Modeling, Validation and Analysis of Degradation Processes of Lithium Ion Polymer Batteries

by

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Abstract

The lithium ion polymer battery (LiPB) has become one of the most widely used energy storage devices because of its high energy and power densities. However, its performance and life span are limited by the degradation processes, such as capacity and power fade, under various operating conditions. In order to study the degradation mechanisms, an accelerated test consisting of large cycling currents was conducted on LiPB. According to the analyses of impedance spectra, morphologies and compositions of the cycled cells, the results have shown that the degradation is predominantly caused by the side reactions at the anode. The side reactions consume lithium ions and produce deposits that increase the thickness of the solid electrolyte interphase (SEI) and deposit layers. By fitting a semi-empirical degradation model to the experimental data obtained from different numbers of cycles, the changes of the internal parameters are extracted and used to describe the degradation processes caused by the side reactions.

In order to better understand the mechanism of the side reactions and predict the degradation of LiPB under various operating conditions, the degradation processes are described using physical principles based on Butler-Volmer and Nernst equations that are integrated into the electrochemical-thermal model. The key parameter for the side reactions used in the model is experimentally determined from the self-discharging behavior of the battery. The model is used to analyze the effects of the loss of ions and active materials on capacity fade. The integrated model is then validated against experimental data obtained from testing the battery under

different state of charge (SOC) cycling limits and charging C-rates (1C = 15.7A) and used to study the effects of the operating conditions on degradation mechanisms.

In addition to the side reactions, another important degradation process reported in the literature is crack formation and fracture of the anode and cathode particles due to mechanical stresses. A stress model is developed to describe the mechanical stresses caused by a non-uniform distribution of lithium ions and inhomogeneous localized volume changes inside an electrode particle. The stress model is then incorporated into the electrochemical-thermal model, which has been validated by studying the volume change of a cell while charging and discharging. The simulation results show that the electrode particles are under cyclic stress when the cell is being cycled, which may cause crack and fracture.

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List of Symbols

Α	sandwich area of the cell (cm^2)
a_s	specific surface area of electrode (cm ⁻¹)
C _s	ion concentration in solid phase (mol L^{-1})
C _e	ion concentration in electrolyte (mol L^{-1})
Cionloss	Amount of ion loss caused by the side reactions (A h)
C_p	heat capacity (J kg ⁻¹ K ⁻¹)
D	diffusion coefficient in electrode (cm ² s ⁻¹)
Ε	Young's modulus (MPa)
F	Faraday constant (96,487 C mol ⁻¹)
g	swelling coefficient
h	height of the cell (mm)
h_c	convective heat transfer coefficient (W K ⁻¹)
Ι	current of the cell (A)
i	current density (A cm ⁻²)
i_0	exchange current density of intercalation (A cm^{-2})
$i_{0,side}$	exchange current density of the side reactions (A cm^{-2})
j^{Li}	reaction rate of intercalation (A cm ⁻³)
\dot{J}^{Li}_{side}	reaction rate of the side reactions (A cm ⁻³)
\dot{J}^{Li}_{total}	total reaction rate (A cm ⁻³)

k _{iso}	isolation coefficient due to SEI
L	thickness of the micro cell (cm)
l	coordinate along the thickness of micro cell
т	mass of a single cell (kg)
Ν	number of microcells in a single cell
n	amount of Li ion (mol)
OCV	open circuit voltage (V)
P _{chem}	power contributing to the increase of chemical energy (W)
Q	capacity of the cell (A h)
Q_{aged}	capacity of an aged cell (A h)
$Q_{\it fade}$	capacity fade (A h)
$Q_{\it fade,ion}$	capacity fade due to loss of ions (A h)
$Q_{\it fade,AM}$	capacity fade due to loss of active anode material (A h)
<i>q</i> _{rev}	reversible heat generation rate (W cm ⁻³)
q_{irr}	irreversible heat generation rate (W cm ⁻³)
q convec	heat convection rate (W cm ⁻³)
R	resistance (Ω cm ²) or universal gas constant (8.3143 J mol ⁻¹ K ⁻¹)
r _s	radius of spherical electrode particle (cm)
r	coordinate along the radius of electrode particle (cm)
SOC	state of charge
Т	cell temperature (K)
T_{∞}	ambient temperature (K)
t	time (s)

U_{eq}	equilibrium potential (V)
$U_{\scriptscriptstyle eq}^{\Theta}$	standard equilibrium potential when $c_e = c_{e0}$ (V)
и	radial displacement in electrode particle (cm)
V	voltage (V) or volume of the composite electrode (cm ³)
V_T	terminal voltage of cell (V)
\widetilde{V}	molar volume (cm ³ mol ⁻¹)
W	width of the single cell (cm)
x	stoichiometric number of the anode
χ_{shift}	change in x due to loss of ions
у	stoichiometric number of the cathode

Greek symbols

α	transfer coefficient of reaction
δ	thickness (mm)
δ_{cell}	thickness of the single cell (mm)
З	volume fraction or strain
E _r	radial strain in electrode particle
\mathcal{E}_t	tangential strain in electrode particle
ϕ_e	electrical potential in electrolyte phase (V)
ϕ_s	electrical potential in solid phase (V)
η	activation overpotential of chemical reactions(V)

κ	ionic conductivity (S cm ⁻¹)
κ _D	concentration driven diffusion conductivity (A cm ⁻¹)
v	Poisson's ratio
ρ	density (g cm ⁻³)
σ	conductivity (S cm ⁻¹) or stress (MPa)
σ_r	radial stress in electrode particle (MPa)
σ_t	tangential stress in electrode particle (MPa)
τ	total operating time (s)
σ_h	hydrostatic stress in electrode particle(MPa)
Ω	theoretical partial molar volume of Li-ion (cm ³ mol ⁻¹)
$arOmega_{ ext{fitted}}$	fitted partial molar volume of Li-ion based on experimental data (cm ³
	mol^{-1})
ω	fractional expansivity of electrode material

Subscripts

AM	caused by loss of active anode material
сс	current collector
cell	single cell
DL	deposit layer
EIS	measured by EIS
EOC	end of charge
EOD	end of discharge

e	electrolyte phase
fresh	fresh cell
ionloss	caused by loss of lithium ions
max	maximum
n	negative electrode (anode)
р	positive electrode (cathode)
r	radial direction in electrode particle
SEI	solid electrolyte interphase
SEM	measured by SEM
S	solid phase (active material)
side	the side reactions
Т	terminal
0%	0% state of charge
100%	100% state of charge
-	negative electrode (anode)
+	positive electrode (cathode)

Superscripts

eff	effective
Li	lithium ion

List of Abbreviations

AM	loss of active (anode) material
BV	the Butler-Volmer equation
DL	deposit layer
ECM	equivalent circuit model
EIS	electrochemical impedance spectroscopy
EOC	end of charge
EOD	end of discharge
LiPB	lithium ion polymer battery
LVDT	linear voltage displacement transducer
OCV	open circuit voltage
SEI	solid electrolyte interphase
SEM	scanning electron microscopy
SOC	state of charge
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

1.1 Background

1.1.1 Battery chemistries

Batteries are principally composed of various chemical compositions. The most common types include lead acid, nickel cadmium (NiCd), nickel metal hydride (NiMH), lithium ion, etc. Each type of battery technology has its own unique characteristics. Lead acid is the most economical for larger power applications where weight is of little concern. NiCd is well established and understood but relatively low in energy density. NiMH has a higher energy density compared to the NiCd at the expense of reduced cycle life. Lithium ion is the fastest growing battery system with high-energy density and light weight.

The chemistry of a battery mostly determines its energy density, which is a measure of the amount of energy per unit weight or per unit volume which can be stored in a battery. Figure 1 shows some typical examples, where the lithium ion batteries appear to have the highest energy density compared to other cell chemistries. Lithium ion batteries also have lower internal resistance and larger allowable load current. However, its cycle life does not have any significant advantages when compared to other cell chemistries and its manufacturing cost is usually the highest.



Figure 1: Energy density of different battery chemistries [1].

1.1.2 Battery packaging

Depending on the desired application, the cells can be manufactured into different types including cylindrical, coin, prismatic and pouch type, as shown in Figure 2.



Figure 2: Ways of packaging [2]-[5]: a) cylindrical, b) coin, c) prismatic and (d) pouch.

The cylindrical cell is one of the most widely used packaging styles for batteries due to ease of manufacture and good mechanical stability, but it makes inefficient use of space. The coin cell, also known as a button cell, offers a small size and easy stacking, but most of them are non-rechargeable. The prismatic cell satisfies the demand for thinner sizes and lower manufacturing costs, but requires a slightly thicker wall to compensate for the decreased mechanical stability [6].

Compared to the three types of cell packaging, the pouch cell makes the most efficient use of space and packaging efficiency. The pouch cell has conductive foil tabs welded to the electrode and sealed to the pouch which connects the positive and negative electrodes to the outside. The pouch design has eliminated the metal enclosure to reduce weight. Lithium-ion polymer batteries (LiPB) batteries are commonly packaged in this way. The pouch cell is the most preferred in new applications such as electric and hybrid vehicles that require increased power and energy density. This can be accomplished by employing a large size of active areas by means of folding electrodes, electrolytes, and separators together.

1.1.3 Working principles of LiPB

A single cell consists of multiple micro cells that are packaged together and connected in parallel, where the micro cell is defined as the sandwich structure that includes a negative current collector, an anode, a separator, a cathode and a positive current collector, as shown in Figure 3. The anode indicates a negative electrode and the cathode indicates a positive electrode.



Figure 3: Schematic diagram of a single cell (right) and micro cell (left) (by Meng Xiao).

When a battery is charged or discharged, chemical reactions take place at the interface between the electrode and electrolyte. In order to have a large reaction area, the electrodes in a high power lithium ion battery are made porous to allow the ingress of the electrolyte. In this case, the composite electrode (either the anode or cathode) is a mixture of electrode particles and electrolyte. This allows the ionic current and electron current to coexist, as shown in Figure 4.



Figure 4: Schematic diagram of a micro cell.

The current inside the battery is composed of ionic current, which flows in the electrolyte, and the electron current that is carried by the electrode. When a cell is charged, the electrons and lithium ions will separate at the cathode, as shown in Figure 5. The electrons are transported to the anode through an external circuit and the lithium ions are transported to the anode through the electrolyte. Both the electrons and the lithium ions finally combine at the anode which completes the battery reaction. When the cell is discharged, the flow of electrons and lithium ions are reversed.



Figure 5: Schematic diagram of current flow under charging (by Meng Xiao).

The morphology of the electrode particle is porous to allow a larger active area. An example of this is shown from the scanning electron microscopy (SEM) for $LiCoO_2$ electrode in Figure 6. Here we can see multiple interspaces among the granular crystalline grains. When the $LiCoO_2$ electrode material is used with lithium ion batteries, $LiCoO_2$ is mixed with the liquid electrolyte. The liquid electrolyte then penetrates into the interspaces between the crystalline grains producing a direct contact. Thus, the lithium ion in the liquid electrolyte can easily diffuse throughout the $LiCoO_2$ electrode, which is beneficial for a good electrochemical performance of the material, as well as a high current density.



Figure 6: SEM images of LiCoO₂ electrode in different scales [7].

In recent years, the most commonly used materials to construct the anode are carbon, Sn and Si-based alloys, metal oxides and $Li_4Ti_5O_{12}$ spinel. The most common cathode materials are Li–S, Li_2MnO_4 (LMO), Li_2MnO_3 ·Li[MnNiCo]O₂ (NMC), LiFePO₄ (LFP) and LiMn_{1.5}Ni_{0.5}O₄ [8]. The separator materials are usually composed of polymers, such as polyethyleneoxide (PEO). The most common salt of electrolyte is LiPF₆ and the solvents are usually ethyl-methyl carbonates (EC) and dimethyl carbonate (DMC).

The electrode material has an intrinsic equilibrium potential, which is a function of the stoichiometric number determined by the concentration of lithium ion in the electrode. This means at the equilibrium state (i.e. no macroscopic current across the surface), there is a potential difference between the electrode and electrolyte that is equal to the equilibrium potential. The difference between the equilibrium potentials of cathode and anode is known as the open circuit voltage (OCV).

The state of charge (SOC) of a battery is defined as the ratio of the usable charge per the maximum charge at a particular time which is usually defined as a percentage. At full SOC, the anode has the highest lithium ion concentration while the cathode has the lowest. The opposite is

true for zero SOC, as shown in Figure 7. Changing SOC is equivalent to moving around the lithium ions between the anode and cathode.



Figure 7: SOC and ion concentration in electrodes (by Meng Xiao).

1.2 Literature review

1.2.1 Electrochemical models considering thermal and mechanical effects

Unlike traditional equivalent circuit models, electrochemical models of LiPB describe the cell mathematically using the principles of electrochemical kinetics, potential theory, mass transports, energy balance and elasticity. These numerical models not only simulate the terminal voltage of LiPB with higher accuracy, but can also predict the changes of internal physical variables for in-depth analysis.

The first electrochemical model proposed by Doyle et al. [9] assumed that a cell is made of several thin-film layers and the working mechanism is described with electrochemical principles. Fuller et al. [10] then extended the model by considering various cathode materials, such as $LiCoO_2$ and $LiMn_2O_4$, to investigate the effects of material properties on the performance of a cell. Further improvements of the model have considered the inclusion of a transference number [11], an activity coefficient for the electrolyte [12], a diffusion coefficient for LiPF₆ electrolyte [13] and multiple particle size distributions [14].

The material properties of the electrode and electrolyte, which are related to ion transport and electrochemical kinetics, are affected by heat generation that takes place during the charging and discharging of the battery due to their temperature dependencies. Song et al. [15] and Smith et al. [16] further improved the electrochemical model by incorporating the energy equations which considered various heat generation terms, such as entropy heating, Joule heating and heat of mixing. Chen and Evans [17] added the principles of heat transfer to the electrochemical model.

Mechanical stress is generated by expansion or contraction of the electrode particles due to the change of ion concentration during charging and discharging. There have been several attempts to investigate the mechanisms of stress generation and volume expansion using models. Christensen and Newman [18][19] first proposed a detailed model based on the theories of transport and elasticity to predict the stress in a single anode particle and cathode particle. It was found that at high power applications of a Li-ion battery, there is an increased likelihood of particle fracture while reducing the size of the particles can help prevent such failures.

An alternative method to describe the mechanical stress induced by change in concentration of solutes was proposed by Prussin et al. [20], who mathematically described the

inclusion of boron and phosphorus into an aqueous silicon solution. Yang et al. [21] used the same methodology to model the mechanical stress of a solute in a thin plate. In 2007, Zhang et al. [22] first applied this method to analyze the mechanical stresses in a lithium ion battery and a model for generation of mechanical stress in a single cathode particle was proposed. The simulation results produced similar predictions as was seen with Christensen and Newman's model [19]. Zhang et al. [23] extended the model by considering the heat generation in ellipsoidal particles. It was concluded that a larger aspect ratio obtained from ellipsoidal particles produces better cell performance than spherical particles.

1.2.2 Degradation caused by side reactions

The performances of lithium ion batteries can degrade over the required lifetimes, which can be categorized into calendar or cycle life. The calendar life is affected by self-discharging rate, while the cycle life is affected by operating conditions. Researchers have previously investigated causes of degradation and have identified side reactions as the predominant mechanism [24]-[37], [38]-[40], [41], [42], [43]. The studies show that the side reactions are caused by the reduction process of the electrolyte components, particularly on a composite anode when the electrochemical potential is out of the stability window of the electrolyte. The reduction process consumes lithium ions and the electrolyte solvents and produces deposits. The two prominent side reactions taking place at the anode side are [30];

$$2Li^{+} + 2e^{-} + EC \longrightarrow CH2 == CH2 + Li_2CO_3 \downarrow$$
(1)

$$2Li^{+} + 2e^{-} + 2EC \longrightarrow CH2 == CH2 + (CH_2OCO_2Li)_2 \downarrow$$
(2)

where the arrow " \downarrow " indicates deposit. The products of the side reactions can form very thin layers that adhere to the surface of the anode particles. This thin layer, called solid electrolyte interphase (SEI) [31], is deliberately created during the initial charging cycles by manufacturers to slow down the side reactions. However, when side reactions continue during the charging and discharging cycles over a long period of time, the produced deposits are accumulated in the SEI which serve as growth of the SEI [24][27] [32][33].

The deposits are ionic conductors, but the ionic conductivity is relatively small. Therefore, growth of the SEI leads to increase in ionic resistance and power fade. In contrast, these deposits are electronic isolators [30]-[33] that can electrically isolate some carbon particles, so that these isolated particles cannot participate in the electrochemical reactions, which causes loss of active carbon material and leads to capacity fade [26][27][30][44][42]. In addition, the ions consumed by the side reactions cannot participate in the electrochemical reactions, which contributes to capacity fade [24][43].

There have been various experimental attempts to characterize the effects of side reactions on the morphology and compositions of materials using SEM, X-ray diffraction (XRD) and transmission electron microscopy (TEM) [30]-[33][35][37][38][41]. In addition, electrochemical impedance spectroscopy (EIS) has been used to extract the changes in electrochemical parameters [34][39][40] caused by side reactions. All these findings have revealed that the side reactions taking place at the anode side are the dominant cause for the degradation of LiPB.

The analysis of the effects on battery degradation due to side reactions has been performed using an electrochemical-thermal model by changing the internal parameters that describe the various degradation processes. Previous research has proposed semi-empirical models that extract the values for the degradation parameters by fitting the performance of the model to the experimental data obtained at a different number of cycles [26][28][29][44]. Typically, the degradation parameters used to model the capacity fade are the anode SOC [26], [27], [44] and the cathode SOC [26][27]. These internal parameters are adjusted at the beginning of every cycle when the cell is fully charged. The diffusion coefficient for lithium ion in the electrode at different temperatures is used to model the decrease in rate capability [44] and the phenomena that the deposits clog pores in the particles [27]. The increase of SEI resistance is used to model power fade [44]. The temperature dependency of the degradation parameters was investigated by Santhanagopalan et al. where the degradation process was accelerated in an elevated ambient temperature [26]. However, no solid physical evidence for the selection and justification of the degradation parameters was shown in the aforementioned literature. In addition, the semi-empirical models are not predictive tools for degradations because their results deviate from experimental data when operating conditions are changed, which limits use of the model to real applications.

Therefore, there has been several attempts to develop physics-based degradation models based on electrochemical principles of the side reactions [24][25][27] [42][43]. Doyle et al. first developed a model to describe the side reactions using the Butler-Volmer equation, but no simulation was carried out [25]. Ramadass et al. extended Dolye's model and simulated capacity fade caused by the loss of ions [24]. Sikha et al. extended the model further for the side reactions, where the effects of the deposits on the porosity are considered [27]. Ning et al. then validated Sikha's model using experimental data obtained by cycling the cell under a small current (1C) [43]. Safari et al. has extended the model to consider the diffusion of the electrolyte solvent in

the SEI [42], but did not provide experimental data that proves the effects of such diffusion process on degradation.

The previous research attempted to physically describe the side reactions and formation of the SEI. However, the two important degradation processes observed experimentally, the formation of the deposit layers and the loss of electrolyte solvents [41][45], were not considered in the physics-based models. In addition, the exchange current density and equilibrium potential of the side reactions were assumed values and not validated [24][25][27][43][42]. The degradation rate caused by the side reactions is dependent on the operating conditions, such as SOC, C-rate and temperature [26][41], which has not been fully quantified in the physics-based models. Doyle et al. showed the degradation rate is dependent on SOC [24], but did not consider the effects of C-rates or provide any experimental validations. Also, self-discharging caused by the side reactions [46][47][48] has not been investigated using the degradation models.

Additionally, the effects of side reactions on capacity fade have not yet been clarified. Since the side reactions are irreversible processes that consume lithium ions, some authors have claimed that capacity fade is caused by loss of ions and the amount of capacity fade is assumed to be the same as the amount of ion loss [24][43][49][50]. Others have attributed the capacity fade primarily to the loss of active carbon material due to SEI isolations [27][30][41] because the product of side reactions forms the electronically insulting SEI layer. More authors believed that loss of ions and loss of active material are both factors that lead to capacity fade [44][26][29][42][51], which were analyzed using semi-empirical models rather than physics-based principles. Only Dubarry et al. and Safari et al. have analyzed the effects on loss of ion and loss of active materials, but the corresponding capacity fade have not been quantified [52][53].

1.2.3 Degradation caused by stress generation

Another important degradation process is crack formation and fracture of both electrodes (anode and cathode) due to stress generation [38][54]-[56]. When a cell is charged or discharged, the non-uniform distribution of lithium ions inside an electrode particle can cause inhomogeneous localized volume changes inducing mechanical stress. The stress generation increases as the current increases. The stress may cause crack initiation inside in an electrode particle, leading to crack propagation and then fracture. Such mechanically induced defects may lead to performance degradation, because fractured electrode particles may lose contact with other electrodes or current collectors causing the amount of active material to be reduced [32], [57], [58]-[60].

Only a few degradation models have considered crack and fracture formation in the electrodes. Harris et al. [61] developed a stress generation model for electrode particles with the presence of small internal cracks and pores based on the equations of elasticity. It was shown that stress generation depends largely on the internal microstructure of particles rather than just the material properties of the electrode. Crack propagation in the electrode is analyzed using fracture mechanics theory [36][62]. The tangential tensile stress in electrode particles is considered as the cause for crack initiation and propagation. The energy release rate as a function of crack length has been considered, as well as the stability index of crack growth [36][62].

Although there are several other causes of degradation, such as phase change of the cathode active material with the formation of an oxide layer, lithium plating, and decomposition

of the separator [63][64], no significant degradation has been observed from these mechanisms based on our previous findings. Therefore, these effects have not been considered in this study.

1.3 Objective and dissertation structure

1.3.1 Motivation

Based on the current literature, the degradation mechanisms of lithium ion batteries are not fully understood, and there is a need to improve the existing degradation models to accurately describe the degradation processes. The semi-empirical models [26][27][44] did not provide solid physical evidence for the selection and justification of the degradation parameters. The physics-based degradation models [24][25][27][42][43] lack experimental validation and have not described the effects of loss of ions and active material on capacity fade. The formation of deposit layers and loss of electrolyte solvents has not been considered in any of the previous modeling efforts. Stress generation and crack formation are only modeled for a single electrode particle [36][62][61] and have not been incorporated into an electrochemical model or validated by experiments.

Therefore, it is crucial to develop an electrochemical-thermal-mechanical model that considers predominate degradation processes caused by the side reactions and stress generations. Such efforts can bring up lots of benefits, such as in-depth analysis of degradation mechanisms, optimization of cell design, as well as the prediction of battery life span under different operating conditions.

1.3.2 Approaches and objectives

The objective of this research is to develop an electrochemical-thermal-mechanical model considering dominant degradation effects for LiPB. The working principles of LiPB are shown in Figure 8. The proposed model describes the electrochemical, thermal and mechanical principles with a consideration of the coupling effects (A, B, C and D) and degradation effects (F, G, and H).



Figure 8: Working principles of LiPB.

The electrochemical properties are described by the equations of electrochemical kinetics, potential theory and mass transport. These properties dominate the performance of a cell, such as terminal voltage, SOC, overpotentials, and concentration of ions. The thermal properties are described by the equations for energy and heat transfer, where heat generation and temperature

increase can be calculated. The mechanical properties are described by the equations of elasticity, where ion-induced stress in electrode can be calculated.

Process A describes the heat generation caused by chemical reaction and ion transport. Process B shows how the change in temperature affects the electrochemical properties. Process C describes the non-uniform distribution of lithium ions inside an electrode that induces mechanical stress. Process D demonstrates how mechanical stress induces stress-driven diffusion which affects the electrochemical properties. Process E indicates thermal stress induced by temperature gradient. In fact, the temperature gradient in a single cell is very small (<2 $^{\circ}$ C), so process E is not considered in this work.

Degradation process F is dominated by the side reactions, which is the predominant degradation factor of the cell performance that has been investigated using both semi-empirical degradation model in Chapter 2 and physics-based degradation model in Chapter 3. Degradation process G indicates that the exchange current density of side reactions is temperature-dependent, which is validated in Chapter 3 by studying self-discharge characteristics under different temperatures. The degradation processes under different temperatures are investigated using semi-empirical model in Chapter 2. Degradation process H shows that mechanical stress may lead to crack and fracture of electrode particles which results in additional loss of active materials, where the generation of stresses is calculated in Chapter 5.

The electrochemical and thermal properties as well as their coupling effects (A and B), as shown in black in Figure 8, have been previously developed by Meng Xiao at Auburn University. This work focuses on extending this model by including equations to describe mechanical properties, the coupling effects between mechanical and electrochemical properties (C and D) and most importantly the degradation processes (F, G and H), as shown in red in Figure 8. In addition to model development, experimental investigations are another important part of this research. The morphology and composition analyses of aged cells help to identify the major degradation mechanisms that serve as the basis for the development of the degradation models. Also, the experimental data obtained from cycling profiles, capacity fade and impedance increase is used to validate with simulation results.

The commercial LiPB cells studied in this work has a pouch type with dimensions of $164 \text{mm} \times 250 \text{mm} \times 5 \text{mm}$. The single cell has 15.7A h capacity and is composed of 30 micro cells connected in parallel, whose schematic diagrams are shown in Figure 9. The active material of the anode and cathode are carbon and NMC (Li[MnNiCo]O₂), respectively. The polymer separator is made of polyvinylidene difluoride (PVdF). The electrolyte salt is LiPF₆ and its solvents are ethyl-methyl carbonates (EC) and dimethyl carbonate (DMC). Both electrode particles and the separator are mixed with the electrolyte.



Figure 9: Schematic diagram of the single cell (right) and micro cell (left).

1.3.3 Dissertation Structure

The basic structure of the dissertation is shown as follows:

1. Introduction:

This chapter includes the background, literature review and scope of this work. The setup of electrochemical-thermal model is introduced.

2. Development of a Semi-empirical Degradation Model based on Experiments:

A highly accelerated test is conducted to the cells to investigate the degradation mechanisms. Based on the experimental finding, a semi-empirical degradation model is developed to extract the degradation parameters in order to describe the degradation process.

3. Development of Physics-based Degradation Model Considering Side Reactions:

The side reactions that dominate the degradation process are described using physicsbased equations, such as the Butler-Volmer and Nernst equations, which are integrated into the electrochemical-thermal model described in Chapter 1. The integrated model is validated against experimental data obtained under different operating conditions. This was used to study the effects of different SOC cycling limits and charging C-rates on performance degradation.

4. Development of Electrochemical-thermal-mechanical Model

A stress model for LiPB is developed and integrated to the electrochemical-thermal model. The model is validated in terms of dimension changes under charging and discharging. Simulations of stress generations are carried out under different applying current.

5. Conclusions

1.4 The electrochemical-thermal model [65]

The cell is mathematically described by a one dimensional sandwiched model considering electrochemical and thermal principles, which is shown in black in Figure 8. Since it was developed by Meng Xiao [65], the model setup is briefly introduced in this chapter. The rest of the efforts, as shown in red in Figure 8, are the core parts of this dissertation and will be described in the following chapters.

The model is composed of a composite anode mixed with electrolyte, a separator and a composite cathode mixed with electrolyte, as shown in Figure 4. The electrode materials are porous. When the cell is charged or discharged, electrons go through external circuit while ions are transported in the electrode and electrolyte. Chemical reactions take place at the surface of electrode particles that contact the electrolyte, followed by ion diffusion inside the electrode particles. The model has two temperature-dependent parameters including SEI resistance and diffusion coefficient of ions in electrode particle, whose temperature dependency are obtained empirically. In addition, three heat source terms are considered for temperature behavior that include change of entropy, Joule heating and heat of mixing.

1.4.1 Ion transport and charge conservation
The equation of the material balance of lithium ion in electrode particles is based on Fick's law;

$$\frac{\partial c_s}{\partial t} = D_s \left(\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r} \frac{\partial c_s}{\partial r} \right)$$
(3)

where c_s and D_s are ion concentration and diffusion coefficient in solid electrode, respectively. r is the coordinate along the radius of electrode particle.

Since the ion concentration inside the particles is spherically symmetric and does not have any sources, the gradient of ion concentration at the center is zero. Also the outer boundary of electrode particles is determined by the rate of the reaction;

$$r^{2} \frac{\partial c_{s}}{\partial r}\Big|_{r=0} = 0$$

$$(4)$$

$$- D_{s} \frac{\partial c_{s}}{\partial r}\Big|_{r=R_{s0}} = \frac{j^{Li}}{a_{s}F}$$

The balance of materials in electrolyte is affected by the gradient of ion concentrations. When the electrodes have pores that are filled with electrolyte, the balance should consider the porosity of the material. Accordingly, the diffusion coefficient is redefined considering the porosity as follows;

$$D_e^{eff} = D_e \cdot \mathcal{E}_e \tag{5}$$

where the diffusion coefficient of electrolyte, D_e , is a constant. The material balance for the electrolyte considering the porosity is

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \frac{\partial}{\partial l} \left(D_e^{eff} \cdot \frac{\partial}{\partial l} c_e \right) + \frac{1 - t_+^0}{F} j^{Li} = 0$$
(6)

where c_e is the concentration of lithium ion in electrolyte, *F* is the Faraday's constant, t_+^0 is the initial transference number, ε_e is the porosity, and j^{Li} is the reaction rate.

Since there is no ionic flow at the left and right boundaries of a micro cell, the change in ion concentration in electrolyte is to equal zero;

$$\frac{\partial c_e}{\partial l}\Big|_{l=0} = \frac{\partial c_e}{\partial l}\Big|_{l=L} = 0$$
(7)

The amount of charges produced in oxidation process should be equal to those consumed in reduction process. This relationship is described using the Ohm's law and expressed as a function of currents and potential gradients [65]. Charge transport in electrolyte is governed by the Nernst-Planck equation as shown in the following equation;

$$\frac{\partial}{\partial l} (\kappa_e^{eff} \cdot \frac{\partial}{\partial l} \phi_e) + \frac{\partial}{\partial l} (\kappa_D^{eff} \cdot \frac{\partial}{\partial l} (\ln c_e)) + j^{Li} = 0$$
(8)

where ϕ_e is the electrolyte potential, κ_e^{eff} is the effective electrolyte conductivity and κ_D^{eff} is the concentration driven diffusion conductivity. The boundary conditions for the potentials of electrolyte is

$$\frac{\partial \phi_e}{\partial l}\Big|_{l=0} = \frac{\partial \phi_e}{\partial l}\Big|_{l=L} = 0$$
(9)

where l=0 represents the interface between the electrode and negative current collector, and l=L represents the interface between the electrode and positive current collector.

The charge transport in solid electrode has no diffusion terms, which is solely governed by the Ohm's law;

$$\frac{\partial}{\partial l} (\sigma^{eff} \cdot \frac{\partial}{\partial l} \phi_s) = j^{Li}$$
(10)

where σ^{eff} is the solid phase electronic conductivity. The boundary conditions for the potentials of electrode is

$$-\sigma_{-}^{eff} \left. \frac{\partial \phi_{s}}{\partial l} \right|_{l=0} = -\sigma_{+}^{eff} \left. \frac{\partial \phi_{s}}{\partial l} \right|_{l=L} = \frac{I}{A}$$

$$\left. \frac{\partial \phi_{s}}{\partial x} \right|_{l=\delta_{-}} = \frac{\partial \phi_{s}}{\partial x} \right|_{l=\delta_{+}} = 0$$
(11)

where $l=\delta_{-}$ and $l=\delta_{+}$ represent the interface between separator and electrode at the negative and positive sides, respectively.

1.4.2 Butler-Volmer equation and equilibrium potentials

The current produced by chemical reactions at the interface between electrode and electrolyte is a function of overpotential governed by the Butler-Volmer equation. Here, only the intercalation process is considered;

$$j^{Li} = a_s \cdot i_0 \left(\exp\left(\frac{\alpha_a \cdot n \cdot F}{R \cdot T} \eta\right) - \exp\left(-\frac{\alpha_c \cdot n \cdot F}{R \cdot T} \eta\right) \right)$$
(12)

where a_s is the specific reaction area. α_a and α_c are the symmetric factors of anodic and cathodic reactions of intercalation, which take values of 0.5. *n* denotes number of ions transferred in intercalation reaction which is equal to 1.

To reduce computational time, Eq. (12) can be simplified to a linear form;

$$j^{Li} = a_s \cdot i_0 \frac{n \; (\alpha_a + \alpha_c) F}{R \cdot T} \eta \tag{13}$$

where the activation overpotential of intercalation is

$$\eta = \phi_s - \phi_e - U_{eq} - \frac{R_{SEI}}{a_s} j^{Li}$$
(14)

where ϕ_s and ϕ_e are electrical potentials of solid electrode particle and electrolyte, respectively. R_{SEI} is the resistance of SEI that is present only on anode side.

The equilibrium potential of an electrode, U_{eq} , is a function of stoichiometric number which is determined by the ratio of ion concentration in solid phase to its maximum value. Smith and Wang [16] approximated the negative equilibrium potential using the equation as a function of stoichiometric number

$$U_{eq-}(x) = 8.002 + 5.065 x - 12.578 x^{1/2} - 8.632 \times 10^{-4} x^{-1} + 2.177 \times 10^{-5} x^{3/2} - 0.460 \exp(15(0.060 - x)) - 0.553 \exp(-2.433(x - 0.920))$$
(15)

The positive equilibrium potential is obtained by adding negative equilibrium potential with open circuit voltage (*OCV*) obtained by experiment;

$$U_{eq+}(y) = \left(U_{OCV}\right)_{\text{experiment}} + U_{eq-}(x)$$
(16)

The stoichiometric numbers are defined as

$$x = \frac{c_{s-}}{c_{s,\max}}$$

$$y = \frac{c_{s+}}{c_{s,\max}}$$
(17)

where $c_{s,\max}$ and $c_{s,\max}$ are maximum allowable ion concentration in anode and cathode electrode, respectively.

The initial conditions of various variables are determined from the initial lithium ion concentration in the electrodes. The initial ion concentration is assumed with no gradient and expressed as a function of stoichiometric numbers and *SOC* of the cell;

$$\overline{c}_{s-} = (x_{\min} + (x_{\max} - x_{\min}) \times SOC) \cdot c_{s-,\max}$$

$$\overline{c}_{s+} = (y_{\min} + (y_{\min} - y_{\max}) \times SOC) \cdot c_{s+,\max}$$
(18)

1.4.3 Energy conservation and heat equations

Cell temperature affects the cell performance and the degradation of materials, which is described using the energy equation;

$$C_{p}m\frac{\partial T}{\partial t} = \int_{V} q_{rev}dV + \int_{V} q_{irr}dV + \int_{A} q_{convec}dA$$
⁽¹⁹⁾

where C_p and m are the heat capacity and mass. q_{rev} , q_{irr} and q_{convec} are the reversible heat source, the irreversible heat source, and the heat convection rate, respectively.

The reversible heat is a result of change of entropy during a chemical reaction ($T\Delta S$). Song and Evans [15] expressed the rate of the heat generated as

$$q_{rev} = j^{Li} \cdot T \cdot \frac{\partial OCV}{\partial T}$$
(20)

Since the irreversible heat generation, q_{irr} , includes a Joule heating and a heat of mixing, Xiao and Choe [65] proposed the following modification. The electrochemical energy can be expressed as follows;

$$E_{chem} = -\frac{3\varepsilon_{s,p}FN\delta_p \int_0^{r_s} c_{s,p} \cdot U_{equi,p} r^2 dr}{\delta_{cell} r_s^3} - \frac{3\varepsilon_{s,n}FN\delta_n \int_0^{r_s} c_{s,n} \cdot U_{equi,n} r^2 dr}{\delta_{cell} r_s^3}$$
(21)

The power contributing to the increase of chemical energy can be obtained by differentiating the electrochemical energy with respect to time;

$$p_{chem} = \frac{dE_{chem}}{dt} \tag{22}$$

The irreversible heat generation rate for a micro cell is the difference between the electrical power supplied to the cell $(-V_T \cdot I)$ and the power contributing to the increase of chemical energy (P_{chem}) ;

$$q_{irr} = -\frac{V_T i}{\delta_{cell}} - P_{chem}$$
(23)

When charging, $0 < P_{chem.} < -V_T \cdot I$. When discharging, $P_{chem} < -V_T \cdot I < 0$. Therefore, q_{irr} is always positive. q_{irr} calculated from Eq. (21)(23) includes the Joule heating generated in electrode, electrolyte and their interfaces. q_{irr} also includes the heat of mixing caused by concentration relaxation in electrode. However, the heat generation caused by concentration relaxation in electrolyte is neglected in this work since the amount of Li ion in electrolyte is much less than that in electrode.

In addition, a heat transfer by convection is considered;

$$q_{convec.} = h_c (T - T_{\infty}) \tag{24}$$

where h_c , T and T_{∞} denote the convective heat transfer coefficient, cell temperature and ambient temperature, respectively.

1.4.4 Numerical method

The equations have been discretized and coded using MATLAB. The composite anode, separator and composite cathode are meshed using 25 grids in the direction of thickness of the cell and each electrode particle is meshed using 10 grids in the radial direction. The conservation of charge in electrolyte (Eq. (8)) and (Eq. (10)) across the cell are solved first. The resulting phase and equilibrium potentials are used to calculate overpotential across the cell and then the reaction rate, j^{Li} , using the Butler-Volmer equation (Eq. (13)). The solved potentials, φ_s and φ_e , as well as reaction rate, j^{Li} , provide the inputs for calculating the conservation of mass in the electrode (Eq.(3)) and electrolyte (Eq. (6)). Next, the change in concentration at each time step is determined. Finally, the heat generation rates are calculated and the cell temperature is updated and used for the next time step.

Chapter 2Development of a Semi-empirical DegradationModel based on Experiments

2.1 Accelerated test for identifying degradation mechanisms

In order to identify the degradation mechanisms, a highly accelerated test involving a large cycling current was conducted to the cells. This can decrease the time needed to reach the end of life of the cells so that the degradation mechanisms could easily be analyzed. The cells were charged and discharged with a current of 7C (110A) using three different number of cycles of 100, 200 and 300 as well as three different ambient temperatures of 40 \degree , 25 \degree and 0 \degree . For each cycle, the cell was discharged using a constant current until the terminal voltage decreased to 2.5V and then charged using the same constant current until the voltage reached 4.15V. This was followed by a constant voltage (CV) charge until the magnitude of the current decreased to 0.8A. The test matrix for the highly accelerated test is summarized in Table 1.

Temperature	Number of	Charge/discharge	SOC cycling
	cycles	current	limits
40^{0} C	100		
	200		
	300		
25 ⁰ C	100		
	200	7C/7C	10%-98%
	300		
$0^0 C$	100		
	200		
	300		

Table 1: Test matrix of highly accelerated tests.

After every 20 cycles, a 1C discharge-resting-charge profile was applied to the cell to measure its capacity. The simulation results from the semi-empirical degradation model are fitted to the terminal voltage measured at this 1C cycle to estimate the degradation parameters. The ambient temperature was set as constant during the entire process as described above. The flow chart shown in Figure 10 summarizes the procedures of testing, parameter estimation and validation, as will be discussed in this chapter.



Figure 10: Flow chart of experiment, parameter extraction and validation.

2.1.1 Experimental setup

A test station to conduct experiments was designed, constructed and calibrated. A schematic diagram of the test station is shown in Figure 11, where a Sorensen DCS8-125E

programmable power supply and a Kikusui PLZ1004W programmable E-load were used to generate charging and discharging profiles, respectively. They were connected in parallel to the battery cell and controlled by LabVIEW. Terminal current, voltage and temperature of the cell were measured and made available for estimation of capacity. Tests were conducted in a thermal chamber where the ambient temperature was controlled at 0 $\$, 25 $\$ and 40 $\$.



Figure 11: Schematic diagram of the test station.

After cycling was finished, the cycled cells were sent to the EIS test station to measure their impedance. Before starting EIS tests, the cells were set at 50% SOC by fully charging the cell and then discharging half of its capacity, where the capacity was measured with 1C current. A Gamry FC350 EIS system was used to measure the impedance. The system sends signals to a bipolar power supply to apply different frequencies of small AC excitation current and meanwhile senses the current flow as well as voltage of battery terminals to calculate the impedance at different frequencies. The AC current has amplitude of 1A with frequency from 2kHz to 1mHz. The cell was enclosed in a chamber that maintains $25 \,^{\circ}$ C ambient temperature during the EIS testing.

2.1.2 Analysis of capacity fade

The capacity of each cell, Q, is measured at 1C discharge current in every 20 cycles. The data are plotted in Figure 12 as a function of number of cycles at 40 °C, 25 °C and 0 °C, where the degradation tests have good reproducibility at the same temperature. Generally, the capacity decreased when the number of cycles increased. At different temperatures, the initial capacity and the rate of capacity fade are different.

To better analyze capacity fade at different temperatures, a dimensionless capacity, Q^* , is introduced and defined as the capacity of the aged cell over that of the fresh cell

$$Q^* = \frac{Q_{aged}}{Q_{fresh}}$$
(25)



Figure 12: Capacity vs. number of cycles at different temperatures.

After averaging Q^* among the repeating tests, the averaged dimensionless capacity fade are plotted in Figure 13 at different temperatures. The decreasing rate at the beginning was relatively high, especially for 40 °C and 0 °C, but became low when the cells have been cycled. The final capacities of cells at 300 cycles at 40 °C, 25 °C and 0 °C were 43.2%, 46.4% and 62.7%, respectively. This large fade of the capacity are most likely caused by charging the cells to a high SOC (98%) with a high current rate (7C) in every cycle.



Figure 13: Averaged dimensionless capacity vs. number of cycles at different temperatures.

2.1.3 Analysis of impedance spectrum and SEI resistance

The impedance characteristics of cycled cells measured by EIS at the different temperatures are plotted as markers in Figure 14. The impedance of baseline plot measured from a fresh cell consists of a complete semicircle followed by a less obvious semicircle and a line with increasing slope. Compared to the baseline plot, the impedances of degraded cells are shifted to the right side with increased radius of the first semicircle. However, the effects of the number of cycles and temperature on impedance were not explicit. Therefore, an equivalent circuit model for EIS fitting (EIS-ECM) is used to extract a set of parameters that represent different electrochemical properties of the battery.



Figure 14: Impedance characteristics measured by EIS .

The EIS-ECM is similar to other models reported in the literatures [66]-[70] and its configuration is shown in Figure 15. In the model, L is used to model the mutual inductance of external wires in high frequency domain (>1kHz) [66][67]. R_0 is the ohmic resistance caused by electrolyte, deposit layer, separator, current collector and electrode, which equals to the left intercept between impedance spectrum and the x-axis at high frequency (\approx 1kHz) [67]-[69]. R_1 and C_1 indicate SEI resistance and capacitance at anode, which dominate the shape of the first semi-circle in high frequency domain from 1kHz to several Hz [66]-[70]. R₂ and C₂ indicate charge transfer resistance and double layer capacitance, respectively. They affect the shape of the second semi-circle, which is less obvious in the lower frequency range (several Hz to several mHz) [67][68]. W_a is the Warburg admittance that represents ion diffusion in the electrolyte [66]-[68] and C_{int} is the intercalation capacitance that indicates the process of ion intercalation [67][68]. Both W_a and C_{int} dominate the impedance in the low frequency region (< several mHz). To extract these parameters, the EIS-ECM is fitted to the impedance spectrum measured by EIS using simplex algorithm. The simulated impedance spectra are then plotted as lines in Figure 14 in comparison with the experimental data plotted as markers.



Figure 15: EIS equivalent circuit model.

In this work, the EIS parameter that is most relevant to the degradation model is the SEI resistance. It is extracted and plotted as a function of cycles and temperature, as shown in Figure

16. The dots and bars indicate the mean value and standard deviation, respectively, of $(R_{SEI})_{EIS}$ of cells from the repeating tests. The increase of the resistance was dependent upon the number of cycles and temperature. At 40 °C and 25 °C, $(R_{SEI})_{EIS}$ increased with increasing number of cycles and ambient temperatures. The resistance increased up to four times larger than that of the fresh cell. At 0 °C, the data shows that most degradation took place between 0 – 100 cycles and the changes of $(R_{SEI})_{EIS}$ among 100, 200 and 300 cycled cells are relatively small.



Figure 16: SEI resistance estimated by impedance spectra and EIS-ECM.

2.1.4 Analysis of morphology and composition

The results in this section are provided by Victor Agubra. To investigate any changes of material compositions and morphologies of the cycled cells, the cycled cells were then discharged and opened. The separators in degraded cells were found dry, which is most likely

caused by consumption of electrolyte due to the side reactions. For each single cell, multiple small samples were cut from different locations in the globe box with a high purity argon atmosphere. The separators were removed from anode and cathode samples when morphology and composition analyses are conducted. Two images for anode of the fresh and degraded cell taken by SEM are shown in Figure 17. The anode particles of the cycled cells were coated by white deposits. These deposits are dispersed randomly all over the carbon surface in a non-uniform manner and its coverage ratio does not change significantly from cell to cell.



Figure 17: SEM of a fresh anode (left) and a degraded anode (right) (by Victor Agubra).

SEM was then used to take images for cross sections of the anode, as shown in Figure 18, where the middle and the right images are the cross-sections of a fresh anode and a degraded anode, respectively. Section A is the composite anode with negative current collector embedded inside. The separators are located at section B, but were removed when the images were taken. Section C indicates layers of the deposit that is called "Deposit Layer".



Figure 18: Cross-section of a fresh (middle) and a aged anode (right) (by Victor Agubra).

The SEM images of the cycled cells are used to measure the thickness of the deposit layers, δ_{DL} , that are depicted as a function of the number of cycles and temperature, as shown in Figure 19. The thickness of the deposit layers is in tens of micrometers compared to that of the SEI which is typically several nanometers.



Figure 19: Thickness of the deposit layers (by Victor Agubra).

The composition of the deposit layers was evaluated using X-ray photoelectron spectroscopy (XPS) and a spectrum from which is shown in Figure 20, where the peaks of Li1s, C1s and O1s are identified. Zoomed-in spectra are shown in Figure 21, where the binding energies for Li1s, C1s and O1s are shown. These binding energies are then summarized in Table 2, including those characterized in Li₂CO₃ by Contarni et al. [71] and Contour et al. [72]. Comparison in the table shows that the binding energies measured for Li1s, C1s and O1s correspond to those found in the two standard Li₂CO₃ studies [71][72] indicating the deposit layer should have a composition of Li₂CO₃, which is also a major composition of SEI [30][31][33]. Therefore, it is concluded that the products of the side reactions not just form SEI, but also form thick deposit layers between composite anode and separator.



Figure 20: XPS spectrum derived from the deposit layer (by Dr. Michael Bozack).



Figure 21: Zoomed in XPS spectra derived from the deposit layer (by Dr. Michael Bozack).

Table 2: Binding energies (eV) for Lithium Carbonate, Li₂CO_{3.} (by Dr. Michael Bozack).

Investigator	C1s	Li1s	O1s
This work	289.5	55.0	531.3
Contarni [71]	289.55	55.12	531.40
Contour [72]	289.80	55.20	531.50

SEM images of a fresh and a degraded cathode are shown in Figure 22 and reveal no significant changes. The XRD spectra in Figure 23 also show no phase change or new phase formation in the active materials of anode and cathode.



Figure 22: SEM images of a fresh (left) and a degraded cathode (right) (by Victor Agubra).



Figure 23: XRD of anode (left) and cathode active material (right) (by Victor Agubra).

2.1.5 Summary of experimental results

The results observed from analysis of the cycled cells are summarized as below:

- i. Large amount of deposits are formed at the surface of anode particles.
- ii. The deposits also forms thick deposit layers between the composite anode and the separator.
- iii. The deposits contain Li_2CO_3 .
- iv. The separator dries out.
- v. No phase change in active material of anode and cathode is observed.
- vi. SEI resistance is increased according to the EIS measurement.

Based on the experimental results, the following statements have been drawn:

- a) Since Li₂CO₃ films act as electronic isolators [30][31][33], based on i and iii and other investigations [26][27][29][30][44], the deposits can completely isolate certain anode particles from electrons, so that these particles are no more available for active chemical reactions, which causes loss of active material and leads to capacity loss.
- b) Based on v, the degradation of active materials is negligible and no effect on capacity fade can be assumed.
- c) Based on i and vi as well as other investigations [24][27][31][32][33], the deposits accumulate on the anode particles, which leads to growth of SEI layers and consequently an increase in internal resistance.
- d) Based on ii and iii, the deposit layer has much lower ion conductivity than that of electrolyte so an extra internal resistance is induced by the deposit layer.
- e) Based on iv, the electrolyte is being consumed, which may lead to decrease in diffusion coefficient of electrolyte and extra internal resistance.

In summary, the anode, rather than cathode, is adversely affected by the side reactions. No significant changes were observed regarding active anode and cathode material. Therefore, we have concluded that the side reactions at the anode side and its deposit are the major causes for capacity loss shown in Figure 13 and increase in internal resistance in Figure 16.

2.2 Analysis of side reactions using a semi-empirical degradation model

The effects of side reactions on degradation based on the experimental results as aforementioned are analyzed using the electrochemical-thermal model by changing internal parameters subject to degradation processes. Based on the electrochemical-thermal model described in Eq. (3) to (24), a semi-empirical degradation model is developed that extract the values for the degradation parameters by fitting performance of the model to the experimental data obtained at different number of cycles, as depicted in Figure 10.

2.2.1 Determination of degradation parameters

Schematic diagrams for a fresh cell and degraded cell are depicted in Figure 24, where the circles with blue color on the anode particles represent the SEI layers. In the degraded cell, thicker blue circles indicate the growth of SEI layer due to the formation of deposits. The particles that are completely isolated by the SEI are marked by extra red crosses to indicate their inaccessibility to electrons needed for chemical reactions. The thick bar between the composite anode and the separator indicates the deposit layer. After the cell is degraded, the overall thickness of the micro cell is increased due to the formation of the deposit layer, while the thickness of composite anode, separator and composite cathode are regarded as constant.



A fresh cell An degraded cell Figure 24: The degradation processes involved in the anode side reactions.

The changes of properties of the cell are considered in four degradation parameters: the volume fraction of accessible active anode, SEI resistance, resistance of deposit layer and diffusion coefficient of electrolyte.

Since the deposits of side reactions are electronic isolators, some anode particles can be completely isolated by the deposits and become inaccessible for electrons anymore and therefore, certain amount of active anode material is lost. This phenomena causes capacity fade and is approximated by decreasing the volume fraction of accessible active material, ε_{s-} . ε_{s-} affects the specific area of the anode;

$$a_{s-} = \frac{4\pi r_s^2}{4/3\pi r_s^3} \varepsilon_{s-} = 3\frac{\varepsilon_{s-}}{r_s}$$
(26)

where a_{s-} is equal to the ratio of particle area to particle volume multiplied by ε_{s-} . r_s is the radius of electrode particles.

In fact, capacity fade is not only a function of loss of active material as described above, but also a function of loss of ions caused by the irreversible side reactions. However, it is impossible to separately analyze both effects using the semi-empirical degradation model and the measurement of capacity fade. Therefore, in this chapter, loss of active material is considered as the only cause for capacity fade.

The deposits are conductive to ions so the growth of the SEI results in an increase of internal resistance and leads to power fade. Increased SEI resistance, R_{SEI} , is reflected in change of the activation overpotential, η_{-} ;

$$\eta_{-} = \phi_{s_{-}} - \phi_{e_{-}} - U_{eq_{-}} - \frac{R_{SEI}}{a_{s_{-}}} j^{Li}$$
(27)

where ϕ_{s-} and ϕ_{e-} are the anode and electrolyte potential, U_{eq-} is the equilibrium potential of anode and j^{Li} is the reaction rate.

The deposit layer formed between the separator and the composite anode has a similar chemical composition as that of SEI. Even though the layers are ion conductive, overall ionic resistance of this extra layer is larger than that of pure electrolyte. Consequently, the total internal resistance increases and power fade occurs. The extra voltage drop caused by the resistance of the deposit layer is calculated using the ionic current that passes through the composite anode and is expressed with $\int_{0}^{\delta_{-}} j^{Li}(l) dl$. The terminal voltage is as follows;

$$V_{T} = \phi_{s}|_{l=L} - \phi_{s}|_{l=0} - R_{cc}i - R_{DL}\int_{0}^{\delta_{-}} j^{Li}(l)dl$$
(28)

where V_T is the terminal voltage, R_{cc} is the resistance of current collector, δ_n is the thickness of composite anode and *i* denotes the current density of the micro cell that represents electron current. The current density in the last term has the same magnitude as that of the electron current.

Both R_{SEI} and R_{DL} contribute to the internal resistance for the battery and it is impossible to separately measure the individual value based on the terminal data acquired from cycling. For parameter estimation of the model, R_{SEI} and R_{DL} are regarded as one value. R_{SEI} in Eq. (27) has a unit of Ω cm², where cm² denotes the total area at the anode side where chemical reactions are taking place. R_{DL} in Eq. (28) has a unit of Ω cm², but cm² denotes the sandwich area of the cell. Therefore, the differences in the unit of R_{SEI} and R_{DL} need to be adjusted by reformatting the equations. First define dV_{SEI} as the voltage drop on SEI in a differential volume of composite anode;

$$dV_{SEI} = \frac{j^{Li}(l)}{a_{s-}} \frac{R_{SEI}dl}{\delta_{-}}$$
(29)

where *l* is the coordinate to the thickness direction of composite anode. Then the total voltage drop on SEI, V_{SEI} , is obtained by integrating dV_{SEI} over the thickness of composite anode;

$$V_{SEI} = \int dV_{SEI} = \int_{0}^{\delta_{-}} \frac{j^{Li}(l)}{a_{s-}} \frac{R_{SEI}dl}{\delta_{-}}$$
(30)

Under the assumption that the specific area of the anode and the thickness of SEI is independent upon the *l* coordinate of the anode, the voltage drop on SEI becomes

$$V_{SEI} = \frac{R_{SEI}}{a_{s-}\delta_n} \int_0^{\delta_-} j^{Li}(l) dl$$
(31)

Since the magnitude of the ionic current, $\int_{0}^{\delta} j^{Li}(l) dl$, is equal to that of the current density of cell *i*, the equivalent SEI resistance, R'_{SEI} , is obtained based on Eq. (31), where the resistance has a

unit of Ω cm² and cm² denotes the sandwich area;

$$R'_{SEI} = \frac{R_{SEI}}{a_{s-}\delta_{-}}$$
(32)

Then R_{SEI} and R_{DL} can be regarded as connected in series;

$$R_{SEI+DL} = R'_{SEI} + R_{DL} = \frac{R_{SEI}}{a_{s-}\delta_{-}} + R_{DL}$$
(33)

Since the side reactions consume the electrolyte solvent, the separator of cycled cells becomes dry. The dryness of the separator is considered by decreasing diffusion coefficient of electrolyte, D_e and consequently the effective diffusion coefficient of electrolyte, D_e^{eff} ;

$$D_e^{eff} = D_e \cdot \mathcal{E}_e \tag{34}$$

where ε_e is the porosity (i.e., volume fraction of electrolyte).

2.2.2 Comparison of terminal voltages between simulation and experiment

Extra 1C discharge-resting-charge cycles were applied in every 20 cycles during cycling, where the terminal voltage was measured to find those parameters, as shown in Figure 10. The parameters are estimated by employing the nonlinear least square method that minimizes the error of the terminal voltage between the model and the experiment. The solver for the method

was trust-region-reflective algorithm. The resulting three parameters are estimated every 20 cycles, so that 15 sets of parameters are available up to 300 cycles at each temperature. Comparison of the terminal voltage at 0, 100, 200 and 300 cycles is shown in Figure 25, where 1C discharge-rest-charge cycle was applied and the ambient temperature was 25 °C. As the number of cycles increases, the duration needed for discharging decreases due to the loss of the active materials and as a result the capacity fade occurs. In addition, the magnitude of the voltage increases during charging and decreases during discharging, which are caused by increased resistance of SEI and the deposit layer as well as decreased diffusion coefficient. Consequently, power fade takes place.



Figure 25: Comparison of the terminal voltage at 1C discharge-rest-charge cycle at 25 °C.

The three parameters for the ambient temperature at $40 \,\text{C}$ and $0 \,\text{C}$ are estimated. Comparisons of the terminal voltage for the two temperatures at the different cycles are shown in Figure 26 and Figure 27. The trend of the terminal voltage is similar to that at 25 $\,\text{C}$, but the degradation process became faster than that at $40 \,\text{C}$. At $0 \,\text{C}$, the terminal voltage during discharge becomes smaller and the CV charge takes much longer because the internal resistance increases at lower temperature. However, it does not mean necessarily that the degradation process became more severe at $0 \,\text{C}$.



Figure 26: Comparison of the terminal voltage at 1C discharge-rest-charge cycle at 40 °C.



Figure 27: Comparison of the terminal voltage at 1C discharge-rest-charge cycle at 0 °C.

2.2.3 Analysis of effects of degradation parameters on degradation

The three parameters estimated above from the terminal voltage during cycling are the volume fraction of the active materials, the consolidated resistance for SEI and deposit layer, and the diffusion coefficient of electrolyte. The error bars shown in plots indicate 95% of the confidence intervals of parameters, which are calculated during the parameter estimation process.

The dimensionless volume fraction of the active material, ε_{s-}^* , is defined as ε_{s-} of the degraded cell over ε_{s-} of the fresh cell as a function of the number of cycles and ambient temperatures, which is plotted in Figure 28. ε_{s-}^* decreases as the number of cycles increases, but

depends upon the temperature. The decrease in ε_{s-}^* can be caused by deposits that isolate some particles from the anode electrode. At 25 °C, ε_{s-}^* has mostly decreased during the first 200 cycles, but at 40 °C and 0 °C, most loss in ε_{s-}^* happens during the first 100 cycles. In addition, elevated temperature induces a higher loss of active materials eventually.



Figure 28: Volume fraction of accessible anode vs. number of cycles.

The estimated total resistance obtained from SEI and deposit layer, R_{SEI+DL} , are plotted in Figure 29, where the resistance increases as the number of cycles increases. At 25 °C, the resistance increases mostly in the first 200 cycles but at 40 °C and 0 °C in the first 100 cycles. When the number of cycles becomes larger, the resistance increases as the temperature increases. The increase of the resistance indicates that deposits accumulate at the surface of anode and increase the resistance and thickness of the SEI layers.



Figure 29: Resistance of SEI and deposit layer vs. number of cycles.

The dimensionless diffusion coefficient of the electrolyte, D_e^* , is defined as D_e of the degraded cell over D_e of the fresh cell. D_e^* is plotted in Figure 30 as a function of the number of cycles and different ambient temperatures. D_e^* decreases as the number of cycles increases and the effects of temperature on the coefficient are similar to the other parameters. The decrease of D_e^* is predominantly caused by consumption of electrolyte solvent.



Figure 30: Diffusion coefficient of electrolyte vs. number of cycles.

The analysis of the effects of the parameters on degradation has shown that the degradation speeds up at the beginning of cycling and slows down after a certain number of cycles. The severe degradation at the beginning might be interpreted by the phenomena that the deposits isolate the anode particles that can be easily isolated because of relative small particle size and poor contact with composite anode. Once these particles have been isolated, isolation of the rest particles is difficult and consequently the capacity fade slows down.

The degradation processes by the side reactions are also affected by ambient temperatures. The higher the temperature is, the more has degradation induced. Cycling cells at 40 °C and 25 °C has higher degradation that at 0 °C. During the first 150 cycles, however, the degradation at 0 °C is severer than that at 25 °C. This phenomenon might be caused by decreased diffusion coefficient in electrode at low temperature environment. In this case, when a cell is being charged, the ion concentration at the surface of anode particles is relatively larger due to smaller diffusion coefficient in electrode at low temperature. Such high surficial ion concentration accelerates the side reactions and increases degradation rate. In addition, other degradation mechanisms might be involved like lithium plating [32] that forms at low temperature.

2.2.4 Validation of the resistance of deposit layer using SEM

One of the extracted parameters for degradation model is the resistance that consists of two parts, one from SEI and another from deposit layer, as shown in Figure 29. The resistance of SEI, $(R_{SEI})_{EIS}$, was measured using EIS, as shown in Figure 16. Therefore, the resistance of the deposit layer can be calculated by the difference between the estimated total resistance of SEI and deposit, and the resistance of SEI measured by EIS

$$R_{DL} = R_{SEI+DL} - (R_{SEI})_{\text{EIS}}$$
(35)

On the other hand, the thickness of the deposit layer, $(\delta_{DL})_{SEM}$, at different temperatures was measured by SEM, as shown in Figure 19. Comparisons between the measured thickness of the deposit layer and the resistance of the R_{DL} at different temperatures are shown in Figure 31, Figure 32 and Figure 33, where the error bars of $(\delta_{DL})_{SEM}$ are the standard deviation of the measurements obtained from different samples of a cell.



Figure 31: R_{DL} vs. $(\delta_{DL})_{SEM}$ for cells cycled at 25 °C.



Figure 32: $R_{\rm DL}$ vs. $(\delta_{\rm DL})_{\rm SEM}$ for cells cycled at 40 °C.


Figure 33: R_{DL} vs. $(\delta_{DL})_{SEM}$ for cells cycled at 0 °C.

At a given temperature, both R_{DL} and $(\delta_{DL})_{\text{SEM}}$ increase as the number of cycles increases and are in good agreement. However, the value of R_{DL} is significantly different at different temperatures, which implies the dependence of the conductivity of the deposit layer on temperature.

This conductivity dependence is estimated by

$$\kappa_{DL} = \frac{\Delta(\delta)_{\text{SEM}}}{\Delta R_{DL}} \tag{36}$$

where ΔR_{DL} and $\Delta(\delta)_{\text{SEM}}$ are based on the results in Figure 31, Figure 32 and Figure 33.

The conductivity of the deposit layer, κ_{DL} , for cells cycled at 0, 25 and 40 °C was 1.37, 0.16 and 0.08 S cm⁻¹, respectively. σ_{DL} at 25 °C is twice as large as σ_{DL} at 40 °C. The large variation might result from different compositions and structures of the deposits. In addition,

 σ_{DL} at 0 °C is much higher than σ_{DL} at the two other temperatures, which might be caused by the mixture of formed deposits and lithium plating [32] at low temperature. Thus, the conductivity of the deposit layer appears much higher for cells cycled at low temperature.

2.3 Conclusions

Experimental investigations on material degradation of a pouch type NMC/Carbon battery using SEM, XRD and XPS have revealed that the major degradation is caused by deposits from the side reactions at the anode. Based on these results and a semi-empirical degradation model, three key parameters are identified and extracted from the terminal voltages obtained during cycles. These parameters are the volume fraction of accessible anode ($\varepsilon_{s,n}$), resistance of SEI and deposit layer (R_{SEI+DL}), and diffusion coefficient of electrolyte (D_e). The set of parameters are incorporated into the electrochemical-thermal model, whose performance is compared with the experimental data. In addition, the effects of those parameters on degradation processes are analyzed. Particularly, the validity of the estimated resistance of the deposit layer is shown by measurement of its thickness using SEM.

2.3.1 Key findings

The anode particles are coated by deposits composed of Li_2CO_3 , which is known as the product of the side reactions that is conductive to ions but nonconductive to electrons, but no phase change of active materials has been observed.

- The deposits lead to growth of SEI layer and increase in ionic resistance causing power fade. In addition, they electrically isolate certain anode particles, reducing the amount of active material and causing capacity fade. This hypothesis is manifested by the simulation results of the decrease in volume fraction of accessible active anode and increase in SEI resistance that are predicted using the model.
- The deposits of the side reactions also formed thick deposit layers coated between composite anode and separator. The deposit layer has lower ion conductivity than that of electrolyte and causes extra power fade. The resistance of the deposit layer estimated by the model has the same trend as its thickness measured by SEM.
- The dryness of the separator was observed which is most likely caused by the consumption of electrolyte solvent. This process can decrease the diffusion coefficient of electrolyte, which is predicted using the model.
- At elevated temperature (40 °C), the side reactions are more extensive and more deposits are formed, according to the experimental results and model predictions. The conductivity of deposits is smaller if the cell is cycled at higher temperature.

2.3.2 Future work

In this part, the EIS-ECM shown in Figure 15 is used to fit the impedance data and extract EIS parameters. It is commonly agreed that R_1 indicate SEI resistance [66]-[70], which determines the size of the first semi-circle of the impedance spectrum. However, the electrochemical meanings of other EIS parameters, such as C_1 , R_2 and C_2 , are not consistent in the literature [66]-[70], which is probably caused by different cell chemistries. Therefore, future

work may include verification of these EIS parameters for our cells. In addition, this work considers R_{DL} as part of R_0 . This is because the deposit layer is close to the separator and R_{DL} is assumed to be connected in series to the resistance of the separator, as shown in Figure 24. However, this assumption requires verification in the future too.

Chapter 3 Development of Physics-based Degradation Model Considering Side Reactions

Experimental investigations described in the previous chapter have revealed that side reactions taking place at the anode are the major factor for degradation of the battery performance and lead to capacity and power fade. The side reactions consume ions and solvents from the electrolyte and produce deposits that increase the thickness of the SEI layer and form a new deposit layer between composite anode and separator. As a result, active anode materials are isolated and the diffusivity of the electrolyte becomes low. These phenomena are described using physical principles based on Butler-Volmer and Nernst equations that are integrated into the electrochemical-thermal model described in Section 1.4. The key parameter for the side reactions used in the model is experimentally determined from self-discharging behavior of the battery. The model is used to analyze the effects of the loss of ions and active materials on capacity fade. The integrated model is then validated against experimental data obtained from testing the battery under different SOC cycling limits and charging C-rates and used to study effects of the conditions on degradation mechanisms.

3.1 Modeling of intercalation and side reactions

When the side reactions take place at the interface between the electrode particles and the electrolyte, the reaction rate governed by the Butler-Volmer (BV) equation shown in Section 1.4 needs to be modified by considering an extra reaction rate induced by the side reactions.

Intercalation reactions occur on both electrodes, while the side reactions occur only on the anode side. The total reaction rate, j_{total}^{Li} , is expressed as a sum of both reaction rates;

$$j_{total}^{Li} = j^{Li} + j_{side}^{Li}$$
(37)

where j^{Li} and j^{Li}_{side} denote the reaction rates caused by intercalation and side reactions, respectively.

The BV equation describes the charge transfer process at the interface between electrodes and electrolyte, so the intercalation process is described as;

$$j^{Li} = a_{S} i_{0} \left(\exp\left(\frac{\alpha_{n} R F}{RT} \eta\right) - \exp\left(-\frac{\alpha_{+} n F}{RT} \eta\right) \right)$$
(38)

where a_s is the specific reaction area. α_- and α_+ are the symmetric factors of anodic and cathodic intercalation reactions, which take values of 0.5. *n* denotes the number of ions transferred in intercalation reaction which is equal to 1 for lithium ion. In this work, the chemical reaction of the intercalation is also regarded as the main reaction of the cell, while the side reactions are reduction of electrolyte solvent, which will be described later.

To reduce computational time, Eq. (38) can be simplified to a linear form;

$$j^{Li} = a_s i_0 \frac{n \ (\alpha_- + \alpha_+)F}{R \cdot T} \eta \tag{39}$$

The activation overpotential of intercalation is

$$\eta = \phi_s - \phi_e - U_{eq} - \frac{R_{SEI}}{a_s} j_{total}^{Li}$$
(40)

where ϕ_s and ϕ_e are electrical potentials of the solid electrode particle and electrolyte, respectively. R_{SEI} is the resistance of SEI that is present only on the anode side. U_{eq} is the equilibrium potential of intercalation. In fact, U_{eq} is not just a function of stoichiometric number of the electrode, but also affected by ion concentration in electrolyte, according to the Nernst Equation;

$$U_{eq-} = U_{eq-}^{\Theta}(x) + \frac{RT}{nF} \ln(\frac{c_{e-}}{c_{e0}})$$
(41)

$$U_{eq+} = U_{eq+}^{\Theta}(y) + \frac{RT}{nF} \ln(\frac{c_{e+}}{c_{e0}})$$
(42)

where $U_{eq}^{\Theta}(x)$ and $U_{eq}^{\Theta}(y)$ are the standard equilibrium potentials when c_e is equal to c_{e0} .

The electrochemical-thermal model developed previously used an empirical polynomial that approximated $U_{eq}^{\Theta}(x)$ [54][65], as shown in as shown in Eq. (15). Since the approximation for $U_{eq}^{\Theta}(x)$ has some errors that result in inaccurate calculation of overpotential and side reaction rate, the polynomial has been replaced by a set of data provided by the manufacturer, which is plotted as the blue curve in Figure 34. On the other hand, open circuit voltage (OCV) is measured experimentally, as plotted as green curve in Figure 34. $U_{eq+}^{\Theta}(y)$ can be obtained from the relationship for OCV that is equal to the difference between the two equilibrium potentials on the cathode and anode;

$$OCV = U_{eq^{+}}^{\Theta}(y) - U_{eq^{-}}^{\Theta}(x)$$
(43)



Figure 34: Equilibrium potentials and OCV.

Reaction rates of the side reactions are calculated using the BV equation. Since the rate of the reduction process is much larger than the oxidation process, the side reactions are irreversible and the BV equation can be simplified as follows;

$$j_{side}^{Li} = -i_{0,side}a_s \exp(-\frac{\alpha_{c,side}n_{side}F}{RT}\eta_{side})$$
(44)

where $i_{0,side}$ is the exchange current density of the side reactions, whose temperature dependency will be discussed later. n_{side} is the number of ions involved in the side reactions which is equal to 2, as shown in Eq. (1) and Eq. (2). η_{side} is the activation overpotential of side reactions;

$$\eta_{side} = \phi_s - \phi_e - U_{eq,side} - \frac{R_{SEI}}{a_s} j_{total}^{Li}$$
(45)

where $U_{eq,side}$ is the equilibrium potential of the side reactions;

$$U_{eq,side} = U_{eq,side}^{\Theta} + \frac{RT}{n_{side}F} \ln(\frac{c_e}{c_{e0}})$$
(46)

Unlike $U_{eq,int}^{\Theta}$, $U_{eq,side}^{\Theta}$ is independent on stoichiometric numbers and has a constant value of 0.4V [24][27][42][45][73].

3.2 Modeling of effect of side reactions on degradation processes

Five degradation processes caused by the side reactions are modeled in this work and they are i) loss of ions, ii) growth of SEI, iii) loss of active anode material, iv) growth of deposit layer (DL) and v) loss of electrolyte. Three of them are graphically depicted in Figure 35, where the thick blue circles, the particles marked with red "X" and the layer with blue color indicate SEI, loss of active material and formation of deposit layers, respectively.

The amount of ion loss, $C_{ionloss}$, can be obtained by integrating the side reaction rate, j_{side}^{Li} , over the volume of composite anode and time;

$$C_{ionloss}(\tau) = \int_{x=0}^{\delta_n} \left(\int_{t=0}^{\tau} \left| j_s^{Li}(l,t) \right| dt \right) A dl$$
(47)

where $C_{ionloss}$ has a unit of A h, δ_n is the thickness of composite anode, τ is the total operating time and A is the cross section of the cell.



Figure 35: Schematic diagram of a degraded cell.

The volume fraction of SEI, ε_{SEI} , is the volume of SEI in a unit volume of composite anode and expressed using the rate of side reactions;

$$\Delta \varepsilon_{SEI}(\tau, l) = \frac{\widetilde{V}_{SEI}}{n_{side}F} \int_{t=0}^{\tau} j_{side}^{Li}(l, t) dt$$
(48)

where \tilde{V}_{SEI} is the molar volume of SEI.

Since the rate of side reactions, j_{side}^{Li} , is a function of thickness l, ε_{SEI} also becomes a function of l. Given a ε_{SEI} , the thickness and resistance of SEI can be calculated as follows;

$$\Delta \delta_{SEI}(\tau, l) = \frac{\Delta \varepsilon_{SEI}(\tau, l)}{a_s} \tag{49}$$

$$\Delta R_{SEI}(\tau, l) = \frac{\Delta \delta_{SEI}(\tau, l)}{\kappa_{SEI}}$$
(50)

where κ_{SEI} is the ionic conductivity of SEI.

Loss of active materials is simply described using an empirical equation as follows;

$$\Delta \varepsilon_{s-}(\tau, l) = -k_{iso} \Delta \varepsilon_{SEI}(\tau, l) \tag{51}$$

where ε_s is the volume fraction of solid active material that is also dependent on thickness *l*. k_{iso} is a dimensionless coefficient that describes how fast the active anode materials are isolated from chemical reactions due to electrical isolation of the SEI.

Since particles are glued together by binders that are mechanically resistive against the growth of SEI, SEI is very thin. In contrast, the DL is formed between the composite anode and the separator so it is much thicker in comparison with SEI [41]. The region that is responsible for the formation of DL can be regarded as the region of composite anode without binder, which is $\delta_{-} - R_{s} < l < \delta_{-}$, where R_{s} denotes the radius of anode particles that are adjacent to the separator. Thus, the increase in the thickness of DL is expressed with;

$$\delta_{DL}(\tau) = \frac{\widetilde{V}_{DL}R_s}{n_{side}F} \int_{t=0}^{\tau} j_{side}^{Li}(\delta_-, t)dt$$
(52)

When ionic current flows through the DL, extra voltage drop is induced due to its resistance that can be simply expressed by dividing its thickness by its ionic conductivity, κ_{DL} ;

$$R_{DL}(\tau) = \frac{\delta_{DL}(\tau)}{\kappa_{DL}}$$
(53)

As a result, the terminal voltage becomes as follows;

$$V_{T} = \phi_{s}|_{l=L} - \phi_{s}|_{l=0} - R_{cc}i - R_{DL}\int_{0}^{\delta_{-}} j^{Li}(l)dl$$
(54)

where $\int_{0}^{\delta_{n}} j^{Li}(l) dl$ denotes the ionic current passing through the DL.

Loss of electrolyte solvent by the side reactions is described using the volume fraction of electrolyte;

$$\Delta \varepsilon_{e^{-}}(\tau) = -\frac{\alpha \tilde{V}_{e} C_{ionloss}(\tau)}{A \delta_{-} F}$$
(55)

where α is a coefficient indicating how many moles of electrolyte is consumed when one mole of lithium ion is consumed, which is equal to 0.5 for the side reaction in Eq. (1) and 1 for the side reaction in Eq. (2). Under assumption that both side reactions have the same reactions rate, an averaged value of 0.75 is taken.

Since the effective diffusion coefficient of electrolyte is dependent on ε_e , loss of electrolyte leads to a decrease in the ion diffusion rate in electrolyte

$$D_e^{eff} = D_e \cdot \mathcal{E}_e \tag{56}$$

The amount of charge participating in the degradation processes caused by the side reactions are the integration of j_{side}^{Li} over a given time and the measure for capacity and power fade, as seen in (47) - (56). However, the reaction rates can have different magnitudes at any instant, which is analyzed later in the section 3.5.3.

3.3 Determination of parameters using self-discharge characteristics

As described in the previous section, the rate of the side reactions, j_{side}^{Li} , determines the rates of all corresponding degradation processes. According to Eq. (44), $i_{0,side}$ is the important parameter of j_{side}^{Li} that can be extracted from self-discharging data obtained experimentally.

Eq. (44) shows that j_{side}^{Li} is always negative and never becomes zero, which implies that the side reactions continue when a cell is resting under open circuit. Since the composite anode has no net current under open circuit, the total reaction rate, j_{total}^{Li} , is equal to zero. Then Eq. (37) yields;

$$j_{-}^{Li} = -j_{side}^{Li}$$
(57)

$$j_{+}^{Li} = 0$$
 (58)

Since j_{-}^{Li} is positive based on Eq. (57), the ions are actually transported anode particles into the electrolyte during resting. This amount of ions are consumed in the side reactions because j_{side}^{Li} has the same magnitude of j_{-}^{Li} , as shown in Eq. (57). Therefore, the equilibrium potential of the anode increases due to reduced amount of ion in anode. On the other hand, since j_{+}^{Li} is equal to zero, the equilibrium potential of cathode remains the same. Hence, the OCV decrease under resting.

The mechanism described above is one of the major causes for self-discharge [46][47][48]. Although some work has reported other causes for self-discharge, such as separator leakage and dissolution of Mn from cathode [25], the investigated cells in this work have not shown evidence of these phenomena, so the side reactions are regarded as the only cause for self-discharge.

Since self-discharge is a slow process and its rate is only determined by the side reaction rate, the self-discharge characteristics are used to determine the exchange current density, $i_{0,side}$, of the side reactions. The exchange current density of the side reactions is dependent upon

temperature and experimentally determined by measurement of the self-discharge rate at different temperatures, i.e. $0 \ C$, 25 $\ C$ and 50 $\ C$.

 $i_{0,side}$ is used to calculate the voltage change during self-discharge using the cell model, which is plotted with lines and compared with experimental data plotted with symbols in Figure 36. The experimental data was collected in every several days for about two months. One cell was used to measure the self-discharge characteristic at each temperature. It shows that the simulation results agree with experimental data with minor discrepancy.



Figure 36: Decrease in terminal voltage under self-discharge tests.

The values of $i_{0,side}$ at different temperatures are obtained by comparing the selfdischarge data between experiment and simulation, as summarized in Table 3.

	0°C	25 °C	50 °C
$i_{0,side}$ (A cm ⁻²)	1.87 ×10 ⁻¹⁷	2.61×10^{-10}	1.53 × 10 ⁻¹⁵

Table 3: Value of $i_{0,side}$ obtained from self-discharge characteristics.

3.4 Analysis of electrical potentials under resting, charging and discharging

When the cell is under resting, charging or discharging, the activation overpotentials of intercalation and side reactions, η and η_{side} , change which lead to changes in their reaction rates, j^{Li} and j_{side}^{Li} . As described in Eq. (40) and (45), η and η_{side} are determined by various electrical potentials, including ϕ_s , ϕ_e , U_{eq} , $U_{eq,side}$ and $\frac{R_{SEI}}{a_s} j_{total}^{Li}$, so schematic diagrams are used to analyze their changes at resting, charging or discharging in this section.

At the anode side, Eq. (40) and (45) can be reformulated as

$$\phi_{s-} = \phi_e + V_{SEI} + U_{eq-} + \eta_- \tag{59}$$

$$\phi_{s-} = \phi_e + V_{SEI} + U_{eq,side} + \eta_{side} \tag{60}$$

where

$$V_{SEI} = \frac{R_{SEI}}{a_s} j_{total}^{Li}$$
(61)

At the cathode side, Eq. (59)-(61) are reduced to one equation;

$$\phi_{s+} = \phi_e + U_{eq+} + \eta_+ \tag{62}$$

since there are no side reactions or SEI formation at the cathode side.

In addition, ϕ_e is regarded as the reference (0V) for analyzing other potentials and the gradient of ϕ_e is not considered in these analyses.

3.4.1 Electrical potentials under resting

The analysis is conducted for a cell at 50% SOC, so U_{eq+} and U_{eq-} are set as 3.8V and 0.1V, respectively. At the cathode side, η_{+} is equal to zero since there is no intercalation reaction taking place during resting. Therefore, the potential at the cathode side is depicted in Figure 37, based on Eq. (62).



Figure 37: Electrical potential at the cathode side during resting.

The potential relationships at the anode are more complex than that at the cathode since both main and side reactions take place simultaneously. Two simple cases (case 1 and case 2) and a realistic case (case 3) are schematically depicted, where case 1, case 2 and case 3 consider neither the SEI layer nor the side reactions, only the SEI layer and both the SEI layers and the side reactions, respectively.



Figure 38: Electrical potentials at the anode side during resting.

The electrical potentials for case 1 are depicted in the left of Figure 38, based on Eq. (59). Since the cell is under resting and the side reactions are not considered, there is no intercalation taking place and as a result η_{-} becomes zero.

The electrical potentials for case 2 are depicted in the middle of Figure 38, based on Eq. (59). Although the SEI layer is considered, there is no potential drop at the SEI layer because j_{total}^{Li} is equal to zero at resting, based on the analysis provided in section 3.3.

The electrical potentials for case 3 are depicted in the right of Figure 38, based on Eq. (59) and (60). Under the consideration of side reactions, there is a small reaction rate, j_{side}^{Li} , taking place at the interface. Since $U_{eq,side}$ is 0.2V as calculated from section 3.3, the sign of η_{side} becomes negative from Eq. (60). On the other hand, there is a self-discharge process because j_{side}^{Li} leads to the same magnitude of intercalation reaction rate, j_{-}^{Li} , with the opposite sign, as described in Eq. (57). This small magnitude of j_{-}^{Li} causes a small magnitude of potential drop, η_{-} , that is positive.

In addition, the terminal voltage is equal to the difference between ϕ_{s+} and ϕ_{s-} , as depicted in Figure 37 and Figure 38, respectively.

3.4.2 Electrical potentials under charging

When the SOC remains at 50%, U_{eq+} and U_{eq-} do not change. At the cathode side, lithium ions are transported from solid phase to electrolyte when charged, which results in a positive j_{+}^{Li} as well as a positive η_{+} . Based on Eq. (62), the potential relationship at the cathode side is depicted in Figure 39. Compared to Figure 37, ϕ_{s+} is increased because of the positive η_{+} produced by charging.



Figure 39: Electrical potentials at the cathode side during charging.

Similarly, the potential relationship at the anode during charging is analyzed at three different cases. Case 1, 2 and 3 consider neither the SEI layer nor side reactions, only the SEI and both of them, respectively. The electrical potentials for case 1 are depicted in the left of Figure 40, based on Eq. (59). There is a negative potential drop, η_{-} , caused by the negative j_{-}^{Li} induced by ion transport from electrolyte to solid phase when charged. Compared to Figure 38, ϕ_{s-} is decreased because of the negative η_{-} under charging.



Figure 40: Electrical potentials at the anode side during charging.

The electrical potentials for case 2 are depicted in the middle of Figure 40, based on Eq. (59). There is a potential drop across the SEI. When j_{-}^{Li} is negative at charging, the sign of the V_{SEI} becomes negative, based on Eq. (61) and as a result ϕ_{s-} is decreased further.

The electrical potentials for case 3 are depicted in the right of Figure 40, based on Eq. (59) and (60). Since ϕ_{s-} is decreased under charging, η_{side} becomes more negative, which induces a higher rate of side reactions, based on Eq. (44).

Because of the increase in ϕ_{s+} and decrease in ϕ_{s-} as described above, the terminal voltage becomes large when the cell is charging than resting at the same SOC.

3.4.3 Electrical potentials under discharging

When the SOC remains at 50%, U_{eq+} and U_{eq-} do not change. At the cathode side, lithium ions are transported from electrolyte to solid phase when discharged, which results in a negative j_{+}^{Li} as well as a negative η_{+} . Based on Eq. (62), the potential relationship at the cathode side is depicted in Figure 41. Compared to Figure 37, ϕ_{s+} is decreased because of the negative η_{+} produced by discharging.



Figure 41: Electrical potentials at the cathode side during discharging.

Similarly, the potential relationship at the anode during discharging is analyzed at three different cases. Case 1, 2 and 3 consider neither the SEI layer nor side reactions, only the SEI and both of them, respectively. The electrical potentials for case 1 are depicted in the left of Figure 42, based on Eq. (59). There is a positive potential drop, η_{-} , caused by the positive j_{-}^{Li}

induced by ion transport from solid phase to electrolyte when discharged. Compared to Figure 38, ϕ_{s-} is increased because of the positive η_{-} during discharging.



Figure 42: Electrical potentials at the anode side during discharging.

The electrical potentials for case 2 are depicted in the middle of Figure 42, based on Eq. (59). There is a potential drop across the SEI. When j_{-}^{Li} is positive at discharging, the sign of the V_{SEI} becomes positive, based on Eq. (61) and as a result ϕ_{s-} is increased further.

The electrical potentials for case 3 are depicted in the right of Figure 42, based on Eq. (59) and (60). Since ϕ_{s-} is increased at discharging, η_{side} becomes less negative, which induces a lower rate of side reactions, based on Eq. (44).

Because of the decrease in ϕ_{s+} and increase in ϕ_{s-} as described above, the terminal voltage becomes small when the cell is during discharging than resting at the same SOC.

3.5 Effect of side reactions on capacity fade

The consequences of the side reactions discussed in previous section are loss of ions, loss of active material, growth of SEI/DL, and loss of electrolyte. The first two factors cause capacity fade, while the last three factors lead to power fade. The power fade can be relatively simply predicted based on increased resistances. Therefore, only the relationship between capacity fade and the first two phenomena is analyzed with the help of equilibrium potentials. Equilibrium potentials for anode and cathode are functions of ion concentrations and can be expressed with stoichiometric numbers.

End-of-charge (EOC) and end-of-discharge (EOD) are defined as the points of the OCV that are equal to OCV_{max} and OCV_{min} , as provided by manufacturers, respectively. Capacity of a battery can be expressed with an amount of charges transferred from EOC to EOD and vice versa as follows;

$$Q = (y_{EOD} - y_{EOC})\varepsilon_{s+}\delta_{+}Ac_{s,\max,+}F = (x_{EOC} - x_{EOD})\varepsilon_{s-}\delta_{-}Ac_{s,\max,-}F$$
(63)

For a fresh cell, x_{EOC} , y_{EOC} , x_{EOD} and y_{EOD} correspond to x_{max} , y_{min} , x_{min} and y_{max} , respectively, so the capacity of a fresh cell is

$$Q_{fresh} = (y_{\max} - y_{\min})\varepsilon_{s+}\delta_{+}Ac_{s,\max,+}F = (x_{\max} - x_{\min})\varepsilon_{s-}\delta_{-}Ac_{s,\max,-}F$$
(64)

A relationship between x and y for a fresh cell can be derived;

$$y = -\frac{\varepsilon_{s-}\delta_{-}c_{s,\max}}{\varepsilon_{s+}\delta_{+}c_{s,\max}} (x - x_{\min}) + y_{\max}$$
(65)

The values of x_{max} , y_{min} , x_{min} and y_{max} are provided by the manufacturer. The equilibrium potentials of a fresh cell are plotted versus stoichiometric numbers, as shown in Figure 43, where EOC and EOD are marked with black "X". The OCV is plotted as green curve in Figure 43.



Figure 43: Equilibrium potentials with EOC and EOD for a fresh cell.

3.5.1 Effect of loss of ions on capacity fade

When ions are lost because of the side reactions at anode, the actual stoichiometric number on the anode side, x, is less than that of the fresh cell. The resulting x is a sum of the previous x with x_{shift} , as expressed below;

$$y = -\frac{\varepsilon_{s-}\delta_{-}c_{s,\max}}{\varepsilon_{s+}\delta_{+}c_{s,\max}} \left(x + x_{shift} - x_{\min} \right) + y_{\max}$$
(66)

where x_{shift} is the amount of shift in *x* axis and graphically presented in Figure 44. x_{shift} is expressed with the amount of ion loss;

$$x_{shift} = \frac{C_{ionloss}}{\varepsilon_{s} - \delta_{-} A c_{s, \max} - F}$$
(67)

where $C_{ionloss}$ is calculated based on Eq. (47).



Figure 44: Equilibrium potentials with EOD and EOC for an aged cell after loss of ion.

When a cell is charged to EOC, the OCV_{max} is described using two equilibrium potentials that are a function of the stoichiometric numbers.

$$U_{eq+}(y_{EOC}) - U_{eq-}(x_{EOC}) = OCV_{\max}$$
(68)

The two variables, x_{EOC} and y_{EOC} are numerically solved using Eq. (68) and Eq. (66) and plotted in Figure 44 with symbols of "X". The result shows that the x_{EOC} and y_{EOC} calculated above are less than x_{max} and y_{min} , respectively. Consequently, given the same OCV_{max} , the anode electrode cannot be fully charged while cathode electrode can be over-discharged. The analysis assumes that the amount of over-discharge is small enough to not damage the cathode active material.

Similarly, when a cell is discharged to EOD, the OCV_{min} is described using two equilibrium potentials as follows;

$$U_{eq+}(y_{EOD}) - U_{eq-}(x_{EOD}) = OCV_{\min}$$
(69)

By numerically solving Eq. (69) and (66), the x_{EOD} and y_{EOD} are plotted in Figure 44 with symbols of "X" and they become less than x_{min} and y_{max} , respectively. Consequently, given the same OCV_{min} , the cathode electrode cannot be fully charged while anode electrode can be over-discharged.

In fact, when the carbon anode is over-discharged, most of lithium ions have deintercalated from carbon material and the lattice structure of carbon would contract significantly. In this case, it becomes more difficult to charge lithium ions back into the carbon. However, this mechanism is not considered in the current model.

By updating x_{EOC} , y_{EOC} , x_{EOD} and y_{EOD} in Eq. (63), the cell capacity considering loss of ions is calculated and plotted as blue curve in Figure 46. The capacity fade increases with an increasing amount of loss of ions. However, the amount of ion loss is not the same as that of capacity loss, as is frequently assumed.

3.5.2 Effect of loss of ion and active material (AM) on capacity fade

When a certain amount of active anode material is lost, its volume fraction, ε_{s-} , decreases and the linear equation describing the relationship between y and x should be changed from Eq. (66) to

$$y = -\frac{(\varepsilon_{s0-} + \Delta \overline{\varepsilon}_{s-})\delta_{-}Ac_{s,\max,-}}{\varepsilon_{s+}\delta_{+}Ac_{s,\max,+}} \left(x + x_{shift} - x_{\min}\right) + y_{\max}$$
(70)

where $\Delta \bar{\varepsilon}_{s_{-}}$ is the averaged value of the change of volume fraction obtained from Eq. (51), which is negative. After $\varepsilon_{s_{-}}$ is decreased, *x* changes faster with respect to *y*, based on Eq. (70). This mechanism can be represented by shrinking the *x* axis, as shown in Figure 45.



Figure 45: Equilibrium potentials for an aged cell after loss of ion and active material.

In addition to ε_{s-} , loss of active material also affects x_{EOC} , y_{EOC} , x_{EOD} and y_{EOD} . In this case, x_{EOC} and y_{EOC} can be recalculated using Eq. (68) and (70). Similarly, x_{EOD} and y_{EOD} can be recalculated using Eq. (69) and (70). Their values are plotted in Figure 45 with symbols of "X".

By updating x_{EOC} , y_{EOC} , x_{EOD} , y_{EOD} and ε_{s-} in Eq. (63), the cell capacity considering both loss of ions and loss of active materials is calculated and plotted in Figure 46. The capacity fade increases with increasing amounts of both loss of ions and active materials.



Figure 46: Capacity fade as a function of loss of ion and active anode material.

3.6 Effects of operating conditions on degradation

To analyze the effects of operating conditions on degradation performance, the model for side reactions previously described has been integrated into the electrochemical-thermal model of a cell and simulations have been carried out using different operating conditions, as shown in Table 4. The number of cycles for baseline data was 600 at 25^oC. C-rates for both charging and discharging were 4C. The SOC cycling limit was 25% - 90%. To study the degradation rate as a function of SOC, the SOC cycling limits were changed from 25% - 90% to 15% - 80% and 5% - 70%. The range of each SOC cycling window was maintained at 65%. Also, the degradation rate as a function of the charging C-rate was considered. Three charging C-rates of 2C, 3C and 4C were used to study the effects on degradation rate. The discharging C-rate, ambient temperature and number of cycles were kept constant. Since the computational effort for 600 cycles is very large, simulation of degradation processes was carried out only for the first cycle. The total degradation is then considered as the degradation calculated in the first cycle multiplied by the ratio of total operating time over the time of the first cycle.

	SOC cycling limits	Charging C- rates	Discharging C-rate	Temperature	Number of cycles
Baseline	25% - 90%		4C	25ºC	600
Effect of SOC cycling limits	15% - 80%	4 C			
	5% - 70%				
Effect of charging C- rate	25% - 90%	3C			
		2C			

Table 4: Test matrix considering different operating conditions.

To validate the model, experiments were conducted under the same operating conditions shown in Table 4. One cell was tested at each operating condition. For each case, a new cell was used. After every 20 cycles, a 1C current rate was applied to measure the cell capacity. Upon completion of the cycle, the cycled cells were set at 50% SOC and their impedances were measured using EIS. After each cycled cell was completely discharged and opened, samples of cells were cut off and analyzed using SEM to investigate the morphology and deposit layers.

3.6.1 Degradation under the baseline condition

Discharging characteristics of the cell at 1C current rate and every 200 cycles are plotted in Figure 47, where voltage drops and discharge times of the model are compared with those of experiments. Generally, as the number of cycles increases, the voltage decreases faster and the discharge time becomes shorter due to capacity fade. The voltage drop of the model tends to follow the experimental data at the beginning and middle of the discharge. At the end of the discharge, the simulated voltage matches the experimental data for the fresh cell and cell at 600 cycles. However, there are some deviations at 200 and 400 cycles, which are caused by inaccurate estimations of capacity.



Figure 47: 1C discharge curves of aged cell under baseline test conditions.

For analysis of capacity fade, the calculated amount of ion loss, C_{ionloss} , capacity fade caused by ion loss, $Q_{fade,\text{ion}}$, and loss of active material, $Q_{fade,AM}$, are plotted in Figure 48. The measured total capacity fade is plotted for validation as well. The total amount of capacity fade from simulations and experiments at different cycles are comparable. Interestingly, the amount of ion loss, C_{ionloss} , is not the same as that of capacity fade caused by the ion loss, $Q_{fade,\text{ion}}$, as explain in section 3.4.1. In addition, the capacity fade caused by loss of active material is slightly larger than that by loss of ions, based on the simulation results.



Figure 48: Analysis of capacity fade under baseline test conditions.

Based on the simulation results, the effects of cycling on SEI, volume fractions of active anode material and electrolyte are analyzed. SEI resistances as a function of anode thickness calculated using Eq. (48), (49) and (50) are plotted in Figure 49. As the number of cycles increases, the SEI resistance tends to increase and the increase is large near the separator on the anode side because of the high ion concentrations that cause a high rate of side reactions.



Figure 49: Change in SEI resistance under baseline test conditions.

The volume fraction of the active anode material, ε_s , and the electrolyte, ε_e , are calculated and plotted in Figure 50. As the number of cycle increases, ε_s becomes less, particularly near the separator because of isolation of the active material by growing SEI layers, which can be seen in Eq. (51). Similarly, ε_e becomes less because of the side reactions that consume the electrolyte. It is assumed that there is no gradient of ε_e in the direction of anode thickness, based on Eq. (55).



Figure 50: Volume fractions of active material and electrolyte.

3.6.2 Effects of SOC cycling limits on degradation

In real world operations, the SOC cycling limits vary depending upon operating modes. The effects of different SOC cycling limits are investigated using the test conditions shown in the second and third row of Table 4. Calculated and measured capacity over the number of cycles under different SOC cycling limits are plotted in Figure 51. Generally, capacity fade of the cell cycled at 25% - 90% is the largest, followed by 15% - 80% and 5% - 70%. The model can predict the capacity fade well. The deviations might be caused by some other neglected degradation mechanism as indicated in literature, such as phase change of the cathode active

material with the formation of an oxide layer, lithium plating, and decomposition of the separator [63][64].



Figure 51: Capacity fade at different SOC cycling limits.

Calculated and measured discharging characteristics of the fresh and cycled cells after 600 cycles under different SOC cycling limits are plotted in Figure 52, where the current rate was 1C. After cycled, cells become quickly discharged because of the faded capacity. The higher the SOC is, the faster the cells are degraded.



Figure 52: 1C discharge curve at 600 cycles at different SOC cycling limits.

Similar to Figure 48, analysis of capacity fade for cells cycled under different SOC limits is shown in Figure 53. The total amount of capacity fade in simulations and experiments at different SOC cycling limits are comparable. The fade caused by ion loss is slightly smaller than that by active material loss.


Figure 53: Analysis of capacity fade at 600 cycles at different SOC cycling limits.

The SOC limits also affect SEI resistance. The simulated and measured SEI resistances as a function of SOC limits are plotted in Figure 54. The measured values of SEI are obtained from EIS analysis, as described in section 2.1.3. SEI resistance significantly increases as the SOC cycling limits move to the upper range. The model tends to follow the experimental data.



Figure 54: SEI resistance of fresh cell and cells after 600 cycles.

Similarly, SOC cycling limits affect the formation of deposit layers. As a result, ion conductivity decreases and internal resistance increases. Calculated and measured thicknesses of the DL using Eq. (52) and SEM are plotted in Figure 55. The thickness increases as SOC cycling limits move to the upper range. The model tends to follow the data extracted from the SEM measurements with some deviations. A few examples of SEM micrographs are provided in the Appendix.



Figure 55: Thickness of DL of fresh cell and cells after 600 cycles.

The results of capacity fade and resistance increase shown above reveal that degradation is most severe in the cell operated at high SOC cycling limits, 25% - 90%, followed by 15% - 80% and 5% - 70%. For more detailed analysis, the rate of side reactions, j_{side}^{Li} , is analyzed since it determines the rates of all degradation processes caused by the side reactions.

The calculated and measured terminal voltages as well as calculated j_{side}^{Li} are plotted in Figure 56 during a single discharge-charge cycle under different SOC cycling limits. When the cells are discharged, the terminal voltages decrease and the magnitude of j_{side}^{Li} decreases. When the cells are being charged with a constant current, the terminal voltages begin to increase and the magnitude of j_{side}^{Li} increases significantly. Finally, when the cell is charged with a constant voltage, the magnitude of j_{side}^{Li} decreases because of decreased charging current. The cell cycled under 25% - 90% has the highest magnitude of j_{side}^{Li} , followed by 15% - 80% and 5% - 70%.



Figure 56: Terminal voltage and side reaction rates in one discharge-charge cycle.

The variation of j_{side}^{Li} shown above is caused by the changes in $i_{0,side}$ and η_{side} , based on Eq. (44). On one hand, j_{side}^{Li} is proportional to $i_{0,side}$, which is a function of temperature, as summarized in Table 3. Since all operating conditions considered in this work have used the same ambient temperature, the temperature variations during operation were small so the effects of temperature on $i_{0,side}$ and j_{side}^{Li} were not significant and thus not analyzed in details. On the other hand, j_{side}^{Li} is very sensitively affected by the change of η_{side} because η_{side} is the variable in the exponential power term, as shown in Eq. (44). In addition, as seen from Eq. (45), η_{side} can be affected by other factors, so detailed analyses are performed. By substituting Eq. (14), (41), (46) with Eq. (45), a new expression for η_{side} is obtained;

$$\eta_{side} = \eta + U_{ce} + U_{eq}^{\Theta}(x) - U_{eq,side}^{\Theta}$$
(71)

where

$$U_{ce} = \frac{RT}{2F} \ln(\frac{c_e}{c_{e0}}) \tag{72}$$

Hence, η_{side} includes four terms, where $U_{eq,side}^{\Theta}$ is considered a constant and the rest three terms, η , U_{ce} and $U_{eq}^{\Theta}(x)$, are analyzed for one discharge-charge cycle, as shown in Figure 57.



Figure 57: Potentials in one discharge-charge cycle at different SOC cycling limits.

The first term is the activation overpotential of intercalation, η . The simulation results in Figure 57 show that η is positive when the cell is being discharged and negative when the cell is being charged. This is true because η is proportional to the reaction rate of intercalation, j^{Li} , based on Eq. (13), so η should have the same sign with j^{Li} .

The second term is the potential change caused by ion concentration in electrolyte, U_{ce} , which originates from the Nernst equation, Eq. (41) and (46). U_{ce} is positive when the cell is discharged and negative when the cell is charged. When the cell is discharged, ions are transported from anode to cathode through electrolyte according to the diffusion process shown in Eq. (6). Ion transport is driven by the gradient of ion concentration from high c_e region to low c_e region. Therefore, in the region of composite anode, c_e is larger than c_{e0} under discharging and smaller than c_{e0} under charging, which explains the signs of U_{ce} shown in Figure 57.

The third term is the equilibrium potential of intercalation at anode, $U_{eq^-}^{\Theta}$. As expected, $U_{eq^-}^{\Theta}$ decreases with the increase of SOC, as shown in Figure 57.

In summary, η_{side} becomes more negative when SOC becomes high and when the cell is being charged rather than discharged. The magnitude of the side reaction rate increases if η_{side} becomes more negative, as shown in Eq. (44). Consequently, charging a cell to higher SOC leads to a larger rate of side reactions, which eventually accelerates degradation.

3.6.3 Effects of charging C-rate on degradation

In real world operations, the C-rates at charging vary depending upon vehicle operating conditions. Effects of charging C-rates on capacity fade are investigated using the test conditions shown in the fourth and fifth row of Table 4. Calculated and measured capacity over the number of cycles under three charging C-rates are plotted in Figure 58. The capacity fade of the cell cycled at 4C charging rate is the largest, followed by 3C and 2C. However, the capacity fade under different charging rates is not clearly distinctive. The model can predict the capacity fade well with some deviations, which might be caused by some other neglected degradation mechanisms as indicated in the literature review.



Figure 58: Effect of charging C-rates on capacity fade.

Calculated and measured discharging characteristics of the fresh and cycled cells after 600 cycles as a function of charging C-rates are plotted in Figure 59, where the current rate was 1C. After being cycled, the cells become discharged quickly because of the faded capacity. When the charging C-rate becomes larger, the capacity fade is slightly increased.



Figure 59: 1C discharge curve at 600 cycles at different charging C-rates.

Similar to Figure 48 and Figure 53, capacity fade for cells cycled under different charging C-rates is analyzed and shown in Figure 60. The total amount of capacity fade in simulations and experiments at different charging C-rates are comparable.



Figure 60: Analysis of capacity fade at 600 cycles at different charging C-rates.

The charging C-rates also affect SEI resistance, too. The simulated and measured SEI resistances as a function of charging C-rates are plotted in Figure 61. SEI resistance slightly increases as the charging C-rate increases. The simulation result tends to follow the experimental data with some deviations.



Figure 61: SEI resistance of fresh cell and cells after 600 cycles.

Similarly, the formation of the DL is affected by charging C-rates. Calculated and measured thicknesses of the DL using Eq. (52) and SEM are plotted in Figure 62. The thickness increases with the increase of charging C-rates. The simulation results tend to follow the data extracted from the SEM measurements.



Figure 62: Thickness of DL of fresh cell and cells after 600 cycles.

The results of capacity fade and resistance increase as shown above reveal that the degradation is worsening when the charging C-rate is high. Similar to the previous section, analyses of j_{side}^{Li} and η_{side} are conducted again with three different charging C-rates.

The calculated and measured terminal voltages as well as calculated j_{side}^{Li} are plotted in Figure 63 for a single discharge-charge cycle under different charging C-rates. When charged with high C-rates, the magnitude of j_{side}^{Li} becomes large as does the instantaneous degradation rate.



Figure 63: Terminal voltage and side reaction rates in one discharge-charge cycle.

As explained previously, j_{side}^{Li} is predominantly affected by η_{side} that is a function of the three variables, η , U_{ce} and U_{eq}^{Θ} . The three variables are calculated and plotted in Figure 64.



Figure 64: Potentials in a discharge-charge cycle at different charging C-rates.

As the charging C-rate increases, η has a negative value and becomes smaller. As explained in the previous section using Eq. (13), η is a function of j^{Li} , so the magnitude of η increases as the charging C-rate increases.

Similarly, U_{ce} also becomes small as charging C-rate increases. The increased charging C-rate leads to a higher gradient of ion concentration in the electrolyte. Consequently, c_e in composite anode becomes low and U_{ce} gets decreased with the increase of charging C-rate.

In addition, U_{eq}^{Θ} decreases rapidly when the cell is charged with increased C-rate because of the resulting high SOC.

The analysis of effects of C-rates on performance show that η_{side} decreases and j_{side}^{Li} becomes significantly high when the charging C-rate is increased. However, dependence of the degradation upon the C-rates was not clearly distinctive at the same number of cycles (Figure 58 to Figure 62) because the degradation is determined by integration of j_{side}^{Li} over time, according to Eq. (47), (48) and (52). When C-rates are high, charging process takes shorter time although the magnitude of j_{side}^{Li} is large. Consequently, contribution of charging C-rates to degradation is limited, as predicted by the model, which agrees with the trend of experimental data (Figure 58 to Figure 62).

3.7 **Conclusion**

A variety of experimental analysis has shown that the side reactions are the main cause for degradation process in lithium ion batteries. The side reactions are mathematically described using the Butler Volmer and Nernst equations and the corresponding degradation processes are modeled based on physical principles. The model is incorporated into the electrochemicalthermal model developed previously. The integrated model is then validated against experimental data obtained from large format LiPB NMC/Carbon cells. Numerical and experimental analysis have shed light on the mechanisms of capacity and power fade as well as their dependencies on different operating conditions.

3.7.1 Summary of findings

- Not only the loss of ion, but also the loss of active anode material are the factors that cause capacity fade. The mechanisms are illustrated by analysis of the two factors on EOC and EOD determined by two equilibrium potentials and OCVs.
- The side reactions produce deposit layers and increase the thickness of SEI layer, which leads to power fade. Simulated growths of both layers are confirmed quantitatively characterized using SEM and EIS.
- The charging process causes more degradation than the discharging process. The overpotential of the side reactions (η_{side}) is small during charging and large during discharge. Consequently, the rate of side reactions during charging is larger than that during discharging.
- Cycling at high SOC accelerates the degradation processes because the equilibrium potential of anode becomes low, which leads to low η_{side} and large rate of side reactions.
- Charging at high C-rate significantly and instantaneously increases the degradation rate. However, the dependence of degradation upon the C-rates was not clearly distinctive at the same number of cycles, because high C-rate leads to not only increase of side reaction rate but also reduction of charging time.

3.7.2 Future work

In order to reduce computational time, the simulation of degradation processes was carried out only for the first cycle and the total degradation under multiple cycles is considered as the degradation calculated in the first cycle multiplied by the ratio of total operating time over the time of the first cycle. However, this method does not consider the effect of historical degradation on the new degradation processes. For example, the degradation process in the 300th cycle should be different from that in the 1st cycle because the internal parameters have been changed due to the degradation during the first 300 cycles. Therefore, future work may include conducting simulation of degradation processes over the entire operating time.

The second mechanism that needs to be considered in the future is the over-discharge of carbon anode due to loss of ion and active materials, as shown in Figure 44 and Figure 45. As described previously, when the carbon anode is over-discharged, most of lithium ions have deintercalated from carbon material and the lattice structure of carbon would contract significantly. In this case, it becomes more difficult to charge lithium ions back into the carbon. This mechanism needs to be investigated, which might be modeled by increasing charge transfer resistance.

In addition, Eq. (51) empirically describes the effect of SEI layers on isolation of active anode materials, which needs verification in the future work too.

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Chapter 4 Development of Electrochemical-thermalmechanical Model

Mechanical stress is generated in electrode particles of batteries during charge and discharge. The stress can cause cracks in the solid particles which eventually leads to a fracture of the electrodes. In order to understand the mechanism, a stress model for a pouch type high power LiPB is developed and incorporated into the electrochemical-thermal model. The integrated model is validated against experimental data in terms of dimension changes.

4.1 **Development of stress model**

When a cell is charged and discharged, stress is generated by a non-uniform distribution of ions inside an electrode, which is shown as process C in Figure 8. On the other hand, the generated stress induces stress-driven diffusion which affects the electrochemical properties, which is shown as process D in Figure 8. In this section, these two processes are modeled mathematically and then incorporated in the electrochemical-thermal model.

4.1.1 Modeling of ion-induced stress and dimension changes

The electrode particles are regarded as elastic materials whose expansion is affected by concentration and partial molar volume of ions that inserted, as shown in Figure 65.



Figure 65: Localized volume changes and stress generation in a spherical electrode particle.

The Hooke's law can be applied by adding an extra term that describes the ion-induced changes in normal strains [22];

$$\varepsilon_{ij} = \frac{1}{E} \left[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij} \right] + \frac{1}{3}c_s\Omega\delta_{ij}$$
(73)

where *i*, *j*, *k* take values of 1, 2 or 3. δ_{ij} is the Kronecker delta that is equal to 1 when i=j and 0 when $i\neq j$. c_s is the ion concentration in solid phase. Ω is the Partial Molar Volume (PMV) of lithium ions in the electrode with a unit of cm³ mol⁻¹. PMV is defined as the volume change in lithiated electrode when the inserted ion increases by one mole. Since the materials of anode and cathode have different lattice constants and structures, the PMV of lithium ion in anode and cathode has a different value.

The second term in Eq. (73) assumes that the volume expansion induced by ion insertion is isotropic in 3 normal directions. The stress equilibrium equation and strain-displacement relationship are

$$\sigma_{ij,i} = 0 \tag{74}$$

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$
(75)

As each electrode particle is approximated as a one-dimensional symmetric elastic sphere, Eq. (73)-(75) can be transformed to one-dimensional polar forms as follows;

$$\varepsilon_r = \frac{1}{E} \left[\sigma_r - \nu (\sigma_t + \sigma_t) \right] + \frac{1}{3} c_s \Omega \tag{76}$$

$$\varepsilon_t = \frac{1}{E} \left[\sigma_t - \nu (\sigma_t + \sigma_r) \right] + \frac{1}{3} c_s \Omega \tag{77}$$

where σ_r , σ_t , ε_r and ε_t are stress and strain components in the radial and tangential direction.

The stress equilibrium for a differential volume, as shown in Figure 65, is

$$\frac{d\sigma_r}{dr} + \frac{2}{r} \left(\sigma_r - \sigma_t\right) = 0 \tag{78}$$

The strain-displacement relations are

$$\mathcal{E}_r = \frac{du}{dr} \tag{79}$$

$$\mathcal{E}_t = \frac{u}{r} \tag{80}$$

where u denotes the displacement in radial direction.

Two boundary conditions are used. Firstly, the radial displacement u at the center of sphere (r=0) is zero since the particle is considered as symmetric sphere. Secondly, the radial

stress σ_r at the particle surface ($r = r_{s0}$) is zero since the particle surface is regarded as a free surface. This boundary condition assumes that the reaction forces between particles are small and negligible.

Based on Eq. (76)-(80) and the boundary conditions, the stress and radial displacement can be solved as a function of r and $c_s(r)$;

$$\sigma_{r} = \frac{2\Omega E}{3(1-\nu)} \left(\frac{1}{R_{s0}^{3}} \int_{0}^{r_{s0}} c_{s} r^{2} dr - \frac{1}{r^{3}} \int_{0}^{r} c_{s} r^{2} dr \right)$$
(81)

$$\sigma_{t} = \frac{\Omega E}{3(1-\nu)} \left(\frac{2}{R_{s0}^{3}} \int_{0}^{r_{s0}} c_{s} r^{2} dr + \frac{1}{r^{3}} \int_{0}^{r} c_{s} r^{2} dr - c_{s} \right)$$
(82)

$$u = \left[\frac{2\Omega(1-2\nu)}{9(1-\nu)} \cdot \frac{3}{r_{s0}^3} \int_{0}^{r_{s0}} c_s r^2 dr + \frac{\Omega(1+\nu)}{9(1-\nu)} \cdot \frac{3}{r^3} \int_{0}^{r} c_s r^2 dr\right] \cdot r$$
(83)

The value of mechanical properties for electrodes, such as Young's modulus and Poisson's ratio, are listed in Table 8 in the appendix. It should be noted that these mechanical properties are considered as isotropic since each electrode particle consists of numerous lattices with different orientations.

The thickness of a cell generally varies at charging or discharging because the volume of an electrode particle is affected by the presence of ions. When a cell is charged, anode particles expand while cathode particles contract. Conversely, cathode particles expand and anode particles contract when a cell is discharged. However, the rates of volume changes in anode and cathode are not the same because the composite anode and composite cathode have different lattice structures, thicknesses and volume fractions. As a result, the overall volume of a cell varies as the SOC does.

The change of particle radius, Δr_s , can be found by setting $r = r_{s0}$ in Eq. (83);

$$\Delta r_s = u(r_{s0}) = \frac{1}{3} \overline{c}_s \Omega r_{s0} \tag{84}$$

where \bar{c}_s is the averaged ion concentration in an electrode particle and r_{s0} is the radius of an electrode particle without the presence of lithium ions.

The volume changes of composite electrode (anode or cathode) mixed with electrolyte is caused by the volume changes of electrode particles [75], which can be described as follows;

$$\frac{V}{V_0} = \left(\frac{V_s}{V_{s0}}\right)^g \tag{85}$$

where V_s and V_{s0} denote the volumes of electrode particles with and without expansion caused by lithiation. V and V_0 denote the volumes of composite electrodes with and without expansion caused by lithiation. g is a swelling coefficient describing how volume changes of particles affect the volumes of composite electrode. However, the value of g is dependent on electrode porosity and the arrangement of particles and is hard to determine. Therefore it is assumed that g is equal to 1 and the volume changes of particles fully contribute to the volume change of composite electrode. Since the volume of spherical particles, V_s , is proportional to r_s^3 , Eq. (85) can be linearized using the Taylor series. Perturbation of the volume of composite electrode becomes

$$\Delta V = 3V_0 \frac{\Delta r_s}{r_{s0}} \tag{86}$$

In fact, the composite electrode is a mixture of the electrode particles, electrolyte and binder. The binder behaves like glue and sticks the electrode particles on the current collectors. When SOC changes, although the volumes of electrode particles change, the volumes of current collectors remain the same. Therefore, it is assumed that volume change of composite electrodes only occur in the through-the-plane (thickness) direction, so does the cell. The schematic diagrams of dimension changes are shown in Figure 66.





Side views (zoomed in)



Figure 66: Dimension changes are assumed to take place only in the thickness direction.

Since the area of composite electrodes is A and assumed to be constant, the volume change in composite electrode is $\Delta V = A\Delta\delta$. Then, Eq. (86) becomes

$$\Delta \delta = 3\delta_0 \frac{\Delta r_s}{r_{s0}} \tag{87}$$

where δ_0 denotes the thickness of composite electrode without expansion caused by lithiation, and $\Delta\delta$ denotes the thickness increase of composite electrode caused by lithiation. Substitute Eq. (84) to Eq. (87), the change of the thickness is expressed as a function of the average concentration;

$$\Delta \delta = \Omega \delta_0 \bar{c}_s \tag{88}$$

By substituting Eq. (18) to Eq. (88), we have

$$\Delta \delta_{-} = \Omega_{-} \delta_{0-} c_{s-,\max} \cdot x_{\min} + \Omega_{-} \delta_{0-} c_{s-,\max} \cdot (x_{\max} - x_{\min}) \cdot SOC$$

$$\Delta \delta_{+} = \Omega_{+} \delta_{0+} c_{s+,\max} \cdot y_{\max} + \Omega_{+} \delta_{0+} c_{s+,\max} \cdot (y_{\min} - y_{\max}) \cdot SOC$$
(89)

where subscripts - and + denote negative electrode (anode) and positive electrode (cathode), respectively. The effect of SOC on the thickness of electrode can be obtained by taking a derivative on Eq. (89);

$$\frac{d\Delta\delta_{-}}{dSOC} = \Omega_{-}\delta_{0-}c_{s-,\max} \cdot (x_{\max} - x_{\min})$$

$$\frac{d\Delta\delta_{+}}{dSOC} = \Omega_{+}\delta_{0+}c_{s+,\max} \cdot (y_{\min} - y_{\max})$$
(90)

Eq. (90) indicates a relationship between the thickness change of a composite electrode (anode or cathode) and the SOC of a cell. The SOC increases at charging and the number of ions in anode increases, so the volume of composite anode increases. Also, x_{max} is larger than x_{min} and the sign of Eq. (90) for anode is positive. Conversely, cathode loses ions and its volume decreases when *SOC* increases. Also, y_{min} is less than y_{max} and the sign of Eq. (90) for cathode is negative.

The maximum ion concentration in anode and cathode can be calculated as

$$c_{s-,\max} = \frac{Q}{(x_{\max} - x_{\min}) \cdot \delta_{-,\max} \cdot \varepsilon_{s-} \cdot A \cdot F \cdot N} = 0.041 \text{ mol cm}^{-3}$$

$$c_{s+,\max} = \frac{Q}{(y_{\max} - y_{\min}) \cdot \delta_{+,\max} \cdot \varepsilon_{s+} \cdot A \cdot F \cdot N} = 0.073 \text{ mol cm}^{-3}$$
(91)

where Q is the cell capacity and N is the number of micro cells of a single cell. Both values are based on the cell specifications. F is the Faraday constant. The volume fraction of active material of electrode, ε_s . $\delta_{-,\max}$ and $\delta_{+,\max}$ are the maximum thickness of composite anode or cathode caused by the expansion due to lithiation.

When the electrode is fully lithiated, the volume of electrode particle expands by a factor of $(1+\omega)$, where ω is defined as the fractional expansivity of the electrode material according to Christensen and Newman [18][19], as shown in Eq. (92);

$$\frac{V_{s,\max}}{V_{s0}} = \left(\frac{r_{s,\max}}{r_{s0}}\right)^3 = 1 + \omega \tag{92}$$

Then, the maximum thickness of composite electrode results in

$$\delta_{\max} = (1+\omega)\delta_0 \tag{93}$$

where δ_0 is obtained from the cell specification. Since no other components (separator or current collector) in the battery are affected by SOC, the thickness change of a single cell can be derived from the thickness changes of all composite electrodes in anode and cathode;

$$\Delta \delta_{cell} = N \left(\Delta \delta_{-} + \Delta \delta_{+} \right) \tag{94}$$

Eq. (94) assumed that there is no compression force from the pouch packaging material when the cell expands. Therefore, the separator should have no deformation and the response of inner and outer micro cells should experience the same mechanical response.

By combing Eq. (89), (90), (91) and (94), the thickness change of a cell due to SOC can be derived as follows;

$$\frac{d\Delta\delta_{cell}}{dSOC} = \frac{Q}{AF} \left(\frac{\Omega_{-}}{\varepsilon_{s-}(1+\omega_{-})} - \frac{\Omega_{+}}{\varepsilon_{s+}(1+\omega_{+})} \right)$$
(95)

The unknown PMVs of ions in anode and cathode, Ω . and Ω_+ , can be derived from the values of expansivity ω provided by Christensen and Newman [18][19]. Firstly obtain the maximum deviation of particle radius from Eq. (84);

$$\Delta r_{s,\max} = \frac{1}{3} \bar{c}_{s,\max} \Omega r_{s0} \tag{96}$$

Secondly substitute Eq. (96) to Eq. (92). The PMVs are now derived for both anode and cathode;

$$\Omega_{-} = \frac{3}{c_{s+,\max}} \left[(1 + \omega_{+})^{\frac{1}{3}} - 1 \right] = 2.77 \text{ cm}^{3} \text{ mol}^{-1}$$

$$\Omega_{+} = \frac{3}{c_{s+,\max}} \left[(1 + \omega_{+})^{\frac{1}{3}} - 1 \right] = 0.93 \text{ cm}^{3} \text{ mol}^{-1}$$
(97)

where $c_{s_{-,\max}}$ and $c_{s_{+,\max}}$ are calculated from Eq.(91) and the values of ω_{-} and ω_{+} are 0.08 and 0.06, respectively [18][19].

At each time step of simulation, after the ion concentrations are solved, the stress and displacement in electrode particles as well as the change of cell thickness are solved at last using Eq. (81)-(83) and Eq. (95) since they are functions of ion concentrations in solid phase.

4.1.2 Ion transport in electrode considering stress-induced diffusion

Based on the principle of thermal dynamics, chemical potential of a substance is affected by the pressure that is equivalent to hydrostatic stress, σ_h , for solid materials [76]. According to this theory, Yang [21] and Zhang et al. [22] derived the species flux of ion in electrode particles driven by concentration and stress gradient;

$$Flux = -D\left(\nabla c_s - \frac{\Omega c_s}{RT} \nabla \sigma_h\right)$$
(98)

where the hydrostatic stress, $\sigma_{\scriptscriptstyle h}$, can be expressed as

$$\sigma_h = \frac{1}{3} \left(\sigma_r + \sigma_t + \sigma_t \right) \tag{99}$$

The change of ion concentration in a differential volume is equal to the gradient of species flux;

$$\frac{\partial c_s}{\partial t} + \nabla \cdot \text{Flux} = 0 \tag{100}$$

Substitute Eq. (100) with Eq. (98) and Eq. (99) and then take derivatives in spherical coordinates, the equation of the material balance in electrode particles is modified from Eq. (3) to

$$\frac{\partial c_s}{\partial t} = D \left(\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r} \frac{\partial c_s}{\partial r} \right) - \frac{2D\Omega E}{9RT(1-\nu)} \left[\left(\frac{\partial c_s}{\partial r} \right)^2 + c_s \left(\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r} \frac{\partial c_s}{\partial r} \right) \right]$$
(101)

where the first and second term denotes the diffusion caused by the concentration gradient and the stress gradient, respectively [22].

4.2 Experimental validation of dimension changes

4.2.1 Dimension changes in the thickness direction

Since the stress in electrodes cannot be measured directly during cell operations, the change in thickness of the cell was measured using two linear voltage displacement transducers (LVDTs). The two LVDTs were placed on both sides of battery with a capability to measure the thickness at different locations of the cell and robustly supported by a fixture, as shown in Figure 67. It should be noted that no gas evolutions were observed during the tests. In addition, the pressure produced by possible gas evolution does not cause any measurement error since the spring of the LVDTs can impose a pressure around several hundreds of Kilo-Pascal on the cell. The device is in synchronization with the cycling test station that was shown in Figure 11, so the change of cell thickness under cycling can be recorded during testing.



Figure 67: Measurement of thickness using two LVDTs (by Yinyin Zhao).

First, the thickness at the center of battery is measured and used to compare with results of simulations. The first experimental data collected using the device at 25° C and the simulated

data are shown in Figure 68, where the thickness is a function of SOC. The thickness tends to follow the SOC, as expected. When SOC increases, the cathode loses ions while the anode gains ions, so the anode particles expand and cathode particles contract. In fact, the volume change rate of anode is larger than that of cathode, as shown in Eq. (95) and (97), so the overall thickness of the cell increases with increasing SOC.



Figure 68: Comparison between simulated and experimental thickness (at center).

The experimental data shows that the change of thickness is not linear to the change of the *SOC*. The data can be divided into three different regions as the SOC increases. The thickness of cell increases rapidly in the low range of *SOC* (0 to 40%), which agrees with the finding from Ohzuku et al. [77] and Hardwick et al. [78]. Then it becomes flat for the mid-range of *SOC* (40% to 70%) and finally increases again when SOC is larger than 70%.

The blue curve plotted in Figure 68 shows a simulated thickness of the cell using the theoretical PMVs based on Eq. (95) and (97). Since it is assumed that the PMVs in anode and cathode are constant and the change of porosity is negligible, the thickness increase linearly with the SOC. Mismatch of the experiments and simulations may be caused by the inaccurate values of fractional expansivity, ω , and the assumption that the expansion of lattice structure of electrodes is linear.

Since the graphite experiences the most expansion in low SOC region [77][78], which agrees with our experimental data, the PMV of ion in anode could be regarded as being negatively proportional to SOC, while the PMV in the cathode side is preserved as constant. The red curve with this fitting is shown in Figure 68, where the theoretical PMV is modified as follows and used to calculate the final thickness;

$$\Omega_{-,fitted} = 2.24 \cdot \Omega_{-} - 2.3 \cdot SOC \tag{102}$$

where Ω_{-} is the original PMV obtained from the Eq. (97).

The data obtained for the change in the cell thickness shown in Figure 68 was measured by locating the LVDTs at the center of the cell. In order to investigate the change in thickness of the entire cell, the position of the LVDTs was adjusted so that the thickness could be measured at 9 different locations. As shown below in Figure 69, each measurement location was marked with an "X" and given a unique numbering index.



Figure 69: Different locations for thickness measurement.

After the LVDTs were fixed at one location, the cell was charged and discharged for several cycles while the thickness was continuously measured. Regardless of the location of the LVDTs, the results always showed that the cell thickness increased with an increasing SOC, which is similar to the results found for the center of the cell as shown in Figure 68. In order to investigate the difference between the change in thickness at the different measurement locations, a new variable, $\Delta \delta_{cell}^{*}$, is introduced and defined as the maximum thickness at 100% SOC subtracted by the minimum thickness at 0% SOC for each location;

$$\Delta \delta_{cell}^* = \delta_{cell,100\%} - \delta_{cell,0\%} \tag{103}$$

Several measurements of $\Delta \delta_{cell}^*$ was recorded at each location. After the thickness at each location was measured, the same procedure was repeated using an additional cell to acquire more data points for the change in thickness. The mean value and standard deviation of $\Delta \delta_{cell}^*$ at each location has been plotted as error bars in Figure 70. Each error bar has the numerical index associated with each measurement location as previously shown in Figure 69.



Figure 70: Measurement of $\Delta \delta^*_{cell}$ at different locations.

As shown in Figure 70, the mean values of $\Delta \delta_{cell}^*$ at the outside locations of "11", "13", "21", "23", "33" and "33" were approximately the same. However, $\Delta \delta_{cell}^*$ at the inside locations of "12", "22" and "32" are smaller. To better interpret the results, the mean values of $\Delta \delta_{cell}^*$ shown in Figure 70 is re-plotted using a two-dimensional contour, as shown in Figure 71. The color bar indicates the value of $\Delta \delta_{cell}^*$ at the different locations. The change in thickness

measured from the experiment is marked as "X" and the data at the unknown locations are determined using interpolation.



Figure 71: Two-dimensional contour of $\Delta \delta^*_{cell}$ based on measurement and interpolations.

The results show that the location with the smallest thickness change is "12", which is located at the top middle of the cell near the terminal tabs. The region of small $\Delta \delta_{cell}^*$ extends to the middle of the cell, while the thickness changes at the sides are relatively larger. The thickness change is symmetric horizontally but asymmetric vertically. These results imply that the

thickness change is affected by the terminal tabs. Since the current collectors are clamped together and connected to the terminal tabs, the nearby electrode may be constrained from expansion.

Based on the data shown in Figure 70 and Figure 71, the mean value of $\Delta \delta_{cell}^*$ measured from different locations of the cell is only 5% larger than the $\Delta \delta_{cell}^*$ measured at the center. Therefore, the change in thickness measured at the center can be deemed acceptable to represent the overall thickness change in the cell, as shown in Figure 68.

4.2.2 In-plane dimension changes

The model used to calculate the volume change of the cell has assumed that the cell dimension only changes in the thickness direction, as shown in Figure 66 and Eq. (87). To validate this assumption, the fixture with LVDTs shown in Figure 67 was modified to measure the in-plane dimension change and is shown below in Figure 72.



Figure 72: Measurement of cell width using LVDTs.

To increase the measurement accuracy, some of the packing material at the edges of the cell was removed so that the LVDTs could be in direct contact with the cell. The key components of the cell, such as the electrodes, separators and current collectors, were not damaged when the packaging material was removed. The change in the cell width during cycling is plotted in Figure 73. The change in the thickness previously measured is also plotted in order to compare the two results. The results show that the width of cell increases as the SOC increases that is similar to what was observed with the change in thickness. However, the largest change in width is only one third of the change in thickness.



Figure 73: Change in thickness and width of a cell under cycling.

Similar to Eq. (103), Δw_{cell}^* is introduced and defined as the maximum width at 100% SOC subtracted by the minimum width at 0% SOC;

$$\Delta w_{cell}^* = w_{cell,100\%} - w_{cell,0\%} \tag{104}$$

The changes in thickness and width have been summarized in Table 5. The analysis shows that the volume change caused by the change in width, $\Delta V_{cell,width}$, is about 1% of the volume change caused by the change in thickness, $\Delta V_{cell,thick}$. Therefore, it is acceptable to use only the change in thickness to represent the volume change of the cell without introducing much error in the results, as assumed in the model.

Description	Symbol	Value
Change in thickness	$\Delta {\delta}^{*}_{cell}$	0.075 mm
Change in width	Δw^*_{cell}	0.023 mm
Volume change caused by change in thickness	$\Delta V_{cell,thick} = A_0 \Delta \delta_{cell}^*$	2250 mm ³
Volume change caused by change in width	$\Delta V_{cell,width} = h_0 \delta_0 \Delta w_{cell}^*$	25.3 mm ³

Table 5: Comparison of changes in thickness and width.

4.3 Analysis of stress generation

Figure 74 shows the simulated current, terminal voltage, temperature, thickness and maximum anode stress under cycling, which are compared with the experimental data. The current rates applied are 0.5C, 1C and 2C for each cycle, respectively. Each cycle includes a constant current discharge, a constant current charge and a constant voltage charge along with a 10 minutes resting period between charging and discharging.


Figure 74: Experimental validations at 0.5C, 1C and 2C cycles.

Comparison shows that the current and voltage are relatively in good match. However, some discrepancies in temperature responses are observed, which might be caused by the inaccurate values of convective heat transfer coefficient. In addition, simulated and experimental thicknesses match well with each other. The change of thickness is only affected by the SOC, but not current rate. Current at high C rate leads to a high amplitude of stress because the stress follows the increase of the gradient of ion concentration in electrode particles. During resting periods, the gradient of ion concentration gets low, so the stress decreases and tends to vanish.

Time evolution of the maximum stress in anode or cathode under different discharge current is shown in Figure 75. When the current rate is low, for example, 1C, the maximum stress increases at the beginning of discharge and tends to stay constant afterwards. When current rate is high, for example, 3C, 5C and 7C, the maximum stress increases significantly to an extreme value and then slowly goes down.



Figure 75: Maximum stress (absolute values) under discharging.

The maximum stress in tangential direction, σ_t , is slightly larger than the stress in radial direction, σ_r . The stress generated in anode is larger than that in cathode, since anode material has a higher PMV of lithium ion. The simulation indicates that a high current rate is most likely to cause electrode material failures at the beginning of discharge and charge.

Maximum stress as a function of the thickness of micro cell is shown in Figure 76. The domain from 0 to 50 µm indicates the composite anode mixed with electrolyte, the domain from

 $50\,\mu\text{m}$ to $75\,\mu\text{m}$ indicates the separator where stress is not considered, and the domain from $75\,\mu\text{m}$ to $112\,\mu\text{m}$ indicates the composite cathode mixed with electrolyte. The plotted stress at each position is the maximum value of the stress in the local electrode particles. Each stress curve is obtained at the time instant when extreme value is reached in Figure 75.



Figure 76: Maximum stress (absolute values) as a function of the thickness.

The results in Figure 76 show that the tangential stress is slightly higher than the radial stress and the stress in anode is larger than that in cathode. In addition, the magnitude of stress is dependent on the locations of composite electrode. The highest value of stress is in the electrode

particles in contact with the separator, which implies that the material failure, such as crack or fracture, is more likely to happen in the electrode particles that are close to the separator. This fact is in line with the experimental work done by Kostecki and McLarnon [79], which showed that the graphite particles near the separator become more disordered under cycling. Horn and White [80] also found cracks in electrode particles near the separator by SEM images at the cross-section of a cell.

In order to study stress distributions in particles, particles near the separator are selected and the stress distributions in a single electrode particle are shown in Figure 77. Each stress curve is obtained at the instant when extreme value is reached in Figure 75. At discharging, the anode electrode loses ions so the particle has a negative radial stress and compressed in radial direction. The magnitude of the radial stress becomes highest at the center of sphere and decays to zero at the surface. In the tangential direction of anode particle, the stress is compressive in the inner part of sphere and tensile in the outer part of sphere. The maximum magnitude of tangential stress is similar to radial stress. Conversely, in the cathode particles, the directions of stresses are opposite to those in the anode since the cathode gains ions. The magnitude of stress in cathode is smaller than anode due to different Young's modulus and PMVs of lithium ion.



Figure 77: Stress as a function of particle radius.

The stresses are generated by the inhomogeneous distribution of ion concentration in electrode particles. As described in Eq. (81) and (82), the distribution of ion concentration determines the magnitude and direction of stress. In most cases, high gradient of ion concentration would induce large stress. Radial stress is proportional to the difference between averaged ion concentration in the entire particle and averaged ion concentration in the "localized region", as indicated in Eq. (81).

The ion concentrations in the electrode particles selected in Figure 77 are plotted in Figure 78. It is observed that a high current induces a large gradient of ion concentration in electrodes, and in turn results in a large stress.

4.4 Analysis of stress-induced diffusion

The effects of electrochemical behavior on stress generation have been analyzed in the previous section. According to the Eq. (98), the gradient of hydrostatic stress influences diffusion flux of ions in electrode. Therefore, the species conservation equation gains an extra term to consider the stress-induced diffusion, as shown in Eq. (101). Based on the equation, the effects of stress-induced diffusion on the cell performance have been studied.

The ion concentrations and radial stresses in an anode particle near the separator with and without considering stress-induced diffusion are shown in Figure 78. When stress-induced diffusion is considered, the gradient of ion concentration and the magnitude of radial stress become smaller. The result shows that stress could help to improve ion diffusion in electrode particles to some extent.



Figure 78: Effect of stress-induced diffusion on ion concentration and stress.

The terminal voltage, cell temperature and maximum radial stress with and without considering stress-induced diffusion are shown in Figure 79. The effect of stress-induced diffusion on the terminal voltage and cell temperature is negligible. However, the maximum radial stress is obviously reduced by stress-induced diffusion, since the stress enhances diffusion flux and decreases the gradient of ion concentration in electrode, which is in coincidence with results from Christensen et al. [80]. It is concluded that stress-induced diffusion has little effect on terminal voltage, but is important to analyze stress generations.



Figure 79: Effect of stress-induced diffusion on terminal voltage, temperature and stress.

4.5 **Conclusions**

4.5.1 Summary of findings

A stress model for LiPB is developed and integrated to the electrochemical-thermal model. The model is validated in terms of dimension changes under charging and discharging. Simulations of stress generations are carried out under different applying current.

Key findings are as follows:

- The battery thickness is a function of *SOC* at a constant temperature. When *SOC* changes from 0 to 100%, the thickness of the battery increases by 1.2%. This is mainly because of the anode material that has a larger expansion rate when ions are intercalated compared to that of the cathode material.
- Stress tends to follow the increase of the ion concentration gradient in an electrode. As a result, high C-rate leads to high amplitude of stress. During resting periods, the gradient of the ion concentration gets low, so the stress decreases and vanishes.
- Stress in anode is higher than that in cathode particles.
- At a high C-rate, stress might reach its maximum value at the beginning of charge and discharge.
- The highest stress is generated particularly in the electrode particles near the separator, where cracking and fracture are most likely to take place.
- The stress-induced diffusion could enhance the ion diffusion in an electrode and reduces the gradient of ion concentration. However, it has little effects on the macro-scale quantities, such as terminal voltage and cell temperature.

4.5.2 Future work

First, the boundary condition of the stress generation model needs to be improved. In the current form, the radial stress σ_r at the particle surface ($r = r_{s0}$) is considered as zero, which is based on the assumption that there is no reaction forces between the particles. However, based on the measurements of thickness and width changes, it is observed that the composite electrodes are free to expand in the thickness direction, but constrained in the in-plane directions. In other words, the reaction forces between particles in the in-plane directions exist and should be considered to better describe the stress generation processes.

Second, future work may include modeling and analysis of the effect of stress generation on formation of crack and fracture. The crack propagation under stress can be analyzed using fracture mechanics theory [36][62], where tangential tensile stress in electrode particles should be considered as the cause for crack opening and growth, as shown in Figure 80.



Figure 80: Proposed crack opening mode for spherical electrode particles.

Based on linear elastic fracture mechanics for radial symmetry, the energy release rate as a function of crack length can be defined and the stability index of crack growth can be calculated [36][62]. The stability index of crack growth should be proportional to crack growth rate. A negative stability index indicates a stable growth and slow propagation. When the stability index increases to zero, crack growth becomes unstable and catastrophic failure is approached. At this moment, critical crack length is reached at which fracture of the electrode takes place.

In addition, this work only analyzed the stress in electrode particles but has not considered the stress in the binder that connects the electrode particles. In fact, the binder is under compression or tension when electrode particles expand or contract. In addition, the formation of SEI and deposit layers may also have effect on stress generation in the binder. If mechanical failure, such as crack and fracture, take place in the binder, certain amount of particles will loss contact with the composite electrode and the amount of active material will decrease. Modeling of this phenomenon can be incorporated in the stress generation model in the future.

Chapter 5 Conclusions

This work has investigated and modeled the predominant degradation processes of LiPB considering the side reactions and stress generations. The research starts with a highly accelerated test in order to study the degradation mechanisms of LiPB. The results show that the predominant degradation is caused by the side reactions at the anode. The change in internal parameters as a function of degradation is calculated using a semi-empirical degradation model.

In order to better understand the mechanism of the side reactions and predict the degradation of LiPB under various operating conditions, a physics-based degradation model is developed. The side reactions are mathematically described using the Butler Volmer and Nernst equations and the corresponding degradation processes are modeled based on physical principles. The model is incorporated into the electrochemical-thermal model developed previously. The integrated model is then validated against experimental data obtained from large format LiPB NMC/Carbon cells. Numerical and experimental analysis have shed light on the mechanisms of capacity and power fade as well as their dependencies on different operating conditions.

In addition to the side reactions, a stress model is developed to describe the mechanical stresses caused by the non-uniform distribution of lithium ions and inhomogeneous localized volume changes inside an electrode particle, which has been validated by studying the volume change of a cell. Simulations show that stress in the anode is higher than that in the cathode and the highest stress is generated particularly in the electrode particles near the separator, where crack and fracture are most likely to take place.

Based on our results, the magnitude of degradation caused by the side reactions is much larger than that caused by stress generations because no observable crack or fracture has been found in our cells. The finding could vary for other types of cells but in most cases, the side reactions play a major role in degradation processes while stress generations play a minor one, based on the literature.

The key findings of this work are summarized below;

- Experimental investigation of degradation mechanism:
 - The side reactions at the anode are the predominant degradation process that leads to capacity and power fade.
 - The anode particles are coated by SEI composed of Li_2CO_3 , which is known as the product of the side reactions that is conductive to ions but nonconductive to electrons, but no phase change of active materials has been observed.
 - The deposits lead to growth of the SEI layer and an increase in ionic resistance causing power fade. In addition, they electrically isolate certain anode particles, reducing the amount of active material and causing capacity fade.
 - The deposits of the side reactions also form thick deposit layers coated between composite anode and separator. The deposit layer has a lower ion conductivity than that of the electrolyte and causes extra power fade.
 - The dryness of the separator was observed which is most likely caused by the consumption of the electrolyte solvent.
 - At elevated temperature (40 °C), the side reactions are more extensive and more deposits are formed.

- Theoretical analysis of the side reactions using the physics-based degradation model and experimental validations:
 - Not only the loss of the active anode material, but also the loss of ions are the factors that cause capacity fade. The mechanisms are illustrated by analysis of the two factors on EOC and EOD determined by two equilibrium potentials and OCVs.
 - The side reactions produce deposit layers and increase the thickness of the SEI layer, which leads to power fade. Simulated growths of both layers are confirmed by experimental data quantitatively characterized using SEM and EIS.
 - The charging process causes more degradation than the discharging process. The overpotential of the side reactions (η_{side}) is small during charging and large during discharge. Consequently, the rate of side reactions during charging is larger than that during discharging.
 - Cycling at high SOC accelerates the degradation processes because the equilibrium potential of the anode becomes low, which leads to low η_{side} and a large rate of side reactions.
 - Charging at high C-rates significantly and instantaneously increases the degradation rate. However, the dependence of degradation upon the C-rates was not clearly distinctive at the same number of cycles, because a high C-rate leads to not only an increase of the side reaction rate but also a reduction of the charging time.
- Analysis of stress generation and volume changes:

- The battery thickness is a function of *SOC* at a constant temperature. When *SOC* changes from 0 to 100%, the thickness of the battery increases by 1.2%. This is mainly because of the anode material that has a larger expansion rate when ions are intercalated compared to that of the cathode material.
- Stress tends to follow the increase of the ion concentration gradient in an electrode. As a result, a high C-rate leads to a high amplitude of stress. During resting periods, the gradient of the ion concentration gets low, so the stress decreases and vanishes.
- Stress in the anode is higher than that in the cathode particles.
- At a high C-rate, stress might reach its maximum value at the beginning of charge and discharge.
- The highest stress is generated particularly in the electrode particles near the separator, where cracking and fracture are most likely to take place.
- The stress-induced diffusion could enhance the ion diffusion in an electrode and reduces the gradient of ion concentration. However, it has little effect on the macro-scale quantities, such as terminal voltage and cell temperature.

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Appendix 1: Parameters

Category	Parameter	Negative electrode	Separator	Positive electrode	unit
Geometry and volume fractions	Thickness, δ	50×10 ⁻⁴	25.4×10 ⁻⁴	36.4×10 ⁻⁴	cm
	Particle radius, r_s	1×10 ⁻⁴		1×10 ⁻⁴	cm
	Active material volume fraction, ε_s	0.58		0.5	
	Polymer phase volume fraction, ε_p	0.048	0.5	0.11	
	Conductive filler volume fraction, ε_f	0.04		0.06	
	Porosity, ε_e	0.332	0.5	0.33	
Li ⁺ concentrations	Stoichiometry at 0% SOC: x_{min} , y_{max}	0.08		0.98	
	Stoichiometry at 100% SOC: x _{max} , y _{min}	0.93		0.21	
	Average electrolyte concentration, c_e	1.2×10 ⁻³	1.2×10 ⁻³	1.2×10 ⁻³	mol cm ⁻³
	Exchange current density coefficient, k_{i0}	12.9		6.28	A cm ⁻²
Kinetic and transport properties	Charge-transfer coefficient, α_{a} , α_{c}	0.5, 0.5		0.5, 0.5	
	Solid phase diffusion coefficient, D	2.0×10^{-12}		3.7×10^{-12}	$\mathrm{cm}^2\mathrm{s}^{-1}$
	Solid phase conductivity, σ	1		0.1	S cm ⁻¹
	Electrolyte phase Li^+ diffusion coefficient, D_e	2.6×10 ⁻⁶	2.6×10 ⁻⁶	2.6×10 ⁻⁶	$\mathrm{cm}^2\mathrm{s}^{-1}$
	Bruggeman's porosity exponent, p	1.5	1.5	1.5	
	Electrolyte phase ionic conductivity,	15.8c _e		15.8c _e	S cm ⁻¹
	κ	$exp(-13472c_{e}^{-1.4})$		$exp(-13472c_e^{-1.4})$	
	Li^+ transference number, t_+^0	0.363	0.363	0.363	

Table 6: Parameters of electrochemical-thermal model [65]

Parameter	Value	Source	
exchange current of side reactions, $i_{0,side}$ (A cm ⁻²)	3.66×10^{-17} at 0 °C 4.15×10^{-16} at 25 °C 2.12×10^{-15} at 50 °C	Optimized by comparing simulation to the self-discharge data	
equilibrium potential of side reacionts, $U_{eq, side}$ (V)	0.4	[24][27][42][45][73]	
cathodic symmetric factor of side reactions, $\alpha_{c,side}$	0.70	Optimized by comparing simulation to the degradation data under different SOC cycling limits. The value falls in an acceptable range provided by [82]	
molar volume of SEI, \widetilde{V}_{SEI} (cm3/mol)	2	Obtained by assuming the initial thickness of SEI is 2 n m	
ionic conductivity of SEI, κ_{SEI} (S cm ⁻¹)	2.3 × 10 ⁻⁸	Optimized by comparing simulation to the SEI resistance obtained from EIS	
isolation rate of active anode materials due to SEI, k_{iso}	27.3	Optimized by comparing simulation to measured capacity fade	
molar volume of DL, \widetilde{V}_{DL} (cm3/mol)	7560	Optimized by comparing simulation to the thickness of DL measured by SEM	
ionic conductivity of DL, κ_{DL} (S cm ⁻¹)	1.26×10 ⁻²	Optimized by comparing simulation to the terminal voltage under cycling	
molar volume of electrolyte, \tilde{V}_{e} (cm3/mol)	325	Optimized by comparing simulation to the terminal voltage under cycling	

Table 7: Parameters of the physics-based degradation model

Parameter	Value	Source
Young's modulus of anode (graphite), <i>E</i> . (MPa)	9 300	Takes an average of the data provided from [83][84]
Young's modulus of cathode (NMC), E_+ (MPa)	10 000	[19][20][23]
Poisson's ratio of anode (graphite), v.	0.3	[18][19][20][23]
Poisson's ratio of cathode (NMC), v_+	0.3	[18][19][20][23]
Fractional expansivity of anode (graphite), ω .	0.08	[18][19]
Fractional expansivity of cathode (NMC), ω_+	0.065	[18][19]

Table 8: Parameters of the stress model

Appendix 2: EIS and SEM analysis of DL



Figure 81: Impedance of cells after 600 cycles using EIS and an equivalent circuit model.



Figure 82: Impedance of cells after 600 cycles using EIS and an equivalent circuit model.



Figure 83: Thickness of DL of cell cycled under 25% to 90% (by Victor Agubra).



Figure 84: Thickness of DL of cell cycled under 15% to 80% (by Victor Agubra).