IDENTIFICATION OF LITHIUM-ION-CELL PHYSICS-MODEL PARAMETER VALUES

by

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ABSTRACT

Due to their computational simplicity and robustness, equivalent-circuit-type cell models are widely used as the basis for control algorithms in battery-management systems. These models execute quickly and have relatively few parameter values to optimize to make the model calculations fit laboratory test data. However, equivalent-circuit models lack the predictive capability of physics-based cell models. For example, while equivalent-circuit models can predict a cell’s current–voltage behaviors well, they cannot predict internal cell electrochemical variables such as lithium concentration or electric potential at different spatial locations internal to the cell. Knowledge of these internal variables is critical to being able to predict and control the instigators of premature aging or unsafe operating conditions. While physics-based models have much greater predictive capabilities, they also have many more parameter values that must be measured or inferred to make the model match the behaviors of a real cell. This “system identification” problem is significant, and in the past has relied on cell tear-down and complex and costly electrochemical experiments to determine the required parameter values. In this dissertation, I propose a methodology that minimizes the need for laborious cell tear-down and electrochemical experimentation. Instead, the model equations are reformulated, and specific cell-level laboratory tests are crafted such that the current–voltage response isolates certain sets of parameter values in the model. These tests are executed on standard cell cycling equipment. A simple and fast optimization procedure then computes the physics-based model parameter values directly from the specialized lab-test data. We present results based on a virtual (simulated) cell, where “truth” values for the electrochemical parameters are known for comparison.
purposes. The virtual cell’s coupled partial-differential equation model is simulated using COMSOL and the same designed experiments as would be used in a laboratory. The current–voltage data from the simulation are used to identify the cell’s parameter values; these identified values are then compared to known “truth” values. In most cases, the identified parameters have error less than 1% when compared to the truth values. We then demonstrate the methods on a physical cell.
DEDICATION

To my wonderful family, Tracy, Elsie, and Amelia. Thanks for being patient with me!
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Lithium-ion batteries have become a very important part of today’s life; they power everything from personal electronics to cars and homes. Lithium-ion technology exhibits certain benefits over other battery-cell technologies such as high energy density and high specific energy as shown in Fig. 1.1. Lithium-ion batteries also exhibit long shelf life with very little self discharge. This low self discharge allows for integration into sensitive electronics with prolonged power-down states. The high open-circuit potential of lithium-ion batteries can deliver high power at low currents that many industrial and automotive markets demand [2]. All of these benefits make lithium-ion technology desirable by many different applications.

The need to further the usability of lithium-ion batteries to other markets requires that lithium-ion technology be pushed to its performance limits while still maintaining acceptable battery-pack longevity. In order to improve the life and performance of these batteries it is necessary to gain insight into the internal dynamics of the battery cell during

**Figure 1.1:** Energy density comparisons of different battery cell technologies.
1.1. Cell background

Present methods of controlling a battery cell are based mainly upon voltage limits. Cell manufacturers set high and low voltage limits that should not be violated during the operation of the battery cell. Due to internal resistances however, this will limit the power available to the system during operation at certain states of charge (SOC) [3]. Many cell degradation models [4–8] have shown that these limits might be artificial and true limits should instead be set on the internal parameters of the cell and not specifically on cell voltage. For this to be possible, an electrochemical model of cells is required. We further need to know all parameter values for these models. Finding these parameter values is the topic of this dissertation.

The goal of a battery cell is to provide electrical energy/power by utilizing a chemical process to free up contained chemical energy. As the cell is discharged the internal chemistry is changed to lower its overall energy state. Some batteries have chemistries that will allow this process to occur in only one direction, meaning that they cannot be recharged, and are referred to as “primary cells.” Other chemistries allow this process to happen in reverse allowing an external power source to store electrical energy, recharging the cell; these are referred to as “secondary cells.” This dissertation will focus on lithium-ion cells, which fall into the secondary-cell category.

A simple cell comprises three sections, a positive electrode, a separator, and a negative electrode. Each electrode contains a solid material and an electrolyte in either a solid or liquid form. The separator ensures that the two electrodes do not internally touch and short the cell. During the operation of a battery, electrical potential energy is stored in the two electrodes of the battery. In the case of a lithium-ion battery, the energy is stored by lithium atoms inside the solid active material. The potential of each electrode corresponds to how many lithium atoms are contained in the solid material. Since each electrode is made of different materials, the potential of each is different and allows the charge to move once
1.2. Battery-cell modeling

the electrodes are connected via an external circuit. During the operation of a battery, the lithium atoms lose an electron as they cross from the solid material to the electrolyte. The electrolyte is unable to accept the electron and the electrolyte will carry only the new lithium-ion. The lithium-ion moves across the separator region to the other electrode. Once at the opposite electrode, the lithium-ion meets an electron and through a chemical reaction is stored once again.

There are two important factors to consider in the state of a battery cell: state of charge (SOC), and state of health (SOH). SOC denotes how “full” a battery cell is, and is related to the capacity, \( Q \), or maximum amount of charge that can be stored in the battery cell. SOC is computed as the ratio of how much charge is left in the battery cell to the total capacity. On the other hand, SOH is the overall health of a battery cell. During the utilization of storing and releasing energy of the battery cell, certain unwanted side reaction can degrade the battery cell over time. This loss of performance is described by the cells SOH.

1.2 Battery-cell modeling

Battery-cell modeling describes how different battery-cell variables respond to an input stimulus through a set mathematical equations. Typically this is done in one of two ways: an equivalent-circuit model (ECM), or a physics-based model (PBM). With an ECM, an equivalent circuit matches the input and output relationship though a network of resistors and capacitors together with a voltage source as shown in Fig. 1.2. The resistors attempt to match certain internal resistances of a battery cell while the capacitors simulate the diffusion process. By expanding the number of resistors and capacitors, a model may be found that closely matches the input–output relationship of a battery cell. While finding an acceptable ECM model can help develop insight into the state of charge and available power/energy, it provides no insight into the internal processes of the battery cell.
1.3 Previous system identification work

There have been significant attempts made to identify equivalent-circuit and physics-based models and their respective model parameter values for various battery cells. Seaman [9] outlines different methods used to model a lithium-ion cell and compares the mathematics between the ECM and the PBM. The majority of system identification work is done by fitting real battery cell voltage-versus-current responses to an ECM model response. Attempts to perform system identification using physics-based models have been accomplished but can often run very slowly and place high computational demand on a system. Some of these system-identification methods involve destructive methods to physically tear apart cells to measure lengths and thicknesses of various internal dimensions.

Let’s first look at system identification done with ECMs. Yann [10] used EIS data over a variety of SOCs along with constant-current discharge profiles to find an ECM. Hu et al. [11] performed a system identification of a nickel-metal-hydride (NiMH) battery cell using charge and discharge tests over a range of SOCs. Hu managed to use his measured time-domain data to fit the RC values of an ECM to match voltages. These ECM models along with various filtering techniques, such as Plett’s Kalman filtering method [12], can provide a very good means to control a battery cell based on power and energy limits, but again this approach provides no method for controlling internal degradation states of the battery cell.

Forman [13] used a genetic algorithm on a Doyle–Fuller–Newman physics-based model to optimize a set of 88 parameters. In this paper, the author ran a set of tests and matched voltage time-domain responses of an actual lithium iron phosphate (LFP) cell to
1.3. Previous system identification work

A simulated physics-based model using a PDE solver. This method was very time consuming, taking up to 63 seconds to run each new set of parameter values to get “fitness” values based on voltage error. The overall identification process took three weeks on a parallel computing cluster. Safari [14] on the other hand used a reduced three-parameter, fourth-order polynomial proposed by Subramanian [15] to model the lithium concentrations inside the particles of the cathode and anode. Safari physically measured certain parameters and fitted the rest of the parameter values based on experimental data.

Many attempts to model the internal behavior of a battery cell have resulted in very complicated nonlinear partial-differential equations containing multiple independent variables. The Doyle–Fuller–Newman [16] pseudo-2d full order model (FOM) describes internal cell potentials and concentrations along with lithium flux. To simplify the system identification process, we make use of the work by Lee and colleagues [17, 18] who produced a reduced-order model (ROM) from the FOM equations in the form of transfer functions for each parameter of interest. These models have multiple independent variables, and must be determined for a specific cell before those equations can produce a model and thus provide any clarity into the cell’s dynamics. With manufacturing companies unwilling to give these parameter values, it is necessary to determine these parameters using different voltage and current tests on the batteries.

Further, the Doyle–Fuller–Newman model was developed to model constant-current events. To describe high frequency transients, a double-layer model was proposed by Ong and Newman [19] who suggested an additional lithium-flux term from the solid particle to the electrolyte. Other models for the additional lithium-flux term are proposed by Dees et al. [20] and Shaju et al. [21] and include various paths and boundaries for the double-layer capacitance. We incorporate these transient models to explain the data collected by laboratory tests.
1.4. Original work

Finally, to add temperature-dependent parameter values, the paper by Gu and Wang [22], suggests that the conductivity of the electrolyte has an Arrhenius-equation dependence on temperature. The paper also suggests that the diffusion coefficients and the reaction rate constant in the Butler–Volmer equation has some temperature dependence as well. Some additional temperature terms were proposed by Ecker et al. [23] and are included in the temperature-dependent models. We adopt these equations into the model to help find parameters once a satisfactory set of data is collected at various temperatures.

1.4 Original work

Identifying all independent parameter values of a physics-based battery-cell model is a challenging task as they are collectively embedded in a set of nonlinear coupled partial-differential equations. Further, common PBM s are over parameterized, so this problem will also involve lumping parameters together to arrive at a minimum set of independent constants that must be identified. From analysis of the reduced model, this dissertation proposes a series of tests to identify all lumped parameters from voltage and current measurements. These tests include a pulse test at various SOCs and current-pulse amplitudes, a small-signal frequency-response analysis, and a steady-state discharge/charge test. Using all of the impedance data gathered from these tests, a set of lumped parameters is produced to closely match the behavior of the cell under test.

The identification method proposed in this dissertation takes the approach of using existing linearization methods with these PDEs to form transcendental transfer functions. Then, parameter values are optimized to match certain frequency characteristics of a battery cell. The method is first applied to find the parameter values of a simulated, or virtual cell where true values of all parameters are known for comparison. It is later applied to a physical cell. Since there is no truth data for this cell, a dynamic time-domain signal is used to simulate the cell with the identified parameter values and compare it to the dynamic data run in the laboratory on the real cell.
1.4. Original work

**Chapter 2:** This chapter reformulates all PDEs to use a minimum set of independent parameters. From these reformulated PDEs, a new set of linearized transfer functions is created that can be combined with nonlinear corrections to model cell behavior. To help speed up the optimization process, some numerical processes needed to be improved for efficiency. For this reason, a new linearization method is developed for finding the transfer function for lithium concentration in the electrolyte.

**Chapter 3:** This chapter focuses on identifying parameter values from simulated frequency responses of a virtual battery cell. It proposes a set of tests to run on the virtual cell in order to isolate certain parameters and ultimately find their values. All parameter values are identified and compared to the original set of values that generated the data.

**Chapter 4:** In chapter 4 modifications are made to the model and the identification process in the quest for identifying models of actual cells. These enhancements are made to the Doyle model to include the dynamics seen by laboratory data. They include a double-layer capacitance between the solid particles and the electrolyte, an Arrhenius temperature model on certain parameters, and an SOC-dependent term on the solid diffusivity parameter. These enhancements are added to the Doyle cell model and simulated to ensure all parameters are still identifiable.

**Chapter 5:** This chapter will discuss applying these methods to a real laboratory cell. Data from a Panasonic PHEV cell are used to identify a model and results are presented. Specialized procedures for testing a cell in the lab are developed with some raw results presented. For certain tests calibration of the test equipment is necessary to ensure accurate parameter values, especially at high frequencies. A new method for determining the OCV for a cell is explored; it turns out this is very important for simulating a cell once all values are found. The data processing for a lab cell is undoubtedly quite different from that for the virtual cell.
1.4. Original work

Chapter 6: This chapter focuses on simulating a real cell’s voltage versus current relationship and comparing it to actual data. To accomplish this, the new model needs to compute the new feed-through and DC gain terms. The blending of the simulation across SOCs is improved by changing from a model blending technique to an output blending scheme. Since the cell produces experimental measurements rather than equation values, a need arises to interpolate OCV tables with SOC and temperature. Finally, the ROM is matched to the original equations to ensure fidelity in the new reduced model.
2.1 Introduction

Before we can discuss identification of model parameters, we must first review the physics-based models used to describe cell dynamics, and then show how to reformulate those models in a form more convenient for parameter identification. This process starts with the fundamental set of coupled nonlinear partial-differential equations developed by Doyle, Fuller, and Newman [16]. These equations describe the concentrations of lithium inside the electrode active-material particles and the electrolyte, the potentials in the solid and electrolyte phases, as well as the flux of lithium between phases [24]. To help simplify these equations to include a minimum number of independent parameters, some of the original parameters are grouped into a smaller set of “lumped” independent parameters and each equation is reformulated. After simplifying the governing partial-differential equations, each equation is linearized using the process described by Smith [25] and expanded by Lee [26]. The transfer functions found from this linearization use the same lumped-parameter set as is used by the full set of nonlinear partial-differential equations. The equation definitions throughout this dissertation will use a generic superscript, “reg” as a placeholder for a region in the cell. The superscript “pos” will refer to the positive electrode, “neg” will refer to the negative electrode, and “sep” refers to the separator.
2.2 Doyle–Fuller–Newman pesudo-2d full-order model

The Doyle–Fuller–Newman continuum-scale model can be derived by starting with a micro-scale model of a lithium-ion cell and using volume-averaging techniques to simplify the equations. The model is most often applied by assuming uniformity across the cell which simplifies the spatial domain to two main dimensions. The first dimension spans the length of the cell. This includes the negative electrode (anode), the separator, and the positive electrode (cathode). This dimension is used to find lithium concentrations and potentials as they vary across the length of the cell. The second dimension is across a spherical radius of a solid particle in either the negative or positive electrode. Every particle in an electrode is assumed to be identical in spherical geometry thus having the same radius. These two dimensions are shown in Fig. 2.1.

There are four main partial-differential equations and one algebraic equation that together model the dynamics of a battery cell. These equations describe the concentration of lithium in the solid particles, the concentration of lithium in the electrolyte, the potential of the solid particles, the potential of the electrolyte, and the flux of lithium out of a particle. The following sections will review the Doyle–Fuller–Newman model and investigate the minimum number of parameters needed to fully describe each equation. This simplification is used in Section 2.2 to find linear approximations and will ultimately be used in the system-identification process.
2.2. Doyle–Fuller–Newman pseudo-2d full-order model

2.2.1 Concentration of lithium in the solid particles

In order to track the concentration of lithium in the solid particles across its radial dimension the first partial-differential equation is defined as,

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

where $c_s(r, x, t)$ is the concentration of lithium at $r$ distance from a particle center, $x$ distance from the current collector, and at time $t$. $D_s$ is the diffusion constant of the electrode and $R_s$ is the full radius of the spherical particle. This equation has boundary conditions that state that lithium cannot move through the center of the particle and that the driving function for concentration change is the flux at the surface of the particle. These boundary conditions are set by:

$$D_s \frac{\partial c_s(0, x, t)}{\partial r} = 0, \quad \text{and} \quad D_s \frac{\partial c_s(R_s, x, t)}{\partial r} = -j(x, t), \quad t \geq 0. \quad (2.1)$$

The first step in reducing the parameters of this partial-differential equation is to lump the diffusion constant and the radius of the particle together. The concentration is normalized over the particle radius by defining $\bar{r} = r/R_s$ where $0 \leq \bar{r} \leq 1$ and $\partial \bar{r}/\partial r = 1/R_s$. After normalizing the particle radius now both the positive electrode and the negative electrode will have the same dimensions.

$$\frac{\partial c_s(\bar{r}, x, t)}{\partial t} = \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left( \frac{D_s}{R_s^2} \frac{\partial c_s(\bar{r}, x, t)}{\partial \bar{r}} \right). \quad (2.2)$$

For this section, the superscripts denoting the region specified are left out for simplicity. Note that these equations are valid only for the region they are defined in. The first lumped parameter is defined as $D_{s,\text{tot}} = \left( \frac{D_s}{R_s^2} \right)$. Both sides of the equation are then multiplied by $\varepsilon_s^\text{reg} AL^\text{reg}$ to get the normalized total number of moles in the electrode, leading to the definition of the first lumped variable, $n_s^\text{reg} = c_s^\text{reg} \varepsilon_s^\text{reg} AL^\text{reg}$:

$$\frac{\partial n_s(\bar{r}, x, t)}{\partial t} = \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left( D_{s,\text{tot}} \bar{r}^2 \frac{\partial n_s(\bar{r}, x, t)}{\partial \bar{r}} \right). \quad (2.3)$$
2.2. Doyle–Fuller–Newman pseudo-2d full-order model

Now that the PDE is redefined using new lumped parameters, the boundary conditions must be changed as well. While working on the boundary conditions to fit the new parameters, the same substitutions are made as in the derivation of the PDE itself. These substitutions allow for the first boundary condition equation from Eq. (2.1) to transform to:

\[ D_{s,\text{tot}} \frac{\partial n_s(0, x, t)}{\partial r} = 0. \]  

(2.4)

The second boundary condition equation in Eq. (2.1) is transformed by making the same substitution, becoming:

\[ \frac{D_s}{R_s} \frac{\partial n_s(1, x, t)}{\partial r} = -j(x, t) \varepsilon_s AL. \]

Recognizing that this equation still has some of the non-lumped parameters, some further simplifications must be derived. To help this simplification, we recognize that the volume fraction of solid material can be written as \( \varepsilon_s = a_s R_s / 3 \). Now, instead of defining the flux in units of moles per unit area per second, a new total flux is defined as \( j_{\text{tot}}(x, t) = j(x, t) a_s AL \) in moles per second. These two substitutions allow the final boundary condition equation to be written as:

\[ D_{s,\text{tot}} \frac{\partial n_s(1, x, t)}{\partial r} = -\frac{j_{\text{tot}}(x, t)}{3}. \]

(2.5)

This new form of the PDE that governs the dynamics is identical to Eq. (2.2). The dynamics are the same with only a change in units of the functions. The rest of this section will redefine the PDEs of the remaining model equations using similar substitutions so all governing equations can work together to define the battery-cell dynamics.

2.2.2 Concentration of lithium inside the electrolyte

We now turn our attention to the equation that describes the dynamics of the concentration of lithium, \( c_e \), inside the electrolyte. This process is modeled by the diffusion equation shown in Eq. (2.6), where \( \varepsilon_e \) is the partial volume fraction of electrolyte in the electrode, \( D_{e,\text{eff}} \) is the effective diffusion coefficient of the electrolyte, \( t_0^+ \) is the charge transference number, and \( a_s \) is the volume fraction of the electrode. This PDE contains old non-lumped
2.2. Doyle–Fuller–Newman pesudo-2d full-order model

parameters and variables and needs to be transformed to work with the previous PDE that
governs the concentration of lithium inside the solid material.

\[
\frac{\partial(\varepsilon_e c_e(x, t))}{\partial t} = \frac{\partial}{\partial x} \left( D_{e,\text{eff}} \frac{\partial c_e(x, t)}{\partial x} \right) + (1 - \theta_0^\circ) a_s j(x, t).
\]

(2.6)

Again, just like the first PDE, the first step in reducing the parameters is to normalize the
electrode lengths to a length of one by defining a new dimensionless spatial variable \( \bar{x} \).
This is done by dividing each of the sections by their actual respective lengths. Different
than in the first section, the length is defined by the normalized distance away from the
negative current collector. This means the separator will start at a normalized distance of 1,
the positive electrode will start at a distance of 2 (and so forth)

\[
\bar{x} = \begin{cases} 
\frac{x}{L_{\text{neg}}}, & 0 \leq x < L_{\text{neg}} \\
1 + \frac{x - L_{\text{neg}}}{L_{\text{sep}}}, & L_{\text{neg}} \leq x < L_{\text{neg}} + L_{\text{sep}} \\
2 + \frac{x - L_{\text{neg}} - L_{\text{sep}}}{L_{\text{pos}}}, & L_{\text{neg}} + L_{\text{sep}} \leq x \leq L_{\text{neg}} + L_{\text{sep}} + L_{\text{pos}}.
\end{cases}
\]

Since the original differential equation for the concentration of lithium in the electrolyte,
Eq. (2.6), uses a derivative with respect to the original length, the derivative of the new
length with respect to the old length is determined by:

\[
\frac{\partial \bar{x}}{\partial x} = \begin{cases} 
\frac{1}{L_{\text{neg}}}, & 0 \leq x < L_{\text{neg}} \\
\frac{1}{L_{\text{sep}}}, & L_{\text{neg}} \leq x < L_{\text{neg}} + L_{\text{sep}} \\
\frac{1}{L_{\text{pos}}}, & L + L_{\text{sep}} \leq x \leq L_{\text{neg}} + L_{\text{sep}} + L_{\text{pos}}.
\end{cases}
\]

Using this new derivative, the old derivative can be replaced using the chain rule substitu-
tion \( \frac{\partial}{\partial x} = \frac{\partial}{\partial \bar{x}} \frac{\partial \bar{x}}{\partial x} \). This causes the derivative in the PDE to be taken with respect to the
new normalized length \( \bar{x} \). By defining a new function of concentration that divides the
lithium concentration by the constant resting concentration,

\[
c_{e,\text{ratio}} = c_e / c_{e,0} = \left( c_{e}^{\text{reg}} A L^{\text{reg}} \right) / \left( c_{e,0}^{\text{reg}} A L^{\text{reg}} \right) = n^{\text{reg}} / n_{e,0}^{\text{reg}} = n_{e,\text{ratio}},
\]

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2.2. Doyle–Fuller–Newman pesudo-2d full-order model


\[
\frac{c_{e,0} \varepsilon_e}{1 - t_0^0} \frac{\partial (n_{e,\text{ratio}}(\bar{x}, t))}{\partial t} = \frac{1}{L^\text{reg}} \frac{\partial}{\partial \bar{x}} \left( \frac{D_{e,\text{eff}} c_{e,0} A}{L^\text{reg}} \frac{\partial}{\partial \bar{x}} n_{e,\text{ratio}}(\bar{x}, t) \right) + \left(1 - t_0^0\right) a_s j(x, t).
\]

The PDE still has many parameters that can be lumped together. By multiplying both sides of the equation by \( AL^\text{reg} / (1 - t_0^0) \), and remembering that \( j_{\text{tot}}(\bar{x}, t) = j(x, t) a_s AL^\text{reg} \), the PDE is transformed to:

\[
\frac{c_{e,0} \varepsilon_e AL^\text{reg}}{(1 - t_0^0)} \frac{\partial (n_{e,\text{ratio}}(x, t))}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( \frac{D_{e,\text{eff}} c_{e,0} A}{L^\text{reg} (1 - t_0^0)} \frac{\partial}{\partial \bar{x}} n_{e,\text{ratio}}(x, t) \right) + j_{\text{tot}}(x, t).
\]

Looking at the equation, there are still several constant terms that can be lumped together. Two new lumped-parameter values are defined to simplify this equation further:

\[
\begin{align*}
n_{e,0}^\text{reg} &= c_{e,0} \varepsilon_e AL^\text{reg} \\
D_{e,\text{tot}}^\text{reg} &= \frac{D_{e,\text{eff}} c_{e,0} A}{L^\text{reg}}.
\end{align*}
\]

The final form of the equation has the same definition of \( j_{\text{tot}}(\bar{x}, t) \) as in the concentration of lithium in the solid and has normalized lengths. The final equation for the lithium concentration in the electrolyte becomes:

\[
\frac{n_{e,0}^\text{reg}}{(1 - t_0^0)} \frac{\partial (n_{e,\text{ratio}}(\bar{x}, t))}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( \frac{D_{e,\text{tot}}^\text{reg}}{(1 - t_0^0)} \frac{\partial}{\partial \bar{x}} n_{e,\text{ratio}}(\bar{x}, t) \right) + j_{\text{tot}}(\bar{x}, t).
\] (2.7)

The boundary equations for this PDE hold the change of concentration with respect to the length to zero at each current collector (or end of the electrode). This is unchanged with the new partial-differential equation except that the length of the electrodes and separator are now normalized. The new boundary equations are now defined as:

\[
\begin{align*}
\frac{\partial n_{e,\text{ratio}}(0, t)}{\partial \bar{x}} &= \frac{\partial n_{e,\text{ratio}}(3, t)}{\partial \bar{x}} = 0.
\end{align*}
\]

### 2.2.3 Potential of the solid particles

Now that the concentration PDEs are transformed, work needs to be done on the potential equations. We look first at the potential of the solid particles at different locations throughout the cell. The potential of the particles is driven by the amount of lithium contained
in the solid particles. The original Newman PDE that models the potential of the solid particles across each electrode is given by:

\[
\frac{\partial}{\partial x} \left( \sigma_{\text{eff}} \frac{\partial}{\partial x} \phi_s(x, t) \right) - a_s F j(x, t) = 0.
\] (2.8)

The first step to transforming this equation is to normalize the electrode length by again using \( \bar{x} \). In order to lump more parameters together, both sides of the equation are multiplied by \( AL^{\text{reg}} \).

\[
\frac{\partial}{\partial \bar{x}} \left( A\sigma_{\text{eff}}^{\text{reg}} \frac{\partial}{\partial \bar{x}} \phi_s^{\text{reg}}(\bar{x}, t) \right) - a_s^{\text{reg}} A L^{\text{reg}} F j^{\text{reg}}(\bar{x}, t) = 0
\]

To help collapse the equation, a new lumped parameter for the conductance of the solid \( \sigma_{\text{tot}}^{\text{reg}} \) is defined by Eq. (2.9). When the now familiar substitution \( j_{\text{tot}}^{\text{reg}}(\bar{x}, t) = j^{\text{reg}}(x, t) a_s^{\text{reg}} A L^{\text{reg}} \) is made for the lithium flux, the final PDE shown by Eq. (2.10) is obtained.

\[
\sigma_{\text{tot}}^{\text{reg}} = \frac{\sigma_{\text{eff}}^{\text{reg}} A}{L^{\text{reg}}}
\] (2.9)

\[
\sigma_{\text{tot}}^{\text{reg}} \frac{\partial^2}{\partial \bar{x}^2} \phi_s^{\text{reg}}(\bar{x}, t) - F j_{\text{tot}}^{\text{reg}}(\bar{x}, t) = 0.
\] (2.10)

The boundary equations of the original PDE force all of the current of the battery cell to be placed on the solid material at the current collectors. In terms of the non-normalized lengths, the boundary equations are:

\[
-\sigma_{\text{eff}}^{\text{neg}} \frac{\partial \phi_s(0, t)}{\partial x} = \sigma_{\text{eff}}^{\text{pos}} \frac{\partial \phi_s(L, t)}{\partial x} = i_{\text{app}} A.
\]

Since the new potential PDE is in terms of the normalized lengths, the derivative is changed and the boundary location of the positive electrode is switched from \( L \) to \( 3 \). After substituting for the new derivative the same substitution for \( \sigma_{\text{tot}}^{\text{reg}} \) is made.

\[
-\frac{\sigma_{\text{eff}}^{\text{neg}}}{L^{\text{reg}}} \frac{\partial \phi_s(0, t)}{\partial \bar{x}} = \frac{\sigma_{\text{eff}}^{\text{pos}}}{L^{\text{pos}}} \frac{\partial \phi_s(3, t)}{\partial \bar{x}} = \frac{i_{\text{app}}}{A}
\]

\[
-\sigma_{\text{tot}}^{\text{neg}} \frac{\partial \phi_s(0, t)}{\partial \bar{x}} = \sigma_{\text{tot}}^{\text{pos}} \frac{\partial \phi_s(3, t)}{\partial \bar{x}} = i_{\text{app}}.
\]
2.2. Doyle–Fuller–Newman pseudo-2d full-order model

2.2.4 Potential of the electrolyte

The potential of the electrolyte is an essential part of modeling a battery cell. The electrolyte will carry all of the battery’s current at the separator boundaries and though the separator. Since the electrolyte is present throughout the cell the PDE will be defined across the whole cell starting at the negative current collector. The electrolyte potential dynamics across the length of the electrode are governed by the following PDE:

$$\frac{\partial}{\partial x} \left( \kappa_{eff} \frac{\partial}{\partial x} \phi_e(x, t) \right) + \frac{\partial}{\partial x} \left( \kappa_D^{eff} \frac{\partial}{\partial x} \ln \left( c_e(x, t) \right) \right) + a_s F j(x, t) = 0.$$

In an effort to group parameters together, this PDE is further expanded by utilizing the following expression for $\kappa_{eff}^D$:

$$\kappa_{eff}^D = \frac{-2RT}{F} \kappa_{eff} \left( 1 - t_+^0 \right) \left( 1 + \frac{d \ln f_\pm}{d \ln c_e} \right).$$

The value of $\frac{d \ln f_\pm}{d \ln c_e}$ is assumed to be zero. Now substituting for $\kappa_{eff}^D$ and changing to the normalized dimension $\bar{x}$ by modifying the derivatives, the new PDE becomes,

$$\frac{\partial}{\partial \bar{x}} \left( \kappa_{tot}^{reg} \frac{\partial}{\partial \bar{x}} \phi_e(\bar{x}, t) \right) + \frac{\partial}{\partial \bar{x}} \left( \frac{-2RT}{F \kappa_{tot}^{reg}} \kappa_{eff} \left( 1 - t_+^0 \right) \frac{\partial}{\partial \bar{x}} \ln \left( c_e(\bar{x}, t) \right) \right) + a_s F j(\bar{x}, t) = 0.$$

Now both sides of the equation are multiplied by $AL^{reg}$ and a new lumped parameter $\kappa_{tot}^{reg}$ is defined as $\kappa_{tot}^{reg} = \kappa_{tot}^{reg} AL^{reg}$. It is also apparent that the total flux defined by $j_{tot}(x, t) = j(x, t) a_s AL$ is formed by this multiplication and is substituted accordingly. The new PDE becomes a function of all new parameters, except that it depends on the concentration of lithium in the electrolyte, and not on the ratio of the concentration and the equilibrium concentration:

$$\frac{\partial}{\partial \bar{x}} \left( \kappa_{tot}^{reg} \frac{\partial}{\partial \bar{x}} \phi_e(\bar{x}, t) \right) + \frac{\partial}{\partial \bar{x}} \left( \frac{-2RT}{F \kappa_{tot}^{reg}} \kappa_{eff} \left( 1 - t_+^0 \right) \frac{\partial}{\partial \bar{x}} \ln \left( c_e(\bar{x}, t) \right) \right) + j_{tot}^{reg}(\bar{x}, t) = 0.$$

Rearranging the equation to get the PDE as a function of the ratio of concentrations, the $\frac{\partial}{\partial \bar{x}} \ln c_e(\bar{x}, t)$ term is modified to get it into the form $n_{e, \text{ratio}} = n_e/n_{e,0}$. Using properties of the natural logarithm, we write,

$$\ln \left( n_{e, \text{ratio}} \right) = \ln \left( \frac{c_e \varepsilon_{reg}^{e,reg} AL^{reg}}{n_{e,0}^{reg}} \right) = \ln \left( c_e \right) - \ln \left( \frac{n_{e,0}}{\varepsilon_{e}^{reg} AL^{reg}} \right).$$
2.2. Doyle–Fuller–Newman pseudo-2d full-order model

To find the equivalent term of \( \frac{\partial}{\partial \bar{x}} \ln c_e(\bar{x}, t) \), we take the derivative of both sides which removes the constant term,

\[
\frac{\partial}{\partial \bar{x}} \ln (c_e(\bar{x}, t)) = \frac{\partial}{\partial \bar{x}} \ln (n_e,\text{ratio}(\bar{x}, t)).
\]

The final equation can now be written in terms of only new lumped parameters and new PDEs,

\[
\frac{\partial}{\partial \bar{x}} \left( \kappa_{\text{tot}} \frac{\partial}{\partial \bar{x}} \phi_e(\bar{x}, t) \right) + \frac{\partial}{\partial \bar{x}} \left( \frac{-2RT}{F} \kappa_{\text{tot}} (1 - t_{\pm}^0) \frac{\partial}{\partial \bar{x}} \ln (n_e,\text{ratio}(\bar{x}, t)) \right) + F j_{\text{tot}}^{\text{reg}}(x, t) = 0.
\]

The boundary equations set the change to the potential with respect to the change in distance to zero at the current collectors of both electrodes. This remains the same for the old PDE except that the new dimension is in terms of \( \bar{x} \),

\[
\frac{\partial \phi_e(0, t)}{\partial \bar{x}} = \frac{\partial \phi_e(3, t)}{\partial \bar{x}} = 0.
\]

2.2.5 Butler–Volmer equation

The Butler–Volmer equation describes how lithium flows in and out of a particle. This is driven by the concentration of lithium at the surface of the particle, the local concentration of lithium in the electrolyte, as well as the overpotential between the solid particle and the electrolyte. The basic Butler–Volmer equation describing the flux of lithium out of a particle is defined as:

\[
j(x, t) = kc_e^{1-\alpha}(c_{s,\text{max}} - c_{s,e})^{1-\alpha} c_{s,e}^\alpha \left( \exp \left( \frac{(1 - \alpha)F}{RT} \eta \right) - \exp \left( -\frac{\alpha F}{RT} \eta \right) \right),
\]

(2.12)

The overpotential term \( \eta \) is a measure of how far the potential difference between the solid and electrolyte are away from equilibrium. This is defined as:

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

First, the equation is split up into two different segments where we assume \( \alpha = 0.5 \).

The first segment deals with the overpotential and can be written as:

\[
\exp \left( \frac{(1 - \alpha)F}{RT} \eta \right) - \exp \left( -\frac{\alpha F}{RT} \eta \right) = 2 \sinh \left( \frac{F}{2RT} \eta \right)
\]
2.2. Doyle–Fuller–Newman pesudo-2d full-order model

The second segment deals with the concentrations of lithium in the solid particle and the electrolyte.

\[ j_0(x, t) = k c_e^{1-\alpha} (c_{s,max} - c_{s,e})^{1-\alpha} c_{s,e}^\alpha \]  \hspace{1cm} (2.13)

By substituting \( j_0 \) and the \( \sinh \) term into the flux Eq. (2.12) the equation can be written as,

\[ j(x, t) = j_0(x, t) 2 \sinh \left( \frac{F}{2RT} \eta(x, t) \right). \] \hspace{1cm} (2.14)

Since all of the transfer functions are dependent on the new function \( j_{\text{tot}}(\bar{x}, t) \) this equation is modified. To transform the flux \( j(x, t) \) into a normalized total flux \( j_{\text{tot}}(\bar{x}, t) \) both sides are multiplied by \( a_s AL \).

\[ j_{\text{tot}}(\bar{x}, t) = 2a_s AL j_0(\bar{x}, t) \sinh \left( \frac{F}{2RT} \eta(\bar{x}, t) \right) \]

The \( j_0 \) term is lumped together with the other constant parameters to simplify notation further. Since \( \alpha \) is assumed to be one half Eq. (2.13) becomes a square root function and the new term becomes,

\[ j_{0,\text{tot}}(\bar{x}, t) = a_s AL j_0(\bar{x}, t) = a_s AL k \sqrt{c_e(\bar{x}, t) (c_{s,max} - c_{s,e}(\bar{x}, t))c_{s,e}(\bar{x}, t)}. \]

Finally, to get everything in terms of the new parameters, the equation is multiplied by \( \frac{\varepsilon_s \sqrt{c_{e,0}}}{\varepsilon_s \sqrt{c_{e,0}}} \) and the concentration terms are converted to total moles by remembering that \( n_{\text{cell}} = c_s \varepsilon_s AL \):

\[ j_{0,\text{tot}}(\bar{x}, t) = a_s AL j_0(\bar{x}, t) = a_s AL k \frac{\varepsilon_s AL \sqrt{c_{e,0}}}{\varepsilon_s AL \sqrt{c_{e,0}}} \sqrt{c_e(c_{s,max} - c_{s,e}(\bar{x}, t))c_{s,e}(\bar{x}, t)} \]

\[ = a_s k \frac{\sqrt{c_{e,0}}}{\varepsilon_s} \sqrt{n_{\text{ratio}}(n_{s,max} - n_{s,e})n_{s,e}}. \]

One last lumped parameter in now identifiable and labeled \( k_{\text{step}} \):

\[ k_{\text{step}}^{\text{reg}} = a_s k \frac{\sqrt{c_{e,0}}}{\varepsilon_s} = \frac{3k}{R_{\text{reg}}} \sqrt{c_{e,0}}. \]
2.2. Doyle–Fuller–Newman pseudo-2d full-order model

![Figure 2.2: Electrode concentration terms](image)

When looking at the electrodes and their capacities some simplifications can be made. First, both electrodes have the same operating region within the cell. This means that lithium leaves one electrode the lithium must be transferred through diffusion into the other electrode. In each electrode there is a starting concentration of lithium that is labeled $n_{s,0}^{\text{reg}}$. At 100% cell SOC the starting number of moles is $n_{s,0}^{\text{neg}} + Q_{\text{cell}}$ in the negative electrode and $n_{s,0}^{\text{pos}}$ in the positive electrode. Similarly, the molar quantity of lithium at 0% SOC in the negative electrode is $n_{s,0}^{\text{neg}}$, and $n_{s,0}^{\text{pos}} + Q_{\text{cell}}$ in the positive electrode. Similarly, there is a certain amount of lithium that could potentially be pushed into the opposite electrode but is left in the electrode under normal operation. This term is referred to as $n_{s,\Delta,\text{max}}^{\text{reg}}$. Finally, the amount of lithium inside an electrode at different SOCs above the $n_{s,0}^{\text{reg}}$ level is $\tilde{n}_{s}^{\text{reg}}$. All of these terms are visualized in Figs. 2.2 and 2.3.

With these new definitions some of the old terms in $j_{0,\text{tot}}(\bar{x}, t)$ can be changed. The first change is the difference between the max/min surface concentration and the present surface concentration. Using the new definition,

$$ (n_{s,\text{max}} - n_{s,e}) = (\tilde{n}_{s,\Delta}^{\text{reg}} + n_{s,\Delta,\text{max}}^{\text{reg}}). $$
2.2. Doyle–Fuller–Newman pseudo-2d full-order model

Furthermore, $n_{s,e}$ is changed too,

$$ n_{s,e} = \left( n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}} \right). $$

First, the $j_{0,\text{tot}}$ terms are changed in terms of the new variables,

$$ j_{0,\text{tot}}^{\text{reg}}(x,t) = k_{\text{step}}^{\text{reg}} \sqrt{n_{e,\text{ratio}}^{\text{reg}} (n_{s,\text{max}}^{\text{reg}} - n_{s,e}^{\text{reg}}) n_{s,e}^{\text{reg}}} $n_{e,\text{ratio}}^{\text{reg}} \left( \tilde{n}_{s,\Delta}^{\text{reg}} + n_{s,\Delta,\text{max}}^{\text{reg}} \right) \left( n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}} \right).$$

(2.15)

Going back to the overpotential term, the flux term is converted to a total flux and the constant $R_{\text{film}}$ term is lumped with the other constants such that $R_{\text{film, tot}}^{\text{reg}} = \frac{r_{\text{film}}^{\text{reg}}}{a_k^{\text{reg}} AL^{\text{reg}}}.$

$$ \eta = \phi_s - \phi_e - U_{\text{ocp}} - j_{\text{tot}} F R_{\text{film, tot}}^{\text{reg}} $$

(2.16)

After all of the substitutions the new equation becomes,

$$ j_{\text{tot}}^{\text{reg}} = 2 k_{\text{step}}^{\text{reg}} \sqrt{n_{e,\text{ratio}}^{\text{reg}} \left( \tilde{n}_{s,\Delta}^{\text{reg}} + n_{s,\Delta,\text{max}}^{\text{reg}} \right) \left( n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}} \right)} \times \sinh \left( \frac{F}{2RT} (\phi_{s-e} - U_{\text{ocp}} - j_{\text{tot}} F R_{\text{film, tot}}^{\text{reg}}) \right).$$

(2.17)

2.2.6 Linearized overpotential

It is necessary to find a transfer function for the overpotential during the system identification process. When simulating the cell, the overpotential is computed using the nonlinear

\[ \eta = \phi_s - \phi_e - U_{\text{ocp}} - j_{\text{tot}} F R_{\text{film, tot}}^{\text{reg}} \]
2.2. Doyle–Fuller–Newman pseudo-2d full-order model

time-dependent Eq. (2.14), but for frequency testing, a linear transfer function is needed. To start, the Butler–Volmer equation is linearized in order to isolate the overpotential term. The equation is simplified by making a definition of the difference in potential between the solid particles and the electrolyte $\phi_s - \phi_e = \phi_{s-e}$:

$$\frac{j_{tot}(\bar{x},t)}{k_{step}\sqrt{n_{e,\text{ratio}}(n_{s,\text{max}} - n_{s,e})n_{s,e}}} = \sinh \left( \frac{F}{2RT} (\phi_{s-e} - U_{\text{ocp}} - j_{tot}(\bar{x},t)FR_{\text{film,tot}}) \right).$$

To linearize this equation the Taylor-series expansion of both sides is computed at a setpoint $j = 0, n_{s,e} = n_{s,0}, n_{e,\text{ratio}} = 1, \phi_{s-e} = U_{\text{ocp}} (n_{s,0}/n_{s,\text{max}})$. The left hand side (LHS) is linearized first:

$$\frac{j_{tot}(\bar{x},t)}{k_{step}\sqrt{n_{e,\text{ratio}}(n_{s,\text{max}} - n_{s,e})n_{s,e}}} \approx \text{LHS} (p^*) + \frac{\partial \text{LHS}}{\partial n_{s,e}} \bigg| _{p^*} (n_{s,e} - n_{s,0})$$

$$+ \frac{\partial \text{LHS}}{\partial n_{e,\text{ratio}}} \bigg| _{p^*} (n_{e,\text{ratio}} - 1) + \frac{\partial \text{LHS}}{\partial j_{tot}} \bigg| _{p^*} (j_{tot} - 0)$$

$$\approx 0 + 0 \times (n_{s,e} - n_{s,0}) + 0 \times (n_{e,\text{ratio}} - 1)$$

$$+ \frac{j_{tot}}{j_{0,tot}} \approx 0$$

The same process is performed for the right hand side (RHS):

$$\text{RHS} (p^*) + \frac{\partial \text{RHS}}{\partial \phi_{s,e}} \bigg| _{p^*} (\phi_{s,e} - U_{\text{ocp}} (n_{s,0}))$$

$$+ \frac{\partial \text{RHS}}{\partial n_{s,e}} \bigg| _{p^*} (n_{s,e} - n_{s,0}) + \frac{\partial \text{RHS}}{\partial j_{tot}} \bigg| _{p^*} (j_{tot})$$

$$\approx 0 + \frac{F}{RT} (\phi_{s,e} - U_{\text{ocp}} (n_{s,0}))$$

$$- \frac{F}{RT} \left( \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \bigg| _{n_{s,0}} \right) (n_{s,e} - n_{s,0}) - \frac{F^2 R_{\text{film,tot}}}{RT} (j_{tot}).$$

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By setting both sides equal to each other and substituting \( \tilde{\phi}_{s-e} = \phi_{s-e} - U_{\text{ocp}}(n_{s,0}) \), and \( \tilde{n}_{s,e} = n_{s,e} - n_{s,0} \) the equation becomes,

\[
\frac{j_{\text{tot}}}{j_{\text{eq, tot}}} = \frac{F}{RT} \left( \tilde{\phi}_{s-e} \right) - \frac{F}{RT} \left( \left. \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \right|_{n_{s,0}} \right) (\tilde{n}_{s,e}) - \frac{F^2 R_{\text{film, tot}}}{RT} (j_{\text{tot}}).
\]

By rearranging terms, the \( j_{\text{tot}} \) term is factored out:

\[
\left( \frac{RT}{F j_{\text{eq, tot}}} + F R_{\text{film, tot}} \right) j_{\text{tot}} (\bar{x}, t) = \left( \frac{\tilde{\phi}_{s-e}(\bar{x}, t)}{ \left. \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \right|_{n_{s,0}} } \right) (\tilde{n}_{s,e}(\bar{x}, t)).
\]

Now a last substitution of a new constant \( R_{ct, \text{tot}} = \frac{RT}{F j_{\text{eq, tot}}} \) is inserted and used with \( \tilde{\phi}_{s-e} = \phi_{s-e} - U_{\text{ocp}}(n_{s,0}) \) to make the equation,

\[
F R_{ct, \text{tot}} j_{\text{tot}} (\bar{x}, t) = \phi_{s-e} - U_{\text{ocp}}(n_{s,0}) - \left( \left. \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \right|_{n_{s,0}} \right) (\tilde{n}_{s,e}(\bar{x}, t)) - F R_{\text{film, tot}} j_{\text{tot}} (\bar{x}, t).
\]

Since the right-hand side of the equation looks like a linear approximation of the full open circuit potential equation,

\[
U_{\text{ocp}}(n_{s,0}) - \left( \left. \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \right|_{n_{s,0}} \right) (\tilde{n}_{s,e}) \approx U_{\text{ocp}}(n_{s,e}).
\]

a substitution is performed:

\[
F R_{ct, \text{tot}} j_{\text{tot}} (\bar{x}, t) = \phi_{s-e}(\bar{x}, t) - U_{\text{ocp}}(n_{s,e}(\bar{x}, t)) - F R_{\text{film, tot}} j_{\text{tot}} (\bar{x}, t).
\]

Finally, the right-hand side of Eq. (2.19) is equal to \( \eta \) from Eq. (2.16) and thus the approximation is shown by,

\[
F R_{ct, \text{tot}} j_{\text{tot}} (\bar{x}, t) \approx \eta (\bar{x}, t).
\]

2.2.7 Summary

After performing an analysis of the old governing PDEs and algebraic equations, the minimum number of parameters is now set. Notice that the governing equations are the same
2.3. The reduced order model (ROM)

as before but are defined in such a way in order to minimize parameters. The summary of all of the equations are shown in Table 2.1. The next steps will be to re-derive the reduced order model by Lee [17] in terms of these new lumped parameters.

2.3 The reduced order model (ROM)

We wish to create a reduced order model of cell dynamics to enable quick simulation and real-time control of internal battery cell parameters. We follow the approach of Lee and colleagues [17], who defined a discrete-time realization algorithm (DRA) to obtain a simple state-space model with nonlinear corrections to compute the internal variables. This model is obtained by first linearizing the nonlinear PDEs around a setpoint to obtain a transfer function for each variable. In order to use these transfer functions to perform system identification, they must be converted to use the new lumped parameter values. The following sections will step through each conversion.

2.3.1 The Jacobsen–West transfer function

The transfer function between the concentration of lithium at the surface of the solid particle and the flux of lithium out of the particle is essential to unlocking the rest of the parameter transfer functions. The original equation was given by,

\[
\frac{\tilde{C}_{s,e}(s)}{J(s)} = \frac{R_s}{D_s}\left(\frac{\tanh(\beta)}{\tanh(\beta) - \beta}\right),
\]

where \(\beta = R_s\sqrt{s/D_s}\). To fit this into the new parameter form it is desired to arrive at \(\frac{\tilde{N}_{s,e}(s)}{J_{tot}(s)}\). First, multiply the transfer function by \(\frac{\varepsilon_s{AL}}{a_s{AL}}\) and substitute for \(\varepsilon_s = \frac{a_s{R_s}}{3}\):

\[
\frac{\tilde{C}_{s,e}(s) \varepsilon_s{AL}}{J(s) a_s{AL}} = \frac{\tilde{N}_{s,e}(s)}{J_{tot}(s)} = \frac{R_s \varepsilon_s{AL}}{D_s a_s{AL}} \left(\frac{\tanh(\beta)}{\tanh(\beta) - \beta}\right) = \frac{R_s^2}{3D_s} \left(\frac{\tanh(\beta)}{\tanh(\beta) - \beta}\right).
\]

This substitution produced the desired equation:

\[
\frac{\tilde{N}_{s,e}(s)}{J_{tot}(s)} = \frac{R_s^2}{3D_s} \left(\frac{\tanh(\beta)}{\tanh(\beta) - \beta}\right).
\]
Table 2.1: Summary of reformulated PDE model

<table>
<thead>
<tr>
<th>PDE</th>
<th>Old Parameters</th>
<th>New Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid Concentration</td>
<td>( \frac{\partial c_s(r,x,t)}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_s(r,x,t)}{\partial r} \right) )</td>
<td>( \frac{\partial n_{cell}(r,x,t)}{\partial t} = \frac{\partial}{\partial r} \left( D_{s,tot} \frac{\partial n_{cell}(r,x,t)}{\partial r} \right) )</td>
</tr>
<tr>
<td>Electrolyte Concentration</td>
<td>( \frac{\partial (\varepsilon e c_e(x,t))}{\partial t} = \frac{\partial}{\partial x} \left( D_{e,eff} \frac{\partial c_e(x,t)}{\partial x} \right) + \frac{1}{1-t_0^+} a_s F j(x,t) )</td>
<td>( n_{e,0} \frac{\partial (n_{e,ratio}(\bar{x},t))}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( D_{e,tot} \frac{\partial n_{e,ratio}(\bar{x},t)}{\partial \bar{x}} \right) + (1-t_0^+) j_{tot}(x,t) )</td>
</tr>
<tr>
<td>Solid Potential</td>
<td>( \frac{\partial}{\partial x} \left( \sigma_{eff} \frac{\partial \phi_s(x,t)}{\partial x} \right) - a_s F j(x,t) = 0 )</td>
<td>( \sigma_{tot} \frac{\partial^2}{\partial \bar{x}^2} \phi_s(\bar{x},t) - F j_{tot}(\bar{x},t) = 0 )</td>
</tr>
<tr>
<td>Electrolyte Potential</td>
<td>( \frac{\partial}{\partial x} \left( \kappa_{eff} \frac{\partial \ln c_e(x,t)}{\partial x} \right) + a_s F j(x,t) = 0 )</td>
<td>( \frac{\partial}{\partial \bar{x}} \left( -\frac{2RT}{F} \kappa_{tot} (1-t_0^+) \frac{\partial}{\partial \bar{x}} \ln n_{e,ratio}(\bar{x},t) \right) + F j_{tot}(\bar{x},t) = 0 )</td>
</tr>
<tr>
<td>Lithium Flux</td>
<td>( j(x,t) = k c_e^{-\alpha} (c_{s,max} - c_{s,e}) - \alpha c_{s,e}^\alpha \times \exp \left( \frac{(1-\alpha)F}{RT} \eta \right) - \exp \left( -\frac{\alpha F}{RT} \eta \right) )</td>
<td>( j_{tot}(\bar{x},t) = k_{step} \sqrt{n_{e,ratio}} \times \sqrt{\left( \bar{n}<em>{cell,\Delta</em>{max}} + n_{cell,\Delta_{max}} \right) \times \sqrt{\left( n_{cell,0} + \bar{n}_{cell} \right) \sinh \frac{F}{2RT} (\eta) \right.} )</td>
</tr>
</tbody>
</table>
2.3. The reduced order model (ROM)

Using the new parameters \( \frac{D_s}{R_s^2} = D_{s,\text{tot}} \), the new transfer function becomes,

\[
\tilde{N}_{s,e}(s) \quad J_{\text{tot}}(s) = \frac{1}{3D_{s,\text{tot}}} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right), \tag{2.20}
\]

where \( \beta = \sqrt{s/D_{s,\text{tot}}} \).

2.3.2 The impedance ratio

The ratio of internal impedances is a term used in nearly all of the transfer functions. This function will be used throughout the following section and can be written as,

\[
\nu(s) = \frac{L \sqrt{\frac{a_s}{\sigma_{\text{eff}}} + \frac{a_s}{\kappa_{\text{eff}}}}}{\sqrt{R_{s,e} + \left[ \left. \frac{\partial U_{\text{ocp}}}{\partial c_{s,e}} \right|_{c_{s,0}} \right] \frac{R_s}{FD_s} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right)}.
\]

To reformulate this ratio to use new parameters, we start by multiplying the top and bottom of the fraction by \( 1/\sqrt{a_s AL} \),

\[
\nu(s) = \frac{\frac{1}{\sqrt{a_s AL}} \sqrt{\frac{a_s L}{\sigma_{\text{eff}}} + \frac{a_s L}{\kappa_{\text{eff}}}}}{\frac{1}{\sqrt{a_s AL}} \sqrt{R_{s,e} + \left[ \left. \frac{\partial U_{\text{ocp}}}{\partial c_{s,e}} \right|_{c_{s,0}} \right] \frac{R_s}{FD_s} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right)}}.
\]

By reducing the equation, some familiar substitutions become evident.

\[
\nu(s) = \frac{\sqrt{\frac{L}{A\sigma_{\text{eff}}} + \frac{L}{A\kappa_{\text{eff}}}}}{\sqrt{\frac{R_{s,e}}{a_s AL} + \left[ \left. \frac{\partial U_{\text{ocp}}}{\partial c_{s,e}} \right|_{c_{s,0}} \right] \frac{R_s}{FD_s a_s AL} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right)}}.
\]

Almost all substitutions can be made, but now focus on the \( \frac{\partial U_{\text{ocp}}}{\partial c_{s,e}} \) term in the equation. This term needs to be transformed in terms of \( n_{s,e} \):

\[
\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}} = \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \frac{\partial n_{s,e}}{\partial c_{s,e}}, \text{ where } n_{s,e} = c_{s,e} \varepsilon_s A L
\]

\[
\frac{\partial n_{s,e}}{\partial c_{s,e}} = \varepsilon_s A L.
\]
2.3. The reduced order model (ROM)

After making this substitutions the impedance ratio term becomes,

\[ \nu(s) = \sqrt{\frac{L}{A\sigma_{\text{eff}}} + \frac{L}{A\kappa_{\text{tot}}}}. \]

Now all terms can be transformed into the new parameter set using \( \sigma_{\text{tot}}^{\text{reg}} = \frac{\sigma_{\text{eff}} A}{L_{\text{reg}}} \), \( \kappa_{\text{tot}}^{\text{reg}} = \frac{\kappa_{\text{eff}} A}{L_{\text{reg}}} \), and \( I_{\text{k},e,\text{tot}}^{\text{reg}} = \frac{I_{\text{k},e}}{R_{s}} \). The new function is now,

\[ \nu^{\text{reg}}(s) = \sqrt{\frac{1}{\sigma_{\text{tot}}^{\text{reg}}} + \frac{1}{\kappa_{\text{tot}}^{\text{reg}}}}. \]

2.3.3 Potential difference between solid surface and electrolyte

The conversion of the potential difference \( \Phi_{s-e}(z,s) \) transfer function is straightforward. The original equations are,

\[ \frac{\Phi_{s-e}^{\text{neg}}(z,s)}{I_{\text{app}}(s)} = \frac{L^{\text{neg}}}{A\nu^{\text{neg}}(s) \sinh(\nu^{\text{neg}}(s))} \left( \frac{1}{\kappa_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{neg}}(s)z) + \frac{1}{\sigma_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{neg}}(s)(z-1)) \right) \]

\[ \frac{\Phi_{s-e}^{\text{pos}}(z,s)}{I_{\text{app}}(s)} = -\frac{L^{\text{pos}}}{A\nu^{\text{pos}}(s) \sinh(\nu^{\text{pos}}(s))} \left( \frac{1}{\kappa_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{pos}}(s)z) + \frac{1}{\sigma_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{pos}}(s)(z-1)) \right) \]

and after substituting in for \( \sigma_{\text{tot}}^{\text{reg}} = \frac{\sigma_{\text{eff}} A}{L_{\text{reg}}} \), \( \kappa_{\text{tot}}^{\text{reg}} = \frac{\kappa_{\text{eff}} A}{L_{\text{reg}}} \), the equations become,

\[ \frac{\Phi_{s-e}^{\text{neg}}(z,s)}{I_{\text{app}}(s)} = \frac{1}{\nu^{\text{neg}}(s) \sinh(\nu^{\text{neg}}(s))} \left( \frac{1}{\kappa_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{neg}}(s)z) + \frac{1}{\sigma_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{neg}}(s)(z-1)) \right), \]

and

\[ \frac{\Phi_{s-e}^{\text{pos}}(z,s)}{I_{\text{app}}(s)} = -\frac{1}{\nu^{\text{pos}}(s) \sinh(\nu^{\text{pos}}(s))} \left( \frac{1}{\kappa_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{pos}}(s)z) + \frac{1}{\sigma_{\text{tot}}^{\text{eff}}} \cosh(\nu^{\text{pos}}(s)(z-1)) \right). \]

2.3.4 Lithium flux

Instead of finding a transfer function of localized lithium flux \( J(z,s) \), it is necessary to derive a transfer function for total localized lithium flux \( J_{\text{tot}}(z,s) \). The original lithium flux equations are,

\[ \frac{J^{\text{neg}}(z,s)}{I_{\text{app}}(s)} = \frac{\nu^{\text{neg}}(s)}{\sigma_{\text{tot}}^{\text{eff}} F L^{\text{neg}} A (\kappa_{\text{tot}}^{\text{neg}} + \sigma_{\text{tot}}^{\text{neg}})} \left( \frac{\kappa_{\text{tot}}^{\text{neg}} \cosh(\nu^{\text{neg}}(s)z) + \sigma_{\text{tot}}^{\text{neg}} \cosh(\nu^{\text{neg}}(s)(z-1))}{\sinh(\nu^{\text{neg}}(s))} \right), \]
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and,

\[
\frac{J_{\text{pos}}(z, s)}{I_{\text{app}}(s)} = -\frac{\nu_{\text{pos}}(s)}{A_{\text{pos}} F L_{\text{pos}} A (\kappa_{\text{eff}} + \sigma_{\text{eff}})} \left( \frac{\sigma_{\text{eff}} \cosh(\nu_{\text{pos}}(s)) + \kappa_{\text{eff}} \cosh(\nu_{\text{pos}}(s)(z - 1))}{\sinh(\nu_{\text{pos}}(s))} \right),
\]

In order to get total lithium flux, both sides of the equation are multiplied by \( \alpha_{\text{reg}} L_{\text{reg}} A \).

After substituting in for \( \sigma_{\text{tot}} = \frac{\sigma_{\text{eff}} A}{L_{\text{reg}}}, \kappa_{\text{tot}} = \frac{\kappa_{\text{eff}} A}{L_{\text{reg}}} \), the final equations become,

\[
\frac{J_{\text{tot}}^{\text{neg}}(z, s)}{I_{\text{app}}(s)} = \frac{\nu_{\text{neg}}(s)}{F (\kappa_{\text{tot}} + \sigma_{\text{tot}})} \left( \frac{\sigma_{\text{tot}}^\text{neg} \cosh(\nu_{\text{neg}}(s)) + \kappa_{\text{tot}}^\text{neg} \cosh(\nu_{\text{neg}}(s)(z - 1))}{\sinh(\nu_{\text{neg}}(s))} \right),
\]

(2.21)

and,

\[
\frac{J_{\text{tot}}^{\text{pos}}(z, s)}{I_{\text{app}}(s)} = -\frac{\nu_{\text{pos}}(s)}{F (\kappa_{\text{tot}} + \sigma_{\text{tot}})} \left( \frac{\sigma_{\text{tot}}^\text{pos} \cosh(\nu_{\text{pos}}(s)) + \kappa_{\text{tot}}^\text{pos} \cosh(\nu_{\text{pos}}(s)(z - 1))}{\sinh(\nu_{\text{pos}}(s))} \right),
\]

(2.22)

2.3.5 Potential in the solid

This transfer function is converted to new parameters using the definitions for \( \sigma_{\text{tot}} \) and \( \kappa_{\text{tot}} \).

The original transfer functions in each electrode are,

\[
\bar{\Phi}_{\text{neg}}^\text{s}(z, s) = -\frac{\nu_{\text{neg}}^\text{s}}{A_{\text{neg}}^\text{s} F L_{\text{neg}}^\text{s} A_{\text{neg}}^\text{s} (\kappa_{\text{neg}}^\text{s} + \sigma_{\text{neg}}^\text{s})} \left( \frac{\sigma_{\text{neg}}^\text{s} \cosh(\nu_{\text{neg}}^\text{s}(s)) + \kappa_{\text{neg}}^\text{s} \cosh(\nu_{\text{neg}}^\text{s}(s)(z - 1))}{\sinh(\nu_{\text{neg}}^\text{s}(s))} \right)
\]

for the negative electrode and,

\[
\bar{\Phi}_{\text{pos}}^\text{s}(z, s) = \frac{\nu_{\text{pos}}^\text{s}}{A_{\text{pos}}^\text{s} F L_{\text{pos}}^\text{s} A_{\text{pos}}^\text{s} (\kappa_{\text{pos}}^\text{s} + \sigma_{\text{pos}}^\text{s})} \left( \frac{\sigma_{\text{pos}}^\text{s} \cosh(\nu_{\text{pos}}^\text{s}(s)) + \kappa_{\text{pos}}^\text{s} \cosh(\nu_{\text{pos}}^\text{s}(s)(z - 1))}{\sinh(\nu_{\text{pos}}^\text{s}(s))} \right)
\]

for the positive electrode. Since \( \sigma_{\text{neg}}^\text{reg} = \frac{\sigma_{\text{neg}}^\text{reg} A_{\text{neg}}^\text{reg}}{L_{\text{neg}}^\text{reg}}, \kappa_{\text{neg}}^\text{reg} = \frac{\kappa_{\text{neg}}^\text{reg} A_{\text{neg}}^\text{reg}}{L_{\text{neg}}^\text{reg}}, \) a simple substitution leads to,

\[
\bar{\Phi}_{\text{neg}}^\text{s}(z, s) = \frac{\nu_{\text{neg}}^\text{s}}{A_{\text{neg}}^\text{s} F L_{\text{neg}}^\text{s} A_{\text{neg}}^\text{s} (\kappa_{\text{neg}}^\text{s} + \sigma_{\text{neg}}^\text{s})} \left( \frac{\sigma_{\text{neg}}^\text{s} \cosh(\nu_{\text{neg}}^\text{s}(s)) + \kappa_{\text{neg}}^\text{s} \cosh(\nu_{\text{neg}}^\text{s}(s)(z - 1))}{\sinh(\nu_{\text{neg}}^\text{s}(s))} \right)
\]

and,

\[
\bar{\Phi}_{\text{pos}}^\text{s}(z, s) = \frac{\nu_{\text{pos}}^\text{s}}{A_{\text{pos}}^\text{s} F L_{\text{pos}}^\text{s} A_{\text{pos}}^\text{s} (\kappa_{\text{pos}}^\text{s} + \sigma_{\text{pos}}^\text{s})} \left( \frac{\sigma_{\text{pos}}^\text{s} \cosh(\nu_{\text{pos}}^\text{s}(s)) + \kappa_{\text{pos}}^\text{s} \cosh(\nu_{\text{pos}}^\text{s}(s)(z - 1))}{\sinh(\nu_{\text{pos}}^\text{s}(s))} \right)
\]

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and

\[ \frac{\tilde{\Phi}_s^{\text{pos}}(z, s)}{I_{\text{app}}(s)} = \frac{\kappa^{\text{pos}}_\text{tot} (\cosh(\nu^{\text{pos}}(s)) - \cosh((z - 1)\nu^{\text{pos}}(s)))}{\sigma^{\text{pos}}_\text{tot} (\kappa^{\text{pos}}_\text{tot} + \sigma^{\text{pos}}_\text{tot}) \nu^{\text{pos}}(s) \sinh(\nu^{\text{pos}}(s))} \]

\[ - \frac{\sigma^{\text{pos}}_\text{tot} (1 - \cosh(z\nu^{\text{pos}}(s)) + z\nu^{\text{pos}}(s) \sinh(\nu^{\text{pos}}(s)))}{\sigma^{\text{pos}}_\text{tot} (\kappa^{\text{pos}}_\text{tot} + \sigma^{\text{pos}}_\text{tot}) \nu^{\text{pos}}(s) \sinh(\nu^{\text{pos}}(s))}. \]

2.3.6 Potential in the electrolyte

The potential in the electrolyte is broken up into two functions: \( [\tilde{\phi}_e(x, t)]_1 \) and \( [\tilde{\phi}_e(x, t)]_2 \). The electrolyte’s dimension is across each length of both electrodes. Since the new parameters lump the lengths inside new constants, the length must be normalized. The original transfer functions are defined in all three cell regions where each one must be transformed individually. The first equation is defined to be,

\[ \frac{\left[\tilde{\phi}_e(x, s)\right]_1}{I_{\text{app}}(s)} = \frac{L^{\text{neg}} \left( \frac{\nu^{\text{neg}}_\text{eff}}{\nu^{\text{neg}}_\text{tot}} \left( 1 - \cosh \left( \frac{x \nu^{\text{neg}}_\text{tot}}{L^{\text{neg}}_\text{tot}} \right) \right) \right) - x \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})}{A(\kappa^{\text{neg}}_\text{tot} + \sigma^{\text{neg}}_\text{tot}) \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})} \]

\[ + \frac{L^{\text{neg}} \left( \cosh(\nu^{\text{neg}}_\text{tot}) - \cosh \left( \frac{(L^{\text{neg}} - x) \nu^{\text{neg}}_\text{tot}}{L^{\text{neg}}_\text{tot}} \right) \right)}{A(\kappa^{\text{neg}}_\text{tot} + \sigma^{\text{neg}}_\text{tot}) \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})}, \]

where \( 0 < x < L^{\text{neg}} \). A new normalized length dimension is defined as \( \bar{x} = x / L^{\text{neg}} \) and substituted into the equation as follows:

\[ \frac{\left[\tilde{\phi}_e(\bar{x}, s)\right]_1}{I_{\text{app}}(s)} = \frac{L^{\text{neg}} \left( \frac{\nu^{\text{neg}}_\text{eff}}{\nu^{\text{neg}}_\text{tot}} \left( 1 - \cosh \left( \frac{x_2 L^{\text{neg}} \nu^{\text{neg}}_\text{tot}}{L^{\text{neg}}_\text{tot}} \right) \right) \right) - \bar{x} L^{\text{neg}} \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})}{A(\kappa^{\text{neg}}_\text{tot} + \sigma^{\text{neg}}_\text{tot}) \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})} \]

\[ + \frac{L^{\text{neg}} \left( \cosh(\nu^{\text{neg}}_\text{tot}) - \cosh \left( \frac{(L^{\text{neg}} - x L^{\text{neg}}_\text{tot}) \nu^{\text{neg}}_\text{tot}}{L^{\text{neg}}_\text{tot}} \right) \right)}{A(\kappa^{\text{neg}}_\text{tot} + \sigma^{\text{neg}}_\text{tot}) \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})}. \]

Since \( \kappa^{\text{neg}}_\text{eff} = \kappa^{\text{neg}}_\text{tot} \) and \( \sigma^{\text{neg}}_\text{eff} = \sigma^{\text{neg}}_\text{tot} \), a substitution leads to the new transfer function,

\[ \frac{\left[\tilde{\phi}_e(\bar{x}, s)\right]_1}{I_{\text{app}}(s)} = \frac{\left( \frac{\nu^{\text{neg}}_\text{tot}}{\nu^{\text{neg}}_\text{tot}} \left( 1 - \cosh \left( x_2 L^{\text{neg}} \nu^{\text{neg}}_\text{tot} \right) \right) \right) - \bar{x} L^{\text{neg}} \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})}{A(\kappa^{\text{neg}}_\text{tot} + \sigma^{\text{neg}}_\text{tot}) \nu^{\text{neg}}_\text{tot} \sinh(\nu^{\text{neg}}_\text{tot})} \]

\[ + \frac{\left( \cosh(\nu^{\text{neg}}_\text{tot}) - \cosh \left( (1 - \bar{x}) \nu^{\text{neg}}(s) \right) \right)}{A(\kappa^{\text{neg}}_\text{tot} + \sigma^{\text{neg}}_\text{tot}) \nu^{\text{neg}}(s) \sinh(\nu^{\text{neg}}(s))}. \]
2.3. The reduced order model (ROM)

In the separator region were \( L^{\text{neg}} < x < L^{\text{sep}} \) the old transfer function was defined as,

\[
\left[ \Phi_e (x, s) \right]_{1} = \frac{L^{\text{neg}} - x}{A \kappa^{\text{eff}}_{\text{sep}}} + \frac{L^{\text{neg}} \left(1 - \frac{\sigma^{\text{neg}}}{\kappa^{\text{eff}}}\right) \tanh \left( \frac{\nu^{\text{neg}}(s)}{2} \right) - \nu^{\text{neg}}(s)}{A \left( \kappa^{\text{neg}} + \sigma^{\text{neg}} \right) \nu(s)}.
\]

Again, a new normalized \( x \) value is defined as,

\[
\bar{x} = 1 + \frac{x - L^{\text{neg}}}{L_{\text{sep}}}, L^{\text{neg}} \leq x < L^{\text{neg}} + L^{\text{sep}}.
\]

and substitution leads to,

\[
\left[ \Phi_e (\bar{x}, s) \right]_{1} = \frac{L^{\text{neg}} - (\bar{x} - 1) L^{\text{sep}} - L^{\text{neg}}}{A \kappa^{\text{eff}}_{\text{sep}}} + \frac{L^{\text{neg}} \left(1 - \frac{\sigma^{\text{neg}}}{\kappa^{\text{eff}}}\right) \tanh \left( \frac{\nu^{\text{neg}}(s)}{2} \right) - \nu^{\text{neg}}(s)}{A \left( \kappa^{\text{neg}} + \sigma^{\text{neg}} \right) \nu(s)}.
\]

Since \( \frac{\kappa^{\text{neg}}}{\sigma^{\text{tot}}} = \frac{\kappa^{\text{neg}}}{\sigma^{\text{tot}}} \) and \( \frac{\nu^{\text{neg}}}{\nu^{\text{tot}}} = \frac{\nu^{\text{neg}}}{\nu^{\text{tot}}} \) substituting leads to the new transfer function,

\[
\left[ \Phi_e (\bar{x}, s) \right]_{1} = \frac{L^{\text{neg}} - (\bar{x} - 1) L^{\text{sep}} - L^{\text{neg}}}{A \kappa^{\text{eff}}_{\text{sep}}} + \frac{L^{\text{neg}} \left(1 - \frac{\sigma^{\text{neg}}}{\kappa^{\text{eff}}}\right) \tanh \left( \frac{\nu^{\text{neg}}(s)}{2} \right) - \nu^{\text{neg}}(s)}{A \left( \kappa^{\text{neg}} + \sigma^{\text{neg}} \right) \nu(s)}.
\]

In the positive region where \( L^{\text{neg}} + L^{\text{sep}} < x < L^{\text{neg}} + L^{\text{sep}} + L^{\text{pos}} \) the old transfer function was defined as:

\[
\left[ \Phi_e (x, s) \right]_{1} = \frac{-L^{\text{sep}}}{A \kappa^{\text{eff}}_{\text{sep}}} + \frac{L^{\text{neg}} \left(1 - \frac{\sigma^{\text{neg}}}{\kappa^{\text{eff}}}\right) \tanh \left( \frac{\nu^{\text{neg}}(s)}{2} \right) - \nu^{\text{neg}}(s)}{A \left( \kappa^{\text{neg}} + \sigma^{\text{neg}} \right) \nu(s)}
\]

\[
\frac{L^{\text{pos}} \left[ 1 + \frac{\sigma^{\text{pos}}}{\kappa^{\text{eff}}} \cosh \left( \nu^{\text{pos}}(s) \right) \right]}{A \left( \kappa^{\text{pos}} + \sigma^{\text{pos}} \right) \nu(s) \nu^{\text{pos}}(s)}
\]

\[
+ \frac{L^{\text{pos}} \left( \frac{\left( L^{\text{neg}} + L^{\text{sep}} - x \right) \nu^{\text{pos}}(s)}{\nu^{\text{pos}}(s)} \right) \nu^{\text{pos}}(s)}{A \left( \kappa^{\text{pos}} + \sigma^{\text{pos}} \right) \nu(s) \nu^{\text{pos}}(s)}
\]

\[
+ \frac{L^{\text{pos}} \left( \frac{\sigma^{\text{pos}}}{\kappa^{\text{eff}}} \sinh \left( \nu^{\text{pos}}(s) \right) \right) \nu^{\text{pos}}(s)}{A \left( \kappa^{\text{pos}} + \sigma^{\text{pos}} \right) \nu(s) \nu^{\text{pos}}(s)} + \frac{L^{\text{neg}} + L^{\text{sep}} - x}{A \left( \kappa^{\text{pos}} + \sigma^{\text{pos}} \right) \nu(s) \nu^{\text{pos}}(s)}.
\]

With \( \bar{x} \) going from two to three the new dimension relationship to the old dimension is,

\[
\bar{x} = 2 + \frac{x - L^{\text{neg}} - L^{\text{sep}}}{L^{\text{pos}}}, L^{\text{neg}} + L^{\text{sep}} \leq x \leq L^{\text{neg}} + L^{\text{sep}} + L^{\text{pos}}.
\]
This substitution leads to a new form,

\[
\frac{\Phi_e(x, s)}{I_{app}(s)} = \frac{-I_{sep} + \nu^\text{neg} (s)}{A\kappa_{\text{eff}} + \nu^\text{neg} (s)} + \frac{L^\text{pos} (1 + \frac{\sigma^\text{pos}}{\kappa_{\text{eff}}} \cosh (\nu^\text{pos} (s)))}{A(\kappa_{\text{eff}} + \sigma^\text{neg}) \nu^\text{neg} (s)}
\]

\[
- \frac{L^\text{pos} \cosh \left( \left( L^\text{neg} + L^\text{sep} - ((\bar{x} - 2)L^\text{pos} + L_{\text{sep}}) \nu^\text{pos} (s) \right) \right)}{A(\kappa_{\text{eff}} + \sigma^\text{pos}) \nu^\text{pos} (s)}
\]

\[
+ \frac{A(\kappa_{\text{eff}} + \sigma^\text{pos}) \nu^\text{pos} (s)}{L^\text{pos} \cosh \left( \left( L^\text{neg} + L^\text{sep} - ((\bar{x} - 2)L^\text{pos} + L_{\text{sep}}) \nu^\text{pos} (s) \right) \right)}
\]

Since \( \kappa_{\text{tot}}^{\text{reg}} = \frac{\kappa_{\text{tot}}^{\text{reg}}}{\kappa_{\text{tot}}} A \) and \( \sigma_{\text{tot}}^{\text{reg}} = \frac{\sigma_{\text{tot}}^{\text{reg}}}{\kappa_{\text{tot}}} A \) substituting leads to,

\[
\frac{\Phi_e(\bar{x}, s)}{I_{app}(s)} = \frac{-1}{\kappa_{\text{tot}}^{\text{sep}}} + \frac{\left( 1 - \frac{\sigma_{\text{tot}}^{\text{neg}}}{\kappa_{\text{tot}}^{\text{neg}}} \right) \tanh \left( \frac{\nu_{\text{neg}} (s)}{2} \right) - \nu_{\text{neg}} (s)}{\left( \kappa_{\text{tot}}^{\text{neg}} + \sigma_{\text{tot}}^{\text{neg}} \right) \nu_{\text{neg}} (s)}
\]

\[
\left( 1 + \frac{\sigma_{\text{tot}}^{\text{pos}}}{\kappa_{\text{tot}}^{\text{pos}}} \cosh (\nu_{\text{pos}} (s)) \right)
\]

\[
- \left( \kappa_{\text{tot}}^{\text{pos}} + \sigma_{\text{tot}}^{\text{pos}} \right) \sinh (\nu_{\text{pos}} (s)) \nu_{\text{pos}} (s)
\]

\[
\cosh ((2 - \bar{x}) \nu_{\text{pos}} (s))
\]

\[
+ \left( \kappa_{\text{tot}}^{\text{pos}} + \sigma_{\text{tot}}^{\text{pos}} \right) \sinh (\nu_{\text{pos}} (s)) \nu_{\text{pos}} (s)
\]

\[
\left( \frac{\sigma_{\text{tot}}^{\text{pos}}}{\kappa_{\text{tot}}} \cosh ((3 - \bar{x}) \nu_{\text{pos}} (s)) \right)
\]

\[
\left( \kappa_{\text{tot}}^{\text{pos}} + \sigma_{\text{tot}}^{\text{pos}} \right) \sinh (\nu_{\text{pos}} (s)) \nu_{\text{pos}} (s)
\]

\[
+ \frac{2 - \bar{x}}{\left( \kappa_{\text{tot}}^{\text{pos}} + \sigma_{\text{tot}}^{\text{pos}} \right)}.
\]

For the second term in the potential \( \tilde{\phi}_e(x, t) \) the equation is specified in the time-domain as,

\[
\left[ \tilde{\phi}_e(x, t) \right]_2 = \frac{2RT}{F} \left( 1 - \frac{t^0}{t^1} \right) \ln \left( \frac{c_e(x, t)}{c_e(0, t)} \right).
\]

Since the concentration of the electrolyte is not found but the ratio of the concentration to the initial resting concentration is found, the equation is changed to

\[
\left[ \tilde{\phi}_e(\bar{x}, t) \right]_2 = \frac{2RT}{F} \left( 1 - \frac{t^0}{t^1} \right) \ln \left( \frac{n_{e,\text{ratio}}(\bar{x}, t)}{n_{e,\text{ratio}}(0, t)} \right).
\]

Using the properties of natural logarithms this can be written as,

\[
\left[ \tilde{\phi}_e(\bar{x}, t) \right]_2 = \frac{2RT}{F} \left( 1 - \frac{t^0}{t^1} \right) \left( \ln \left( n_{e,\text{ratio}}(\bar{x}, t) \right) - \ln \left( n_{e,\text{ratio}}(0, t) \right) \right).
\]
2.3. The reduced order model (ROM)

To find the transfer function we need to linearize \( \ln \left( n_{e,\text{ratio}}(\bar{x}, t) \right) \) using Taylor-series expansion.

\[
\ln \left( n_{e,\text{ratio}}(\bar{x}, t) \right) \approx \ln \left( n_{e,\text{ratio}}(\bar{x}, 0) \right) + \frac{\partial \ln \left( n_{e,\text{ratio}}(\bar{x}, t) \right)}{\partial t} \bigg|_{t=0} \left( n_{e,\text{ratio}}(\bar{x}, t) - n_{e,\text{ratio}}(\bar{x}, 0) \right) \\
= \frac{n_{e,\text{ratio}}(\bar{x}, t) - n_{e,\text{ratio}}(\bar{x}, 0)}{n_{e,\text{ratio}}(\bar{x}, 0)} = \tilde{n}_{e,\text{ratio}}(\bar{x}, t)
\]

This linearization creates the approximation transfer function for the second term,

\[
\frac{\left[ \tilde{\Phi}_e(\bar{x}, s) \right]}{I_{\text{app}}(s)} \approx \frac{2RT(1 - t_0^0)}{F} \left( \frac{\tilde{N}_{e,\text{ratio}}(\bar{x}, s)}{I_{\text{app}}(s)} - \frac{\tilde{N}_{e,\text{ratio}}(0, s)}{I_{\text{app}}(s)} \right). 
\tag{2.25}
\]

2.3.7 Concentration of lithium in the electrolyte

While investigating the conversion of the PDE to a transfer function, the need arose to redevelop this transfer function. This section will go through similar steps as performed by Lee but with added simplicity in order to run an optimization for system identification. The original PDE is defined as

\[
\frac{\partial (\varepsilon_e c_e(x, t))}{\partial t} = \frac{\partial}{\partial x} \left( D_{e,\text{eff}} \frac{\partial c_e(x, t)}{\partial x} \right) + (1 - t_0^0) a_s j(x, t).
\]

With the substitution made with lumped parameters and \( \tilde{n}_{e,\text{ratio}}(\bar{x}, t) = n_{e,\text{ratio}}(\bar{x}, t) - 1 \), the new PDE is defined as,

\[
\frac{n_{e,0}}{(1 - t_0^0)} \frac{\partial (\tilde{n}_{e,\text{ratio}}(\bar{x}, t))}{\partial t} = \frac{\partial}{\partial x} \left( \frac{D_{e,\text{tot}}}{(1 - t_0^0)} \frac{\partial \tilde{n}_{e,\text{ratio}}(\bar{x}, t)}{\partial x} \right) + j_{\text{tot}}(x, t).
\]

2.3.7.1 Homogeneous case

To find the homogeneous case, the input to the differential equation is removed and \( n_{e,\text{ratio}}(\bar{x}, t) \) is broken into a function of space multiplied by a function of time:

\[
\tilde{n}_{e,\text{ratio}}(\bar{x}, t) = h(t)\Psi(x).
\]
2.3. The reduced order model (ROM)

This causes the new PDE to become,

\[
\frac{n_{e,0}}{(1 - t_0^+)} \frac{\partial (h(t)\Psi(\bar{x}))}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( \frac{D_{e,\text{tot}}}{(1 - t_0^+)} \frac{\partial h(t)\Psi(\bar{x})}{\partial \bar{x}} \right).
\]

After rearranging the PDE to have functions of time on one side and functions of space on the other the equation becomes,

\[
\frac{1}{h(t)} \frac{\partial (h(t))}{\partial t} = \frac{1}{n_{e,0}\Psi(\bar{x})} \frac{\partial}{\partial \bar{x}} \left( D_{e,\text{tot}} \frac{\partial \Psi(\bar{x})}{\partial \bar{x}} \right).
\]

Since both sides equal each other and have different independent variables they both must equal a constant. This results in two equations,

\[
\frac{1}{h(t)} \frac{\partial (h(t))}{\partial t} = -\lambda
\]

\[
\frac{1}{n_{e,0}\Psi(\bar{x})} \frac{\partial}{\partial \bar{x}} \left( D_{e,\text{tot}} \frac{\partial \Psi(\bar{x})}{\partial \bar{x}} \right) = -\lambda.
\]

To start deriving a transfer function the function of space is analyzed. An eigenfunction over the entire region is defined in terms of the normalized dimension.

\[\bar{x}_1 = \bar{x}\]

The eigenfunction across the negative electrode becomes,

\[\Psi_1(\bar{x}_1, \lambda) = \cos \left( \sqrt{\frac{\lambda n_{e,0}}{D_{e,\text{neg}}}} \bar{x}_1 \right), 0 \leq \bar{x}_1 < 1\]

The eigenfunction across the separator,

\[\bar{x}_2 = \bar{x} - 1\]

\[\Psi_2(\bar{x}_2, \lambda) = k_1 \cos \left( \sqrt{\frac{\lambda n_{e,0}}{D_{e,\text{sep}}}} \bar{x}_2 + \theta \right), 0 \leq \bar{x}_2 \leq 1\]

Finally the eigenfunction across the positive electrode,

\[\bar{x}_3 = -\bar{x} + 3\]
2.3. The reduced order model (ROM)

\[ \Psi_3(\bar{x}_3, \lambda) = k_2 \cos \left( \sqrt{\frac{\lambda n_{e,0}^{pos}}{D_{e,0}^{pos}}} \bar{x}_3 \right), \quad 0 \leq \bar{x}_3 < 1. \]

To ensure the eigenfunction is continuous over the entire region, the function and the derivatives must be equal at the electrode and separator boundaries. This results in four equations which must be met.

\[
\begin{align*}
\cos \left( \sqrt{\frac{\lambda n_{e,0}^{neg}}{D_{e,0}^{neg}}} \right) &= k_1 \cos (\theta) \\
k_1 \cos \left( \sqrt{\frac{\lambda n_{e,0}^{sep}}{D_{e,0}^{sep}}} + \theta \right) &= k_2 \cos \left( \sqrt{\frac{\lambda n_{e,0}^{pos}}{D_{e,0}^{pos}}} \right) \\
\sqrt{\frac{\lambda n_{e,0}^{neg}}{D_{e,0}^{neg}}} D_{e,0}^{neg} \sin \left( \sqrt{\frac{\lambda n_{e,0}^{neg}}{D_{e,0}^{neg}}} \bar{x}_1 \right) &= k_1 D_{e,0}^{sep} \sqrt{\frac{\lambda n_{e,0}^{sep}}{D_{e,0}^{sep}}} \sin (\theta) \\
\sqrt{\frac{\lambda n_{e,0}^{neg}}{D_{e,0}^{neg}}} D_{e,0}^{neg} \sin \left( \sqrt{\frac{\lambda n_{e,0}^{neg}}{D_{e,0}^{neg}}} \bar{x}_1 \right) &= -k_2 D_{e,0}^{pos} \sqrt{\frac{\lambda n_{e,0}^{pos}}{D_{e,0}^{pos}}} \sin \left( \sqrt{\frac{\lambda n_{e,0}^{pos}}{D_{e,0}^{pos}}} \right) .
\end{align*}
\]

To help simplify the equations new constants are defined:

\[
\begin{align*}
b_1 &= \sqrt{\frac{n_{e,0}^{neg}}{D_{e,0}^{neg}}} \\
b_2 &= \sqrt{\frac{n_{e,0}^{sep}}{D_{e,0}^{sep}}} \\
b_3 &= \sqrt{\frac{n_{e,0}^{pos}}{D_{e,0}^{pos}}} \\
c_1 &= \sqrt{n_{e,0}^{neg}} D_{e,0}^{neg} \\
c_2 &= \sqrt{n_{e,0}^{sep}} D_{e,0}^{sep} \\
c_3 &= \sqrt{n_{e,0}^{pos}} D_{e,0}^{pos}
\end{align*}
\]
2.3. *The reduced order model (ROM)*

These four equalities now become,

\[
\cos (\sqrt{\lambda b_1}) = k_1 \cos (\theta) \quad (2.26)
\]
\[
k_1 \cos (\sqrt{\lambda b_2 + \theta}) = k_2 \cos (\sqrt{\lambda b_3}) 
\]
\[
c_1 \sin (\sqrt{\lambda b_1}) = k_1 c_2 \sin (\theta) \quad (2.28)
\]
\[
k_1 c_2 \sin (\sqrt{\lambda b_2 + \theta}) = -k_2 c_3 \sin (\sqrt{\lambda b_3}) \quad (2.29)
\]

With four equations and four unknowns \((\lambda, \theta, k_1, k_2)\) all variables are uniquely identified. By taking Eq. (2.28) and dividing by Eq. (2.26), and Eq. (2.29) by Eq. (2.27), the set of four equations is reduced to two equations:

\[
c_1 \tan (\sqrt{\lambda b_1}) = c_2 \tan (\theta)
\]
\[
c_2 \tan (\sqrt{\lambda b_2 + \theta}) = -c_3 \tan (\sqrt{\lambda b_3})
\]

Using trigonometric identities the two function can be written as one equation,

\[
\frac{c_2}{c_3} \tan (\sqrt{\lambda b_1}) + \frac{c_2^2}{c_1 c_3} \tan (\sqrt{\lambda b_2}) + \frac{c_2}{c_1} \tan (\sqrt{\lambda b_3}) = \tan (\sqrt{\lambda b_1}) \tan (\sqrt{\lambda b_2}) \tan (\sqrt{\lambda b_3}) 
\]

The intention is to find a solution for the value of \(\lambda\). Noticing, if the equation were

\[
\tan (\sqrt{\lambda b_1}) + \tan (\sqrt{\lambda b_2}) + \tan (\sqrt{\lambda b_3}) = \tan (\sqrt{\lambda b_1}) \tan (\sqrt{\lambda b_2}) \tan (\sqrt{\lambda b_3})
\]

the value of \(\lambda\) must solve the equation,

\[
\sqrt{\lambda b_1} + \sqrt{\lambda b_2} + \sqrt{\lambda b_3} = n\pi
\]

Rearrange the equation the values of \(\lambda\) would have to be close to,

\[
\lambda_n \approx \left( \frac{n\pi}{b_1 + b_2 + b_3} \right)^2
\]
2.3. The reduced order model (ROM)

Since there are terms in front of each tangent term in Eq. (2.30), \( \lambda \) is found by iteratively searching for values that solve Eq. (2.30), starting with an initial guess found above. Assuming \( \lambda \) is found the rest of the three variables can be found.

\[
\theta = \arctan \left( \frac{c_1 \tan \left( \sqrt{\lambda} b_1 \right)}{c_2} \right)
\]

\[
k_1 = \frac{\cos \left( \sqrt{\lambda} b_1 \right)}{\cos (\theta)}
\]

\[
k_2 = \frac{k_1 \cos \left( \sqrt{\lambda} b_2 + \theta \right)}{\cos \left( \sqrt{\lambda} b_3 \right)}
\]

\[
k_2 = \frac{\cos (\theta) \cos \left( \sqrt{\lambda} b_3 \right)}{c_2 \cos \left( \sqrt{\lambda} b_1 \right) \cos \left( \sqrt{\lambda} b_2 \right) - c_1 \sin \left( \sqrt{\lambda} b_2 \right) \sin \left( \sqrt{\lambda} b_1 \right)}
\]

In order to have found an eigenfunction of the system, the eigenfunctions must be orthonormal. To ensure that the eigenfunctions are orthonormal, the integral of the squared function multiplied by its weighting term across the whole region must be equal to one.

\[
\int_{0}^{3} \psi^2(\bar{x}, \lambda) n_{e,0}^{\text{reg}} \, d\bar{x} = 1
\]

\[
\int_{0}^{3} \psi^2(\bar{x}, \lambda) n_{e,0}^{\text{reg}} \, d\bar{x} = \int_{0}^{1} \psi_1^2(\bar{x}_1, \lambda) n_{e,0}^{\text{neg}} \, d\bar{x}_1 + \int_{0}^{1} \psi_2^2(\bar{x}_2, \lambda) n_{e,0}^{\text{sep}} \, d\bar{x}_2 + \int_{0}^{1} \psi_3^2(\bar{x}_3, \lambda) n_{e,0}^{\text{pos}} \, d\bar{x}_3
\]

This integration is broken into three areas across each region in the cell:

\[
\int_{0}^{1} \cos^2 \left( \frac{\lambda n_{e,0}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}} \bar{x}_1 \right) n_{e,0}^{\text{neg}} \, d\bar{x}_1 = \frac{\sqrt{n_{e,0}^{\text{neg}} D_{e,\text{tot}}^{\text{neg}}} \sin \left( 2 \frac{\lambda n_{e,0}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}} \right)}{4 \sqrt{\lambda}} + \frac{n_{e,0}^{\text{neg}}}{2}
\]
2.3. The reduced order model (ROM)

\[
\int_0^1 k_1^2 \cos^2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{sep}} D_{e,\text{tot}}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}}} x_2 + \theta \right) n_{e,0}^{\text{sep}} \, dx_2 = \frac{k_1^2 \sqrt{n_{e,0}^{\text{sep}} D_{e,\text{tot}}^{\text{sep}}} \sin \left( \frac{2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{sep}}}{D_{e,\text{tot}}^{\text{sep}}} + \theta} \right)}{4\sqrt{\lambda}} \right)}{4\sqrt{\lambda}} - \frac{k_1^2 n_{e,0}^{\text{sep}}}{4\sqrt{\lambda}} + \frac{k_1^2 n_{e,0}^{\text{sep}}}{2}.
\]

\[
\int_0^1 k_2^2 \cos^2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{pos}} D_{e,\text{tot}}^{\text{pos}}}{D_{e,\text{tot}}^{\text{pos}}}} x_3 \right) n_{e,0}^{\text{pos}} \, dx_3 = \frac{k_2^2 \sqrt{n_{e,0}^{\text{pos}} D_{e,\text{tot}}^{\text{pos}}} \sin \left( \frac{2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{pos}}}{D_{e,\text{tot}}^{\text{pos}}} + \theta} \right)}{4\sqrt{\lambda}} \right)}{4\sqrt{\lambda}} + \frac{k_2^2 n_{e,0}^{\text{pos}}}{2}.
\]

The sum of these terms must be equal to one. To help simplify these equations some trigonometric substitutions are needed. The term of interest is the integration across the separator region. To start, the \( \sin \left( 2 \sqrt{\frac{\lambda n_{e,0}^{\text{sep}}}{D_{e,\text{tot}}^{\text{neg}}} + \theta} \right) - \sin (2\theta) \) term is converted. The first part of the term is converted by,

\[
\sin \left( 2 \sqrt{\frac{\lambda n_{e,0}^{\text{sep}}}{D_{e,\text{tot}}^{\text{neg}}} + \theta} \right) = 2 \sin \left( \sqrt{\frac{\lambda n_{e,0}^{\text{sep}}}{D_{e,\text{tot}}^{\text{sep}}} + \theta} \right) \cos \left( \sqrt{\frac{\lambda n_{e,0}^{\text{sep}}}{D_{e,\text{tot}}^{\text{sep}}} + \theta} \right)
\]

\[
= \frac{2k_2^2 \sqrt{n_{e,0}^{\text{pos}} D_{e,\text{tot}}^{\text{pos}}} \sin \left( \sqrt{\frac{\lambda n_{e,0}^{\text{pos}}}{D_{e,\text{tot}}^{\text{pos}}} + \theta} \right)}{k_1^2 \sqrt{n_{e,0}^{\text{sep}} D_{e,\text{tot}}^{\text{sep}}}} + \frac{k_2^2 n_{e,0}^{\text{pos}}}{k_1^2 \sqrt{n_{e,0}^{\text{sep}} D_{e,\text{tot}}^{\text{sep}}}}.
\]

Now the second part of the sum is converted to,

\[
\sin (2\theta) = 2 \sin (\theta) \cos (\theta) = \frac{2 \sqrt{n_{e,0}^{\text{neg}} D_{e,\text{tot}}^{\text{neg}}} \sin \left( \sqrt{\frac{\lambda n_{e,0}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}} + \theta} \right)}{k_1^2 \sqrt{n_{e,0}^{\text{sep}} D_{e,\text{tot}}^{\text{sep}}}} \cos \left( \sqrt{\frac{\lambda n_{e,0}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}} + \theta} \right)
\]

\[
= \frac{\sqrt{n_{e,0}^{\text{neg}} D_{e,\text{tot}}^{\text{neg}}} \sin \left( \sqrt{\frac{\lambda n_{e,0}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}} + \theta} \right)}{k_1^2 \sqrt{n_{e,0}^{\text{sep}} D_{e,\text{tot}}^{\text{sep}}}}.
\]

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2.3. The reduced order model (ROM)

The equivalent integration across the separator now becomes,

\[
\int_{0}^{1} k_1^2 \cos^2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{sep}}}{D_{e,\text{tot}}^{\text{sep}}}} \bar{x}_2 + \theta \right) n_{e,0}^{\text{sep}} d\bar{x}_2 = \frac{k_1^2 \sqrt{\frac{n_{e,0}^{\text{pos}} D_{e,\text{tot}}^{\text{pos}}}}}{4\sqrt{\lambda}} \left( 2 \sqrt{\frac{\lambda n_{e,0}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}}} \right)
\]

Finally putting all three terms together the integration becomes,

\[
\int_{0}^{3} \Psi^2(\bar{x}, \lambda) n_{e,0} d\bar{x} = \int_{0}^{1} \cos^2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{neg}}}{D_{e,\text{tot}}^{\text{neg}}}} \bar{x}_1 \right) n_{e,0}^{\text{neg}} d\bar{x}_1
\]

\[
+ \int_{0}^{1} k_1^2 \cos^2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{sep}}}{D_{e,\text{tot}}^{\text{sep}}}} \bar{x}_2 + \theta \right) n_{e,0}^{\text{sep}} d\bar{x}_2
\]

\[
+ \int_{0}^{1} k_2^2 \cos^2 \left( \sqrt{\frac{\lambda n_{e,0}^{\text{pos}}}{D_{e,\text{tot}}^{\text{pos}}}} \bar{x}_3 \right) n_{e,0}^{\text{pos}} d\bar{x}_3
\]

\[
\int_{0}^{3} \Psi^2(\bar{x}, \lambda) n_{e,0} d\bar{x} = \left( \frac{n_{e,0}^{\text{neg}} D_{e,\text{tot}}^{\text{neg}}}{4\sqrt{\lambda}} \right) + \frac{n_{e,0}^{\text{neg}}}{2}
\]

\[
+ \left( \frac{k_1^2 \sqrt{n_{e,0}^{\text{pos}} D_{e,\text{tot}}^{\text{pos}}}}{4\sqrt{\lambda}} \right) - \frac{n_{e,0}^{\text{neg}} D_{e,\text{tot}}^{\text{neg}}}{4\sqrt{\lambda}} + \frac{k_2^2 n_{e,0}^{\text{sep}}}{2}
\]

\[
+ \left( \frac{k_2^2 \sqrt{n_{e,0}^{\text{pos}} D_{e,\text{tot}}^{\text{pos}}}}{4\sqrt{\lambda}} \right) + \frac{k_2^2 n_{e,0}^{\text{pos}}}{2}
\]

\[
= \frac{n_{e,0}^{\text{neg}}}{2} + \frac{k_1^2 n_{e,0}^{\text{sep}}}{2} + \frac{k_2^2 n_{e,0}^{\text{pos}}}{2}.
\]
2.3. The reduced order model (ROM)

To ensure that the integral equals one, the eigenfunctions are multiplied by

\[ k_0 = \sqrt{\frac{2}{n_{e,0} \neg + k_1^2 n_{e,0} \text{sep} + k_2^2 n_{e,0} \text{pos}}} \]

The final set of eigenfunctions are now defined as,

\[ \bar{x}_1 = \bar{x} \]

\[ \Psi_{\text{neg}}(\bar{x}_1, \lambda) = k_0 \cos \left( \sqrt{\frac{\lambda n_{e,0} \neg}{D_{e,\text{tot}}} \bar{x}_1} \right), 0 \leq \bar{x}_1 < 1 \]

\[ \bar{x}_2 = \bar{x} - 1 \]

\[ \Psi_{\text{sep}}(\bar{x}_2, \lambda) = k_0 k_1 \cos \left( \sqrt{\frac{\lambda n_{e,0} \text{sep}}{D_{e,\text{tot}}} \bar{x}_2 + \theta} \right), 0 \leq \bar{x}_2 \leq 1 \]

\[ \bar{x}_3 = -\bar{x} + 3 \]

\[ \Psi_{\text{pos}}(\bar{x}_3, \lambda) = k_0 k_2 \cos \left( \sqrt{\frac{\lambda n_{e,0} \text{pos}}{D_{e,\text{tot}}} \bar{x}_3} \right), 0 \leq \bar{x}_3 < 1. \]

2.3.7.2 Heterogeneous case

Going back to the new PDE with the driving function included,

\[ \frac{n_{e,0}}{\partial t} \frac{\partial (\bar{n}_{e,\text{ratio}}(\bar{x}, t))}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( D_{e,\text{tot}} \frac{\partial \bar{n}_{e,\text{ratio}}(\bar{x}, t)}{\partial \bar{x}} \right) + j_{\text{tot}}(x, t) \quad (2.31) \]

Following the same steps from Lee, using Green’s identity and using the eigenfunctions found earlier,

\[ \frac{d\bar{n}_{e,\text{ratio},n}(t)}{dt} = -\lambda_n \bar{n}_{e,\text{ratio},n}(t) + \int_0^3 j_{\text{tot}}(\bar{x}, t)\Psi(\bar{x}, \lambda)d\bar{x}. \]
2.3. The reduced order model (ROM)

We define $j_{\text{tot},n}$ corresponding to the $n$th eigenvalue,

$$\int_{0}^{3} j_{\text{tot}}(\bar{x}, t)\Psi(\bar{x}, \lambda) d\bar{x} = j_{\text{tot},n}(t)$$

Therefore, taking Laplace transforms of Eq. (2.31),

$$s \tilde{N}_{\text{e},\text{ratio},n}(s) = -\lambda_{n} \tilde{N}_{\text{e},\text{ratio},n}(s) + J_{\text{tot},n}(s)$$

Collecting terms gives a transfer function for $\tilde{N}_{\text{e},\text{ratio},n}(s)$

$$\frac{\tilde{N}_{\text{e},\text{ratio},n}(s)}{I_{\text{app}}(s)} = \frac{1}{s + \lambda_{n}} \frac{J_{\text{tot},n}(s)}{I_{\text{app}}(s)}$$

where,

$$\int_{0}^{3} \frac{J_{\text{tot}}(\bar{x}, s)}{I_{\text{app}}(s)}\Psi(\bar{x}, \lambda) d\bar{x} = \frac{J_{\text{tot},n}(s)}{I_{\text{app}}(s)}.$$
2.3. The reduced order model (ROM)

To simplify this equation a new function of \( s \) is defined as

\[
\int^{\text{neg}}(s) = \frac{\nu^{\text{neg}}(s) \sinh(\nu^{\text{neg}}(s))}{\nu^{\text{neg}}(s) + \lambda_n b_1^2} \left( \sigma^{\text{neg}}_{\text{tot}} \cos(\sqrt{\lambda_1 b_1}) + \kappa^{\text{neg}}_{\text{tot}} \right)
\]

\[
= \frac{\nu^{\text{neg}}(s) \sqrt{\lambda_1 b_1} \sin(\sqrt{\lambda_1 b_1})}{\nu^{\text{neg}}(s) + \lambda_n b_1^2} \left( \sigma^{\text{neg}}_{\text{tot}} \cosh(\nu^{\text{neg}}(s)) + \kappa^{\text{neg}}_{\text{tot}} \right).
\]

(2.32)

Now using \( \int^{\text{neg}}(s) \) the equation becomes just

\[
\frac{J^{\text{neg}}_{\text{tot,n}}(s)}{I_{\text{app}}(s)} = k_0 \int^{\text{neg}}(s).
\]

The positive electrode follows the same procedure, where by \( b_3 = \sqrt{\frac{n^{\text{pos}}_{e,0}}{D_{e,\text{tot}}}} \),

\[
\frac{J^{\text{pos}}_{\text{tot,n}}(s)}{I_{\text{app}}(s)} = -k_0 k_2 \nu^{\text{pos}}(s) \sinh(\nu^{\text{pos}}(s)) \left( \sigma^{\text{pos}}_{\text{tot}} \cos(\sqrt{\lambda_3 b_3}) + \kappa^{\text{pos}}_{\text{tot}} \right)
\]

\[
\frac{\nu^{\text{pos}}(s) \sqrt{\lambda_3 b_3} \sin(\sqrt{\lambda_3 b_3})}{\nu^{\text{pos}}(s) + \lambda_n b_3^2} \left( \sigma^{\text{pos}}_{\text{tot}} \cosh(\nu^{\text{pos}}(s)) + \kappa^{\text{pos}}_{\text{tot}} \right)
\]

\[
- \frac{\nu^{\text{pos}}(s) \sqrt{\lambda_3 b_3} \sin(\sqrt{\lambda_3 b_3})}{\nu^{\text{pos}}(s) + \lambda_n b_3^2} \left( \sigma^{\text{pos}}_{\text{tot}} \cosh(\nu^{\text{pos}}(s)) + \kappa^{\text{pos}}_{\text{tot}} \right) \text{ sinh}(\nu^{\text{pos}}(s))
\]

(2.32)

Similarly, we define \( \int^{\text{pos}}(s) \) as,

\[
\int^{\text{pos}}(s) = \frac{\nu^{\text{pos}}(s) \sinh(\nu^{\text{pos}}(s))}{\nu^{\text{pos}}(s) + \lambda_n b_3^2} \left( \sigma^{\text{pos}}_{\text{tot}} \cos(\sqrt{\lambda_3 b_3}) + \kappa^{\text{pos}}_{\text{tot}} \right)
\]

\[
= \frac{\nu^{\text{pos}}(s) \sqrt{\lambda_3 b_3} \sin(\sqrt{\lambda_3 b_3})}{\nu^{\text{pos}}(s) + \lambda_n b_3^2} \left( \sigma^{\text{pos}}_{\text{tot}} \cosh(\nu^{\text{pos}}(s)) + \kappa^{\text{pos}}_{\text{tot}} \right)
\]

(2.33)

which simplifies our answer to:

\[
\frac{J^{\text{pos}}_{\text{tot,n}}(s)}{I_{\text{app}}(s)} = -k_0 k_2 \int^{\text{pos}}(s).
\]

Putting everything back together, the transfer function for the \( n \)th eigenfunction of lithium concentration in the electrolyte becomes,

\[
\frac{\tilde{N}_{e,\text{ratio},n}(s)}{I_{\text{app}}(s)} = \frac{1}{s + \lambda_n} \left( \frac{J^{\text{neg}}_{\text{tot,n}}(s)}{I_{\text{app}}(s)} + \frac{J^{\text{pos}}_{\text{tot,n}}(s)}{I_{\text{app}}(s)} \right)
\]

\[
= \frac{1}{s + \lambda_n} \left[ \frac{J^{\text{neg}}_{\text{tot,n}}(s)}{I_{\text{app}}(s)} + \frac{J^{\text{pos}}_{\text{tot,n}}(s)}{I_{\text{app}}(s)} \right]
\]

\[
= \frac{k_0, n}{s + \lambda_n} \left( \int^{\text{neg}}_{\text{n}}(s) - k_2, n \int^{\text{pos}}_{\text{n}}(s) \right)
\]
2.3. **The reduced order model (ROM)**

To find the total transfer function \( \tilde{N}_{e,\text{ratio}}(\bar{x}, s) \), the all transfer function are summed,

\[
\frac{\tilde{N}_{e,\text{ratio}}(\bar{x}, s)}{I_{\text{app}}(s)} = \sum \frac{\tilde{N}_{e,\text{ratio,n}}(s)}{I_{\text{app}}(s)} \Psi(\bar{x}, \lambda_n).
\]

The total transfer function for any region is,

\[
\tilde{N}_{e,\text{ratio}}(\bar{x}, s) = \begin{cases} 
\sum \frac{k_{1,n}^2}{s+\lambda_n} (int_{n}^{\text{neg}}(s) - k_{2,n} int_{n}^{\text{pos}}(s)) \cos \left( \sqrt{\frac{\lambda_{n,n,e,0}}{D_{e,\text{tot}}}} \bar{x} \right) , & 0 \leq \bar{x} \leq 1 \\
\sum \frac{k_{1,n}^2}{s+\lambda_n} (int_{n}^{\text{neg}}(s) - k_{2,n} int_{n}^{\text{pos}}(s)) \cos \left( \sqrt{\frac{\lambda_{n,n,e,0}}{D_{e,\text{tot}}}} (\bar{x} - 1) + \theta \right) , & 1 < \bar{x} < 2 \\
\sum \frac{k_{1,n}^2 k_{2,n}}{s+\lambda_n} (int_{n}^{\text{neg}}(s) - k_{2,n} int_{n}^{\text{pos}}(s)) \cos \left( \sqrt{\frac{\lambda_{n,n,e,0}}{D_{e,\text{tot}}}} (-\bar{x} + 3) \right) , & 2 \leq \bar{x} \leq 3
\end{cases}
\]  

(2.34)

### 2.3.8 Linearized overpotential

Since a transfer function for the overpotential is needed in frequency analysis, a simple Laplace transformation is performed on the linear time-domain equation,

\[
R_{\text{ct,reg,tot}}^{\text{reg}}(\bar{x}, t) \approx R_{\text{ct,reg,tot}}^{\text{reg}}(\bar{x}, t)
\]

\[
\eta_{\text{reg}}^{\text{reg}}(z, s) \approx R_{\text{ct,reg}}^{\text{reg}} \frac{J_{\text{tot}}^{\text{reg}}(z, s)}{I_{\text{app}}(s)}.
\]

(2.35)

### 2.3.9 Summary

A new set of transfer functions has been reformulated in terms of the new lumped parameters yet still retains the variables of interested for battery cell control. These new transfer functions, along with associated nonlinear functions are used in the following chapters to calculate impedances.
In this chapter, we describe a new process to identify the parameters of a lithium-ion cell model by utilizing only cell current and voltage relationships. To begin, the system identification is broken up into different methods, where each identifies a subset of battery-cell parameters. If the chemistries in each electrode do not have a known open-circuit voltage to depth-of-discharge relationship, the battery cell is physically taken apart to separate the anode and cathode to obtain voltage measurements. With some of the parameters identified, other non-physically measurable properties of the cell are obtained through a series of tests aimed at identifying the impedance of the cell. Once a set of satisfactory data is collected, the data can be related back to the partial-differential equations that govern the cell’s dynamics. An optimization routine finds the set of PDE parameters that best matches the actual cell impedance values.

3.1 Open-circuit voltage (OCV) testing

The system-identification process starts by finding the open-circuit potential (OCP) of a half cell for both the anode and the cathode and the open-circuit voltage (OCV) of the whole cell. This test will find the open-circuit potential of an electrode over a range of SOCs and identify the $U_{ocp}$ function of each electrode, as well as an estimate of $n_{s,0}^{reg}$ and $n_{s,\Delta_{max}}^{reg}$. Fig. 3.1 shows a cell’s $U_{ocp}$ function and its relationship to the $U_{ocp}$ functions of the two separate electrodes.
3.1. Open-circuit voltage (OCV) testing

Figure 3.1: Open circuit voltage breakdown between two electrodes

The potential of each electrode is needed in order to find parameter values for each electrode individually. For the “Doyle” cell, these functions are given explicitly [16]. For an actual cell, half cells are obtained by physically separating the electrodes and attaching a pure lithium electrode to each half, thus resulting in two half cells. It is possible to run a constant slow discharge/charge test to find the separate $U_{ocp}$ functions at various levels of capacity. The separated electrodes form new cell’s that are referred to as a coin cells.

Since, the initial capacities of the cell and electrodes are unknown, an optimization routine finds the best fit for each $U_{ocp}$ curve. To start, the manufacturer’s upper limit on voltage corresponds to the $U_{ocp}^{cell}$ at 100% SOC. Similarly the manufacture’s lower voltage limit corresponds to the $U_{ocp}^{cell}$ at 0% SOC. To find the OCP curves of each electrode, we will use the known facts:

$$U_{ocp,100\%}^{cell} = U_{ocp,100\%}^{pos} - U_{ocp,100\%}^{neg}$$

$$U_{ocp,0\%}^{cell} = U_{ocp,0\%}^{pos} - U_{ocp,0\%}^{neg}$$

Further, we define coin-cell capacities as:

$$\tilde{n}_{coin,100\%}^{neg} - \tilde{n}_{coin,0\%}^{neg} = Q_{coin}^{neg}$$
3.1. Open-circuit voltage (OCV) testing

\[ \tilde{n}_{\text{pos}}^{\text{coin},0\%} - \tilde{n}_{\text{pos}}^{\text{coin},100\%} = Q_{\text{coin}}^{\text{pos}} \]

To relate the coin-cell capacities to the full-cell capacity (\(Q_{\text{cell}}\) is known), two scaling factors are introduced, \(\text{Scale}^{\text{neg}}\), \(\text{Scale}^{\text{pos}}\). This relationship becomes,

\[
Q_{\text{coin}}^{\text{neg}} \cdot \text{Scale}^{\text{neg}} = Q_{\text{coin}}^{\text{pos}} \cdot \text{Scale}^{\text{pos}} = Q_{\text{cell}}
\]

\[
\left( \tilde{n}_{\text{coin},100\%}^{\text{neg}} - \tilde{n}_{\text{coin},0\%}^{\text{neg}} \right) \cdot \text{Scale}^{\text{neg}} = Q_{\text{cell}}
\]

\[
\left( \tilde{n}_{\text{coin},0\%}^{\text{pos}} - \tilde{n}_{\text{coin},100\%}^{\text{pos}} \right) \cdot \text{Scale}^{\text{pos}} = Q_{\text{cell}}
\]

The potential of each coin cell is then combined to estimate the potential of the full cell and given by,

\[ U_{\text{ocp}}^{\text{pos}} (\tilde{n}_{\text{coin}}^{\text{pos}}) - U_{\text{ocp}}^{\text{neg}} (\tilde{n}_{\text{coin}}^{\text{neg}}) = U_{\text{ocp}}^{\text{cell}} (\tilde{n}) . \]

We now define a cost function that penalizes the potential difference between the full-cell and the combined half cells. Ideally this error should approach zero when the operating points of both half cells match the operating points of the individual electrodes in the full-cell,

\[ J = \left( U_{\text{ocp}}^{\text{cell}} (\tilde{n}) - \left( U_{\text{ocp}}^{\text{pos}} (\tilde{n}_{\text{coin}}^{\text{pos}}) - U_{\text{ocp}}^{\text{neg}} (\tilde{n}_{\text{coin}}^{\text{neg}}) \right) \right)^2 \]

for

\[ 0 < \tilde{n} < Q_{\text{cell}} \]

\[ \tilde{n}_{\text{coin},0\%}^{\text{neg}} < \tilde{n}_{\text{coin}}^{\text{neg}} < \tilde{n}_{\text{coin},100\%}^{\text{neg}} \]

\[ \tilde{n}_{\text{coin},100\%}^{\text{pos}} < \tilde{n}_{\text{coin}}^{\text{pos}} < \tilde{n}_{\text{coin},0\%}^{\text{pos}} \]

The cost function is described in terms of three independent variables. To change this everything is modified to be dependent on \(\tilde{n}\) and shown by adjusting the domains of the variables to be the same,

\[ 0 < \left( \tilde{n}_{\text{coin}}^{\text{neg}} - \tilde{n}_{\text{coin},0\%}^{\text{neg}} \right) \cdot \text{Scale}^{\text{neg}} < Q_{\text{cell}} \]

\[ -Q_{\text{cell}} < \left( \tilde{n}_{\text{coin}}^{\text{pos}} - \tilde{n}_{\text{coin},0\%}^{\text{pos}} \right) \cdot \text{Scale}^{\text{pos}} < 0. \]
3.2. \( R_0 \) testing

Now the variables, \( \bar{n}_{\text{coin}}^{\text{neg}}, \bar{n}_{\text{coin}}^{\text{pos}} \) are put in terms of \( \bar{n} \) by writing,

\[
\begin{align*}
\left( \bar{n}_{\text{coin}}^{\text{neg}} - \bar{n}_{\text{coin}}^{\text{neg},0\%} \right) \text{Scale}^{\text{neg}} &= \bar{n} \\
- \left( \bar{n}_{\text{coin}}^{\text{pos}} - \bar{n}_{\text{coin}}^{\text{pos},0\%} \right) \text{Scale}^{\text{pos}} &= \bar{n}.
\end{align*}
\]

Solving each variable separately we can define the relationship between the independent variables as,

\[
\begin{align*}
\bar{n}_{\text{coin}}^{\text{neg}} &= \frac{\bar{n}}{\text{Scale}^{\text{neg}}} + \bar{n}_{\text{coin}}^{\text{neg},0\%} = \frac{\bar{n}}{Q_{\text{cell}}} \left( \bar{n}_{\text{coin}}^{\text{neg},100\%} - \bar{n}_{\text{coin}}^{\text{neg},0\%} \right) + \bar{n}_{\text{coin}}^{\text{neg},0\%} \\
\bar{n}_{\text{coin}}^{\text{pos}} &= -\frac{\bar{n}}{\text{Scale}^{\text{pos}}} + \bar{n}_{\text{coin}}^{\text{pos},0\%} = -\frac{\bar{n}}{Q_{\text{cell}}} \left( \bar{n}_{\text{coin}}^{\text{pos},0\%} - \bar{n}_{\text{coin}}^{\text{pos},100\%} \right) + \bar{n}_{\text{coin}}^{\text{pos},0\%}.
\end{align*}
\]

Finally, plugging back into the cost function,

\[
J = \left[ U_{\text{ocp}}^{\text{cell}} (\bar{n}) \right. \\
\left. - U_{\text{ocp}}^{\text{pos}} \left( \frac{\bar{n}}{Q_{\text{cell}}} \left( \bar{n}_{\text{coin}}^{\text{pos},100\%} - \bar{n}_{\text{coin}}^{\text{pos},0\%} \right) + \bar{n}_{\text{coin}}^{\text{pos},0\%} \right) \right] ^2
\]

for,

\[0 < \bar{n} < Q_{\text{cell}},\]

the only independent variable remaining is \( \bar{n} \), with parameters, \( \bar{n}_{\text{coin}}^{\text{pos},0\%}, \bar{n}_{\text{coin}}^{\text{neg},0\%}, \bar{n}_{\text{coin}}^{\text{pos},100\%}, \) and \( \bar{n}_{\text{coin}}^{\text{neg},100\%} \). This final cost function is used in an optimization routine to find the four parameters shown in Table 3.1; these parameters produce an initial estimate of the \( \bar{n}_{\text{cell},0}^{\text{reg}}, \bar{n}_{\text{cell},\Delta_{\text{max}}}^{\text{reg}}, \bar{n}_{\text{cell},0}^{\text{reg}} \) and the \( U_{\text{ocp}}^{\text{reg}} \) functions.

3.2 \( R_0 \) testing

After the thermodynamic open-circuit potential functions have been found, the next step is to find parameters related to the instantaneous resistance at different current-pulse magnitudes and different starting states of charge. These pulse tests can be run on a real cell
3.2. \( R_0 \) testing

<table>
<thead>
<tr>
<th>Negative electrode</th>
<th>Positive electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tilde{n}_{\text{coin},0%} )</td>
<td>( \tilde{n}_{\text{coin},0%} )</td>
</tr>
<tr>
<td>( \tilde{n}_{\text{coin},100%} )</td>
<td>( \tilde{n}_{\text{coin},100%} )</td>
</tr>
</tbody>
</table>

by finding the instantaneous voltage change when the cell is subjected to a current-pulse. The data in this chapter assumes an ideal virtual lithium-ion cell using the Doyle-cell parameters. The Doyle cell is simulated using a full-order model (FOM) created with known parameter values in COMSOL. The pulse tests are set up to run at initial SOCs from 0% to 100% in increments of 10%. This is easily configured in Matlab but will take precise calibration when running on an unknown real cell. At each of these SOCs the current-pulse magnitude is changed from 0.1C to 10C using step sizes chosen by the user. For this chapter the C-rates and initial SOCs used are shown in Table 3.4. The resistance is measured by using the current-pulse height and the resulting voltage change at the time the pulse was applied to arrive at a value for the feedthrough or instantaneous resistance. This is performed in Matlab at all initial SOCs and current magnitudes to span a set of resistance values that characterize the battery cell.

Next, we develop analytic equations for the resistance value with initial SOC and C-rate as independent variables. First we define the equation for the the measured voltage and overpotential as,

\[
v(t) = \phi_s^{\text{pos}}(0, t) - \phi_s^{\text{neg}}(0, t)
\]

\[
\eta_{\text{reg}}(\vec{x}, t) = \phi_s^{\text{reg}}(\vec{x}, t) - \phi_e(\vec{x}, t) - U_{\text{ocp}}(\vec{x}, t) - j_{\text{tot}}(\vec{x}, t) F \eta_{\text{film, tot}},
\]

Combining these two equations gives the time-domain representation of the cell voltage as,

\[
v(t) = \left( \eta_{\text{pos}}(0, t) + \phi_e(3, t) + U_{\text{ocp}}(0, t) + j_{\text{tot}}(0, t) F \eta_{\text{film, tot}} \right) - \left( \eta_{\text{neg}}(0, t) + \phi_e(0, t) + U_{\text{ocp}}(0, t) + j_{\text{tot}}(0, t) F \eta_{\text{film, tot}} \right),
\]

where,

\[
\phi_e(\vec{x}, t) = \left[ \phi_e(\vec{x}, t) \right]^1 - \phi_s^{\text{reg}}(0, t) + \phi_e^{\text{reg}}(0, t) + \left[ \phi_e(\vec{x}, t) \right]^2.
\]
3.2. \( R_0 \) testing

This equation can be separated into linear and nonlinear parts by defining,

\[
v_{\text{linear}}(t) = (j_{\text{tot}}^{\text{pos}}(0, t) R_{\text{film,tot}}^{\text{pos}} - j_{\text{tot}}^{\text{neg}}(0, t) R_{\text{film,tot}}^{\text{neg}}) F + \left[ \tilde{\phi}_e(3, t) \right]_1.
\]

The total voltage equation is now,

\[
v(t) = v_{\text{linear}}(t) + (\eta^{\text{pos}}(0, t) - \eta^{\text{neg}}(0, t)) + \left[ \tilde{\phi}_e(3, t) \right]_2 + \left( U_{\text{ocp}}^{\text{pos}}(0, t) - U_{\text{ocp}}^{\text{neg}}(0, t) \right).
\]

The linear portion can now be made into a transfer function with \( I_{\text{app}}(s) \) as an input,

\[
\frac{V_{\text{linear}}(s)}{I_{\text{app}}(s)} = \left( R_{\text{film,tot}}^{\text{pos}} I_{\text{app}}(s) - R_{\text{film,tot}}^{\text{neg}} I_{\text{app}}(s) \right) F + \left[ \tilde{\Phi}_e(3, s) \right]_1. \tag{3.2}
\]

To find the resistance value, we use the linear voltage transfer function, and let \( s \) approaches infinity in all of the transfer functions to give,

\[
\lim_{s \to \infty} \frac{V_{\text{linear}}(s)}{I_{\text{app}}(s)} = R_{0, \text{linear}}.
\]

Next, we find the limit of the impedance ratio as \( s \) approaches infinity, where \( \beta = \sqrt{s/D_{s,\text{tot}}} \),

\[
\nu^{\text{reg}}(\infty) = \lim_{s \to \infty} \nu^{\text{reg}}(s) = \frac{\sqrt{\frac{1}{\sigma_{\text{tot}}^{\text{pos}}} + \frac{1}{\nu^{\text{reg}}(s)}}}{\sqrt{R_{\text{reg}}}}.
\]

Next, we move to the lithium flux equation

\[
\lim_{s \to \infty} j_{\text{tot}}^{\text{pos}}(0, s) = -\frac{\nu^{\text{pos}}(\infty)}{F(\nu^{\text{pos}}(\infty) + \sigma_{\text{tot}}^{\text{pos}})} \left( \frac{\sigma_{\text{tot}}^{\text{pos}} + \kappa_{\text{tot}}^{\text{pos}} \cosh(\nu^{\text{pos}}(\infty))}{\sinh(\nu^{\text{pos}}(\infty))} \right).
\]

And finally to the last transfer function where,

\[
\lim_{s \to \infty} \left[ \frac{\Phi_e(3, s)}{I_{\text{app}}(s)} \right]_1 = -\frac{1}{\kappa_{\text{tot}}^{\text{neg}}} + \frac{\left( 1 - \frac{\sigma_{\text{tot}}^{\text{neg}}}{\kappa_{\text{tot}}^{\text{neg}}} \right) \tanh \left( \frac{\nu^{\text{neg}}(\infty)}{2} \right) - \nu^{\text{neg}}(\infty)}{\left( \kappa_{\text{tot}}^{\text{neg}} + \sigma_{\text{tot}}^{\text{neg}} \right) \nu^{\text{neg}}(\infty)}
\]

\[
\frac{\left( 1 + \frac{\sigma_{\text{tot}}^{\text{neg}}}{\kappa_{\text{tot}}^{\text{neg}}} \right) \cosh(\nu^{\text{pos}}(\infty))}{\sinh(\nu^{\text{neg}}(\infty))} \cosh(\nu^{\text{pos}}(\infty))
\]

\[
+ \frac{\left( \kappa_{\text{tot}}^{\text{neg}} + \sigma_{\text{tot}}^{\text{neg}} \right) \sinh(\nu^{\text{pos}}(\infty)) \nu^{\text{pos}}(\infty)}{\left( \kappa_{\text{tot}}^{\text{pos}} + \sigma_{\text{tot}}^{\text{neg}} \right) \nu^{\text{neg}}(\infty)}
\]

\[
+ \frac{\sigma_{\text{tot}}^{\text{neg}}}{\kappa_{\text{tot}}^{\text{neg}}}
\]

\[
- \frac{1}{\kappa_{\text{tot}}^{\text{pos}} + \sigma_{\text{tot}}^{\text{neg}}}.
\]
3.2. $R_0$ testing

This function can be simplified by combining terms in the fractions,

$$\lim_{s \to \infty} \left[ \Phi_e (3, s) \right]_1 = \frac{-1}{\kappa_{\text{tot}}^{\text{sep}}} + \frac{\left( 1 - \frac{\kappa_{\text{tot}}^{\text{neg}}}{\kappa_{\text{tot}}^{\text{pos}}} \right) \tanh \left( \frac{\nu_{\text{pos}}(\infty)}{2} \right) - \nu_{\text{neg}}(\infty)}{\left( \kappa_{\text{tot}}^{\text{neg}} + \sigma_{\text{tot}}^{\text{neg}} \right) \nu_{\text{neg}}(\infty)} \cosh \left( \nu_{\text{pos}}(\infty) \right) - \left( 1 + \frac{\kappa_{\text{tot}}^{\text{pos}}}{\kappa_{\text{tot}}^{\text{neg}}} \cosh \left( \nu_{\text{pos}}(\infty) \right) \right)$$

Finally using the trigonometric substitution

$$\frac{\cosh (x) - 1}{\sinh (x)} = \tanh \left( \frac{x}{2} \right),$$

we get the simplified result,

$$\lim_{s \to \infty} \left[ \Phi_e (3, s) \right]_1 = \frac{-1}{\kappa_{\text{tot}}^{\text{sep}}} + \frac{\left( 1 - \frac{\kappa_{\text{tot}}^{\text{neg}}}{\kappa_{\text{tot}}^{\text{pos}}} \right) \tanh \left( \frac{\nu_{\text{pos}}(\infty)}{2} \right) - \nu_{\text{neg}}(\infty)}{\left( \kappa_{\text{tot}}^{\text{neg}} + \sigma_{\text{tot}}^{\text{neg}} \right) \nu_{\text{neg}}(\infty)} \cosh \left( \nu_{\text{pos}}(\infty) \right) - \left( 1 + \frac{\kappa_{\text{tot}}^{\text{pos}}}{\kappa_{\text{tot}}^{\text{neg}}} \cosh \left( \nu_{\text{pos}}(\infty) \right) \right)$$

To find the total instantaneous resistance, the nonlinear portion of the voltage equation is examined and combined with the linear portion $R_{0,\text{linear}}$, such that,

$$R_0 = R_{0,\text{linear}} + R_{0,\text{nonlinear}}.$$

Since a transfer function is not possible for the nonlinear equations to get the instantaneous resistance, the limit of the time-domain expressions as time goes to zero is found,

$$R_{0,\text{nonlinear}} = \lim_{t \to 0} \eta (3, t) - \eta (0, t) + \lim_{t \to 0} \frac{\left[ \tilde{\phi}_c (3, t) \right]_2}{i_{\text{app}} (t)} + \lim_{t \to 0} \frac{\left( U_{\text{pos}} (0, t) - U_{\text{neg}} (0, t) \right)}{i_{\text{app}} (t)}.$$
3.2. \( R_0 \) Testing

Let’s start with the nonlinear overpotential term,

\[
j_{\text{tot}}(\bar{x}, t) = j_{0, \text{tot}} \sinh \left( \frac{F}{2RT} \eta \right).
\]

This equation can be solved for the variable \( \eta \) as,

\[
\frac{2RT}{F} \text{asinh} \left( \frac{j_{\text{tot}}(\bar{x}, t)}{j_{\text{eq, tot}}} \right) = \eta (\bar{x}, t).
\]

Now taking the limit of \( \frac{\eta(\bar{x}, t)}{i_{\text{app}}(t)} \) as time goes to zero gives,

\[
\lim_{t \to 0} \eta (\bar{x}, t) = \frac{2RT}{F} \text{asinh} \left( \frac{j_{\text{tot}}(\bar{x}, 0)}{j_{0, \text{tot}}} \right) i_{\text{app}}(0^+) - \frac{2RT}{F} \text{asinh} \left( \frac{j_{\text{tot}}(0, 0)}{j_{0, \text{tot}}} \right) i_{\text{app}}(0^+).
\]

Since the concentrations of lithium cannot change instantaneously, the rest of the terms in \( R_{0, \text{nonlinear}} \) become,

\[
\lim_{t \to 0} \left[ \frac{\Phi_e(3, t)}{i_{\text{app}}(t)} \right] = 0
\]

\[
\lim_{t \to 0} \left( \frac{U_{\text{ocp}}^+(0, t) - U_{\text{ocp}}^-(0, t)}{i_{\text{app}}(t)} \right) = 0
\]

Putting everything together, the resistance term can be written as a function of SOC and current-pulse amplitude \( i_{\text{app}}(0^+) \),

\[
R_0 \left( \text{SOC}, i_{\text{app}}(0^+) \right) = -\frac{R_{\text{film}, \text{pos}}}{F(\kappa_{\text{tot}} + \sigma_{\text{tot}})} \left( \frac{\sigma_{\text{tot}}^{\text{pos}} + \kappa_{\text{tot}}^{\text{pos}} \cosh(\nu_{\text{pos}}^{\text{pos}}(\infty))}{\sinh(\nu_{\text{pos}}^{\text{pos}}(\infty))} \right)
\]

\[
-\frac{R_{\text{film}, \text{neg}}}{F(\kappa_{\text{tot}} + \sigma_{\text{tot}})} \left( \frac{\sigma_{\text{tot}}^{\text{neg}} + \kappa_{\text{tot}}^{\text{neg}} \cosh(\nu_{\text{neg}}^{\text{neg}}(\infty))}{\sinh(\nu_{\text{neg}}^{\text{neg}}(\infty))} \right)
\]

\[
-\frac{1}{\kappa_{\text{sep}}^{\text{pos}}} + \left( \frac{1 - \frac{\sigma_{\text{tot}}^{\text{pos}}}{\kappa_{\text{tot}}^{\text{pos}}}}{\nu_{\text{tot}}^{\text{neg}} + \sigma_{\text{tot}}^{\text{neg}}} \right) \frac{\nu_{\text{neg}}^{\text{neg}}(\infty) - \nu_{\text{neg}}^{\text{neg}}(\infty)}{2}
\]

\[
+ \frac{1}{\kappa_{\text{sep}}^{\text{neg}}} + \left( \frac{1 - \frac{\sigma_{\text{tot}}^{\text{neg}}}{\kappa_{\text{tot}}^{\text{neg}}}}{\nu_{\text{tot}}^{\text{pos}} + \sigma_{\text{tot}}^{\text{pos}}} \right) \frac{\nu_{\text{pos}}^{\text{pos}}(\infty) - \nu_{\text{pos}}^{\text{pos}}(\infty)}{2}
\]

\[
+ \frac{2RT}{F} \text{asinh} \left( \frac{j_{\text{tot}}(3, 0)}{j_{0, \text{tot}}} \right) i_{\text{app}}(0^+) - \frac{2RT}{F} \text{asinh} \left( \frac{j_{\text{tot}}(0, 0)}{j_{0, \text{tot}}} \right) i_{\text{app}}(0^+). \quad (3.3)
\]
3.3 Frequency response testing

<table>
<thead>
<tr>
<th>Table 3.2: List of parameters found with pulse testing</th>
<th>Negative Electrode</th>
<th>Separator</th>
<th>Positive Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_{\text{neg}}$</td>
<td>$\kappa_{\text{tot}}$</td>
<td>$\kappa_{\text{pos}}$</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\text{neg}}$</td>
<td>$\sigma_{\text{tot}}$</td>
<td>$\sigma_{\text{pos}}$</td>
<td></td>
</tr>
<tr>
<td>$k_{\text{step}}$</td>
<td>$k_{\text{step}}$</td>
<td>$k_{\text{step}}$</td>
<td></td>
</tr>
<tr>
<td>$P_{\text{film}}^{\text{tot, neg}}$</td>
<td>$P_{\text{film}}^{\text{tot, pos}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_{\text{cell},0}$</td>
<td>$n_{\text{cell},0}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n_{\text{cell}, \triangle, \text{max}}$</td>
<td>$n_{\text{cell}, \triangle, \text{max}}$</td>
<td></td>
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</tr>
</tbody>
</table>

Using the expression for the instantaneous resistance, the parameter values identified in Table 3.2 are able to be uniquely identified though optimizing measured pulse data.

3.3 Frequency response testing

When looking at the instantaneous resistance of a battery cell, the frequency involved in all of the transfer functions is considered only as it approaches infinity. To gain further insight into the cell, it is instructive to excite the cell over a wide range of frequencies. For these reasons a test was created to match the model’s frequency response to that obtained from a set of data collected from the cell. This frequency response testing identifies all of the remaining constant parameters as shown in Table 3.3. Frequency testing assumes that the tests are performed around equilibrium. This is approximated by using a small signal as an input at different SOCs and frequencies. For this test, $s = j\omega$ is substituted into all of the transfer functions, where the range of frequencies is determined by the user. Almost all transfer functions can be evaluated directly except for $\frac{N_{\text{ratio}}(\bar{x}, s)}{I_{\text{app}}(s)}$ which takes some effort to arrive at values for $\lambda$. This process of identifying the frequency response of a model starts with using the linear portion of the voltage equation shown by Eq. (3.2). The nonlinear portion needs to be linearized to find a total linear estimate of the cell’s potential with respect to a small-signal current input i.e,

$$v_{\text{nonlinear}}(t) = (\eta_{\text{pos}}(0, s) - \eta_{\text{neg}}(0, s)) + \left[\varphi_{e}(3, t)\right]_{2} + (U_{\text{ocp}}^{\text{pos}}(0, t) - U_{\text{ocp}}^{\text{pos}}(0, t)).$$
3.3. Frequency response testing

The impedance value at each frequency of the nonlinear cell voltage equation is computed starting with the open-circuit potential term in the voltage equation shown by Eq. (3.1). Using a first-order Taylor-series expansion this is written as,

\[ U_{ocp}(n^{reg}_{s,e}) \approx \frac{\partial U_{ocp}(n^{reg}_{s,e})}{\partial n^{reg}_{s,e}} n^{neg}_{s,e}(0, s) + U_{ocp}(n^{reg}_{s,0}) \]

A de-biased voltage function is defined as the resting potential of the cell subtracted from the actual potential of the cell,

\[ \tilde{v}(t) = v(t) - [U_{ocp}(n^{neg}_{s,0}) - U_{ocp}(n^{pos}_{s,0})] \]

This causes the de-biased nonlinear voltage function to become,

\[ \tilde{v}_{\text{nonlinear}}(t) = (\eta^{pos}(0, s) - \eta^{neg}(0, s)) + \left[ \tilde{\phi}_{e}(3, t) \right]_{2}^{2} \]

Moving on to the next terms, the linear transfer function of the overpotential term, \( \eta \), has already been performed in Chapter 2 and is shown by Eq. (2.35). Finally the transfer function for \( \frac{[\tilde{\phi}_{e}(s, s)]_{2}}{I_{\text{app}}(s)} \) shown by Eq. (2.25) is used with the final linearized transfer function of the nonlinear voltage terms,

\[ \frac{\tilde{V}_{\text{nonlinear}}(s)}{I_{\text{app}}(s)} = \left( R_{\text{ct,tot}} \frac{J_{\text{pos}}(s)}{I_{\text{app}}(s)} - R_{\text{ct,tot}} \frac{J_{\text{neg}}(0, s)}{I_{\text{app}}(s)} \right) + \frac{2RT(1-t_{0}^{\text{t}})}{F} \left( \frac{\tilde{N}_{e,\text{ratio}}(3, s)}{I_{\text{app}}(s)} - \frac{\tilde{N}_{e,\text{ratio}}(0, s)}{I_{\text{app}}(s)} \right) \]

\[ + \left( \frac{\partial U_{ocp}(n^{pos}_{s,e})}{\partial n^{reg}_{s,e}} n^{neg}_{s,e}(0, s) \right) \]

\[ - \left( \frac{\partial U_{ocp}(n^{neg}_{s,e})}{\partial n^{reg}_{s,e}} n^{neg}_{s,e}(0, s) \right) \]
3.3. Frequency response testing

Combining the linearized nonlinear and linear voltage transfer functions the total transfer function for the cell voltage is now,

\[
\frac{\tilde{V}(s)}{I_{\text{app}}(s)} = F \left( \frac{P_{s,e,\text{tot}}^\text{pos}}{I_{\text{app}}(s)} \frac{J_{\text{tot}}^\text{pos}(s)}{I_{\text{app}}(s)} - R_{s,e,\text{tot}}^\text{reg} \frac{J_{\text{tot}}^\text{reg}(0,s)}{I_{\text{app}}(s)} \right)
\]

\[
+ \frac{[\tilde{\Phi}_e(3,s)]}{I_{\text{app}}(s)} + \frac{2RT(1-t^0_+)}{F} \left( \frac{\tilde{N}_{e,\text{ratio}}(3,s)}{I_{\text{app}}(s)} - \frac{\tilde{N}_{e,\text{ratio}}(0,s)}{I_{\text{app}}(s)} \right)
\]

\[
+ \frac{\partial U_{\text{ocp}}(n_{s,e})}{\partial n_{s,e}} \bigg|_{n_{s,e,0}} \frac{\tilde{N}_{s,e}^\text{pos}(0,s)}{I_{\text{app}}(s)} - \frac{\partial U_{\text{ocp}}(n_{s,e})}{\partial n_{s,e}} \bigg|_{n_{s,e,0}} \frac{\tilde{N}_{s,e}^\text{neg}(0,s)}{I_{\text{app}}(s)} \bigg) .
\] (3.4)

Figure 3.2: Nyquist plot of the Doyle cell

Notice that the transfer function of \( \eta\) is combined with \( R_{\text{reg}}^\text{tot} \) to form \( R_{s,e,\text{tot}}^\text{reg} \). To find the impedances at different frequencies, Eq. (3.4) uses the linear approximation to the \( [\tilde{\Phi}_e(x,s)] \) transfer function shown by Eq. (2.25), along with Eq. (2.23), (2.22), and (2.20). The expanded form of Eq. (3.4) uses all of the parameters in Table 3.2 as well as the new parameters shown in Table 3.3. Generating a Nyquist plot parametrically plots the imaginary portion of the frequency response versus the real portion. This gives a window into the magnitude and phase response as frequencies are increased at different SOC setpoints. Figure 3.2 shows the Nyquist plot of the linearized cell model using the Doyle parameter values.

In order to reduce the number of parameters to the minimum set, recall the equation for \( \kappa_{\text{tot}}^\text{reg} \) which is found in pulse testing. Defining a ratio of \( \kappa_{\text{tot}}^\text{reg} \) terms in each electrode, and noting that \( \kappa_{\text{tot}}^\text{reg} = \frac{\kappa_{\text{reg}}}{L_{\text{reg}}} \), and \( \kappa_{\text{eff}} = \kappa(\varepsilon^e_{\text{reg}})^{\text{brug}} \), we arrive at,
3.4. $R_{ss}$ testing

<table>
<thead>
<tr>
<th>Negative Electrode</th>
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<tbody>
<tr>
<td>$n_{e,0}^{neg}$</td>
<td>$n_{sep}$</td>
<td>$n_{e,0}^{pos}$</td>
</tr>
<tr>
<td>$D_{e,tot}^{neg}$</td>
<td>$D_{sep}$</td>
<td>$D_{e,tot}^{pos}$</td>
</tr>
<tr>
<td>$D_{s,tot}^{neg}$</td>
<td></td>
<td>$D_{s,tot}^{pos}$</td>
</tr>
</tbody>
</table>

Looking at the $D_{reg e}^{eff}$ terms, where $D_{reg e}^{eff} = D_{e}^{e} (\varepsilon_{reg e})^{brug}$, and using the definitions of $\text{ratio}_1$ and $\text{ratio}_2$,

$$D_{e,tot}^{sep} = \frac{D_{e,0}^{sep} c_{e,0} A}{L_{sep}^{sep}} = \frac{D_{e}^{sep} (\varepsilon_{e}^{sep})^{brug} e_{e,0} A}{L_{sep}^{sep}} = D_{e,tot}^{sep} \text{ratio}_2$$

$$D_{e,tot}^{pos} = \frac{D_{e,0}^{pos} c_{e,0} A}{L_{sep}^{pos}} = \frac{D_{e}^{pos} (\varepsilon_{e}^{pos})^{brug} e_{e,0} A}{L_{pos}^{pos}} = D_{e,tot}^{pos} \text{ratio}_1.$$  

Assuming that the $R_{0}$ testing found the correct valued for $\kappa_{tot}^{neg}$, $\kappa_{tot}^{pos}$, and $\kappa_{tot}^{sep}$, both $D_{e,tot}^{sep}$ and $D_{e,tot}^{pos}$ can be eliminated as parameters during the optimization process.

3.4 $R_{ss}$ testing

The last impedance test for a cell is one that measures a steady-state resistance. This test determines resistance at various SOCs during a constant-current discharge/charge profile. The measured voltage of the cell is compared to the open circuit voltage at different SOCs. The SOC of the cell is evaluated by integrating the constant current with respect to time and using the total capacity of the cell to find the average SOC of the cell. With the measured
3.4. \( R_{ss} \) testing

voltage and the OCV known for each SOC the steady-state resistance is measured by the equation,

\[
R_{ss} = \frac{V_{ss} - OCV}{I} \tag{3.5}
\]

Since this equation uses the steady-state voltage we turn to the total voltage equation using the transfer functions already established. The total voltage equation using the transfer functions and nonlinear corrections is simply,

\[
v(t) = F \left( j_{tot}^{pos}(0,t) R_{lim,tot}^{pos} - j_{tot}^{neg}(0,t) R_{lim,tot}^{neg} \right) + \left[ \tilde{\phi}_e (3,t) \right]_1 + \left( \eta^{pos}(0,t) - \eta^{neg}(0,t) \right) + \left[ \tilde{\phi}_e (3,t) \right]_2 + \left( U_{ocp}^{pos}(0,t) - U_{ocp}^{neg}(0,t) \right)
\]

To find the steady-state voltage each transfer function, the limit is taken as time goes to infinity, and shown by the equation;

\[
V_{ss} = \lim_{t \to \infty} v(t).
\]

Because the steady-state resistance is desired, the Laplace domain representation of the input is shown by a step input with a constant charge/discharge magnitude \( i_{app} \). This is shown in Laplace domain as,

\[
I_{app}(s) = \frac{i_{app}}{s}.
\]

3.4.1 Linear terms

We first consider the portion of the total voltage equation made up of linear transfer functions. Using the final value theorem \([27]\) the calculation of the the final estimated steady-state voltage equation is given by,

\[
v_{ss,linear} = \lim_{t \to \infty} v_{linear}(t) = \lim_{s \to 0} sV_{linear}(s) = \lim_{s \to 0} \frac{V_{linear}(s)}{I_{app}(s)} I_{app}(s) = \lim_{s \to 0} \frac{V_{linear}(s)}{I_{app}(s)} i_{app}
\]

All of the linear transfer functions rely on the impedance ratio \( \nu^{reg}(s) \); the limit of the impedance ratio at \( s \) approaches zero is,

\[
\lim_{s \to 0} \nu^{reg}(s) = 0.
\]
3.4. $R_{ss}$ testing

With the impedance ratio approaching zero, the limit is taken for the flux out of the particle at the negative current collector boundary, $J_{\text{tot}}^{\text{neg}}(0, s)$,

$$J_{\text{tot, ss}}^{\text{neg}} = \lim_{s \to 0} \frac{J_{\text{tot}}^{\text{neg}}(0, s)}{I_{\text{app}}(s)} i_{\text{app}} = \frac{i_{\text{app}}}{F}. $$

This is reasonable since the total flux of moles entering an electrode for a given current is $i_{\text{app}}/F$. The flux limit for the positive current collector is simply,

$$J_{\text{tot, ss}}^{\text{pos}} = \lim_{s \to 0} \frac{J_{\text{tot}}^{\text{pos}}(0, s)}{I_{\text{app}}(s)} i_{\text{app}} = -\frac{i_{\text{app}}}{F}. $$

Finally, the last linear term remaining contains the first portion of the de-biased potential of the electrolyte. Using Mathematica this limit is calculated and shown by,

$$\lim_{s \to 0} \left[ \frac{\tilde{\phi}_e(3, t_1)}{I_{\text{app}}(s)} \right] = - \left[ \frac{1}{2\kappa_{\text{tot}}^{\text{neg}}} + \frac{1}{\kappa_{\text{sep}}} + \frac{1}{2\kappa_{\text{tot}}^{\text{pos}}} \right].$$

The final form for the linear resistance contains the results of the flux through the film resistance and the first electrolyte potential equation,

$$V_{ss, \text{linear}} = \left( R_{\text{film, tot}}^{\text{pos}} - R_{\text{film, tot}}^{\text{neg}} - \left[ \frac{1}{2\kappa_{\text{tot}}^{\text{neg}}} + \frac{1}{\kappa_{\text{sep}}} + \frac{1}{2\kappa_{\text{tot}}^{\text{pos}}} \right] \right) i_{\text{app}}$$

### 3.4.2 Nonlinear terms

Now the focus shifts to the nonlinear terms in Eq. (3.6). For this set of equations the total number of moles on the surface of the particle is needed. The first step re-linearizes the Butler-Volmer equation around a new operating point. Because the flux into the particle in steady-state is far away from the old operating value of zero, the Bulter-Volmer equation is linearized around a new flux, $J_{\text{tot,0}}$. Using the method from Lee [17], the Bulter-Volmer equation is fully expanded to,

$$J_{\text{tot}}^{\text{reg}} = J_{\text{step}}^{\text{reg}} \left( n_e^{\text{reg}} \right)^{1-\alpha} \left( \tilde{n}_{s, \Delta}^{\text{reg}} + n_{s, \Delta, \text{max}}^{\text{reg}} \right)^{1-\alpha} \left( n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}} \right)^{\alpha}$$

$$\times \left( \exp \left( \frac{(1-\alpha)F}{RT} \eta^{\text{reg}} \right) - \exp \left( -\frac{\alpha F}{RT} \eta^{\text{reg}} \right) \right).$$

55
3.4. $R_{ss}$ testing

The overpotential term inside the Butler-Volmer equations is simply,

$$\eta = \phi_s - \phi_e - U_{ocp} - j_{tot}FR_{film,tot}$$

Since $n_{s,e}^{\text{reg}} + \tilde{n}_{s,e}^{\text{reg}} = n_{s,e}$ and $n_{s,e,\Delta}^{\text{reg}} + n_{s,e,\Delta,\max}^{\text{reg}} = n_{s,max} - n_{s,e}$, moving terms around an implicit-function definition for the Butler-Volmer equation is now,

$$F(\phi_{s,e}, n_{s,e}, n_{e,ratio}, j_{tot}) = \exp\left(\frac{(1 - \alpha) F}{RT} \eta\right) - \exp\left(-\frac{\alpha F}{RT} \eta\right) - \frac{j_{tot}}{k_{\text{step}}(n_{e,ratio})^{1-\alpha}(n_{s,max} - n_{s,e})^{1-\alpha}(n_{s,e})^{\alpha}} = 0.$$

To linearize this equation the Taylor series expansion is performed around the setpoint $p^* = \{\phi_{s,e} = \phi_{s,e,0}, n_{s,e} = n_{s,e,0}, n_{e,ratio} = n_{e,ratio,0}, j_{tot} = j_{tot,0}\}$, with $F(p^*) = 0$,

$$\frac{\partial F}{\partial \phi_{s,e}} |_{p^*} (\phi_{s,e} - \phi_{s,e,0}) + \frac{\partial F}{\partial n_{s,e}} (n_{s,e} - n_{s,e,0}) + \frac{\partial F}{\partial n_{e,ratio}} (n_{e,ratio} - n_{e,ratio,0}) + \frac{\partial F}{\partial j_{tot}} (j_{tot} - j_{tot,0}) \approx 0.$$

To help simplify the form of the Taylor-series expansion, a function is created that is dependent on the overpotential at the setpoint, $p^*$, shown by,

$$E(\eta_0) = (1 - \alpha) \exp\left(\frac{(1 - \alpha) F}{RT} \eta_0\right) + \alpha \exp\left(-\frac{\alpha F}{RT} \eta_0\right) = \cosh\left(\frac{F}{2RT} \eta_0\right),$$

Where we assume $\alpha = 0.5$.

Taking the partial derivative with respect to each variable, the separate differential functions are shown by Eq. (3.7), Eq. (3.8), Eq. (3.9), and Eq. (3.10):

$$\frac{\partial F}{\partial \phi_{s,e}} |_{p^*} = \frac{F}{RT} E(\eta_0) \quad \text{(3.7)}$$

$$\frac{\partial F}{\partial n_{s,e}} |_{p^*} = \frac{j_{tot,0}(\alpha n_{s,max} - n_{s,e,0})}{j_{eq,tot}(n_{s,max} - n_{s,e,0})n_{s,e,0}} - \frac{F}{RT} E(\eta_0) \frac{\partial U_{ocp}}{\partial n_{s,e}} |_{n_{s,e,0}} \quad \text{(3.8)}$$

$$\frac{\partial F}{\partial n_{e,ratio}} |_{p^*} = \frac{j_{tot,0}(1 - \alpha)}{j_{eq,tot}n_{e,ratio,0}} \quad \text{(3.9)}$$

$$\frac{\partial F}{\partial j_{tot}} |_{p^*} = -\frac{1}{j_{eq,tot}} - \frac{F^2 R_{film,tot}}{RT} E(\eta_0) \quad \text{(3.10)}$$
3.4. $R_{ss}$ testing

With these values for the partial derivatives, the Taylor-series expansion is solved for $\phi_{s-e}$,

$$-\frac{\partial F}{\partial \phi_{s-e}} (n_{s,e} - n_{s,e,0}) - \frac{\partial F}{\partial n_{e,ratio}} (n_{e,ratio} - n_{e,ratio,0}) - \frac{\partial F}{\partial j_{tot}} (j_{tot} - j_{tot,0}) + \phi_{s-e,0} \approx \phi_{s-e}.$$ 

This equation can be simplified around the de-biased variable by using the equalities, $\tilde{n}_{e,ratio} = n_{e,ratio} - 1$, $\tilde{n}_{e,ratio,0} = n_{e,ratio,0} - 1$, and $\tilde{n}_{s,e} = n_{s,e} - n_{s,e,0}$, where $n_{e,ratio,0} = 1$ and $\tilde{n}_{e,ratio,0} = 0$. The new value for the charge-transfer resistance is now defined as $R_{ct,tot,j} = \frac{RT}{F^2 j_{eq,tot}^2 (\eta_0)}$. Now with all substitutions made the linear approximation for $\phi_{s-e}$ can be written,

$$\phi_{s-e} \approx \left(-FR_{ct,tot,j} j_{tot,0} \left(\frac{\alpha n_{s,max} - n_{s,e,0}}{(n_{s,max} - n_{s,e,0})n_{s,e,0}}\right) + \frac{\partial U_{ocp}}{\partial n_{s,e}} \right)(\tilde{n}_{s,e})$$

$$+ (-FR_{ct,tot,j} j_{tot,0} (1 - \alpha)) (\tilde{n}_{e,ratio})$$

$$+ F (R_{ct,tot,j} + R_{film,tot}) \tilde{j}_{tot} - F (R_{ct,tot,j} + R_{film,tot}) \tilde{j}_{tot,0} + \tilde{\phi}_{s-e,0}.$$ 

Three new variables are created to simplify the notation, these are defined as,

$$W_{s,e} = F \left(1 - \frac{\partial U_{ocp}}{\partial n_{s,e}} \right) - R_{ct,tot,j} j_{tot,0} \left(\frac{\alpha n_{s,max} - n_{s,e,0}}{(n_{s,max} - n_{s,e,0})n_{s,e,0}}\right)$$

$$W_{e} = -FR_{ct,tot,j} j_{tot,0} (1 - \alpha)$$

$$W_{j} = F (R_{ct,tot,j} + R_{film,tot}).$$

Finally with all of the substitutions the approximation can be written as,

$$W_{s,e} \tilde{n}_{s,e} + W_{e} \tilde{n}_{e,ratio} + W_{j} \tilde{j}_{tot} - W_{j} \tilde{j}_{tot,0} + \tilde{\phi}_{s-e,0} \approx \phi_{s-e}.$$ 

A relationship is desired between the total faradaic flux and the de-biased potential difference of the particle and electrolyte. To help find this value, the linear approximation is simplified by noting,

$$\phi_{s-e,0} - W_{j} \tilde{j}_{tot,0} = \phi_{s-e,0} - FR_{ct,tot,j} j_{tot,0} - FR_{film,tot} \tilde{j}_{tot,0}$$

$$= \phi_{s-e,0} - \eta_0 - FR_{film,tot} \tilde{j}_{tot,0}$$

$$= U_{ocp} (n_{s,e,0}).$$
3.4. $R_{ss}$ testing

Using the definition of the de-biased potential difference, $\tilde{\phi}_{s-e} = \phi_{s-e} - U_{ocp}(n_{s,e,0})$ the equation is written as,

$$\tilde{\phi}_{s-e} \approx W_{s,e} \tilde{n}_{s,e} + W_e \tilde{n}_{e,\text{ratio}} + W_j j_{tot}.$$

Transforming to the Laplace domain the equation becomes,

$$\tilde{\Phi}_{s-e}(\bar{x}, s) \approx W_{s,e} \tilde{N}_{s,e}(\bar{x}, s) + W_e \tilde{N}_{e,\text{ratio}}(\bar{x}, s) + W_j J_{tot}(\bar{x}, s).$$

This equation can be expanded to,

$$\tilde{\Phi}_{s-e}(\bar{x}, s) \approx W_{s,e} \frac{\tilde{N}_{s,e}(\bar{x}, s)}{J_{tot}(\bar{x}, s)} J_{tot}(\bar{x}, s) + W_e \frac{\tilde{N}_{e,\text{ratio}}(\bar{x}, s)}{J_{tot}(\bar{x}, s)} J_{tot}(\bar{x}, s) + W_j J_{tot}(\bar{x}, s)$$

Now by solving for $J_{tot}(\bar{x}, s)$, a relationship in the Laplace domain is finally established as,

$$\frac{\tilde{\Phi}_{s-e}(\bar{x}, s)}{W_{s,e} \frac{\tilde{N}_{s,e}(\bar{x}, s)}{J_{tot}(\bar{x}, s)} + W_e \frac{\tilde{N}_{e,\text{ratio}}(\bar{x}, s)}{J_{tot}(\bar{x}, s)} + W_j} \approx J_{tot}(\bar{x}, s)$$

With this relationship a new equation for the impedance ratio is established,

$$\nu_{reg}(s) = \left[ F \left( \frac{1}{\eta_{0,tot,avg}} + \frac{1}{\eta_{reg}} \right) \right]^{\frac{1}{2}} W_j + W_e \frac{\tilde{N}_{e,\text{ratio}}(\bar{x}, s)}{J_{tot}(\bar{x}, s)} + W_s e^{\frac{1}{2}D_s,\text{tot}} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right).$$

From here we need to find the value for $W_{s,e,\text{avg}}$ centered around the setpoint $p^* = \{n_{s,e} = n_{s,\text{avg}}, n_{e,\text{ratio}} = 1, j_{tot} = j_{tot,ss}\}$. First we rewrite $j_{0,tot}$ as,

$$j_{0,tot,avg} = \eta_{\text{step}} \sqrt{(n_{s,\text{max}} - n_{s,\text{avg}})(n_{s,\text{avg}})}.$$

Using this value and the non-linearized equation for the over-potential, the set point becomes,

$$\eta_{0,\text{avg}} = \frac{2RT}{F} \text{asinh} \left( \frac{i_{\text{app}}}{2F \eta_{0,tot,avg}} \right).$$

The average value for the charge transfer resistance around this new non-zero flux is now,

$$R_{ct,tot,avg}^{\text{reg}} = R_{ct,tot,j} = \frac{RT}{F^2 J_{0,tot,avg} \nu_{0,\text{avg}}^{\text{reg}}} = \frac{RT}{F^2 \sqrt{\frac{1}{\mu} (\frac{\eta_{0,\text{avg}}}{\eta_{0,tot,avg}})^2 + (\frac{j_{0,tot,avg}}{j_{0,tot,avg}})^2}}. \quad (3.11)$$
Finally the value for $W_{s,e,avg}$ is set to,

$$W_{s,e,avg} = \frac{\partial U_{ocp} (n_{s,e}^{\text{neg}})}{\partial n_{s,e}^{\text{neg}}}_{n_{s,e}^{\text{avg}}} - F R_{c,\text{tot},j,\text{avg}} J_{\text{tot,ss}}^{\text{neg}} \left( \alpha n_{s,max} - n_{s,avg}^{\text{neg}} \right) \left( n_{s,max} - n_{s,avg}^{\text{neg}} \right) n_{s,avg}.$$ 

To help find the steady-state value for the number of moles on the surface of the particles, the Jacobsen–West transfer function along with the lithium-flux transfer function are used to find the limit as $s$ goes to zero. This limit is calculated in Mathematica and is shown by:

$$\tilde{n}_{s,e,ss}^{\text{neg}}(0,t) = \lim_{s \to 0} \frac{\tilde{N}_{s,e}^{\text{neg}}(0,s)}{I_{\text{app}}(s)} = \lim_{s \to 0} \frac{\tilde{N}_{s,e}^{\text{neg}}(0,s)}{J_{\text{tot}}^{\text{neg}}(0,s)} \frac{J_{\text{tot}}(0,s)}{I_{\text{app}}(s)} = \frac{2n_{s,avg}^{\text{neg}} - \sigma_{s,avg}^{\text{neg}}}{6W_{s,e,avg}^{\text{neg}} \kappa_{s,avg}^{\text{neg}}} - \frac{1}{15FD_{s,ss}^{\text{neg}}}.$$

$$\tilde{n}_{s,e,ss}^{\text{pos}}(0,t) = \lim_{s \to 0} \frac{\tilde{N}_{s,e}^{\text{pos}}(0,s)}{I_{\text{app}}(s)} = \lim_{s \to 0} \frac{\tilde{N}_{s,e}^{\text{pos}}(0,s)}{J_{\text{tot}}^{\text{pos}}(0,s)} \frac{J_{\text{tot}}(0,s)}{I_{\text{app}}(s)} = -\frac{2n_{s,avg}^{\text{pos}} - \sigma_{s,avg}^{\text{pos}}}{6W_{s,e,avg}^{\text{pos}} \kappa_{s,avg}^{\text{pos}}} + \frac{1}{15FD_{s,ss}^{\text{pos}}}.$$

Since this limit is only the change from the equilibrium point, the average surface number of moles is added to this offset. The average total number of moles on the surface of the particle is calculated by integrating the constant current and adding the starting number of moles. For the negative and positive electrodes this calculated by Eq. (3.12) and Eq. (3.13) respectively.

$$n_{s,avg}^{\text{neg}}(0,t) = \left( n_{s,0}^{\text{neg}} + \int_{0}^{t} \frac{i_{\text{app}}}{F} dt \right)$$

$$n_{s,avg}^{\text{pos}}(0,t) = \left( n_{s,0}^{\text{pos}} + Q_{\text{cell}} - \int_{0}^{t} \frac{i_{\text{app}}}{F} dt \right)$$

Putting all of this together, the steady-state value for the total number of moles on the surface of the particles is now given by,

$$n_{s,e,ss}^{\text{reg}} = \lim_{t \to \infty} n_{s,e}^{\text{reg}}(0,t) = n_{s,avg}^{\text{reg}} + \tilde{n}_{s,e,ss}^{\text{reg}}.$$

To find the over-potential at steady-state, the steady-state value for $n_{e,\text{ratio}}^{\text{reg}}$ needs to be derived. First, the total ratio is found by adding one to the de-biased transfer function shown in Eq. (2.34). This gives the the Laplace representation of the total electrolyte concentration ratio, shown by,

$$N_{e,\text{ratio}}(\bar{x},s) = 1 + \frac{\tilde{N}_{e,\text{ratio}}(\bar{x},s)}{I_{\text{app}}(s)} I_{\text{app}}(s).$$
3.4. \( R_{ss} \) Testing

Finding the limit at the current-collector boundaries is first evaluated by finding the limit as \( s \) approaches zero of Eq. (2.32) and Eq. (2.33). This is shown for both current collectors by,

\[
\lim_{s \to 0} \int t_{n}^{\text{neg}} (s) = \frac{\sin \left( \sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}}} \lambda_n \right)}{\sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n}}, \quad (3.14)
\]

and,

\[
\lim_{s \to 0} \int t_{n}^{\text{pos}} (s) = -\frac{\sin \left( \sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n} \right)}{\sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n}}, \quad (3.15)
\]

Finally, the total steady-state value for the electrolyte concentration ratio is found by substituting Eq. (3.14) and Eq. (2.33), into Eq. (2.34). This is now shown for both electrodes as,

\[
n_{\text{e,ratio,ss}}^{\text{neg}} = 1 + \lim_{s \to 0} \frac{\tilde{N}_{\text{e,ratio}} (0, s)}{I_{\text{app}} (s)} i_{\text{app}}
\]

\[
= 1 + \sum_{n=1}^{\infty} k_{2,n}^{2} \left( \frac{\sin \left( \sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n} \right)}{\sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n}} + k_{2,n} \frac{\sin \left( \sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n} \right)}{\sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n}} \right) i_{\text{app}},
\]

and,

\[
n_{\text{e,ratio,ss}}^{\text{pos}} = 1 + \lim_{s \to 0} \frac{\tilde{N}_{\text{e,ratio}} (3, s)}{I_{\text{app}} (s)} i_{\text{app}}
\]

\[
= 1 + \sum_{n=1}^{\infty} k_{2,n}^{2} \left( \frac{\sin \left( \sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n} \right)}{\sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n}} + k_{2,n} \frac{\sin \left( \sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n} \right)}{\sqrt{\frac{n_{\text{e,0}}}{D_{\text{e,0}}} \lambda_n}} \right) i_{\text{app}}.
\]

The second electrolyte potential term is easily found by using the result of the steady-state electrolyte ratio inside Eq. (2.24). This is now shown by,

\[
\lim_{s \to 0} \left[ \frac{\Phi_e (3, s)}{I_{\text{app}} (s)} \right] = \frac{2RT (1 - t_{+}^0)}{F} \ln \left( \frac{n_{\text{e,ratio,ss}}^{\text{pos}}}{n_{\text{e,ratio,ss}}^{\text{neg}}} \right)
\]
3.4. \( R_{ss} \) testing

Now that the values for \( \tilde{n}_{e,\text{ratio},ss}^{\text{reg}} \) and \( n_{s,e,ss}^{\text{reg}} \) are found, the overpotential terms can be calculated. Let’s first define the nonlinear equation for the total lithium flux at the current collector as a function of \( \eta_{\text{reg}} \) by,

\[
j_{\text{tot}}^{\text{reg}}(0, t) = 2j_{\text{eq},tot}^{\text{reg}}(0, t) \sinh \left( \frac{F}{2RT} \eta_{\text{reg}}^{\text{reg}}(0, t) \right).
\]

(3.16)

Because the value for the equilibrium flux \( j_{0,\text{tot},ss}^{\text{reg}} \) is needed, the steady-state value for \( n_{s,e,ss}^{\text{reg}} \), and \( n_{e,\text{ratio},ss}^{\text{reg}} \) are used inside Eq. (2.15) and shown by,

\[
j_{0,\text{tot},ss}^{\text{reg}} = \sqrt{n_{e,\text{ratio},ss}^{\text{reg}} (n_{s,\text{max}}^{\text{reg}} - n_{s,e,ss}^{\text{reg}}) (n_{s,e,ss}^{\text{reg}})}.
\]

Rearranging Eq. (3.16), and solving for \( \eta_{\text{reg}}^{\text{reg}} \), the steady-state overpotential term becomes,

\[
\eta_{\text{ss}}^{\text{reg}} = 2 \frac{RT}{F} \text{asinh} \left( \frac{j_{\text{tot},ss}^{\text{reg}}}{2j_{0,\text{tot},ss}^{\text{reg}}} \right).
\]

Substituting the value for \( j_{\text{tot},ss}^{\text{reg}} \) for both electrodes gives the final version of the steady-state over-potential,

\[
\eta_{\text{ss}}^{\text{pos}} = 2 \frac{RT}{F} \text{asinh} \left( \frac{i_{\text{app}}}{2Fj_{0,\text{tot},ss}^{\text{reg}}} \right),
\]

and,

\[
\eta_{\text{ss}}^{\text{neg}} = 2 \frac{RT}{F} \text{asinh} \left( \frac{-i_{\text{app}}}{2Fj_{0,\text{tot},ss}^{\text{reg}}} \right).
\]

Using both the linear and nonlinear terms, the final steady-state potential of the cell is now shown by,

\[
v_{\text{ss}} = \left( R_{\text{film,tot}}^{\text{pos}} - R_{\text{film,tot}}^{\text{neg}} - \left[ \frac{1}{2\kappa_{\text{tot}}^{\text{reg}}} + \frac{1}{\kappa_{\text{tot}}^{\text{pos}}} + \frac{1}{2\kappa_{\text{tot}}^{\text{neg}}} \right] \right) i_{\text{app}}
\]
\[
+ \left( \frac{F}{2RT} \text{asinh} \left( \frac{i_{\text{app}}}{2Fj_{\text{eq},\text{tot},ss}^{\text{reg}}} \right) - \frac{F}{2RT} \text{asinh} \left( \frac{-i_{\text{app}}}{2Fj_{\text{eq},\text{tot},ss}^{\text{reg}}} \right) \right)
\]
\[
+ 2RT \left( 1 - i_{+}^{0} \right) \ln \left( \frac{\tilde{n}_{e,\text{ratio},ss}^{\text{pos}}}{\tilde{n}_{e,\text{ratio},ss}^{\text{neg}}} \right)
\]
\[
+ \left( U_{\text{ocp}}^{\text{pos}}(n_{s,e,ss}^{\text{pos}}) - U_{\text{ocp}}^{\text{neg}}(n_{s,e,ss}^{\text{neg}}) \right).
\]

(3.17)
3.5 Results

Using Eq. (3.5) with this new $v_{ss}$ and an applied DC current, the Doyle parameters produce a plot of the $R_{ss}$ versus SOC shown in Fig. 3.3. The $R_{ss}$ estimation gives a much better fit to the FOM simulation when the current magnitude is small. When applying this test to a laboratory cell a small steady state current is essential when measuring steady state resistances as various SOCs.

![Figure 3.3: Estimated steady-state resistance of the Doyle cell](image)

**Figure 3.3:** Estimated steady-state resistance of the Doyle cell

To gather a set of test data, a virtual lithium-ion cell is implemented in COMSOL to arrive at voltage–current data. To begin finding the parameters that characterize a battery cell, an optimization routine is created in Matlab. The system-identification process initially starts with pulse testing to arrive at the first set of parameter values. With the equations for resistance as a function of initial SOC and current-pulse magnitude, a cost function is developed that uses the calculated resistance and the measured resistance,

$$ f(x) = Cost\ (SOC,\ Amplitude) = R_{0,\ measured} - R_{0,\ estimated}. $$

The nonlinear least square function in Matlab is used with bounds to estimate the 13 parameters values that minimizes the cost function,

$$ \min_x \|Cost(x)\| = \min_x \left( f_1(x)^2 + f_2(x)^2 + \ldots + f_n(x)^2 \right). $$
3.5. Results

<table>
<thead>
<tr>
<th>Table 3.4: Test variation on initial SOC and C-rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOC setpoint</td>
</tr>
<tr>
<td>C-rate</td>
</tr>
<tr>
<td>C-rate</td>
</tr>
</tbody>
</table>

![Resistance values versus SOC & C-rate](image)

**Figure 3.4:** Resistance values versus SOC and C-rate

To obtain the current-pulse data, the Doyle cell is simulated in COMSOL using the FOM. A current-pulse is generated and input to the virtual cell. The instantaneous voltage change of the cell at the time of application of the current-pulse is recorded and divided by the current magnitude to find the instantaneous resistance. This was done at various magnitudes of current and different starting SOCs. Once all of the data were collected the resistance at all of the operating locations is calculated with the results plotted in Fig. 3.4.

The next step involved running the optimization script to find the 13 parameters that minimize the cost function without any prior knowledge of the cell’s parameter values. The errors from the truth data (FOM results) and the results of the optimization routine are shown in Fig. 3.5. The optimization quickly found parameters values that produced an almost perfect match with resistance errors around $10^{-7}$ mΩ.

After obtaining the initial set of 13 parameters, the other 7 parameters were found using the frequency response of the virtual cell. The frequency response of the virtual cell was gathered from the ROM in Matlab. The cost function for the frequency test is different from the one used for the pulse test due to the huge range of the resistance values between high and low frequencies. To help the optimization routine optimize over all of
3.5. Results

![Resistance Error versus SOC & C-rate](image)

Figure 3.5: Resistance error values versus SOC and C-rate

The resistance values, the measured data points are normalized by the measured value as shown by,

\[ f(x) = \text{Cost}(\text{SOC}, s) = \left( \frac{\text{real}(Z_{\text{estimated}})}{\text{real}(Z_{\text{measured}})} - 1 \right)^2 + \left( \frac{\text{imag}(Z_{\text{estimated}})}{\text{imag}(Z_{\text{measured}})} - 1 \right)^2 \]

\[
\min_x \| \text{Cost}(x) \| = \min_x \left( f_1(x)^2 + f_2(x)^2 + \ldots + f_3(x)^2 \right).
\]

The set of generated frequencies range from $10^{-10}$ to $10^{10}$ rads$^{-1}$ with the SOC ranging from 0 to 100%. The generated impedances at these data points are shown in Fig. 3.6. After the optimization routine arrives at set of parameter values the resulting error between the measured data and the estimated data was computed and is shown in Fig. 3.7. This optimization took more time since the number of data points was dramatically increased as compared to the instantaneous resistance test. The errors was minimized to an order of $10^{-4}$ mΩ and fit the measured data almost perfectly.

Now that a full set of parameter values has been found to minimize the instantaneous impedances as well as impedances at various frequencies, a full PBM of the cell is produced. A table showing the true parameter values compared to the estimated values is shown in Table 3.5. These results show excellent matching with the truth values and provide hope for finding values of a laboratory cell using actual data. The $n_{\text{reg}}$ terms have the worst error and is due to the limited effect these terms have on the impedance responses.
3.5. **Results**

![Nyquist Plot](image)

**Figure 3.6:** Frequency testing data versus SOC and $\omega$

![Re(Z) Error](image)

![Im(Z) Error](image)

![Impedance Magnitude Error](image)

**Figure 3.7:** Frequency error versus SOC and $\omega$
### Table 3.5: Truth versus estimated values for all 21 parameter values

<table>
<thead>
<tr>
<th>Negative Electrode</th>
<th>Truth</th>
<th>Estimated</th>
<th>Separator</th>
<th>Truth</th>
<th>Estimated</th>
<th>Positive Electrode</th>
<th>Truth</th>
<th>Estimated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_{\text{tot}}^{\text{neg}}$</td>
<td>$1.757 \times 10^2$</td>
<td>$1.756 \times 10^{-2}$</td>
<td>$\kappa_{\text{tot}}^{\text{neg}}$</td>
<td>$8.544 \times 10^2$</td>
<td>$8.545 \times 10^2$</td>
<td>$\kappa_{\text{tot}}^{\text{pos}}$</td>
<td>$1.641 \times 10^2$</td>
<td>$1.641 \times 10^2$</td>
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<tr>
<td>$\sigma_{\text{tot}}^{\text{neg}}$</td>
<td>$3.680 \times 10^5$</td>
<td>$3.820 \times 10^5$</td>
<td>$D_{\text{sep},\text{tot}}^{\text{neg}}$</td>
<td>$2.996 \times 10^{-3}$</td>
<td>$2.983 \times 10^{-3}$</td>
<td>$\sigma_{\text{tot}}^{\text{pos}}$</td>
<td>$5.940 \times 10^3$</td>
<td>$5.946 \times 10^3$</td>
</tr>
<tr>
<td>$R_{\text{film},\text{neg}}$</td>
<td>$0$</td>
<td>$1.400 \times 10^{-7}$</td>
<td>$n_{\text{sep}}^{\text{neg}}$</td>
<td>$2.712 \times 10^{-1}$</td>
<td>$3.122 \times 10^{-1}$</td>
<td>$R_{\text{film},\text{pos}}$</td>
<td>$0$</td>
<td>$1.391 \times 10^{-11}$</td>
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<td>$2.077 \times 10^{-4}$</td>
<td>$k_{\text{pos}}$</td>
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<td>$k_{\text{step}}$</td>
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<td>$3.070 \times 10^{-1}$</td>
<td>$3.070 \times 10^{-1}$</td>
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<tr>
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<td>$7.477 \times 10^{-1}$</td>
<td>$D_{\text{s},\text{tot}}^{\text{neg}}$</td>
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<td>$4.005 \times 10^3$</td>
<td>$D_{\text{s},\text{tot}}^{\text{pos}}$</td>
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<td>$D_{\text{e},\text{tot}}^{\text{neg}}$</td>
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<td>$5.756 \times 10^{-4}$</td>
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<td>$4.158 \times 10^{-1}$</td>
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<td>$4.158 \times 10^{-1}$</td>
<td>$1.936 \times 10^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.6 Summary

The accumulation of all this work successfully identified all of the necessary parameters needed to simulate a lithium-ion physics-based model of a Doyle-cell. The optimization process used here was significantly faster (approximately 30 minutes) than using an optimization routine that relies on the FOM time-domain simulation as performed by Forman [13]. All of the parameters match very closely with the truth values with the exception of the $n_{e,0}$ terms. To help further refine the estimates of these parameter values, the $R_{ss}$ test must be run long enough to converge on a solution.

Our next step is to apply these methods to identify the parameter values for a physical cell and address the challenges of moving from virtual data to actual lab-collected data. A prime example of this is the collection of the frequency-dependent impedance data. When collecting the “truth” data on the virtual cell any value of $\omega$ is possible. However collecting this data from a lab cell will require significant time to collect frequencies below $10^{-3}$ rad s$^{-1}$. Other factors that must be taken into account include contact resistances, non-ideal pulse data, mutual inductance, and data processing.

Some early results of data obtained from a lab cell led to the realization that the model was missing some dynamics. This was especially true when looking at the Nyquist plot from the frequency testing in, Fig. 3.8. The current model has no way to deal with the “bump” at high frequencies. For this reason the model needs to add a double-layer capacitor. This changes only some aspects of the model with most of the model intact. Other additions to the model include adding SOC dependence on the $D_s$ terms, adding temperature dependence on certain parameters, and finding error bounds on parameters, which is discussed next.
3.6. Summary

![Nyquist plot of lab cell](image)

**Figure 3.8:** Nyquist plot of lab cell
CHAPTER 4

*Enhancing the Model to Fit Lab Cell Characteristics*

4.1 Introduction

Identifying parameter values on a laboratory cell proves to be more complicated than finding values on a virtual cell. After initially testing some laboratory cells with the EIS test equipment, some frequency-response characteristics were discovered that were unexplained by the partial-differential equations investigated in Chapter 2. This included observing a “bump” at high frequencies on a Nyquist plot. This bump looked quite similar to that produced by a capacitor in parallel with a resistor. After investigating some previous work done by Ong and Newman on a lithium-ion cell, we determined that the model needed to include a double-layer capacitor. The double-layer capacitor suggested by Ong and Newman would explain the “bump” in the Nyquist plot at high frequencies but would also add an additional non-faradaic lithium flux in the model.

The model of this lithium flux due to the double-layer capacitor is not clearly defined in the literature, so three different models are investigated. Fig. 4.1 shows the potential sources of lithium flux out of the solid particles. The first and simplest model contains just a single double-layer capacitor, bridging the solid particle and electrolyte shown in Fig. 4.2. The other models add different lithium fluxes between various particle, film, and electrolyte interfaces.

Other issues arose when looking at defining models at various temperatures. In the current cell model this would involve computing a new set of all the parameter values at
4.1. Introduction

Figure 4.1: Different lithium flux mechanisms.

![Figure 4.1](image1)

Figure 4.2: Nonlinear double-layer model 1.

![Figure 4.2](image2)

every temperature setpoint. This would allow independent models at different temperatures to have unique and unrelated parameter values. To help the optimization find consistent values between the models, the parameters that are dependent on temperature are identified and modeled with various Arrhenius equations. These Arrhenius equations match different methods in literature but add additional thermal-modeling parameters to the model that also need to be identified.

In order to improve the model even further an Einstein equation was found by [23] that relates the diffusivity of the electrolyte to its conductivity. This will ultimately reduce the number of parameter values needed by the model. The last improvement creates an SOC-dependent solid diffusivity to help match different time constants at various SOCs in
4.2 Double-layer capacitance

the laboratory cells. To accomplish this a Baker–Verbrugge relationship [28] is added to the constant \( D_{s,tot}^{reg} \) term.

4.2 Double-layer capacitance

Different models for the double-layer capacitance inside a lithium-ion cell are proposed in the literature. Ong and Newman proposed a change to the potential of the solid particle Eq. (2.8) to include a new non-faradaic lithium-flux term that enters through a double-layer capacitance and is given by,

\[
\frac{\partial}{\partial x} \left( \sigma_{eff} \frac{\partial}{\partial x} \phi_s(x, t) \right) - a_s F j(x, t) - a_s C_{dl} \left( \frac{\partial \phi_{dl}(x, t)}{\partial t} \right) = 0.
\]

To put this new PDE in terms of the new lumped parameters, the same procedure is used as before. The new form of the PDE that includes the non-faradaic flux is now given by,

\[
\sigma_{tot}^{reg} \frac{\partial^2}{\partial x^2} \phi_s^{reg}(\bar{x}, t) - F j_{f,tot}^{reg}(\bar{x}, t) - a_s A L C_{dl}^{reg} \left( \frac{\partial \phi_{dl}^{reg}(\bar{x}, t)}{\partial t} \right) = 0.
\]

Now a new lumped parameter is discovered for the double-layer capacitance \( a_s A L C_{dl}^{reg} = \frac{3s}{R_s} A L C_{dl}^{reg} = C_{dl,tot}^{reg} \) which results in a new non-faradaic flux term,

\[
j_{dl}^{reg} = \frac{C_{dl,tot}^{reg}}{F} \left( \frac{\partial \phi_{dl}^{reg}(\bar{x}, t)}{\partial t} \right). \tag{4.1}
\]

The form of the solid-potential PDE with the lumped parameters and new flux terms is now just,

\[
\sigma_{tot}^{reg} \frac{\partial^2}{\partial x^2} \phi_s^{reg}(\bar{x}, t) - F j_{f,tot}^{reg}(\bar{x}, t) - F j_{dl}^{reg}(\bar{x}, t) = 0.
\]

In order to include this new flux term in the other PDEs, a new flux term is created to include the lithium flux from the double-layer capacitor. To accomplish this the original faradaic flux term dependent on the over-potential \( \eta \) is combined with the non-faradaic flux through the double-layer capacitor. The old variable \( j_{tot}^{reg}(\bar{x}, t) \) was the faradaic flux due to the chemical reaction at the surface of the particle and thus is renamed \( j_{f,tot}^{reg}(\bar{x}, t) \). The new non-faradaic flux is named \( j_{dl}^{reg}(\bar{x}, t) \) and can vary between the double-layer models. Regardless
4.2. **Double-layer capacitance**

of which model is used, the total flux entering the solid particle is labeled \( j_{\text{sum,tot}}(\bar{x}, t) \), and is initially defined as,

\[
j_{\text{sum,tot}}(\bar{x}, t) = j_{\text{f,tot}}(\bar{x}, t) + j_{\text{dl}}(\bar{x}, t).
\] (4.2)

The final PDE for the solid-particle potential is now defined with total flux term and not just the faradaic flux term, and is defined as

\[
\sigma_{\text{tot}} \frac{\partial^2}{\partial \bar{x}^2} \phi_{\text{s}}(\bar{x}, t) - F j_{\text{sum,tot}} = 0.
\]

Since there is a new lithium-flux term, which includes the faradaic \( j_{\text{tot}}^{\text{reg}} \) and non-faradaic flux \( j_{\text{dl}}^{\text{reg}} \), the other PDEs in Eq. (2.1) need to include both flux terms. The PDE for the concentration of lithium in the solid particle Eq. (2.3) remains unchanged but the second boundary equation Eq. (2.5) is affected by the new flux term. The new boundary value contains the total flux term \( j_{\text{sum,tot}}(\bar{x}, t) \) and is now given by,

\[
D_{\text{s,tot}} \frac{\partial n_s(1, \bar{x}, t)}{\partial \bar{r}} = - \frac{j_{\text{sum,tot}}(\bar{x}, t)}{3}.
\]

The concentration ratio of the electrolyte described by Eq. (2.7) also needs the new total flux term and can now be defined as,

\[
\frac{n_{e,0}^{\text{reg}}}{(1 - t_0^+)} \frac{\partial (n_{\text{e, ratio}}(\bar{x}, t))}{\partial t} = \frac{\partial}{\partial \bar{x}} \left( D_{e,tot}^{\text{reg}} \frac{\partial}{\partial \bar{x}} n_{e, \text{ ratio}}(\bar{x}, t) \right) + j_{\text{sum,tot}}^{\text{reg}}(\bar{x}, t).
\]

The final change to the set of PDEs in Chapter 2 is made to the PDE describing the potential of lithium in the electrolyte PDE Eq. (2.11). The new flux source term is changed to include the non-faradaic flux from the double-layer as well and is shown by,

\[
\frac{\partial}{\partial \bar{x}} \left( \kappa_{\text{tot}}^{\text{reg}} \frac{\partial}{\partial \bar{x}} \phi_e(\bar{x}, t) \right) + \frac{\partial}{\partial \bar{x}} \left( \frac{-2RT}{\kappa_{\text{tot}}^{\text{reg}} (1 - t_0^+)} \frac{\partial}{\partial \bar{x}} \ln n_{\text{e, ratio}}(\bar{x}, t) \right) + F j_{\text{sum,tot}}(\bar{x}, t) = 0.
\] (4.3)

The Butler–Volmer equation remains unchanged since it describes only the faradaic lithium flux process.

### 4.2.1 Adding double-layer effects to the ROM

To start the process of reducing the new set of PDEs, the PDE for the potential of the solid and electrolyte are combined by subtracting one from the other. It is assumed that the term
4.2. Double-layer capacitance

\[ \frac{\partial}{\partial x} \ln n_{e,\text{ratio}}(x, t) = 0 \] in the potential of the electrolyte PDE eliminates the the second term in Eq. (4.3). This assumption is not always valid and may introduce error into our models and thus the corresponding parameter values that are found. It is beyond the scope of this dissertation to explore the error introduced by the assumption\(^1\). By moving the source term \( j_{\text{sum,tot}}(x, t) \) to the left side of the equality in both PDEs, the resulting combined equation becomes,

\[
\sigma_{\text{tot}}^\text{reg} \frac{\partial^2}{\partial x^2} \phi_{s}^\text{reg} (x, t) - \frac{\partial^2}{\partial x^2} \phi_{e}^\text{reg} (x, t) = F \left( \frac{1}{\sigma_{\text{tot}}^\text{reg}} + \frac{1}{\kappa_{\text{tot}}^\text{reg}} \right) j_{\text{sum,tot}}^\text{reg} (x, t).
\]

In order to reduce the PDE, a new potential is defined as \( \phi_{s-e}^\text{reg} (x, t) = \phi_{s}^\text{reg} (x, t) - \phi_{e}^\text{reg} (x, t) \) which is the potential difference between the solid particle and the electrolyte. Another step in reducing the complexity is to de-bias the solid potential from the resting potential,

\[ \tilde{\phi}_{s}^\text{reg} (x, t) = \phi_{s}^\text{reg} (x, t) - U_{\text{ocp}} (n_{s,0}). \]

Since, \( U_{\text{ocp}} (n_{s,0}) \) is constant we may write,

\[ \frac{\partial^2}{\partial x^2} (\phi_{s}^\text{reg} (x, t) - U_{\text{ocp}} (n_{s,0})) = \frac{\partial^2}{\partial x^2} \phi_{s}^\text{reg} (x, t). \]

Now that the equality \( \frac{\partial^2}{\partial x^2} \phi_{s}^\text{reg} (x, t) = \frac{\partial^2}{\partial x^2} \tilde{\phi}_{s}^\text{reg} (x, t) \) is defined, this equation can simply be written in Laplace domain as,

\[
\frac{\partial^2}{\partial x^2} \tilde{\phi}_{s-e}^\text{reg} (x, s) = F \left( \frac{1}{\sigma_{\text{tot}}^\text{reg}} + \frac{1}{\kappa_{\text{tot}}^\text{reg}} \right) j_{\text{sum,tot}}^\text{reg} (x, s). \tag{4.4}
\]

This new equation contains a Laplace function of \( j_{\text{sum,tot}}^\text{reg} (x, s) \) and needs to be written in terms of \( \tilde{\phi}_{s-e}^\text{reg} (x, s) \). This is where the literature differs with regard to how the different flux terms impact \( \tilde{\phi}_{s-e}^\text{reg} (x, s) \). To move on from here let’s first take a look at the expanded form of \( j_{\text{sum,tot}}^\text{reg} (x, t) \) from Eq. (4.1) and set the non-faradaic flux \( j_{\text{dl}}^\text{reg} (x, t) \) to zero thus yielding \( j_{\text{sum,tot}}^\text{reg} (x, t) = j_{\text{tot}}^\text{reg} (x, t) \). Shown in Fig. 4.3 the flux through \( R_{\text{ct}} \) and \( R_{\text{film}} \) will be strictly a

\(^1\)Albert Rodriguez Marco, another Ph.D. student in our research group, is investigating a way to eliminate this assumption. He will develop it in his own Ph.D. dissertation.
4.2. Double-layer capacitance

\[
\begin{align*}
\phi_s &\quad + \quad J_{\text{sum,tot}} \quad Z_{\text{part}} \quad \phi_e \\
U_{\text{ocp}}(n_{s,0}) &\quad \quad R_{\text{ct}} \quad \phi_f \quad R_{\text{film}} \\
\end{align*}
\]

**Figure 4.3:** Original linearized model

faradaic flux in all of the double-layer models. By remembering that the faradaic flux was renamed from \( j_{\text{tot}}^{\text{reg}}(\bar{x}, t) \) to \( j_{\text{tot}}^{\text{reg}}(\bar{x}, t) \) and using Eq. (2.18), the new form is simply,

\[
\begin{align*}
FR_{s,e,\text{tot}}^{\text{reg}}j_{\text{reg}}^{\text{f,tot}}(\bar{x}, t) &= \phi_{s-e}(\bar{x}, t) - \left( \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \bigg|_{n_{s,0}} \right) (\bar{n}_{s,e}(\bar{x}, t)).
\end{align*}
\]

We need a transfer function to map \( J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \) to the de-biased potential \( \widetilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) \). Since \( \left( \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \bigg|_{n_{s,0}} \right) \) is a constant value at a specific \( n_{s,0} \), the Laplace-domain transfer function can be written as,

\[
\begin{align*}
FR_{s,e,\text{tot}}^{\text{reg}}J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, t) &= \widetilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - \left( \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \bigg|_{n_{s,0}} \right) (\bar{N}_{s,e}(\bar{x}, s)). \tag{4.5}
\end{align*}
\]

The transfer function for \( \bar{N}_{s,e}(s) \) with respect to the total lithium flux, has already been evaluated in Eq. (2.20). With the new total lithium flux term entering the particle, \( J_{\text{sum,tot}}(s) \), the new Jacobsen–West transfer function becomes,

\[
\begin{align*}
\frac{\bar{N}_{s,e}(s)}{J_{\text{sum,tot}}(s)} &= \frac{1}{3D_{s,tot}} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right). \tag{4.6}
\end{align*}
\]

Now using Eq. (4.6), the \( \bar{N}_{s,e}(\bar{x}, s) \) in Eq. (4.5) can be replaced with \( \frac{\bar{N}_{s,e}(s)}{J_{\text{sum,tot}}(s)}J_{\text{sum,tot}}(\bar{x}, s) \) and the result is:

\[
\begin{align*}
FR_{s,e,\text{tot}}^{\text{reg}}j_{\text{reg}}^{\text{f,tot}}(\bar{x}, s) &= \widetilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - \left( \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \bigg|_{n_{s,0}} \right) \left( \frac{1}{3D_{s,tot}} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right) \right) J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s). \tag{4.7}
\end{align*}
\]

To help simplify the new ROM equations, the slope expression of the \( U_{\text{ocp}} \) function along with the Jacobsen–West function are combined and the following expression below is written as a single impedance,

\[
\begin{align*}
\frac{1}{F} \left( \frac{\partial U_{\text{ocp}}}{\partial n_{s,e}} \bigg|_{n_{s,0}} \right) \left( \frac{1}{3D_{s,tot}} \left( \frac{\tanh(\beta)}{\tanh(\beta) - \beta} \right) \right) &= Z_{\text{part}}^{\text{reg}}.
\end{align*}
\]
4.2. Double-layer capacitance

Incorporating this new impedance term, the linearized Butler–Volmer equation can be depicted as a simple circuit as shown in Fig. (4.3). By rearranging terms, the linearized Butler–Volmer equation can be brought into the form of Kirchhoff’s voltage-law,

\[ F R_{s,e,tot}^{reg} j_{f,tot}^{reg} (\bar{x}, s) - F Z^{reg}_{part} (\bar{x}, s) J_{sum,tot}^{reg} (\bar{x}, s) = \tilde{\Phi}^{reg}_{s-e} (\bar{x}, s) . \]

There is still work remaining to identify the new ROM with the double-layer capacitance, though several different models exist in literature. For this reason the three most prominent models will be investigated here.

4.2.2 Double-layer capacitor model 1

The first model investigated will include the double-layer capacitor located around the \( R_{ct} \) and \( R_{film} \) terms. This will add the additional flux term \( j_{dl}^{reg} \) shown in Fig. 4.4.

Because the \( j_{dl}^{reg} \) term is dependent on the derivative of the potential with respect to time, we need to define the potential across the capacitor. This model has a potential function across the double-layer capacitor that is expressed in terms of \( j_{f,tot}^{reg} (\bar{x}, t) \) and given by,

\[ \phi_{dl} (\bar{x}, t) = F R_{s,e,tot}^{reg} j_{f,tot}^{reg} (\bar{x}, t) . \]

Using this potential equation inside the definition of the double-layer flux Eq. (4.1), the non-faradaic flux becomes,

\[ j_{dl}^{reg} = C_{dl,tot}^{reg} R_{s,e,tot}^{reg} \left( \frac{\partial j_{f,tot}^{reg} (\bar{x}, t) }{\partial t} \right) . \]

**Figure 4.4:** Double-layer model 1.
4.2. Double-layer capacitance

A transfer function for \( J_{\text{dl}}^{\text{reg}} \) is required to move forward from here. A Laplace transform of the differential equation results in,

\[
J_{\text{dl}}^{\text{reg}}(\bar{x}, s) = sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}} \tilde{f}_{\text{tot}}^{\text{reg}}(\bar{x}, s) .
\]

By using the Laplace domain representation of Eq. (4.1) and using the equality \( J(\bar{x}, s) = J_{\text{f,\text{tot}}}^{\text{reg}}(\bar{x}, s) + J_{\text{dl}}^{\text{reg}}(\bar{x}, s) \) we can get a relationship between \( J_{\text{f,\text{tot}}}^{\text{reg}}(\bar{x}, s) \) and \( J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x}, s) \) shown by,

\[
J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x}, s) = \left( 1 + sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}} \right) J_{\text{f,\text{tot}}}^{\text{reg}}(\bar{x}, s) .
\]

Now Eq. (4.7) is simplified with this substitution and can be written as,

\[
\left( \frac{FR_{s,e,\text{tot}}^{\text{reg}}}{1 + sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}}} \right) J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x}, s) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - Z_{\text{part}}^{\text{reg}} J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x}, s) .
\] (4.8)

Moving all of the total flux terms together Eq. (4.8) can be simplified as,

\[
J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x}, s) \left( \frac{FR_{s,e,\text{tot}}^{\text{reg}}}{1 + sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}}} + FZ_{\text{part}}^{\text{reg}} \right) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) .
\]

In order to use Eq. (4.4) a relationship is established between \( J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x}, s) \) and \( \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) \),

\[
J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x}, s) = \frac{\tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s)}{F} \left( \frac{R_{s,e,\text{tot}}^{\text{reg}}}{1 + sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}}} + Z_{\text{part}}^{\text{reg}} \right)^{-1} .
\]

Using this relationship Eq. (4.4) can now be written only in terms of \( \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) \).

\[
\frac{\partial^2}{\partial \bar{x}^2} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - \left( \frac{1}{\sigma_{\text{tot}}^{\text{reg}}} + \frac{1}{\kappa_{\text{tot}}^{\text{reg}}} \right) \left( \frac{R_{s,e,\text{tot}}^{\text{reg}}}{1 + sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}}} + Z_{\text{part}}^{\text{reg}} \right)^{-1} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) = 0
\]

Solving this differential equation results in a generic solution to

\[
\frac{\partial^2}{\partial \bar{x}^2} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - \left( \nu^{\text{reg}}(s) \right)^2 \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) = 0
\]

where,

\[
\nu^{\text{reg}}(s) = \sqrt{\left( \frac{1}{\sigma_{\text{tot}}^{\text{reg}}} + \frac{1}{\kappa_{\text{tot}}^{\text{reg}}} \right) \left( \frac{R_{s,e,\text{tot}}^{\text{reg}}}{1 + sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}}} + Z_{\text{part}}^{\text{reg}} \right)} .
\]
4.2. Double-layer capacitance

<table>
<thead>
<tr>
<th>SOC (%)</th>
<th>Re(Z) (mΩ)</th>
<th>Im(Z) (mΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>50%</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>10%</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>

**Figure 4.5:** Nyquist plot of the Doyle cell using the first double-layer model $C_{dl} = 1 \text{ F}$

<table>
<thead>
<tr>
<th>SOC (%)</th>
<th>Re(Z) (mΩ)</th>
<th>Im(Z) (mΩ)</th>
</tr>
</thead>
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<tr>
<td>10%</td>
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<td>4</td>
</tr>
</tbody>
</table>

**Figure 4.6:** Nyquist plot of the Doyle cell using the first double-layer model $C_{dl}^{neg} = 1 \text{ F}$ and $C_{dl}^{pos} = 100 \text{ F}$

Using this expression for $\nu^{reg}(s)$ in the transfer function of Eq. (3.4) one can generate a frequency response for the cell with the new double-layer capacitor. Using the “Doyle” parameter values, a Nyquist plot of the frequency response at three different SOC setpoints is generated and shown in Fig. 4.5. The “bump” at high frequencies now appears and the low frequencies still match the original Nyquist plot generated without the double-layer physics. Due to the ability of each electrode to have vastly different double-layer capacitance values, a second Nyquist plot is generated with $C_{dl}^{neg} = 1 \text{ F}$ and $C_{dl}^{pos} = 100 \text{ F}$ in Fig. 4.6. These new models can now vary greatly with different capacitance and the additional degrees of freedom have a much better ability to match laboratory collected data.
4.2. Double-layer capacitance

The drawback of this added double-layer capacitor is eliminating the SOC and current magnitude dependence on the instantaneous resistance values. The plot of the $R_0$ data is shown in Fig. 4.7.

4.2.3 The second double-layer capacitor model

We now move on to explore the second model for the double-layer capacitor shown in Fig. 4.8. This new model has the double-layer capacitor, $C_{dl,tot}^{reg}$, in parallel with $R_{ct}$, $R_{film}$, and $Z_{part}^{reg}$. $Z_{part}^{reg}$ is the impedance due to the potential change in the open-circuit potential as a result of the lithium flux. Since the double-layer capacitor bridges $Z_{part}^{reg}$, this means that the non-faradaic flux of lithium through the capacitor does not affect the change in the open-circuit potential. This model is contained in various cell modeling papers [19] but does not make physical sense. It implies that the capacitance bridges between the electrolyte and some imaginary node inside the particle where potential is always a function of only the average lithium concentration and not the local concentration. No such node exists.

Again, to arrive at a transfer function for the non-faradaic lithium flux, with respect to the faradaic flux we need to define the potential across the double-layer capacitor. The potential across the double-layer capacitor in this new model is now defined as,

$$\phi_{dl}(x, t) = F \left( R_{6,\epsilon,tot}^{reg} + Z_{part}^{reg} \right) J_{t,tot}^{reg}(\bar{x}, t).$$
4.2. Double-layer capacitance

By introducing this expression into Eq. (4.1) and utilizing the properties of the Laplace transform, the new definition for $J_{\text{reg\_dl}}$ becomes,

$$ J_{\text{reg\_dl}}(\bar{x}, s) = sC_{\text{dl\_tot}}^{\text{reg}} \left( R_{s,e,\text{tot}}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right) J_{\text{Ltot}}^{\text{reg}}(\bar{x}, s). $$

Using this equation in conjunction with Eq. (4.2) the new definition for the total flux entering the particle becomes,

$$ J_{\text{sum\_tot}}^{\text{reg}}(\bar{x}, s) = \left( 1 + sC_{\text{dl\_tot}}^{\text{reg}} \left( R_{s,e,\text{tot}}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right) \right) J_{\text{Ltot}}^{\text{reg}}(\bar{x}, s). \quad (4.9) $$

Notice that since the lithium flux due to the double-layer capacitor does not contribute to changing the total moles of lithium on the particle itself, the $\tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s)$ term is simply,

$$ F \left( R_{s,e,\text{tot}}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right) J_{\text{Ltot}}^{\text{reg}}(\bar{x}, s) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s). $$

Using Eq. (4.9) and solving for the faradaic lithium flux, the new relationship between $J_{\text{sum\_tot}}^{\text{reg}}(\bar{x}, s)$ and $\tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s)$ becomes,

$$ \frac{F \left( R_{s,e,\text{tot}}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right)}{\left( 1 + sC_{\text{dl\_tot}}^{\text{reg}} \left( R_{s,e,\text{tot}}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right) \right)} J_{\text{sum\_tot}}^{\text{reg}}(\bar{x}, s) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s). $$

Finally, using this relationship together with Eq. (4.4) the PDE for the de-biased potential difference between the solid particle and the electrolyte for the second double-layer model becomes,

$$ \frac{\partial^2}{\partial \bar{x}^2} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - \left( \frac{1}{\sigma_{\text{tot}}^{\text{reg}}} + \frac{1}{\kappa_{\text{tot}}^{\text{reg}}} \right) \left( \frac{R_{s,e,\text{tot}}^{\text{reg}} + Z_{\text{part}}^{\text{reg}}}{1 + sC_{\text{dl\_tot}}^{\text{reg}} \left( R_{s,e,\text{tot}}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right)} \right)^{-1} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) = 0. $$
4.2. Double-layer capacitance

Using the same generic solution to the PDE defined as

\[
\frac{\partial^2}{\partial \bar{x}^2} \Phi_{s-e}^{\text{reg}}(\bar{x}, s) - (\nu_{\text{reg}}^{\text{reg}}(s))^2 \Phi_{s-e}^{\text{reg}}(\bar{x}, s) = 0,
\]

the new \( \nu_{\text{reg}}^{\text{reg}}(s) \) is defined as,

\[
\nu_{\text{reg}}^{\text{reg}}(s) = \frac{\frac{1}{\sigma_{\text{reg}}^{\text{tot}}} + \frac{1}{\kappa_{\text{reg}}^{\text{tot}}}}{\left( R_{\text{s-e,tot}} + Z_{\text{part}}^{\text{reg}} \right) \left( 1 + sC_{\text{dl,tot}}(R_{\text{s-e,tot}} + Z_{\text{part}}^{\text{reg}}) \right)}.
\]

The Nyquist plot of this new model is shown in Fig. 4.9. The first double-layer model is preferred to this derived model since for this model the plot does not vary significantly compared to the first double-layer model. Furthermore, placing a node in-between the constant and the concentration dependent potentials for the Taylor series expansion of the open circuit potential function is not physically realistic.

4.2.4 The third double-layer capacitor model

The third double-layer model includes two double-layer capacitors, the first in parallel with \( R_{\text{ct}} \) and the second capacitor in parallel with \( R_{\text{film}} \). The \( Z_{\text{part}}^{\text{reg}} \) term is pulled out in front of the \( RC \) circuit, meaning that the \( j_{\text{sum,tot}} \) flux term flows through \( Z_{\text{part}}^{\text{reg}} \) and thus all of the flux contributes to the change in lithium contained in the solid particles. This model is shown in Fig. 4.10.
4.2. Double-layer capacitance

\[ \phi_{dl}(x, t) = F(R_{ct}) J^{\text{reg}}_{f,tot}(\bar{x}, t) . \]

The potential difference across the second double-layer capacitor \( C_{\text{film,tot}}^{\text{reg}} \) is the result of the lithium flux \( j_{\text{film,tot}}^{\text{reg}}(\bar{x}, t) \), going through the \( R_{\text{film}} \) term and is shown below by,

\[ \phi_{\text{film}}(x, t) = F(R_{\text{film}}) j_{\text{film,tot}}^{\text{reg}}(\bar{x}, t) . \]

Using \( j_{\text{di}}^{\text{reg}} = C_{\text{dl,tot}}^{\text{reg}} \frac{\partial \phi_{\text{di}}(x,t)}{\partial t} \) and transforming to the Laplace domain, a relationship between \( j_{\text{di}}^{\text{reg}}(\bar{x}, s) \) and \( j_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) \) can be written as,

\[ J_{\text{di}}^{\text{reg}}(\bar{x}, s) = sC_{\text{dl,tot}}^{\text{reg}}(R_{\text{ct}}) J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) . \] (4.10)

Also, by the same means, since \( j_{\text{film,dl}}^{\text{reg}} = C_{\text{film,dl}}^{\text{reg}} \frac{\partial \phi_{\text{film,dl}}(x,t)}{\partial t} \), a Laplace-domain relationship is established between \( J_{\text{film,dl}}^{\text{reg}}(\bar{x}, s) \) and \( J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) \),

\[ J_{\text{film,dl}}^{\text{reg}}(\bar{x}, s) = sC_{\text{film,tot}}^{\text{reg}}(R_{\text{film}}) J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) . \] (4.11)

The sum of the \( j_{\text{di}}^{\text{reg}}(\bar{x}, s) \) and \( j_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) \) terms gives the same result as the total lithium flux flowing through \( Z_{\text{part}}^{\text{reg}} \), and can be written as

\[ J_{\text{di}}^{\text{reg}}(\bar{x}, s) + J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) = J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) . \]

Now using the relationship established by Eq. (4.10) this can be written as a relationship between \( J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \) and \( J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) \),

\[ (1 + sC_{\text{dl,tot}}^{\text{reg}}(R_{\text{ct}})) J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) = J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) . \]
4.2. Double-layer capacitance

The sum of \( J_{\text{film,dl}}^{\text{reg}}(\bar{x}, s) \) and \( J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) \), is also the same as the total lithium flux flowing through \( Z_{\text{part}}^{\text{reg}} \), and can be written as

\[
J_{\text{film,dl}}^{\text{reg}}(\bar{x}, s) + J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) = J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s).
\]

Using the relationship established by Eq. (4.11), this can now be written as a relationship between \( J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \) and \( J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) \),

\[
\left(1 + sC_{\text{film,tot}}^{\text{reg}}(R_{\text{flim}})\right) J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) = J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s).
\]

\( \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) \) can be defined as a summation of lithium flux terms and is given by,

\[
FR_{\text{ct}} J_{l,tot}^{\text{reg}}(\bar{x}, s) + FR_{\text{film}} J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) + FZ_{\text{part}} J_{\text{part}}^{\text{reg}}(\bar{x}, s) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s).
\]

Using the relationships derived between the individual flux terms \( J_{l,tot}^{\text{reg}}(\bar{x}, s) \) and \( J_{\text{film,tot}}^{\text{reg}}(\bar{x}, s) \) and the total flux, \( J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \), the \( \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) \) can be written in terms of \( J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \) as,

\[
\tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) = \frac{FR_{\text{ct}}}{(1 + sC_{\text{dl,tot}}^{\text{reg}}(R_{\text{ct}}))} J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s)
+ \frac{FR_{\text{film}}}{(1 + sC_{\text{film,tot}}^{\text{reg}}(R_{\text{film}}))} J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s)
+ FZ_{\text{part}} J_{\text{part}}^{\text{reg}}(\bar{x}, s).
\]

This can be simplified by factoring out the \( J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \) term to obtain

\[
\left(\frac{FR_{\text{ct}}}{(1 + sC_{\text{dl,tot}}^{\text{reg}}(R_{\text{ct}}))} + \frac{FR_{\text{film}}}{(1 + sC_{\text{film,tot}}^{\text{reg}}(R_{\text{film}}))} + FZ_{\text{part}}\right) J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s).
\]

Using this transformation between the total flux \( J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \) and the potential \( \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) \), the new PDE becomes,

\[
\frac{\partial^2}{\partial \bar{x}^2} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - \left(\frac{1}{\sigma_{\text{tot}}} + \frac{1}{\kappa_{\text{tot}}}\right) \left(\frac{FR_{\text{ct}}}{(1 + sC_{\text{dl,tot}}^{\text{reg}}(R_{\text{ct}}))} + \frac{FR_{\text{film}}}{(1 + sC_{\text{film,tot}}^{\text{reg}}(R_{\text{film}}))} + FZ_{\text{part}}\right) \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) = 0.
\]

Finally the corresponding impedance ratio becomes,

\[
\nu_{\text{reg}}(s) = \sqrt{\frac{\frac{1}{\sigma_{\text{tot}}} + \frac{1}{\kappa_{\text{tot}}} R_{\text{ct}}}{\frac{1}{R_{\text{ct}}} + \frac{1}{R_{\text{film}}}} + \frac{Z_{\text{part}}}{\frac{1}{R_{\text{film}}} + \frac{1}{R_{\text{part}}}}}
\]

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4.2. Double-layer capacitance

![Nyquist plot of the Doyle cell using the third double-layer model](image)

**Figure 4.11:** Nyquist plot of the Doyle cell using the third double-layer model $C_{dl}^{reg} = 1 \text{ F}$, $R_{film}^{reg} = 1 \text{ m}\Omega$

![Model 1 with series resistance](image)

**Figure 4.12:** Model 1 with series resistance

### 4.2.5 Adding a series resistance to the double-layer capacitor

After observing that the double-layer capacitor will essentially “short” both $R_{ct}$ and $R_{film}$ at high frequencies, the SOC and current magnitude dependence on the instantaneous resistance goes away using these double-layer models. Some of the early laboratory tests suggested that this was not the case, so a resistance was added to the model in series with the double-layer capacitors. The first model was changed to add a series resistance and is shown in Fig. 4.12.

This model will have a potential function across the double-layer capacitor given by,

$$\phi_{dl}(\bar{x}, t) = F R_{s, e, tot}^{reg} J_{i, tot}^{reg}(\bar{x}, t) - F R_{dl, tot}^{reg} J_{dl}(\bar{x}, t).$$

Using this expression inside the definition of the double-layer flux Eq. (4.1) the flux becomes,
4.2. Double-layer capacitance

\[
J_{\text{dl}}^{\text{reg}}(\bar{x}, t) = C_{\text{dl,tot}}^{\text{reg}} \left( \frac{\partial}{\partial t} \left( R_{s,e,\text{tot}}^{\text{reg}} J_{\text{f,tot}}^{\text{reg}}(\bar{x}, t) - R_{\text{dl,tot}}^{\text{reg}} J_{\text{dl}}^{\text{reg}}(\bar{x}, t) \right) \right).
\]

Transforming to the Laplace domain this can be written as,

\[
J_{\text{dl}}^{\text{reg}}(\bar{x}, s) = sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}} J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) - sC_{\text{dl,tot}}^{\text{reg}} R_{\text{dl,tot}}^{\text{reg}} J_{\text{dl}}^{\text{reg}}(\bar{x}, s).
\]

Since a transfer function is needed between \(J_{\text{dl}}^{\text{reg}}(\bar{x}, s)\) and \(J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s)\), the equation above is solved for the non-faradaic flux flowing through the double-layer capacitor and the series resistor. This can be written as,

\[
J_{\text{dl}}^{\text{reg}}(\bar{x}, s) = \frac{sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}}}{sC_{\text{dl,tot}}^{\text{reg}} R_{\text{dl,tot}}^{\text{reg}} + 1} J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s).
\]

Because the total flux \(J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s)\) is just the sum of the faradaic and non-faradaic flux terms, \(J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) = J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) + J_{\text{dl}}^{\text{reg}}(\bar{x}, s)\), an expression for \(J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s)\) is found by,

\[
\left( \frac{sC_{\text{dl,tot}}^{\text{reg}} R_{s,e,\text{tot}}^{\text{reg}}}{sC_{\text{dl,tot}}^{\text{reg}} R_{\text{dl,tot}}^{\text{reg}} + 1} + 1 \right) J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) = J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s).
\]  
(4.12)

The relationship between the de-biased potential of the solid particle and the electrolyte, and the flux flowing through the different paths is simply given by,

\[
J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) Z_{\text{part}}^{\text{reg}} + J_{\text{f,tot}}^{\text{reg}}(\bar{x}, s) R_{s,e,\text{tot}}^{\text{reg}} = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s).
\]  
(4.13)

Using both Eq. (4.12) and Eq. (4.13), a final relationship is found between the total flux \(J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s)\) and the potential \(\tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s)\),

\[
J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s) \left( Z_{\text{part}}^{\text{reg}} + \frac{(sC_{\text{dl,tot}}^{\text{reg}} R_{\text{dl,tot}}^{\text{reg}} + 1) R_{s,e,\text{tot}}^{\text{reg}}}{sC_{\text{dl,tot}}^{\text{reg}} (R_{s,e,\text{tot}}^{\text{reg}} + R_{\text{dl,tot}}^{\text{reg}}) + 1} \right) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s).
\]

Going back to Eq. (4.4) and using the new relationship between \(J_{\text{sum,tot}}^{\text{reg}}(\bar{x}, s)\) and \(\tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s)\) the final PDE becomes,

\[
\frac{\partial^2}{\partial \bar{x}^2} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) - \left( \frac{1}{\sigma_{\text{tot}}^{\text{reg}}} + \frac{1}{\kappa_{\text{tot}}^{\text{reg}}} \right) \left( Z_{\text{part}}^{\text{reg}} + \frac{(sC_{\text{dl,tot}}^{\text{reg}} R_{\text{dl,tot}}^{\text{reg}} + 1) R_{s,e,\text{tot}}^{\text{reg}}}{sC_{\text{dl,tot}}^{\text{reg}} (R_{s,e,\text{tot}}^{\text{reg}} + R_{\text{dl,tot}}^{\text{reg}}) + 1} \right)^{-1} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x}, s) = 0.
\]

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4.2. Double-layer capacitance

This results in a new impedance-ratio term that is used in all of the ROM equations, and is given by,

\[ \nu_{\text{reg}}(s) = \sqrt{\frac{Z_{\text{reg part}}}{Z_{\text{reg}}^2 + \frac{1}{s C_{\text{reg} \text{dl, tot}} R_{\text{dl, tot}} (R_{\text{s, e, tot}} + R_{\text{dl, tot}}) + 1}}} + \frac{1}{s C_{\text{reg} \text{dl, tot}} R_{\text{dl, tot}} (R_{\text{s, e, tot}} + R_{\text{dl, tot}}) + 1}}. \]

Using this equation for \( \nu_{\text{reg}}(s) \) the Nyquist plot of the frequency response is shown in Fig. 4.13. When looking at the high frequencies, which is where the imaginary values go to zero, all SOCs cross at different values. This shows how the new series resistance, \( R_{\text{dl, tot}} \), adds SOC dependence to the instantaneous resistance. When taking into account both the current magnitude and the SOC the cell’s instantaneous resistance is shown by Fig. 4.14. The series resistance introduces both current and SOC dependence to the instantaneous resistance. As the series resistance is increased and approaches infinity, the plot of the instantaneous resistance starts completely flat and approaches the shape of the “tent” as shown in Fig. 3.4.

We can also add a resistance in series with the double-layer capacitor in the second model as shown in Fig. 4.15. The second model includes the linearized change in \( U_{\text{oep}} \) as a function of resistance \( Z_{\text{part}}^\text{reg} \), which is again placed in parallel with the double-layer capacitor. Similar to the first model, the potential across the double-layer capacitor (now with a series resistance) is derived. To find this new potential term, the faradaic flux path is used to find the potential across the capacitor. Because of the added series resistance, there
4.2. Double-layer capacitance

Figure 4.14: $R_0$ plot of the Doyle cell using the first double-layer model with $R_{dl,tot} = \text{1 m\,$\Omega}$

Figure 4.15: Model 2 with series resistance

is a slight potential drop across $R_{dl,tot}$ which must be subtracted from the overall potential term. This is easily shown by,

$$
\phi_{dl}(\vec{x},t) = F \left( R_{s,e,tot}^{reg} + Z_{part}^{reg} \right) j_{f,tot}(\vec{x},t) - F R_{dl,tot} j_{dl}(\vec{x},t).
$$

From here, the $\phi_{dl}(\vec{x},t)$ term is used within Eq. (4.1) to find the flux through the double-layer capacitor as,

$$
j_{dl}^{reg}(\vec{x},t) = C_{dl,tot}^{reg} \left( \frac{\partial}{\partial t} \left( \left( R_{s,e,tot}^{reg} + Z_{part}^{reg} \right) j_{f,tot}(\vec{x},t) - R_{dl,tot} j_{dl}^{reg}(\vec{x},t) \right) \right).
$$

Using the Laplace transform, the $s$-domain representation for the non-faradaic flux is written as,

$$
j_{dl}^{reg}(\vec{x},s) = s C_{dl,tot}^{reg} \left( R_{s,e,tot}^{reg} + Z_{part}^{reg} \right) j_{f,tot}^{reg}(\vec{x},s) - s C_{dl,tot}^{reg} R_{dl,tot} j_{dl}^{reg}(\vec{x},s).
$$
4.2. Double-layer capacitance

Solving this equation for $J_{dl}^{\text{reg}}(\bar{x}, s)$, a relationship between the non-faradaic flux $J_{tot}^{\text{reg}}(\bar{x}, s)$ and the faradaic flux $J_{dl}^{\text{reg}}(\bar{x}, s)$ is established by,

$$J_{dl}^{\text{reg}}(\bar{x}, s) = \frac{sC_{dl,tot}^{\text{reg}} \left( R_{s,e,tot}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right)}{(sC_{dl,tot}^{\text{reg}} R_{dl,tot}^{\text{reg}} + 1)} J_{tot}^{\text{reg}}(\bar{x}, s)$$

Since a relationship for $\Phi_{s-e}^{\text{reg}}(\bar{x}, s)$ and $J_{sum,tot}^{\text{reg}}(\bar{x}, s)$ is the ultimate goal, we see that the equality

$$J_{sum,tot}^{\text{reg}}(\bar{x}, s) = J_{dl}^{\text{reg}}(\bar{x}, s) + J_{tot}^{\text{reg}}(\bar{x}, s),$$

allows for a quick transformation to relate the faradaic flux to the total flux,

$$\left( \frac{sC_{dl,tot}^{\text{reg}} \left( R_{s,e,tot}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right)}{(sC_{dl,tot}^{\text{reg}} R_{dl,tot}^{\text{reg}} + 1)} + 1 \right)^{-1} J_{sum,tot}^{\text{reg}}(\bar{x}, s) = J_{tot}^{\text{reg}}(\bar{x}, s) \quad (4.14)$$

Because the de-biased potential $\Phi_{s-e}^{\text{reg}}(\bar{x}, s)$ is a direct result of $J_{tot}^{\text{reg}}(\bar{x}, s)$ flowing through $R_{s,e,tot}^{\text{reg}}$ and $Z_{\text{part}}^{\text{reg}}$, the equality is set such that the following holds,

$$J_{tot}^{\text{reg}}(\bar{x}, s) \left( R_{s,e,tot}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right) = \Phi_{s-e}^{\text{reg}}(\bar{x}, s).$$

Using Eq. (4.14) together with this equality we finally arrive at the desired relationship between the total flux and the de-biased potential difference,

$$J_{sum,tot}^{\text{reg}}(\bar{x}, s) \left( \frac{(sC_{dl,tot}^{\text{reg}} R_{dl,tot}^{\text{reg}} + 1) \left( R_{s,e,tot}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right)}{(sC_{dl,tot}^{\text{reg}} \left( R_{s,e,tot}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} + R_{dl,tot}^{\text{reg}} \right) + 1)} \right)^{-1} \Phi_{s-e}^{\text{reg}}(\bar{x}, s) = 0.$$

Substituting this equality into Eq. (4.4) finally produces the governing PDE in terms of $\Phi_{s-e}^{\text{reg}}(\bar{x}, s)$ and is given by,

$$\frac{\partial^2}{\partial \bar{x}^2} \Phi_{s-e}^{\text{reg}}(\bar{x}, s) - \left( \frac{1}{\sigma_{tot}^{\text{reg}}} + \frac{1}{\kappa_{tot}^{\text{reg}}} \right) \left( \frac{sC_{dl,tot}^{\text{reg}} R_{dl,tot}^{\text{reg}} + 1) \left( R_{s,e,tot}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} \right)}{(sC_{dl,tot}^{\text{reg}} \left( R_{s,e,tot}^{\text{reg}} + Z_{\text{part}}^{\text{reg}} + R_{dl,tot}^{\text{reg}} \right) + 1)} \right)^{-1} \Phi_{s-e}^{\text{reg}}(\bar{x}, s) = 0.$$
4.2. Double-layer capacitance

![Nyquist plot of the Doyle cell using the second double-layer model with \(R_{dl,tot} = 1\, \text{m}\Omega\)](image)

**Figure 4.16:** Nyquist plot of the Doyle cell using the second double-layer model with \(R_{dl,tot} = 1\, \text{m}\Omega\)

![Resistance values versus SOC & C-rate](image)

**Figure 4.17:** \(R_0\) plot of the Doyle cell using the second double-layer model with \(R_{dl,tot} = 1\, \text{m}\Omega\)

![Model 3 with series resistance](image)

**Figure 4.18:** Model 3 with series resistance

The Nyquist plot of the frequency response using the second double-layer model is shown in Fig. 4.16. The second model does not exhibit much change from the first model using the series resistance. Indeed by comparing the instantaneous resistance plots of the first model (Fig. 4.14) to the second model, (Fig. 4.17) the plots are almost identical.
4.2. **Double-layer capacitance**

With the third model the series resistance is placed in series with $C_{dl,tot}^{reg}$ as to prevent the double-layer capacitor from shorting out $R_{ct}$ at high frequencies. The capacitance term $C_{film,tot}^{reg}$ is left alone and will short out the $R_{film}$ term at high frequencies. The resistor is added to $C_{dl,tot}^{reg}$ because $R_{ct}$ is dependent on both the current magnitude and the SOC of the cell. We start our search for the new impedance-ratio term term $\nu^{reg}(s)$ by first examining the linearized circuit shown by Fig. 4.18. The potential difference across the first double-layer capacitor $C_{dl,tot}^{reg}$ is simply the result of the faradaic lithium flux $J_{f,tot}^{reg}(\bar{x}, t)$ going through the $R_{ct}$ term minus the potential drop of $J_{dl}^{reg}(\bar{x}, t)$ going through $R_{dl,tot}$. This equality for the potential difference is shown by,

$$\phi_{dl}(x, t) = F(R_{ct}) J_{f,tot}^{reg}(\bar{x}, t) - FR_{dl,tot} J_{dl}^{reg}(\bar{x}, t).$$

Using $J_{dl}^{reg} = C_{dl,tot}^{reg} \left( \frac{\partial \phi_{dl}(x,t)}{\partial t} \right)$, and going to the Laplace domain a relationship between $J_{dl}^{reg}(\bar{x}, s)$ and $J_{f,tot}^{reg}(\bar{x}, s)$ is given by,

$$J_{dl}^{reg}(\bar{x}, s) = sC_{dl,tot}^{reg} (R_{ct}) J_{f,tot}^{reg}(\bar{x}, s) - sC_{dl,tot}^{reg} R_{dl,tot} J_{dl}^{reg}(\bar{x}, s). \quad (4.15)$$

The sum of $J_{dl}^{reg}(\bar{x}, s)$ and $J_{f,tot}^{reg}(\bar{x}, s)$ is the same as the total lithium flux flowing through $Z_{part}^{reg}$, and can be written as

$$J_{dl}^{reg}(\bar{x}, s) + J_{f,tot}^{reg}(\bar{x}, s) = J_{sum,tot}^{reg}(\bar{x}, s).$$

Now using the relationship established by Eq. (4.15) this can be written as a relationship between $J_{sum,tot}^{reg}(\bar{x}, s)$ and $J_{f,tot}^{reg}(\bar{x}, s)$,

$$\left( \frac{sC_{dl,tot}^{reg} R_{ct}}{sC_{dl,tot}^{reg} R_{dl,tot} + 1} + 1 \right) J_{f,tot}^{reg}(\bar{x}, s) = J_{sum,tot}^{reg}(\bar{x}, s).$$

$\Phi_{s-e}^{reg}(\bar{x}, s)$ can be defined as a summation of lithium flux terms and is given by,

$$FR_{ct} J_{f,tot}^{reg}(\bar{x}, s) + FR_{film} J_{film,tot}^{reg}(\bar{x}, s) + FZ_{part} J_{sum,tot}^{reg}(\bar{x}, s) = \Phi_{s-e}^{reg}(\bar{x}, s)$$
4.2. Double-layer capacitance

Using the relationships derived between the individual flux terms \( J_{\text{reg}}^{\text{tot}}(\bar{x},s) \) and \( J_{\text{film,\text{tot}}}^{\text{reg}}(\bar{x},s) \) with respect to the total flux \( J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s) \), \( \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x},s) \) can be written in terms of \( J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s) \) as

\[
\tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x},s) = \frac{FR_{\text{ct}}}{sC_{\text{dl,\text{tot}}}^{\text{reg}}} R_{\text{dl,\text{tot}}} + 1 \, J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s) + FR_{\text{film}} \left( 1 + sC_{\text{film,\text{tot}}}^{\text{reg}}(R_{\text{film}}) \right) J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s). 
\]

This can be simplified by factoring out the \( J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s) \) term,

\[
\left( \frac{FR_{\text{ct}}}{sC_{\text{dl,\text{tot}}}^{\text{reg}}(R_{\text{ct}} + R_{\text{dl,\text{tot}}}) + 1} + \frac{FR_{\text{film}}}{1 + sC_{\text{film,\text{tot}}}^{\text{reg}}(R_{\text{film}})} + FZ_{\text{part}} \right) J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s) = \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x},s). 
\]

Using this transformation between the total flux \( J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s) \) and the potential \( \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x},s) \), the new PDE becomes,

\[
\frac{\partial^2}{\partial \bar{x}^2} \tilde{\Phi}_{s-e}^{\text{reg}}(\bar{x},s) - \left( \frac{1}{\sigma_{\text{tot}}} + \frac{1}{Z_{\text{tot}}} \right) = 0 
\]

Finally the resulting impedance ratio becomes,

\[
\nu_{\text{reg}}(s) = \left( \frac{1}{\sigma_{\text{tot}}} + \frac{1}{Z_{\text{tot}}} \right)^{-1} \frac{FR_{\text{ct}}(sC_{\text{dl,\text{tot}}}^{\text{reg}}(R_{\text{dl,\text{tot}}}) + 1) + FR_{\text{film}}}{1 + sC_{\text{film,\text{tot}}}^{\text{reg}}(R_{\text{film}})} J_{\text{sum,\text{tot}}}^{\text{reg}}(\bar{x},s) + FZ_{\text{part}}. 
\]

The Nyquist plot of this final double-layer model is shown in Fig. 4.19 and shows the same double bump expected because of the two capacitances. The plot of the instantaneous resistances versus SOC and current magnitude is shown in Fig. 4.20. Now all three models have been developed both with and without a series resistance and will be used to find parameter values of a laboratory cell. This allows for greater flexibility in the process of finding physics-based parameter values for a real cell.
4.2. **Double-layer capacitance**

![Diagram of Nyquist plot of Doyle cell using the third double-layer model with $R_{dl,tot} = 1 \text{ m}\Omega$](image)

**Figure 4.19:** Nyquist plot of the Doyle cell using the third double-layer model with $R_{dl,tot} = 1 \text{ m}\Omega$

![Diagram of Resistance values versus SOC & C-rate](image)

**Figure 4.20:** $R_0$ plot of the Doyle cell using the third double-layer model with $R_{dl,tot} = 1 \text{ m}\Omega$

<table>
<thead>
<tr>
<th>Table 4.1: Added parameters with the double-layer models</th>
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<tbody>
<tr>
<td><strong>Negative Electrode</strong></td>
</tr>
<tr>
<td>$C_{dl,tot}^{neg}$</td>
</tr>
<tr>
<td>$C_{dl,tot}^{neg}$</td>
</tr>
<tr>
<td>$R_{dl,tot}^{neg}$</td>
</tr>
</tbody>
</table>

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4.3 Adding temperature dependence

An earlier method to identify parameters of a cell at different temperatures involved fitting all parameters to a single isothermal data set without utilizing any insight on how individual parameters may change with temperature. This caused the erroneous effect of some parameters that were known not to be dependent on temperature to in fact be different from one temperature model to the other. A new method using Arrhenius equations on certain parameters allows a much quicker process for finding battery-cell models at any temperature. The old parameters $\sigma_{\text{reg},\text{tot}}$, $\kappa_{\text{reg},\text{tot}}$, $k_{\text{step}}$, and $D_{s,\text{tot}}$ are still valid at the reference temperature of 298.15 K and are now referred to as $\sigma_{\text{reg},\text{tot},T_{\text{ref}}}$, $\kappa_{\text{reg},\text{tot},T_{\text{ref}}}$, $k_{\text{step},T_{\text{ref}}}$, and $D_{s,\text{tot},T_{\text{ref}}}$. To add temperature-dependent parameter values, the paper by Gu and Wang [22] suggests that the conductivity of the electrolyte contains an Arrhenius equation $e^{\left(\frac{E_{\text{act}}}{R\left(1/T-1/T_{\text{ref}}\right)}\right)}$, dependence on temperature. The paper also suggests that the diffusion coefficients and the reaction rate constant in the Butler–Volmer equation exhibit some temperature dependence as well. These equations are easily incorporated into the model and can help find parameters once a satisfactory set of data is collected at various temperatures. The three equations all contain the original values for the parameters plus an extra parameter $E_{\text{act}}$ that sets the degree to which each parameter is dependent on temperature. The first parameter we will examine that includes the Arrhenius temperature dependence is the conductivity of the solid particle and is shown by,

$$
\sigma_{\text{tot}}^{\text{reg}}(T) = \sigma_{\text{tot},T_{\text{ref}}}^{\text{reg}} e^{\left(\frac{E_{\text{act}}}{R\left(1/T-1/T_{\text{ref}}\right)}\right)}.
$$

To show what effect the Arrhenius equation has on the overall frequency response, the Nyquist plot is generated at five different temperatures. By adding this Arrhenius equation to the $\sigma_{\text{tot},T_{\text{ref}}}^{\text{reg}}$ value and keeping the state of charge at 50%, five different Nyquist plots are shown in Fig. 4.21. These plots are generated by simply adjusting $\sigma_{\text{tot}}^{\text{reg}}(T)$ for each temperature and using the first double-layer capacitor model without the series resistance.
4.3. Adding temperature dependence

![Nyquist plot of the second model with Arrhenius $\sigma_{\text{tot}}^{\text{reg}}(T)$](image1)

**Figure 4.21:** Nyquist plot of the second model with Arrhenius $\sigma_{\text{tot}}^{\text{reg}}(T)$

![Nyquist plot of the second model with Arrhenius $\kappa_{\text{tot}}^{\text{reg}}(T)$](image2)

**Figure 4.22:** Nyquist plot of the second model with Arrhenius $\kappa_{\text{tot}}^{\text{reg}}(T)$

Next we consider the conductivity of the electrolyte, which after adjusting with the Arrhenius equation is shown by,

$$\kappa_{\text{tot}}^{\text{reg}}(T) = \kappa_{\text{tot},T_{\text{ref}}}^{\text{reg}} \exp \left( \frac{E_{\text{act}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right),$$

The corresponding Nyquist plot, shown in Fig. 4.22, is generated at the five different temperatures by only adding the temperature dependence only to $\kappa_{\text{tot}}^{\text{reg}}(T)$. When comparing the temperature dependence between $\kappa_{\text{tot}}^{\text{reg}}(T)$ and $\sigma_{\text{tot}}^{\text{reg}}(T)$ the effect is vastly different and offers some hope in identifying both activation energies, $E_{\text{act}}$, separately.
4.3. Adding temperature dependence

Figure 4.23: Nyquist plot of the second model with Arrhenius $k_{\text{step}}^{\text{reg}}(T)$

As suggested by Gu and Wang [22], temperature dependence is also added to the reaction-rate constant. Because the reaction-rate constant is wrapped into the lumped parameter $k_{\text{step}}^{\text{reg}}$, the Arrhenius equation for the reaction rate is written,

$$k_{\text{step}}^{\text{reg}}(T) = k_{\text{step,ref}}^{\text{reg}} e^{\left(\frac{E_{\text{act}}^{\text{reg}} \cdot k_{\text{norm}} \cdot R}{1 + (T^{-1} - T_{\text{ref}}^{-1})}\right)}.$$  

Since $k_{\text{step}}^{\text{reg}}(T)$ is inversely proportional to the resistance $R_{\text{ct}}^{\text{reg}}$, as the value for $k_{\text{step}}^{\text{reg}}(T)$ is decreased the value for $R_{\text{ct}}^{\text{reg}}$ is increased. From the Nyquist plot of Fig. 4.23 we note how the width of the bump increases as the temperature decreases. This is the direct result of $R_{\text{ct}}^{\text{reg}}$ being in parallel to the double-layer capacitor $C_{\text{dl, tot}}^{\text{reg}}$ in the second model.

The diffusivity of the solid particle is the final parameter to exhibit temperature dependence. Similar to the other parameters, the equation for this temperature dependence is,

$$D_{\text{s, tot}}^{\text{reg}}(T) = D_{\text{s, tot, ref}}^{\text{reg}} e^{\left(\frac{E_{\text{act}}^{\text{reg}} \cdot D_{\text{s}}}{1 + (T^{-1} - T_{\text{ref}}^{-1})}\right)}.$$  

The solid diffusivity parameter is included only in the $\beta$ function as part of $Z_{\text{part}}$ and approaches zero as the frequency increases. As shown by Fig. 4.24, the temperature dependence on the solid diffusivity affects only the low frequency behavior as the temperature is changed.

Other changes to the model included adding an additional temperature dependence on the conductivity of the solid, $\sigma_{\text{tot}}^{\text{reg}}(T)$. The new temperature dependence includes a $T_{\text{ref}}/T$
4.3. Adding temperature dependence

![Figure 4.24: Nyquist plot of the second model with Arrhenius $D_{s,\text{tot}}^\text{reg}(T)$](image)

![Figure 4.25: Nyquist plot of the second model with Arrhenius $T_{\text{ref}}/T$](image)

Visually, the effects of this added temperature-dependent term to the Arrhenius equation is shown by the Nyquist plot in Fig. 4.25. Even though this effect is small it does provide a small change to the model even when the activation energy $E_{\text{act}}$ is zero.

Finally, in order to help explain the $R_0$ dependence on both SOC and current-pulse magnitude, the resistor $R_{\text{dl,\text{tot}}}$ was added in series to the double-layer capacitor. By observing test data from laboratory cells, it was noted that the degree of the SOC and current...
4.3. Adding temperature dependence

\[ R_{dl,tot}(T) = R_{dl,tot,ref} e^{-\left(\frac{E_{act,R}}{RT} + \frac{1}{T_{ref}}\right)} \]

To see these effects, the Doyle cell values are used with a double-layer capacitor and the new temperature dependent \( R_{dl,tot}(T) \) term. The instantaneous resistance of the cell are plotted at two different temperatures to see the effects of this new temperature dependence and is shown in Fig. 4.26. This plot demonstrates how the “tent” like behavior of instantaneous resistance may not be observable until the cell reaches a cold temperature.

When including the temperature dependence on only the applicable parameters, a new model is created by finding only seven additional parameter values shown in Table 4.2. This represents a vast improvement in the efficiency of finding models since not all parameter values are estimated at each temperature. To help find these values, multiple tests are run at various temperatures and used as a single data set to optimize all the parameter values.
4.4 Einstein equation

Table 4.2: Added parameters using Arrhenius equations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Negative Electrode</th>
<th>Separator</th>
<th>Positive Electrode</th>
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<tbody>
<tr>
<td>$E_{act,\kappa}$</td>
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<td>$E_{act,\kappa}$</td>
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</tr>
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<td>$E_{act,R_{dl}}$</td>
<td>$E_{act,R_{dl}}$</td>
<td>$E_{act,R_{dl}}$</td>
</tr>
</tbody>
</table>

4.4 Einstein equation

The next improvement to the model of a lithium-ion cell tried to reduce the number of parameters by one. To aid this process, we make use of a relationship between the conductivity of the electrolyte and the diffusivity term. This relationship was referred to by the “Einstein equation” by Ecker et al. [23]. Ecker et al. proposed defining the electrolyte diffusivity with the equation,

$$D_{reg}^{e, eff} = \frac{k_B T}{e^2 N_A c_e}$$

where, $k_B$ is the Boltzmann constant, $e$ the elementary charge, $N_A$ the Avogadro constant and $c_e$ the lithium concentration of the electrolyte. Multiplying both sides of this equation by $A c_{e,0} / L_{reg}$ we derive the lumped parameter $D_{e,tot}^{reg} = \frac{D_{e,0}^{reg} c_{e,0} A}{L_{reg}}$ yielding,

$$D_{e,tot}^{reg} (T) = \frac{A k_{eff} k_B T c_{e,0}}{L_{reg} e^2 N_A c_e}$$

Using the lumped parameter for the conductance of the electrolyte $k_{tot} = k_{eff} A/L_{reg}$ and the equality, $c_e/c_{e,0} = n_{e,reg}/n_{e,0} = n_{e,ratio}$, this expression simplifies to,

$$D_{e,tot}^{reg} (T) = \frac{k_{tot} (T) k_B T}{e^2 N_A n_{e,ratio} (\bar{x}, t)}.$$  

Finally, a substitution is made with familiar constants such that $k_B / (e^2 N_A) = R/F^2$ to arrive at a new estimation of the diffusivity of the electrolyte shown by,

$$D_{e,tot}^{reg} (T) = \frac{k_{tot} (T) R T}{F^2 n_{e,ratio} (\bar{x}, t)}.$$
4.5 \textit{SOC-dependent diffusivity}

<table>
<thead>
<tr>
<th>Equation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{\text{reg},\text{tot}}^\text{neg}(T)) $\frac{RT}{F^2}$</td>
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</tr>
<tr>
<td>(\kappa_{\text{tot}}^\text{neg}(T)) $\frac{RT}{F^2}$</td>
<td>4.536e - 05</td>
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<td>(D_{\text{reg},\text{tot}}^\text{sep}(T)) $\frac{RT}{F^2}$</td>
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<td>4.239e - 05</td>
</tr>
</tbody>
</table>

This new definition for \(D_{\text{reg},\text{tot}}(T)\) is dependent on the electrolyte concentration, here it is assumed that the electrolyte concentration is near equilibrium, where \(n_{\text{e,ratio}}(x,t) \approx 1\), and the electrolyte diffusivity term is constant at a certain temperature giving the equation,

\[
D_{\text{reg},\text{tot}}(T) = \frac{\kappa_{\text{tot}}(T) RT}{F^2}. \tag{4.16}
\]

For the Doyle cell, the electrolyte diffusivity term provided in the literature is slightly different from using Eq. (4.16) in conjunction with the provided \(\kappa_{\text{tot}}(T)\) parameter value. The differences between the provided value and the result of the Einstein equation are shown in Table 4.3.

4.5 SOC-dependent diffusivity

Baker and Verbrugge [28] suggested that the diffusivity of the solid is dependent on the local state of charge of individual cell electrodes. This dependence includes two main terms, the percentage of lithium contained in the electrode as compared to the maximum amount of lithium the electrode could contain \((\theta)\), and the slope of the open-circuit potential at certain \(\theta\) values. This new equality does not contain any additional parameters but does contain the constant \(F/RT\). The units of this constant are \(V^{-1}\).

The total dependence on \(\theta\) by the solid diffusivity is shown by,

\[
D_{\text{reg},\text{tot}}^\text{neg}(\theta, T) = -D_{\text{reg},\text{tot}}^\text{neg}(T) \frac{F}{RT} \theta^\text{reg} (1 - \theta^\text{reg}) \frac{\partial U_{\text{ocp}}^\text{reg}}{\partial \theta^\text{reg}}.
\]
4.6  Adding a terminal resistance

Figure 4.27:  SOC-dependent $D_s$ values at various values of $\theta$

Notice that the additional term does not add any units to the original diffusivity terms but does change the value. Because the diffusivity is also a function of temperature the new equation for the solid diffusivity is now a combination of the Arrhenius and Verbrugge equations. This is best shown by,

$$D_{s,\text{tot}}^{\text{reg}}(\theta, T) = D_{s,\text{tot},\text{ref}}^{\text{reg}} e^{\frac{E_{\text{act}}^{\text{reg}}}{RT} \left( 1 - \frac{1}{T_{\text{ref}}} \right) + \frac{F}{RT} \theta^{\text{reg}} (\theta_{\text{reg}} - 1) \frac{\partial U_{\text{oCP}}^{\text{reg}}}{\partial \theta_{\text{reg}}}}$$

To show the effects of this new equation, the “Doyle” cell was used as a starting point where the new dependence on temperature and $\theta$ is added. The two plots in Fig. 4.27, show the diffusivity of the solid for both the negative and positive electrode at different values of theta.

4.6  Adding a terminal resistance

After some actual data from a laboratory cell was gathered, it was discovered that another parameter value was needed to model the resistance of the terminals in the setup involving the laboratory cell. Larger capacity cells exhibit very low internal resistances which are within the values of the terminal resistances. When trying to optimize the values of the cell parameters without modeling the terminal resistances, it turns out that many values of the internal cell parameters are skewed to try to account for this offset. This terminal
4.7 Constant-phase element (CPE)

resistance was therefore added to the model and assumed to be an ideal resistor in series with the cell under test. This relationship between the measured impedance and the actual cell impedance is shown by the equality,

\[ R_{\text{cell}} + R_{\text{term}} = R_{\text{measured}}. \]

Ideally, a single test setup should be used to perform all of the tests on the cell, but if the test setup configuration is changed for different tests, then multiple terminal resistances may be needed.

4.7 Constant-phase element (CPE)

After examining preliminary results from frequency response impedance data it was observed that, the double-layer effect does not exhibit perfect double-layer capacitor impedance behavior as predicted by our models. The double layer effect was investigated by Bisquert et al. [29] where the authors suggest a constant-phase element to replace the standard ideal capacitor. Because the cell’s solid particle radius has neither uniform radius nor spherical shape, the added ideal double-layer capacitor was changed to a constant-phase element. The impedance of the ideal double-layer capacitor is given by,

\[ sC_{\text{reg}}^{\text{dl,tot}} = \left( \frac{s}{R_s} \right)^{3\varepsilon_s ALC_{\text{dl}}} \]

In order to add the CPE to the double-layer model, an exponential term is added to the frequency dependent term, giving

\[ sC_{\text{dl,tot}}^{\text{reg}} = \left( \frac{s}{R_s} \right)^{n_{\text{CPE}}} 3\varepsilon_s ALC_{\text{dl}} \]

A Nyquist plot comparing the original double-layer model to the new CPE model is shown in Fig. 4.28. The new CPE term essentially flattens the “bump” as \( n_{\text{CPE}} \) is decreased from a value of one.
4.8. Results

To ensure that the same impedance testing procedure can be used to find all of the parameters for the new models, the Doyle-cell parameter set is used with the additional new parameters to generate all “truth” impedance data. The optimization routine is initiated and run to see if the values can be independently found using just the impedance frequency response matching techniques. This was performed by using the first model with and without the series resistance $R_{dl,tot}$.

4.8.1 Finding Values for the first $C_{dl}$ model

To start, the first model was used with “truth” data at a single temperature without the series resistance $R_{dl,tot}$. The instantaneous resistance is used as an additional DOF to help the optimization but is constant for both SOC and C-rate. This does not help relate the dynamics of the current-dependent nonlinear behavior to the cell parameters but does provide a good basis for the optimization to start. The plots of the instantaneous resistance of the truth and estimated data set along with a plot of the error are shown in Fig. 4.29.

The all-important frequency test finds the remaining parameter values and is essential in predicting the cell’s overall behavior. The optimization found a close match with a generated Nyquist plot as shown in Fig. 4.30.
4.8. Results

Figure 4.29: Plots of the truth and estimated instantaneous resistances (left) and the error (right)

Figure 4.30: Nyquist plot the truth frequency data and estimated frequency data with $C_{dl}$

Figure 4.31: Steady-state resistance values for Doyle parameters with $C_{dl}$

Finally, the steady-state resistance ($R_{ss}$) test was used to help refine the parameter values and separate the $t_{plus}$ terms from the $D_{e,tot}$ and $n_{e,0}$ values. The plots of the estimated and truth steady-state resistance values are shown in Fig. 4.31.
4.8. Results

Finally, after optimizing all of the parameters using the three different tests, the truth and estimated data are shown in Table 4.4. Almost all of the parameters are found within 10% of the truth values except $\sigma_{\text{tot}}^{\text{reg}}$, and $D_{v,\text{tot}}^{\text{reg}}$ are found within 20%. Values that were typically found using the instantaneous resistance now rely heavily on the frequency and steady-state tests for identification.

4.8.2 Finding values for the $C_{\text{dl}}$ model with series resistance

The next model included placing a resistance in series with the double-layer capacitor. This effectively allows for SOC and C-rate dependence to show up in the instantaneous resistance to help find the original 13 parameter values plus the value for $R_{\text{dl}}$. The instantaneous results show excellent matching between the estimated and truth values with errors on the order of $10^{-4}$ Ω and are shown in Fig. 4.32.

After optimizing both the instantaneous resistance and the frequency response impedances simultaneously, the estimation vastly improved. The Nyquist plot for the truth and estimated impedances is shown in Fig. 4.33.

Lastly, the steady-state resistance test can help further narrow down on some important parameters involved in the electrolyte concentration; the plots of the estimated and true values are shown in Fig. 4.34. The optimization routine quickly converged to the set of parameters shown in Table 4.5.

![Resistance values versus SOC & C-rate](image1)

![Resistance Error versus SOC & C-rate](image2)

**Figure 4.32:** Plots of the truth and estimated instantaneous resistances (left) and the error (right)
Table 4.4: Truth vs. estimated for all 21 parameter values with \( \kappa \) total.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Truth</th>
<th>Estimated</th>
<th>Separator</th>
<th>Truth</th>
<th>Estimated</th>
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<td>$1.757 \times 10^2$</td>
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4.9. Summary

In this chapter we introduce a number of improvements to the model in hopes of describing the main characteristics of an actual laboratory cell. The addition of the double layer models as well as temperature and SOC dependence on certain parameters provides a much better cell description. After demonstrating the ability to identify a model with the added enhancements, the next chapter will investigate testing and optimization of a laboratory cell. This process is similar to finding the virtual cell parameter values but has added challenges being a physical cell with actual data and the limitations that accompany the real world.

**Figure 4.33:** Nyquist plot the truth frequency data and estimated frequency data with $C_{dl}$ and $R_{dl}$

**Figure 4.34:** Steady-state resistance values for Doyle parameters with $C_{dl}$ and $R_{dl}$
This chapter focuses on using all of the techniques developed in Chapter 4 to identify parameter values of a virtual cell and then applies them to the identification of parameter values of an actual laboratory cell. The identification process now involves the test setup, data processing, optimization, and validation. The cell under test for this section will be a Panasonic cell, shown in Fig 5.1 having a nominal capacity of 25 Ah. The first section will focus on setting up the laboratory tests as well as provides an overview of the equipment used. After collecting the test data, the second section covers how the measured data are processed and calibrated to arrive at a close approximation to the “true” impedance data. The final section will show optimization tools that were created to help identify all cell parameter values and the results of the optimization.
5.1 Cell testing setup

Three main tests are performed on the cell to gather impedance data. These tests include an instantaneous-resistance test, a small-signal frequency test, and a steady-state impedance test. Ideally these tests are performed on a single piece of equipment, but due to hardware restrictions different setups were needed for each test. During the process of performing each test, a strict three to four step procedure is followed to obtain repeatable results. This process starts by fully charging the cell to 100% SOC. The second step discharges the cell according a specific current profile based on the selected test. Step three fully discharges the cell to 0% SOC to get an estimate of the cell’s capacity. Depending on the selected test, a charge-current profile can be performed to get additional impedance data.

Each test starts with the cell at 100% SOC which requires the manufacturer to provide the maximum voltage for the cell under test. To ensure the test starts off at 100% SOC the cell is put into a controlled climatized environment and set to a temperature of 25°C. After allowing the cell to rest for five to six hours the cell is charged to its maximum voltage using a constant current/constant voltage charging technique. To ensure the cell stays at the maximum voltage, the cell is subjected to a dithering routine that oscillates a small current into and out of the cell. This helps mitigate the effects of hysteresis and ensures that the cell is fully charged.

The next step involves discharging the cell using a specified current profile depending on the test. The cell is soaked at a specific temperature for five to six hours depending on the cell. After reaching the desired temperature the current profile can involve both positive and negative currents as long as the maximum or minimum voltage constraints are not violated. The instantaneous resistance test involved a series of discharge pulses with varying magnitudes around a setpoint SOC, and a constant discharge designed to move the cell’s SOC to the next setpoint. Frequency-response testing involves a sweep of small magnitude signals at different frequencies around a setpoint SOC with a constant-current discharge in between sweeps to move the SOC to the next setpoint. Finally, the steady-state
5.1. Cell testing setup

resistance test discharges the cell using constant current at a specified magnitude until the minimum voltage constraint is reached.

The third step discharges the cell to 0% SOC. The cell is brought back to 25°C and then is fully discharged to the minimum voltage. Again, the cell is subjected to a dithering current to minimize the hysteresis effect. The cell is held at the minimum voltage for a set period of time and then allowed to rest. The cell terminal voltage often recovers somewhat as it is resting but the cell is still assumed to be near the 0% SOC mark. The current data is integrated with respect to time to find the net ampere-hours that were discharged during steps two and three in order to estimate the total capacity of the cell.

Finally a fourth step can be added if testing requires an overall charge-current profile at a specific temperature. This is not always needed but certain tests do require a charge profile, such as when accomplishing OCV testing. If this step is not needed, the cell starts again at the first step, which returns the cell to 100% SOC.

5.1.1 Open-circuit voltage (OCV) testing

The open-circuit voltage for a laboratory cell is often unknown. However, OCV function and its derivative is vital to performing parameter estimation. In order to obtain an acceptable cell potential as a function of cell SOC, a series of tests is performed. The first such test involves a constant-current profile conducted at a very low current levels to measure the voltage continuously over the entire SOC range from 100% to 0%. The second test discharges and rests at various intermediate SOCs to get an estimate of the resting voltages at these points. From these two tests an approximation to the cell’s true potential curve is made.

The first series of tests are made to estimate the shape of the potential curve. After the cell is fully charged, a slow discharge at C/30 provides a discharge potential curve over a range of SOCs. These data provide an estimate of the shape but do not give reliable estimates of the resting potentials. A second charge profile is performed after fully discharging the cell to gain insight into the shape of the potential curve during a charge event.
5.1. Cell testing setup

Figure 5.2: OCV resting test for the Panasonic cell

The potential measurements from the two tests bound the true resting OCV curve and also provides the shape information.

The second series of tests discharge the cell for a certain period of time to move the cell’s SOC. Once at a desired SOC, the cell is allowed to rest for several hours in order to find a resting potential. Ideally the resting potential at each one of the these points would be exactly the OCV value we are looking for, but due to the hysteresis effect this only helps to bound the final OCV curve estimate. The potential plot versus SOC for the Panasonic test is shown in Fig. 5.2. After performing the discharge and rest current profile, the cell is fully discharged and the same test is performed while charging the cell.

With an estimate of the shape of the curve and multiple bounds on the OCV function itself, an optimization routine finds the best OCV curve. The shape information from the two constant current tests is averaged using a weighted value that minimizes the error between the charge and discharge resting voltages. For the Panasonic cell these results are plotted in Fig. 5.3.

The same procedure is applied to the negative-electrode half cell to find $U_{neg_{ocp}}$ and to the positive electrode half cell to find $U_{pos_{ocp}}$. We then optimize the $n_{coin,100\%}$ and $n_{coin,0\%}$ values to find a range for each half cell that when subtracted from each other produces the best match for the total estimate cell OCV. The results from the optimization are shown below in Fig. 5.5. When looking at the potential curves for each electrode the curve extends
5.1. Cell testing setup

Figure 5.3: OCV plot of the Panasonic cell

Figure 5.4: Estimated and measured OCV function of the Panasonic cell

Figure 5.5: OCP functions of each electrode in the Panasonic cell, the portion utilized during normal cell operation is highlighted in red.

Beyond the portion used to find the cell OCV. These “unused” sections provide an estimate of $n_{s,△,max}^{reg}$ and $n_{s,0}^{reg}$. 
5.1. Cell testing setup

Figure 5.6: Arbin test equipment and setup

5.1.2 Instantaneous-resistance testing.

The instantaneous resistance testing is performed on an Arbin BT-2000, using a 200A channel, as shown in Fig. 5.6. This allows for pulses up to 8C on the Panasonic cell, which provides insight on certain hard-to-find parameter values. The interface software to the Arbin is called “MITS Pro” which has the ability to generate user-customized schedules. An example of the scheduling tool is shown in Fig. 5.7. The schedule allows the ability for counters and loops depending on multiple control variables. The control variables can be set to measure voltage, current, energy and other quantities of interest. For example, the schedule for the pulse test included a control variable on the cell's voltage, which decremented a counter if a pulse violated the minimum-voltage constraint. This counter prevents the schedule from twice attempting a current-pulse whose magnitude violates a voltage constraint.

The schedule for the pulse testing resulted in the current profile shown in Fig. 5.8. A total of 11 pulses were performed at a single SOC with varying magnitudes. Since each pulse does move the SOC slightly, the ampere-hours value provided by every pulse is measured and the SOC at the beginning each pulse is recorded. In between each pulse the
5.1. Cell testing setup

Figure 5.7: MITS Pro schedule for pulse testing

cell is allowed to rest for a period of time to help the cell reach equilibrium. After each set of pulses the schedule performs a constant-current discharge to move the cell’s SOC by an estimated 10%. After the cell arrives at its new SOC the cell rests for 5 hours to make sure the cell is near equilibrium. This process continues until the cell’s measured voltage during the constant-current discharge reached the minimum voltage constraint.

Within each pulse are five short pulses each having a duration of 10 ms. The plots of current verses time and voltage versus time for each set of smaller pulses is shown in Fig. 5.9. This provides five different measurement of the instantaneous resistance for each magnitude. Since the duration of each pulse is so small we assume that the cell does not deviate from equilibrium for each successive pulse.
5.1. Cell testing setup

Figure 5.8: Voltage and current versus time plots for pulse testing

Figure 5.9: The voltage and current plots for the five short pulses at 1C
5.1. Cell testing setup

![Figure 5.10: \( R_0 \) raw data versus pulse magnitude and SOC](image)

After the test has been run, the data are collected into an Excel spreadsheet with all measured values in separate columns. The data are imported into Matlab using the “xlspread.m” function which saves the data into a matrix. After the import, the data are extracted by columns and saved in voltage, current, SOC, and time variables. The current data are examined to find when the current changes from a value near zero. At this point the change in voltage is compared to the change in current to get an estimate of the instantaneous resistance. This is shown by the equality,

\[
R_0 = \left| \frac{V_{\text{meas}}[k+1] - V_{\text{meas}}[k]}{i_{\text{app}}[k+1] - i_{\text{app}}[k]} \right|. 
\]

All of the data are processed to extract all of the pulses and sub-pulses to arrive at multiple instantaneous-resistance values. The total ampere hours discharged during the test are recorded by the MITS Pro software and used to find the SOC at the beginning of each pulse. After the cell is fully discharged with the third step of the test procedures the total capacity can be calibrated. After all of the data are extracted, the resistance data along with the ampere-hour discharge, pulse magnitude, and temperature are saved within a structure in Matlab. A plot of the raw data is shown in Fig. 5.10.

At very low current magnitudes the data from the five sub-pulses do not agree and show a huge variance in the resistance. To investigate further the raw data at those small currents are examined and shown in Fig. 5.11. Due to the very small changes in voltage with such a small current-pulse the measurement error plays a huge role in the calculated
5.1. Cell testing setup

![Cell Voltage versus Time](image1)

![Cell Current versus Time](image2)

**Figure 5.11:** The voltage and current plots for the five short pulses at C/10

![R₀ data vs SOC and C-rate](image3)

![R₀ data vs SOC and C-rate](image4)

**Figure 5.12:** $R₀$ averaged data versus pulse magnitude and SOC

resistance. To help combat this effect the five pulses are averaged to get a single value for the resistance. If the data from the five pulses show a variance over a user-defined threshold the data point is thrown away. The result of this filtering is shown in Fig. 5.12.

5.1.3 Frequency-response testing

Frequency-response testing was performed using a Gamry Reference 3000 unit, shown in Fig. 5.13, using a four-wire interface to the cell. The Gamry unit allows for customizable current profiles and is programmed using a “sequence wizard” as shown in Fig. 5.14. The sequence is set to apply sinusoidal signals at a magnitude of 250 mA at frequencies ranging from $10^{-3}$ to $10^5$ Hz. The electrochemical impedance spectroscopy (EIS) tool within the sequence wizard provided a simple means of performing these steps. The galvanostatic
5.1. Cell testing setup

![Gamry Reference 3000](image)

**Figure 5.13:** Gamry Reference 3000 used for frequency-response testing

EIS tool applies a specified current to the cell at the magnitude and frequencies determined by the user. The Gamry provided much better data using the galvanostatic EIS versus the potentiostatic EIS test due to the Gamry’s ability to control current much better than it controls voltage. The number of frequencies inside the EIS test is controlled by selecting the number of points per decade for each frequency range. Before the EIS testing is performed, the cell is first fully charged and a loop counter is initiated inside the sequence wizard to control the SOC location for each test.

After running the sequence, the Gamry saves the data into text files from each individual step in the sequence. To import the data into Matlab a series of commands is performed inside a loading function and saves the frequency data as a structure. To estimate the SOC at each EIS test performed, the discharge step in the sequence wizard outputs the total ampere-hours discharged in a separate file. By using the ampere hour discharge data, along with the overall capacity of the cell, an estimate of the cell’s SOC is obtained. After processing this data a Nyquist plot is generated for each temperature. An example is shown in Fig. 5.15.
5.1. Cell testing setup

5.1.3.1 Calibrating EIS data

The raw data from the EIS testing needs to be calibrated in order to reduce/eliminate the tail in the Nyquist plot that cross the $x$-axis. The tail was hypothesized to be a result of mutual inductance in the four-wire interface to the cell. At high frequencies, the current-carrying wires can induce a voltage inside the measurement wires. This voltage is proportional to the frequencies of the current inside the current carrying wires. From the plots in Fig. 5.15, this effect is shown by the high-frequency data gaining magnitude and approaching a phase angle of 90 degrees. To help correct this data the setup was analyzed to show how this effect can be removed. To start, the equation for the added potential from the mutual-inductance term is given by,

$$v_m(t) \approx M \frac{di_{app}(t)}{dt}$$

Going to the Laplace domain and setting $s = j\omega$ the equation becomes,

$$V_m(j\omega) \approx j\omega MI_{app}(j\omega)$$

Now the total measured resistance by the Gamry will be,

$$R_{meas}(j\omega) = \frac{V_{cell}(j\omega) + V_m(j\omega)}{I_{app}(j\omega)} = R_{cell}(j\omega) + j\omega M$$
5.1. Cell testing setup

Figure 5.15: Raw Nyquist data for Panasonic cell
5.1. Cell testing setup

The new mutual-inductance term can explain the increase in the imaginary part of the impedance at high frequencies. This new term however, cannot explain the increase in the real impedance values at those higher frequencies. It is assumed that the cell’s real impedance term does not increase at higher frequencies, so the mutual-inductance term is modified to include a constant-phase element (CPE). A constant-phase element is used to model a non-ideal inductance and can be applied to the imperfections of the test setup. This new mutual-inductance term is shown by,

\[ V_m(j\omega) \approx j^n\omega^n M_{\text{app}}(j\omega) \]

In the frequency domain this impedance can be broken into a real and imaginary impedance that is dependent on \( \omega \),

\[ M j^n \omega^n = \omega^n M \left( \cos \left( \frac{\pi n}{2} \right) + j \sin \left( \frac{\pi n}{2} \right) \right). \]

Breaking the equation into its real and imaginary components shows how this new mutual-inductance term can add real impedance values at high frequencies,

\[ \text{real} [M j^n \omega^n] = \omega M \cos \left( \frac{\pi n}{2} \right) \]

\[ \text{imag} [M j^n \omega^n] = \omega^n M \sin \left( \frac{\pi n}{2} \right). \]

Now the total measured impedance by the Gamry device is shown by,

\[ R_{\text{meas}}(j\omega) = R_{\text{cell}}(j\omega) - \omega^n M \cos \left( \frac{\pi n}{2} \right) - j\omega^n M \sin \left( \frac{\pi n}{2} \right) \]

Rearranging this equation provides a solution to calculate the cell-impedance value from the measured data,

\[ R_{\text{cell}}(j\omega) = R_{\text{meas}}(j\omega) + \omega^n M \cos \left( \frac{\pi n}{2} \right) + j\omega^n M \sin \left( \frac{\pi n}{2} \right) \]
5.1. Cell testing setup

The values for $M$ and $n$ can be estimated by replacing the cell in the setup with a highly calibrated resistor near the same impedance of the cell. A variety of resistor values are used to estimate the calibration parameters for the test setup. An optimization routine was developed that chooses the values for $M$ and $n$ that minimize the error between the actual and estimated frequency response. The value of the resistor is estimated by averaging the low-frequency impedance values. The measured imaginary impedance contains measurement noise at low frequencies and is corrected by linearizing the high-frequency values using a decibel plot of the magnitude. The measured data and the corrected data for the imaginary values are shown in Fig. 5.16.

After estimating a value of $M = 1.0367 \times 10^{-7}$ and a value for $n = 0.9719$, the plots of the magnitude of the actual and estimated calibration resistor data for the EIS testing are shown in Fig. 5.17. Very good estimates of the real and imaginary impedances using a calibration resistor meant that this method of using a CPE to correct for the mutual inductance proved to be viable.

When changing the test setup to evaluate the method for different resistance values the calculated $M$ and $n$ values changed significantly simply by moving the connections and wires. Fig. 5.18, shows multiple magnitude and phase responses for different calibration-resistance values. The best method used to calibrate the EIS impedance measurement from EIS testing was to create a setup such that the cell and the calibrated resistor can be easily switched without moving any connections or wires. For the setup used in the EIS testing of
5.1. Cell testing setup

To calibrate directly from the cell’s EIS data some assumptions needed to be made. The first assumption was that the imaginary impedance at high frequencies of the cell

the Panasonic cell this was not possible and the values for $M$ and $n$ needed to be estimated directly from the EIS testing of the cell.

Figure 5.17: Measured and estimated values for the impedance of the calibration resistor

Figure 5.18: Magnitude and phase response of multiple calibration resistors prior to correction via CPE method
5.1. Cell testing setup

should be equal to zero, implying that the cell is a pure ohmic resistance at those frequencies. This allowed for an equality between \( M \) and \( n \) such that,

\[
\text{imag} [Z_{\text{meas}} (\omega_{\text{highest frequency}})] - M \omega_{\text{highest frequency}}^n \sin \left( \frac{\pi n}{2} \right) \approx 0
\]

Rearranging terms provides an equation for \( M \) that is dependent on \( n \),

\[
M (n) \approx \frac{\text{imag} [Z_{\text{meas}} (\omega_{\text{highest frequency}})]}{\omega_{\text{highest frequency}}^n \sin \left( \frac{\pi n}{2} \right)}
\]

The second assumption was that the real value of impedance at high frequencies can only decrease in magnitude. This allowed for the cells EIS measurement data to be directly calibrated. The plots of the calibrated data for the EIS testing are shown in Fig. 5.19.

5.1.3.2 Change in SOC

Another artifact of testing on a laboratory cell is the cell’s SOC movement as a function of frequency. Because the EIS testing applies a sinusoidal signal with a peak value of \( i_{\text{peak}} \), the operating point of the cell will change. By integrating the sinusoidal signal, shown in Fig. 5.20, to a value of 1/4 of the period the total amp hour discharged is,

\[
\text{Ampere-hour}_{\text{delta}} (\omega) = \int_0^{\frac{\pi}{2}} i_{\text{peak}} \sin (\omega t) \, dt = \frac{1}{3600} \frac{i_{\text{peak}}}{\omega} \frac{1}{3600}.
\]

By adding this term to all of the operating set-points of each EIS test, the final SOC for each frequency is individually determined.

5.1.4 Steady-state impedance testing

Steady-state impedance testing starts with the OCV curve found during OCV testing. Once an acceptable curve is established, the C/30 discharge/charge data are used to estimate the cell’s resistance at each SOC.

\[
R_{\text{ss,discharge}} (SOC) = \frac{V_{\text{cell,discharge}} (SOC) - OCV (SOC)}{i_{\text{app}}}
\]
5.1. Cell testing setup

Figure 5.19: Calibrated Nyquist data for Panasonic cell

Figure 5.20: Area of a sinusoidal current input used to move cell’s SOC at each frequency.
5.2. Optimization and parameter estimation

\[ R_{ss,\text{charge}}(SOC) = \frac{V_{cell,\text{charge}}(SOC) - OCV(SOC)}{i_{\text{app}}} \]

Because the cell does not reach the steady-state potential instantaneously, when first starting the test the discharge data are taken after the cell reaches 90% SOC and 10% for the charge test. The tests must start with the cell fully charged for the discharge \( R_{ss} \) test and fully discharged for the charge \( R_{ss} \) test. The discharge \( R_{ss} \) test must finish at 0% SOC using step three of the testing procedure while the charge \( R_{ss} \) test must finish at 100% SOC using step one. The SOC information is estimated by integrating the current over time and diving by the total capacity.

5.2 Optimization and parameter estimation

After a set of impedance data is collected and calibrated from the laboratory cell, the model parameter values are estimated by using an optimization routine. The optimization process starts by estimating a few parameter values directly from the Nyquist plots as shown in Fig. 5.22. Since most or all of the cells measured in the lab exhibit double-layer capacitance behavior, associated parameter values may be estimated. The “bump” in the Nyquist plot has a certain width, which can be directly measured. The width of the bump corresponds to the value for \( R_{ct} + R_{\text{film}} \), but the initial estimate of the film resistance \( R_{\text{film}} \) is set to zero. The value for \( R_{ct,\text{lot,est}} \) is found by first finding the real value of the impedance where the
5.2. Optimization and parameter estimation

bump has a slope of zero. Once found, this value can serve as the basis for other estimates of parameter values using the equality,

\[ R_{ct,tot,est} = \frac{RT}{F^2 j_{eq,tot}} = \frac{RT}{F^2 k^{reg}_{step} \sqrt{n_{e,ratio} \left( \tilde{n}^{reg}_{s,\triangle} + n^{reg}_{s,\triangle,max} \right) \left( \tilde{n}^{reg}_{s,0} + \tilde{n}^{reg}_{s} \right)}}. \]

The values of \( n^{reg}_{s,\triangle,max} \) and \( n^{reg}_{s,0} \) are initially estimated when finding the OCV curve of the cell from the OCP curves of the electrodes. If the OCP data are not available, \( n^{reg}_{s,\triangle,max} \) and \( n^{reg}_{s,0} \) are set equal to half the total molar capacity of the cell. To find the molar capacity, the total cell capacity in ampere-hours is multiplied by 3600 and divided by Faraday’s constant,

\[ Q_{moles} = \frac{Q_{cell} \cdot 3600}{F}. \]

With these values estimated, an initial estimate for \( k^{reg}_{step} \) can be made from the equation,

\[ k^{reg}_{step,est} \approx \frac{RT}{R_{ct,tot,est} F^2 \sqrt{n_{e,ratio} \left( \tilde{n}^{reg}_{s,\triangle} + n^{reg}_{s,\triangle,max} \right) \left( \tilde{n}^{reg}_{s,0} + \tilde{n}^{reg}_{s} \right)}}. \]

The other parameter value estimated is \( C_{dl,tot} \). Since the value for \( \omega \) is already known for the top of the Nyquist bump, an estimate for \( C_{dl,tot} \) is computed from,

\[ C_{dl,tot,est} \approx \frac{1}{\omega R_{ct,tot,est}}. \]

Finally, estimates are made for \( \kappa^{neg}_{tot}, \kappa^{sep}_{tot}, \kappa^{pos}_{tot}, \sigma^{neg}_{tot}, \) and \( \sigma^{pos}_{tot} \). Initially, the cell is assumed to exhibit behavior with no series resistance to the double-layer capacitor. With this assumption the total instantaneous resistance is equal to,

\[ R_0 = \frac{1}{\kappa^{sep}_{tot}} + \frac{1}{\kappa^{neg}_{tot} + \sigma^{neg}_{tot}} + \frac{1}{\kappa^{pos}_{tot} + \sigma^{pos}_{tot}}. \]

Assuming all of the solid-particle conductivity values for both electrodes, and the electrolyte parameters are an order of magnitude less than that of the solid particle, the estimate can be written,

\[ R_0 = \frac{1}{x} + \frac{1}{x + 10x} + \frac{1}{x + 10x} = \frac{13}{11x} \]

\[ x = \frac{13}{11 R_0} \]
5.2. Optimization and parameter estimation

Going back to the estimates for the electrolyte and solid particle conductance, $\kappa_{\text{reg}}^{\text{tot}} = x$ and $\sigma_{\text{reg}}^{\text{tot}} = 10x$.

Once an initial guess is made at the cell parameter values, the optimization routine fits the estimated impedance to the actual data, using Eqs. (3.3), (3.17), and (3.4). In order to help manage the optimization, a graphical user interface (GUI) was developed in Matlab. A screenshot of the optimization tool is shown in Fig. 5.23. This tool allows a user to visualize and adapt the optimization process by using options that allow the user to: select which parameters to optimize, change the double-layer capacitor model, select a specific or multiple impedance tests, manually adjust values, generate plots of the estimated and actual data, and other various options.

5.2.1 $R_0$ optimization for the laboratory cell

The model parameter values are first optimized to match the laboratory data for the instantaneous resistance values. This optimization follows the same process as with the virtual cell in Sec. 3.5. Only the first 13 parameter values are involved with the computation of the instantaneous resistance. For this reason they are optimized first to best match the estimated instantaneous resistance. The optimization starts by focusing only on the data collected at a single user-defined temperature. After the optimization converges to a set of parameter
5.2. Optimization and parameter estimation

values for the data at the specific temperature, the parameter values for $E_{\text{act},\sigma}^{\text{reg}}$, $E_{\text{act},\kappa}$, and $E_{\text{act},R_{\text{dl}}}$ are optimized. This optimization finds the best set of activation energies that control how the parameter values change with temperature. Once the optimization finds the estimate for the activation energies, the parameter values for all temperature values are optimized together to match all measured instantaneous resistance data at all temperatures to arrive at a final estimate of the parameter values. The result of this optimization process is shown in Fig. 5.24.

5.2.2 Frequency-response optimization for the laboratory cell

Complex impedance computed at various frequencies contains both magnitude and phase information. The amount of data gathered in this test greatly outnumbers the data from the $R_0$ and $R_{\text{ss}}$ tests combined. Getting the optimization to converge on the global solution proved to be very challenging. Because of the assumptions that the cell’s electrolyte concentration stays near the equilibrium point, and all particles have uniform radius, the
5.2. Optimization and parameter estimation

![Graph showing resistance values versus SOC & C-rate](image)

**Figure 5.24:** Instantaneous resistance estimate versus measured for the Panasonic cell

measured data and the estimation data do not converge to a single optimal solution. The model does arrive at a set of parameter values that produce computed impedances near the measured data, but they are not exact. The results of the frequency test are shown in Fig. 5.25.

5.2.3 $R_{ss}$ optimization for the laboratory cell

The steady-state resistance test provided the final set of data used in the optimization process. The steady-state current $i_{app}$ is set to be at a relatively low magnitude of C/30 to avoid issues with estimation errors at large C rates. The steady-state resistance test depends on all of the parameter values except those involved with the double-layer capacitor. The optimization routine is mainly used to separate the $t_+^0$ and $D_{e,tot}$ values that were lumped together from linearizing the electrolyte-concentration PDE. The results of the optimization process are shown in Fig. 5.26 and show good agreement.

5.2.4 Optimization parameter values

In a final step, all of the tests data are incorporated into a single optimization that finds the best fit to all of the impedance tests. Since some of the data is not in alignment from test to test the optimization finds the best parameter values that fit all of the tests together. A great example is shown when plotting the small signal instantaneous resistance from the
5.2. Optimization and parameter estimation

Figure 5.25: EIS estimate versus measured for the Panasonic cell

Figure 5.26: Steady-state resistance estimate versus measured for the Panasonic cell
5.2. Optimization and parameter estimation

![Resistance values versus SOC & C-rate](image1)

![R₀ values versus SOC at all C-Rates](image2)

Figure 5.27: Instantaneous resistance estimate versus measured for the Panasonic cell

frequency test compared to the standard instantaneous resistance test at multiple C-rates, this is shown in Fig. 5.27. The data is not aligned, which shows some issues my arise when testing on the Arbin. The rise time of the pulse is theorized to be too slow on the Arbin test equipment thus causing a greater separation in resistance values between SOCs.

In general, the frequency results show excellent results, although the low frequency data is slightly skewed due to the optimization method trying to find $D_{e,tot}$ values that fit the $R_{ss}$ testing. This is shown in Fig. 5.28, and plotted for multiple temperatures.

The final set of values found in the optimization is shown below in Table 5.26. These values produce the best match to the all of the measured data and can be used to simulate the cell as will be shown in the next chapter. The simulation process will require all of the identified parameter values along with transfer functions of cell variables and non-linear corrections that help match the real cell’s behavior.
5.2. Optimization and parameter estimation

Figure 5.28: EIS estimate versus measured for the Panasonic cell
### Table 5.1: Panasonic estimated parameter values

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5.2. Optimization and parameter estimation

![Figure 5.29: $R_{ss}$ estimate versus measured for the Panasonic cell](image)
This chapter will cover simulating the cell with the new parameter values. Much of this work was performed by Lee et al. [17] but needs modifications to work with the new lumped parameter values. The first section will use the parameter values found in Chapter 5 and extend them into transfer functions at numerous frequencies both above and below those that were optimized. Using these transfer functions, the continuous-time realization algorithm (CRA) developed by DePalma [30] generates the state-space model at each SOC set-point. Finally the state-space systems are used inside the reduced order model (ROM) to simulate the cell under any current profile.

6.1 Transfer functions

Electrochemical based transfer functions are created using the equations derived in Chapter 2, where the equations are modified depending on which double-layer capacitor model is selected. To arrive at a voltage equation for the cell, we make use of the transfer functions \( \frac{\Phi_e(3,s)}{I_{app}(s)} \), \( \frac{\tilde{N}_{e,\text{rat}(3,s)}}{I_{app}(s)} \), \( \frac{\tilde{N}_e(0,s)}{I_{app}(s)} \), \( \frac{\tilde{N}_{e,s,e}(0,s)}{I_{app}(s)} \), \( \frac{\tilde{N}_{e,s,n}(0,s)}{I_{app}(s)} \), \( \frac{\tilde{N}_{f,s,n}(0,s)}{I_{app}(s)} \), and \( \frac{\tilde{N}_{f,s,e}(0,s)}{I_{app}(s)} \). With these transfer functions the total time-domain voltage equation can be written,

\[
v(t) = F \left( j_t^{\text{pos}}(0,t) P_{\text{film,tot}}^{\text{pos}} - j_t^{\text{neg}}(0,t) P_{\text{film,tot}}^{\text{neg}} \right) + \left[ \tilde{\phi}_e(3,t) \right]_1 + (\eta^{\text{pos}}(0,t) - \eta^{\text{neg}}(0,t)) + \left[ \phi_e(3,t) \right]_2 + (U_{\text{ocp}}^{\text{pos}}(0,t) - U_{\text{ocp}}^{\text{neg}}(0,t)).
\]

The values for \( \tilde{\phi}_e(3,t) \), \( j_t^{\text{neg}}(0,t) \), and \( j_t^{\text{pos}}(0,t) \) are solved directly through the transfer functions and their associated state-space modes generated from the CRA. The other values
6.2 Frequency response fitting

needed in the voltage equation are nonlinear but are dependent on variables that are solved through linear transfer functions. To start, the value for \[\tilde{\phi}_e(3, t)\] is given by,

\[\left[\tilde{\phi}_e(3, t)\right]_2 = \frac{2RT(1 - t_0)}{F} \ln \left( \frac{n_{e,\text{ratio}}(3, t)}{n_{e,\text{ratio}}(0, t)} \right)\]

where,

\[n_{e,\text{ratio}}(3, t) = 1 + \tilde{n}_{e,\text{ratio}}(3, t)\]
\[n_{e,\text{ratio}}(0, t) = 1 + \tilde{n}_{e,\text{ratio}}(0, t)\]

The values for \(\tilde{n}_{e,\text{ratio}}(3, t)\) and \(\tilde{n}_{e,\text{ratio}}(0, t)\) can be found through the transfer functions \(\tilde{N}_{e,\text{ratio}}(0, s) / I_{\text{app}}(s)\) and \(\tilde{N}_{e,\text{ratio}}(3, s) / I_{\text{app}}(s)\), respectively. Next, the overpotential terms are equal to a nonlinear function,

\[\eta_{\text{reg}}(0, t) = \frac{2RT}{F} \text{asinh} \left( \frac{j_{\text{reg}}^0(0, t)}{2Fj_{\text{reg}}^e} \right),\]

and are dependent on the faradaic flux \(j_{\text{reg}}^e(0, t)\), which is found through the linear transfer function \(\tilde{j}_{\text{reg}}^e(0, s) / I_{\text{app}}(s)\). Finally, \(U_{\text{reg}}(0, t)\) is found through look-up tables and has a dependence on electrode SOC. To find the SOC of each electrode, the value for \(n_{s,e,\text{reg}}(0, t)\) is required and is equal to,

\[n_{s,e,\text{reg}}(0, t) = n_{s,e,\text{reg}}(0, t) + \tilde{n}_{s,e,\text{reg}}(0, t)\]

The values for \(\tilde{n}_{s,e,\text{reg}}(0, t)\) can be found through the transfer functions and the equivalent state-space model for \(\tilde{N}_{s,e,\text{reg}}(0, s) / I_{\text{app}}(s)\). The total Nyquist plot of the cell’s impedance is derived from from the linear transfer functions together with the linearized equations of the nonlinear terms. A plot of the Nyquist frequency data from the transfer functions along with the estimated data from the optimization is shown in Fig. 6.1.

6.2 Frequency response fitting

In order to simulate the cell with any given current profile, the transcendental transfer functions are converted into a linear state-space model. To accomplish this, a sub-space-based system identification method introduced by DePalma [30] generated constant coefficient
6.2. Frequency response fitting

![Nyquist plot of Transfer functions vs Estimated Data](image)

**Figure 6.1:** The extended Nyquist plot from the transfer functions estimates of $A, B, C,$ and, $D$ matrices to form a linear model at a specific SOC. Since the transfer functions are expressed in continuous-time, the CRA produces a continuous-time state-space representation. After the continuous-time state-space system is created, Nyquist plots generated from the state-space system and from the original transfer functions are compared. These are shown in Fig. 6.2. Each state-space model produced by the CRA is dependent on the total number of poles used in the estimation as well as an “oversizing parameter”, used for tuning.

The oversizing parameter used to generate the state-space model can greatly influence the model fit. In order to help find the best oversizing parameter, a cost function is created to compare the Nyquist fit of the produced ROM and the transfer function created with the estimated parameters. The cost function for the Nyquist plot is given by,

$$\text{Cost}(SOC, s) = \sqrt{\text{mean} \left[ (\text{Re}(Z_{\text{est}}(s)) - \text{Re}(Z_{\text{ROM}}(s)))^2 + (\text{Im}(Z_{\text{est}}(s)) - \text{Im}(Z_{\text{ROM}}(s)))^2 \right]}.$$ 

Where $Z_{\text{est}}(s)$ are the impedances produced by the transfer functions and $Z_{\text{ROM}}(s)$ are the cell impedances produced by the ROM.

One potential problem with the CRA relates to complex poles. During the constructions of the state-space model the “$A$” matrix is forced to be in a block-diagonal form. If the system has complex poles, then this diagonal form will contain block matrices for each set of complex poles. In order to find an oversizing parameter that produce a state-space model without complex poles, candidate system having complex poles are discarded from
6.3 Reduced-order model

This ensures that all produced ROMs contain the most appropriate oversizing parameters that fit the transfer functions well and contain only real poles. The best oversizing parameters are saved to the Matlab structure containing the cell’s data and the final ROM estimates are saved to a simulation directory. The frequency-domain magnitudes of each transfer function along with the CRA’s produce linear model (four poles) with non-linear corrections are shown in Fig. 6.3 at both the positive and negative current collectors.

6.3 Reduced-order model

The simulation process uses the continuous-time realization algorithm (CRA)-generated state-space matrices inside the reduced order model (ROM) framework to estimate the cell’s voltage along with other internal parameters of interest. The continuous-time state-space equations are ultimately converted to discrete time equivalent matrices at a sampling rate of 1 Hz. This causes much of the higher frequency dynamics to be ignored but due to the current applications of the cell model this is not a concern. The ROM takes the linear outputs of each transfer function and performs the nonlinear corrections in the time-domain to calculate a time response for the cell properties of interest. The ROM changes models
6.3. Reduced-order model

Figure 6.3: Cell voltage transfer functions and CRA state-space system magnitudes (dB) versus frequency (rad/s⁻¹)
6.3. Reduced-order model

According to the cell’s calculated SOC at every time instant. This means the ROM has to perform blending of some form in between the generated models.

An earlier method of blending the models interpolated the $A, B, C,$ and, $D$ matrices in-between the SOC set-points of the generated models using an approach termed “model blending” [17], which we will review next. First we note that the state-space system generated by the CRA is in diagonal canonical form,

$$
\begin{align*}
\begin{bmatrix}
\dot{x}_1 \\
\dot{x}_2 \\
\vdots \\
\dot{x}_n 
\end{bmatrix} &= \begin{bmatrix}
-p_1 & 0 & 0 & 0 \\
0 & -p_2 & 0 & 0 \\
0 & 0 & \ddots & 0 \\
0 & 0 & 0 & -p_n
\end{bmatrix} \begin{bmatrix}
x_1 \\
x_2 \\
\vdots \\
x_n
\end{bmatrix} + \begin{bmatrix}
1 \\
1 \\
\vdots \\
1
\end{bmatrix} u \\
\begin{bmatrix}
y_1 \\
y_2 \\
y_3 \\
y_m
\end{bmatrix} &= \begin{bmatrix}
c_{11} & c_{12} & \cdots & c_{1n} \\
c_{21} & c_{22} & \cdots & c_{2n} \\
c_{31} & c_{32} & \cdots & c_{3n} \\
c_{m1} & c_{m2} & \cdots & c_{mn}
\end{bmatrix} \begin{bmatrix}
x_1 \\
x_2 \\
\vdots \\
x_n
\end{bmatrix} + \begin{bmatrix}
d_1 \\
d_2 \\
\vdots \\
d_m
\end{bmatrix} u.
\end{align*}
$$

Each state-space system is blended based on the current SOC set-point (around which the model is linearized) and the nearest computed linear models. For example, if the current

![Figure 6.4: $\Phi_{s-e}$ transfer functions versus CRA state space system magnitudes (dB) versus frequency (rad s$^{-1}$)](image)

![Figure 6.4: $\Phi_{s-e}$ transfer functions versus CRA state space system magnitudes (dB) versus frequency (rad s$^{-1}$)](image)
6.3. Reduced-order model

cell’s SOC is at 13% with the nearest produced models at 10% and 20% the formulation of the model is,

\[ SOC = 13\% \]
\[ \alpha = \frac{13\% - 10\%}{20\% - 10\%} \]
\[ A_{10\%}(1 - \alpha) + A_{20\%}(\alpha) = A_{13\%} \]
\[ C_{10\%}(1 - \alpha) + C_{20\%}(\alpha) = C_{13\%} \]

This method of blending produces reasonable results when the dynamics of the current profile are high such as in an urban dynamic drive schedule (UDDS) profile. Issues arose however when performing a constant-current discharge profile having very little dynamics. After investigating the states of the models, each produced ROM contained a state-space system where the state definitions did not necessarily agree with one another. In particular when crossing a set-point SOC, the model changed its state definition abruptly and took time to correct the state definition.

To help improve this, a new method was developed that instead blended the outputs from all models instead of the \( A, B, C, \) and \( D \) matrices directly. Because the \( A \) matrix of each model is diagonal, every model’s states can be updated by placing all models in a single matrix with the diagonals of each \( A \) matrix into separate columns. The states of each model are updated individually using the equation,

\[
\dot{x}_{all} = A_{all} \circ x_{all} = \begin{bmatrix}
-p_{1,0\%}x_{1} & -p_{1,10\%}x_{1} & \cdots & -p_{1,100\%}x_{1} \\
-p_{2,0\%}x_{2} & -p_{2,10\%}x_{1} & \cdots & -p_{2,100\%}x_{1} \\
\vdots & \vdots & \ddots & 0 \\
-p_{n,0\%}x_{n} & -p_{n,10\%}x_{1} & \cdots & -p_{n,100\%}x_{1}
\end{bmatrix} + \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix} u
\]

The \( C \) matrix of all models are kept in a 3-dimensional matrix with the outputs formed in a loop by multiplying each model’s states by each corresponding \( C \) matrix,

\[
\begin{bmatrix} y_{0\%} & y_{10\%} & \cdots & y_{100\%} \end{bmatrix} = \begin{bmatrix} C_{0\%,0\%} & C_{10\%,10\%} & \cdots & C_{100\%,100\%} \end{bmatrix}
\]

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6.3. Reduced-order model

Now, to blend the models the outputs of the nearest models are blended with respect to the cell’s current SOC, such that,

\[
SOC = 13%
\]
\[
\alpha = \frac{13\% - 10\%}{20\% - 10\%}
\]
\[
y_{10\%} (1 - \alpha) + y_{20\%} (\alpha) = y_{13\%}.
\]

This blending method does require more computations now since every model needs to be run at every time instant, but due to the low computational demand of simulating a state-space system, this effect was not noticeable. To show the effects of the new versus the old blending methods, a constant-current discharge of C/10 is simulated with the full order model (COMSOL), the old ROM with model blending, and the new ROM with output blending. This is shown in Fig. 6.5. This new method reduced the RMS error from the FOM simulation from 1.02 mΩ to 0.45 mΩ at a C/10 discharge rate, 2.35 mΩ to 1.64 mΩ at a C/4 discharge rate, and 5.38 mΩ to 4.85 mΩ at a C/2 discharge rate. From this result a slower discharge rate has a better estimation as compared to the FOM, and thus a slow discharge rate should be used when testing a laboratory cell.

The last improvement to the ROM was to correct the OCV data when using a laboratory cell. In order to create an error vector, the OCP estimated data from the negative and positive electrodes are compared to the OCV data taken from the cell. The OCV error as a function of SOC is created by,

\[
OCV_{\text{error}}(SOC) = OCV_{\text{cell}}(SOC) - OCP_{\text{pos}}(SOC) - OCP_{\text{neg}}(SOC)
\]

The plot of the voltage error for the Panasonic cell is shown in Fig. 6.6. This OCV error function is used to correct the cell’s potential in the ROM but does not correct the individual electrode estimated potentials. The corrected ROM voltage equation is,

\[
v_{\text{cell}}[k] = F(j_{f}^{\text{pos}}[0,k]R_{\text{film,tot}}^{\text{pos}} - j_{f}^{\text{neg}}[0,k]R_{\text{film,tot}}^{\text{neg}}) + \left[\tilde{\phi}_{e}[3,k]\right]_{1} + (\eta^{\text{pos}}[0,k] - \eta^{\text{neg}}[0,k])
\]  
\[
\hspace{1cm} + \left[\tilde{\phi}_{e}[3,k]\right]_{2} + \left(U_{\text{ocp}}^{\text{pos}}[0,k] - U_{\text{ocp}}^{\text{neg}}[0,k]\right) + i_{\text{app}}[k]R_{\text{term}} + U_{\text{ocv, error}}[k].
\]
6.3. Reduced-order model

Figure 6.5: Constant-current discharge simulation with the model blending versus output blending
6.3. Reduced-order model

![Diagram of OCV error function for the Panasonic cell](image1)

**Figure 6.6:** OCV error function for the Panasonic cell

![Diagram of UDDS simulation of the Panasonic cell and estimated ROM](image2)

**Figure 6.7:** UDDS simulation of the Panasonic cell and estimated ROM

### 6.3.1 Urban dynamometer driving schedule simulation

After the ROM is generated at each user-defined SOC, a current profile is loaded onto the Arbin for testing the laboratory cell. The urban dynamometer driving schedule (UDDS) current profile contains the most dynamic profile and was chosen to compare the results of the ROM to the actual cell. A series of UDDS cycles are used to move the cell though all of the cell’s SOC range to apply the dynamics at various SOCs. The same current profile was tested on the Panasonic cell with the Arbin as was used in the ROM. The results of the tests are shown in Fig. 6.7, and exhibit an RMS error of 3.14 mV.
6.4. Conclusion

6.3.2 C/30 simulation

To test the cell against very slow dynamics, the C/30 discharge profile was run on the Panasonic cell and the estimated ROM. This process tests the accuracy of the DC gain of the transfer functions and helps test the solid-diffusivity fit. Again the cell is subject to a current profile on the Arbin with measurement recorded every second. The current profile is saved from the Arbin and tested on the estimated cell using the ROM. The result of this test is shown in Fig. 6.8, with a corresponding RMS error of 12.4 mV.

6.4 Conclusion

This chapter presented a method for simulating a lithium ion cell using any defined current profile, and provides not only cell voltage but all internal electrochemical variables of interest. The voltage match between the actual cell and the estimated model shows that matching impedance values at a variety of frequencies can provide a suitable model for the cell. The model identification process contains multiple steps that help avoid finding local minimum values in the optimization process. A flow chart describing the identification process steps used for the Panasonic cell is shown in Fig. 6.9. After showing that the minimum cost from each impedance does not produce the same parameter values, it requires some additional enhancements for further accuracy improvement. The final chapter will
6.4. Conclusion

Figure 6.9: Flow chart of the identification process

provide suggestions for future work to help match the cells impedance results of all tests simultaneously.
CHAPTER 7

Conclusions

This dissertation provides the framework for systematic identification of a cell’s parameter values and the corresponding ability to simulate the cell under different current profiles. This new model represent a significant departure from the equivalent circuit model in common use, and can provide far more insight into the internal concentrations and potentials that drive unwanted side reactions [31]. The methods introduced here were used to not only find parameters of a virtual cell but also the parameter values of a laboratory cell. Validating the parameter values of the laboratory cell is difficult but demonstrated excellent voltage matching of a highly dynamic current profile. The model was improved to better match a laboratory cell but further refinements are possible.

7.1 Future work

The full process of finding the parameter set for a cell is a lengthy one requiring significant mathematical modeling. The optimization process used to identify the parameters of a virtual cell is straightforward and shows very good results. The process used to identify a laboratory cell is much more difficult. Working with a laboratory cell takes a huge amount of time for data collection as well as very careful calibration of the test equipment. The focus here was to identify a laboratory cell with single chemistries in each electrode, and must be changed slightly to include a mixed chemistry cell. Other improvements that can be made to the model include adding other constant phase elements to the model due to the distribution of particle sizes in each electrode, and including a hysteresis model to predict
steady-state potentials with better accuracy. Finally the process of finding the states space models for the linear terms involved in the reduced order model needs to be improved.

### 7.1.1 Single test setup

A very important part of the cell parameter value identification process involves setting up the test to minimize the amount of unknown errors. This difficulty was exacerbated by having to change the test setup for each test. The setup becomes even more complicated if tests need to be rerun, requiring a whole new set of calibration parameters need to be identified. Using a single test platform such as the Arbin Reference 3000 with a power booster would allow for a single set of calibration parameters. In this case the data for each test can be directly compared without concern over different terminal resistances or mutual inductances.

A better method of collecting the data is also needed. The data collecting process involves a significant time demand with user intervention between each test step. Changing temperatures and allowing the cell to regain equilibrium values can take time. A single test script that communicates with the Arbin and the thermo-chambers would eliminate testing time while running all of the tests with no user intervention. This would save significant time and would meet the suggestion of using a single test setup.

### 7.1.2 Mixed chemistries model

Newer chemistries of lithium-ion batteries are trying to maximize the benefits of different chemistries and combining these to make a new cell. The model for the lithium-ion cell can thus be modified to include these multiple chemistries as was done by Albert Rodriguez [32]. This new model needs to be modified to include the new “lumped” parameters in order to take advantage of the techniques introduced here. These new chemistries will involve more parameter value estimations but can help to pinpoint when unwanted side reactions for each individual chemistry will happen [31]. With this new model, the battery
7.1. Future work

Figure 7.1: SEM of the Panasonic cell for the negative and positive electrodes shown particle sizes can theoretically be controlled to ensure conditions do not arise that promote these side reactions.

7.1.3 Distribution of particle sizes

The current model uses a single particle radius in each electrode. The particle sizes in a commercial lithium-ion cell can vary greatly and affect the performance of the cell [33]. A Scanning electron microscope (SEM) image of the Panasonic cell was completed and shown in Fig. 7.1. This particle size distribution can effect the low frequency responses which causes errors when comparing to a model with a single particle radius. Adding the effects of multiple particles with different radius will help improve the model fit to the measured data.

7.1.4 Hysteresis model

As seen with the steady-state resistance test, the resting voltages for a charge and discharge test do not converge to the same value. The culprit of this was hypothesized to be a result of the cells hysteresis effect [34]. By taking the fits of the resting voltages and simple
hysteresis model developed by Plett [12], this new potential term can help improve the cells potential fit to the measured data.

### 7.1.5 Alpha value

The work in this dissertation assumes the alpha value is set to a half. This assumption is necessary to solve (in closed form) the overpotential term when given a specific lithium flux, $j_{\text{reg}}^{\text{tot}}$, shown by,

$$
\begin{align*}
    j_{\text{tot}}^{\text{reg}} &= k_{\text{step}}^{\text{reg}} (n_{\text{e}, \text{ratio}})^{1-\alpha} (\tilde{n}_s^{\text{reg}} + n_{s, \Delta, \text{max}}^{\text{reg}})^{1-\alpha} (n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}}) \alpha \\
    &= k_{\text{step}}^{\text{reg}} \sqrt{(n_{\text{e}, \text{ratio}}) (\tilde{n}_s^{\text{reg}} + n_{s, \Delta, \text{max}}^{\text{reg}}) (n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}}) 2 \sinh \left( \frac{F}{2RT\eta} \right) ^{\alpha} \\
    &= k_{\text{step}}^{\text{reg}} \sqrt{(n_{\text{e}, \text{ratio}}) (\tilde{n}_s^{\text{reg}} + n_{s, \Delta, \text{max}}^{\text{reg}}) (n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}}) 2 \sinh \left( \frac{F}{2RT\eta} \right)}
\end{align*}
$$

Because the assumption is not always valid, a numerical solution can be found by finding the solution to,

$$
\begin{align*}
    k_{\text{step}}^{\text{reg}} (n_{\text{e}, \text{ratio}})^{1-\alpha} (\tilde{n}_s^{\text{reg}} + n_{s, \Delta, \text{max}}^{\text{reg}})^{1-\alpha} (n_{s,0}^{\text{reg}} + \tilde{n}_s^{\text{reg}}) \alpha \\
    - \left( \exp \left( \frac{F}{RT\eta} \right) \right) \exp \left( -\alpha \frac{F}{RT\eta} \right) - \exp \left( -\frac{\alpha F}{RT\eta} \right) = 0.
\end{align*}
$$

Solving for the overpotential term with any given alpha value, produces an instantaneous resistance plot versus SOC and C-rate that is non-symmetrical. Before the instantaneous resistance was exactly the same whether a discharge or charge pulse of the same magnitude was applied. As shown in Fig. 7.2 this is quite different when alpha is not assumed to be a half.

### 7.1.6 New reduced order model

Models produced using the CRA (even when used with optimal over-sizing parameters) do not match the transfer functions to a satisfactory degree. A need exists to improve the method of finding a linear system that best fits the measured data. These new linear systems
7.1. Future work

![Resistance values versus SOC & C-rate](image)

**Figure 7.2:** $R_0$ versus C-rate and SOC plot of Doyle cell when $\alpha = 0.9$

need to be easily adapted into the reduced order model and need to be able to blend at every instant in time to provide reliable steady-state responses.

The ROM has a limitation of blending models for a given temperature and SOC at every time step. In order to help improve the steady-state response for a constant charge/discharge current profile, models must be generated at set-points of lithium flux from the solid particles. Using the same equations from the $R_{ss}$ optimization section these models can be created using the new impedance ratio term. The ROM must be adapted to use these new models and switch based on the current flux value.
Bibliography


Bibliography


Bibliography


