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Mathematical Modeling of Lithium-Sulfur Batteries

Niloofer Kamyab

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MATHEMATICAL MODELING OF LITHIUM-SULFUR BATTERIES

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DEDICATION

To my mother, who stood by my side when seeing the light at the end of the tunnel seemed like an illusion.

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My deep gratitude goes to my Ph.D. advisor, Prof. Ralph White, for his unwavering support, guidance, and encouragement throughout the journey. He made me believe in myself and taught me perseverance is the key to success in every endeavor. I also greatly appreciate my fellow research group members, Dr. Coman, Shiv Krishna Maddy Reddy. Without their help and support along the way, this would not have been possible.

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ABSTRACT

Energy storage market transformed by utilization of lithium-ion batteries, will demand high and affordable deliverable energy in the near future which it would be impossible for the current employed technologies to meet those needs. Among new generation of lithium batteries, high theoretical energy density, good low-temperature performance, and abundance of inexpensive nontoxic raw material, make the lithium-sulfur batteries (LiS) a promising candidate to outperform the current lithium-ion batteries and transform the technology of the future. However, the problems and challenges that LiS batteries are currently facing with, which stem from the inherent complex mechanism of these cells, are hindering their successful development, commercialization, and implementation.

In this regard, mathematical models can be used as a powerful tool to provide a better mechanistic understanding, address the issues and challenges, clarify the existing misconceptions and guide experimental studies toward an optimum configuration and performance. In the present research study, different aspects of the performance of LiS cells including lithium capacity loss, multicomponent transport, phase change and precipitation, porosity and volume change of the cathode, and the shuttling process are thoroughly studied through proposing mathematical models to gain a mechanistic understanding of the phenomena occurring inside the cell. First, the focus will be on the anode side of the cell and developing a mechanistic model for the solid electrolyte

interphase (SEI) growth on the anode surface. As dissolution, diffusion, and shuttling of the dissolved polysulfides result in parasitic reactions and substantial capacity loss for LiS cells, in the second step and in order to study the shuttling phenomena as the main performance issue and source of capacity loss of the LiS cells, a 1D porous electrode model is developed for the entire LiS cell which uses a semi-empirical loss approximations for the shuttling induced capacity fade mechanism to dig deeper into the underlying mechanism and investigate this process. Finally, by focusing on the future of the LiS cells, a simple lumped model with minimum number of parameters is proposed and developed based on the idea of having an empirical state of charge (SOC) expression for the LiS cells.

TABLE OF CONTENTS

DEDICATION	iii
ACKNOWLEDGMENT.....	iv
ABSTRACT	v
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF SYMBOLS	xii
LIST OF INDEXES	xv
CHAPTER 1: INTRODUCTION	1
1.1 Energy Market	1
1.2 Mechanism and Challenges	5
CHAPTER 2: LITERATURE REVIEW	12
2.1 LiS Modeling Literature Review	12
2.2 Present Research Study	16
CHAPTER 3: MIXED MODE SEI GROWTH MODEL.....	21
3.1 Introduction.....	21
3.2 Results and Discussion	30
3.3 Conclusion and Future Directions	35
CHAPTER 4: SHUTTLING INDUCED MODEL.....	48
4.1 Electrochemical/ Chemical Reactions	48
4.2 Model Development	52

4.3	Results and Discussion	61
4.4	Conclusions and Future Directions	66
CHAPTER 5: STATE OF CHARGE LUMPED MODEL		77
5.2	Model Development	80
5.3	Results and Discussions	81
5.4	Conclusion and Further Developments	82
BIBLIOGRAPHY		87

LIST OF TABLES

Table 3.1. Published and assumed characteristics	46
Table 3.2. Model Parameters	47
Table 4.1. Kinetic and Thermodynamic Properties ^[16]	73
Table 4.2. Transport Properties and Reference Concentrations ¹	74
Table 4.3. Separator and Cathode Parameters	74
Table 4.4. Parameters for Precipitation Reactions ^[16]	74
Table 4.5. Stoichiometric coefficients ^[16]	75
Table 4.6. List of remaining parameters	76
Table 5.1. Model parameters for SPAN cells	86

LIST OF FIGURES

Figure 1.1. Historical evolution of lithium-ion battery.....	9
Figure 1.2. (a) A schematic of Li-S cells	10
Figure 1.3. Typical discharge and charge performance of a LiS cell ^[13]	10
Figure 1.4. Challenges facing the LiS battery ^[4]	11
Figure 2.1. Comparison of topics addressed in research articles.....	20
Figure 3.1. Schematic of the formation of the SEI	38
Figure 3.2. Data for HE prototypes and Sanyo cells.....	39
Figure 3.3. Measured and simulated capacity loss	40
Figure 3.4. Measured and simulated capacity loss for different ϵ	41
Figure 3.5. Solvent concentration versus SEI thickness	42
Figure 3.6. Solvent concentration at the electrode surface	43
Figure 3.7. SEI thickness as function of time	44
Figure 3.8. Analytical SEI thickness as a function of time.....	45
Figure 4.1. Sketch showing the potential proposed reaction pathway.....	67
Figure 4.2. Sketch showing the components of a typical LiS cell.....	67
Figure 4.3. Comparison between the model and the experiments.	68
Figure 4.4. Concentration profiles of different species.....	69
Figure 4.5. Plots showing the concentration of S8(l)	70
Figure 4.6. Plots of volume fractions for the no-shuttling case	70

Figure 4.7. Cycling voltage data with and without shuttling.....	71
Figure 4.8. Cycling voltage data with and without shuttling.....	72
Figure 4.9. Concentration profiles of species with shuttling	73
Figure 5.1. Different sulfur electrochemitsry	84
Figure 5.2. Discharge predictions for SPAN	85

LIST OF SYMBOLS

A_{anode}	Anode surface area, m^2
a	Specific surface area, m^{-1}
a_0	Initial value of specific surface area, m^{-1}
b	Bruggeman coefficient, ($b = 1.5$)
c_p	Molar concentration of the product (P), mol m^{-3}
C_S^0	Bulk solution concentration, mol m^{-3}
$C_{\text{Li, max}}$	Maximum concentration of the lithium in the anode, mol m^{-3}
C_i	Concentration of species i , mol m^{-3}
$C_{i,\text{ref}}$	Reference concentration of species i , mol m^{-3}
$D_{i,\text{eff}}$	Effective diffusion coefficient of species i , $\text{m}^2 \text{s}^{-1}$
D_i	Diffusion coefficient of species i in the bulk medium, $\text{m}^2 \text{s}^{-1}$
E_{eq}	Equilibrium potential of the electrode, V
F	Faraday constant, $96485 \text{ sA mol}^{-1}$
I_{app}	Applied current density, A m^{-2}
i_l	Current density in the liquid phase, A m^{-2}
i_j	Current density due to reaction j , A m^{-2}
$i_{j0,\text{ref}}$	Exchange current density of electrochemical reaction j , A m^{-2}
i_s	Current density in the solid phase, A m^{-2}
k_k	Rate constant of species k , units vary
$K_{\text{sp},k}$	Solubility product of species k , units vary

k_{SEI}	Rate constant of the solvent reduction reaction, m s^{-1}
J_{SEI}	Rate of the solvent reduction reaction, $\text{mol m}^{-2}\text{s}^{-1}$
L	SEI thickness, m
L_{c}	Thickness of the cathode, m
L_{s}	Thickness of the separator, m
L^0	Initial SEI thickness, m
L^*	Characteristic SEI thickness, m
M_{P}	Molecular weight of the product (P), $73.89 \text{ gr mol}^{-1}$
N_0	Initial number of moles of lithium ions, mol
$N_{\text{i,m}}$	Superficial flux of species i, $\text{mol m}^2 \text{s}^{-1}$
n_{j}	Number of electrons transferred in electrochemical reaction j
$p_{\text{i,j}}$	Anodic reaction order of species i in electrochemical reaction j
$q_{\text{i,j}}$	Cathodic reaction order of species i in electrochemical reaction j
P	Product formed as a result of the solvent reduction reaction
R	Gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
R_{i}	Production rate of species i due to precipitation reactions, $\text{mol m}^3 \text{s}^{-1}$
R_{cell}	Cell resistance, Ω
r_{i}	Production rate of species i due to electrochemical reactions, mol m^3
R_{k}	Rate of precipitation of solid species k, $\text{mol m}^3 \text{s}^{-1}$
$s_{\text{i,j}}$	Stoichiometric coefficient of species i in electrochemical reaction j
SOC	State of charge
t	Time, s
t^*	Characteristic SEI growth time, s

T	Temperature, K
U_j^0	Standard OCP of electrochemical reaction j , V
U_{SEI}	Equilibrium potential of the solvent reduction reaction, V
V_k	Molar volume of the species k , $\text{m}^3 \text{mol}^{-1}$
v	Mass average velocity, m/s
x	Fractional capacity loss
z	Coordinate direction normal to the anode, m
Z_P	Number of atoms of lithium in the product (P)
z_i	Charge number of species i

LIST OF INDEXES

i	Index corresponding to different species
m	Index corresponding to separator and cathode (m = sep or cat)
k	Index corresponding to solid state species ($k=S_{8(s)}$, $Li_2S_{(s)}$)
j	Index corresponding to the number of reactions

CHAPTER 1

INTRODUCTION

1.1 Energy Market

The trend of market protrusion of batteries increases almost exponentially every year, and it is therefore important to work on improving the battery systems, especially in an era where petroleum dependency can make society fragile in case of a crisis globally. The field of electrochemical engineering seems to receive growing attention in the recent years as today not only United States but also the world faces energy challenges on two main frontiers: shifting electricity production from burning fuel to sustainable energy sources, and moving ground transportation towards electrical propulsion, namely, using electric vehicles (EVs) instead of cars driven by internal combustion engines (ICEs).

The sources of sustainable energy fluctuate during the day and hence, the use of sustainable energy for electricity production requires the availability of suitable technology for energy storage, namely, batteries. Although we have seen very impressive progress in recent years in the development of technology for harvesting sustainable energy, e.g., better wind turbines, photothermal receivers, and photovoltaic cells, the development of storage devices are still lagging far behind. Another important requirement of modern society is to reduce the use of oil for transportation as quickly as possible due to very limited resources.

According to the report released by the U.S. Department of Energy's Energy Information Administration (EIA) in 2019, in just the first half of 2019 alone, we have seen more than 1.4 billion dollars invested in battery technologies in the United States. According to the report, the total investment in battery manufacturing, both previous and planned, until 2023, represents around 150 billion dollars. What's more is that projections of the advancement that these investments can drive are not linear. What that means is that as the capital cost for new planned battery manufacturing capacity drops technologies become cheaper and that money can drive even greater adoption. These projections, along with the 2.5 GW of battery storage Predicted by the US departments of energy to be on-line by 2023 portray a rapidly changing energy future. To date, the United States has only completed 899 MW of operating battery storage. From the end of 2014 to this past March, the volume of installed battery storage increased more than four times from 214 MW to 889.

As batteries are the heart of an EV and any other device using batteries as their power source, the development of novel and advanced rechargeable batteries that can safely store sustainable energy with long term stability, very prolonged cycle life, and meeting environmental constraints is an important challenge for modern electrochemistry. The revolution of all the applications which they use batteries in some way, depends on the Research & Development success of new generation batteries possessing the necessary qualification. Consequently, many research groups and industries throughout the world work intensively towards developing new strategies for improving the current battery technologies and exploring different alternative battery chemistries to meet the future energy need.

1.1.1 Lithium-Ion Batteries

Lithium-ion batteries as one of the most popular energy storage devices for their high energy density, enhanced rate capabilities, superior safety features, and environmental suitability and can be considered to be the most impressive success story of modern electrochemistry in the last two decades. They power most of today's portable devices and seem to overcome the psychological barriers against the use of such high energy density devices on a larger scale for a variety of applications ranging from small portable devices to large grid applications, aerospace devices, and the next generation of automotive applications.

The study of lithium-ion cells is currently of huge scientific and technological interest because although, lithium-ion battery technology has gained a significant market share as the principal energy storage solution for many industrial applications. Every year more and more electric vehicles are released into the market and Li-ion batteries have protruded in almost every application that requires electrical power. The trend of market protrusion of Li-ion increases almost exponentially every year, and it is therefore important to work on improving the battery systems.

However, their performance is known to decline over time and use and also safety is another important concern that needs to be thoroughly investigated to keep the battery and users safe from potential hazards[1]–[5]. Also, the high cost and limited mileage of present lithium-ion powered cars are due to the intrinsic limited capacities of the lithium-ion insertion cathodes, which are nearing their practical limits and even a two-fold increase

in energy density of current lithium-ion cells is insufficient for the long-term demands of transport and electricity storage [6].

In other words, energy storage market transformed by utilization of lithium ion batteries, will demand high and affordable deliverable energy in the near future which it would be impossible for the current employed technologies to meet those needs [7] Hence, for a wide deployment of EVs and maximizing electrification of the road transportation system, drastic improvements in today's battery pack performance is needed. As it can be seen in Figure 1.1, although lithium-ion technology introduced in late 90s has taken a long journey of improvements and modifications through extensive research endeavors, since 2010 researchers have started exploring other chemistries such as lithium-air and lithium-sulfur cells to replace the current lithium-ion battery technologies to achieve the goal of employing safer and cheaper batteries with higher energy and power densities.

1.1.2 Lithium-Sulfur Batteries

Among new generation of lithium batteries, high theoretical energy density ($\sim 600 \text{ Wh Kg}^{-1}$) that may be 4-5 times higher compared to that of Li-ion batteries, good low-temperature performance, and abundance of inexpensive nontoxic raw material, make the lithium-sulfur batteries (LiS) a promising candidate for major energy applications. Due to their high energy density, LiS batteries have the potential to outperform the current lithium ion batteries and transform the technology of the future [8]. Such batteries can significantly increase the current mileage, from a maximum of 600 miles (the most performant EV) or approximately 300-400 in average to more than one thousand miles on a single charge. Considering the fact that “Range Anxiety” is one of the main barriers to the developments and widespread implications of EVs, highlights the importance of this matter even more.

This means that the implementation of long-lasting LiS cells will revolutionize the electrical mobility and portability.

However, short lifetime (200 – 300 cycles) of LiS cells is hindering their successful development, commercialization, and implementation, and it is critical to push the advancement of such batteries as soon as possible. The problems and challenges that LiS cells are currently facing with, stem from the inherent complex mechanism of these cells which include various electrochemical and chemical reactions, transport phenomena, precipitation and porosity and volume change. Hence, in the next section, we dive into the explaining the structure and operation manner of these cells to gain better understanding of the underlying mechanism which gives rise to the current LiS performance issues.

1.2 Mechanism and Challenges

1.2.1 Mechanism

A LiS cell as shown in Figure 1.2, is consisted of a lithium metal strip as the anode and the cathode consists of insulating sulfur (present as cyclo-S₈ rings) embedded into a conducting carbon host. The cell operates by reduction of sulfur at the cathode on discharge which results in production of different polysulfides. S₈(l) reduces to S²⁻ in steps and through a set of consecutive reactions. The details of this cascade reactions and the exact reaction mechanism is not known yet and some experimental evidence strongly suggests that the reaction pathway for charge and discharge might be different [9]. The complex redox chemistry of sulfur on the cathode side of the lithium sulfur batteries, makes the understanding of the cell performance challenging.

The overall reaction in a lithium-sulfur cell ($\text{S}_8 + 16 \text{Li} \leftrightarrow 8 \text{Li}_2\text{S}$) is highly reversible with a potential of ~2.15 V versus Li/Li⁺. Although the voltage of LSBs is

relatively lower than LIBs (3.4-3.8 V vs. Li/Li⁺), sulfur has the highest specific capacity for a solid electrode material at 1675 mAh g⁻¹ and consequently a LiS cell has a theoretical energy density of 2500 Wh kg⁻¹ which makes them a great candidate for EVs and other applications

As shown in Figure 1.3, a typical LiS cell discharge/charge curve consists of a sloping high plateau voltage, a flat low plateau voltage, and a voltage dip in between. The shape of voltage- capacity curve depends on the solubility of the intermediate polysulfides. During discharge, in the first part (2.45-2.1 V), the voltage drop is significant and high order polysulfides (x=6,8, and 4) are produced. Whereas, in the second part (~2.1 V) the voltage is almost constant and low order of polysulfides are generated. Simultaneous production and consumption of lower polysulfide (S⁻²) flatten the second part of the voltage curve. The theoretical capacities for the higher and lower voltage plateaus are 419 mAh g⁻¹ and 1256 mAh g⁻¹, respectively. In order to understand the voltage curve, we need to obtain a good understanding of the complex interaction between electrochemical and chemical reactions occurring inside the cell during discharge and charge.

1.2.2 Challenges

LiS batteries, as future candidates to outperform current lithium ion batteries and transform the battery technology, as shown in Figure 1.4 suffer from different challenges which hinder their successful development, commercialization and implementation and limit their current application to UAVs, space applications, robotics and defense applications where the lightness and high energy is more important than life cycle. As mentioned earlier, Cyclo-S₈ undergoes a series of structural and morphological changes during the charge-discharge process involving the formation of soluble lithium

polysulfides Li_2S_x ($8 \leq x \leq 3$) and insoluble polysulfides., $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ in the liquid electrolyte (see Figure 1.2).

Soluble polysulfides shuttle between the anode and cathode during the charge process involving side reduction reactions with the lithium anode and re-oxidation reactions at the cathode. The so-called shuttle mechanism involved in the charge-discharge of LiS is as follows: i) formation of soluble polysulfides at the cathode, ii) polysulfides transport to the anode through the electrolyte, iii) reduction of polysulfides to lower polysulfides (see Figure 1.2), and iv) return to the cathode for re-oxidation. However, the undesired redox reactions in steps iii) and iv) produce insoluble Li_2S_2 or Li_2S , which precipitate onto the electrodes leading to increased resistance and volume change of the cathode. The insulating nature and poor intrinsic conductivity of sulfur ($5 \times 10^{-30} \text{ S cm}^{-1}$ at 25°C) and solid reduction product, Li_2S leads to the poor electrode conductivity and reachability and rate capability issues.

Another major issue with intercalation/ de-intercalation S-cathodes is the volume expansion. Upon the insertion of lithium ions, electrodes containing sulfur are known to more than double their volume possibly leading to cracks and delamination of the cathode. Furthermore, the deposition of insoluble polysulfides such as Li_2S leads to 80% volume expansion compared to solid S. In this regard, the cathode porosity and architecture must be carefully designed to accommodate these volume changes without compromising the performance in terms of energy density. Overall, the structural changes and increased internal resistance result in a low utilization of active material, poor cycle life, and low system efficiency.

Regardless of the complexities of the chemical and electrochemical reactions on the cathode side, and the shuttle processes in the electrolyte, the anode/ electrolyte interface is poorly controlled and limits the cycle life of the lithium sulfur cells. Although, use of Li metal anodes allows high energy densities in rechargeable batteries, but the interface of the lithium metal and the electrolyte can be a major source for capacity loss and cell degradation. During the first charge of the battery, a passivating layer, called the “Solid-Electrolyte Interphase or SEI”, forms on the surface of the electrodes as a result of reaction between electrode and electrolyte. Ideally, the SEI layer prevents further electrolyte degradation by blocking the electron transport through it while concomitantly allowing the transport of lithium ions. However, the solvent continuously diffuses through the layer and gets reduced on the anode which results in the continuous thickening of the SEI layer and major capacity loss since the layer traps the active and cyclable lithium ions.

Also, another challenge that all the cell chemistries with lithium metal as anode are facing with, is the dendrite formation and propagation which occurs during the electrochemical plating-stripping process and can lead to the increase in irreversible capacity loss, reduce the columbic efficiency (CE), drying the electrolyte, and most importantly, piercing through the battery separator and short-circuiting of the cell.

Significant research studies by many groups of researchers have been done in the past and have attempted to understand and capture the important aspects of LiS cells to address the current issues and improve their overall performance. In the next chapter, by reviewing these works and focusing on the modeling and theoretical studies, the motivation, scope, steps, and proposed models of the present research study will be discussed.

Figure 1.1. Historical evolution of lithium-ion battery.

Figure 1.2. (a) A schematic of Li-S cell showing the charge (red)/discharge (black) processes. (b) Charge/discharge processes are accompanied by the formation of soluble lithium polysulfides or LiPS (Li₂S₈, Li₂S₆, Li₂S₄, and Li₂S₃) and insoluble Li₂S₂/Li₂S [10].

Figure 1.3. Typical discharge and charge performance of a LiS cell [11].

Figure 1.4. Challenges facing the LiS battery [8]

CHAPTER 2

LITERATURE REVIEW

2.1 LiS Modeling Literature Review

Theoretical modeling plays crucial role in the exploration of the phenomena happening in the LiS cells. The complexity of the lithium sulfur chemistry induces a large number of parameters which need to be identified to characterize the cell and the difficulty and infeasibility of experimentally measuring some of these parameters, highlights the importance of mathematical models as a powerful tool to provide a better mechanistic understanding of the complex phenomena occurring inside the cell, address the issues and challenges, guide experimental studies toward an optimum configuration and performance, and clarify the existing misconceptions. For instance, a misconception that can be found in the open literature when referring to shuttling. That is, in some relevant papers such as the one in Ref. [11], it is stated that shuttling effect causes continuous anode corrosion during operation. This cannot be correct because the anode becomes cathodically protected during operation, but it is true during self-discharge. This implies that the shuttling mechanism is also dependent on the operating regime, whether it is charging, resting, or discharging.

Several modeling studies have attempted to provide a mechanistic study and capture important aspects of LiS behavior through proposing zero dimensional (0D), one

dimensional (1D) and higher dimensional models which will be reviewed in the following sections.

2.1.1 Lumped models

Several modeling studies have attempted to capture important aspects of lithium sulfur behavior also through proposing fast zero-dimensional models (OD) or lumped models. The lumped models are powerful tools which can be used to guide higher dimensional models but lack the in-depth control of the design parameters and kinetics. In attempt to study the shuttling effect and resulting heat generation via a constant shuttle rate, a zero-dimensional Nernst description model was developed by Mikhaylik et al. [12] A two-step reaction pathway was considered for the high and low plateau of the discharge curve in which elemental sulfur converts to the different polysulfides. They assumed fast kinetics for the reactions and developed two Nernstian equations to describe the potential of cell for each region including charge-discharge current and shuttle phenomena. In addition to this, they report that the total high plateau polysulfide dynamic could be expressed using a formulation that contains a heterogeneous reaction constant or a shuttle constant. Such an approximation can lead to the development of a higher-scale mathematical modeling of shuttling.

The modeling team from Imperial College London brought a strong contribution concerning lumped modeling of LiS. Marinescu et al.[9] extended Mikhaylik's et al. [12] model by adding the voltage-over-potential relation (kinetics limitation) and precipitation and nucleation via a constant precipitation rate including nucleation and the effect of a saturation concentration. They introduced a similar degradation mechanism, by allowing a fraction of the shuttled polysulfide to become permanently inactive, leading to capacity

fade. Zhang et al. [13] developed a lumped model that includes precipitation and kinetics of the reactions and takes into account for the concentration dependency of electrolyte resistance. They extended the reaction mechanism to include all the generated polysulfide (S_n^{-2} ($n=0,2,4,6,8$)). Therefore, their model considers six electrochemical reactions for the cathode side.

2.1.2 Higher scale models

Significant modeling work was done on higher scales in the past by many groups of researchers. The model pioneered by the PI's battery group was published by Kumaresan et al. [14] using the porous electrode theory. The model predicts the voltage profile characteristic to these types of batteries and provides a good analysis of the time and one-dimensional spatial distribution and precipitation of polysulfide species. The model was used as a guideline for several noteworthy modeling works, but this particular model only considers the discharge process and no capacity loss. Ghaznavi et al. [15]–[17] carried out a sensitivity analysis, demonstrating that Kumaresan's model yields some numerical issues when modeling charging and that it needs further developments because the precipitation expression does not reproduce re-dissolution of Li_2S upon charging. Their study indicated that transport affects the predictions of the Kumaresan model only if the diffusion coefficients get reduced by more than two orders of magnitude. However, the study is focused only on discharge and does not include charge or capacity fade.

Following Ghaznavi's et al. analysis, Zhang et al [18], developed a 1D model based on the framework introduced by Kumaresan to study the transport limitations during discharge and analyze the capacity recovery at different rates. They concluded that with low ionic diffusion, the trapped polysulfides in the separator might lead to the

experimentally observed reduction of the low-plateau capacity at high discharge rates. However, no charging process or cycling was included in their study. Ren et al. [19] focused only on discharge but provided a one-dimensional model by incorporating the surface nucleation and growth dynamics to study the precipitation of Li_2S . They studied the rate-dependency of precipitation phenomena and showed the growth of precipitated Li_2S particles as the final discharge product and compared the active material loss with experimental data. Even though there are some differences between experiments and model results, the authors observed that increasing the discharge rate leads to a higher active material loss both experimentally and numerically, demonstrating that material loss is an important phenomenon to model.

Charging process was included by Hofmann et al. [20], which assumed a simplified reaction mechanism by including two-steps redox reactions and a chemical precipitation reaction on the cathode side in their 1D model. Their framework is more flexible for modeling multiple phases (Solid/liquid/gases) in batteries and fuel cells. For example, in Li-O_2 battery and SOFC where multi-phase management can be tedious, as systems of rate equations need to be implemented manually. However, these frameworks are particularly not useful for integrating multi-step electrochemical reaction mechanisms and 2D/3D transport on structurally complex domains. Hence, they have assumed a simplified reaction mechanism by including two-steps.

Hofmann et. al. [20] were the first authors to introduce an anode study domain for studying shuttling. They also showed that the volume fraction of Li_2S precipitate increases on the anode with each cycle, indicating that precipitation of lithium sulfide in the anode can cause the capacity to drop. Although their model is a very good contribution to the

field, they included Butler-Volmer equations both at anode and cathode but only for a simplified reaction mechanism. In addition to this, they are using extremely small values for the reaction constants (See Table 2 in Ref. [20]) which require special numerical solvers or advance solver settings for dealing with the numerical instabilities. In addition to this, a good fit to the discharge experimental measurements is shown at low currents but fails to provide a satisfactory fit at higher rates. Yoo et al. [21] also focused on both discharge and charge processes by extending the precipitation/dissolution expressions in Kumaresan's model. They showed that the model can predict capacity loss, but it cannot be replicated, and the physics are not fully modeled using kinetics at the anode.

Moy et al. [22] developed a simplified 1D model which aimed to predict the capacity fade caused by shuttling. They show that shuttle current measurements can be used to predict capacity fade in Li-S, but although their model provides a good fit to the shuttle rate measurements, it is limited to the constant voltage mode and the model is overly simplified. Danner et al.[23] presented a pseudo-2D model using the framework of the classical theory of nucleation and growth (CNG) and, in contrast to the precipitation model proposed by Ren et al. [19] treated the electrochemical reactions and the particle nucleation and growth as individual processes, separating the reduction/oxidation of polysulfides and particle growth. However, the model fails to provide a suitable fit to the charge measurements.

2.2 Present Research Study

In order to address these issues and improve the performance of LiS cells, conducting experimental and modeling research studies in recent years have become increasingly important. A perspective review study which categorized 1524 related articles

published until May 2017 based on the topics addressed in these studies [24], concluded that although a wide range of experimental researches have investigated novel strategies, material and designs for the cells (papers published per year has increased dramatically from less than 50 in 2010 to over 900 in 2016), the mathematical and theoretical studies are scarce (9%) and focusing only 2% of the research studies on the anode, makes it a neglected research area, as shown in Figure 2.1[24].

Most of the previous research work was focused on the cathode for solving the issue of low-electric-conductivity of LiS and the polysulfide shuttling at the cathode, which pushed the field significantly, Despite this, almost all the papers acknowledged the importance of studying the anode and recommended the studies, but for some unknown reasons it was neglected by many. The numerical issues which arise due to the low concentration of polysulfides on the anode surface and the lack of previous comprehensive models impeded the advancement of this field.

None of the existing models has included all the known features of the LiS performance and involved degradation mechanisms. Therefore, a good mechanistic understanding of LiS degradation is lacking due to limited number of modeling and characterization studies. Also, all the existing degradation models only take into account the loss of sulfur species due to the precipitation and shuttling and fail to consider the capacity loss due to the SEI growth on the anode. To the best of our knowledge, there is no mathematical model that focuses on the anode side of the lithium sulfur cell to directly study three main phenomena occurring on the anode surface including the SEI growth.

In the present research study, different aspects of the performance of LiS cells including lithium capacity loss, multicomponent transport, phase change and precipitation

leading to porosity change of the cathode, and the shuttling process as the main capacity loss mechanism are thoroughly studied through proposing mathematical models to gain a mechanistic understanding of the phenomena occurring inside the cell. First, the focus will be on the anode side of the cell and developing a mechanistic model for the solid electrolyte interphase (SEI) growth on the anode surface which the details of this model are elaborated in chapter 3.

A mixed mode SEI growth model is presented that includes both the influence of the kinetics of the solvent reduction reaction at the SEI/electrode interface and diffusion of the solvent through the SEI layer. The governing equations are solved numerically to predict the solvent concentration profile, the SEI layer thickness, and the capacity loss. Capacity loss predictions are fitted to two sets of experimental data from the literature. The high quality of the fits demonstrates that the mixed mode model provides a useful description of the capacity loss in the cell due to the growth of the SEI layer on the anode under constant voltage storage condition. Also, analytical expressions are presented for SEI growth for both the combined kinetics/diffusion mode (mixed mode model) and the limit of a fast solvent reduction reaction (diffusion limited mode model) as a function of cell characteristics.

As dissolution, diffusion, and shuttling of the dissolved polysulfides result in parasitic reactions and substantial capacity loss for LiS cells, in the second step and in order to study the shuttling phenomena as the main performance issue and source of capacity loss of the LiS cells, chapter 4 digs deeper into the underlying mechanism of this phenomena by including the details of a 1D porous electrode model developed for the

entire LiS cells which uses a semi-empirical loss approximations for the shuttling induced capacity fade mechanism.

To provide a better understanding of the shuttling process, a 1D porous electrode mathematical model has been developed. An approximation method is used to account for the shuttling-induced capacity loss by adding an extra source/sink term in the material balance equations for the species involved in the parasitic reactions. Shuttling constants used in the source terms can be determined through fitting the model predictions to the experimental measurements. The results showed that by including the approximation method, the model was able to predict the active material loss and the continuous decrease of volume fractions of Li_2S on the cathode surface. The model sheds light on the capacity loss mechanism occurring inside the cell as a result of shuttling of polysulfides.

Finally, chapter 5 concludes the discussion by focusing on the future of the LiS and proposing a state of charge (SOC) based lumped model for a LiS Cells. In order to develop a simple LiS cell model with minimum number of parameters, a lumped model is developed based on the idea of having an empirical state of charge (SOC) expression for the cell. In the model, by defining the SOC for the cell and having open circuit potential (OCP) versus SOC measurements, all the kinetics and polarizations expressions are lumped into one to model the charge and discharge performance of the cell. The model is applied to a novel polymer-based cathode types in which the existence of polysulfides (PS) anions is completely avoided at its source. The model predictions for discharge which are fitted to the experimental measurements in the literature, provide satisfactory fit to the experimental data by capturing the main features of LiS discharge profile.

Figure 2.1. Comparison of topics addressed in research articles, from the abstract of 1524 articles. Reproduced from [24].

CHAPTER 3

MIXED MODE SEI GROWTH MODEL

3.1 Introduction

Lithium metal, which is used as the anode in LiS cells, has a high theoretical specific capacity (3860 mA h g^{-1}), low density (0.59 g cm^{-3}), and the lowest negative electrochemical potential (3.040 V vs. the standard hydrogen electrode). With the emergence of post lithium-ion batteries, Li metal anode is thus considered as the “Holy Grail” in energy storage and the ultimate solution for next-generation high-energy-density batteries. However, as its interface with the electrolyte is poorly controlled, the practical applications of Li metal anode have been facing numerous challenges over the past 40 years, such as complicated interfacial reactions between Li metal anode and electrolytes, the uncontrollable growth of lithium dendrites, and “dead” lithium [25]. The fatal issues of Li metal anode are still far away from solved due to the lack of a basic understanding of the fundamental chemistry in Li metal anode, such as the mechanism of the interfacial interactions between anodes and electrolytes and Li metal deposition.

The growth of the solid electrolyte interphase (SEI) layer on the anode surface, which results in the loss of active lithium ions in the layer, is recognized to be the dominant

capacity loss mechanism in the lithium ion batteries. Many studies have been presented in the literature to investigate the capacity loss due to the growth of the SEI layer [26]–[59].

In general, these studies can be categorized into two main groups in terms of the model assumptions. In the first group [26], [28], [31], [33], [34], [36], [38], [42]–[46], [48]–[50], [59], [60], the authors assumed that the SEI layer is composed of two distinct layers, a compact layer of inorganic products (e.g., Li_2CO_3 , LiF , LiCl , Li_2O) and a porous layer of reduced organic products, which are made of a solvent dependent organic group (e.g., $(\text{CH}_2\text{OCO}_2\text{Li})_2$, ROLi , ROCO_2Li) [61]. They assumed electrons diffuse through the compact layer and react with the solvent and lithium ions at the compact SEI/porous SEI interface, which leads to the continuous thickening of the porous layer. The other group of authors assumed a single porous SEI layer which allows the diffusion of solvent and salt components, resulting in the reduction reaction of the solvent at the electrode/SEI interface [27], [39], [47], [52], [54]–[58], [62]. These authors assumed that the electrons are located on the electrode surface and the SEI is an ionic conducting and electronically insulating layer that is either a solid or a slightly porous layer.

In some of the SEI studies, the SEI growth was assumed to be under either kinetic control [26], [28], [34], [38], [40], [57], [59] or transport control only [27], [32], [47], [49]. Although, considering both the diffusion of the involved species and the kinetics of the formation reaction is required to create a precise growth model, only a few studies in the past combined the kinetics and diffusion aspects to develop a mixed mode SEI growth model [33], [35], [36], [39], [40], [54], [58], [62], [63]. A brief summary of these studies is provided here to review these models and their limitations.

Colclasure et al.[36], Christensen et al.[45], and Tang et al. [63] developed mixed mode models based on the diffusion of the electrons through the SEI. However, they did not validate their equations against any experimental measurements. Single et al.[48][50] applied porous electrode theory to the porous SEI and included both the diffusion of the solvent in the electrolyte and the conduction of electrons in the SEI material. In all of these studies, the authors did not support their hypothesis of diffusion of electrons through the SEI layer with any SEI experimental data. According to the several experimental studies [53], [64]–[68] which have investigated the composition and structure of the SEI layer, the SEI layer acts as a lithium ion conductor and an electron insulator. These studies question the feasibility of the physical picture which considers diffusion of the electrons through the SEI layer to reduce the solvent at either the SEI/electrolyte interface or the compact SEI/porous SEI interface.

Safari et al. in 2009 [54], developed a mixed mode model based on the two extreme cases of diffusion and kinetic limited SEI growth. They overlaid their predictions for constant voltage storage results over 450 days of storage to the experimental data reported by Broussely et al.[49] (see their Fig.4 in Ref. [54]). However, since their kinetically controlled predictions deviated drastically from the experimental data points, they concluded that the SEI growth is more under diffusion control. They also included deintercalation of lithium ions from the carbon during constant voltage storage. However, it is unlikely that lithium ions will deintercalate from the carbon if the constant potential condition is being held by the trickle charging. Delacourt et al.[58] in 2012, extended the Safari et al. model and proposed an alternative form for their kinetic expression for the solvent reduction reaction, but the electrode potential (Φ_s) in their kinetic expression which

determines the driving force for the SEI formation reaction was not clarified (see their Eq.1 in Ref.[58]).

Pinson et al. [51] and Deshpande et al. [62] provided mixed mode models that combine the diffusion of solvent through the SEI with a first order kinetic expression in which the constant reaction rate unlike the Tafel equation, does not depend on the over-potential of the solvent reduction reaction and the state of charge of the electrode. Their model predictions failed to provide a reasonable fit to the experimental data reported by Broussely et al.[49] (see Fig 8 in Ref. [51] and Fig 8 in Ref.[62]). Similarly, Sankarasubramanian et al. [40] used a first order kinetic expression with a constant reaction rate and related this reaction rate to the rate of change of concentration by using a volume-based material balance equation at the SEI/electrode interface. However, they provide an unclear analysis that yields a capacity loss that varies linearly with time (see their Fig.4 in Ref.[40]). A model by Yang et al.[39] included a SEI resistance term in their kinetics expression for the solvent reduction reaction and substituted the solvent diffusion equation with an approximate equation to describe diffusion of the solvent through the SEI. Zhao et al.[37] proposed a mixed mode model that fails to provide a reasonable solvent concentration profile. Their predictions show that the solvent, ethylene carbonate, concentration at the carbon/SEI interface is initially zero and increases over time as the SEI layer grows (see their Fig.4 and Fig.5 in Ref.[37]). Ekstrom et al. [35] proposed a zero-dimensional model which combines two extreme conditions of diffusion limited and kinetic limited cases to obtain a mixed mode approximation for the rate of the SEI formation. Hao et al. [52] developed a model which related the solvent diffusion to the SEI growth. They assumed that solvent diffusion in the SEI film obeys a hopping mechanism

and the rate is described by an Arrhenius formulation (see their Eq.11 in Ref.[52]). However, they did not validate their results against any experimental data.

All of the previous mixed mode models reviewed here have limitations such as neglecting the state of charge effect on the driving force for the solvent reduction reaction, replacing the governing equations with simplified expressions, lack of experimental validation, unreported kinetics and diffusion parameters. In the mixed mode model presented here, diffusion of the solvent through the SEI layer is combined with solvent reduction at the SEI/electrode interface, based on Tafel kinetics which provides the opportunity to study the dependency of the SEI formation driving force on the state of charge (SOC) of the electrode. This feature also enables our model to be extended to include other operational modes (e.g., open circuit potential (OCP), cycling, pulsing). The governing equations are solved numerically to predict the solvent concentration profile, the SEI layer thickness, and the capacity loss. The capacity loss predictions are fitted to two sets of experimental data for constant-voltage charging (trickle charging) from the literature (HE prototypes cells ($\text{LiNi}_{0.91}\text{Co}_{0.09}\text{O}_2$) stored at 90% SOC over 625 days [49] and Sanyo UR18650E cells ($\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC)) stored at 50% SOC over 500 days [69]). The effective diffusion coefficient of the solvent (D_s^{eff}) and the reaction rate constant of the solvent reduction reaction (k_{SEI}) for these two different cell types were obtained from curve fitting to the experimental data and the confidence interval is obtained to provide an accuracy range for these estimated parameters. The model was used to predict the capacity loss for different SOC and the SEI layer porosity (ϵ). Also, we have developed an analytical solution for the growth of the SEI by assuming a linear solvent concentration profile through the SEI. The governing equations were solved analytically for both the mixed

mode model and the diffusion limited mode model, to obtain analytical expressions for the SEI growth as functions of cell characteristics.

3.1.1 Model Development

3.1.1.1 Assumptions

Figure 3.1 presents the schematic of the SEI growth on the electrode. The solvent (S) and lithium ions diffuse through the SEI layer and react with the electrons on the surface which results in the production of an insoluble product (P) at the electrode/SEI interface:

In order to develop a mixed mode model to predict the growth of the SEI, the solvent (S) was assumed to have a constant effective diffusion coefficient and the solid product (P) was assumed to have a constant molar density. In terms of the SEI formation mechanism, the multi-step formation reaction in Eq.1 was treated as a one-step solvent decomposition reaction on the surface. We also assumed that the SEI layer is completely inorganic and has a slightly porous structure, which allows continuous diffusion of the electrolyte (i.e., solvent components and solution phase lithium ions).

3.1.1.2 Governing equations

Solvent (S) diffusion through the SEI layer follows Fick's second law:

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial z^2} \quad 2$$

where C_s is the solvent concentration in the pores and D_s is the effective diffusivity of the solvent components. Since we assume a porous structure for the SEI layer, the liquid electrolyte fills the pores of the SEI and reaches the electrode surface. Therefore, the

effective solvent (S) concentration at the electrolyte/SEI determines our first boundary condition to be:

$$at\ z = 0 \quad C_S = \varepsilon C_S^0 \quad 3$$

where C_S^0 is the bulk solution concentration and ε is the porosity of the layer. A Tafel expression is used to describe the kinetics of the irreversible formation reaction of the product (P) as:

$$at\ z = L(t) \quad J_{SEI} = -k_{SEI} C_S \exp\left(\frac{-\alpha_c F(E_{eq}(SOC) - U_{SEI})}{RT}\right) \quad 4$$

where k_{SEI} is the rate constant and U_{SEI} is the equilibrium potential of the solvent reduction reaction. Also, E_{eq} is the open circuit potential of the anode, which is a function of SOC.

The flux of the solvent at the SEI/electrode interface is proportional to the rate of the solvent reduction reaction, J_{SEI} , and the growth rate of the SEI layer ($\frac{dL}{dt}$) caused by the formation of the insoluble product, P.

$$-D_s \frac{dC_S}{dz} \Big|_{z=L(t)} = -J_{SEI} = c_P \frac{dL}{dt} \quad 5$$

where c_P is the molar density of the reaction product (P) and L is the thickness of the SEI layer. The capacity loss, $x(t)$, is defined to be the ratio of lost number of moles of lithium ions in the SEI to the initial number of moles of lithium ions [27] as:

$$x(t) = \frac{Z_P c_P A_{anode}}{N_0} L(t) \quad 6$$

where Z_p is the number of atoms of Li in the product (P), A_{anode} is the anode surface area, N_0 is the initial number of moles of lithium ions in the cell.

3.1.1.3 Analytical Solution

An analytic expression for the SEI thickness can be obtained by solving equations 4 and 5, by assuming that the solvent concentration changes linearly through the SEI layer as follows:

$$\frac{dC_s}{dz} = \frac{C_s - C_s^0 \varepsilon}{L(t)} \quad 7$$

combining Eq.4, 5, and 7 results in a first order differential equation for L

$$\frac{dL}{dt} = \frac{D_s C_s^0 \varepsilon}{c_p (L^* + L(t))} \quad 8$$

we can define characteristic parameters to be:

$$L^* = \frac{D_s}{k_{SEI}} \exp \left(\frac{\alpha_c F (E_{eq}(SOC) - U_{SEI})}{RT} \right) \quad 9$$

$$t^* = \frac{c_p L^{*2}}{D_s C_s^0 \varepsilon} \quad 10$$

and we can use them to form two dimensionless variables as:

$$\tau = \frac{t}{t^*} \quad 11$$

$$\delta = \frac{L(t)}{L^*} \quad 12$$

thus Eq.8 becomes

$$\frac{d\delta}{d\tau} = \frac{1}{1+\delta} \quad 13$$

where

$$\delta = 0 \quad \text{at} \quad \tau = 0 \quad 14$$

integrating Eq.13 gives

$$\delta = \sqrt{1+2\tau} - 1 \quad 15$$

or

$$L(t) = \sqrt{L^{*2} + \frac{2D_s C_s^0 \varepsilon t}{c_p}} - L^* \quad 16$$

combining Eq.5 and 7 gives the solvent concentration at the SEI/electrode interface

$$C_s(t) = \frac{C_s^0 \varepsilon}{1 + \frac{L(t)}{L^*}} \quad 17$$

in the limit of a fast solvent reduction reaction where $C_s \approx 0$ at $z = L(t)$ (i.e., $k_{SEI} \rightarrow \infty$ and $L^* \rightarrow 0$), we obtain our diffusion limited equation for the thickness of the SEI:

$$L(t) = \sqrt{\frac{2D_s C_s^0 \varepsilon t}{c_p}} \quad 18$$

3.2 Results and Discussion

Equations 2, 4, and 5 were solved numerically using the general PDE interface in COMSOL to predict the solvent concentration profile through the SEI and the SEI thickness as function of time. The “Deformed Geometry” feature in COMSOL was used to take into account the SEI layer movement. The main domain in the model includes a small length as the initial SEI thickness (L^0) in which its boundaries represent the electrode/SEI and SEI/electrolyte interfaces. The solvent diffuses through this domain as

Eq.2 and the rate of its reduction at the electrode surface is controlled by Eq.4. Equations 3 and 5 are defined in the model to describe the boundary conditions at the interfaces. Over time, the SEI layer grows and the SEI/electrolyte boundary moves with the velocity derived in Eq.5. By increasing the layer thickness, the capacity loss caused by the SEI growth can be calculated by using Eq.6.

We define trickle charging, as applying a small charging current to maintain a constant voltage so that all the intercalated lithium ions stay inside the electrode, and, therefore, the state of charge of the electrode does not change over time. The model only applies to the anode side of the cell, which we assume is either lithium metal or graphite. Also, since ethylene carbonate (EC) is known to be the most reactive alkyl carbonates[70][71], we assume that the solvent (S) is EC which reacts with 2 electrons and 2 lithium ions to produce Li_2CO_3 (P) [72] according to Eq.1. The cell characteristics based on the design specifications of the HE prototypes and Sanyo cells, and the SEI parameters used in the model are listed in Table 3.1 and Table 3.2, respectively.

3.2.1 Capacity Loss

The capacity loss of HE prototype cells and capacity ratio of Sanyo UR18650E cells as functions of time were reported in the literature by Broussely et al. [49] and Schmalsteig et al.[69], respectively. Table 3.1 summarizes the design specifications and a list of characteristics of these cells. The carbon surface area (A_{anode}) of the HE prototypes and Sanyo cells and equilibrium solvent molar concentration (C_s^0) of the Sanyo cells were not reported in the literature. Hence, the estimated value for A_{anode} by Ploehn et al.[27] is used in the model for HE prototype cells, and we used the capacity ratio of the HE prototype and Sanyo cells to estimate a value for A_{anode} for the Sanyo cells. Also, the same C_s^0 value

which was reported by Broussely et al. [49] for HE prototypes, was used for the Sanyo cells. The capacity loss and the SEI thickness definitions presented in Eq.6 and Eq.16, provides a better understanding of how different parameters such as A_{anode} , k_{SEI} , $D_{\text{S}}^{\text{eff}}$, and C_{S}^0 are correlated with each other to obtain a certain capacity loss value and how a variation in one of them may affect the output.

The logarithmic capacity loss vs. $\sqrt{t}$ data points for the HE prototypes cells and Sanyo cells, and the mixed mode model fit are shown in Figure 3.2. The diffusion limited model by the Ploehn et al.[27], is also reproduced by assuming that the SEI growth occurs at the diffusion limited rate (i.e., the concentration of the solvent is approximately zero at the carbon/SEI interface). Ploehn et al.[27] assumed the SEI layer to be a non-porous solid phase and predicted that the capacity loss caused by the SEI growth changes linearly with the square root of time. As shown in Figure 3.2. here, and also, in Figure 2 in Ref.[27], in which they fit their diffusion limited model predictions to the measurements by Broussely et al.[49], it can be seen that the diffusion limited model is only an approximate model. Also, the diffusion coefficient which is extracted from their fit is almost two orders of magnitude smaller ($3.07 \times 10^{-23} \pm 2.68 \times 10^{-24}$ m/s) than the diffusion coefficient in our mixed model. As shown in Figure 3.2., the overall quality of the mixed mode model predictions of the capacity loss data for both HE prototypes cells and Sanyo cells, demonstrates that the mixed mode model provides a satisfactory description of the capacity loss due the growth of the SEI, which is valid for the entire time period that the lithium ion cells were stored under constant voltage charging.

The kinetic rate constant (k_{SEI}) and the effective diffusion coefficient ($D_{\text{S}}^{\text{eff}}$) which have been extracted from the curve fitting to the experimental data points for both the HE

prototypes and the Sanyo cells, and the SEI parameters used in the model are listed in Table 3.2. Confidence intervals were obtained to provide an accuracy range for the estimated parameters. As the values in Table 3.2 indicate, the kinetics and diffusion parameters for two different cells are reasonably close to each other (by factor of almost 6) which demonstrates the credibility of the mixed mode model to simulate the growth of the SEI layer. In order to account for the effect of porosity and tortuosity, the Bruggeman approximation has been used to relate the effective diffusion coefficient (D^{eff}) to the bulk diffusion coefficient (D^0) as:

$$D^{\text{eff}} = \varepsilon^{1.5} D^0 \quad 19$$

where ε is the porosity of the SEI layer and 1.5 is the standard Bruggeman coefficient in the porous media.

3.2.2 State of Charge and Porosity Parametric Study

The properties of the SEI film such as the thickness, composition and compactness of the SEI layer or operating conditions like SOC are critical in estimating capacity loss and SEI thickness. In order to investigate the effect of the SOC of the electrode, capacity loss predictions for different SOC values are shown in Figure 3.3 for HE prototypes. As shown in Figure 3.3, the higher state of charge of the electrode results in more capacity loss. In other words, the film growth rate at the negative electrode is greater for the fully charged batteries rather than for the uncharged ones or the cells with a lower state of charge. The dependency of the capacity loss on the SOC of the electrode can be explained through the correlation between the Tafel kinetics and the growth rate of the SEI layer shown in Eq.5. Any variation in the SOC, leads to a change of the potential difference which is the driving force of the solvent reduction reaction at the SEI/electrode interface, which results

in the thicker SEI layer and consequently, the greater capacity loss. This dependency becomes even more important when the battery experiences self-discharge under OCP storage condition in which the SOC of the electrode constantly decreases as a result of the de-intercalation of the lithium ions.

A similar parametric study was conducted to evaluate the effect of the porosity of layer on the capacity loss and capacity loss predictions for different ϵ values are shown in Figure 3.4 for HE prototypes. The variations among different ϵ values, demonstrate the importance of the assumed structure and compactness of the SEI layer. The solid curves fitted to the measurement data points are the simulation result for $\epsilon=0.05$. As Figure 3.4 illustrates, a more porous layer leads to the thicker SEI layer and the larger capacity loss. As shown in Eq.3, any change in the ϵ , alters the effective solvent concentration which determines the boundary condition at the SEI/electrolyte interface for the solvent diffusion through the SEI.

3.2.3 Mixed Mode Model and Diffusion Limited Model

In order to understand fully the SEI growth mechanism, the differences between the mixed and the diffusion limited modes and how these two regimes transform into each other must be studied. The numerical solvent concentration (C_s) profile predictions during the growth of the SEI layer on the electrode surface over the period of 625 days for both models are displayed in the Figure 3.5 for the parameters listed in Table 3.2. According to the coordinate and the direction of the transport (z) (Figure 3.1), when the SEI layer grows on the electrode surface without any kinetic limitation and the solvent reduction reaction is occurring at the highest possible rate, all the solvent (S) which diffuses through the SEI layer is consumed at the SEI/electrode interface. Consequently, at the electrode surface

($z=L(t)$), the solvent concentration is zero (Figure 3.5.a). However, Figure 3.5.b shows that in the mixed mode model, the kinetics of the reduction reaction limits the consumption of the solvent and changes the solvent concentration at the electrode surface to a non-zero value. While the concentration of the solvent at the electrode surface diminishes over time, the SEI layer continuously grows and ultimately at low concentration, the growth will cease.

The transition of the mixed mode model to the diffusion limited model is illustrated in Figure 3.6 in which the solvent concentration at the electrode surface, is displayed for different k_{SEI} values as function of time. By increasing the k_{SEI} value, the mixed mode model predictions approach to the diffusion limited model limit in which the concentration of the solvent at the electrode surface is assumed to be zero. Also, as shown in Figure 3.7, as the k_{SEI} values become larger, the diffusion limitations dominate the SEI formation process. As a result, the SEI thickness predictions of the mixed mode model advance toward the diffusion limited model prediction. Comparing Eq. 16 and 18 also helps to understand the fact of having thicker SEI layer when the SEI forms on the electrode without kinetics limitations.

3.2.4 SEI Thickness

The analytic expression for the SEI thickness was obtained by assuming that the solvent concentration changes linearly through the SEI layer. In order to validate the analytical solution, the relative error of the numerical SEI thickness prediction and the analytical solution for the mixed kinetics/diffusion mode (Eq. 16) for the parameters listed in Table 3.2, is calculated to be 0.0346% and for the diffusion limited mode (Eq.18) to be 0.076%. The small relative error values confirm the validity of the linear assumption and

the analytical solution. Also, the error of the analytical solution for the diffusion limited mode (Eq. 18) relative to the exact solution derived by Ploehn et al. is calculated to be 1.5%. Ploehn et al. [27] used a similarity solution to obtain an analytical expression for the diffusion limited mode (see Eq.24 in Ref. [27]). The analytical solution provided here for this case (Eq.18) has the advantage of simplicity over Ploehn et al. [27] solution.

Among different SEI studies in the literature, Tang et al.[63] and Hao et al.[52] have derived an expression for the SEI thickness by considering both diffusion and kinetics effects. However, they did not validate their expressions against any experimental data. Figure 3.8 shows a comparison among analytical solutions from these two studies and the present work. Eq.15 in Tang et al.[63] was derived for the SEI growth limited by electron migration through an assumed compact layer on the electrode.

The conductivity in this equation, was treated as an adjustable parameter to get the best fit to our mixed mode model predictions. As shown in Figure 3.8, the best fit was obtained with an electronic conductivity of the SEI of 2.5×10^{-14} S/m, which is unrealistic and demonstrates the improbability of the diffusion of electrons through the SEI. Also, the SEI thickness expression by Hao et al.[52] which is a function of non-adjustable parameters (see Eq.17 in Ref.[52]), greatly deviates from our predictions as shown in Figure 3.8.

3.3 Conclusion and Future Directions

The SEI layer was assumed to be a single, porous non-electrically conductive layer which grows gradually on the negative electrode due to solvent reduction at the electrode surface during constant voltage storage. A mixed mode SEI growth model is presented that includes both the influence of the kinetics of the solvent reduction reaction at the SEI/electrode interface and diffusion of the solvent components through the SEI layer. The

governing equations are solved numerically to predict the solvent concentration profile, the SEI layer thickness, and the capacity loss. The high quality of the fits to two sets of experimental data for constant-voltage charging (HE prototypes cells stored at 90% SOC over 625 days [49] and Sanyo UR18650E cells stored at 50% SOC over 500 days [69]) from the literature, demonstrates that the mixed mode model provides a useful description of the capacity loss in the cell due to the growth of the SEI layer on the anode under constant voltage storage condition (trickle charging). Since during constant voltage charging, all the intercalated lithium ions stay inside the anode in the lithium ion cell, choosing the constant voltage storage mode makes the model generic for other anodes such as Li metal. An analytical expression for the SEI thickness for both the mixed and diffusion limited modes was derived by assuming a linear solvent concentration profile through the SEI. The small relative error of the analytical solution compared to the numerical solution confirms the validity of the analytical solution.

This transformative research part of the project was focused on the SEI on the anode to gain in-depth understanding of the composition, formation mechanism, and property of SEI films and also understanding the functionalities of SEI. The SEI modeling and establishing the underlying fundamental knowledge to guide the design of LiS cell with long cycle life that can be obtained by using additives (e.g. LiNO_3 , P_2S_5 and fluorinated ether) in the liquid electrolytes. The previous works [73] [74] reveal that LiNO_3 plays opposite roles in the Li anode and sulfur cathode of LiS battery.

On the Li anode surface, the LiNO_3 promotes the formation of a stable passivation film, which is known to significantly suppress the redox shuttle of lithium polysulfides. LiNO_3 is beneficial to LiS battery only when its irreversible reduction on the cathode is

avoided, which can be easily achieved by raising the discharge cutoff voltage. However, the fundamental, electrolytic mechanism and the reasons for the enhanced cycling performance of these additives are not known. Similarly, the effect and role of the different types and amounts of additives in the electrolyte remain elusive. Once the formation mechanism of the SEI layer on the anode surface in different electrolytes is identified as the first step, a SEI growth model by focusing on the anode during charge can be developed to study the effect of different electrolyte compositions and additives such as LiNO_3 , on the stabilizing the SEI and cell performance which later can be implemented into the complete model for the entire cell to investigate the effect of different additives and electrolyte compositions on the coulombic efficiency, cell resistance, and overall performance of the cell.

Figure 3.1. Schematic of the formation of the SEI at the SEI/ electrode interface. Solvent (S) and solution phase lithium ions continuously diffuse through the pores of the SEI layer and react with the electrons on the electrode surface resulting in the formation of insoluble product (P).

Figure 3.2. Data for HE prototypes cells ($\text{LiNi}_{0.91}\text{Co}_{0.09}\text{O}_2$) stored at 90% SOC over 625 days $\blacklozenge$ [49] and Sanyo UR18650E cells ($\text{Li}(\text{NiMnC})\text{O}_2$ (NMC)) stored at 50% SOC over 500 days. The lines are from the numerical solution of mixed mode model (—) and our diffusion limited model [27] (---) for capacity loss as a function of the square root of time in days.[75]

Figure 3.3. Measured [27] (◆) and simulated (—) capacity loss as function of time for different SOC Values. The higher state of charge of the electrode results in thicker SEI layer and more capacity loss.

Figure 3.4. Measured [27] (◆) and simulated (—) capacity loss as a function of time for different ε values. A more porous layer leads to a thicker SEI layer and greater capacity loss.

Figure 3.5. Solvent concentration versus SEI thickness in a) diffusion limited model b) mixed mode model over 625 days. In the mixed mode model, the kinetics of the reduction reaction limits the consumption of the solvent and changes the solvent concentration at the electrode surface to a non-zero value over the period of 625 days.

Figure 3.6. Solvent concentration at the electrode surface as function of time in the mixed mode model (-) and diffusion limited model (--). By increasing the k_{SEI} value, the mixed mode model predictions approach to the diffusion limited model limit in which the concentration of the solvent at the electrode surface is assumed to be zero.

Figure 3.7. SEI thickness as function of time in the mixed mode model (—) and diffusion limited model (--). As k_{SEI} values become larger, the SEI thickness predictions of the mixed mode model advance toward the diffusion limited model prediction.

Figure 3.8. Analytical SEI thickness as a function of time in mixed mode model(—) and reproduced solutions from Tang et al.[63] (---) and Hao et al. [52] (-.-) models. Tang et al. [63] analytical solution approaches our prediction with a really small electronic conductivity for the SEI of $2.5 \times 10^{-14} \text{ S m}^{-1}$.

Table 3.1. Published and assumed characteristics of the HE and Sanyo cells [27], [49], [69]

Characteristics	HE prototype	Sanyo
Positive electrode	$\text{LiNi}_{0.91}\text{Co}_{0.09}\text{O}_2$	Li (NiMnCo)O_2 (NMC)
Negative electrode	Graphite	Graphite
Initial capacity (Ah)	50.93	2.15
Initial number of moles of Li based on initial capacity, N_0 (mol)	1.9	0.08
Float potential (V)	3.8	3.699
Temperature ($^{\circ}\text{C}$)	30	50
Cs^0 (mol/m ³)	2636	2636
Anode surface area, A_{anode} (m ²)	173	7.33*
SOC	90	50
*Estimated (see text)		

Table 3.2. Model Parameters for HE Li-ion prototype and Sanyo UR18650E cells.

Estimated kinetics and diffusion parameters		
	HE prototypes	Sanyo UR18650
k_{SEI} (m/s)	$4.3 \times 10^{-16} \pm 9.932 \times 10^{-17}$	$2.28 \times 10^{-15} \pm 6.04 \times 10^{-17}$
D_s^{eff} (m ² /s)	$1.084 \times 10^{-21} \pm 1.789 \times 10^{-22}$	$6.23 \times 10^{-21} \pm 2.48 \times 10^{-22}$
D_s^0 (m ² /s) = $D_s^{\text{eff}} \times \epsilon^{-1.5}$	9.7×10^{-20}	5.57×10^{-19}
SEI parameters		
U_{SEI} (V)	0.4	
ϵ_{SEI}	0.05	
c_p (mol/m ³)	28556 [29]	
Z_p	2	

CHAPTER 4

SHUTTling INDUCED MODEL

4.1 Electrochemical/ Chemical Reactions

The structure and operation of LiS cells was touched on earlier in chapter 2, explaining the general mechanism of these cells. Here, we dig deeper into the set of electrochemical and chemical reactions occurring inside the battery in order to develop a model for the entire cell to study the charge/discharge performance and investigate the shuttling phenomena in more details. During the discharge process, lithium metal is oxidized to form lithium ions and electrons. The Li-ions (Li^+) travel to the cathode while the elemental sulfur in the cathode side first dissolves in the electrolyte and then is reduced through a set of redox reactions to produce a long-chain lithium polysulfide species which either are soluble or insoluble in the electrolyte. The reaction at the anode side is given as:

On the cathode side, the elemental sulfur in the solid phase ($\text{S}_{8(\text{s})}$) dissolves into the electrolyte and forms $\text{S}_{8(\text{l})}$. It is assumed that no solid sulfur $\text{S}_{8(\text{s})}$ precipitates on the anode. In the cathode, the dissolved sulfur, $\text{S}_{8(\text{l})}$, is reduced to lower order polysulfide anions through a chain of electrochemical reactions as seen in Ref.[14]:

The set of electrochemical reactions are accompanied with a group of chemical reactions between lithium and polysulfides and Li_2S_i ($i=1,2,4, 6, 8$) form as [14]:

The insoluble polysulfides precipitate on the cathode surface, imposing a decrease in the electric conductivity of the cathode host due to the insulating nature of the sulfur and a decrease in the porosity of the cathode porous structure by clogging the pores. The soluble polysulfides which react with the lithium ions existing in the vicinity of the electrode, owing to the driving force from the concentration gradient and electro-osmotic effect, tend to diffuse with lithium-ions across the cell from the cathode to the anode side during charge, giving rise to the phenomena called the shuttling process as illustrated in Figure 4.1.

In other words, although according to experimental studies [76]–[78] Li_2S is the only species that precipitates on the cathode surface as a result of chemical reaction of last order polysulfide with lithium according to reaction 31, however, the reaction of remaining polysulfides with lithium according to reaction 27-30, initiates the shuttling process. As it can be seen in Figure 4.1, during charge, the chain of sulfur redox reaction (reaction 22 to 26) occurs on the anode surface leading to the deposition of Li_2S on the surface which might also result in coulombic inefficiency, capacity loss for the cell, and resultant fast cell failure. Part of the deposited Li_2S on the electrode surfaces dissolve back into the electrolyte during charge for the cathode and discharge for the anode. However, as it was first reported by Hofmann et. al [20] (see Figure 8 in Ref. [20]), during cycling, the overall volume fraction of Li_2S on the cathode surface has a descending trend that explains the capacity loss which LiS cells experience.

Although it seems obvious that LiS cells experience capacity loss due to the shuttling process, however, the underlying details of this phenomena and how it might directly or indirectly affect the cell capacity is not well understood yet as the isolation of each polysulfide to study its behavior is almost impossible. The polysulfide anions

transport and commute back to the cathode during discharge to participate in the cascade redox reaction which runs in reverse, but a portion of them might get stuck and remain on the anode side leading to an active material capacity loss.

During charge, transported polysulfides get reduced on the anode surface leading to the formation and deposition of insoluble lithium sulfides on the metallic lithium. Although the exact mechanism of these side reactions is not well studied yet, they might adversely affect cell performance by reducing Coulombic efficiency, deteriorating, and deforming lithium anode and causing an increase in interfacial resistance between the anode and electrolyte. These reactions also result in an irreversible capacity degradation through both sulfur and lithium loss as the precipitation of last order polysulfide on the anode surface (Li_2S) is not completely reversible and consequently, a portion of the lithium and sulfur which do not dissolve back into the electrolyte can be considered as dead sulfur and lithium. Also, the occurrence of these reactions on the anode surface which its interface is already poorly controlled and suffer from various issues, leads to the formation of an unstable solid-electrolyte interface (SEI) and propagation of dendrite growth, which both have the potential to be considered as active lithium capacity loss mechanism.

Although, the physics occurring inside a LiS cell is not fully understood yet, however, the sharp capacity loss in LiS is commonly known to be associated with the polysulfides which shuttle between the electrodes and due to the precipitation of lithium sulfides. It is therefore important to continue the work in this direction and develop modeling tools that will help to improve and predict the capacity life which corresponds to this phenomenon.

4.2 Model Development

The mathematical model is based on the schematics from Figure 4.2. The model was built based on the porous electrode theory framework. In this approach, transport in the matrix phase and in the solution phase enters into material balances and involves coupling through polarization relations in such a way that the electrolytic processes appear as homogenous terms in the material balances. The material balance and charge balance equations were solved to find the time and spatial dependence of the concentrations and potentials that are tightly coupled and satisfy nonlinear partial differential equation [79].

Based on the 1D geometry of the cell, the governing equations in the porous medium of separator and cathode can be categorized into transport (material balance equations), thermodynamic, kinetics (Butler-Volmer equations), charge transfer (solid and solution phase potential equations), porosity change, precipitation expressions and shuttling approximation. The time-dependent model is one-dimensional (1D) and consists of two domains: one corresponding to the separator and the second one to the cathode. The cathode consists of a carbon-sulfur blend and the anode consists of a lithium metal foil, which will be modeled at the boundary of the separator, as seen at the bottom of Figure 4.2.

Modeling shuttling currents at the anode by including the kinetic expressions of the parasitic reactions, would yield a more accurate mechanistic approach to study the shuttling effect. However, the very low concentration of species at the end of discharge, can significantly complicate the simulation by increasing the computation time and creating the need for advanced non-linear solvers. Therefore, including the Butler-Volmer formulation for modeling the current densities associated with the side reactions on the

anode during charge is an exceedingly difficult numerical approach and no attempt has been made to include these equations for the side reactions in any mathematical framework proposed for LiS cells in the past. Hence, to simplify the model and in order to avoid including the numerical complications imposed by these kinetic expressions, it is assumed that the entire cell capacity fade is associated with loss of active material as a result of shuttling back and forth of polysulfide anions.

4.2.1 Material Balance

For a multicomponent electrolyte system in a porous medium, the material balance of each individual species in the separator and the cathode can be written as [14][79]:

$$\frac{\partial(\epsilon_m C_i)}{\partial t} = -\frac{dN_i}{dx} + r_i + R_i + R_{ps,i} \quad 32$$

where ϵ_m is the pore volume fraction of the porous cathode or separator, and C_i is the concentration of species i ($i = \text{Li}^+$, $\text{S}_{8(l)}$, S_8^{2-} , S_6^{2-} , S_4^{2-} , S_2^{2-} , S^{2-} , and A^- , which is the anion of the lithium salt used in the electrolyte) in mol m^{-3} and the index m corresponds to each domain (*sep* for separator and *cat* for cathode).

For a dilute solution, the flux of the species i , N_i can be written as follows [14]:

$$N_{i,m} = -D_{i,eff,m} \frac{dC_i}{dx} - z_i \frac{D_{i,eff,m}}{RT} F C_i \frac{d\phi_l}{dx} \quad 33$$

where $D_{i,eff,m}$ is the effective diffusion coefficient of species i for domain m , corrected for porosity and tortuosity using the Bruggeman expression ($D_{i,eff,m} = D_{i,0}\epsilon_m^b$, where $b = 1.5$), z_i is the charge number of species i , and ϕ_l is the liquid-phase potential.

4.2.2 Kinetics

The current density due to electrochemical reaction j at the solid/liquid interface is given by the Butler–Volmer equation as follows[14]:

$$i_j = i_{0,jref} \left\{ \prod_i \left(\frac{C_i}{C_{i,ref}} \right)^{p_{i,j}} \exp \left(\frac{\alpha_{a,j} F}{RT} \eta_j \right) - \prod_i \left(\frac{C_i}{C_{i,ref}} \right)^{q_{i,j}} \exp \left(\frac{-\alpha_{c,j} F}{RT} \eta_j \right) \right\} \quad 34$$

where $p_{i,j}=s_{i,j}$ for anodic species and $q_{i,j}=-s_{i,j}$ for cathodic species. The system is assumed isothermal and the temperature is set to $T = 298$ K. The exchange current densities are fitted to match experimental data and are presented in Table 4.1. The overpotential for reaction j is given by [14]:

$$\eta_j = \phi_s - \phi_l - U_{j,ref} \quad 35$$

the potential of the solid phase (ϕ_s) in the anode boundary is set to zero.

The second term on the right side of Eq. 32 r_i , is the rate of production of species i in the cathode, which is related to the current densities due to each of the electrochemical reactions as follows [14]:

$$r_i = -a \sum_j \frac{s_{i,j} i_j}{n_j F} \quad 36$$

where a represents the specific area of the porous cathode, n_j denotes the number of electrons transferred in reaction j , and $s_{i,j}$ is the stoichiometric coefficient of species i in electrochemical reaction j (Table 4.5).

The specific surface area of the cathode varies according to the expression [14]:

$$a = a_0 \left(\frac{\epsilon_{cat}}{\epsilon_{cat,0}} \right)^\xi \quad 37$$

where ξ is the empirical parameter describing the morphology of the precipitate, which is assumed to be 1.5.

4.2.3 Thermodynamics

The open-circuit potential (OCP) for reaction j at the reference concentrations $C_{i,\text{ref}}$ (assumed to be equal to initial concentration) of species i is given by the Nernst equation as follows [14]:

$$U_{j,\text{ref}} = U_j^\theta - \frac{RT}{n_j F} \sum_i \left\{ s_{i,j} \ln \left[\frac{C_{i,\text{ref}}}{1000} \right] \right\} \quad 38$$

Equation 38 is valid only when the concentrations are expressed in moles per liter, consequently the reference concentration in mol m^{-3} are divided by the factor 1000 for conversion. The terms U_j^θ are given in Table 4.1.

4.2.4 Precipitation/ Dissolution Rates

The third term on the right side of Eq. 32, R_i , is the rate of production of species i due to precipitation/dissolution reactions, which is related to the rate of precipitation/dissolution reaction k , R_k , as follows [14]:

$$R_i = - \sum_k \gamma_{i,k} R_k \quad 39$$

where R_k is the rate of precipitation of the solid species k , $\gamma_{i,k}$ is the number of moles of ionic species i in the solid species k . The rate of precipitation of species Li_2S , assuming that the precipitation reaction is kinetically controlled can be written as [21]:

$$R_{\text{Li}_2\text{S}} = k_{\text{Li}_2\text{S}} \epsilon_{\text{Li}_2\text{S}} \left(\prod_i C_{\text{Li}_2\text{S}}^{\gamma_{i,\text{Li}_2\text{S}}} - K_{\text{sp},\text{Li}_2\text{S}} \right) + k_{\text{Li}_2\text{S},2} \frac{c_{\text{Li}}^2 c_{\text{S}^{2-}}}{\epsilon_{\text{Li}_2\text{S}}} \quad 40$$

where $K_{\text{sp},\text{Li}_2\text{S}}$ is the solubility product of Li_2S in the electrolyte and $k_{\text{Li}_2\text{S}}$ is the rate constant (Table 4.4) and $\epsilon_{\text{Li}_2\text{S}}$ is the solid volume fraction of the species Li_2S . For $\text{S}_{8(\text{s})}$, the precipitation is modified by adding an extra term, as follows [21]:

$$R_{S_{8(s)}} = k_{S_{8(s)},1} \epsilon_{S_{8(s)}} \left(C_{S_{8(l)}} - K_{sp,S_{8(l)}} \right) + k_{S_{8(s)},2} \frac{C_{S_{8(l)}}}{\epsilon_{S_{8(s)}}} \quad 41$$

More details on the importance of two terms at the end of Eqs. 41 and 42 will be discussed in the results section.

4.2.5 Porosity Change

Using the rate of precipitation R_k and the partial molar volume V_k ($k = S_{8(s)}, Li_2S_{(s)}$) of the species (Table 4.4) the variation of porosity of the cathode with time can be expressed as [14]:

$$\frac{d\epsilon_m}{dt} = - \sum_k V_k R_k \quad 42$$

and the solid volume fraction of each specie k depends on time [16]:

$$\frac{d\epsilon_k}{dt} = V_k R_k \quad 43$$

4.2.5.1 Conservation of Charge

The liquid-phase current density, i_l , is related to flux of species i

$$i_l = F \sum_i z_i N_i \quad 44$$

and the solid-phase charge transfer can be defined by the Ohm's law:

$$i_s = -\sigma_{eff} \frac{d\phi_s}{dx} \quad 45$$

where σ_{eff} is the effective electrical conductivity of the cathode, which is calculated using the initial porosity of the anode and cathode ($\sigma_{eff} = \sigma_s(1 - \epsilon_{cat})^b$) and $\sigma_s = 60 \text{ S m}^{-1}$ (Table 4.6). The fact that charge can enter or leave the liquid phase only by electrochemical reactions at the solid/liquid interface in the porous cathode gives an extra constraint for the liquid-phase current density in the cathode [14]:

$$\frac{di_l}{dx} = a \sum_j i_j \quad 46$$

Finally, charge is conserved in the porous medium is defined as [14]:

$$\frac{di_l}{dx} + \frac{di_s}{dx} = 0 \quad 47$$

4.2.6 Shuttling approximation

Although the sulfur redox reactions on the anode surface during charge and other unforeseen precipitation reactions will not be included directly in the model, but their effect on the active material loss will be accounted by included reaction source/sink terms in the material balance for each polysulfide. To accommodate this assumption, a sink term will be added to the material equations of each species that contributes to the material loss to reflect the irreversible shuttling-induced capacity loss, similar to the approach first introduced in Ref. [12] to account for the shuttling effect (see equation 5 in Ref. [12]).

The source/sink term is defined for each polysulfide in the cathode and separator as follows:

$$R_{ps,i} = -k_{ps,j}C_i \quad 48$$

where i in this case corresponds to S_8^{2-} , S_6^{2-} , S_4^{2-} , S_2^{2-} , S^{2-} and k_{ps} is the heterogeneous reaction constant or shuttle constant, which is a fitted parameter. As according to the reaction 27-31, each polysulfide reacts with two lithium, the same term will be added to the material balance equation of lithium as well to account for the shuttling effect as:

$$R_{Li} = -s_{Li} \sum k_{ps,j}C_i \quad 49$$

the terms $R_{ps,i}$ represent the reaction sink terms which account for the shuttling-induced active material loss. It should be noted that since the parasitic reactions occur on the anode

surface only during charge, this term will be automatically disabled in the model during discharge.

4.2.7 Boundary Conditions

Two types of boundary conditions including conditions for the transport of species and conditions for the solid and solution phase potentials, are defined at three interfaces (e.g. anode/separator, separator/cathode, cathode/current collector).

4.2.7.1 Transport

At the cathode/current collector interface (at $x = L_c$ in Figure 4.2), a boundary condition for each specie is needed to solve the material balance equations. Due to the presence of a physical barrier (cathode current collector), the flux of each specie i ($i = \text{Li}^+$, $\text{S}_{8(l)}$, S_8^{2-} , S_6^{2-} , S_4^{2-} , S_2^{2-} , S^{2-} , and A^-) is set equal to zero at this boundary:

$$N_{i,cat} = 0 \quad \text{at } x = L \quad 50$$

at the separator/cathode interface (at $x = L_s$), the flux of each of the eight species is continuous:

$$N_{i,sep} = N_{i,cat} \quad \text{at } x = L_s \quad 51$$

Because lithium is the only reacting specie at the anode/separator interface ($x = 0$) (in the absence of the polysulfide reactions), the flux of all species i ($i = \text{S}_{8(l)}$, S_8^{2-} , S_6^{2-} , S_4^{2-} , S_2^{2-} , S^{2-} , and A^-) except Li^+ is set equal to zero:

$$N_{i,sep} = 0 \quad (i \neq \text{Li}^+) \quad \text{at } x = 0 \quad 52$$

$$N_{\text{Li}^+} = -\frac{s_{\text{Li}^+,1} i_1}{n_1 F} \quad \text{at } x = 0 \quad 53$$

where i_1 is the current density on the anode, which is given by the Butler–Volmer equation.

4.2.7.2 Solid and Solution Phase Potentials

At the cathode/current collector interface (at $x = L$), the solution-phase current density at this boundary is zero and the current density in the solid phase is equal to the applied current density:

$$i_e = 0 \quad \text{at} \quad x = L \quad 54$$

$$-\sigma_{eff} \frac{d\phi_s}{dx} = I_{app} \quad \text{at} \quad x = L \quad 55$$

and at the separator/cathode interface (at $x = L_s$), all the current is carried by the solution phase alone and the solution-phase current density is continuous through the interface:

$$i_{l,sep} = i_{l,cat} \quad \text{at} \quad x = L_s \quad 56$$

$$-\sigma_{eff} \frac{d\phi_s}{dx} = 0 \quad \text{at} \quad x = L_s \quad 57$$

at the anode/separator interface (at $x = 0$), the solid-phase potential is set equal to zero to have a reference point for the potential and the liquid-phase current density is given by the flux of the lithium-ion:

$$\phi_s = 0 \quad \text{at} \quad x = 0 \quad 58$$

$$i_l = FN_{Li^+} \quad \text{at} \quad x = 0 \quad 59$$

4.2.7.3 Initialization

The initial concentrations are given in Table 4.2. Although the solution and solid phase potential equations do not depend explicitly on time, their concentration dependency creates the need to specify proper initial conditions for these two as well. The initial values for the solid and solution phase potentials are defined as follows:

$$\phi_s = U_{1,ref} + U_{2,ref} \quad \text{at} \quad t = 0 \quad 60$$

$$\phi_l = -U_{1,ref} \text{ at } t = 0$$

61

The initial porosities for the cathode and the anode and the initial solid volume fraction for $S_{8(s)}$ and Li_2S are given in Table 4.3.

4.2.7.4 Parameter Values

Most of the transport and geometric parameters used in the Kumarasan et al.[14] model, are used to predict the discharge and charge profiles of the cell under constant current density. In order to charge the model, the solubility of Li_2S and the precipitation rate provided in Kumarasan et al. [14] needed to be changed (See Table 4.4).

4.2.7.5 Numerical Scheme

The time-dependent mathematical model consisting of equations 32 - 61 was built using COMSOL Multiphysics v5.4. The ODE's and PDE's equations were implemented using the General Form PDE physics. The geometry with two one-dimensional domains corresponding to the separator and cathode was used, as seen in Figure 4.2. To eliminate any numerical instabilities associated with the geometrical discretization, a higher density mesh was applied near the boundaries (at $x = 0$, $x = L_s$ and $x = L_c$). A predefined number of 60 elements are assigned to the separator and 150 to the cathode domain as seen in Figure 4.2. The distribution in each domain was symmetric with an element ratio of 0.3, which means a coarser mesh in the middle of the domains and a very fine mesh close to the boundaries, as seen in Figure 4.2.

To charge the model, the “Events” interface was added to switch the direction of the current between the two cutoff voltage limits ($V_{high} = 2.6V$ and $V_{low} = 2V$). The Events interface create state variables such as “Charge” and “Discharge” which need to be

manually scaled in COMSOL's solver in order to make the events stop at precise limits. In this model, the state variables were scaled with a scaling factor of $f_s = 10^{-3}$.

The applied current density, for both charge and discharge, is $I_{app} = \pm 1.97 \text{ A m}^{-2}$ (corresponding to C/10 for a 2.5Ah cell). Since the governing equations are coupled and highly nonlinear, the model suffers from convergence issues specifically during charge. This matter highlights the need to modify strategically the solver to deal with nonlinearity limitations. Switching the nonlinear method for solving equations to a damped Newton's approach, decreasing the tolerance value to 10^{-4} , and adding mesh distribution at all the edges helps with the convergence problems and makes the model stable. Also, it should be noted that the model is highly sensitive to the precipitation/dissolution parameters. Small Li_2S solubility values can make the model numerically unstable once the charging process starts and limit the rechargeability of the model.

4.3 Results and Discussion

4.3.1 Model without shuttling

The cell considered for this study is a typical LiS battery with a maximum capacity of 2.5Ah. The no-shuttling case is assumed when the extra source term (R_{ps}) in the material balance (Equation 32) is set to zero. As no in-house experimental measurements were available, the model was initially fitted and validated against the experimental data for 0.1C (0.25A) presented in Ref. [21], as seen in Figure 4.3.

The predicted voltage as shown in Figure 4.3 yields a typical discharge/charge curve which consists of a sloping high plateau voltage, a flat low plateau voltage, and a voltage dip in between. The shape of voltage curve depends on the solubility of the intermediate polysulfides. During discharge, in the first part (2.45-2.1V), the voltage drop

is significant and high order polysulfides ($x=8,6,4$) are produced. Whereas, in the second part ($\sim 2.1\text{V}$) the voltage is almost constant and low order of polysulfides are generated. Once the last redox reaction according to reaction 26 starts to occur in the cathode, the concentration of S^{2-} in the electrolyte continuously increases as a result of conversion of S_2^{2-} to S^{2-} , until it reaches the saturation limit and the local voltage minimum appears in the discharge curve. After passing this value, the voltage slightly increases and simultaneous production and consumption of lower polysulfide (S^{2-}) flatten the second part of the voltage curve. The precipitation of Li_2S starts according to reaction 23 and as a result of chemical reaction between lithium ions and S^{2-} , the Li_2S particles depending on the solubility of Li_2S and precipitation rate starts to form on the cathode surface till the end of discharge.

Once the charging process starts, the set of redox reaction (equation 22-26) begins to occur in the opposite direction to eventually reproduce elemental sulfur again. Before the production of polysulfides begins, Li_2S exists as a single phase with a lithium-poor shell on the surface. The resulting sluggish charge transfer creates a potential barrier in the beginning of charge which improves over time, as polysulfides are generated and ends with a fast kinetics of high order polysulfides. Once the charge barrier is passed, the dissolution of precipitated Li_2S begins which creates the charge plateau. Toward the end of charge, as a result of fast conversion of high order polysulfides, the voltage rapidly increases until it reaches the end of charge voltage. The Li_2S solubility value ($K_{\text{Li}_2\text{S}}$) determines the end of discharge concentration of the last polysulfides, S^{2-} . The higher the solubility value is, the less precipitation occurs during discharge and the greater the concentration at the end of discharge would be.

There are some slight differences between the experimental voltage and the model predictions. This is caused by the fact that the experiments described in Ref. [21] are given for a rate of 0.1C, but the parameters were taken from Ref.[14], which state that their cell had a capacity of 2.5 Ah. For fitting the voltage in Figure 4.3 the capacity of the cell was set to 2.5Ah. Better fitting can be obtained by further fitting the parameters, but this is beyond the scope of the paper. It is important to capture the phase changes and the precipitation, which are reflected in both curves, at approximately $t = 2.5$ h and $t = 17$ h, where the curves follow the same tendencies. The chain of reactions and the formation of polysulfides start from the beginning of discharge, as seen in Figure 4.4. This figure displays the cascade sulfur redox reactions (Eqs. 22-26) and how the concentration of different polysulfides varies as the discharge proceeds through different steps and how by switching to the charge mode, these reactions and concentration trends run in reverse. The concentration profile for each species follows a same trend in a sense that concentration starts to increase, reaches a highpoint, and decreases as a certain reaction starts and finishes.

Due to the high solubility, the concentration of $S_{8(l)}$ in the cathode stays almost constant at the beginning of discharge and then starts to dissolve and consumed for the formation of high order polysulfides. The concentration drops significantly from 19 mol m^{-3} to less than 1 mol m^{-3} and by the end of discharge reaches extremely low values ($c_{S_{8(l)}} = 9.3 \times 10^{-10} \text{ mol m}^{-3}$). Such low concentration values can lead to numerical instabilities which require an increase of number of iterations and a decrease in the tolerance factor for the fully coupled solver.

Yoo et al. [21] proposed including an extra term in the precipitation expressions to tackle the numerical issues corresponds with charging the framework by Kumarasan et al.

[14]. Adding these terms, resolves the limiting numerical issues which the volume fraction of Li_2S and $\text{S}_{8(s)}$ create for the model during precipitation and toward the end of charge. Without the extra term, the concentration continues to increase to some unrealistic values, as seen in Figure 4.5.b which accentuates the importance of including those stabilizing terms in the precipitation/ dissolution expressions. It can also be observed both from Figure 4.4 and Figure 4.5 that the concentration curves for the anode and cathode almost overlap, which indicates that the concentration gradient in both domains is extremely small at low rates.

The volume fraction of Li_2S and S_8 in the cathode as shown in Figure 4.6 indicate that the $\text{S}_{8(s)}$ dissolves almost completely after $t = 1.8$ h and after approximately 2.5 h, it can be seen that the Li^+ ions from the oxidized anode react with the last polysulfide according to reaction 31 and form Li_2S in the cathode as the precipitation process starts in the cathode. Here, it is assumed that dissolution process during charge occurs at an equal rate of the precipitation which as it can be seen in Figure 4.6 Figure 4.6, results in symmetry in Li_2S and S_8 solid volume fraction profiles as it keeps the third term on the right side of Eq.31, R_i the same for both discharge and charge. Therefore, the model can be charged by switching the sign of the applied current density and the increase and decreases in solid volume fraction of Li_2S represents the precipitation and dissolution occurring in the cathode, respectively.

4.3.2 Model with shuttling and capacity loss

As it was explained earlier, shuttling-induced capacity loss is modeled by adding an extra source term (R_{ps} in Equation 32 which only gets enabled during charge) in the material balance equations for the involved polysulfides in both cathode and separator.

Cycling simulation has been performed to investigate the shuttling process and active material loss, as the effect of commuting of polysulfides between the electrodes can be observed by switching from discharge to charge frequently. As shown in Figure 4.7, the voltage curve illustrates a significant capacity loss as the with-shuttling case lags no-shuttling voltage predictions considerably. The shuttle constants $k_{ps,i}$ were randomly chosen to accelerate the capacity loss for illustration purposes. For practical matters, treating these constants as fitted parameters the parameters can help to predict the capacity life of a LiS cell. By looking at the concentrations of lithium from Figure 4.8, one can see that with each cycle, there is less and less Li^+ available for the discharge and charge process and the concentration of S_8^{2-} and S_6^{2-} , S_4^{2-} .

Figure 4.9 in which the volume fraction of the Li_2S and $\text{S}_{8(s)}$ in the cathode decrease with every cycle, indicates a descending trend reflecting the shuttling-induced capacity loss. This observation was also apprehended by Hofmann et. al [20] in their Figure 8a. The volume fraction of solid $\text{S}_{8(s)}$ indicates that with each cycle, more and more active material is lost, which confirms the theory behind the proposed capacity loss mechanism. The same observation can be seen by looking at the volume fraction of Li_2S on the cathode surface, where less and less active material is available to produce S^{2-} and therefore less precipitation occurs by each passing cycle. This indicates that by using a loss approximation method leads to a physical interpretation of a cycled LiS cell and can be used to predict capacity loss without sacrificing numerical resources and with a relatively smaller number of parameters that need to be fitted.

4.4 Conclusions and Future Directions

To provide a better understanding of the shuttling process of polysulfides and investigate how this process can affect the performance of the battery during charge and discharge, a 1D mathematical model developed by Kumaresan et al.[14] has been extended by eliminating the limitations of the existing model to simulate the charging process and to include an approximation for the shuttling-induced capacity loss. It was shown that adding such the approximation the model can be used to predict the capacity loss. This method simplifies the modeling method which would otherwise require the kinetic expressions using of Butler-Volmer formulation in the anode, which adds numerical complexity to the model. The model can be further used to identify the parameters that have the highest contribution to the capacity loss such as separator porosity and thickness. As a future development, adding the Butler-Volmer formulations for capturing the reaction kinetics on the anode, although is computationally expensive due to the extremely low concentration of different chemical species and requires complex solvers and strategies, seems necessary to grasp the real mechanism of the parasitic reactions of polysulfides on the anode surface. Including the physics on the anode side will significantly contribute to the understanding the nature of shuttling induced capacity loss, and also how the shuttling process affects other aspects of the cell performance such as energy efficiency and volume change caused by the deposition of Li_2S on both electrodes.

Figure 4.1. Sketch showing the potential proposed reaction pathway occurring in both electrodes during a) discharging process and b) charging.

Figure 4.2. Sketch showing the components of a typical LiS cell, which consists of a Li metal anode, a polymeric separator, a sulfur-carbon-blend cathode and an ether based electrolyte.

Figure 4.3. Plot showing the comparison between the model predictions and the experimental measurements from Ref. [21] during a C/10 discharge/charge cycle on a 2.5Ah cell.

Figure 4.4. Plots showing the concentration profiles of different species during a full discharge-charge C/10 cycle.

Figure 4.5. Plots showing the concentration of S_8 or two cases: a) when the precipitation formulation have an extra term and b) without the extra term.

Figure 4.6. Plots showing the volume fractions for the no-shuttling case (no reaction sinks in the material balance) in the cathode.

Figure 4.7. Plot showing the voltage for multiple cycles for both cases – shuttling and no-shuttling effects, indicating the capacity loss associated with shuttling.

Figure 4.8. Plots showing the concentration of all the species during four discharge-charge cycles, indicating the capacity loss when shuttling of polysulfides is modeled.

Figure 4.9. Plot showing the volume fractions of different precipitates in the cathode during four full discharge-charge cycles, indicating the decrease of a) $S_{8(s)}$ b) Li_2S due to loss of active material.

Table 4.1. Kinetic and Thermodynamic Properties [14]

Reaction (j)	$i_{0j,ref}$ (A m^{-2})	$\alpha_{a,j}$	$\alpha_{c,j}$	n_j	U_j^0 (V)
1	0.394	0.5	0.5	1	0.0
2	1.972	0.5	0.5	1	2.39
3	0.019	0.5	0.5	1	2.37
4	0.019	0.5	0.5	1	2.24
5	$1.97 \cdot 10^{-4}$	0.5	0.5	1	2.04
6	$1.97 \cdot 10^{-7}$	0.5	0.5	1	2.01

Table 4.2. Transport Properties and Reference Concentrations [14]

Specie (i)	z_i	$D_{i,0}(\text{m}^2 \text{s}^{-1})$	$C_{i,\text{ref}}(\text{mol m}^{-3})$
Li^+	1	$1 \cdot 10^{-10}$	1001.04
$S_8(l)$	0	$1 \cdot 10^{-9}$	19
S_8^{2-}	-2	$6 \cdot 10^{-10}$	0.178
S_6^{2-}	-2	$6 \cdot 10^{-10}$	0.324
S_4^{2-}	-2	$1 \cdot 10^{-10}$	0.02
S_2^{2-}	-2	$1 \cdot 10^{-10}$	$5.229 \cdot 10^{-7}$
S^{2-}	-2	$1 \cdot 10^{-10}$	$8.267 \cdot 10^{-10}$
A^-	-1	$4 \cdot 10^{-10}$	1000

Table 4.3. Separator and Cathode Parameters[14]

Parameter	Separator	Cathode
$L_m(\text{m})$	$9 \cdot 10^{-6}$	$41 \cdot 10^{-6}$
$\epsilon_{m,0}$	0.37	0.778
$\epsilon_{m,S_8(s),0}$	$1 \cdot 10^{-12}$	0.16
$\epsilon_{m,\text{Li}_2\text{S}(s),0}$	$1 \cdot 10^{-7}$	$1 \cdot 10^{-7}$
$a_{m,0}(\text{m}^{-1})$	0	132,762

Table 4.4. Parameters for Precipitation Reactions [14]

Precipitate (k)	Rate Constant (k _k)	Solubility Product (K _{sp,k})	Molar volume V _k (m ³ mol ⁻¹)
S _{8(s)}	1.0 [s ⁻¹]**	19 [mol m ⁻³]	1.239 · 10 ⁻⁴
Li ₂ S _(s)	10 ⁻⁴ [m ⁶ mol ² s ⁻¹]	1 · 10 ⁵ [mol ³ m ⁻⁹] ^a	2.768 · 10 ⁻⁵
a – Assumed ** The second term in Eq. 42 is assumed $k_{S_{8(s),2}} = 1e^{-12} [s^{-1}]$			

Table 4.5. Stoichiometric coefficients [14]

Specie (i)	Stoichiometric coefficient Reaction (j)					
	(S _{i,1})	(S _{i,2})	(S _{i,3})	(S _{i,4})	(S _{i,5})	(S _{i,6})
Li ⁺	-1	0	0	0	0	0
S ₈ (l)	0	-1/2	0	0	0	0
S ₈ ²⁻	0	1/2	-3/2	0	0	
S ₆ ²⁻	0	0	2	-1	0	0
S ₄ ²⁻	0	0	0	3/2	-1/2	
S ₂ ²⁻	0	0	0	0	1	-1/2
S ²⁻	0	0	0	0	0	1
A ⁻	0	0	0	0	0	0

Table 4.6. List of remaining parameters

Parameter	Value and Unit	Reference
T	298 K	Assumed
ξ	1.5	Assumed
b	1.5	Assumed
σ_s	60 S m ⁻¹	Assumed

CHAPTER 5

STATE OF CHARGE LUMPED MODEL

As it was explained in the previous chapter, in the conventional cathode, dissolved polysulfide anions are generated as a result of interaction between sulfur and solvent molecules. However, since dissolution, diffusion, and shuttling of the dissolved polysulfide results in parasitic reactions on the anode side and capacity loss for the cell, various research studies have been focusing on the novel electrode structural designs to explore different alternative cathodes to eliminate or minimize the formation of polysulfide in the LiS cell. Hence, research developments have created two main categories of sulfur electrochemistry for the cathode of LiS cells, e.g. solid sulfur conversion and solid-liquid sulfur. These two conversion mechanisms induce specific shapes in the voltage curve which identifies the type of the system [11].

The other group functions as a polysulfide-bypass cells in which the existence of polysulfide anions is completely avoided at its source by keep the sulfur conversion only in solid phase. As an example for this group of cathodes, sulfurized polyacrylonitrile (SPAN), polymerized from sulfur and polyacrylonitrile, first developed by Wang et al. [80], is a typical sulfur containing compound which has been designed to mitigate the polysulfide generation and shuttling process and improve stability due to having a C-S bond. Figure 5.1 depicts the two groups of cathodes for LiS cells containing different types of sulfur electrochemistry as it was discussed above.

In chapter 2, a thorough literature review of the modeling studies on LiS batteries was provided. As informative as one (or higher) dimensional models are, the model development requires identifying a large number of the chemical and physical parameters such as reaction rate constants, diffusion coefficients, equilibrium potentials, etc. Considering the complexity of the lithium sulfur chemistry, even larger number of properties should be determined compared to the other chemistries. Consequently, although, transport aspects or dimensional volume change cannot be studied in a lumped or 0D model, these models can still provide valuable information about the cell performance and set the basis for the mechanistic studies. Also, due to the computational simplicities, reduced order models are especially important and useful for the control and management purposes.

In all of the mentioned studies in chapter 2, the reaction mechanism on the cathode side is hypothesized to be a consecutive set of reactions in which during discharge the dissolved elemental sulfur is reduced to sulfide ions with lower state of charge resulting in the production of different polysulfides [14]. However, the details of this cascade reaction and the exact reaction mechanism is not known yet and some experimental evidence strongly suggests that even the reaction pathway might be different for charge and discharge [81]. Even though the assumed reaction pathway for the sulfur species has been frequently used in the modeling studies in the literature, the identity of all polysulfide intermediates and their reaction equilibrium are still unknown [82]. Modeling this reaction mechanism requires determining the relevant physical parameters for all the reactions which lead to the production/consumption of polysulfides. The difficulty of isolating each reaction and the resulting polysulfide, makes the measuring of these parameters (e.g.

diffusion coefficient, exchange current density, and equilibrium potential) almost impossible. Hence, most of these parameters in the existing LiS models are assumed values which this matter limits the reliability of these model predictions.

Also, in all the previous modeling studies, the cathode is assumed to be a conventional sulfur cathode which goes through various phase changes while cell operates under charge and discharge. Hence, in order to develop a simple LiS cell model with minimum number of parameters, a lumped model is developed here, which is based on the idea of having an empirical state of charge (SOC) expression for the cell. In other words, by defining the SOC for the cell and having open circuit potential (OCP) versus SOC measurements, all the kinetics and polarizations expressions can be lumped into one to model the charge and discharge performance of the cell. The model is applied to a novel polymer-based electrochemistry for the cathode in which the existence of polysulfide anions is completely avoided at its source. To the best of our knowledge, no modeling effort has been made in the literature to simulate and capture the performance of the cells with solid sulfur conversion cathode.

5.1 Model Development

Various research studies have demonstrated the capability, cycling performance and capacity retention of SPAN as promising cathode in LiS cells [83]–[86]. Although, the molecular structure and reaction mechanism are not fully understood yet, discharge and charge process of this cathode involves lithiation and de-lithiation of the compound which resembles the cathode in lithium ion batteries. For this cathode, as shown in Figure 5.1, since all the sulfur is embedded into the compound, charge and discharge of the cell occurs through bonding and un-bonding of the lithium ions with the polymer structure. According

to the reaction pathway proposed by Wang et al. [80] for SPAN to store lithium (see figure 6 in [80]) each lithium ion which inserts the structure, bonds with one sulfur atom to produce LiS. Their study also proved the absence of lithium polysulfides which causes the stable performance of SPAN.

Considering the resemblance to lithium ion batteries, Zhang et al. [87] modeled the lithium extraction/insertion in a spherical particle in a way that lithium ions are intercalated into solid manganese dioxide resulting in reducing the oxidation state of manganese from 4 to 3.5 (see Eq.1 in [87]). In this case, the state of charge was defined as concentration of lithium-ions within the spinel particle to initial concentration of lithium ions within the spinel particle. Similarly, in case of SPAN cathode, the lithium ions insert the compound which leads to reducing the oxidation state of sulfur from 0 to -1. Therefore, based on the same analogy, the SOC can be defined as:

$$SOC = \frac{C_{Li^+}}{C_{0,Li^+}} \quad 62$$

Based on the lumped framework introduced by Zhang et al. [13], the concentration of lithium varies with time due to the reduction reaction as

$$\frac{d(\varepsilon C_{Li^+})}{dt} = \frac{s a i_L}{nF} \quad 63$$

in which ε is the spatially-averaged cell porosity, i_L is the current density due to the reduction reaction, s is the stoichiometric coefficient of lithium in the reaction, a is the specific surface area for the electrochemical reaction, F is the Faraday constant, and n is the number of electrons transferred in the reaction. By assuming both anodic and cathodic transfer coefficient, α to be 0.5, the kinetics expression as modified Butler-Volmer:

$$i_L = 2i_0 \sinh\left(\frac{nF\eta}{2RT}\right) \quad 64$$

in which i_0 is the exchange current density, R is the ideal gas constant, T is the temperature, and η is the over potential of the reaction as:

$$\eta = \phi_s - U(SOC) + R_{es}I \quad 65$$

in this expression $R_{es}I$ represents the potential drop due to electrolyte resistance, ϕ_s is the potential of the cell, $U(SOC)$ is the open circuit potential of the cell as a function of state of charge. We assume the electrochemical reactions on the anode sides are fast enough so we can neglect the anode overpotential. We need an extra constraint to solve the equations as follows

$$ai_L = \frac{I_{app}}{AL} \quad 66$$

in which I_{app} is the charge/discharge applied current, A is the cross-section area of the cell and L is the cell thickness.

5.2 Results and Discussions

For comparing the model predictions with experimental measurements, a model consisting of equations 62-66 is used and solved in COMSOL Multiphysics to give the discharge predictions for the cell with SPAN cathode. The SPAN coated GF was assembled into coin cells using solid Li as the anode to make 1675 mAh g⁻¹ coin cells at Clemson Nanomaterial Institute. Since to the best of our knowledge, no OCP versus state of charge measurements was found in the literature for the SPAN cathode LiS cell, open circuit as function of state of charge is extracted based on the first cycle of measurements available at low rate ($\sim 0.1C$) as shown in Figure 5.2. The model predictions are compared with the discharge measurements as shown in Figure 5.3 and the fitting parameters are listed in Table 5.1.

As shown in Figure 5.3, the model predictions are matched to the experimental data with satisfactory accuracy. The difference between two types of cathode can be seen by comparing the discharge curve predictions shown in Figure 5.3 and Figure 4.3 in the previous chapter. The discharge curve for the SPAN cathode (Figure 5.3) lacks typical characteristics of lithium sulfur discharge curve, e.g. two distinct stages with a voltage dip in between. The voltage range is between 2.3 and 1 and there is no noticeable plateau in the curve. In the contrary, in case of conventional sulfur cathode (Figure 4.3), the cell experience large concentration gradient resulting in the first steep part of the curve, local voltage minimum, and then a relatively flat plateau. The voltage range in this case is approximately between 2.4 and 1.5. Although, generation of polysulfides during charge/discharge in conventional elemental sulfur cathode gives rise to serious issues such as shuttling and fast capacity loss, but the solid-liquid phase conversion also brings positive aspects including fast sulfur redox reaction, improved sulfur utilization, and as it can be seen in Figure 4.3, flatter discharge curve due to the precipitation of the last polysulfide.

5.3 Conclusion and Further Developments

To model the cell performance and obtain the main features of the typical LiS discharge curve, the material balances, kinetics, and precipitation/dissolution expressions should be solved simultaneously for all the involved species, e.g. S_8 and S_n^{-2} ($n=0..8$). In this study, it was shown how by defining the state of charge for the cell and having OCP versus state of charge measurements, all the kinetics and polarizations expressions can be lumped into one to model the charge and discharge performance of the cell. The framework can be applied to the conventional sulfur cathode and by focusing only on the dissolved elemental sulfur and define the state of charge based on the ratio of its concentration at

each moment to the initial concentration. Reaction Eq. 21 might proceed further to generate different orders polysulfides through any proposed mechanism, but by focusing on the total amount of sulfur (S_8) which starts the chain of reactions, the SOC of the cell can be defined as function of its ratio at each moment. The main reason to define SOC, is the necessity of including this important characteristic parameter in the physics and governing equations of the cell.

When it comes to accurate battery modeling, the relationship of OCP versus SOC is critical, as the obtained SOC coupled with the battery polarization dictates the cell dynamics and determines the framework for different chemical and electrochemical performance of the cell. This matter gains increasing importance considering the fact that electro/chemical mechanism occurring inside of the LiS cell is not well understood yet and not matter how non-destructive an experimental set-up could be, still isolating each reaction to study each single polysulfide is almost impossible to confirm or deny any existing hypothesis in this regard.

Also, it is quite possible that the trajectory of sulfur dissolution be different or more complicated from what is conventionally being assumed to be the reaction pathway for LiS cells. Hence, similar to lithium-ion battery modeling, having OCP versus SOC, can act as the fingerprint of the cell and by eliminating the need to know the detailed reaction mechanism, provides necessary information about the cell performance.

Figure 5.1. Sketch showing different sulfur electrochemistry for LiS cathodes a) conventional cathode. The elemental sulfur $\text{S}_8(\text{s})$ embedded into a conducting carbon b) a polymer-based cathode, SPAN. Charge and discharge of the cell occurs through bonding and un-bonding of the lithium ions with the polymer structure.

Figure 5.2. OCP vs state of charge reproduced based on the first cycle of measurements available at low rate ($\sim 0.1C$) measured experimentally at Clemson Nanomaterial Institute.

Figure 5.3. Discharge predictions for SPAN cathode LiS cell at 0.75C and experimental data by Clemson Nanomaterial Institute.

Table 5.1. Model parameters for SPAN cells

SPAN Coin Cell	
$C_{Li,0}$ (mol/m ³)	191*
i_0 (A/m ²)	0.02*
a (1/m)	1×10^2 *
ϵ	0.51*
R (Ω)	1*
I_{app} (mA)	1.256*
Sulfur Loading(mg)	1*
A (cm ²)	0.76 *
Fitted *	
Clemson Nanomaterials Institute ▶	

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