EXPERIMENTAL PARAMETER IDENTIFICATION OF
A PHYSICS-BASED MODEL FOR
SOLID-ELECTROLYTE INTERPHASE (SEI) LAYER
GROWTH IN LITHIUM-ION BATTERIES

by

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Experimental parameter identification of a physics-based model for solid-electrolyte interphase (SEI) layer growth in lithium-ion batteries

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ABSTRACT

Lithium-ion batteries are prevalent in our society. With the demand for better durability of batteries in portable devices and vehicles, it is imperative that cell degradation be observed and mitigated. A challenge of using a physics-based model is that many parameters are needed to populate the model. One way of obtaining cell parameters is to break open the cell and take physical measurements. However, breaking apart a cell is costly and requires specialized equipment to perform the task. Another way is to use nondestructive means to identify these parameters. Some nondestructive methods include XRM, neutron diffraction, and voltage relaxation. However, most of the non-destructive methods also require specialized equipment. Another way to populate a model is to search the literature and leverage work about the cell of interest. This thesis presents a method to obtain \( \bar{k}_{\text{sei}} \) using regular cycling equipment and without the need to tear down the cell.
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CHAPTER 1

Introduction

Energy storage concerns span centuries and civilizations. Evidence of people trying to solve this problem range from the first century B.C. with the Baghdad Battery to the seventeenth century with Luigi Galvani and Alessandro Volta, who are universally accepted as the creators of the first electrochemical battery [1]. As society evolves, so does its need to develop methods for the effective use of energy, with perhaps the greatest example being modern transportation.

Electric vehicles were developed in parallel with gas-powered vehicles at the beginning of the 20th century. However, due to poor infrastructure surrounding the electric car, gas powered vehicles dominated and continue to dominate the market. However, consumers began to seek an alternative to gas-powered vehicles as a result of growing concern about the effects of emissions on the environment [2, 3].

While the electric car is not the sole solution to the energy or environmental problem, it does speak to our time, and is a stepping stone toward the development of new sources for powering vehicles. While present-day electric cars are more efficient and reliable than their older counterparts, the main problems that were faced in the beginning of the 20th century remain problems that challenge us today: limited range and high cost. Current research aims toward better battery management systems that extend life and improve performance models for state estimation and advance controls of the batteries. One approach to achieving these aims is implementing more accurate battery models, specifically, improved degradation models that work in conjunction with ideal cell models can supply important information to an advanced control algorithm, such as model-predictive control (MPC), in order to reduce the effects of degradation and ultimately extend the life of a battery pack.
1.1 A Brief History of Cell Modeling

There are many types of cell models. They can generally be categorized as either: i) empirical, or ii) physics-based. Empirical models, such as the equivalent-circuit model (ECM) are the most widely used due to their inherit simplicity. ECMs utilize circuit components to emulate observed external cell behavior when exposed to different input stimuli. While most battery-management systems currently use ECMs due to their robustness and simplicity, they do not offer much insight into the internal electrochemical reactions that happen within a cell. By contrast, physics-based models (PBMs) are based on first principles, and although they are more mathematically and computationally complex, they offer a method for exploiting of internal cell behavior, including various cell degradation mechanisms for purposes of advanced cell-level control [4].

John Newman, Thomas Fuller, and Marc Doyle were the first to generate an ideal model of electrochemical battery behavior [5]. Their full-order model (FOM) comprises of four partial-differential equations and one algebraic equation. Jobman [6] and Chu [7] modified on the Full-Order Model (FOM) using lumped parameters, which is a systematic method of identifying parameters by grouping those that frequently appear together in the first-principle equations. Lumping the parameters in this manner makes it possible that reduces the number of discrete parameters to be identified thorough experimentation. It is not possible to identify unobservable parameters uniquely without teardown.

The ideal PBM does not include degradation effects. However, this model can also be used to describe degradation effects by coupling the original ideal equations with additional expressions that account for degradation effects. Aldrich [8] presented ROMs developed by coupling the ideal-cell model with degradation principles. Lithium-plating degradation was initially described by Arora [9]. Ramadass developed the first solid electrolyte interphase (SEI) model [10]. Safari et al. created a SEI model using a diffusion kinetics-limited model which is useful for modeling cells in storage [11].
1.2 The Problem: Mitigating Cell Degradation

One significant challenge in using a physics-based model for degradation modeling is that many parameters are often needed to populate the model. One way of obtaining certain cell parameters is to break open the cell and take physical measurements. However, cell tear-down is costly and requires specialized equipment to perform. It is therefore appealing to use nondestructive means to identify parameters instead. Some nondestructive methods include XRM, neutron diffraction, and voltage relaxation [12, 13, 14].

Using these methods, teams have been successful in utilizing in-situ methods of determining SEI formation. Owejan et al. [12] demonstrated that neutron reflectivity can help investigate the formation of SEI in-situ and gain direct measurements of several critical SEI parameters such as film thickness and porosity of the layer on an operating cell. Further study from Lee et al. [15] provided a method for quantitative study of SEI composition using in operando neutron reflectivity. This work showed in operando evidence for the dual-layer SEI structure and also showed that SEI can be irreversible during cycling. However, most of the non-destructive methods for examining SEI formation also require specialized equipment. Another way to populate a model is to search the literature and leverage work performed by other teams, however, the value will not be exact for the cell of interest. Fu et al. [16] presented a method of estimating $i_{0,\text{side}}$ and $U_{\text{eq,side}}$ SEI side reaction parameters.

The idea is that because the cell is not actively being cycled, all voltage drop can be attributed to SEI side reaction. The self-discharge test takes approximately two months to gather enough voltage measurements to see a trend. Cells kept at 100% SOC over prolonged time will start to degrade, this behavior is exacerbated at extreme temperatures. Lewerenz et al. [17] performed an experiment using a floater device as a source to keep the voltage at 100% SOC. Tuveri presented a similar approach with a potentiostat [18] to reduce the time between design and market introduction. The device can help identify abnormal cell behavior in a matter of hours. The industry uses similar tests to determine the leakage current, which is defined as the current loss after three days [19]. This approach could be used to extract an SEI parameter of in less time.
1.3 Original Contributions

It is important to note that ideal-cell models describe pristine cells, but all real cells eventually deviate from the ideal-cell behavior due to degradation and aging effects. Figure 1.1 a) shows two paradigms for including cell degradation models. The left-hand figure depicts an open loop model for degradation that is convenient for simulation studies, while the right-hand diagram shows a feedback model, which actually modifies aspects of the original ideal cell model to account for aging.

![Figure 1.1: Open loop degradation model (left) and Feedback loop “real” degradation model (right)]

This thesis focuses on estimating parameters to populate a model of SEI formed during self-discharge at cell equilibrium. Future work will include a full model for SEI formed during dynamic loading. SEI parameters from experimental data as highlighted in the red block in Figure 1.1, and is only a milestone in appending an SEI model to the existing lumped parameter ideal cell model. As such, Chapter 2 discusses the ideal cell model highlighted in the purple block, and Chapter 3 discusses the lithium plating model developed by Xavier [20] highlighted in blue in Figure 1.1.

1.3.1 Organization of Thesis

Chapter 2 presents the ideal PBM. This description is necessary in order to understand the existing infrastructure used for electrochemical modeling of cells. The chapter introduces the Doyle-Fuller-Newman [5] model and the lumped-parameter model developed by Jobman [6]. Typically, the Doyle-Fuller-Newman model is used for modeling, however, parameter values for this model are unknown for the Panasonic cell used in this thesis. There
1.3. Original Contributions

is also a brief explanation of ROMs and realization algorithms, which is not relevant for the SEI estimation process, but is relevant for the Xavier lithium-plating model in Chapter 3.

Chapter 3 presents the basics for understanding degradation models. This includes the Arora [21] lithium-plating model and the modified lithium plating model developed by Xavier [20] using MPC techniques. This chapter also describes the kinetics-limited SEI model created by Ramadass [10] and the diffusion-limited SEI model developed by Safari [11]. It also discusses a coupled degradation model developed by Yang [22]. Chapter 3 also presents the publications by Fu [16] and Tuveri [18] that inspired the self-discharge test and leakage current test undertaken within this thesis, respectively.

Chapter 4 presents the identified physical/electrochemical parameters derived from tests, nondestructively. It also discusses the methods used to experimentally derive the SEI side reaction parameter, \( \tilde{k}_{\text{sei}} \). This chapter also discusses the results of reference performance tests conducted intermittently between self-discharge tests. Two methods are presented, one is a self-discharge test and the other is a shorter leakage current test. The parameters are extracted by fitting the experimental data to a cost function.

Chapter 5 presents some conclusions and suggestions for future work. This chapter discusses limitations and improvements for the main SDT and leakage current tests. Future work includes extending the SEI degradation model to account for SEI growth within cells undergoing dynamic profiles. Another future endeavor would be to couple SEI with other degradation mechanisms in order to better understand battery cell degradation and aging.
CHAPTER 2

Battery Models

2.1 Chapter Introduction

The most common models used for battery dynamic simulation and prediction are equivalent-circuit models (ECMs). Alternatively, physics-based models (PBMs), although far more complex, contain information about the underlying electrochemical processes, which can be used to great advantage.

This chapter introduces physics-based full order models (FOMs) that simulate the electrochemical behavior of cells. The derivation is based on the DFN model [5] and incorporates the lumped-parameter approach [6, 7]. Further, reduced-order models that are used to estimate battery parameter values in real-time applications are briefly explained. The following sections describe ECMs and PBMs. To understand the governing first-principles equations of a physics-based model, the following section first describes how a lithium-ion battery functions.

2.2 Battery Fundamentals

Pseudo-two-dimensional (P2D) battery models describe different aspects of the cell referenced to the electrode width dimension, $x$, and the radius of the electrode particles, $r$, which are assumed to be uniformly spherical as seen in Figure 2.1. Thus, it is important to understand how a battery is constructed and operates. The cell experiments presented in Chapter 4 use a Panasonic Li-ion Nickel Manganese Cobalt (NMC) cell, and discussions are focused to the specific structure and operation of this cell for brevity. The Panasonic cell is a rechargeable (secondary) cell meaning that it can be discharged and charged numerous times before the cell reaches the end of its life. Batteries can be used to perform
2.2. Battery Fundamentals

work when connected to an external circuit via redox reactions. Cells provide this service by discharging, and internally the electrons are pushed through the external circuit to the cathode in an oxidation reaction in the anode. While the cathode accepts the electrons in a reduction process, the cations move to the anode via the electrolyte. The anode by definition is the component that is oxidized during the electron exchange, hence the anode and cathode will switch depending on whether the cell in being discharged or charged. To avoid confusion, this document will use the terms negative electrode and positive electrode to distinguish the sections of the cell instead of anode and cathode [4].

![Figure 2.1: Illustration of a cross-section of a lithium-ion cell adopted from G. Plett, "Battery Management Systems, Volume 1 - Battery Modeling" 2015 [4]](image)

### 2.2.1 Negative Electrode

Most negative electrodes in commercial lithium-ion cells for most commonly used lithium-ion cells are made of natural or synthetic graphite ($C_6$). Graphite consists of graphene layers of $C_6$ rings that are themselves tightly bonded. These graphene layers are loosely stacked so that lithium can be inserted between them in a process known as intercalation.

### 2.2.2 Positive Electrode

There are more options for choosing a suitable positive electrode material. One common choice is NMC electrode, which has a layered crystal structure, which comprises an oxide of nickel, cobalt, and manganese. Sometimes coatings are used to slow manganese dissolution.
2.2.3 Electrolyte

The electrolyte is the medium that allows the transfer of ions between the electrodes but does not take part in the reaction. Because lithium reacts violently with water, a non-aqueous organic solvent and a lithium salt make up the electrolyte, for most lithium-ion batteries. Additives may be included to prevent manganese from dissolving into the electrolyte. Methods for choosing suitable positive electrodes and additives to prevent degradation of the electrode are beyond the scope of this thesis.

2.2.4 Separator

The separator is an electronically insulative, permeable membrane that allows lithium ions to pass through but prevents the negative and positive electrodes from making contact, which would short-circuit the cell.

Knowledge of the battery operation is essential to understand where and how processes are happening within the cell. In the next section, ECMs are discussed to explain how they are created to model the output of a cell.

2.3 Equivalent Circuit Models (ECMs)

Equivalent circuit models see wide industrial implementation due to their robustness and ease of use in real-time applications. The ECM is empirical in nature and utilizes common circuit components to emulate the external behavior of a cell; thus, circuit analysis can relate terminal voltage to applied current [4]. System-identification techniques have been developed to estimate equivalent-circuit component values by using input-output measurements from cells.

A number of different ECM topologies are used for battery modeling in [23, 24]. In a comprehensive, systematic comparative study, twelve lumped models were evaluated based on their practicality and complexity when applied to model training accuracy and validation, as well as evaluated based on generalization of model application to other similar cell chemistries. An MPSO algorithm was used to optimize parameter values. This study
2.3. Equivalent Circuit Models (ECMs)

found that first-order RC models, such as the Thévenin model (Figure 2.2a), are better at representing NMC chemistries. Similarly, a first-order RC model with one-state hysteresis, the Enhanced Self-Correcting model (ESC) (Figure 2.2b) was found to represent LiFePO$_4$ chemistries better than other ECMs [24].

![Thévenin Equivalent Circuit Model (Left) and Enhanced Self-Correcting Model (Right) adopted from G. Plett, "Battery Management Systems, Volume 2 - Equivalent-Circuit Methods" 2015 [25]](image)

The Thévenin model, as seen in Figure 2.2, comprises of a single resistor and RC component; $R_0$ represents the instantaneous (Ohmic) resistance giving rise to a direct feed-through term, $R_1$ is the polarization resistance, and $C_1$ is the electric double-layer capacitor. The RC component is analogous to the diffusion process, and the capacitor describes the transient portion of the response during charge and discharge. The Enhanced Self-Correcting (ESC) model, mentioned previously, contains the same components as the Thévenin model but with the addition of a hysteresis element. Hysteresis is a phenomenon seen in cells where the terminal voltage as a result of discharge and the voltage as a result of charge are unequal when allowed to rest at the same SOCs, and this effect is dependent on the recent cycling history of the cell. For a more detailed account, please see reference [26].

While this thesis will not use ECMs, it is included in the discussion of ideal models as there are many uses for this type of model in industry. Although ECMs are convenient and have fast computational speeds, they are limited to predicting only terminal voltage and SOC estimates; importantly, they do not give insight into the internal electrochemical
reactions happening within the cell. For this, physics-based models are needed for that application. The next section explains the first-principles governing equations of a PBM used to simulate battery behavior.

2.4 Physics-Based Models (PBMs)

PBMs (eg. the DFN model) utilize a set of coupled, partial-differential equations and one algebraic closure term to describe the internal behavior of a lithium-ion cell; such models when made computationally compact, can enable the implementation of advanced control strategies to mitigate degradation effects.

2.4.1 Full-Order Models (FOMs)

A FOM encompasses all cell electrochemical behavior utilizing four coupled, partial-differential equations and one algebraic equation. These are known as the first-principles governing equations of a PBM.

Electrochemical models of battery cell derived from first principles

Doyle et al. [5] introduced the pseudo two-dimensional (P2D) model, with expressions for: 1) Potential in the solid phase, 2) Potential in the electrolyte phase, 3) Concentration of lithium in the solid phase, 4) Concentration of lithium in the electrolyte phase, and 5) lithium flux. The Butler-Volmer equation describes lithium movement between different phases. The charge-balance equations are described in terms of potentials and the mass-balance equations in terms of concentrations.

Potential in the solid phase

The potential in the solid phase equation models the movement of electrons within the solid part of an electrode,

\[ \frac{\partial}{\partial x} \sigma_{\text{eff}} \frac{\partial}{\partial x} \phi_s = a_s F j, \]
where $\sigma_{\text{eff}}$ is the effective solid particle conductivity, $\phi_s$ is the potential of the solid, $a_s$ is the specific interfacial surface area, $F$ is Faraday’s constant, and $j$ is the rate of intercalation.

The corresponding boundary conditions are:

$$\sigma_{\text{eff}} \frac{\partial \phi_s}{\partial x} \bigg|_{x=0} = \sigma_{\text{eff}} \frac{\partial \phi_s}{\partial x} \bigg|_{x=L_{\text{tot}}} = -\frac{i_{\text{app}}}{A}$$

and

$$\frac{\partial}{\partial x} \phi_s \bigg|_{x=L_{n}} = \frac{\partial}{\partial x} \phi_s \bigg|_{x=L_{n}+L_{s}} = 0.$$

**Potential in the electrolyte phase**  The potential in the electrolyte phase equation relates the movement of ions within the electrolyte,

$$\frac{\partial}{\partial x} \kappa_{\text{eff}} \left( \frac{\partial \phi_e}{\partial x} + \frac{2RT(t^0_+ - 1)}{F} \left( 1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln c_e}{\partial x} \right) + a_s F j = 0$$

where $\kappa_{\text{eff}}$ is the effective conductivity of the ions in the electrolyte, $\phi_e$ is the potential of the electrolyte, and $c_e$ is the lithium concentration in the electrolyte, $R$ is the universal gas constant, $T$ is the temperature, and $t^0_+$ is the charge transference number of the lithium ion with respect to the solvent.

The potential in the electrolyte phase has the following boundary conditions:

$$-\kappa_{\text{eff}} \left[ \frac{\partial \phi_e}{\partial x} + \frac{2RT(t^0_+ - 1)}{F} \left( 1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln c_e}{\partial x} \right] \bigg|_{x=0} = 0,$$

$$-\kappa_{\text{eff}} \left[ \frac{\partial \phi_e}{\partial x} + \frac{2RT(t^0_+ - 1)}{F} \left( 1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln c_e}{\partial x} \right] \bigg|_{x=L_{\text{tot}}} = 0$$

$$-\kappa_{\text{eff}} \left[ \frac{\partial \phi_e}{\partial x} + \frac{2RT(t^0_+ - 1)}{F} \left( 1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \frac{\partial \ln c_e}{\partial x} \right] \bigg|_{x=L_{n}} = \frac{i_{\text{app}}}{A}$$

and
2.4. Physics-Based Models (PBM)

\[-k_{\text{eff}} \left[ \frac{\partial \phi_e}{\partial x} + \frac{2RT}{F} \left( t^0_+ - 1 \right) \left( 1 + \frac{\partial \ln f_\pm}{\partial \ln c_e} \right) \frac{\partial \ln c_e}{\partial x} \right] \bigg|_{x=L^n+L^s} = \frac{i_{\text{app}}}{A}.

Concentration of lithium in the solid phase  The concentration in the solid phase equation describes the concentration of ions within the solid,

\[ \frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_s r^2 \frac{\partial c_s}{\partial r} \right), \]

where \( c_s \) is the concentration of lithium in the solid 2.1, \( r \) is the radius of the solid particle, and \( D_s \) is the diffusivity of lithium in the solid.

The concentration of the lithium in the solid phase equation has the following boundary conditions:

\[ D_s \frac{\partial c_s}{\partial r} \bigg|_{r=0} = 0 \]

and

\[ D_s \frac{\partial c_s}{\partial r} \bigg|_{r=R_s} = -j. \]

Concentration of lithium in the electrolyte phase  The concentration of lithium in the electrolyte phase equation relates the concentration of ions within the electrolyte

\[ \frac{\partial (\varepsilon_e c_e)}{\partial t} = \frac{\partial}{\partial x} D_e,\text{eff} \frac{\partial c_e}{\partial x} + a_s \left( 1 - t^0_+ \right) j, \]

with boundary conditions

\[ \frac{\partial c_e}{\partial x} \bigg|_{x=0} = \frac{\partial c_e}{\partial x} \bigg|_{x=L^\text{tot}} = 0, \]

\[ D_{e,\text{eff}} \frac{\partial c_e}{\partial x} \bigg|_{x=(L^n)^-} = D_s \frac{\partial c_e}{\partial x} \bigg|_{x=(L^n)^+}, \]
2.4. Physics-Based Models (PBM)

\[ D_{e,\text{eff}}^e \frac{\partial c_e}{\partial x} \bigg|_{x=(L^n+L^s)^-} = D_{e,\text{eff}}^p \frac{\partial c_e}{\partial x} \bigg|_{x=(L^n+L^s)^+}, \]

and

\[ c_e \bigg|_{x=(L^n)^-} = c_e \bigg|_{x=(L^n)^+}, \]

where \( \varepsilon_e \) is the porosity, or volume fraction of the electrolyte, and \( D_{e,\text{eff}}^e \) is the effective diffusivity in the electrolyte.

**Butler-Volmer** The Butler-Volmer equation models the rate of intercalation or de-intercalation of lithium ions occurring at the surface of the solid-mass and the electrolyte,

\[ j = j_0 \left\{ \exp \left( \frac{(1-\alpha)F}{RT} \eta - \exp \left( -\frac{\alpha F}{RT} \eta \right) \right) \right\} \]

and

\[ j_0 = k_{\text{norm},0} \left( \frac{c_e}{c_{e,0}} \right)^{1-\alpha} \left( 1 - \frac{c_{s,e}}{c_{s,\text{max}}} \right)^{1-\alpha} \left( \frac{c_{s,e}}{c_{s,\text{max}}} \right)^{\alpha}, \]

where \( k_{\text{norm},0} \) is the rate constant for the electrochemical reaction, \( \alpha \) is the charge transfer coefficient, \( c_e \) is the concentration of lithium in the electrolyte phase, \( c_s \) is the concentration of lithium in the solid phase, \( c_{s,e} \) is the concentration in the solid at the solid/electrolyte boundary, and \( \eta \) is the overpotential. The overpotential is expressed by

\[ \eta = \phi_s - \phi_e - U_{\text{ocp}} \left( \frac{c_{s,e}}{c_{s,\text{max}}} \right) - FR_{\text{film}}. \]

Here \( U_{\text{ocp}} \) is the open-circuit potential, \( c_{s,\text{max}} \) is the maximum concentration in the solid, and \( R_{\text{film}} \) is the resistivity of the resistance layer formed. Typically, \( R_{\text{film}} \) is assumed to be negligible, however, it becomes important in the presence of degradation.

The information presented in this section is an abridged version of Newman and Doyle’s work. For a comprehensive development of their model, refer to their original publications [4]. The next section introduces an alternative approach to developing a PBM.
2.4. Physics-Based Models (PBM)

Lumped parameters

Jobman created a framework for systematic identification of PBM parameter values that match the behavior of actual cells. He was able to minimize the need to tear down cells and perform electrochemical experiments by restructuring the original first-order equations into lumped parameter versions. However, this thesis utilizes a version of the lumped parameter equations that reflect more of the work presented by Chu in [7]. The lumped parameters are a result of grouping redundant and unobservable constants that regularly appear together in the calculations, which makes these parameters possible to identify experimentally. It is not possible to identify unobservable parameters uniquely without teardown.

Mass conservation in the solid phase

The potential in the solid phase equation relates the movement of ions within the solid part of an electrode, that is,

\[
\bar{\sigma} \frac{\partial^2 \phi_s}{\partial \bar{x}^2} = F \hat{n},
\]

with boundary conditions

\[
\bar{\sigma}^n \frac{\partial (\bar{x}, t)}{\partial \bar{x}} \bigg|_{\bar{x}=0} \phi_k = -i_{\text{app}}
\]

and

\[
\bar{\sigma}^p \frac{\partial (\bar{x}, t)}{\partial \bar{x}} \bigg|_{\bar{x}=3} \phi_k = -i_{\text{app}}
\]

The lumped parameters are \(\bar{\sigma}\) and \(\hat{n}\), where

\[
\bar{\sigma} = \frac{\sigma_{\text{eff}} A}{L}
\]

in \(S\), and

\[
\hat{n} = a_s AL j
\]

in mol s\(^{-1}\). The lumped parameter \(\hat{n}\) is the combination of the same variables as the previous equation with the addition of total amount of positive charge (\(\text{Li}^+\), \(j\), meaning

\[
\hat{n} = a_s AL j
\]
2.4. **Physics-Based Models (PBM)**

in mol s\(^{-1}\).

**Potential in the electrolyte phase**  The concentration of lithium in the electrolyte phase equation relates the movement of ions within the electrolyte, that is,

\[
\bar{n}_e \frac{\partial \theta_e}{\partial t} = \bar{\psi} \frac{\partial}{\partial \tilde{x}} \bar{\kappa} \frac{\partial}{\partial \tilde{x}} \theta_e + \dot{n}
\]

with boundary conditions

\[
\theta_e \bigg|_{\text{left}} = \theta_e \bigg|_{\text{right}}
\]

and

\[
\bar{\kappa}_{\text{left}} \frac{\partial \theta_e}{\partial \tilde{x}} \bigg|_{\text{left}} = \bar{\kappa}_{\text{left}} \frac{\partial \theta_e}{\partial \tilde{x}} \bigg|_{\text{right}}
\]

The lumped parameter \(\bar{\psi}\), where

\[
\bar{\psi} = \frac{D^n_e}{\kappa^n_e} = \frac{D^s_e}{\kappa^s_e} = \frac{D^p_e}{\kappa^b}
\]

in mol S\(^{-1}\) s\(^{-1}\), and

\[
\bar{D}_e = \frac{D_{e,\text{eff}} A \bar{c}_e}{L (1 - 0^\circ)}
\]

in mol s\(^{-1}\).

**Concentration of lithium in the solid phase**  The potential in the solid phase equation relates the movement of ions within the solid part of an electrode, that is,

\[
\frac{\partial n_s(\bar{r}, x, t)}{\partial t} = \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left( D_{s,\text{tot}} \bar{r}^2 \frac{\partial n_s(\bar{r}, x, t)}{\partial \bar{r}} \right),
\]

with boundary conditions

\[
\bar{D}_s \frac{\partial \theta_s}{\partial t} \bigg|_{\bar{r}=1} = -\frac{[\theta_{100} - \theta_0]}{3Q} \dot{n}.
\]

The lumped parameter \(\bar{D}_s\) is the combination of the diffusivity constant, \(D_s\), and the particle radius, \(R_s\), meaning
2.4. Physics-Based Models (PBMs)

\[ \bar{D}_s = \frac{D_s}{R_s^2} \]

measured in \( s^{-1} \).

**Concentration of lithium in the electrolyte phase**  The concentration of lithium in the electrolyte phase equation relates the movement of ions within the electrolyte, that is,

\[ \frac{\partial \theta_e}{\partial t} \left( \kappa \left( \frac{\partial}{\partial \bar{x}} \phi_e + \bar{\kappa}_D T \frac{\partial \ln (\phi_e)}{\partial \bar{x}} \right) \right) + F \dot{n} = 0, \]

where

\[ \bar{\kappa}_D = \frac{2R (\rho^0 - 1)}{F} \left( 1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \]

with boundary conditions

\[ -\bar{\kappa} \left[ \frac{\partial}{\partial \bar{x}} \phi_e + \bar{\kappa}_D T \frac{\partial \ln (\theta_e)}{\partial \bar{x}} \right]_{\bar{x}=1,2} = i_{\text{app}}. \]

The lumped parameter \( \bar{\kappa} \) is the combination of the diffusivity constant, \( \kappa_{\text{eff}} \), and the particle radius, \( R_s \), meaning

\[ \bar{\kappa} = \frac{\kappa_{\text{eff}} A}{L} \]

measured in \( S \).

**Lithium Flux**  The Butler-Volmer equation relates the rate of intercalation or de-intercalation of lithium ions in the electrode, that is,

\[ \dot{n} = \dot{n}_0 \left\{ \exp \left( \frac{(1 - \alpha) F}{RT \eta} \right) - \exp \left( -\alpha F \frac{1}{RT} \eta \right) \right\} \]

and

\[ \dot{n}_0 = \bar{k}_0 (\theta_e)^{1-\alpha} (1 - \theta_{s,e})^{1-\alpha} (\theta_{s,e})^\alpha \]

and

\[ \eta = \phi_s - \phi_e - U_{\text{ocp}} (\theta_{s,e}) - F R_i \dot{n}. \]
2.4. Physics-Based Models (PBM)

The lumped parameters consist of $R_f$, $n$, and $k_0$. The lumped parameter $k_0$ is the combination of the total resistance on particle surface film, $a_s$, the initial rate constant of the electrochemical reaction, $k_0$, the initial concentration of lithium in the electrolyte phase, $c_{e,0}$, and the volume fraction of the electrolyte phase in the positive electrode, $\varepsilon_s$, meaning

$$k_0 = \frac{k_{\text{norm},0}}{j} = a_sALk_{\text{norm},0}.$$  

Alternatively, the lumped parameter $k_{\text{norm},0}$ can be expressed as the combination of

$$k_{\text{norm},0} = k_0 (c_{e,0})^{1-\alpha} c_{s,\text{max}}$$

in mol m$^{-2}$ s$^{-1}$. The lumped parameter $R_f$ is the combination of the total resistance on particle surface film, $R_f$, specific surface area of the porous electrode, $a_s$, A, and L, meaning

$$R_f = \frac{R_f}{a_sAL}$$

in $\Omega$. This Butler-Volmer equation operates on the assumption that alpha is 0.5.

In addition to the modification of these equations, experiments were crafted to isolate parameter values in the model on standard cycling equipment. An optimization procedure was performed on the data to regress model parameter values. The information presented in this section is an abridged version of Jobman’s and Chu’s work. For a comprehensive development of his model, refer to their original publications [6, 7].

A FOM encompasses all cell behavior but is too complex for implementation into real-time applications. That is why the models are “reduced” in complexity to be able to apply to systems [6].
2.5 Reduced-Order Models (ROMs) Derived From Electrochemical Models

Realization algorithms operate on continuous-time transfer functions to produce discrete-time reduced-order state-space models. The purpose of realization algorithms are to reduce infinite order transfer functions into discrete-time models. Lee [27] developed, the Discrete-time Realization Algorithm (DRA), which produces a ROM using discrete-time pulse response data. The DRA model incorporates linearization that needs to be operated near the set-point but can not be implemented in real-time because the model generation is slow. De Palma [28] created the Continuous-time Realization Algorithm (CRA) in which produces a reduced order state-space model using continuous-time frequency-response data. Neither realization algorithm is better than the other. The battery is an infinite dimensional system with a transcendental transfer function, which is difficult to work with mathematically. However, this transfer function will still admit a frequency response. The CRA shows the frequency response in the frequency domain while the DRA shows the frequency response in the time domain with an impulse response, which contains all dynamic information. With the use of the Hankel matrix, subspace based system identification is used to extract the subspace projection to discern linear state-space representation system that optimally captures the most important dynamic elements. The result is a state-space system that matches the behavior of the battery. There have been many advances in the creation of physics-based FOMs and ROMs with the implementation of realization algorithms to produce higher fidelity models. ROMs were created by Jobman with parameters developed with his optimization procedure. The ROMs were created using the lumped parameter equations and reduced with the CRA. In the next chapter, degradation mechanisms are presented to provide background about degradation modeling.
2.6 Chapter Conclusion

This chapter explains PBM modeling for an ideal cell model. ECMs were briefly discussed. This section also explored the generation of FOMs and the implementation of lumped parameters, and briefly touched on ROM generation. The following section describes degradation mechanisms and degradation modeling.
3.1 Chapter Introduction

In the pursuit of safer and more durable batteries, degradation mechanisms must be mitigated. It is important to note that this thesis assumes that the cathode does not participate in degradation. This section discusses the theory of the degradation mechanisms that can affect cells during their lifetimes, with some examples shown in Figure 3.1. While there are numerous degradation mechanisms that affect aging of cells, the primary methods of degradation are lithium plating, solid electrolyte interphase (SEI) growth and manganese dissolution [10, 11, 13, 21, 22, 29, 30, 31, 32].

Figure 3.1: Possible Degradation Causes and Effects Self-discharge adopted from C. R. Birk, "Degradation diagnostics for lithium ion cells," 2017 [30]

Xavier developed a method of coupling the ideal cell model and lithium plating in [20] and uses MPC to mitigate the affects of lithium plating by controlling the current supplied to the cell under many cycling environments.
This chapter has three sections. The first addresses lithium plating to explain how SEI and lithium plating are coupled while the second presents the mechanism of SEI growth, which is the central focus of the work presented in chapter 4. Many interacting degradation mechanisms can affect batteries, as seen in Figure 3.2, and lead to capacity fade and power loss. Due to the complexity of degradation modeling, this thesis will only touch on lithium plating and focus on SEI growth, which have been discussed frequently in the literature as primary methods of cell aging.

3.2 Lithium Plating

Lithium plating is an irreversible process that converts lithium-ions into metallic lithium. This is significant because active lithium is taken from circulation and leads to capacity fade, which means that over time the battery will not hold charge as well as it once did. Arora et al. [21, 9] initially developed the first-principles degradation model for lithium plating, and Xavier implemented Model-Predictive Control (MPC) using this model to mitigate potential lithium plating. MPC is beyond the scope of this thesis; for more information.
on this powerful technique, please refer to the original work in [23]. It does however highlight the potential applications of using advanced control techniques and PBMs to improve battery performance. Lithium plating typically happens at colder temperatures, high current charge rates, and can be instigated by SEI formation as seen in Figure 3.8. The effects of lithium plating can be devastating, rendering a battery dead in a matter of a few cycles under extreme temperatures and cycling.

### 3.2.1 Lithium Plating Degradation Modeling

This section reviews the model presented by Arora to the extent that is relevant to the development of basic understanding. For the complete development of the model, refer to the original work presented by Arora in [21]. Arora assumes that lithium plating is an irreversible process that forms over a solid particle, which results in loss of active lithium within the solid and the electrolyte. Lithium plating primarily forms near the negative electrode separator region due to localization caused by SEI formation as seen in Figure 3.8. Capacity fade occurs as a result of remaining lithium being unable to intercalate and de-intercalate from the solid because the pores are covered with a film of metallic lithium. While Arora developed equations for the rate of film growth and cell resistance, our work only is interested in capacity fade effects.

The rate of lithium involved in lithium plating is calculated using a modified Butler-Volmer equation,

\[
j_{oc} = \min \left\{ 0, \frac{i_{0,oc}}{F} \left( \exp \left( \frac{(1 - \alpha_{oc}) F \eta_{oc}}{RT} \right) - \exp \left( -\frac{\alpha_{oc} F \eta_{oc}}{RT} \right) \right) \right\}.
\]  

(3.1)

where \( i_{0,oc} \) is the exchange current, \( F \) is Faraday’s constant, \( R \) is the gas constant, \( \alpha_{oc} \) is the transient, \( T \) is temperature, \( \eta_{oc} \) is the overpotential of the side reaction. The overpotential can be expressed as

\[
\eta_{oc} = \phi_s - \phi_s - U_{ref,oc} - Fj_{ref,oc} - Fj_{oc}R_{film}.
\]  

(3.2)
3.2. Lithium Plating

This reaction is assumed to be an irreversible process. The side-reaction exchange current density is

\[ i_{0,oc} = F (k_{a,oc})^{\alpha_{oc}} (k_{c,oc})^{1-\alpha_{oc}} (c_e)^{1-\alpha_{oc}}. \]  

(3.3)

Xavier used the Arora model to control lithium plating degradation by applying model predictive control.

3.2.2 Lithium Plating Degradation Modeling with MPC Control

This section reviews the work presented by Xavier in [20] to the extent that it is relevant to the development of basic understanding of his lithium plating model. Lithium plating occurs in regions along the negative electrode and separator interface where the overpotential, \( \eta_{ls} \), becomes negative as presented in Figure 2.1 in Chapter 2.

![Figure 3.3: Overpotential as demonstrated in terms of position along the anode](image)

In order to better determine the integral along the anode, a parabolic curve is assumed between positions \( x = 0 \) and \( x = 1 \) as seen in Figure 3.3. This assumption is used in order to determine \( x_c \) which is the point across the anode at which the overpotential side reaction, \( \eta(x,t) \), becomes negative. This step allows further specification of the bounds for the integration of the flux density, \( j_s(x,t_0) \), as \( [x_c, L_n] \). Thus the equation from Step 1 in the previous section can be written as,
3.2. Lithium Plating

\[ \frac{dQ_{\text{Loss}}}{dt} \bigg|_{t=t_k} = A \int_{x_c}^{L_n} j_s(x, t_k) \, dx. \]

Taken one step further, the equation above can be expressed for \( Q_{\text{Loss}}(t) \) as

\[ Q_{\text{Loss}}(t) = A \int_{t_0}^{t_f} \int_{0}^{L_n} j_s(x, t) \, dx \, dt \quad (3.4) \]

where \( A \) is the cross sectional area and \( j_s(x, t) \) is the flux of the side reaction. It is important to note that capacity is determined as the integration over the electrode integrated over time.

In addition, it is needed to determine this relationship at every time-point in order to generate the function, \( \frac{dQ(t)}{dt} \), from \( t_0 \) to \( t_f \). The equation above is then differentiated in order to obtain the capacity loss, \( Q_{\text{Loss}} \) as seen in Figure 3.4. At this point, it is important to distinguish \( Q_{\text{Loss}} \) from \( Q \); \( Q_{\text{Loss}} \) denotes the amount of lithium-ion inventory loss while \( Q \) denotes the total capacity loss, which can be measured in the lab. Inventory loss is always greater than total capacity loss.

![Figure 3.4: Capacity loss due to lithium plating](image)

This plating model developed by Xavier uses Jobman’s lumped parameter model ROM to determine the overpotential values used to calculate lithium plating. A ROM is needed in this case because lithium plating forms when cells are actively being charged,
that is why the lithium plating model relies on the internal cell dynamics of the ROM to propagate the formation of lithium plating as a result of the applied current. For the purposes of the SEI model presented in this thesis, a ROM is not needed as there are no applied cell dynamics occurring as the cell is assumed to be at constant equilibrium and all electrochemical reactions are a result of parasitic reactions in the negative electrode only. SEI can develop either: i) as a result of cycling; or ii) when the cell is at rest. This thesis examines SEI development while the cell is at rest. The following section present the background necessary to understand SEI modeling.

3.3 Solid Interphase Electrolyte (SEI) Growth

SEI is always present in cells. Peled [13] proved that the transfer of electrons from the electrode to the electrolyte should be avoided except when forming the initial layer of SEI. The initial layer of SEI acts like a protective shell for the negative electrode. Unfortunately, further cycling encourages SEI growth. If the layer continues to grow after the initial formation process, it can cause blocking of the electrode pores, leading to capacity fade, thus producing the ideal conditions for lithium plating [22]. SEI forms under all conditions. It does not matter whether the cell is at rest or being cycled; electrochemical reactions are always happening. SEI is composed of several compounds, which are formed by the electrochemical reactions.

3.3.1 Ramadass SEI Model

Ramadass et al. [10] developed a first-order principles, capacity fade model for SEI. Doyle et al. uses the Butler-Volmer kinetic expression to model intercalation lithium flux density. Thus, the negative electrode flux density can be described as follows,

\[ j_{\text{total}}(x, t) = j_{\text{int}}(x, t) + j_{\text{sei}}(x, t) \]
where \( j_{\text{int}}(x,t) \) is the intercalation-flux density and \( j_{\text{sei}} \) is the side-reaction lithium-flux density. The side-reaction flux density can be reflected as the Tafel equation

\[
j_{\text{sei}}(x,t) = -\frac{i_{0,\text{sei}}}{F} \exp\left(\frac{\alpha F}{RT} \eta_{\text{sei}}(x,t)\right),
\]

where \( i_{0,\text{sei}} \) is the exchange-current density for the side-reaction. The side-reaction overpotential is expressed by

\[
\eta_{\text{sei}}(x,t) = \phi_s(x,t) - \phi_e(x,t) - U_{\text{ref,sei}} - j_{\text{total}}(x,t) FR_{\text{film}},
\]

where \( U_{\text{ref,sei}} \) is the equivalent reference potential of the SEI side reaction.

In addition, Ramadass presents a method to calculate the capacity loss as

\[
\frac{\partial Q_{\text{Loss}}}{\partial t} = \int_{0}^{L_{\text{neg}}} F j_{\text{sei}}(x,t) a_s dx,
\]

where capacity loss is calculated by integrating the lithium loss with respect to time as open-loop. Again, this capacity is amount of lithium-ion inventory loss.

### 3.3.2 Safari Kinetic and Diffusion SEI model

Safari et al. [11] developed an SEI model that considers a kinetic limited mode and a diffusion limited mode. He presents a single-particle SEI model which does not include the electrolyte phase. This model assumes that the SEI layer that forms around a particle has a uniform thickness. In doing so, this model is only accurate for low current rates. The film layer follows a parabolic growth law. The diffusion model is better suited to capture the behavior of a cell during cell storage.

Safari begins development of the SEI degradation model with the flux equation

\[
j_{\text{int}} = j_0 \left( \exp\left(\frac{(1 - \alpha) F}{RT} \eta_{\text{int}}\right) - \exp\left(-\frac{\alpha_{\text{oc}} F}{RT} \eta_{\text{int}}\right) \right)
\]
3.3. Solid Interphase Electrolyte (SEI) Growth

where

\[ \eta_{\text{int}} = \phi_s - U_{\text{ocp}}(\theta_{\text{neg}}) - \frac{\delta F}{\kappa_{\text{sei}}} j_{\text{total}}. \]

The total flux is the combination of all side reactions,

\[ j_{\text{total}} = j_{\text{int}} + j_{\text{sei}}, \]

where

\[ j_{\text{sei}} = -k_{\text{sei}} c_{EC} \exp \left( -\frac{\alpha F}{RT} \eta_{\text{sei}} \right) \]

and

\[ \eta_{\text{sei}} = \phi_s - \frac{\delta F}{\kappa_{\text{sei}}} j_{\text{total}}. \]

Ramadass and Safari have access to physical parameters of the cells to populate the models needed to simulate SEI degradation. There are no individual parameters available for the Panasonic cell. As discussed in Chapter 2, the lumped model returns unobservable parameters as a group. A way to identify the needed parameters for the Ramadass and Safari models is to conduct a post-mortem test on the Panasonic cell and take physical measurements. This is costly to do and not feasible to do at UCCS. The following section provides the background for the methodology used to extract the necessary parameters for commercial cells nondestructively to populate an SEI model.

3.3.3 Fu SEI Self-Discharge Tests

This section builds upon the degradation mechanisms presented above. Fu et al. [16] presents a PBM for SEI side reactions. There, the authors claim that it is possible to extract the exchange current density \( i_{0,\text{side}} \) and the equilibrium potential \( U_{\text{eq,side}} \) of the SEI side reactions from the self discharging characteristics of the battery. Fu proposed extracting degradation parameters by taking voltage measurements of cells at rest over an extended period of time, typically experiments last up to two months. Specifically, by using the
3.3. Solid Interphase Electrolyte (SEI) Growth

Experimental self-discharge data and plotting the change in terminal voltage versus time (Figure 3.5), one can determine constant values for \( i_{0,\text{side}} \) and \( U_{\text{eq,side}} \) (Figure 3.5).

Fu et al. then incorporated these parameters into their SEI model and validated the integrated model against experimental data obtained under cycling with different static aging environments. The cell studied was a 15.7 Ah capacity LiPB pouch type cell with 164mm × 250mm × 5mm dimensions. The active material of the anode is carbon, the cathode is NMC (Li[MnNiCo]O₂), and the polymer separator is PVdF. The electrolyte salt was LiPF₆ with ethylmethyl carbonates (EC) and dymethyl carbonate (DMC) solvents [16].

SEI formation can be explained using the following equations. Having both equations and the lumped parameter model, it is possible to extract the rate of SEI degradation. Fu begins development of the SEI degradation model with the flux equation,

\[
j_{\text{SEI}}^{\text{Li}} = -i_{0,\text{side}} \exp\left(-\frac{\alpha_{\text{c,side}} n_{\text{side}} F}{R F} \eta_{\text{side}}\right)
\]

![Figure 3.5: Curve fit figure presented in Fu publication self-discharge adopted from R. Fu, "Development of a physics-based degradation model for lithium ion polymer batteries considering side reactions" 2015 [16]](image)
3.3. Solid Interphase Electrolyte (SEI) Growth

where \( i_{0,\text{side}} \) is the exchange current density of the side reaction, \( n_{\text{side}} \) is the number of ions involved in side reaction, and \( \eta_{\text{side}} \) is the activation overpotential of side reaction. The overpotential can be expressed as

\[
\eta_{\text{side}} = \phi_p - \phi_e - U_{\text{eq,side}} - R_{\text{SEI}} j_{\text{SEI}}^{\text{Li}}
\]

where \( \phi_p \) is the potential of the solid, \( \phi_e \) is the potential of the electrolyte, and \( U_{\text{eq,side}} \) is the potential of the equilibrium of the side reactions. The potential of the equilibrium can be expressed as

\[
U_{\text{eq,side}} = U_{\text{eq,side}}^\Theta + \frac{RT}{n_{\text{side}} F} \ln \left( \frac{c_e}{c_{e,0}} \right)
\]

where \( U_{\text{eq,side}}^\Theta \) is the derived or manufacturer provided value, \( U_{\text{eq}}^\Theta \) is assumed to be 0.4 V [16], \( c_e \) is the concentration in the electrolyte, \( c_{e,0} \) is the initial concentration in the electrolyte.

Fu’s publication [16] is the basis of the approach used in this thesis. The publication has been referenced mainly for the work done on parameter extraction of side reactions using non-destructive methods. Please reference Fu’s version of SEI and subsequent equations below:

Flux of the SEI side reaction can be expressed as

\[
J_{\text{SEI}}^{\text{Li}} = -i_{0,\text{side}} \exp \left( -\frac{\alpha_{c,\text{side}} n_{\text{side}} F}{RT} \eta_{\text{side}} \right), \quad (3.5)
\]

where, \( i_{0,\text{side}} \) is the exchange current density, \( n_{\text{side}} \) is the number of ions involved in the side reaction, and \( \eta_{\text{side}} \) is activation overpotential of the side reaction.

The over potential of the SEI side reaction can be expressed as

\[
\eta_{\text{side}} = \phi_p - \phi_e - U_{\text{eq,side}} - R_{\text{SEI}} j_{\text{SEI}}^{\text{Li}},
\]

where, \( U_{\text{eq,side}} \) is the potential of the equilibrium of the side reactions and \( R_{\text{SEI}} \) is the film thickness as a result of the side reaction.
3.3. Solid Interphase Electrolyte (SEI) Growth

The potential at equilibrium is

\[ U_{\text{eq,side}} = U_{\text{eq,side}}^{\Theta} + \frac{RT}{n_{\text{side}}F} \ln \left( \frac{c_e}{c_{e,0}} \right), \]

where, \( U_{\text{eq,side}}^{\Theta} \) is a constant independent of stoichiometric numbers [16].

The Fu method is robust but takes a long time to gather the sufficient data to estimate the needed parameters for the model because it takes months for lithium batteries to self-discharge. Section 3.3.5 explains the background of another method that is more time efficient. It uses a potentiostat to track the changes in current needed to keep the SOC of the cell under test at 100%.

3.3.4 Lumped Ramadass SEI Model

There are many key differences between Fu’s experiment and the experiment presented in this work. First, the cells used were new Panasonic 25 Ah prismatic cells. More about experiment details are presented in 4. Another defining difference is that the approach presented here uses a Ramadass lumped-parameter model to estimate the side-reaction parameters. The Ramadass model to lumped-parameter format and allow for estimation of only one parameter, \( \bar{k}_{\text{sei}} \). The conversion process starts with a Tafel equation for the side-reaction and corresponding overpotential relationship,

\[ j_{\text{sei}} (x, t) = -\frac{i_{0,\text{sei}}}{F} \exp \left( -\frac{\alpha_s F}{RT} \eta_s (x, t) \right) \quad (3.6) \]

and

\[ \eta_{\text{sei}} (x, t) = \phi_s (x, t) - \phi_e (x, t) - U_{\text{ref,sei}} - j_{\text{total}} (x, t) F R_{\text{film}}. \quad (3.7) \]

Now to convert Eq. 3.6 into lumped parameter form, recall that \( \dot{n} = a_s AL \dot{j} \), then the equation becomes

\[ \dot{n}_s (x, t) = -\bar{n}_{0,s} \exp \left( -\frac{\alpha_s F}{RT} (\phi_s (x, t) - \phi_e (x, t) - U_s - F R_{\text{film}} \dot{n} (x, t)) \right). \]
3.3. Solid Interphase Electrolyte (SEI) Growth

At this step \( U_s \) can be factored out as a constant term (along with other constants that are associated with this term), so the equation becomes

\[
\dot{n}_s (x, t) = - \left[ \tilde{n}_{0,s} \exp \left( \frac{\alpha_s F}{R T} U_s \right) \right] \exp \left( - \frac{\alpha_s F}{R T} (\phi_s (x, t) - \phi_e (x, t) - F R_{\text{film}} \dot{n} (x, t)) \right)
\]

and in this way we can define a new lumped parameter,

\[
\bar{k}_{\text{sei}} = \tilde{n}_{0,s} \exp \left( \frac{\alpha_s F}{R T} U_s \right).
\]

Thus the Tafel equation can be rewritten as

\[
\dot{n}_s (x, t) = \bar{k}_{\text{sei}} \exp \left( - \frac{\alpha_s F}{R T} (\phi_s (x, t) - \phi_e (x, t) - F R_{\text{film}} \dot{n} (x, t)) \right).
\]

It is also important to mention that now the units of the constant and \( \dot{n}_s \) is in \( \text{mol s}^{-1} \). In the next section, details about the systematic data collection process and the results of the estimated \( \bar{k}_{\text{sei}} \) are presented. For \( \bar{k}_{\text{sei}} \) estimation, optimizations were conducting using the following cost function:

\[
p^* = \arg \min_p \sum (OCV_{\text{model}} (k) - OCV_{\text{data}} (k))^2.
\]

In order to obtain the simulated voltage, \( OCV_{\text{model}} (k) \), a function was created to iterate voltage in a loop. Plett [8, 25] developed a method for solving for the current density
and was able to generate an algebraic solution to estimate SEI side reaction values. That strategy is implemented here to propagate simulated voltage.

\[
\theta^n_{ss,k} = \theta^n_{ss,k-1} - \frac{|\theta^n_{100} - \theta^n_0| \Delta t}{FQ} \left( i_{app,k-1} - F\dot{n}_{s,k-1} \right)
\]

\[
\theta^p_{ss,k} = \theta^n_{ss,k-1} - \frac{|\theta^n_{100} - \theta^n_0| \Delta t}{FQ} \left( -i_{app,k-1} \right)
\]

\[
Q_k = Q_{k-1} + \Delta t \cdot \dot{n}_{s,k-1}
\]

\[
\dot{n}_{0,k} = k_0 \sqrt{\theta^n_{ss,k} \left( 1 - \theta^n_{ss,k} \right)}
\]

\[
A = -k_{sei} \exp \left( -\frac{F}{2RT} U^m_{ocp} \left( \theta^n_{ss,0} \right) \right)
\]

\[
B = -\frac{i_{app,k}}{2F\dot{n}_{0,k}}
\]

\[
C = \frac{1}{2F\dot{n}_{0,k}}
\]

\[
\dot{n}_{s,k} = \frac{AB + A \sqrt{B^2 + (1 - 2AC)}}{1 - 2AC}
\]

\[
V_{cell} = U^p_{ocp} \left( \theta^p_{ss,k} \right) - U^m_{ocp} \left( \theta^n_{ss,k} \right)
\]

There are three components that affect the propagation of voltage in the simulation, which are \( \theta_{ssn} \) and \( \dot{n}_{s,k} \). Please note that while \( Q_k \) is being calculated, \( \theta^n_{ss,k} \) and \( \theta^p_{ss,k} \) are propagated using, \( Q \), total capacity, which remains constant. In the case for self discharge, the applied current is zero and thus \( i_{app} \) is zero. One of the main issues found was that the initial \( k_{sei} \) estimated values resulted in voltage simulations that did not match the experimental data. Self discharge data was used to not only estimate the \( k_{sei} \) constant, but also estimate the corresponding \( \theta^n_0, \theta^n_{100}, \theta^p_0, \theta^p_{100} \) values because they were found to not be reliable. OCP boundary values were initialized by running an amended version of \( \text{fitOCP} \) function [33] using the FORD negative and positive half cell data as well as the FORD OCV full cell data. The result was \( \bar{\theta}^n_0 = -0.0015212, \bar{\theta}^n_{100} = 0.753549, \bar{\theta}^p_0 = 0.749474, \text{and } \bar{\theta}^p_{100} = 0.0815161 \). With this method two parameters are reduced to one parameter and consolidates the degrees of freedom.

At this point it is important to distinguish between relative stoichiometric boundaries, \( \bar{\theta} \), and absolute stoichiometric boundaries, \( \theta \). Absolute stoichiometric boundaries determine
3.3. **Solid Interphase Electrolyte (SEI) Growth**

![Diagram](image)

**Figure 3.6:** Relative and absolute stoichiometries adopted from Dongliang Lu, "Identifying Physical Model Parameter Values for Lithium-ion Cells" 2021 [34]

the minimum and maximum cutoff voltages, $V_{\text{min}}$ and $V_{\text{max}}$, respectively, where $\theta^n_{0}$ and $\theta^n_{100}$ correspond to $V_{\text{min}}$ and $\theta^p_{0}$ and $\theta^p_{100}$ correspond to $V_{\text{max}}$. These boundaries capture only a portion of the cell capacity as both electrodes will always have a higher capacity, as seen in Figure 3.6. However, relative stoichiometric bounds are unscaled. The relative bounds can be refined and horizontally shifted with a scaling factor, $k_{c\text{v}}$, and a shifting factor, $\theta_{c\text{v}}$, (for the negative and positive electrodes, respectively) with pulse data [33]. The pulse test required to determine these scaling and shifting factors is a comprehensive test that would optimize 15 parameters. The pulse test presented in this work was performed with the sole intention of estimating the instantaneous resistance, lacking the detail necessary to extract these parameters.

### 3.3.5 **Tuveri Leakage Current Test Application**

A Keysight paper [18] proposed using a potentiostat to measure the current of a cell to determine the rate of self-discharge current as seen in Figure 3.7. The purpose of this paper was to propose a method of optimizing the time needed from design to production of lithium-ion batteries via potentiostat current tests.

Typically self-discharge is determined by measuring OCV; however, since, Li-ion cells typically lose 0.5 to 1% of charge per month, it takes months to detect a significant change in SOC. Electrochemical processes within lithium-ion cells cause self-discharge, depleting the stored energy of the cell, causing the terminal voltage to decrease over time when stored [18]. It is possible that the same leakage current test used to determine if a cell is market ready can also be used to determine side reaction parameters like in [35]. Shang
3.3. **Solid Interphase Electrolyte (SEI) Growth**

Figure 3.7: Self-discharge potentiostat set-up and Self-discharge from BT2152A cell adopted from Giacomo Tuveri, "Keysight Technologies How to Shorten Li-Ion Self-Discharge Test Time?" 2017 [18]

*et al.* used the leakage current data to estimate the exchange current of oxygen reduction by fitting the leakage current data to the expression for exchange current of oxygen reduction. This same technique may be applicable to SEI by assuming that all parasitic side reactions are a result of SEI. Plett’s algebraic iterative solution is implemented once again to analyze leakage current data. The next section presents a model where SEI may be coupled with other degradation mechanisms as a result of changing internal dynamics.

### 3.3.6 SEI Degradation Equations Coupled with Lithium Plating

There have been two authors that have coupled SEI with another degradation mechanism. Yang’s publication [22] coupled lithium plating degradation with SEI. Yang *et al.* [22] presented a PBM for quantifying the amount of lithium plating and SEI formation across the negative electrode. This model also implements a method for determining linear and nonlinear degradation. It is important to note that the author refers to the overpotential, $\eta$, as lithium deposition potential (LDP). SEI is the dominant degradation mechanism during the linear degradation. SEI causes a drop in porosity, thus affecting the local electrolyte potential gradient in the anode. This causes the overpotential to go negative. Once the overpotential is negative, the conditions are favorable for lithium plating to deposit in between the anode and separator region as the voltage cut-off is approached. Figure 3.8 shows what degradation behavior is present across the electrode with respect to time, depicting the linear and non-linear degradation described above. This linearity can be seen experimentally,
but more on that subject in the next chapter. Lithium plating can be instigated by SEI formation as seen in Figure 3.8. The effects of lithium plating can be devastating, rendering a battery dead in a matter of a few cycles under extreme temperatures and cycling. The information in this section is presented for completeness in the discussion of model degradation and demonstrates how interconnected SEI is with other forms of cell degradation, which is why it is important to develop an SEI model for aging purposes.

Figure 3.8: Relationship Between SEI formation and Lithium Plating adopted from Xiao-Guang Yang, "Modeling of lithium plating induced aging of lithium-ion batteries: Transition from linear to nonlinear aging." 2017[22]

Below are Yang’s equations to describe SEI and lithium plating reactions. The total volumetric current as

\[ j_{\text{tot}} = j_{\text{int}} + j_{\text{sei}} + j_{\text{lpl}}. \]

The current density of the lithium intercalation is defined as

\[ j_{\text{int}} = -a i_{0,\text{int}} \left( \exp \left( -\frac{\alpha_{a,\text{int}} F}{RT} \eta_{\text{int}} \right) - \exp \left( -\frac{\alpha_{c,\text{int}} F}{RT} \eta_{\text{int}} \right) \right). \]

The local current density of SEI formation is defined as

\[ j_{\text{sei}} = -a F k_{0,\text{sei}} c_{\text{EC}}^{s} \exp \left( -\frac{\alpha_{c,\text{side}} F}{RT} \left( \phi_{s} - \phi_{u} - \frac{j_{\text{tot}}}{a} \alpha R_{\text{film}} - U_{\text{sei}} \right) \right), \]

where \( k_{0,\text{sei}} \) is the kinetic rate constant, and \( c_{\text{EC}}^{s} \) is the concentration of ethylene carbonate.

The transfer current density of lithium deposition is defined as
$$\dot{j}_{lpl} = -\alpha i_{i0,lpl} \exp\left(-\frac{\alpha e_{lpl} F}{RT} \left(\phi_s - \phi_e - \frac{\dot{j}_{tot}}{a} R_{film}\right)\right)$$ (3.8)

Yang’s proposed method offers a way to determine the transition between linear and nonlinear aging affected by the lithium plating rate. In addition, this method accounts for a drop in negative electrode porosity due to lithium plating. Furthermore, there is a relationship between lithium plating and porosity drop. Coupling degradation models is beyond the scope of this thesis. The focus of this thesis is to determine an experimental way to estimate $\bar{k}_{sei}$ nondestructively in order to populate an SEI model. This section is included to show that degradation models are coupled and affect each other in ways that are not fully known.

### 3.4 Chapter Conclusion

This chapter explains degradation modeling for lithium plating and SEI, showing that SEI is a precursor to lithium plating. Lithium plating alone is devastating without exacerbating the effects with SEI. This section also touched briefly on ways that degradation can be coupled together. The following section describes the method of estimating SEI lumped side reaction constant, $\bar{k}_{sei}$, experimentally through two tests: i) a SDT by measuring voltage and ii) a leakage current test by measuring current loss directly.
CHAPTER 4

Experimental extraction of SEI side-reaction parameters

4.1 Chapter Introduction

In an effort to extract degradation parameters experimentally, this chapter describes the experimental method developed to estimate SEI side-reaction constant, $\bar{k}_{\text{sei}}$, and $z_0$ as well as the OCP absolute boundaries: $\theta_0^n$, $\theta_{100}^n$, $\theta_0^p$, and $\theta_{100}^p$. The first method was inspired by the work developed by Fu in [16] and Tuveri in [18]. In addition, an investigation into the health of cells was also studied to keep track of the state of health of the batteries during experimentation.

4.2 Experiment Preparation & Reference Performance Tests

This section describes the tests used to prepare the cells for experimentation, and the development of reference performance tests to evaluate changes in cells, and SDTs. Nine new Panasonic Lithium-ion Nickel Manganese Cobalt (Li-ion graphite anode +NMC cathode) cells were cycled nine times to circulate the lithium. Cells were maintained in Cincinnati Sub-Zero ZP-8 thermal chamber controlled environments. Reference performance tests include an Open Circuit Voltage (OCV) test and an instantaneous pulse resistance test. The cells were labeled as FP07-FP15.
4.2. Experiment Preparation & Reference Performance Tests

4.2.1 Experimental set-up

A long-term cell aging experiment was performed in stages. However, the actual experiment timeline looked more like that of Fig. 4.1 because there was only one Gamry Potentiostat and Power Booster set that was able to produce the 30 A pulse needed for the pulse test. Thus the timeline catered to making the data process more efficient due to that limiting factor with 9 test articles.

![Figure 4.1: All Experiments Sample Timeline for all cells](Image)

4.2.2 Results and Analysis

The results of the SDTs were compiled and analyzed utilizing a curve fit in Matlab. Since not all cells are identical, Post Reference Performance Tests (RPTs) were performed to characterize each new cell. All RPTs were performed at 25 °C using a script tailored for the Panasonic cell. The open circuit characterization RPT contains two parts: i) a capacity test and ii) a pulse test. The reason for performing the baseline characterization of cell performance in this manner is to gain data without impacting future aging tests. For easier comparison of the data, all raw data sets are plotted on the same axis.

4.2.3 Pre and Post Reference Performance Tests (RPTs)

The main focus of this thesis is to identify parameters extracted from the self-discharge data. Yet, there are many other age related changes that occur by storing cells at 100% SOC for prolonged periods of time. To make such observations, RPTs were added to the
4.2. Experiment Preparation & Reference Performance Tests

experimental design such OCV and abridged OCV tests to determine changes in capacity, and pulse tests to determine changes in cell high-frequency instantaneous resistance. The OCV test was performed using an Arbin BT2000 while storing in the same thermal chambers as stated before. Pulse tests were performed using a Gamry Instruments Reference 3000 Potentiostat and a 30k Power-Booster in a Tenney thermal chamber at 25°C. All RPTs were performed at 25°C after each subsequent SDT. This work was initially developed by Jobman in [6] and refined by Cromer in [36]. While the original test was performed at different magnitudes and temperatures, the pulse test presented in this section was amended to include one pulse at 30 A and was only performed at 25°C.

Four-step Open Circuit Voltage Tests (OCV)

Open Circuit Voltage Tests (OCV) Test were used primarily in this study to determine capacity of the cell before and after all subsequent Self Discharge Tests and Reference Performance Tests were completed. An OCV test is used to establish a relationship between OCV and SOC. The OCV used in the experiment consists of four scripts, each detailing a specific groups of steps:

1. Assume that the cell is already charged to 100% SOC, soak the cell at the desired test temperature, and discharge the cell at a rate of C/30 until the minimum voltage boundary, $V_{\text{min}}$, is reached;

2. Perform a dither test at the minimum voltage boundary, $V_{\text{min}}$, at 25°C;

3. Charge the cell at a rate of C/30 at the desired test temperature until the maximum voltage boundary, $V_{\text{max}}$, is reached;

4. Perform a dither test at the maximum voltage boundary, $V_{\text{max}}$, at 25°C.

Voltage boundaries are defined by the cell manufacturer. Due to the nature of this experiment, voltage boundaries were carefully observed to prevent unnecessary degradation to the test articles. Dither cycles are sinusoidal current applied to the cell to ensure that the cell does achieve being at the minimum or maximum voltage boundaries [4].
4.2. Experiment Preparation & Reference Performance Tests

Figure 4.2: Capacity Pre-SDTs

Figure 4.2 shows the visual comparison of all nine Panasonic cells after the initial OCV Test. Table 4.1 shows the values of each cell. The highest capacity was of FP10 at 24.85 Ah and the lowest capacity was 24.73 Ah. Showing that the cell estimated capacity measurement was within 0.12 Ah of each other.

Table 4.1: Capacity Measurements Post all SDTs

<table>
<thead>
<tr>
<th>Row</th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>24.78</td>
<td>24.84</td>
<td>24.85</td>
<td>24.83</td>
<td>24.79</td>
<td>24.76</td>
<td>24.78</td>
<td>24.73</td>
<td>24.86</td>
</tr>
</tbody>
</table>

4.2.4 Intermittent Reference Performance Tests

The RPTs were designed to be performed in between the SDTs. The capacity test was an abridged version of the OCV four step test that was performed pre and post all of the SDTs. This test was used to estimate the capacity of the cell after each SDT; however, this test did not contain the dithers present in the original OCV test. The dithers were omitted due to time constraints. With this in mind, this test served to give an estimation of the capacity, but could not be compared directly to the capacity estimation of the OCV tests and was used to check that the battery’s state of health was not severely degraded that the cell could not continue with the next experiment. The test allowed the cell to rest for three hours for the cell to climatize to the correct temperature. Then, the cell was discharged at a C/30 rate. The cell was allowed to rest for one hour. The cell was then charged at a rate of C/30. Again, the cell was allowed to rest for one hour.
4.2. Experiment Preparation & Reference Performance Tests

**Short-Version Open Circuit Voltage Capacity Test (CAP)**

Once the SDT had been successfully completed, a short OCV capacity test was performed. While a capacity measurement was calculated with this abridged version of the experiment, the capacity calculated from the four step OCV test and this short OCV test cannot be compared directly. This is because the four step OCV test contains two steps that run dither profiles at the lower and upper voltage boundaries. Dithers ensure that a cell was exercised at the voltage boundaries, and the sum voltage of the dither tests are added to the capacity calculated. The abridged CAP test calculates total capacity by subtracting the charge amp hours from discharge amp hours approximated by the ARBIN software at the end of step one.

**Gamry Electrochemical Impedance Spectroscopy Pulse Test (PUL)**

Once the capacity test had been successfully completed, then a pulse test was performed. The sequence assumed that the test article was at 100% State of Charge (SOC); otherwise, the cell would operate at unsafe conditions. The cell was exposed to one 20 millisecond 30 A charge and discharge pulse in a loop for four SOCs: 20% SOC, 40% SOC, 60% SOC, and 80% SOC. The test discharged the cell using a constant current C/10 rate, and the cell was allowed to rest for three hours in order to let the cell reach equilibrium. Voltage measurements were taken for three hours as the cell attempted to return to equilibrium. Equilibrium is defined as the state when the cell voltage stops fluctuating, which typically takes three hours to achieve on a NMC battery at 25°C.

![Figure 4.3: Resistance Pre-SDTs](image-url)
4.3 Experiment Analysis

Figure 4.3 shows the initial resistance measurements for the charge and discharge pulse. Table 4.2 and Table 4.3 show the resistance values from the charge pulse and discharge pulse at 20% SOC, 40% SOC, 60% SOC, and 80% SOC for all cells, respectively. Figure 4.3 shows that all resistances were similar for all cells. The pulse test analysis indicated that the highest resistance was produced at 20% SOC while the lowest resistance typically happened at 80% SOC.

<table>
<thead>
<tr>
<th>Row</th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC20</td>
<td>1.385</td>
<td>1.428</td>
<td>1.486</td>
<td>1.515</td>
<td>1.449</td>
<td>1.441</td>
<td>1.356</td>
<td>1.467</td>
<td>1.466</td>
</tr>
<tr>
<td>SOC40</td>
<td>1.3023</td>
<td>1.334</td>
<td>1.3923</td>
<td>1.390</td>
<td>1.369</td>
<td>1.380</td>
<td>1.303</td>
<td>1.381</td>
<td>1.392</td>
</tr>
<tr>
<td>SOC60</td>
<td>1.276</td>
<td>1.2767</td>
<td>1.4062</td>
<td>1.358</td>
<td>1.310</td>
<td>1.384</td>
<td>1.261</td>
<td>1.370</td>
<td>1.341</td>
</tr>
<tr>
<td>SOC80</td>
<td>1.249</td>
<td>1.258</td>
<td>1.343</td>
<td>1.326</td>
<td>1.299</td>
<td>1.376</td>
<td>1.287</td>
<td>1.305</td>
<td>1.311</td>
</tr>
</tbody>
</table>

This section introduced the reference performance tests used to determine cell state of health. The pre Self Discharge Test data was introduced to establish understanding of the four step OCV test to calculate total capacity, Q, in order to extract $\bar{k}_{sei}$ from the Self-Discharge Tests and leakage current.

4.3 Experiment Analysis

This section describes how to estimate $\bar{k}_{sei}$ and $z_0$ as well as the OCP absolute boundaries: $\theta^0_0$, $\theta^m_{100}$, $\theta^p_0$, and $\theta^p_{100}$. This method can be applied to all commercial lithium-ion cells. For
4.3. Experiment Analysis

optimization, there are three functions that come to mind. While there are many Matlab optimization routines, some stand out: fminsearch, fmincon, and particleswarm. fminsearch is a useful all around function but can not directly apply constraints, although, there is a way to apply a penalty for undesirable outcomes. Nevertheless, there are better functions to apply constrains to systems. fmincon is a function that will work for constrained systems, however, this function may get stuck in a local minima. Lastly, particleswarm is better for determining a global minimum. Figure 4.4 demonstrates the way particleswarm works in Matlab [37]. Particles of different velocities are uniformly created, distributed and used to evaluate the lowest function value at each particle location. Particles that return the lowest function values are used to determine new velocities along with the values of neighboring particles. Then the particles are iteratively updated until optimization criterion are met for the objective function.

![Diagram](image)

**Figure 4.4:** General system Particle Swarm iteration improvements

The following code was implemented to analyze the data:

```matlab
%% Estimate SEI parameters
% Setup the optimization
bestcost = Inf;
custom_init = [1e-4,0.1,0.85,0.75,0.6,0.9;...  
               1e-5,0.1,0.85,0.75,0.6,0.9;...  
               1e-6,0.1,0.85,0.75,0.6,0.9;...  
               1e-7,0.1,0.85,0.75,0.6,0.9;...  
               1e-8,0.1,0.85,0.75,0.6,0.9;...  
               1e-9,0.1,0.85,0.75,0.6,0.9;...]
```
4.3. Experiment Analysis

\[
\begin{align*}
1e-10,0.1,0.85,0.75,0.6,0.9; \\
1e-11,0.1,0.85,0.75,0.6,0.9; \\
1e-12,0.1,0.85,0.75,0.6,0.9; \\
1e-13,0.1,0.85,0.75,0.6,0.9; \\
1e-14,0.1,0.85,0.75,0.6,0.9; \\
1e-15,0.1,0.85,0.75,0.6,0.9; \\
\end{align*}
\]

% PARTICLESWARM
fminconopts = optimoptions('fmincon','Algorithm','sqp');
options = optimoptions('particleswarm','SwarmSize',10000,...
    'InitialSwarmMatrix',custom_init,'HybridFcn',{fmincon',
    fminconopts});
kseiest = particleswarm(@simLC,6,[1e-15 0.001 0.8 0.55 0.4 0.85],...
    [1e-4 0.2 0.95 0.95 0.7 1.2],options)

Please note that this is the code used to optimize for the leakage current data. The SDT and leakage current data are analyzed essentially in the the same way and will become more clear later in what ways the analysis differs. There are some important elements of this code to point out. In this case, the particleswarm function uses 10,000 particles to optimize. Of the 10,000 particles, 12 particles have been defined as particles of interest in matrix custom_init and appended as an option for particleswarm’s ‘InitialSwarmMatrix’.

The following code implements Plett’s algebraic iterative solution to simulate voltage:

```matlab
function currentLeakage = DTAscan(fileID,fieldnames)
    if fileID>1
        A = textscan(fileID,'%s %s %s %s %s %s %s %s %s %s %s %s');
        for i = 1:5
            data = str2double(A{i});
            data = data(~isnan(data)<1);
            if i > 1
                if length(data)>length(currentLeakage.(sprintf('%s',
                    fieldnames{1})))
                    data = data(length(data)-length(currentLeakage.(sprintf('%s',fieldnames{1}))))+1:end;
                end
            end
        end
    end
```
4.3. Experiment Analysis

```matlab
function cost = simLC(varargin)

    global Q T testtemp negmodel posmodel time f
    global bestcost volt R F dt cellname rmserror $z0

    ksei = varargin{1}(1);
    theta0n = varargin{1}(2);
    theta100n = varargin{1}(3);
    theta0p = varargin{1}(4);
    theta100p = varargin{1}(5);
    z0 = varargin{1}(6);

    % CONVERT ABSOLUTE ESTIMATION TO RELATIVE FOR STOIC. BOUNDS
    % -------------------------------------------
    % xx = [theta0n_rel 1;theta100n_rel 1]/[theta0n;theta100n];
    % kcvn = xx(1); thetacvn = xx(2);
    % xx = [theta0p_rel 1;theta100p_rel 1]/[theta0p;theta100p];
    % kcvp = xx(1); thetacvp = xx(2);
    % STRUC: x0 = [ksei,theta0n,theta100n,theta0p,theta100p];
    % x0 = [1e-7,-0.0015212,0.753549,0.749474,0.0815161];
    % relative bounds estimated w/ OCPfit
    xx = [-0.0015212 1;0.753549 1] \ [theta0n;theta100n];
    kcvn = xx(1); thetacvn = xx(2);
    xx = [0.749474 1;0.0815161 1] \ [theta0p;theta100p];
    kcvp = xx(1); thetacvp = xx(2);

    k0_ref = 9.231e-3;
    Ea_k0 = 3.315e4;
```

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4.3. **Experiment Analysis**

\[
k_0 = k_{0\text{ ref}} \exp \left( \frac{E_{a_k} R}{k_0} \left( \frac{1}{298.15} - \frac{1}{T} \right) \right);
\]

\[
d_{Qn} = \text{abs} (\theta_{100n} - \theta_{0n});
\]

\[
d_{Qp} = \text{abs} (\theta_{100p} - \theta_{0p});
\]

\[
U_n = \Theta(x) \text{ OCVfromSOCtemp}((x - \theta_{cvn})/k_{cvn}, \text{testtemp}, \text{negmodel});
\]

\[
U_p = \Theta(x) \text{ OCVfromSOCtemp}((x - \theta_{cvp})/k_{cvp}, \text{testtemp}, \text{posmodel});
\]

\[
\%
INITIALIZE
\%
-------------------------------------------------------------
\%
Step 1: compute initial surface stoichiometry
\%
\%
theta_{sn} = \theta_{0n} + z_0 (\theta_{100n} - \theta_{0n});
\%
theta_{sp} = \theta_{0p} + z_0 (\theta_{100p} - \theta_{0p});
\%
\%
I_{app} = -f;
\%
Q_{cell} = \text{zeros} (\text{length} (\text{time}), 1);
\%
Q_{cell}(1) = Q;
\%
V_{cell} = \text{zeros} (\text{length} (\text{time}), 1);
\%
V_{cell}(1) = U_p (\theta_{asp}) - U_n (\theta_{asn});
\%
N_{side} = \text{zeros} (\text{length} (\text{time}), 1);
\%
N_{side}(1) = -k_{sei} \exp \left( -F/\left( 2 \times R \times T \right) \times U_n (\theta_{asn}) \right);
\%
theta_{asn} = \text{zeros} (\text{length} (\text{time}), 1);
\%
theta_{asn}(1) = theta_{asn};
\%
theta_{assp} = \text{zeros} (\text{length} (\text{time}), 1);
\%
theta_{assp}(1) = theta_{assp};
\%
\%
SIMULATION LOOP
\%
-------------------------------------------------------------
\%
for k = 2: \text{length} (\text{time})
\%
\%
Step 2: update surface stoichiometries
\%
\%
theta_{asn}(k) = theta_{asn}(k-1) - d_{Qn} \times \text{dt} \times (I_{app}(k-1) - F \times N_{side}(k-1)) / Q / F;
\%
theta_{assp}(k) = theta_{assp}(k-1) - d_{Qp} \times \text{dt} \times \left( -I_{app}(k-1) - F \times 0 \right) / Q / F;
\%
\%
Step 3: update cell capacity (mole)
\%
Q_{cell}(k) = Q_{cell}(k-1) + \text{dt} \times N_{side}(k-1);
4.3. Experiment Analysis

% Step 4: update side reaction molar rate
ndot0 = k0*sqrt(Thetassn(k)*(1-Thetassn(k)));
A = -ksei*exp(-F/(2*R*T)*Un(Thetassn(k)));
B = -Iapp(k)/(2*F*ndot0);
C = 1/(2*ndot0);
Nside(k) = (A*B+A*sqrt(B^2+1-2*C*A))/(1-2*C*A);

% Step 5: update cell OCV
Vcell(k) = Up(Thetassp(k)) - Un(Thetassn(k));
end

% DEFINE COST, CALCULATE RMS ERROR, PLOT RESULTS
%------------------------------------------------------------
cost = sum((Vcell(:)-volt(:)).^2);

% Plot real-time fitting results
if cost < bestcost
    bestcost = cost;
    rmserro3 = rms(Vcell(:)-volt(:));
    fprintf(' Best rms error to data: %.4f mV\n',...
        rmserro3*1000);
    fprintf(' cost: %.4f mV\n',cost*1000); close;
    figure;clf;plot(time/60*24,volt(:),'b',time/60*24,...
    Vcell(:),'r');
    xlabel('Time (days)'); ylabel('Open-circuit voltage (V)');
    axis([0 3 3.97 4.11]);
    title(sprintf('FORD %s Leakage Current @ %d^oC',...
        cellname,testtemp),...
        'FontSize',9);
    legend('Data','Estimated','Location','SouthWest');
    grid on; thesisFormat([0.1 0 0.05 0]);
end
end
4.3. Experiment Analysis

Here it is important to point out that $\theta^n_0$, $\theta^n_{100}$, $\theta^p_0$, and $\theta^p_{100}$ are being optimized; however, the open circuit potential of the positive and negative electrodes are determined with debiased elements $\tilde{\theta}^n_0 = -0.0015212$, $\tilde{\theta}^n_{100} = 0.753549$, $\tilde{\theta}^p_0 = 0.749474$, and $\tilde{\theta}^p_{100} = 0.0815161$. That is why there is a section in the simLC cost function taking in the initial estimates, the optimization parameters, and converting the biased estimates into debiased estimates. The conversion is employed by using the following relationship:

$$\theta^r = k^r_cv \tilde{\theta}^r_s + \theta^r_{cv},$$

where $r$ is the electrode region, and $s$ refers to the solid phase. Here, $\theta^r_s$ is the absolute stoichiometric number, $k^r_cv$ is the scaling factor, $\tilde{\theta}^r_s$ is the relative stoichiometric number, and $\theta^r_{cv}$ is the shifting factor. In section 3.3.4 it was discussed that typically $k^r_cv$ and $\theta^r_{cv}$ are optimized using a comprehensive pulse test[33], but in order to convert from absolute to relative bounds, $k^r_cv$ and $\theta^r_{cv}$ can be estimated by using the debiased bounds estimated using fitOCP.m [33]. To do this, $\tilde{\theta}^r_s$ must be isolated, hence the equation becomes

$$\tilde{\theta}^r_s = \frac{\theta^r_s - \theta^r_{cv}}{k^r_cv}.$$

In order to find $k^r_cv$ and $\theta^r_{cv}$ use

$$\begin{bmatrix} k^r_cv \\ \theta^r_{cv} \end{bmatrix} = \begin{bmatrix} \tilde{\theta}^r_0 & 1 \\ \tilde{\theta}^r_{100} & 1 \end{bmatrix}^{-1} \begin{bmatrix} \theta^r_0 \\ \theta^r_{100} \end{bmatrix}.$$  

The SOC, $z_0$, is another parameter that was optimized; otherwise, the cell dynamics were incorrect because starting point for the model will yield deviant solutions.

The main difference between this leakage current code and the code used for SDT is that with leakage current, there is a small applied current and with SDT the applied current is 0. Thus, in the SDT analysis code B is also zero and thus the B term in negligible. Again, only for the SDT case. Constants are presented in Table 4.4.
4.4 Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

As part of this experiment, nine new Panasonic cells were tested; these cells were first charged to 100% SOC, then allowed to self-discharge (rest in thermal chamber) over an extended period of time. The cells were placed in an inert controlled environment while taking regular non-intrusive voltage measurements every hour. The experiment was performed at three different temperatures: 0°C, 25°C, and 50°C while resting in ARBIN BT2000 cycler. Cells FP07-FP15 were divided into three subgroups. FP07-FP09 would undergo testing in a Cincinnati Sub-Zero MCB-1.2-.33-.33-H/AC thermal chamber at 0°C. FP10-FP12 would undergo testing in a Cincinnati Sub-Zero MCB-1.2-.33-.33-H/AC thermal chamber at 50°C. FP13-FP15 would undergo testing in a EPS Tenney TC20 thermal chamber at 25°C. At the end of the test, all data was imported into Matlab and analyzed with hopes of extracting constant values for $\bar{k}_{sei}$ and $z_0$ and OCP absolute boundaries: $\theta^n_0$, $\theta^{100}_0$, $\theta^n_{100}$, and $\theta^{100}_{100}$ from the collected experimental SDT data. Although voltage measurements were taken every hour, one measurement per day was used in the analysis. This can be done without losing detail because Li-ion batteries lose voltage slowly; however, the optimization will not be as perform as well due to the time interval being larger. Utilizing the OCV to SOC relationship, each voltage measurement was used to determine each corresponding SOC to initialize the optimization.

This section displays the results of the experimental method developed to extract the rate of SEI formation. This section is organized sequentially. The results are presented in the order of the SDT test iteration with the results of the intermittent RPT test. Voltage boundaries are defined by the cell manufacturer. The results of the OCV was used to

<table>
<thead>
<tr>
<th>Table 4.4: Table of Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>F</td>
</tr>
<tr>
<td>R</td>
</tr>
<tr>
<td>T</td>
</tr>
</tbody>
</table>
obtain a capacity measurement, which will be used in the simulation to propagate simulated voltage. Due to the nature of this experiment, voltage boundaries were carefully observed to prevent unnecessary degradation to the test articles. Dither cycles are sinusoidal current applied to the cell to ensure that the cell does achieve being at the minimum or maximum voltage boundaries. Figure 4.1 shows the ideal outline of the experiment used to gather the data. The timeline was greatly limited by having only one Gamry Potentiostat and Power Booster available. While the instantaneous resistance measurements do not play a role in identifying $\bar{k}_{\text{sei}}$, the explanation of the RPT pulse test is discussed because it was part of collecting the multiple SDT data sets.

Also, in this section, the simulated voltage is compared to the experimental data in an attempt to validate the estimation of the lumped Ramadass SEI model. Part of the validation was presented in the results section where the rms error was calculated for each set of identified parameters. The data returned conflicting results. Between temperatures, we expect $k_{\text{sei}}$ to change but the values for $\theta_{0}^{n}$, $\theta_{100}^{n}$, $\theta_{0}^{p}$, and $\theta_{100}^{p}$ should remain consistent across all temperatures, except they are always moving as the cell ages.

Before examining the results, we must first discuss what we expect for $k_{\text{sei}}$, $\theta_{0}^{n}$, $\theta_{100}^{n}$, $\theta_{0}^{p}$, and $\theta_{100}^{p}$. The applicable insight that we can borrow from Fu’s research [16] is that the $k_{\text{sei}}$ constant estimated should be a small and a positive value. Although we have relaxed some of the restrictions for the absolute OCP boundaries ($\theta_{0}^{n}$, $\theta_{100}^{n}$, $\theta_{0}^{p}$, $\theta_{100}^{p}$) because some boundaries may not be correct. It is important to remember that $k_{\text{sei}}$ lumps the $i_{0,\text{side}}$ and the $U_{\text{eq,side}}$ terms together. To make the comparison between the work presented here and Fu’s work, the following relationship must be used

$$
\bar{k}_{\text{sei}} = \tilde{n}_{0,\text{a}} \exp \left( \frac{\alpha_{s} F U_{\text{a}}}{RT} \right),
$$

using measurements from Fu, whose values are presented in Figure 3.5. The reaction rate constant is $\tilde{n}_{0,\text{a}}$ is calculated by

$$
\tilde{n}_{0,\text{a}} = \frac{i_{0,\text{side}} a_{s} AL}{F}.
$$

Table 4.5 contains Fu’s identified parameters converted to lumped parameters.
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

**Table 4.5: Fu Lumped Parameter Results.** [16]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\bar{k}_{\text{sei}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°C</td>
<td>5.44E-10</td>
</tr>
<tr>
<td>25°C</td>
<td>1.0664E-9</td>
</tr>
<tr>
<td>50°C</td>
<td>1.3004E-9</td>
</tr>
</tbody>
</table>

Using Fu’s results as a reference, it is shown that for all SDTs and leakage current tests, the $\bar{k}_{\text{sei}}$ component has a lower order of magnitude than those identified by Fu. Unfortunately, there was no conformity of the $\theta^n_0$, $\theta^{100}_0$, $\theta^p_0$, and $\theta^{100}_p$ terms across all temperatures. While exact matches were not required, more consistency for $\theta^n_0$, $\theta^{100}_0$, $\theta^p_0$, and $\theta^{100}_p$ across all temperatures was expected. In the next section, simulated voltage results will be validated against the experiment voltage.

**SDT #1 at 0°C**

Table 4.6 shows the results of all cells at 0°C for SDT#1, SDT#2, and SDT#3. For SDT#1 at 0°C, the $\bar{k}_{\text{sei}}$ constant is very different for FP07 than for FP08 and FP09. Though by SDT#3, the estimations are more similar between FP07 and FP08 and FP09 seems more like an outlier. The shift may have happened because FP09 was damaged during SDT#3. Condensation had formed on the terminal due to the thermal chamber being set at 0°C. As a result, the terminal corroded and changed the characteristics of the cell such as increasing instantaneous resistance. FP08 in SDT#1 had a loose terminal but that issue was resolved after SDT#1 and became better for SDT#2 and SDT#3. Overall, $\bar{k}_{\text{sei}}$ is very variable even within the data of cells within the same SDT. There is also not a lot of consistency among the values for the $\theta^n_0$, $\theta^{100}_0$, $\theta^p_0$, and $\theta^{100}_p$ across SDTs. Though, damage to cells might offer some explanation as to why the estimations for this data seems very irregular in some cases.
### 4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

<table>
<thead>
<tr>
<th>Table 4.6: Identified SEI parameters for at 0°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>$\tilde{k}_{sei}$</td>
</tr>
<tr>
<td>$\theta_{0}^{n}$</td>
</tr>
<tr>
<td>$\theta_{100}^{n}$</td>
</tr>
<tr>
<td>$\theta_{0}^{p}$</td>
</tr>
<tr>
<td>$\theta_{100}^{p}$</td>
</tr>
<tr>
<td>$z_{0}$</td>
</tr>
<tr>
<td>cost [mV]</td>
</tr>
<tr>
<td>rms error [mV]</td>
</tr>
</tbody>
</table>

**Figure 4.5:** SDT using Ramadass Method-$\tilde{k}_{sei}$ at 0°C for SDT#1

Figures 4.5 at 0°C showed great fidelity between the simulation and the experiment data even though the optimization did have good congruency among $\tilde{k}_{sei}$, $\theta_{0}^{n}$, $\theta_{100}^{n}$, and $\theta_{100}^{p}$. The results are surprising and may show that there may be many solutions that satisfy the optimization for 0°C using our current model for the Panasonic cell, and tighter bounds may be needed to optimize for $\theta_{0}^{n}$. Please note that although every effort was made to make sure that each cell starts the SDT at 100% SOC, realistically, cells cannot start at 100% SOC. In the case of FP08 for SDT#1, one of the cell terminals was loose, which resulted in abnormal charging behavior. That is why, FP08 started at a lower voltage.

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4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

SDT #1 at 25°C

Table 4.7: Identified SEI parameters for at 25°C

<table>
<thead>
<tr>
<th></th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{k}_{\text{sei}}$</td>
<td>2.47137E-07</td>
<td>2.5307E-07</td>
<td>2.52195E-07</td>
</tr>
<tr>
<td>$\theta_n^0$</td>
<td>0.110890671</td>
<td>0.00118925</td>
<td>0.03334188</td>
</tr>
<tr>
<td>$\theta_{n100}$</td>
<td>0.898285304</td>
<td>0.8</td>
<td>0.924132654</td>
</tr>
<tr>
<td>$\theta_p^0$</td>
<td>0.95</td>
<td>0.947894299</td>
<td>0.571090095</td>
</tr>
<tr>
<td>$\theta_{p100}$</td>
<td>0.505754239</td>
<td>0.611406302</td>
<td>0.647230324</td>
</tr>
<tr>
<td>$z_0$</td>
<td>1.004143043</td>
<td>1.004672686</td>
<td>1.005056517</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.272607425</td>
<td>0.355532587</td>
<td>0.364153984</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>2.113994838</td>
<td>2.414208579</td>
<td>2.443304617</td>
</tr>
</tbody>
</table>

Figures 4.6 at 25°C showed good fidelity between the simulation and the experiment data even though the optimization did not have good congruency among $\tilde{k}_{\text{sei}}, \theta_n^0, \theta_{n100},$ and $\theta_{p100}$. The 25°C data showed good results among $\tilde{k}_{\text{sei}}, \theta_n^0, \theta_{n100},$ and $\theta_{p100},$ but not $\theta_p^0$. Yet, results between the simulated data and the raw experiment data are okay, but here the affects of using less time points are seen. The results are also surprising and may show that there may be many solutions that satisfy the optimization for 25°C, as well, as seen by Figure 4.5, which are similar to the figures for 0°C cases. The results are surprising and may show that there may be many solutions that satisfy the optimization for 25°C using our current model for the Panasonic cell, like the 0°C.
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

SDT #1 at 50°C

<table>
<thead>
<tr>
<th>Table 4.8: Identified SEI parameters for at 50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>$k_{sei}$</td>
</tr>
<tr>
<td>$\theta_0^n$</td>
</tr>
<tr>
<td>$\theta_{100}^n$</td>
</tr>
<tr>
<td>$\theta_0^p$</td>
</tr>
<tr>
<td>$\theta_{100}^p$</td>
</tr>
<tr>
<td>$z_0$</td>
</tr>
<tr>
<td>cost [mV]</td>
</tr>
<tr>
<td>rms error [mV]</td>
</tr>
</tbody>
</table>

Figure 4.7: SDT using Ramadass Method-$k_{sei}$ at 50°C for SDT#1

Figure 4.7 at 50°C did not show great fidelity between the simulation and the experiment data. Although, $k_{sei}$ and $z_0$ had great consistency for the test group, $\theta_0^n$, $\theta_{100}^n$, $\theta_0^p$, and $\theta_{100}^p$ but and did not have good congruency.

RPT POST SDT #1

Figure 4.8 shows that there is a major loss of capacity by the 50°C test group. Again, this capacity test can not be compared to the four step OCV test.

Figure 4.9 shows the initial resistance measurements for the charge and discharge pulse. Table 4.9 and Table 4.10 shows the resistance values from the charge pulse and discharge pulse at 20% SOC, 40% SOC, 60% SOC, and 80% SOC for all cells, respectively. Figure 4.9 shows that the 50°C test group have deviated from their previous measurements.
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

![Figure 4.8: Capacity approximation after SDT #1](image1)

![Figure 4.9: Resistance Pre-SDTs](image2)

when compared to Figure 4.3, which shows that all resistances are similar for all cells for Pulse Test 1.

<table>
<thead>
<tr>
<th>Table 4.9: Results from Charge Pulse 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Row</strong></td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td><strong>SOC20</strong></td>
</tr>
<tr>
<td><strong>SOC40</strong></td>
</tr>
<tr>
<td><strong>SOC60</strong></td>
</tr>
<tr>
<td><strong>SOC80</strong></td>
</tr>
</tbody>
</table>
4.4. **Self-Discharge Tests (SDTs) with ARBINs Results and Discussion**

The pulse test analysis indicated that the highest resistance is produced at 20% SOC while the lowest resistance typically happened at 80% SOC. The trend remains: The resistance is similar for test articles that were held at 0°C or 25°C, yet the test articles at 50°C developed the highest resistance.

**SDT #2**

This section presents the results of all cells at 0°C, 25°C, and 50°C for SDT#2

**SDT #2 at 0°C**

<table>
<thead>
<tr>
<th>Row</th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC20</td>
<td>1.524</td>
<td>1.381</td>
<td>1.434</td>
<td>1.567</td>
<td>1.707</td>
<td>1.600</td>
<td>1.327</td>
<td>1.390</td>
<td>1.439</td>
</tr>
<tr>
<td>SOC40</td>
<td>1.476</td>
<td>1.317</td>
<td>1.28</td>
<td>1.541</td>
<td>1.647</td>
<td>1.526</td>
<td>1.293</td>
<td>1.254</td>
<td>1.369</td>
</tr>
<tr>
<td>SOC60</td>
<td>1.43</td>
<td>1.288</td>
<td>1.345</td>
<td>1.499</td>
<td>1.564</td>
<td>1.407</td>
<td>1.251</td>
<td>1.282</td>
<td>1.335</td>
</tr>
<tr>
<td>SOC80</td>
<td>1.396</td>
<td>1.285</td>
<td>1.295</td>
<td>1.459</td>
<td>1.537</td>
<td>1.465</td>
<td>1.237</td>
<td>1.289</td>
<td>1.301</td>
</tr>
</tbody>
</table>

**Table 4.10:** Results from Discharge Pulse 2

<table>
<thead>
<tr>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{k}_{sei} )</td>
<td>9.70398E-08</td>
<td>9.71621E-08</td>
<td>8.6185E-08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta_0^n )</td>
<td>0.172827304</td>
<td>0.024309983</td>
<td>0.145021667</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta_{100}^n )</td>
<td>0.800052541</td>
<td>0.8</td>
<td>0.917478571</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta_0^p )</td>
<td>0.807903201</td>
<td>0.944460439</td>
<td>0.728251462</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta_{100}^p )</td>
<td>0.510968529</td>
<td>0.56221766</td>
<td>0.597019899</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Z_0 )</td>
<td>1.010556199</td>
<td>1.010453144</td>
<td>1.009569813</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.022046895</td>
<td>0.0188968</td>
<td>0.007406659</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>0.601185924</td>
<td>0.556582071</td>
<td>0.348454656</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.11:** Identified SEI parameters for at 0°C

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4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

**Figure 4.10:** SDT using Ramadass Method- $\tilde{k}_{\text{sei}}$ at 0°C for SDT#2

**SDT #2 at 25°C**

**Table 4.12:** Identified SEI parameters for at 25°C

<table>
<thead>
<tr>
<th></th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{k}_{\text{sei}}$</td>
<td>2.53615E-07</td>
<td>2.58363E-07</td>
<td>2.59143E-07</td>
</tr>
<tr>
<td>$\theta_0^\phi$</td>
<td>0.037720608</td>
<td>0.2</td>
<td>0.199607792</td>
</tr>
<tr>
<td>$\theta_{100}^\phi$</td>
<td>0.8003121</td>
<td>0.8</td>
<td>0.800010201</td>
</tr>
<tr>
<td>$\theta_0^p$</td>
<td>0.565838735</td>
<td>0.709264184</td>
<td>0.787128262</td>
</tr>
<tr>
<td>$\theta_{100}^p$</td>
<td>0.7</td>
<td>0.522019012</td>
<td>0.644616313</td>
</tr>
<tr>
<td>$z_0$</td>
<td>1.005230747</td>
<td>1.004927987</td>
<td>1.005477433</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.314938362</td>
<td>0.334648206</td>
<td>0.364744917</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>2.272206851</td>
<td>2.342228887</td>
<td>2.445286256</td>
</tr>
</tbody>
</table>

**Figure 4.11:** SDT using Ramadass Method- $\tilde{k}_{\text{sei}}$ at 25°C for SDT#2
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

SDT #2 at 50 °C

| Table 4.13: Identified SEI parameters for at 50 °C |
|-----------------|-----------------|-----------------|
|                 | FP10            | FP11            | FP12            |
| \( \bar{k}_{\text{sei}} \)       | 1.13201E-06     | 1.13132E-06     | 1.16849E-06     |
| \( \theta^n_0 \)                | 0.001930372     | 0.001239439     | 0.001           |
| \( \theta^n_{100} \)            | 0.8             | 0.8             | 0.801442        |
| \( \theta^p_0 \)                | 0.837988133     | 0.902387693     | 0.553326451     |
| \( \theta^p_{100} \)             | 0.658530327     | 0.566196951     | 0.7             |
| \( z_0 \)                       | 0.98464936      | 0.980848614     | 0.989960946     |
| cost [mV]                     | 3.702985759     | 3.91734798      | 4.282730573     |
| rms error [mV]               | 7.791321105     | 8.013664539     | 8.379063069     |

Figure 4.12: SDT using Ramadass Method-\( \bar{k}_{\text{sei}} \) at 50 °C for SDT#2

Figure 4.10 showed good fidelity between the data and model, but Figures 4.11, and 4.12 demonstrated that the simulation and experiment data did not have great fidelity. Tables 4.11, 4.12, and 4.13 all the data in this experiment expose interesting inconsistencies within the results much like results from SDT#1 and SDT#2.

Overall, there was good congruency among \( \bar{k}_{\text{sei}} \) and \( z_0 \), but inconsistencies for \( \theta^n_0 \), \( \theta^n_{100} \), \( \theta^p_0 \), and \( \theta^p_{100} \); like the results of SDT#1. Presently, it is not certain what may be the main cause of the problem; the strategy used to optimize or the model used. What is known is that there is room for improvement in both the optimization and the model especially in case of 50 °C. There may be dynamics at 50 °C that are not being accounted for in the current model. For instance, the cells from the 50 °C group swelled up during SDT#1, which was not expected.
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

RPT POST SDT #2

![Capacity approximation after SDT #2](image)

**Figure 4.13:** Capacity approximation after SDT #2

Figure 4.13 like 4.8 shows that there is a major loss of capacity by the $50^\circ C$ test group. In addition there is more capacity loss in the $25^\circ C$ test group then after CSL1. Again, this capacity test can not be compared to the four step OCV test because it does not contain the dither steps needed to make a complete capacity estimation.

![Resistance Post-SDTs](image)

**Figure 4.14:** Resistance Post-SDTs

Figure 4.14 shows the initial resistance measurements for the charge and discharge pulse. Table 4.14 and Table 4.15 shows the resistance values from the charge pulse and discharge pulse at 20% SOC, 40% SOC, 60% SOC, and 80% SOC for all cells, respectively. Figure 4.14 shows that the $50^\circ C$ test group have deviated more from their previous measurements when compared to Figures 4.3 and 4.9, which shows that all resistances are
similar for all cells for Pulse Test 1 and 2, respectively. Cell FP09 has deviated from the other cells in due to oxidation on the positive terminal.

<p>| Table 4.14: Results from Charge Pulse 3 |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Row</th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC20</td>
<td>1.615</td>
<td>1.416</td>
<td>1.899</td>
<td>1.835</td>
<td>1.819</td>
<td>1.780</td>
<td>1.400</td>
<td>1.423</td>
<td>1.465</td>
</tr>
<tr>
<td>SOC40</td>
<td>1.531</td>
<td>1.348</td>
<td>1.841</td>
<td>1.791</td>
<td>1.695</td>
<td>1.678</td>
<td>1.394</td>
<td>1.363</td>
<td>1.390</td>
</tr>
<tr>
<td>SOC60</td>
<td>1.5443</td>
<td>1.331</td>
<td>1.877</td>
<td>1.712</td>
<td>1.656</td>
<td>1.625</td>
<td>1.347</td>
<td>1.405</td>
<td>1.375</td>
</tr>
<tr>
<td>SOC80</td>
<td>1.447</td>
<td>1.265</td>
<td>1.754</td>
<td>1.649</td>
<td>1.608</td>
<td>1.616</td>
<td>1.271</td>
<td>1.309</td>
<td>1.318</td>
</tr>
</tbody>
</table>

<p>| Table 4.15: Results from Discharge Pulse 3 |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Row</th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC20</td>
<td>1.592</td>
<td>1.380</td>
<td>1.856</td>
<td>1.848</td>
<td>1.759</td>
<td>1.753</td>
<td>1.417</td>
<td>1.413</td>
<td>1.455</td>
</tr>
<tr>
<td>SOC40</td>
<td>1.538</td>
<td>1.323</td>
<td>1.791</td>
<td>1.755</td>
<td>1.682</td>
<td>1.664</td>
<td>1.333</td>
<td>1.320</td>
<td>1.405</td>
</tr>
<tr>
<td>SOC60</td>
<td>1.490</td>
<td>1.270</td>
<td>1.766</td>
<td>1.687</td>
<td>1.612</td>
<td>1.619</td>
<td>1.31</td>
<td>1.344</td>
<td>1.3723</td>
</tr>
<tr>
<td>SOC80</td>
<td>1.462</td>
<td>1.208</td>
<td>1.651</td>
<td>1.656</td>
<td>1.571</td>
<td>1.549</td>
<td>1.260</td>
<td>1.178</td>
<td>1.309</td>
</tr>
</tbody>
</table>

The pulse test analysis indicated that the highest resistance is produced at 20% SOC while the lowest resistance typically happened at 80% SOC. The trend remains: The resistance is similar for test articles that were held at 0°C or 25°C, yet the test articles at 50°C developed the highest resistance. FP09, which was a cell part of the 0°C test group, had a higher SOC than the other cells because the terminal came in contact with water and became rusted.

**SDT #3**

This section presents the SDT results of all cells at 0°C, 25°C, and 50°C for SDT#3.
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

**SDT #3 at 0°C**

Table 4.16: Identified SEI parameters for at 0°C

<table>
<thead>
<tr>
<th></th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{k}_{sei}$</td>
<td>8.63018E-08</td>
<td>8.05769E-08</td>
<td>8.30802E-08</td>
</tr>
<tr>
<td>$\theta_0^n$</td>
<td>0.183928026</td>
<td>0.2</td>
<td>0.010492611</td>
</tr>
<tr>
<td>$\theta_{100}^n$</td>
<td>0.815773843</td>
<td>0.867507676</td>
<td>0.894930159</td>
</tr>
<tr>
<td>$\theta_0^p$</td>
<td>0.839632065</td>
<td>0.597979541</td>
<td>0.844718776</td>
</tr>
<tr>
<td>$\theta_{100}^p$</td>
<td>0.441565661</td>
<td>0.527331385</td>
<td>0.472555823</td>
</tr>
<tr>
<td>$z_0$</td>
<td>1.015896305</td>
<td>1.016397969</td>
<td>1.015737111</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.010053616</td>
<td>0.011220361</td>
<td>0.010777675</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>0.405972143</td>
<td>0.428882669</td>
<td>0.420337008</td>
</tr>
</tbody>
</table>

Figure 4.15: SDT using Ramadass Method-$\tilde{k}_{sei}$ at 0°C for SDT#3

**SDT #3 at 25°C**

Table 4.17: Identified SEI parameters for at 25°C

<table>
<thead>
<tr>
<th></th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{k}_{sei}$</td>
<td>2.5556E-07</td>
<td>2.62213E-07</td>
<td>2.61596E-07</td>
</tr>
<tr>
<td>$\theta_0^n$</td>
<td>0.166991965</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$\theta_{100}^n$</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$\theta_0^p$</td>
<td>0.565818326</td>
<td>0.60362346</td>
<td>0.749261803</td>
</tr>
<tr>
<td>$\theta_{100}^p$</td>
<td>0.675877391</td>
<td>0.480289959</td>
<td>0.673621532</td>
</tr>
<tr>
<td>$z_0$</td>
<td>1.003858464</td>
<td>1.004964259</td>
<td>1.004912038</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.363564646</td>
<td>0.39186958</td>
<td>0.383440284</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>2.441326721</td>
<td>2.534579151</td>
<td>2.507170976</td>
</tr>
</tbody>
</table>
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

**Figure 4.16:** SDT using Ramadass Method-$\tilde{k}_{\text{sei}}$ at 25°C for SDT#3

**SDT #3 at 50°C**

**Table 4.18:** Identified SEI parameters for at 50°C

<table>
<thead>
<tr>
<th></th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{k}_{\text{sei}}$</td>
<td>1.06434E-06</td>
<td>1.08811E-06</td>
<td>1.10615E-06</td>
</tr>
<tr>
<td>$\theta^n_0$</td>
<td>0.001</td>
<td>0.160253652</td>
<td>0.002003052</td>
</tr>
<tr>
<td>$\theta^n_{100}$</td>
<td>0.8</td>
<td>0.800096266</td>
<td>0.925042519</td>
</tr>
<tr>
<td>$\theta^p_0$</td>
<td>0.910593316</td>
<td>0.576137306</td>
<td>0.936729001</td>
</tr>
<tr>
<td>$\theta^p_{100}$</td>
<td>0.509792436</td>
<td>0.453521207</td>
<td>0.7</td>
</tr>
<tr>
<td>$z_0$</td>
<td>0.989602612</td>
<td>0.993992217</td>
<td>0.995638091</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>2.802692263</td>
<td>2.818132222</td>
<td>3.076708617</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>6.77833127</td>
<td>6.873246092</td>
<td>7.101960727</td>
</tr>
</tbody>
</table>

**Figure 4.17:** SDT using Ramadass Method-$\tilde{k}_{\text{sei}}$ at 50°C for SDT#3

Figure 4.15 showed good fidelity between the data and model, but Figures 4.16, and 4.17 demonstrated that the simulation and experiment data did not have great fidelity. Tables 4.16, 4.17, and 4.18 all the data in this experiment expose interesting inconsistencies within the results much like results from SDT#1 and SDT#2.
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

Overall, there was good congruency among $k_{sei}$ and $z_0$, but inconsistencies for $\theta^n_0$, $\theta^n_{100}$, $\theta^p_0$, and $\theta^p_{100}$. Presently, it is not certain what may be the main cause of the problem; the strategy used to optimize or the model used. What is known is that there is room for improvement in both the optimization and the model especially in case of $50^\circ C$. There may be dynamics at $50^\circ C$ that are not being accounted for in the current model. For instance, the cells from the $50^\circ C$ group swelled up during SDT#1, which was not expected.

4.4.1 Effects of Degradation

Reference performance tests were conducted before, after, and intermittently during each subsequent SDT to determine state of health of the cells under testing. While every effort was made to reduce the effects of degradation on the cells, by the end of all experiments, all cells had degraded in some way.

![Figure 4.18: Capacity Post SDTs](image)

Figure 4.18 shows the visual comparison of all nine Panasonic cells OCV Test after all three SDT tests. Table 4.19 shows the capacity estimations of each cell. The highest capacity was of FP09 at 24.85 Ah and the lowest capacity was of FP10 at 24.73 Ah; each cell estimated capacity measurement was within 0.1217 Ah of each other. Table 4.20 shows the total capacity loss after all three SDT tests and all RPTs had been performed for the nine Panasonic cells. The $0^\circ C$ group containing cells FP07 - FP09 experienced the smallest capacity loss while the the $50^\circ C$ group containing cells FP10 - FP12 experience the greatest capacity loss. The $0^\circ C$ group experienced an average capacity loss of 0.40Ah, the $25^\circ C$
4.4. Self-Discharge Tests (SDTs) with ARBINs Results and Discussion

group experienced an average capacity loss of 0.5642Ah, and the 50°C group experienced an average capacity loss of 1.97 Ah. An explanation for this is that cell dynamics are slowed when a cell is soaked at cold temperatures while electrochemical reactions are exacerbated at hot temperatures. Though it is not surprising that degradation was present in all cell groups because the cells were stored at 100% SOC, which are known to degrade cells [4].

<table>
<thead>
<tr>
<th>Table 4.19: Capacity Measurements Post all SDTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Row</td>
</tr>
<tr>
<td>---</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4.20: Capacity Lost Post all SDTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>cell #</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Q</td>
</tr>
</tbody>
</table>

Figure 4.19 shows the initial resistance measurements for the charge and discharge pulse. Table 4.21 and Table 4.22 shows the resistance values from the charge pulse and discharge pulse at 20% SOC, 40% SOC, 60% SOC, and 80% SOC for all cells, respectively. Figure 4.19 shows that the 50°C test group have deviated more from their previous measurements when compared to Figures 4.3, 4.9, and 4.14, which shows that all resistances are similar for all cells for Pulse Test 1 and 2, respectively. Cell FP09 has deviated from the other cells in due to oxidation on the positive terminal. FP10 has also started to deviate after abnormal charging happened during CSL2. The pulse test analysis indicated that the
highest resistance is produced at 20% SOC while the lowest resistance typically happened at 80% SOC.

**Table 4.21:** Results from Charge Pulse 4

<table>
<thead>
<tr>
<th>Row</th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC20</td>
<td>1.492</td>
<td>1.410</td>
<td>2.068</td>
<td>3.932</td>
<td>2.248</td>
<td>2.150</td>
<td>1.447</td>
<td>1.461</td>
<td>1.456</td>
</tr>
<tr>
<td>SOC40</td>
<td>1.444</td>
<td>1.369</td>
<td>2.004</td>
<td>3.789</td>
<td>2.015</td>
<td>1.910</td>
<td>1.385</td>
<td>1.382</td>
<td>1.410</td>
</tr>
<tr>
<td>SOC60</td>
<td>1.418</td>
<td>1.378</td>
<td>1.959</td>
<td>3.691</td>
<td>1.997</td>
<td>1.847</td>
<td>1.334</td>
<td>1.366</td>
<td>1.385</td>
</tr>
<tr>
<td>SOC80</td>
<td>1.395</td>
<td>1.309</td>
<td>1.963</td>
<td>3.618</td>
<td>1.905</td>
<td>1.769</td>
<td>1.330</td>
<td>1.330</td>
<td>1.354</td>
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</table>

**Table 4.22:** Results from Discharge Pulse 4

<table>
<thead>
<tr>
<th>Row</th>
<th>FP07</th>
<th>FP08</th>
<th>FP09</th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC20</td>
<td>1.488</td>
<td>1.425</td>
<td>2.054</td>
<td>3.796</td>
<td>2.080</td>
<td>1.891</td>
<td>1.463</td>
<td>1.438</td>
<td>1.462</td>
</tr>
<tr>
<td>SOC40</td>
<td>1.403</td>
<td>1.371</td>
<td>1.992</td>
<td>3.687</td>
<td>2.001</td>
<td>1.879</td>
<td>1.395</td>
<td>1.409</td>
<td>1.397</td>
</tr>
<tr>
<td>SOC60</td>
<td>1.395</td>
<td>1.322</td>
<td>1.930</td>
<td>3.628</td>
<td>1.945</td>
<td>1.842</td>
<td>1.309</td>
<td>1.366</td>
<td>1.348</td>
</tr>
<tr>
<td>SOC80</td>
<td>1.332</td>
<td>1.2956</td>
<td>1.905</td>
<td>3.578</td>
<td>1.905</td>
<td>1.800</td>
<td>1.323</td>
<td>1.294</td>
<td>1.338</td>
</tr>
</tbody>
</table>

The pulse test analysis indicated that the highest resistance is produced at 20% SOC while the lowest resistance typically happened at 80% SOC. The trend remains: The resistance is similar for test articles that were held at 0 °C or 25 °C, yet the test articles at 50 °C developed the highest resistance. FP09, which was a cell part of the 0 °C test group, had a higher resistance than the other cells because the terminal came in contact with water and became rusted.

### 4.4.2 Errors

The CSZ ZP-8 thermal chambers that were originally going to store the 0 °C and 50 °C cells had capacitor issues, which stopped the fan and froze the cells. Thankfully, the cells were not performing tests and no degradation is believed to have affected the cells. The Cincinnati MCB-1.2-.33-.33-H/AC had trouble holding temperatures. The thermal chamber oscillated within ±2 degrees from the set point periodically within the test. This also is not believed to influence the results of the SDTs or RPTs.
4.5 Leakage Current Tests with GAMRY's Results and Discussion

While the estimated side reaction constant from the voltage experiments were acceptable, there is another method that is faster than measuring voltage. There is no need to perform a long term self-discharge test. The second method was inspired by Tuveri [18] whose work was presented in chapter 3. This test can measure leakage current, which correlates to the side-reaction rate, and the task can observe its effort quicker compared to the self discharge test.

4.5.1 Experimental set-up

The leakage current test was performed on a Gamry Instruments Potentiostat Reference 3000. A cell completely at rest was connected to the potentiostat and allowed to undergo the leakage current test designed by Gamry Instruments. The test is an explain script that produces a dialog box when run as seen in Fig. 4.20. The min ESR value of 0 is a placeholder. An Electrochemical Impedance Spectroscopy (EIS) test was performed in order to extract the ESR term needed for better reliability in the leakage current test. The leakage current test was performed over the course of three days. The potentiostat measured current and voltage every second; however, only one measurement per hour was used for the optimization. The leakage current test was conducted after the SDTs.

Figure 4.20: Gamry leakage current Tests Experiment Setup
4.5. Leakage Current Tests with GAMRYs Results and Discussion

leakage current at 0°C

Figure 4.21 and Table 4.23 display the results of the leakage current test for 0°C. The table only showed results for FP07-08 because FP09 suffered a rusted terminal and was unfit to proceed with the leakage current test.

Table 4.23: Identified SEI parameters for at 0°C

<table>
<thead>
<tr>
<th></th>
<th>FP07</th>
<th>FP08</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\vec{k}_{{\text{sei}}}$</td>
<td>5.35862E-07</td>
<td>4.33584E-08</td>
</tr>
<tr>
<td>$\theta^n_0$</td>
<td>0.054319818</td>
<td>0.147161696</td>
</tr>
<tr>
<td>$\theta^n_{100}$</td>
<td>0.94856105</td>
<td>0.907473655</td>
</tr>
<tr>
<td>$\theta^p_0$</td>
<td>0.827667545</td>
<td>0.779619179</td>
</tr>
<tr>
<td>$\theta^p_{100}$</td>
<td>0.626840831</td>
<td>0.621209306</td>
</tr>
<tr>
<td>$z_0$</td>
<td>0.99022332</td>
<td>1.017025131</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.023061072</td>
<td>0.000841631</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>0.562054355</td>
<td>0.107374087</td>
</tr>
</tbody>
</table>

Figure 4.21: SDT using Ramadass Method-$\vec{k}_{{\text{sei}}}$ at 0°C for SDT#3

leakage current at 25°C

Figure 4.22 and Table 4.24 display the results of the leakage current test for 25°C.
4.5. Leakage Current Tests with GAMRY’s Results and Discussion

Table 4.24: Identified SEI parameters for at 25°C

<table>
<thead>
<tr>
<th></th>
<th>FP13</th>
<th>FP14</th>
<th>FP15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{k}_{sei}$</td>
<td>1.60257E-06</td>
<td>2.64881E-06</td>
<td>1.59121E-06</td>
</tr>
<tr>
<td>$\theta_n^0$</td>
<td>0.183595898</td>
<td>0.108518137</td>
<td>0.009572201</td>
</tr>
<tr>
<td>$\theta_n^{100}$</td>
<td>0.946988885</td>
<td>0.842078981</td>
<td>0.835248633</td>
</tr>
<tr>
<td>$\theta_p^0$</td>
<td>0.717558694</td>
<td>0.828692852</td>
<td>0.94415514</td>
</tr>
<tr>
<td>$\theta_p^{100}$</td>
<td>0.448401203</td>
<td>0.545157409</td>
<td>0.490456751</td>
</tr>
<tr>
<td>$z_0$</td>
<td>1.018508282</td>
<td>1.014102185</td>
<td>1.018817503</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.006083797</td>
<td>0.025977383</td>
<td>0.005114414</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>0.288686131</td>
<td>0.596535468</td>
<td>0.264689385</td>
</tr>
</tbody>
</table>

Figure 4.22: SDT using Ramadass Method-$\bar{k}_{sei}$ at 25°C for SDT#3

leakage current at 50°C

Figure 4.23 and Table 4.23 display the results of the leakage current test for 50°C.

Table 4.25: Identified SEI parameters for at 50°C

<table>
<thead>
<tr>
<th></th>
<th>FP10</th>
<th>FP11</th>
<th>FP12</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{k}_{sei}$</td>
<td>4.3191E-06</td>
<td>4.44488E-06</td>
<td>4.60042E-06</td>
</tr>
<tr>
<td>$\theta_n^0$</td>
<td>0.001</td>
<td>0.001</td>
<td>0.035364842</td>
</tr>
<tr>
<td>$\theta_n^{100}$</td>
<td>0.95</td>
<td>0.95</td>
<td>0.800976526</td>
</tr>
<tr>
<td>$\theta_p^0$</td>
<td>0.583001399</td>
<td>0.628257114</td>
<td>0.62781975</td>
</tr>
<tr>
<td>$\theta_p^{100}$</td>
<td>0.680805237</td>
<td>0.69326578</td>
<td>0.698357407</td>
</tr>
<tr>
<td>$z_0$</td>
<td>1.021928225</td>
<td>1.020611599</td>
<td>1.026358415</td>
</tr>
<tr>
<td>cost [mV]</td>
<td>0.014571527</td>
<td>0.027047421</td>
<td>0.036380835</td>
</tr>
<tr>
<td>rms error [mV]</td>
<td>0.446777309</td>
<td>0.608697474</td>
<td>0.705951555</td>
</tr>
</tbody>
</table>
4.6. Chapter Conclusion

Tables 4.23, 4.24, and 4.25 show that the results are comparable to the results gathered from the long term SDT for $\theta_0^0$, $\theta_{100}^0$, $\theta_0^p$, $\theta_{100}^p$, and $z_0$, but with a larger magnitudes for $\bar{k}_{sei}$. Figures 4.21, 4.22, and 4.23 demonstrated that the simulation and experiment data had great fidelity. The results of the SDT tests and the leakage current test are comparable for all test temperatures. One disadvantage of performing shorter time tests is that the measurements are more susceptible to measurement noise.

Although, $\bar{k}_{sei}$ and $z_0$ had great consistency within each respective test temperature group, the lack of consistency among the optimized results for $\theta_0^0$, $\theta_{100}^0$, $\theta_0^p$, and $\theta_{100}^p$ (in some cases even $\bar{k}_{sei}$) show that the optimizations are still not robust enough for the SDT and leakage current analysis. Thus, sensitivity studies of the parameters are needed because some parameters may not be sensitive to voltage dynamics. However, such studies are beyond the scope of this thesis, please refer to [34]. A possible improvement would be to identify some of the parameters optimized in this work with other tests.

Figure 4.23: SDT using Ramadass Method-$\bar{k}_{sei}$ at 50°C for SDT#3

This work presented a systematic method to estimate the $\bar{k}_{sei}$ and $z_0$ as well as the OCP absolute boundaries: $\theta_0^0$, $\theta_{100}^0$, $\theta_0^p$, and $\theta_{100}^p$. This chapter presented two different methods of analysis used to extract six parameters using voltage measurement or leakage current data. The Self Discharge Tests were conducted at 0°C, 25°C, 50°C for two months periods per subsequent test. SEI is a primary form of cell degradation that affects the internal behavior of a cell since the first cycling by the manufacturer. The experiment used to collect the data was developed in a way that isolated SEI formation. Here are the key findings:
4.6. Chapter Conclusion

1. The side reaction parameter estimations can be simplified by implementing a lumped–parameter Ramadass model to optimize for one constant, $\bar{k}_{\text{sei}}$:

2. Four more parameters were added, $\theta^n_{0}$, $\theta^n_{100}$, $\theta^p_{0}$, and $\theta^p_{100}$, to the optimization as consequence of current limitations of the available model;

3. The SOC, $z_0$, needs to be optimized to ensure correct initial conditions and correct simulated dynamics;

4. This strategy can be applied to all commercial cells without the need to tear-down the cell;

5. There may be many estimation values for that satisfy the optimization at $0\,^\circ\text{C}$ and $25\,^\circ\text{C}$;

6. The current model may not accurately account for cell dynamics present at $50\,^\circ\text{C}$;

7. No absolute OCP boundaries ($\theta^n_{0}$, $\theta^n_{100}$, $\theta^p_{0}$, and $\theta^p_{100}$) values were able to be optimized for all temperature data.
CHAPTER 5

Conclusion and Future Work

This document presented the importance of including degradation models in PBMs. These improvements aim at better battery management systems and extending the life of the batteries. They can be made by implementing more accurate degradation models in conjunction with ideal cell models to extend the life of a battery or battery pack. These models supply important information to control strategies such as the MPC algorithm in order to reduce the effects of degradation mechanisms.

Chapter 4 presented the findings of experimental degradation validation of an ideal SEI cell model of a Panasonic NMCs. Furthermore, this research presents the identified physical/electrochemical parameters derived from SDTs and leakage current tests. In addition, this document explains the experimental approach for degradation of model validation and the analysis of the results. While the first method, self discharge, presented was a long term degradation test, the second method, leakage current, using the potentiostat was non-destructive and time efficient. The work presented in this document can be applied to all commercial li-ion cells.

5.1 Improvements to Experimental Process

The RPTs were incorporated into the experimental design to track the performance of the cells’ state of health. Instead of performing a quick capacity test after each finished SDT, a more complete approach would be to perform a four step OCV test with rests. This was not done during the experiment due to time constraints; however, it would be a good way to accurately compare the capacity measurements conducted in the intermediary RPTs. In addition, it would have been helpful to charge cells using dithers after each SDT and RPT. In addition, an EIS test could be conducted, however, care must be taken to make sure that the
cables are static to minimize the cable inductance effort. Another important amendment to the test would be to attach thermal couples to the cells and compare the temperature measured by the thermo couples compared to the reference temperature measured by the thermal chamber. In addition the cells produced gas while in the 50°C test, and this is because the cells were not under compression; so, a better version of this test should allow cells to be under compression for tests at this temperature. This section described improvements may be applied to an experimental approach for SEI and state of health RPTs, and future work will be discussed in the next section.

5.2 Future Work

As mentioned in the introduction, this work is a milestone in an overall degradation model picture as seen in Figure 5.1. This thesis focuses on establishing an SEI component to the already existing ideal cell model and lithium plating model.

![Open loop degradation model (left) and Feedback loop “real” degradation model (right)](image)

**Figure 5.1:** Open loop degradation model (left) and Feedback loop “real” degradation model (right)

SEI is only one component of degradation. In future work, the overall model should contain SEI degradation coupled with other methods of degradation such as lithium plating described in Chapter 3. Methods for coupling lithium plating and SEI growth are presented in [22] and could be a way forward in creating a more realistic battery model. Peled in [13] mentioned that there was a phenomenon that appears in the positive electrode that behaves like SEI in the negative electrode. Several imaging techniques such as neutron diffraction and neutron reflectometry have been developed to observe SEI formation in vivo. This could be a way of validating or disproving some of the assumptions made in developing...
5.2. Future Work

the SEI model presented in this thesis. Additionally, $R_{\text{film}}$ can be measured directly by performing a post-mortem test and imaging the cross-section of the negative electrode to compare the results of a SEI aged cell and a new cell, a new cell which contains solely the initial SEI protective layer. Both of these suggested validation methods are beyond the scope of the resources available at UCCS. Future work will include incorporating better battery models to optimize for $\bar{k}_{\text{sei}}$ solely. There is still work to be done to obtain better estimations for the OCP boundaries applicable to all temperatures and to obtain a better estimations for data taken at 50°C.


APPENDIX A

Nomenclature

A.1 Primary Symbols

\( \alpha_s \) specific interfacial surface area \([m^2m^{-3}]\)

\( A \) current collector plane area \([m]\)

\( c \) concentration of lithium \([molm^{-3}]\)

\( c_{s,0} \) steady-state lithium concentration in the solid particle \([molm^{-3}]\)

\( c_{e,0} \) steady-state lithium concentration in the electrolyte \([molm^{-3}]\)

\( c_{s,e} \) surface concentration \([molm^{-3}]\)

\( D_e \) effective diffusivity in the electrolyte

\( D_s \) effective diffusivity in the solid lithium

\( F \) Faraday’s constant

\( j \) faradaic flux \([molm^{-2}s^{-1}]\)

\( k_{sei} \) lumped sei constant

\( L \) electrode region thickness

\( Q \) capacity \([mol]\)

\( r \) distance to partial center

\( R \) universal gas constant
### A.1. Primary Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
<td>solid particle average radius</td>
<td>[m]</td>
</tr>
<tr>
<td>$R_{film}$</td>
<td>surface film resistance of a particle</td>
<td>[$\Omega m^2$]</td>
</tr>
<tr>
<td>$\bar{R}_f$</td>
<td>lumped film resistance</td>
<td></td>
</tr>
<tr>
<td>$t^0_+$</td>
<td>charge transference number</td>
<td>[unitless]</td>
</tr>
<tr>
<td>$T$</td>
<td>cell environment temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$U$</td>
<td>Potential</td>
<td>[V]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>charge transfer coefficient</td>
<td>[unitless]</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>volume fraction of a porous medium</td>
<td></td>
</tr>
<tr>
<td>$\phi$</td>
<td>potential</td>
<td>[V]</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>lumped conductivity of the solid particle</td>
<td>[S]</td>
</tr>
<tr>
<td>$\bar{\kappa}$</td>
<td>lumped conductivity of the ionic in electrolyte</td>
<td>[S]</td>
</tr>
<tr>
<td>$\theta^n_0$</td>
<td>relative stoichiometric, lower bound negative electrode</td>
<td></td>
</tr>
<tr>
<td>$\theta^n_{100}$</td>
<td>relative stoichiometric, higher bound negative electrode</td>
<td></td>
</tr>
<tr>
<td>$\theta^p_0$</td>
<td>relative stoichiometric, lower bound positive electrode</td>
<td></td>
</tr>
<tr>
<td>$\theta^p_{100}$</td>
<td>relative stoichiometric, higher bound positive electrode</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>conductivity of the solid particle</td>
<td>[$Sm^{-1}$]</td>
</tr>
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<td>$\bar{\sigma}_e$</td>
<td>lumped conductivity of the solid particle</td>
<td>[S]</td>
</tr>
<tr>
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<td>lumped conductivity of the solid particle</td>
<td>[S]</td>
</tr>
<tr>
<td>$\bar{\Psi}$</td>
<td>lumped effective electrolyte diffusivity</td>
<td>[$molS^{-1}s^{-1}$]</td>
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<td>lumped stoichiometric electrolyte concentration ratio</td>
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<tr>
<td>$\theta_s$</td>
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A.2 Primary Subscripts and Superscripts

EC  ethylene carbonate
int intercalation
lpl lithium plating
n  negative electrode
p  positive electrode
ocp open circuit potential
sei solid electrolyte interphase
tot total