline for Further Work

The further work discussed in this Chapter was split into immediate, intermediate and long-term work. The aim of the work was to improve the predictions for coin-cells, and the scaling to larger cell formats, predominately pouch-cells, without the requirement for higher dimensionality. Further work is still required within the community to confirm the exact mechanisms occurring in the cell, and how these vary between cell formats. Using a 0D model includes only the fundamental mechanisms confirmed to occur, and tests these with the fewest number of assumptions and fitting parameters, increasing the trustworthiness. It attempts to predict qualitative trends, rather than quantitative results.

The immediate work that has started has been discussed in the relevant sections, with the impact the preliminary testing had on model predictions. Improvements to the precipitation dynamics to capture the correct dissolution of species under all conditions is required to ensure trust in the model, and degradation mechanisms are required to match Boenke et al. [28] experimental coin-cell results. Potential methods to implement these changes have been discussed. The intermediate work focuses on capturing scaling variations and further tests the hypotheses about the cause of the experimentally observed changes in Boenke et al. [28], including further degradation and chemistry-based features. Long-term work involves a potential increase in dimensionality, or the inclusion of implied mechanisms. For clarity, all the future work is summarised in Table 14.

Immediate	Intermediate	Long-Term
• Inclusion of lithium • Dynamic diffusion • Precipitation dynamics (dissolution) • Degradation (capacity fade)	• Depletion of electrolyte • Materials and chemistry • Sulfur content variations • C-rate dependence (beyond diffusion)	• Activation cycles • Volumetric expansion • Spatial variations (e.g. inhomogeneity, pore size)

Table 14: Summary of all discussed further work, separated into immediate, intermediate and long-term work to complete

7 Conclusion

7.1 Summary of Work

For Li-S, coin-cells are predominately used for new material testing, whilst pouch-cells are likely to be used for commercial applications. Previous research has found that the behaviour observed at coin-cell level does not directly translate up to larger cell formats; this is an important consideration when designing and testing new materials. It is hypothesised that the physical differences lead to mechanistic differences within the cell. To improve understanding of what these are and the impact they have, models of varying complexity can be used to test the behaviour. Models can also test the behaviour under conditions not possible experimentally, for example, at low E/S ratios or very high C-rates. The use of a well-designed and parameterised model will save significant experimental time designing, creating and testing new materials and cells. Most models currently available are parametrised for pouch-cells; without vigorous testing, it is unclear how well these models work when scaled to predict coin-cell behaviour.

Therefore, the overall aim of the project was to test and develop a model with the capability to accurately predict the behaviour of a Li-S coin-cell under varying conditions. To do this, experimental work was first completed, as discussed in Chapter 2. This involved learning and understanding the manufacturing process, by first testing commercial materials, and then manufacturing positive electrodes from new materials within the laboratory; the goal was to obtain a reproducible data set under optimum conditions. Difficulties associated with manufacturing consistent positive electrodes preventing this from being directly achieved, but the knowledge gained was vital in selecting an alternative parametrisation data set and understanding the limitations when using the information. The process of selecting this alternative data is discussed in Chapter 3, alongside the requirements based on the type and complexity of the model selected. The decision was made to use a 0D model, which included the fundamental mechanisms known to occur within a coin-cell; each of these mechanisms had been proven to capture a specific behaviour within Li-S pouch-cells. The aim was to reproduce the experimental results found from a study by Boenke et al. [28]. The use of a physics-based model allowed the results to be directly compared to the experimental hypotheses for the observed behaviour. Where the causes aligned, it was likely the model predictions could be trusted with confidence.

As discussed in Chapter 3, a selected model by Cornish et al. [3] was first re-parameterised, to understand the capability and highlight the areas for further development. Similarly to the experimental work, a significant amount of knowledge was gained understanding the way in which models were created and run using PyBaMM [90]. This process also highlighted the importance of open source models, and a clear description of how the model was formulated; without this information, a large amount of time can be spent trying to understand why the models have been derived in a specific way, repeating work previously completed by other researchers.

Following on from the re-parameterisation of Cornish et al. [3], Chapter 4 summarised the incremental changes made to the model. Some of the changes were made to improve the alignment to experimental results by Boenke et al. [28], whilst others combined and adapted different mechanisms as required to match the trends in coin-cell behaviour. To summarise, the first of these adaptations involved updating the area from a fixed parameter to a variable and introducing it into the precipitation dynamics to account for the influence of precipitated sulfur and pore blocking on the rate of reactions. Secondly, the porosity was recalculated to remove the dependence on electrolyte volume. By also accounting for pore volume, the assumption of total material utilisation was removed. Following this, the precipitation terms were separated into nucleation and particle growth and saw a further update to the area to improve the magnitude and causality of predictions. With the electrolyte volume and distribution within the cell now accounted for, diffusion of species between the regions in the cell captured C-rate dependence within the model. With these updates, the final model was able to capture a large number of the experimentally observed features for varying cell formats. For example, the removal of the assumption of total material

utilisation was applicable to all cell formats, although more significant in coin-cells with a larger quantity of excess electrolyte.

Once all changes had been introduced, the impact on the model predictions under varying conditions was discussed in Chapter 5, along with the alignment to the experimental hypotheses made by Boenke et al. [28]. Whilst significant improvements had been made to the capability, the discussion also highlighted the limitations associated with the work, linked to the mechanisms included and the complexity of the model. The work to improve or resolve these limitations was discussed as part of the proposed further work in Chapter 6, with the likely impact of each further change.

To prevent repeated work, the final model will be made available open source on GitHub, alongside the submission of the paper that predominately summarises Chapter 5. The aim is to improve dissemination of work and encourage testing by others within the community, to build upon and improve the model capability. Collaboration across the research community aims to accelerate the process of understanding and solving some of the key problems with Li-S.

7.1.1 Summary of Scaling between Cell Formats

When scaling between cell formats, the key components remain the same, but the magnitude of these components varies; for example, a pouch-cell has a larger geometric surface area but a lower electrolyte volume. The additional components also vary when scaling; for example, pouch-cells include tabs to connect to the external circuit, whilst coin-cells include springs and spacers to maintain constant pressure. The casing differs between cell formats, and the method of manufacturing can impact the behaviour; for example, the vacuum filling process in pouch-cell manufacturing could improve wetting of the electrodes, but the springs, spacers and hard casing for coin-cells ensure constant contact between components, minimising volumetric expansion. When using a model to investigate this behaviour, it must include the capability to vary these in this way.

In the current form, the model includes physical variations but does not account for the tabs and associated resistance, the pressure correlating to the casing type, or the quantitative changes such as electrolyte depletion or volumetric expansion during cycling. The impact of each variation involves further work to determine all the potential associated mechanisms, and which are likely to be dominant. For example, the concentration in pouch-cells is higher due to lower E/S ratios, resulting in higher electrolyte resistance. Pouch-cells also have a larger geometric size resulting in larger transport distances to reach reaction sites, along with a hypothesised increased impact of volumetric change due to the soft casing, leading to potential loss of contact between components and reduced reaction pathways. For coin-cells, a lower electrolyte concentration results in lower electrolyte resistance but a larger proportion of species floating around in the excess volume. Alongside a smaller initial surface area, this could influence the pore blocking and available reaction sites, along with the homogeneity over the entire positive electrode. The work towards optimising coin-cells to increase similarity to pouch-cells is an important experimental step in understanding how these physical changes lead to mechanistic changes. The use of a model alongside experimental work can then test each of these individually.

7.2 Achievement of all Research Objectives

The initial aims set out at the beginning of this project worked towards understanding the physical and mechanistic differences between coin and pouch-cells, and the reasons why these lead to differences in the observed behaviour. Experimental work was initially carried out with the aim of obtaining a reliable data set to parameterise a coin-cell model, which would later be scaled up to predict pouch-cell behaviour. Whilst this was not achieved due to the irreproducibility of the results using Organosolv Lignin material, significant knowledge was gained that became essential when making decisions about model development and analysis. The alternative data used to parameterise the coin-cell model included significant detail for both coin and pouch-cells [28]. Further information was provided by the author,

ensuring correct understanding of the results and removing assumptions through the provision of additional data [97]. This also removed the requirement to complete further experimental work for pouch-cells.

Alongside the experimental knowledge, analysis of the existing models and rigorous testing to understand what changes were required, and how these could be implemented, highlighted the impact of the key physical differences between coin and pouch-cells. Whilst the existing models, developed predominately for pouch-cells, could be re-parametrised to capture coin-cell behaviour, various areas were highlighted to improve the capability and capture all the fundamental features. After implementation, these upgrades were tested under various conditions to determine the results aligned with expectation, based on the hypotheses made. With the aim to improve the capability, the qualitative model predictions were not solely focused upon, but also the alignment with the hypotheses made for the experimental results. These results were verified against other experimental results and hypotheses at various stages of development, to confirm Boenke et al. [28] findings. Alignment confirmed the mechanisms included were correct and were at least one cause for the observed behaviour; for example, diffusion captured C-rate dependence through concentration gradients, but there are other transport mechanisms that could be implemented, at higher dimensionality, to capture this behaviour. The further work discussed focuses on the changes that could be implemented into the model, with the aim of fully capturing coin to pouch-cell variations in a 0D model, to match the experimental data obtained by Boenke et al. [28]. This will work towards using the model alongside experimental testing, to help determine the optimum conditions during cell manufacture.

8 References

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9 Appendices

9.1 Experimental Details

9.1.1 Experimental Build of Coin-Cells

9.1.1.1 Pre-Assembly Preparation of Coin-Cell Materials

To study the impact of the various solutions considered for the positive electrode, following the LiSTAR project guidelines [37], [57], the other components used for coin-cell testing were composed of standard materials. The **electrolyte** was a solution of a solvent, a salt and an additive. The solvent 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME) was used. This solvent was ether-based, due to the high solubility of lithium polysulfides [118]. The salt LiTFSI was used, based on work by Agostini et al. [119]. An additive of LiNO₃ was added to the solvent and salt solution. As previously discussed, whilst this is not a commercially viable additive, it is used for coin-cell testing to minimise the impact of polysulfide shuttle when attempting to observe the performance of components within the cell. A ratio of 1M LiTFSI in DOL/DME (1:1: v/v) + 0.8M LiNO₃ was selected for the reference testing case, as found by Agostini et al. [119], with concentrations and volumes further varied as necessary during testing. Following the LiSTAR guidelines [37], to form the electrolyte solution, the anhydrous solvent was dried using molecular sieves before being filtered. The salt, LiTFSI, and additive, LiNO₃, were dried under a vacuum at 120°C, for approximately three days. These components were combined in the glovebox and stirred to ensure full dissolution. The electrolyte mixture was predicted to be stable, with respect to degradation, for a period of several months [37].

The **negative electrode** was fresh, pure lithium, purchased as a pre-rolled film of approximately 12mm thickness [37]. It was cut into 14mm electrodes using a hollow punch, a circular cutting tool. The lithium was not cleaned before use, as the assumption was made that no contaminants were present, nor any surface reactions occurring while being stored in the argon-filled glovebox. When handling the lithium foil, clean plastic tweezers were used, rather than metal ones, to prevent cross contamination and to reduce the risk of damage.

A Celgard-2400 **separator** was used [37] [57]. It is a monolayer microporous membrane, with a thickness of 25µm and a porosity of 41% [120]. The separator was cut into 16mm diameter discs and dried at 60°C for approximately 12 hours. It was handled with gloves and placed only on clean surfaces to prevent cross-contamination.

A standard CR2032 **casing** was used, with 0.5mm stainless steel **spacers** and a steel wave **spring**. These were washed in isopropanol (IPA) in an ultrasonic bath for approximately 1 hour, before being soaked in ethanol. They were then dried at 80°C-100°C before use [37]. The cell was crimped to approximately 50kg m⁻² [37].

9.1.1.2 Coin-Cell Assembly

A schematic of a coin-cell build, for reference, is shown in Figure 2.

In experimental testing, similarly to the negative electrode, the positive electrode is typically cut using the hollow punch to ensure reproducibility of dimensions. The circular shape maximises the contact area between the electrodes, through the separator [37]. Alternatively, square electrodes are often preferred when using a fragile positive electrode material; these are relatively simple to manufacture in a laboratory using a sharp blade, ruler and glass plate. Throughout this project, square positive electrodes were used. Before assembly, the positive electrode was weighed, and the quantity of sulfur was recorded or calculated depending on the sulfur loading. The dimensions of the electrode were also recorded.

To manufacture the cell, one component was added at a time, directly into the lid of the casing. The order could be reversed, but for this work the positive electrode was added first, followed by the electrolyte on top, using a pipette to ensure accurate quantities. The volume and concentration were recorded during manufacturing. If a catholyte solution was used to load the sulfur, it was added at this stage. The various sulfur loading methods are discussed in detail in Section 9.1.2.5. A varying period was given for the electrolyte or catholyte to wet the positive electrode; a longer time allowed it to fill the pores rather than remaining suspended on top. The partially assembled cell could also be placed onto a hot plate to speed up the absorption process into the positive electrode; both the time and temperature influenced the extent to which the electrode was wetted. It was important to consider that sulfur sublimates above 40°C, so only temperatures below this value were used [37]. The separator was then added, followed by the negative electrode. As previously discussed, both electrodes were manufactured significantly smaller than the separator to prevent possibility of contact, if the separator was not perfectly aligned. However, the smaller size also increased the likelihood of misalignment of the electrodes, reducing the achievable capacity of the cell as all the active material would not be utilised. The springs and spacers were then placed on top, as necessary, to maintain contact.

When all the components had been assembled, the coin-cell was crimped to 50kg m⁻², ensuring the casing was fully sealed. Care had to be taken that the cell was aligned within the crimping tool, to prevent damage to the casing, as shown in Figure 37. When excess volumes of electrolyte were used, it was common for a quantity to spill out of the cell during this process. While it was difficult to quantify the exact amount released, this needed to be taken into consideration when interpreting the observed cell performance; the electrode wetting, along with the pressure inside the cell due to electrolyte volume, and due to crimping, were likely to influence the behaviour.



Figure 37: Casing damage of a coin-cell due to misalignment when crimping

When manufacturing the cell in the glovebox, plastic tweezers were used when handling all components. The cell was built upon an insulating mat to prevent shorting from contact with the metal base of the glovebox. Depending on the materials used, when assembled, the cell voltage was typically expected to represent a fully charged state, which was observed to be approximately 2.9V. Voltages at or below 2.5V indicated a potential error, typically a shorted cell. Figure 38 shows the information provided by the LAND software system when the cell was set up to cycle.

9.1.1.3 Preparing the Cells for Cycling

The time between manufacturing the complete cell and beginning cycling can vary. For example, it is common to manufacture coin-cells in large batches, but cycle them in smaller batches, using the results to tailor the cycling protocol. For this project, cells were built in maximum batches of 10. As most of the experimental work within the Titirici group involved new materials with moderate cyclability, there was typically sufficient channels available on the cycler to set up and run all cells made within the batch together. A selection of cells set up for cycling is shown in Figure 39. If stored before use, the period of storage before cycling was recorded and considered when analysing the results; for example,

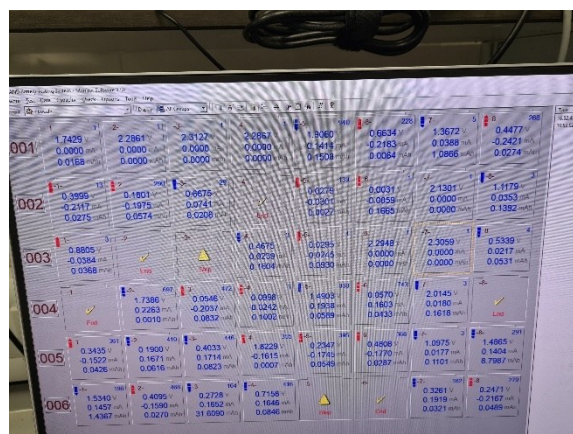


Figure 38: Measurements from cell cycler on LAND Software

self-discharge could occur [6] when stored, influencing the SoC of the cell. To ensure consistency across results when cycling, activation cycles were implemented, using the same protocol regardless of the initial SoC. This is discussed in Section 9.1.1.4.

9.1.1.4 Cycling the Cells

Specific cycling protocols were created dependent on the aim of experimental testing. Voltage and current were measured, and the protocol was created by setting time, current rate and voltage limits. A cycling capacity limit was also applied, calculated based on the amount of sulfur within the cell, as recorded during manufacture. These limits were implemented to ensure the cell cycled as expected and attempted to prevent unsafe testing or unintentional degradation. For example, an upper voltage limit of approximately 2.6V was set during charging to reduce the likelihood of polysulfide shuttle occurring. The current rates used were a compromise between performance and cyclability, dependent on the aim of testing. Time limits prevented the cell infinitely charging or discharging, for example, due to short-circuits occurring and preventing the cell reaching maximum capacity or voltage.



Figure 39: Several coin-cells set up for cycling

As discussed, before standard cycling, activation cycles were introduced. Within commercial cells, these are designed to create optimum conditions within the cell, including a stable SEI layer on the negative electrode [6]. The number and conditions of these activation cycles is not reported by commercial manufacturers. Within the experimental work, one activation cycle was implemented at a very low C-rate, set to 0.05C, with the aim to remove any variations in the initial cycle. The slow rate allowed sufficient time for all reactions, and consistent initial conditions to be obtained before the standard cycling.

9.1.2 Organosolv Lignin Manufacturing

9.1.2.1 Materials

To begin the electrospinning manufacturing process, a solution was created, composed of lignin, a polymer and a solvent. It was important to consider the impact of materials in terms of safety and environment; for example, some work had used dimethylformamide (DMF) as the solvent during manufacture [26] to obtain high performance, although it is highly toxic and reactive [121]. At a lab-scale, and when being considered for commercial applications, more environmentally friendly and less toxic solvents should be used, for example, sodium hydroxide (NaOH). As previously discussed, a compromise between performance and viability, with regards to all aspects leading to commercialisation, needs to be considered.

For experimental work, the polymer used was poly(ethylene oxide) (PEO) and the solvent used was sodium hydroxide, NaOH. The quantities of each component were approximately 1.2wt% PEO (0.12g), 10.8wt% lignin (1.08g), and 88wt% of 0.5M NaOH (8.8g), or a ratio of 1:9 (PEO:OSL).

These quantities were selected based on previous experimental work by Dr. Julien Roman. The components were combined, as shown in Figure 40, and stirred for approximately 2-3 hours, to ensure the lignin was fully dissolved.



Figure 40: Organosolv lignin solution before mixing

9.1.2.2 Electrospinning

Once manufactured, the solution was decanted into a syringe. This syringe was placed externally to a glovebox, to later be used to control the flow of solution. It was connected internally via a tube to a metal needle at the other end, where the solution would come out from to then be deposited. It was essential to ensure there were no air bubbles in the syringe or tube, as this could cause spluttering, leading to damage to the fibre mat during the electrospinning process. This was checked by slowly squeezing the solution through the tube until it flowed out, ensuring no blockages. This needle was positioned perpendicular to a flat target plate, with the tip approximately 20cm away from the target. This could be adjusted as necessary dependent on conditions such as the flow rate or volume of solution. A clip was attached to the needle to apply a voltage. Aluminium foil was placed on the target plate using a grounded clip, and a beaker placed underneath the needle to catch any dripping solution. It was important to ensure the needle did not drip into the clip attached, as this could lead to short circuiting.

Within the glovebox, the humidity was regulated at 25%. The glovebox was filled with compressed air, set to 1 bar. Due to the age and type of glovebox used, external conditions, such as the temperature within the laboratory, influenced the electrospinning conditions; this impact was assumed minimal and not measured.

The electrospinning process worked by creating a potential difference between the target and the needle. When a voltage was applied to the needle, the solution flowing out of the needle was drawn to the centre of the grounded target, gathering fibres. A flow rate of approximately 2ml/hour was set, and the generator was set to $\sim 20\text{kV}$ and $0.02 - 0.04\text{mA}$. These values were selected based on previous experimental work by Dr. Julien Roman. It was essential that the flow rate or voltage were not too high, to prevent spluttering occurring and damaging the surface of the fibre mat.

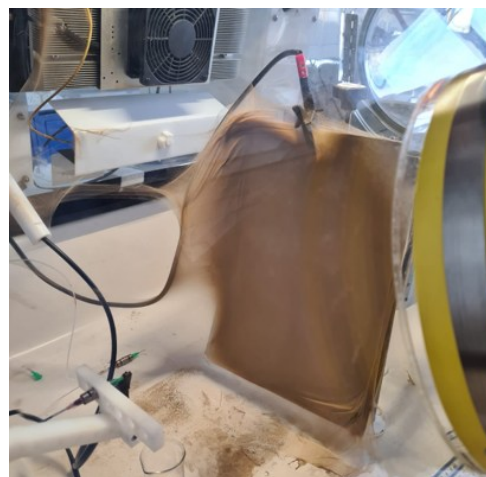


Figure 41: Manufacturing of lignin fibre mat through an electrospinning process

As the solution continued to flow, the fibres dispersed outwards away from the centre, located directly opposite the needle. This created a fibre mat approximately 30cm by 20cm in size, as shown in Figure 41. Deposition layers were created through the electrospinning process; as the underneath layers dried, new, wet layers formed on top. The influence of temperature and humidity on the rate at which layers dried was assumed minimal. Due to the manufacturing process, the thickness of the lignin fibre mat was found to vary dependent on location. The centre, closest to where the needle was located, was the thickest. The edges of the mat, furthest away from the needle, were the thinnest. During manufacturing, the thickness of the lignin fibre mat could be optimised through the total volume of solution, or the flow rate applied. Beyond the thickness, it was unclear how the properties of the mat changed with location. To investigate this, along with the potential influence of temperature or humidity, characterisation was required, such as scanning electron microscopy (SEM), to analyse the morphology.

Once the full solution had been electrospun, the flow rate and generator were turned off, and the fibre mat was moved away from the needle. It was essential to do this as soon as the electrospinning process was complete to prevent any remaining solution spluttering and damaging the mat. All other equipment was then turned off and cleaned with distilled H_2O . To remove the lignin fibre mat from the aluminium foil, tweezers were carefully used. The fibre mat before removal is shown in Figure 42. The fibre mat was then cut into smaller sections and placed into a storage box. Ideally, the mat would be carbonised within one week of manufacturing, to prevent possible side reactions or changes to the material properties.

The lignin electrode mat manufactured via electrospinning was sufficiently strong to be free-standing, meaning it did not require a current collector. Commercially, this is ideal as it reduces the mass and space consumed by inactive components in the cell.

9.1.2.3 Carbonisation of the Fibre Mat

The lignin fibre mat was non-conductive after electrospinning. As previously discussed, carbonisation at a high temperature converts the material, or parts of it, into carbon, making it conductive. To carbonise the fibre mat, it was cut to size to fit into the furnace tube, approximately 10cm by 5cm. It was placed between two pieces of carbon felt to prevent damage during the process. The time and temperature intervals varied depending on testing; a typical routine began at 20°C, before increasing the temperature to the maximum value, for example 800°C, at 5°C per minute. It was held at the maximum temperature for approximately 2 hours, before being cooled to 20°C at 5°C per minute. The temperature at which the fibre mat was carbonised could be varied, influencing the properties and conductivity [67]. Carbonisation was done under nitrogen. The final carbonised mat is shown in Figure 43.

Sublimation of sulfur occurs at temperatures above 40°C [18], making it uncommon to incorporate the sulfur into the fibre before carbonisation; it would be difficult to quantify the amount remaining after carbonisation, based on a portion being lost. The addition of sulfur during the lignin manufacturing process could also alter the properties of the material compared to when using the standard solution, as described in Section 9.1.1. Instead, it is typical to load the sulfur after manufacturing, before or during cell assembly, as discussed in Sections 2.5.3.1 and 9.1.2.5.

9.1.2.4 Washing of the Fibre Mat

After carbonisation, the fibre mat was washed to remove any residual salts. To do this, it was placed in a beaker of water, either tap or distilled H₂O, and heated gradually to 80°C. It was kept at this temperature for approximately 2 hours, before being removed and washed with distilled H₂O to remove any remaining surface salts. It was then washed with ethanol. To dry, the fibre mat was wrapped in foil with pierced holes, to ensure ventilation but prevent possible cross contamination. It was labelled and placed in the vacuum chamber to dry for at least 12 hours.

Once dried, the fibre mat was cut into the required electrode dimensions, as shown in Figure 44. Different methods of sulfur loading, as discussed in Section 9.1.2.5, caused differences in the properties, specifically the brittleness or robustness of the electrode. For this reason, to reduce the risk of damage, square electrodes were cut using a grid method, with a ruler and sharp blade. Cutting the electrodes in straight lines also reduced the impact of crushing or compression around the cut lines, as observed when using the circular punch, which could have influenced the



Figure 42: Electrospun lignin fibre mat after removal from glovebox



Figure 43: Lignin fibre mat after carbonisation



Figure 44: Lignin fibre mat cut into square electrodes

properties of the electrode. The square electrodes were approximately 10mm by 10mm. Before being used for cell manufacture, the electrodes were dried in the glovebox chamber under vacuum at 80°C for approximately 2 hours.

9.1.2.5 Sulfur Content and Loading

If sulfur could not be added during the electrospinning process, other methods of sulfur loading were required. As previously discussed in Section 2.5.3.1, a drop-casting method, also referred to as catholyte, can be used. The concentration and chain length of sulfur species in the catholyte solution can be manipulated to optimise performance. The inclusion of species in a solution also reduces the energy barrier required to dissolve the species, which is likely to increase the achievable capacity for the initial cycles [6]. An alternative method of sulfur loading is sulfur melting, where solid elemental sulfur is melted onto the surface of the positive electrode. When tested experimentally, this process resulted in brittle electrodes which were difficult to handle. It is also an unlikely method for use when considering scaling to larger quantities, or to large cell formats.

Based on these observations, similarly to use with ICFs, the sulfur loading method used was catholyte. The catholyte solution was added to the cell using a pipette to ensure exact quantities, making it easier and more controlled. Once added, various factors could impact the cell performance. For example, the time allowed for the catholyte to absorb into the electrode before full cell assembly could impact the utilisation of sulfur within the pores. The use of a hot plate speeds up the absorption process but can impact the properties of both the electrode and catholyte solution, dependent on the temperature and time. Based on this, and the sublimation that occurs at higher temperatures, it was ideal to weigh the electrodes after the drying step, if used, to ensure accurate measurements [26], [37].

9.2 PyBaMM

Following the submission of the thesis, the latest version of the model was updated to enable it to run in the latest version of PyBaMM (v25.1.1). It has been tested using Python 3.9.13. The details below act as the documentation and include details on installation, set up and use of the model. However, to run earlier iterations of the model that are also available on GitHub, installation of an earlier version is required; this is shown in Section 9.2.1. The GitHub repository is available at <https://github.com/l-olisa>.

9.2.1 Installation (PyBaMM v21.9)

These instructions apply to running the older versions of the model available in the GitHub repository. As discussed throughout the thesis, during various stages of development, the model was unable to run on the latest versions of PyBaMM. The regular updates, to both Python and PyBaMM, also caused differences in the output results across operating systems. To overcome this, a stable version was found and implemented into a virtual environment, to use to develop the models. The step-by-step commands to install on each operating system, using the Command Prompt or equivalent, are shown in this Section.

Running in Mac:

```
apt install python==3.9
python3.9 -m venv env-name
source env-name/bin/activate
python --version
pip install wheel casadi jax jaxlib
pip install pybamm==21.9
pip install jupyter
ipython kernel install --name "env-name" --user
```

Note: if unsuccessful, this installation may require python3, or pip3 versions

Running in Linux:

```
conda create --name env-name python=3.9
conda activate env-name
pip install wheel casadi jax jaxlib
pip install pybamm==21.9
pip install jupyter
ipython kernel install --name "env-name" --user
jupyter notebook % (optional: --browser=firefox, e.g.)
conda deactivate
```

Note: if unsuccessful, this installation may require pip3 version

Running in Windows (*in Anaconda PowerShell Prompt*):

```
conda create --name env-name python=3.9  
conda activate env-name  
pip install wheel casadi jax  
pip install pybamm==21.9  
pip install jupyter  
ipython kernel install --name "env-name" --user  
jupyter notebook
```

Note: if unsuccessful, this installation may require pip3 version

9.2.2 Installation (PyBaMM v25.1.1)

This Section includes instructions to upgrade the older versions of the model available in the GitHub repository to run on the latest version of PyBaMM (at the time of writing, v25.1.1). Further development of PyBaMM since the initial model development, along with focus by the developers to implement existing Li-S models into the later versions, has enabled the models to be run successfully after several modifications. The instructions apply when updating the existing files but could be adjusted for the creation new files.

- 1) Update, or create a model (.py) file, and update the `__init__` file
- 2) Update the model to read in the correct .ipynb file
- 3) Update 'self.set_external_circuit' to 'self.variables'
- 4) Update I variable definition to:
`I = param.dimensionless_current_with_time`
- 5) Update 'self.variables[]' to 'pybamm.Variable()'
Ensure terminal voltage variable added (`V_terminal`)
- 6) Update 'self.variables.update' to 'self.variables' (also removing brackets)
- 7) Remove any timescale and lengthscale terms
- 8) Update 'self.initial.conditions' (remove .update and brackets)
- 9) Update `get_parameter_values()` at top of model (rather than reading in .csv file)
- 10) Update `@property default_parameter_values(self)` (located at the bottom of the script)
- 11) Add any further imports required
- 12) Update to `.parameters.[name of parameter file] import [class in parameter file]` (i.e. add .parameters at top of model)
- 13) Remove minimum and maximum conditions at the end of the model (keep the voltage conditions)

The model should now run in the updated PyBaMM version, ensuring the correct kernel is used.

9.2.3 Overview of GitHub Repository

The folder named ‘Lizzy’ in the repository includes all the scripts (.ipynb files) to run the models and obtain the required outputs. It includes all iterations of the model development, as discussed throughout this thesis. The folder also includes the voltage and capacity results from the experimental data set, to use to compare with model outputs; this information was extrapolated from the voltage-capacity graphs in the publication by Boenke et al. [28], as the raw data was unavailable. The data collected from running the scripts is also saved in this folder. The scripts are set up to run 10 cycles, with 2 cycles at each C-rate, or specified variation.

The folder named ‘models’ in the repository includes all the models created and modified throughout this project. It also includes the initial model, as published by Cornish et al. [3], for reference. The base lithium sulfur model replaces the base model typically used for Li-ion models in PyBaMM, and sets the external variables including voltage, current and capacity. This was not modified from the publication by Cornish et al. [3], other than to enable it to run on a later version of PyBaMM. Each script begins with defining the parameters, some of which are updated when running the script. Each of these parameters are included in the ‘input’ folder and the ‘parameter’ folder, defining the full name and the associated parameter value. The variables are then defined, before introducing the model equations. Comments are included throughout to clearly identify each equation, or group of equations. The model then defines the variables that are constantly updated, along with the initial conditions. Limits are set to prevent the model from running outside of the intended conditions; the formulation of the equations should ensure this does not occur, but the limits are included in the case of numerical errors, or inappropriate parameter selection. The developed models are all ODEs; partial differential equations (PDEs) would be required for higher dimensionality. There are no sub-models used; all information is included in the current model or the base model.

9.2.4 Example

Each of the scripts are named with details of the functionality. For example, `Olisa_2024_POUCH_BP_2_0mgcm2_4_Regions` is the script to run coin-cell parameters for the BP material (as included in Boenke et al. [28]), at a sulfur loading of 2.0mg/cm² and with four regions within the cell (positive electrode, separator, positive electrode reservoir and separator reservoir).

☐	 Olisa_2024_COIN_BP_2_0mgcm2_50wt%_DynamicDiffusion_4_Regions_Shuttled-S_Loss.ipynb	3 months ago	10.4 MB
☐	 Olisa_2024_POUCH_BP_1_0mgcm2_33wt%_4_Regions.ipynb	4 hours ago	48.1 MB
☐	 Olisa_2024_POUCH_BP_1_0mgcm2_50wt%_4_Regions.ipynb	4 hours ago	50.3 MB
☐	 Olisa_2024_POUCH_BP_1_5mgcm2_50wt%_4_Regions.ipynb	4 hours ago	48.2 MB
☐	 Olisa_2024_POUCH_BP_2_0mgcm2_50wt%_4_Regions.ipynb	3 hours ago	49.1 MB
☐	 Olisa_2025_COIN_4_Regions_DynamicElectrolyte.ipynb	3 months ago	993 kB

The first section of the script sets up the details and initialises the model, including importing all the required libraries. It then updates the parameters as required; they are updated here, rather than in the input file, for ease when testing and optimising. Those that do not vary under any conditions are not updated from the input file value. Initial conditions are then verified to ensure consistency.

```
In [2]: import os
os.chdir('../') # ensures use of models folder as python module
# Any figures saved or data pickled in the current working
# directly will be saved up one folder from here.
import pybamm
import models
import numpy as np
import pickle
import pandas
import pandas as pd
import matplotlib.pyplot as plt
from scipy import interpolate
import scipy.integrate as integrate
from scipy.integrate import quad
#from joblib import Parallel, delayed
from IPython.display import clear_output
#from mpl_toolkits import mplot3d
from tabulate import tabulate
import statistics

from multiprocessing import Process
from multiprocessing import Pool
import time
import math

In [6]: #Set current
initial_current = 0 #Units: A

#Set parameters
E_S_ratio = 4 #Units: uL/mg
Ms = 32 #Units: g/mol
MLi = 6.941 #Units: g/mol
ih0 = 2e0 #Units: A
il0 = 2e0 #Units: A

R = pybamm.constants.R.value #Units: #J mol-1.K-1 (Gas Constant)
T = 303.15 #Units: K
nH = 4
nL = 6
iH_coef = nH * F / (2 * R * T)
iL_coef = nL * F / (2 * R * T)
EH0 = 2.35 #Units: V
EL0 = 2.05 #Units: V
ns8 = 8
ns4 = 4
ns1 = 1
nsli = 2

voltage_low_cut = 1.9 #Units: V
voltage_high_cut = 2.6 #Units: V

print('Number of Layers in Pouch Cell:', number_layers)

geom_area = 0.003266*number_layers
print('Geometric Area [m2]:', geom_area)
```

The simulation details are then set up; adaptive time stepping is used, and errors appear when conditions are not met for the model to run. This is followed by reading in the updated parameters for each charge and discharge, to ensure the parameters are correctly updated at each cycle. The tolerances are set and adjusted here, along with the cut-off time and capacity for each cycle. The solver used is Casadi, but there are various other solvers that can be used or trialled [122]. The experimental data from Boenke et al. [28] is read in to make comparisons.

```
time = 0
sim.step(0.0002)
time += 0.0002
clear_output()

while time < time_in_seconds:
    try:
        sim.step(5)
        time += 5
        clear_output()
    except:
        clear_output()
        try:
            sim.step(.03)
            time += .03
            clear_output()
        except:
            print('Smallest time step reached!')
            break

return sim

# Instantiate the model
model = models.Olisa2024_Nucleation_Growth_DynamicDiffusion_4_Regions_Modified_0D()

# Obtain model parameter dictionary
param = model.default_parameter_values

# Base parameters for this series of simulations
param.update(
    {
        "Current function [A]": initial_current,
        "Initial Condition for S8 ion [g]": S8_initial,
        "Initial Condition for S4 ion [g]": S4_initial,
        "Initial Condition for S ion [g]": S1_initial,
        "Initial Condition for Nucleated Precipitated Sulfur [g]": Sp_initial_nuc,
        "Initial Condition for Growth Precipitated Sulfur [g]": Sp_initial_growth,
        "Initial Condition for Li ion [g]": Li_initial,

        "Cathode reservoir S8 initial mass [g]": S8_cath_r_initial,
        "Cathode reservoir S4 initial mass [g]": S4_cath_r_initial,
        "Cathode reservoir S1 initial mass [g]": S1_cath_r_initial,

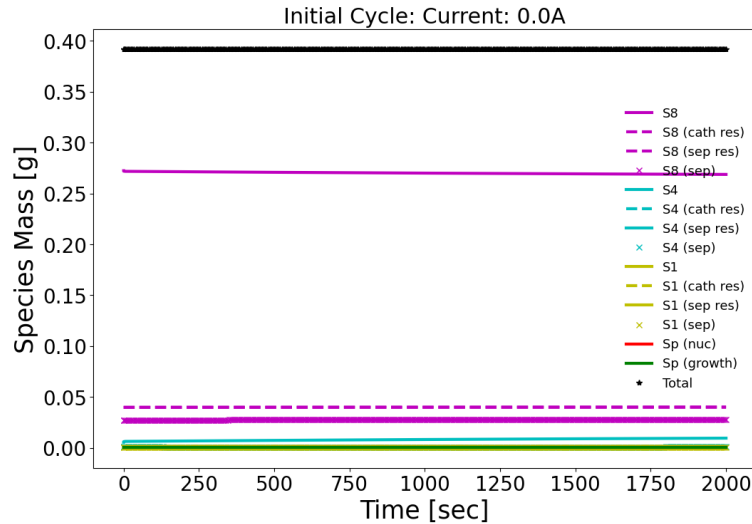
        "Separator reservoir S8 initial mass [g]": S8_sep_r_initial,
        "Separator reservoir S4 initial mass [g]": S4_sep_r_initial,
        "Separator reservoir S1 initial mass [g]": S1_sep_r_initial,

        "Separator S8 initial mass [g]": sep_S8_initial,
        "Separator S4 initial mass [g]": sep_S4_initial,
        "Separator S1 initial mass [g]": sep_S1_initial,
    }
)

# Instantiate simulation object
sim_dis_0A = pybamm.Simulation(
    model,
    parameter_values = param,
    solver=pybamm.CasadiSolver(
        atol= 1e-6,
        rtol= 1e-6,
        extra_options_setup={"max_step_size": 0.01},
    ),
)
target_capacity = hyper_params['capacity target [Ah]']
current = params['Current function [A]']
target_time_in_seconds = 2000
sim_dis_0A = run_simulation(sim_dis_0A, time_in_seconds = target_time_in_seconds)

return sim_dis_0A
```

The first cycle run is the 0A cycle. The main purpose of the output plots is to investigate how the species change during ‘rest’, caused by chemical reactions only (shuttle, diffusion and the precipitation dynamics).



Conditions for the following cycles are then set up, including the currents and corresponding C-rates. The final conditions, including the species distribution, from the end of the previous cycle become the input conditions for the following cycle, allowing the model to capture the history effect. The script then runs three discharge and charge activation cycles, at the lowest current. As discussed in the thesis, these are designed to obtain stable initial conditions before standard cycling occurs. Unlike in a real cell, these have no relation to SEI formation, or other changes that are hypothesised to occur. Following the activation cycles, the cell then runs 10 standard cycles, with 2 cycles at each C-rate. The conditions at the end of the third activation cycle are set as the global initial conditions; these are used when the C-rate is increased to ensure behaviour is due to that C-rate only, with no history from the previous C-rate tested.

Setting Global Initial Conditions

```
In [88]: S8_initial_global = sim.solution['S8 concentration [moles.L-1]'].entries[-2]*Ms*ns8*v
S4_initial_global = sim.solution['S4 concentration [moles.L-1]'].entries[-2]*Ms*ns4*v
S1_initial_global = sim.solution['S1 concentration [moles.L-1]'].entries[-2]*Ms*ns1*v
Sp_initial_nuc_global = sim.solution['Sp nucleation concentration [moles.L-1]'].entries[-2]*Ms*ns1*v
Sp_initial_growth_global = sim.solution['Sp growth concentration [moles.L-1]'].entries[-2]*Ms*ns1*v
Li_initial_global = sim.solution['Li concentration [moles.L-1]'].entries[-2]*MLi*nsli*v

S8_initial = S8_initial_global
S4_initial = S4_initial_global
S1_initial = S1_initial_global
Sp_initial_nuc = Sp_initial_nuc_global
Sp_initial_growth = Sp_initial_growth_global
Li_initial = Li_initial_global

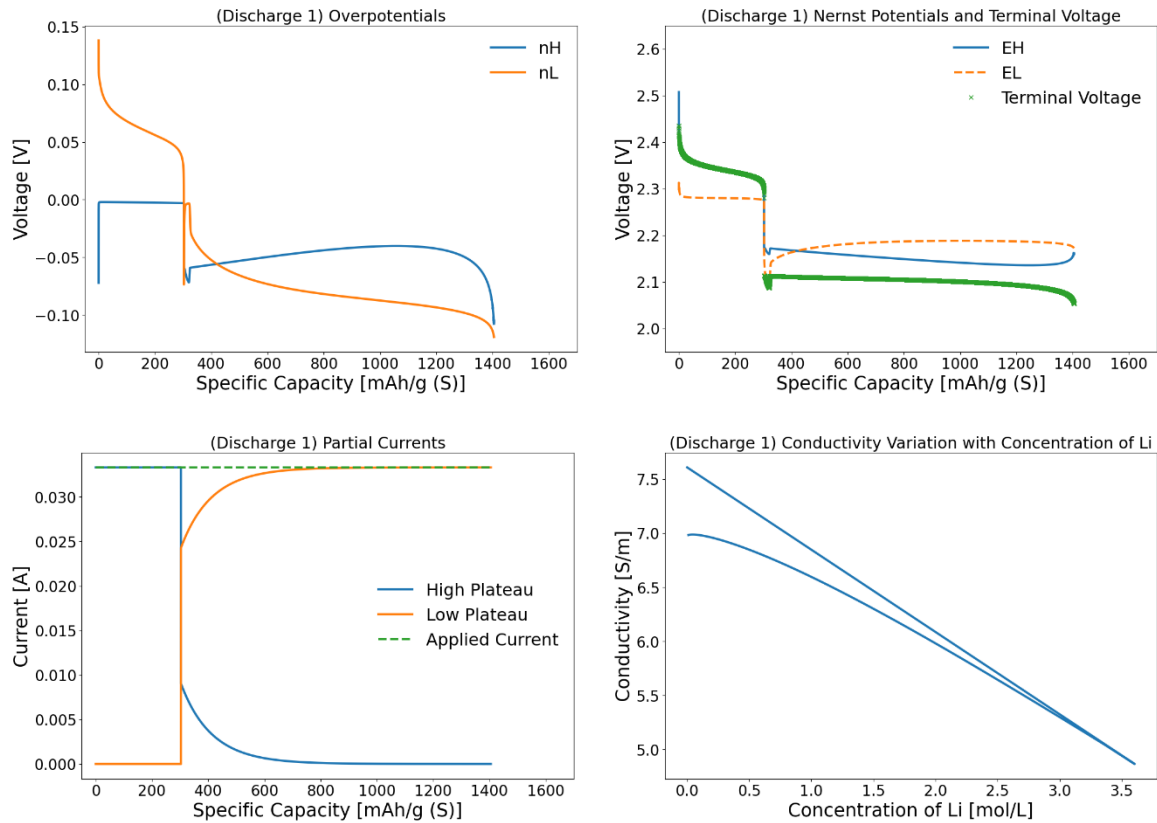
print('S8 Initial: ', S8_initial)
print('S4 Initial: ', S4_initial)
print('S1 Initial: ', S1_initial)
print('Sp Nucleation Initial: ', Sp_initial_nuc)
print('Sp Growth Initial: ', Sp_initial_growth)
print('Li Initial: ', Li_initial)

S8_cath_r_initial_global = sim.solution['S8 cathode reservoir concentration [moles.L-1]'].entries[-2]*Ms*ns8*v_cath_r
S4_cath_r_initial_global = sim.solution['S4 cathode reservoir concentration [moles.L-1]'].entries[-2]*Ms*ns4*v_cath_r
S1_cath_r_initial_global = sim.solution['S1 cathode reservoir concentration [moles.L-1]'].entries[-2]*Ms*ns1*v_cath_r

S8_cath_r_initial = S8_cath_r_initial_global
S4_cath_r_initial = S4_cath_r_initial_global
S1_cath_r_initial = S1_cath_r_initial_global

print('S8 (r) Initial: ', S8_cath_r_initial)
print('S4 (r) Initial: ', S4_cath_r_initial)
print('S1 (r) Initial: ', S1_cath_r_initial)
```

Each cycle includes plots relating to at least the voltage and capacity, voltage and specific capacity, mass and concentration distribution of all species, surface area, electrolyte resistance, conductivity and voltage variation and partial currents. Some cycles include other variations when specific behaviour is being investigated in detail. At the end of the 10 cycles, this information is compared to analyse the behaviour changes under all the varying conditions. *Within this thesis, only relevant plots relating to the discussed behaviour are included.*



In the scripts, only the C-rate is varied. However, any included parameter could be varied to test the behaviour. Alternatively, new parameters or variables could be introduced and tested, for example, the impact of temperature variation. This would require the introduction of new mechanisms, building upon the model's capability.