INVERSE MODELING OF LI TRANSPORT IN MULTIPHASE ELECTRODES

INVERSE MODELING BASED ON MRI MEASUREMENTS TO COMPARE CAHN-HILLIARD MODELS USING MULTIPHASE POROUS ELECTRODE THEORY

BY

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| | pare Cahn-Hilliard Models Using Multiphase Porous |
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Abstract

In this study, a computational approach to the solution of an inverse modeling problem is developed to reconstruct unknown material properties of a Li-ion battery. Insitu MRI measurements performed on a layered graphite electrode during charging are used in comparison with Stefan-Maxwell concentrated electrolyte theory, Butler-Volmer reaction kinetics, and multiphase porous electrode theory to explore the overall accuracy of models for Li transport processes in the active material. In particular, the main research goal here is to determine if the original Cahn-Hilliard formulation for phase-separation can be improved upon through extension to a periodic bilayer model (two-layer Cahn-Hilliard). The original model contains a pair of two stable phases at low and high concentrations that produces the "shrinking core" behavior for lithiated graphite. The comparative advantage of the periodic bilayer model stems from the capturing of a third stable phase of intermediate concentration as the average between one concentrated layer and one dilute layer. Calibration is done simultaneously on concentration and cell voltage profiles through multi-objective optimization where the accuracy of a model is assessed based on the quantification of agreement with experimental data. The periodic bilayer model is found to improve upon the least-squares error for fitting of concentration profiles by roughly 20%, while the voltage fittings are too similar to be conclusive.

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Notation, Symbols, and Abbreviations

Notation

| ÷ | nondimensionalized variable |
|------------|-----------------------------|
| • | experimental data |
| ÷ | averaged value |
| := | defined to be |
| \approx | approximately |
| \in | contained within |
| U | union |
| đ | inexact differential |
| ∂ | partial differential |
| ∇ | gradient |

dot product

 \times cross product

•

Symbols and Units

| a | particle radius | m |
|------------------|-------------------------------------|-------------------------------|
| A | vacancy designation | |
| A_p | surface area | m^2 |
| a_j | ionic conductivity coefficient | |
| b | ionic diffusivity coefficient | |
| $b_{j,1}$ | fit OCV coefficient | V |
| $b_{j,k \neq 1}$ | fit OCV dimensionless coefficient | |
| В | lithiated particle designation | |
| В | magnetic induction | $\rm Vsm^{-2}$ |
| С | concentration | $ m molm^{-3}$ |
| C | probability of a particle at a site | |
| dA | surface area element | m^2 |
| dV | volume element | m^3 |
| D | diffusion coefficient | $\mathrm{m}^2\mathrm{s}^{-1}$ |

| \mathcal{D} | diffusion coefficient | $\mathrm{m}^2\mathrm{s}^{-1}$ |
|------------------|--------------------------|-----------------------------------|
| D | electric displacement | ${ m C}{ m m}^{-2}$ |
| e | electron charge | С |
| E_{Θ} | reference energy | V |
| E_{jk} | intermolecular potential | J |
| Ε | electric field | ${\rm Vm^{-1}}$ |
| \mathbf{F} | species flux | $\rm molm^{-2}s^{-1}$ |
| g | molar Gibbs free energy | $\rm Jmolm^{-3}$ |
| G | total Gibbs free energy | $\rm Jmolm^{-3}$ |
| h | molar enthalpy | $\rm Jmolm^{-3}$ |
| н | magnetic field | ${\rm Am^{-1}}$ |
| i | net reduction current | $\mathrm{Am^{-2}}$ |
| i_0 | exchange current | $\mathrm{Am^{-2}}$ |
| i | current density | ${\rm Am^{-2}}$ |
| j | index | |
| \mathbf{J}_{e} | energy flux | ${\rm J}{\rm m}^{-2}{\rm s}^{-1}$ |
| ${\cal J}$ | error functional | |
| k | index | |

| k_0 | exchange rate constant | ${ m A}{ m m}^{-2}$ |
|---------------|------------------------------------|----------------------------|
| k_B | Boltzmann constant | $ m JK^{-1}$ |
| K | drag coefficient | $\mathrm{Jmolsm^{-5}}$ |
| L | battery length | m |
| L_{jk} | Onsager coefficient | $ m molm^{-1}s^{-1}J^{-1}$ |
| L | battery position domain | |
| М | mobility | $m^2 s^{-1} J^{-1}$ |
| \mathbb{M} | mobility tensor | |
| Μ | magnetization | ${\rm Am^{-1}}$ |
| \mathcal{M} | molar mass | ${\rm kgmol^{-1}}$ |
| n | number of electrons | |
| n | unit normal vector | |
| N | integer quantity | |
| Р | number of particle layers | |
| P_j | crystal polarization component | Jm |
| P_L | percent loading of active material | |
| P_{jk} | probability of forming a bond | |
| Р | polarization | ${ m C}{ m m}^{-2}$ |

| q | heat flux | $J m^{-2} s^{-1}$ |
|-------------------|----------------------------------|--------------------------------|
| Q | heat | J |
| r | radial position within particles | m |
| r | radius vector | m |
| R | entropy production rate | $\mathrm{Jm^{-3}s^{-1}}$ |
| R_V | volume-averaged reaction rate | $molm^{-3}s^{-1}$ |
| ${\cal R}$ | radial domain within particles | |
| S | molar entropy | ${ m J}{ m m}^{-3}{ m K}^{-1}$ |
| s_j | stoichiometric coefficient | |
| S | entropy | $\rm JK^{-1}$ |
| S_j | lattice site | |
| t | time | S |
| t^0 | transference number | |
| ${\mathcal T}$ | time domain | |
| Т | temperature | Κ |
| u | molar internal energy | $\mathrm{Jm^{-3}}$ |
| U | internal energy | J |
| $U_{\mathbf{eq}}$ | fitted open-circuit voltage | V |

| V | species velocity | ${ m ms^{-1}}$ |
|-------------------|--|--------------------|
| $V_{\mathbf{eq}}$ | open-circuit voltage | V |
| V_p | particle volume | m^3 |
| V_{j} | volume fraction of individual particle | |
| w | molar configurational work | $\mathrm{Jm^{-3}}$ |
| W_c | configurational work | J |
| W | ways to configure particles on lattice | |
| x | battery position | m |
| x_j | particle coordinate | m |
| z | charge number | |
| Z_n | coordination number | |
| α | transfer coefficient | |
| γ | side reaction parameter | |
| δ_{jk} | Kronecker delta | |
| ϵ | porosity | |
| ϵ_0 | permittivity of free space | ${\rm Fm^{-1}}$ |
| η | activation overpotential | V |
| κ | gradient penalty | ${ m Jm^{-1}}$ |

| $\kappa^{(1)}_{ij}$ | crystal symmetry tensor | $\mathrm{J}\mathrm{m}^2$ |
|---------------------|---------------------------------------|--------------------------|
| $\kappa^{(2)}_{ij}$ | crystal symmetry tensor | $\mathrm{Jm^5mol^{-1}}$ |
| λ | characteristic interface width | m |
| μ | chemical or electrochemical potential | J |
| μ_0 | permeability of free space | ${\rm Hm^{-1}}$ |
| ν | dissociation number | |
| ϕ | electric potential | V |
| $\hat{\Phi}$ | experimental cell voltage | V |
| σ | conductivity | ${ m Sm^{-1}}$ |
| τ | tortuosity | |
| ω | SEI reaction fraction | |
| Ω | regular solution parameter | J |

Abbreviations

| BDF | backward differentiation formula |
|-----|----------------------------------|
| BV | Butler-Volmer |
| CHR | Cahn-Hilliard reaction |
| DAE | differential algebraic equation |

| \mathbf{FVM} | finite volume method |
|----------------|------------------------------------|
| Li-ion | lithium ion |
| LiPF6 | lithium hexafluorophosphate |
| LIT | linear irreversible thermodynamics |
| LP | linear programming |
| MPET | multiphase porous electrode theory |
| MRI | magnetic resonance imaging |
| NLP | nonlinear programming |
| NP | Nernst-Planck |
| OCV | open-circuit voltage |
| PDE | partial differential equation |
| PEEK | polyether ether ketone |
| PET | porous electrode theory |
| SEI | solid-electrolyte interphase |
| \mathbf{SM} | Stefan-Maxwell |
| А | ampere |
| С | coulomb |
| F | farad |

xxiv

| Н | henry |
|-----|------------|
| h | hour |
| J | joule |
| К | kelvin |
| kg | kilogram |
| m | meter |
| μΑ | microamp |
| μm | micrometer |
| М | Molar |
| mol | mole |
| nm | nanometer |
| S | second |
| S | siemens |
| V | volt |

Chapter 1

Introduction

1.1 Electrochemistry and Batteries

The entirety of the planet is experiencing rapid climate change at what is a critical junction in human history. With global emissions at an all-time high, it is a necessity to innovate clean energy solutions to satisfy power consumption. Renewable energy sources like solar, tidal, and wind have become cheaper, though are intermittent and have variable power outputs that fluctuate over time. To compete with the steady supply from burning fossil fuels, energy storage systems must be put in place to convert and retain excess electricity generated during times of overproduction, helping maintain the supply of green energy otherwise. While there are many forms of energy able be stored for later use (e.g., mechanical, thermal), a rechargeable battery with one or more electrochemical cells remains one of the most popular and effective methods. In particular, the lithium-ion (Li-ion) battery has low self-discharge when not being used and one of the best energy-to-mass ratios. Companies such as Tesla have already demonstrated the effectiveness of large-scale grid storage through installation

of their Megapack in regions with unreliable networks like South Australia. These large clusters of Li-ion batteries are also positioned to replace "peaker" power plants that are dirty and expensive to burn natural gas in times of increased demand. On a local consumer level, Tesla envisions their Solar Roof and Powerwall providing this approach to electricity generation and storage in each individual household.

While retaining energy represents an important aspect of converting the electrical grid infrastructure to be green and sustainable, portable modern technology also requires reliable and mobile sources of power. Smaller electronics like cell phones and laptops are hugely dependent on energy-dense batteries with goals including the lightest materials with the highest charge capacity. For larger systems able to burn fossil fuels, improved battery technology is the most important path forward to reducing these emissions. The automotive industry has targeted a "million mile" battery with a price of \$100/kW h as the threshold at which the production cost of an electric vehicle (EV) becomes less than that using a combustion engine. Certain limitations like capacity fade from numerous charge/discharge cycles present formidable challenges when designing a long lasting battery. As such, huge investment has gone into testing a wide array of battery materials for better performance.

1.2 Ionic Transport

To create a predictive model that can assist in the design of industrial applications, the main physics of the battery must first be captured. In a conventional Li-ion battery, one electrochemical cell has two electrodes and an electrolyte as primary components. Like many physical processes, the system seeks a state of equilibrium in accordance with a free energy minimization. An electrical circuit connecting the electrodes allows for negatively charged electron flow from one to the other, with free energy able to be either added during charging or extracted when discharging. This electrical current is made possible by two simultaneous half-cell reactions occurring at the surface of each electrode. During charging, neutral lithium particles undergo oxidation by losing their electrons to become ions in the electrolyte when extracted from a solid Li metal electrode. At the same time, Li-ions undergo reduction by gaining electrons when intercalated into the solid graphite electrode. At both of these surfaces, the amount of lithium entering or exiting the electrode is as per a reaction driving force being the difference in potential between the reduced state and the oxidized state. The increased internal energy of lithium in the active material is then accessible at a later time by reversing the reactions.

The electrolyte within the cell can be liquid or solid and serves to complete the circuit by transporting ionic current between electrodes with both the anion and cation dissociated species carrying charge. In the present study, the focus is on a liquid binary electrolyte containing only one solvent and one salt. In general, ions move in response to the electric field (migration), concentration gradients (diffusion), and bulk fluid motion (convection is neglected in this work). The fundamental relation from the first law of thermodynamics is used with conservation of species and charge to obtain an expression for ionic flux and ionic current. The use of Ohm's law also allows for consideration of a total cell voltage measured as the potential difference between electrodes, which is an important aspect of battery operation. The open-circuit condition is achieved when the outer electrical circuit has no current and the system is in a state of equilibrium.

An electrochemical cell can be considered as two halves where half-cell reactions

occur at the surface of each electrode. The "foil" counter electrode is a thin, solid Li metal and treated as an inexhaustible source of ions where consideration of interior dynamics is not required. Within the active graphite particles in the porous electrode, however, similar nonequilibrium thermodynamic principles as those used for the electrolyte are also applied on the microscopic scale to model Li transport on a lattice. Here, a particular free energy is formulated where calculus of variations can then be used to find a thermodynamic driving force that evolves the system along a minimal energy trajectory. The porous electrode also consists of added binder and conductive material that serve to support and transport current between the active particles. In this work, simplifications made during mathematical modeling neglect the consideration of such additives.



Figure 1.1: Battery schematic.

1.3 Mathematical and Computational Modeling

An essential tool in battery research and development is a predictive model that saves on having to run expensive experimental tests. Calibration can be done on this model using the minimum amount of experimental data required to then extrapolate the results of untested configurations. The better able the model is to account for physical phenomena and capture features of the dataset used in calibration, the more faith can be put in using it to guide the improvement of battery performance. However, certain physical limitations exist in that a full particle simulation across all length scales is intractable and would require a vast amount of computational effort. The goal of any mathematical formulation is hence to distill and simplify the system into essential elements that do well to approximate the complicated physics of a battery.

The Newman model, as decribed in Section 3.1 with fundamental theory discussed in Fuller *et al.* [10], is an example of a streamlined mathematical framework where arguments made regarding the disparities in length scales reduce the dimensionality of the problem. While there are many length scales to be considered, the macroscopic scale in this work is treated as the distance between parallel current collectors over the length of the full electrochemical cell. The dynamics in the electrolyte can be modeled independently on the macroscopic scale with the Stefan-Maxwell concentrated solution theory. Graphite particles are represented as volumetric sink/source terms of Li-ions as they intercalate/deintercalate with reaction rates determined from the Butler-Volmer reaction type model. Macroscopic quantities like electric potentials, current densities, and volume-averaged lithium concentrations can then be compared to measurable laboratory data. This approach is known as porous electrode theory and was popularized by John Newman and his colleagues. Simplified versions of the model use homogenized, solid-state electrode particles with thermodynamics accounted for by using a reaction driving force determined from an open-circuit voltage that is fitted to experimental data.

An extension of the standard model is to be multi-scale in that macroscopic quantities are strongly coupled to volume-averaged, microscopic graphite particle dynamics. Taking advantage of disparities in length scales of the problem simplifies to a pseudo two-dimensional model that has equations dependent on the macro-scale length of the battery and the micro-scale radii of electrode particles. It is common to use a simplified Fickian diffusion first derived by Fick [9] to determine the evolution of intercalated lithium from gradients in concentration. The Cahn-Hilliard formulation Cahn and Hilliard [3] for free energy can instead be used to resolve phase transformations within the solid electrode particles. This added capability produces a "shrinking core" where during charging, a high concentration exterior is separated by a phase interface from a low concentration core which diminishes as the particle becomes fully charged. The stable phases are referred to as "stages" and are observed by Ferguson and Bazant [8] to produce a measurable change in color of the graphite depending on degree of saturation with lithium.

One extension of the original model from Smith and Bazant [22] to account for phase separation is known as multiphase porous electrode theory with the accompanying software MPET from Smith, Raymond B. [24]. Here, the numerous coupled partial differential equations (PDE's) that define the model are evolved over time as the system would in reality over the duration of an experiment. An extension of the Cahn-Hilliard free energy is implemented to capture the higher staging known to occur in layered graphite material. The periodic bilayer model features two different repeating layers that are independently able to phase separate into high and low concentrations as before. Based on competing inter-layer and intra-layer forces, a third stable phase of an intermediate average concentration is made possible by simultaneously having one layer full with the other dilute in a particular volume.

To obtain meaningful results from simulating battery dynamics, the various parameters and material properties that are used in the model must be based on actual measurements. To simplify the computation, estimations in the literature are used to fix many of the properties related to the electrolyte dynamics where any errors made in this regard will notably change the overall simulation outcomes. In the work here, a number of key electrode and reaction parameters of interest are left unknown and subject to reconstruction during calibration of the model based on experimental data. This is known as the inverse problem with one approach being to infer the unknown values by solving an optimization problem to fit resulting model data. The accuracy of the mathematical model can then be assessed by the magnitude of the optimal least-squares error between the datasets. At the end of an optimization algorithm that iteratively improves upon the fit, the set of parameters producing matching results to measured quantities can then be used by the model to accurately predict the behavior of the battery under different conditions.

1.4 Goals & Summary of Main Results

The main focus of this study is in assessing the relative fidelity of the original Cahn-Hilliard model compared to the extended periodic bilayer (two-layer Cahn-Hilliard) model. It is hypothesized that additional phases from the increased complexity of two-layer free energy considerations will result in macroscopic outputs with closer resemblance to experimental concentration and voltage profiles. Physically, it is known that cross-layer interaction effects between intercalated lithium particles and vacancies play a significant role in determining the higher graphite staging observed experimentally in Ferguson and Bazant [8] that is unable to be captured by the single layer Cahn-Hilliard model. Given its nature as an extension, the two-layer model should perform better or just as well by collapsing to the original Cahn-Hilliard model. Multiobjective optimization is used to simultaneously fit both sets of measurements to solve the inverse problem and infer effective parameters that characterize the physical system. Success is measured by the smallness of error functionals quantifying the least-squares difference between optimal model data and experimental results.

The novelty of this work comes from adapting the inverse modeling approach from Morales Escalante *et al.* [15] to use the more advanced computational software MPET. Doing so enabled the exploration of the 2-layer Cahn-Hilliard model to assess its ability to reproduce experimental results relative to the original model. Proper configuration was required to ensure consistency of the mathematical models with the particular physical experimental setup. This included hard-coded modifications to account for side reactions from Section 3.1.2.2 and the inclusion of an open-circuit voltage fit to experimental data in the Bulter-Volmer reaction from Section 3.1.2.1. These concepts also needed to be extended to apply to the periodic bilayer model which had not been done before. A wrapper around the MPET software was then created to implement all aspects of optimization and data handling.

The optimal "Pareto front" for each model was obtained by solving the family of multi-objective optimization problems with various weights between concentration and voltage error functionals. The periodic bilayer model was indeed found to improve upon the fitting obtained to both available datasets. In particular, the concentration error functional saw the most improvement with the increased complexity of higher staging in the 2-layer model being better able to capture certain features of the experimental data. The change in voltage profile fitting between models was only marginal such that a strong conclusion in this regard was unable to be drawn. However, the results of the multi-objective optimization indicate that the models simultaneously fit both sets of measurements rather well such that a significant trade-off between concentration or voltage agreement is not necessary.

1.5 Thesis Structure

This work begins by detailing the experimental setup and corresponding datasets in Chapter 2. Understanding this physical setup is important to then motivate the specific derivations of governing equations in Chapter 3 that constitute the mathematical model of transport processes. By comparing the experimental concentration and voltage profiles to those produced through simulation, the problem of calibrating the predictive model by reconstructing unknown parameters is formulated through inverse modeling in Chapter 4. The computational approach to simulating the battery and the optimization algorithm used to infer material properties from data is then detailed in Chapter 5. Finally, results of the inverse modeling are presented and discussed in Chapter 6 with concluding remarks on the outlook of research given in Chapter 7.

Chapter 2

Experiments

Physical measurements of voltage and lithium concentration profiles taken over the course of an experiment provide a valuable dataset for inferring thermodynamic battery properties. Inverse modeling discussed in Chapter 4 seeks to most accurately reconstruct unknown parameters and obtain good agreement with experimental results. Furthermore, close consideration of the battery and testing procedure is required to establish known quantities in a mathematical model. In this chapter, the experimental setup and data is summarized from the original work of Krachkovskiy *et al.* [11]. The description is also consistent with Morales Escalante *et al.* [15] where it appears in a similar context as here.

The electrochemical cell is made up of two copper current collectors with a metallic lithium counter electrode attached to one and a copper-foil-supported graphite electrode attached to the other. The polyether ether ketone (PEEK) cylindrical body was hermetically sealed by means of PEEK Super Flangeless high-performance liquid chromatography fittings. Electrodes were separated by three glass microfiber filter membrane discs (# 691, VWR Scientific Products) and soaked in a 1 M LiPF6
in ethylene carbonate/diethyl carbonate (1:1 v/v) battery-grade electrolyte solution (Sigma-Aldrich). The interelectrode spacing was approximately 200 μ m and the thickness of the graphite electrode was 300 μ m. The thickness of the solid Li metal counter electrode is disregarded and does not play a role in this work.

A constant current of $45 \,\mu\text{A}$ was applied to the cell for 26 h to partially charge the graphite. Lithium concentration profiles $\hat{c}_s(x, t_k)$, $k = 1, \ldots, N$, were collected every 2.5 h at $t_1 = 2.5$, $t_2 = 5, \ldots, t_N = 25$ h with N = 10 being the total number of acquired concentration profiles. They were acquired using the one-dimensional 7Li in operando MRI measurement technique described by Krachkovskiy *et al.* [11] and are shown as functions of the space coordinate x at different time levels in Figure 2.1. The measurements are not taken instantaneously at each given time but rather assumed to be an averaged value over some finite acquisition interval much less than the 2.5 h separation between measurements. Comparison during inverse modeling assumes a reasonable snapshot approximation and does not take the acquisition interval into account by time averaging portions of the higher resolution simulation data.

The time dependence of the total amount of Li measured as being intercalated into graphite can be obtained as the spatial mean of the instantaneous concentration profiles $\hat{c}_s(x, t_k)$, k = 1, ..., N. The total filling fraction or state of charge over time is shown in Figure 2.2. The galvanostatic current gives a linear relation between time and total lithium being reduced at the surface of the graphite electrode. Section 3.1.2.4 expresses the current using a charge rate (C-rate) of $C_r = 1/44$ h, written as C/44 and interpreted as the inverse of the number of hours required to achieve maximum charge. The experimental measurements of intercalated lithium normalized by the known maximum graphite capacity $c_{s,\max}$ instead show a departure from the Crate prediction of state of charge at later times. Possible lithium plating or deposition on the graphite surface begins growing at a constant rate upon achieving a certain critical state of charge. The Li here still contributes electrically to the overall circuit but is not measured in the concentration profiles.

Finally, Figure 2.3 shows how the measured cell voltage $\Phi(t)$ as the potential between current collectors evolves throughout the experiment. Similarly, the same experiment but with a slower C-rate of C/100 produces a measurable cell voltage that can be used as an approximation of the open-circuit voltage (OCV), where the current is close to zero. Like is done in solid-state variants of the electrode models, better thermodynamic agreement with experiment is done by using this OCV in the reaction driving force. The focus in the following chapters will be to develop the mathematical and computational framework to simulate approximations of the C/44 experimental concentration and voltage profiles.



Figure 2.1: Experimentally obtained concentration profiles $\hat{c}_s(x, t_k)$ of lithium in solid-phase electrode as functions of spatial coordinate x at time levels $t_k = 2.5, 5, \ldots, 25$ h. Concentrations are normalized by the total Li site capacity to

 $t_k = 2.5, 5, \dots, 25$ in Concentrations are normalized by the total in site capacity to be represented by a filling fraction. The dashed vertical line demarcates the 200 µm long separator from the 300 µm long electrode.



Figure 2.2: Time dependence of the total amount of lithium $\Delta x \sum \hat{c}_s(x, t_k)$ in solid-phase electrode normalized by the total Li site capacity as a filling fraction for the experimental data is the red line with markers. The green line represents the state of charge as calculated directly from the C/44 charge rate. The difference between these two is the black line to demonstrate possible existence of a side reaction diverting lithium to an SEI layer.



Figure 2.3: Comparison of experimentally obtained voltage profiles as functions of filling fraction at two different C-rates. The C/44 curve in red was collected along with MRI measurements while the C/100 in black demonstrates the distinct voltage plateaus expected in near open-circuit conditions.

Chapter 3

Mathematical Models

In this chapter, the mathematical framework for a multi-scale battery model is established using nonequilibrium thermodynamics to obtain equations for the Li-ion transport processes. First, the well known Newman model is discussed which serves to couple dynamics in the macroscopic liquid electrolyte to those in the microscopic solid electrode particles. The electrode model is then expanded using the Cahn-Hilliard formulation to capture the effects of phase separation in layered graphite material. Finally, an extension to the Cahn-Hilliard model will allow for multiple phases and higher staging within solid particles through the use of a periodic bilayer model.

3.1 Newman's Model

Consider the physical battery model as illustrated in Figure 3.1. On either end of a narrow container are two copper current collectors connected by a circuit allowing galvanostatic electron flow from left to right while measuring the cell voltage found



Figure 3.1: Battery schematic with overlayed MRI and simulation data.

later in (3.1.81). The counter electrode is displayed as a thin gray lithium metal from which Li^+ is stripped and transported away. Ions move through the electrolyte which permeates both separator and electrode. The full electrode to be modeled is approximated using graphite spheres of radii *a* which undergo lithiation as time progresses. The concentration of lithium within the particles is demonstrated using a heatmap at a late time. Strong phase separation shown here produces a dilute graphite core distinct from the concentrated graphite shell. The bottom part of the schematic depicts this model data in the pseudo two-dimensional domain (x, r) which accounts for the full electrode volume given particles here are spherically symmetric. The total amount of lithium in each particle over the battery length x as comparable to experimental measurement is given as a bar graph at the top of the schematic.

In the sections to follow, names are assigned to the open spatial domains of the pseudo two-dimensional system to simplify notation. The dynamics on the macroscopic scale occur over the battery length x on the order of hundreds of μ m while the microscopic dynamics of the electrode occur over the particle radius r on the order of 10 µm. The x coordinate is defined in the following regions,

$$x = 0,$$
 current collector/counter electrode, (3.1.1a)

$$x \in \mathcal{L} \coloneqq (0, L_s + L_c), \quad \text{battery cell},$$
 (3.1.1b)

$$x = L_s + L_c,$$
 current collector, (3.1.1c)

where L_s is the length of separator and L_c is the length of solid electrode. Electrolyte is present in the entire battery domain \mathcal{L} which can be segmented into a separator domain \mathcal{L}_s and an electrode domain \mathcal{L}_c ,

$$x \in \mathcal{L}_s \coloneqq (0, L_s),$$
 separator, (3.1.2a)

 $x = L_s$, separator/electrode interface, (3.1.2b)

$$x \in \mathcal{L}_c \coloneqq (L_s, L_s + L_c), \quad \text{graphite electrode}, \quad (3.1.2c)$$

such that $\mathcal{L} = \mathcal{L}_s \cup \mathcal{L}_c$. For the spherical solid electrode particles with $x \in \mathcal{L}_c$,

the following values are possible in the radial coordinate r,

$$r = 0,$$
 particle center, (3.1.3a)

$$r \in \mathcal{R} \coloneqq (0, a),$$
 interior volume, (3.1.3b)

$$r = a,$$
 particle surface, (3.1.3c)

Finally, equations will be evolved in time t over the temporal domain \mathcal{T} ,

$$t = 0,$$
 initial time, (3.1.4a)

$$t \in \mathcal{T} \coloneqq (0, t_f],$$
 experiment duration, (3.1.4b)

where t_f is the final time. For generality, vector notation is used in the following sections. Specializing then to the pseudo two-dimensional x-r domain in the summary Section 3.3 will take advantage of the disparities in length scales in spherical graphite particles and the orthogonal battery coordinates. Initial conditions will also be specified there.

3.1.1 Electrolyte Model

Consider the electrolyte mixture of a dissociating salt and solvent from the experimental description in Chapter 2. The cation and anion concentrations $c_{l,\pm}$ are assigned to components of the binary salt while the solvent has a neutral species concentration $c_{l,0}$. The thermodynamic treatment of transport in Latz and Zausch [14] reduces the three component system to just one by imposing two constraints. Assuming there is no heat transfer from bulk fluid transport as convection, any volume element has a center of mass at rest,

$$\mathcal{M}_0 dc_{l,0} + \mathcal{M}_+ dc_{l,+} + \mathcal{M}_- dc_{l,-} = 0.$$
(3.1.5)

Here, $dc_{l,j}$ is an infinitesimal change in concentration and \mathcal{M}_j are molar masses of each component $j = 0, \pm$.

The second assumption of local electroneutrality is also detailed in Latz and Zausch [14] where they assert the electric field would need to be much larger than those present to induce charge separation on the µm scale that the electrolyte is modeled. On such length scales, it is a reasonable approximation the charge density vanishes $\rho_e \approx 0$. It is noted that the approximation breaks down at the neglected double layer surrounding solid particles on the scale of 10 - 20 nm, though the present theory is restricted to scales greater than 100 nm. For a binary electrolyte in a Li-ion battery, charge neutrality is expressed as,

$$e(\nu_{+}z_{+}c_{l,+}+\nu_{-}z_{-}c_{l,-})=0, \qquad (3.1.6)$$

where the cation/anion dissociation numbers $\nu_{\pm} = 1$ represent the degree each component participates in a reaction. The charge numbers or valences $z_{\pm} = \pm 1$ quantify the amount of charge for each component in increments of the electron charge e. The electrolyte Li concentration is then chosen as c_l with (3.1.6) giving,

$$c_l(x,t) = \frac{c_{l,-}}{\nu_-} = \frac{c_{l,+}}{\nu_+}, \qquad t \in \mathcal{T} \quad x \in \mathcal{L}.$$
 (3.1.7)

The model equations that govern the evolution of lithium transport in the electrolyte

are then obtained by imposing conservation laws on species, charge, and energy.

3.1.1.1 Thermodynamic Potentials & Conservation Equations

The first law of thermodynamics is stated by Carter [4] to equate the increase in internal energy dU to the configurational work done on the system dW_c , plus the heat flow into the system dQ = TdS where S is entropy and T is temperature. Changing now to the corresponding molar densities u, s, w, internal energy also increases from chemical reactions through added matter $dc_{l,j}$ with chemical potentials $\mu_{l,j}$ for species $j = 0, \pm$,

$$du = Tds + \mu_{l,+}dc_{l,-} + \mu_{l,-}dc_{l,-} + \mu_{l,0}dc_{l} + dw.$$
(3.1.8)

Given the system in question is isochoric, the configurational work excludes pressure and volume as PdV = 0. Instead, Carter [4] gives intensive variables electric field \mathbf{E} and magnetic field \mathbf{H} with corresponding extensive variables polarization \mathbf{P} and magnetization \mathbf{M} in determining the work $dw = \mathbf{E} \cdot d\mathbf{P} + \mathbf{H} \cdot d\mathbf{M}$. Now, the electric displacement \mathbf{D} can be used in equation for polarization $\mathbf{P} = \mathbf{D} - \epsilon_0 \mathbf{E}$ where ϵ_0 is the permittivity of free space. Similarly, the magnetic induction \mathbf{B} can be used in equation for magnetization $\mathbf{M} = \mathbf{B} - \mu_0 \mathbf{H}$ where μ_0 is the permeability of free space. Since $\mathbf{E} \cdot d\mathbf{E} = 0$ and $\mathbf{H} \cdot d\mathbf{H} = 0$, the fundamental thermodynamic relation can be written as that found in Latz and Zausch [14],

$$du = Tds + \mu_l dc_l + \mathbf{E} \cdot d\mathbf{D} + \mathbf{H} \cdot d\mathbf{B}.$$
(3.1.9)

Here, a combined chemical potential is found using (3.1.5) and (3.1.7),

$$\mu_l = \mu_{l,+} + \mu_{l,-} - \frac{\mathcal{M}_- + \mathcal{M}_+}{\mathcal{M}_0} \mu_{l,0}.$$
(3.1.10)

In the treatment by Latz and Zausch [14], a Maxwell equation is written as

$$\mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} + \mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} = -\boldsymbol{\nabla} \cdot (\mathbf{E} \times \mathbf{H}) - \mathbf{i}_l \cdot \mathbf{E}, \qquad (3.1.11)$$

such that substitution into the rate of change of internal energy (3.1.9) gives,

$$\frac{\partial u}{\partial t} = T \frac{\partial s}{\partial t} + \mu_l \frac{\partial c_l}{\partial t} - \boldsymbol{\nabla} \cdot (\mathbf{E} \times \mathbf{H}) - \mathbf{i}_l \cdot \mathbf{E}, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}.$$
(3.1.12)

Here, \mathbf{i}_l is the electrolyte current density.

Conservation laws can be expressed in a stronger form as a local continuity equation that describes the transport of some quantity. Following Smith and Bazant [22], the differential forms of the continuity equations for the conservation of species are expressed as

$$\epsilon(x)\frac{\partial c_{l,-}}{\partial t} = -\boldsymbol{\nabla}\cdot\mathbf{F}_{l,-}, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}, \qquad (3.1.13a)$$

$$\epsilon(x)\frac{\partial c_{l,+}}{\partial t} = -\boldsymbol{\nabla}\cdot\mathbf{F}_{l,+} + \frac{R_V}{\nu_+}, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}, \quad (3.1.13b)$$

where the reaction rate $R_V = R_{V,+}$ for cations is later determined in (3.1.88a). The electrolyte species fluxes $\mathbf{F}_{l,\pm}$ require that only one be simulated and the other postcalculated using (3.1.7). Hence, it is better to use an effective flux $\mathbf{F}_l = \mathbf{F}_{l,-}$ as the anion flux where the volumetric source/sink term is $R_{V,-} = 0$ since only cations are reacting at the electrode surfaces. Note that concentration is defined per unit volume of electrolyte while flux is per unit area of porous medium as a whole. Accordingly, the porosity $\epsilon(x)$ is the electrolyte liquid fraction of the total volume with dependence on x specifying a different constant value for separator \mathcal{L}_s and electrode \mathcal{L}_c ,

$$\epsilon(x) \coloneqq \begin{cases} \epsilon_{l,s}, & x \in \mathcal{L}_s, \\ \epsilon_l, & x \in \mathcal{L}_c. \end{cases}$$
(3.1.14)

The compliment $(1 - \epsilon_l)$ for $x \in \mathcal{L}_c$ is the volume fraction occupied by the active material in the solid electrode.

The current density \mathbf{i}_l depends on both anion and cation fluxes, weighted by the amount of charge they carry,

$$\mathbf{i}_{l} = z_{-}e\mathbf{F}_{l,-} + z_{+}e\mathbf{F}_{l,+}.$$
 (3.1.15)

Consider now the charge density with the result of local electroneutrality (3.1.7),

$$\rho_e = z_+ e c_{l,+} + z_- e c_{l,-} = 0. \tag{3.1.16}$$

Taking the divergence of electrolyte current density (3.1.15) and substituting conservation of species equations (3.1.13) then gives the continuity equation for conservation of charge,

$$-\boldsymbol{\nabla} \cdot \mathbf{i}_l + z_+ e R_V = \epsilon(x) \frac{\partial \rho_e}{\partial t} = 0, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}.$$
(3.1.17)

The reference Latz and Zausch [14] proceeds to suggest an additional continuity

equation as a local conservation law for entropy,

$$\frac{\partial s}{\partial t} = -\boldsymbol{\nabla} \cdot \left(\frac{\mathbf{q}}{T}\right) + \frac{R}{T}, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}, \tag{3.1.18}$$

where \mathbf{q} is heat flux and R is the rate of entropy production. The conservation of total energy in the system gives a further constraint in that the local change in energy must also satisfy a continuity equation for energy flux \mathbf{J}_e with no source/sink terms,

$$\frac{\partial u}{\partial t} = -\boldsymbol{\nabla} \cdot \mathbf{J}_e, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}.$$
(3.1.19)

Substitution of (3.1.13a), (3.1.18), and (3.1.19) into (3.1.12) yields the expression,

$$-\boldsymbol{\nabla}\cdot\mathbf{J}_{e} = -\boldsymbol{\nabla}\cdot\left(\mathbf{q} + \mu_{l}\frac{\mathbf{F}_{l}}{\nu_{-}} + \mathbf{E}\times\mathbf{H}\right) + R + \mathbf{F}_{l}\cdot\boldsymbol{\nabla}\mu_{l} - \mathbf{i}_{l}\cdot\mathbf{E},\qquad(3.1.20)$$

Here, note the product rule was used to write $\mu_l \nabla \cdot \mathbf{F}_l = \nabla \cdot (\mu_l \mathbf{F}_l) - \mathbf{F}_l \cdot \nabla \mu_l$.

The absence of a sink/source term in (3.1.19) constrains all the terms not under the divergence $\nabla \cdot \ldots$ in (3.1.20) to sum to zero. The entropy production R is then found such that it negates the other terms. Simplified from that in Latz and Zausch [14],

$$R = -\mathbf{F}_l \cdot \nabla \mu_l + \mathbf{i}_l \cdot \mathbf{E}. \tag{3.1.21}$$

Here, the model is reduced as in Smith and Bazant [22] to be isothermal such that there is no heat flux $\mathbf{q} = 0$ and no temperature gradient $\nabla T = 0$. Constitutive relations are then needed for independent thermodynamic fluxes \mathbf{F}_l and \mathbf{i}_l . The general expressions for fluxes can be written as linear combinations of the forces $\nabla \mu_l$ and \mathbf{E} . Here, note the electric field is conservative $\nabla \times \mathbf{E} = 0$ and able to be written as $\mathbf{E} = -\nabla \phi_l$, where ϕ_l is the electrolyte electric potential. In such a case, the Onsager's reciprocal relations can be written in matrix form using the constitutive relations,

$$\begin{pmatrix} \mathbf{F}_l \\ \mathbf{i}_l \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \boldsymbol{\nabla} \mu_l \\ \boldsymbol{\nabla} \phi_l \end{pmatrix}.$$
 (3.1.22)

The second law of thermodynamics constrains the total entropy production R in (3.1.21) to be zero or positive. As such, the associated Onsager's coefficient matrix must then be symmetric $L_{12} = L_{21}$ and positive semidefinite $L_{11}L_{22} - L_{12}L_{21} \ge 0$.

Since the chemical potential μ_l is hard to measure, Latz and Zausch [14] also gives (3.1.21) using c_l as an independent variable instead of μ_l through the chain rule,

$$R = -\frac{\partial \mu_l}{\partial c_l} \mathbf{F}_l \cdot \boldsymbol{\nabla} c_l + \mathbf{i}_l \cdot \mathbf{E}.$$
(3.1.23)

The alternate form of Onsager's reciprocal relations is similarly,

$$\begin{pmatrix} \frac{\partial \mu_l}{\partial c_l} \mathbf{F}_l \\ \mathbf{i}_l \end{pmatrix} = \begin{pmatrix} \left(\frac{\partial \mu_l}{\partial c_l}\right)^2 L_{11} & \frac{\partial \mu_l}{\partial c_l} L_{12} \\ \frac{\partial \mu_l}{\partial c_l} L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \boldsymbol{\nabla} c_l \\ \boldsymbol{\nabla} \phi_l \end{pmatrix}, \quad (3.1.24)$$

Finally, the more standard presentation of equations is

$$\mathbf{F}_{l} = \frac{\partial \mu_{l}}{\partial c_{l}} L_{11} \nabla c_{l} + L_{12} \nabla \phi_{l}, \qquad x \in \mathcal{L}$$
(3.1.25a)

$$\mathbf{n} \cdot \mathbf{F}_l = 0,$$
 $x = 0, \quad x = L_s + L_c,$ (3.1.25b)

and,

$$\mathbf{i}_{l} = \frac{\partial \mu_{l}}{\partial c_{l}} L_{21} \nabla c_{l} + L_{22} \nabla \phi_{l}, \qquad x \in \mathcal{L}$$
(3.1.26a)

$$\mathbf{n} \cdot \mathbf{i}_l = i_{\text{cell}}, \qquad \qquad x = 0, \qquad (3.1.26b)$$

$$\mathbf{n} \cdot \mathbf{i}_l = 0, \qquad \qquad x = L_s + L_c, \qquad (3.1.26c)$$

where $t \in \mathcal{T}$ and **n** is the unit normal vector at the impermeable current collectors. The boundary condition at the counter electrode (3.1.26b) is detailed in (3.1.77) in terms of its Butler-Volmer kinetics for a thin Li metal foil. Opposite the separator, current through the full graphite electrode $x \in \mathcal{L}_c$ completing the galvanostatic circuit is instead found later in (3.1.86) as the sum of charge from lithium reduced in the solid particle surface reactions. The current collector in (3.1.26c) is electrically connected to the conductive active material in the graphite electrode and has no electrolyte current contribution, as is the case for flux boundary conditions (3.1.25b). The electrolyte model is then defined by (3.1.25) and (3.1.26) with conservation equations (3.1.13a) and (3.1.17).

3.1.1.2 Nernst-Planck Dilute Solution

In the discussion on linear irreversible thermodynamics (LIT) of diffusion in Bazant [2], the diagonal Onsager coefficient L_{11} is given in terms of an anion mobility M_{-} as $L_{11} = M_{-}\nu_{-}c_{l}$. Mobility is then further tied to diffusivity using the Einstein relation $D_{-} = M_{-}k_{B}T$ where k_{B} is the Boltzmann constant and T is the temperature. Applying the same approach to current density \mathbf{i}_{l} expressed in terms of fluxes in

(3.1.15), the off-diagonal term is accordingly,

$$L_{21} = c_l \frac{\nu_- z_- eD_- + \nu_+ z_+ eD_+}{k_B T}.$$
(3.1.27)

Fick's first law of diffusion gives coefficients D_{\pm} to be the constants of proportionality between the fluxes $\mathbf{F}_{l,\pm}$ and the gradients of concentrations $\nabla c_{l,\pm}$. The current density from (3.1.15) as a net sum of fluxes is the Fickian relation $-(\nu_{-}z_{-}D_{-}+\nu_{+}z_{+}D_{+})e\nabla c_{l}$. From the Onsager coefficient matrix (3.1.24) with substitution of (3.1.27), comparison of the ∇c_{l} term gives,

$$-(\nu_{-}z_{-}D_{-}+\nu_{+}z_{+}D_{+})e = \frac{\partial\mu_{l}^{\rm NP}}{\partial c_{l}} \left(-\frac{\nu_{-}z_{-}D_{-}+\nu_{+}z_{+}D_{+}}{k_{B}T}ec_{l}\right), \qquad (3.1.28)$$

which further reduces to,

$$\frac{\partial \mu_l^{\rm NP}}{\partial c_l} = \frac{k_B T}{c_l}.$$
(3.1.29)

Satisfying such an equality is the Nernst-Planck expression for electrolyte chemical potential,

$$\mu_l^{\rm NP} = k_B T \ln\left(\nu_- \frac{c_l}{c_{l,\rm ref}}\right), \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}, \tag{3.1.30}$$

where the reference $c_{l,ref}$ is the initial lithium concentration in the electrolyte.

Imposing symmetry of the Onsager's matrix $L_{21} = L_{12}$, flux in (3.1.25a) can then be expressed,

$$\mathbf{F}_{l}^{\mathrm{NP}} = -\frac{\epsilon}{\tau} c_{l} \left(\frac{\nu_{-} D_{-}}{k_{B} T} \boldsymbol{\nabla} \mu_{l} + \frac{\nu_{-} z_{-} D_{-} + \nu_{+} z_{+} D_{+}}{k_{B} T} e \boldsymbol{\nabla} \phi_{l} \right).$$
(3.1.31)

Important to note is the inclusion tortuosity τ as a function of porosity ϵ which is

commonly that of the Bruggeman relation $\tau = \epsilon^{-1/2}$. Flux from (3.1.31) can then be expressed as,

$$\mathbf{F}_{l}^{\mathrm{NP}} = -\frac{\epsilon}{\tau} \left(\nu_{-} D_{-} \boldsymbol{\nabla} c_{l} + \frac{\nu_{-} z_{-} D_{-} + \nu_{+} z_{+} D_{+}}{k_{B} T} e c_{l} \boldsymbol{\nabla} \phi_{l} \right), \qquad (3.1.32)$$

where the simplification $c_l \nabla \ln (\nu_{\pm} c_l / c_{l,ref}) = \nabla c_l$ results from the gradient of (3.1.30). Similarly, current density from (3.1.24) is expressed as,

$$\mathbf{i}_{l}^{\mathrm{NP}} = -\frac{\epsilon}{\tau} \left([\nu_{-} z_{-} D_{-} + \nu_{+} z_{+} D_{+}] e \boldsymbol{\nabla} c_{l} + \sigma_{l}^{\mathrm{NP}} c_{l} \boldsymbol{\nabla} \phi_{l} \right), \qquad (3.1.33)$$

where the electrolyte conductivity comes from $L_{22} = \sigma_l^{\text{NP}} c_l$.

Consider a simplified case of (3.1.32) such that electrolyte flux for anions has no electromagnetic influence from cations, valid in the limit of a dilute solution. Now in the form presented in Smith and Bazant [22], the Nernst-Planck flux is,

$$\mathbf{F}_{l}^{\mathrm{NP}} = -\frac{\epsilon}{\tau} \nu_{-} \left(D_{-} \boldsymbol{\nabla} c_{l} + \frac{D_{-} z_{-} e}{k_{B} T} c_{l} \boldsymbol{\nabla} \phi_{l} \right).$$
(3.1.34)

Conversely, it follows that the cation flux in the absence of anion interaction is

$$\mathbf{F}_{l,+}^{\mathrm{NP}} = -\frac{\epsilon}{\tau} \nu_{+} \left(D_{+} \boldsymbol{\nabla} c_{l} + \frac{D_{+} z_{+} e}{k_{B} T} c_{l} \boldsymbol{\nabla} \phi_{l} \right).$$
(3.1.35)

It is useful to express the diffusional electrochemical potential of the oxidized state as,

$$\mu_O^{\rm NP} = k_B T \ln\left(\nu_+ \frac{c_l}{c_{l,\rm ref}}\right) + z_+ e\phi_l, \qquad (3.1.36)$$

where the cation flux could simplify to,

$$\mathbf{F}_{l,+}^{\mathrm{NP}} = -\frac{\epsilon}{\tau} \nu_{+} \frac{D_{+}}{k_{B}T} c_{l} \boldsymbol{\nabla} \mu_{O}^{\mathrm{NP}}, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}.$$
(3.1.37)

The new expression for current density is obtained by substituting fluxes into (3.1.15) as,

$$\mathbf{i}_{l}^{\mathrm{NP}} = -\frac{\epsilon}{\tau} \left((\nu_{-} z_{-} D_{-} + \nu_{+} z_{+} D_{+}) e \boldsymbol{\nabla} c_{l} + \frac{\nu_{-} z_{-}^{2} D_{-} + \nu_{+} z_{+}^{2} D_{+}}{k_{B} T} e^{2} c_{l} \boldsymbol{\nabla} \phi_{l} \right). \quad (3.1.38)$$

Note that in this case, (3.1.33) is compared to determine the form of electrolyte conductivity σ_l^{NP} ,

$$\sigma_l^{\rm NP} = \frac{\nu_- z_-^2 D_- + \nu_+ z_+^2 D_+}{k_B T} e^2, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}.$$
 (3.1.39)

The Nernst-Plank dilute electrolyte model is then defined by (3.1.37) and (3.1.38) with conservation equations (3.1.13a) and (3.1.17).

3.1.1.3 Stefan-Maxwell Concentrated Solution

It is often the case that elements of flux corresponding to cross electromagnetic effects between anions and cations play a significant role in more concentrated solutions. The equations are tractable for a binary electrolyte but can be difficult when presented with a many component system. The approach taken by Newman and Thomas-Alyea [17] reformulates the diffusion equation in terms of species velocities \mathbf{v}_j for $j = 0, \pm$,

$$c_{l,j}\boldsymbol{\nabla}\mu_{l,j} = \sum_{k} K_{jk}(\mathbf{v}_k - \mathbf{v}_j) = k_B T \sum_{k} \frac{c_{l,j}c_{l,k}}{c_{l,T}\mathcal{D}_{jk}}(\mathbf{v}_k - \mathbf{v}_j).$$
(3.1.40)

Here, drag coefficients $K_{jk} = K_{kj}$ are functions of species concentrations, corresponding diffusion coefficients \mathcal{D}_{jk} , and total concentration $c_{l,T} = \sum_j c_{l,j}$ for $j = 0, \pm$. It is now useful to express a net diffusion coefficient of the electrolyte \mathcal{D} as

$$\mathcal{D} = \frac{\mathcal{D}_{0+}\mathcal{D}_{0-}(z_+ - z_-)}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}}.$$
(3.1.41)

The transference numbers t^0_{\pm} are the fraction of total electrical current carried by each individual species,

$$t_{+}^{0} = 1 - t_{-}^{0} = \frac{z_{+}\mathcal{D}_{0+}}{z_{+}\mathcal{D}_{0+} - z_{-}\mathcal{D}_{0-}}.$$
(3.1.42)

Rearranging \pm cation/anion diffusion equations (3.1.40) and using a combined chemical potential,

$$\mu_{l,e} = \nu_+ \mu_{l,+} + \nu_- \mu_{l,-}, \qquad (3.1.43)$$

it is then possible to recover the fluxes $\mathbf{F}_{l,\pm} = c_{l,\pm} \mathbf{v}_{\pm}$,

$$\mathbf{F}_{l}^{\mathrm{SM}} = -\frac{\epsilon}{\tau} \frac{\mathcal{D}}{k_{B}T} \frac{\nu_{-}}{\nu} c_{l} \boldsymbol{\nabla} \mu_{l,e} + \frac{1 - t_{+}^{0}}{z_{-}e} \mathbf{i}_{l}^{\mathrm{SM}}, \qquad (3.1.44)$$

where the term with current density \mathbf{i}_l^{SM} uses its definition in terms of fluxes (3.1.15) and the combined dissociation number $\nu = \nu_+ + \nu_-$. Similarly, the cation flux is given as

$$\mathbf{F}_{l,+}^{\mathrm{SM}} = -\frac{\epsilon}{\tau} \frac{\mathcal{D}}{k_B T} \frac{\nu_+}{\nu} c_l \boldsymbol{\nabla} \mu_{l,e} + \frac{t_+^0}{z_+ e} \mathbf{i}_l^{\mathrm{SM}}.$$
(3.1.45)

The solvent here is assumed to vary negligibly with salt concentration and is used as the frame of reference such that $\mathbf{v}_0 = 0$. Note that the constituitive relations for fluxes have cross interaction terms with thermodynamic driving forces from gradients in the chemical potential of other species. The reference Newman and Thomas-Alyea [17] proceeds to substitute the fluxes (3.1.44) and (3.1.45) into the diffusion equation (3.1.40) to obtain,

$$\frac{1}{z_{-}}\boldsymbol{\nabla}\mu_{l,-} = -\frac{e}{\sigma_{l}^{\mathrm{SM}}}\mathbf{i}_{l}^{\mathrm{SM}} - \frac{t_{+}^{0}}{z_{+}\nu_{+}}\boldsymbol{\nabla}\mu_{l,e}.$$
(3.1.46)

Here, the conductivity $\sigma_l^{\rm SM}$ was defined as

$$\sigma_l^{\rm SM} = -\frac{c_{l,T} z_+ z_- e^2}{k_B T} \left(\frac{c_{l,+} \mathcal{D}_{+-} \mathcal{D}_{0-}}{c_{l,+} \mathcal{D}_{0-} + c_{l,0} t_-^0 \mathcal{D}_{+-}} \right).$$
(3.1.47)

Consider now the treatment in Newman and Thomas-Alyea [17] where the equilibrium electrode reaction equation gives potentials that follow from thermodynamic principles as,

$$s_{-}\boldsymbol{\nabla}\mu_{l,-} + s_{+}\boldsymbol{\nabla}\mu_{l,+} + s_{0}\boldsymbol{\nabla}\mu_{l,0} = -ne\boldsymbol{\nabla}\phi_{l}, \qquad (3.1.48)$$

where s_j are stoichiometric coefficients and n is the number of electrons transferred in the reaction. Recall that electroneutrality gives a charge density (3.1.16) of zero, allowing for the first two terms of (3.1.48) to be modified as,

$$s_{-}\nabla\mu_{l,-} + s_{+}\nabla\mu_{l,+} = s_{-}\nabla\mu_{l,-} + s_{+}\left[\nabla\mu_{l,+} + \left(\frac{\nu_{-}}{\nu_{+}} + \frac{z_{+}}{z_{-}}\right)\nabla\mu_{l,-}\right].$$
 (3.1.49)

The relation $s_+z_+ + s_-z_- = -n$ and a substitution of $\mu_{l,e}$ from (3.1.43) to eliminate $\mu_{l,+}$ then gives that found in Newman and Thomas-Alyea [17],

$$s_{-}\nabla\mu_{l,-} + s_{+}\nabla\mu_{l,+} = \frac{s_{+}}{\nu_{+}}\nabla\mu_{l,e} - \frac{n}{z_{-}}\nabla\mu_{l,-}.$$
 (3.1.50)

At this point, the remaining term $\nabla \mu_{l,0}$ in (3.1.48) can be expressed in terms of the other variables by noting that not all chemical potentials are independent and must

satisfy the Gibbs-Duhem equation,

$$c_{l,-}\nabla\mu_{l,-} + c_{l,+}\nabla\mu_{l,+} + c_{l,0}\nabla\mu_{l,0} = 0.$$
(3.1.51)

Applying then the relation between concentrations (3.1.7),

$$\boldsymbol{\nabla}\mu_{l,0} = -\frac{c_l}{c_{l,0}} (\nu_- \boldsymbol{\nabla}\mu_{l,-} + \nu_+ \boldsymbol{\nabla}\mu_{l,+}) = -\frac{c_l}{c_{l,0}} \boldsymbol{\nabla}\mu_{l,e}.$$
 (3.1.52)

The above, along with the substitution of (3.1.50) then allows for the potentials in (3.1.48) to be expressed as,

$$-e\boldsymbol{\nabla}\phi_{l} = \left(\frac{s_{+}}{n\nu_{+}} - \frac{s_{0}c_{l}}{nc_{l,0}}\right)\boldsymbol{\nabla}\mu_{l,e} - \frac{1}{z_{-}}\boldsymbol{\nabla}\mu_{l,-}.$$
(3.1.53)

Using (3.1.46) to eliminate $\mu_{l,-}$ in (3.1.53), the particular form of electrolyte current density \mathbf{i}_l is finally found to be,

$$\mathbf{i}_{l}^{\mathrm{SM}} = -\frac{\epsilon}{\tau} \sigma_{l}^{\mathrm{SM}} \left(\boldsymbol{\nabla} \phi_{l} + \frac{1}{e} \left(\frac{s_{+}}{n\nu_{+}} + \frac{t_{+}^{0}}{\nu_{+}z_{+}} - \frac{s_{0}c_{l}}{nc_{l,0}} \right) \boldsymbol{\nabla} \mu_{l,e} \right).$$
(3.1.54)

As was the case in (3.1.30), the chemical potential in (3.1.43) is able to be expressed as,

$$\mu_{l,e} = k_B T \left[\nu_+ \ln \left(\nu_+ \frac{c_l}{c_{l,\text{ref}}} \right) + \nu_- \ln \left(\nu_- \frac{c_l}{c_{l,\text{ref}}} \right) \right], \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}.$$
(3.1.55)

The standard form of equations as presented in Smith and Bazant [22] substitutes

the above in fluxes (3.1.44) and (3.1.45) as,

$$\mathbf{F}_{l}^{\mathrm{SM}} = -\frac{\epsilon}{\tau} \mathcal{D}\nu_{-} \nabla c_{l} + \frac{1 - t_{+}^{0}}{z_{-}e} \mathbf{i}_{l}^{\mathrm{SM}}, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T},$$
(3.1.56)

and,

$$\mathbf{F}_{l,+}^{\mathrm{SM}} = -\frac{\epsilon}{\tau} \mathcal{D}\nu_{+} \nabla c_{l} + \frac{t_{+}^{0}}{z_{+}e} \mathbf{i}_{l}^{\mathrm{SM}}, \qquad x \in \mathcal{L}, \quad t \in \mathcal{T}.$$
(3.1.57)

The current density (3.1.54) is similarly expressed as,

$$\mathbf{i}_{l}^{\mathrm{SM}} = -\frac{\epsilon}{\tau} \sigma_{l}^{\mathrm{SM}} \left(\boldsymbol{\nabla} \phi_{l} + \nu \frac{k_{B}T}{e} \left(\frac{s_{+}}{n\nu_{+}} + \frac{t_{+}^{0}}{\nu_{+}z_{+}} - \frac{s_{0}c_{l}}{nc_{l,0}} \right) \frac{\boldsymbol{\nabla} c_{l}}{c_{l}} \right).$$
(3.1.58)

Though left in the general form, note that in a Li-ion battery, $s_{+} = -1$ and $s_{-} = s_{0} = 0$ allows for further simplification. In Smith and Bazant [22] for the Stefan-Maxwell model, the diffusional electrochemical potential of the oxidized state is given by only the electric potential in the electrolyte,

$$\mu_O^{\rm SM} = z_+ e \phi_l. \tag{3.1.59}$$

The replacement of a constant diffusivity with that having concentration dependance is able to better match experimental data. The functional dependance on electrolyte concentration and temperature is originally given in Valøen and Reimers [25] where coefficients were fit to results from experiment for LiPF₆. Under constant temperature conditions, this appears as

$$\mathcal{D}(c_l) = \mathcal{D}_0 \exp\left(b\frac{c_l}{c_{l,\text{ref}}}\right),\tag{3.1.60}$$

where \mathcal{D}_0 is the electrolyte dimensional diffusivity prefactor. Again following the functional form with experimentally fit coefficients a_0, a_1, a_2 from Valøen and Reimers [25], the ionic conductivity for constant temperature is

$$\sigma_l^{\rm SM}(c_l) = \sigma_0 \frac{c_l}{c_{l,\rm ref}} \left[a_0 + a_1 \frac{c_l}{c_{l,\rm ref}} + a_2 \left(\frac{c_l}{c_{l,\rm ref}} \right)^2 \right]^2, \qquad (3.1.61)$$

where σ_0 is the dimensional conductivity prefactor. The Stefan-Maxwell concentrated electrolyte model is then defined by (3.1.56) and (3.1.58) with conservation equations (3.1.13a) and (3.1.17).

3.1.2 Reaction Rates

Lithium ions intercalate into the solid electrode by reacting with available sites (vacancies) at the surface of the particle in contact with electrolyte liquid. In doing so, the ions accept an electron as per the chemical equation,

$$\mathrm{Li}^+ + e^- + \theta_s \leftrightarrows \mathrm{Li} - \theta_s, \qquad (3.1.62)$$

where θ_s denotes a lattice site in the solid-phase electrode particle.

3.1.2.1 Butler-Volmer Reaction

The kinetics of the reaction can be described using the Butler-Volmer formulation which expresses a dependence of the interfacial reaction rate on the reaction driving force, or activation overpotential η_s . For equivalent anodic and cathodic transfer coefficients $\alpha_a = \alpha_c = 1/2$, the net reduction current *i* differs from the reaction rate needed for (3.1.72) and (3.2.24c) by electron charge *e*. The Arrhenius type equation gives net reduction current at the surface of graphite particles as,

$$i = i_0 \left[\exp\left(\frac{-e\eta_s}{2k_BT}\right) - \exp\left(\frac{e\eta_s}{2k_BT}\right) \right].$$
(3.1.63)

In general, the exchange current density i_0 has functional dependance on the activity coefficients of the species. In Smith and Bazant [22], inclusion of the transition state activity coefficient is able to make predictions on structure such as a decline in reaction rate as lattice sites become populated. Also diminishing reaction rates are collapsing empty layers accepting less lithium ions at low filling fractions. Following the particular formulation of Fuller *et al.* [10], activity coefficients are taken to be equal to species concentrations in the expression for exchange current density,

$$i_0 = k_0 \left(\frac{c_l}{c_{l,\text{ref}}}\right)^{1/2} \left(1 - \frac{c_s}{c_{s,\text{max}}}\right)^{1/2} \left(\frac{c_s}{c_{s,\text{max}}}\right)^{1/2}, \qquad (3.1.64)$$

where k_0 is the exchange rate constant. The concentration at the surface of the solid particle is denoted as $c_s(x, r = a; t)$. Note however the use of corresponding nondimensional composition $\tilde{c}_s \coloneqq c_s/c_{s,\max}$ such that dimensionality of reduction current *i*, exchange current i_0 , and the exchange rate constant k_0 are equivalent. The form chosen for (3.1.64) is such that the net reduction current is maximized when the surface concentration is nearest to half-full.

The surface overpotential as the reaction driving force for (3.1.63) is given in Smith and Bazant [22] as the difference between the electrochemical potential of the reduced state μ_R and the combined electrochemical potential of the oxidized state μ_O with the electrochemical potential of electrons μ_e ,

$$e\eta_s = \mu_R - (\mu_O + \mu_e), \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.1.65)

The electrochemical potential of the reduced state $\mu_R = \mu(x, r = a; t) - E_{\Theta}$ is the chemical potential at the surface of the solid-phase electrode particle from (3.2.23) differenced from a reference energy. The electrochemical potential of electrons is related to the solid electric potential by $\mu_e = -e\phi_s(x, t)$ giving the general expression for surface overpotential,

$$\eta_s = \frac{\mu}{e} - E_{\Theta} - \left(\frac{\mu_O}{e} - \phi_s\right), \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.1.66)

Substitution of the diffusional electrochemical potential of the oxidized state for a Nernst-Planck dilute electrolyte solution (3.1.36) gives the result,

$$\eta_s^{\rm NP} = \frac{\mu}{e} - E_\Theta - \frac{k_B T}{e} \ln\left(\nu_+ \frac{c_l}{c_{l,\rm ref}}\right) - z_+ \phi_l + \phi_s, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.1.67)

The Stefan-Maxwell formulation with $\mu_O^{\rm SM}$ from (3.1.59) then gives,

$$\eta_s^{\rm SM} = \frac{\mu}{e} - E_\Theta - z_+ \phi_l + \phi_s, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.1.68)

Newman and Thomas-Alyea [17] describe the surface overpotential η_s as being the difference in electric potential between the electrode and electrolyte, minus the opencircuit potential V_{eq} . This description is consistent with how Smith *et al.* [23] gives the near equilibrium Nernstian OCV,

$$V_{\rm eq} = E_{\Theta} - \frac{\mu_0}{e}, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}, \tag{3.1.69}$$

where $\mu_0 = \partial g_0 / \partial c_s$ is the homogenous chemical potential seen later as the first term in the variational derivative of free energy (3.2.23). In Morales Escalante *et al.* [15], the open-circuit voltage V_{eq} is substituted with the cell voltage from the same experiment at a much slower charge rate of (C/100) seen earlier in Figure 2.3. An approximation of the OCV as a function of the surface filling fraction is introduced as U_{eq} . The surface overpotential (3.1.68) can then be rewritten using (3.1.69) in (3.2.23) as,

$$\eta_s = -U_{eq}(\tilde{c}_s) - \kappa \nabla^2 \tilde{c}_s - z_+ \phi_l + \phi_s, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.1.70)

Note that the nonhomogeneous term $-\kappa \nabla^2 \tilde{c}_s$ does not appear in Morales Escalante et al. [15] though is found to have a negligible effect on results. In such a case where an analytical expression is required, Safari and Delacourt [21] suggests the OCV form for graphite,

$$U_{\text{eq}}(\tilde{c}_{s}) = b_{0,1} + b_{1,1} \exp(b_{1,2}\tilde{c}_{s}) + \sum_{j=2}^{8} b_{j,1} \tanh\left(\frac{\tilde{c}_{s} + b_{j,2}}{b_{j,3}}\right),$$

$$x \in \mathcal{L}_{c}, \quad r = a, \quad t \in \mathcal{T},$$
(3.1.71)

where extra terms were added to the summation to account for the particular voltage plateaus here. The coefficients are able to be fit to the experimental C-100 cell voltage data to minimize the absolute difference between the two as done in Appendix C and shown in Table C.1. The full expression for the net reduction current (3.1.63) can then be used as boundary conditions for flux out of the electrolyte and into the solid particle.

3.1.2.2 SEI Layer

In practice, loss of charge capacity is common in the form of lithium plating or dendrite formation known as the solid-electrolyte interphase (SEI) layer on the surface of the graphite electrode particles. Consider again the experimentally obtained total intercalated lithium amount integrated over the solid electrode volume as a function of time shown in Figure 2.2. The deflection in the rate of intercalation beginning near 10 h is illustrated by the upwards trending line representing the difference from the idealized C-44 charge rate. This departure is an indication that a significant amount of lithium being reacted as per the galvanostatic constant current does not end up being intercalated into active material volume. Without accounting for the nonzero side reaction, significant overestimation of solid electrode lithium concentrations would occur at later times during simulation.

Modifications to the model with varying degrees of complexity can be made to address the formation of the SEI layer. In the present state of the simulation software MPET, Smith and Bazant [22] mentions that predicting battery aging and capacity fade are left to future extensions. However, an optional specification of film resistance on surfaces with Butler-Volmer reaction kinetics could give an effective overpotential that modifies (3.1.66) and (3.1.78) through Ohm's law. In this work, film resistances are neglected in favor of an ad-hoc modification that does well to empirically capture the effects observed in Figure 2.2. Alternatively, the work by Arora [1] may be considered as they take a more physical approach to implementing capacity fade and explore the phenomenon in depth.

Assuming that the rate of Li⁺ ions leaving the electrolyte and being reduced at the surface is that of the unaltered Butler-Volmer reaction, a new variable ω is introduced in Morales Escalante *et al.* [15] to represent the fraction of lithium that is actually intercalated into the solid active material. The compliment $1 - \omega$ then represents the remaining fraction of lithium that undergoes the side reaction into a new phase on the surface of the particle, denoted with concentration c_{side} . The SEI layer formed is reasonably assumed to be sufficiently thin such that volumetric effects can be neglected with c_{side} being dimensionally consistent with averaged particle concentration \bar{c}_s .

The growth rate of side reaction concentration is the fraction $1 - \omega$ of the net reduction current *i* from (3.1.63) that does not enter the solid particle surface in the boundary condition (3.2.24c),

$$\frac{\partial c_{\text{side}}}{\partial t} = \frac{A_p}{V_p} (1 - \omega) \frac{i}{e}, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.1.72)

The ratio of surface area to volume of the particle takes a surface to volumetric density and is given in terms of the particle radius a as

$$V_p = \frac{4}{3}\pi a^3, \qquad A_p = 4\pi a^2, \qquad \frac{A_p}{V_p} = \frac{3}{a}.$$
 (3.1.73)

The functional form of ω is then chosen by Morales Escalante *et al.* [15] as

$$\omega(c_s) = \tanh\left(\gamma\left[1 - \frac{c_s}{c_{s,\max}}\right]\right), \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}, \tag{3.1.74}$$

such that at early times when the surface concentration in the particle is low, the SEI layer undergoes minimal growth in (3.1.72). The parameter γ controls the sharpness of the step down characteristic of a hyperbolic tangent function. In the case of strong phase-separation, going from low to high filling fractions happens rapidly. Intermediate surfacial concentrations at the elbow in the hyperbolic tangent are passed over briefly to the effect of a sudden change in slope of total intercalated lithium in Figure 2.2 resembling a piecewise linear deflection.

3.1.2.3 Counter Electrode

In Chapter 2, the counter electrode is described only as metallic lithium on a current collector. Note here the departure from Morales Escalante *et al.* [15] which uses an electrolyte reservoir at x = 0 held at the initial concentration $c_{l,ref}$. Instead, for counter electrodes with no volume, Smith and Bazant [22] account for an infinitely thin Li-foil by assuming Butler-Volmer kinetics apply at the Li metal attached to the current collector x = 0. Analogous to (3.1.64), the Arrhenius reaction gives the exchange current density as,

$$i_{0,\text{wall}} = k_{0,\text{foil}} \sqrt{\frac{c_l}{c_{l,\text{ref}}}},$$
 (3.1.75)

where $k_{0,\text{foil}}$ is the foil rate constant. The cell current boundary condition from (3.1.26b) constrains the dependence on overpotential to satisfy counter electrode current density,

$$i_{\text{cell}} = -i_{0,\text{wall}} \left[\exp\left(-\frac{e\eta_{\text{wall}}}{2k_BT}\right) - \exp\left(\frac{e\eta_{\text{wall}}}{2k_BT}\right) \right], \qquad x = 0, \quad t \in \mathcal{T}.$$
(3.1.76)

This is rewritten using trigonometric identities as,

$$i_{\text{cell}} = -2i_{0,\text{wall}}\sinh\left(\frac{e\eta_{\text{wall}}}{2k_BT}\right), \qquad x = 0, \quad t \in \mathcal{T}.$$
 (3.1.77)

The overpotential at the surface of the counter electrode can then be solved for in terms of i_{cell} as,

$$\eta_{\text{wall}} = \frac{2k_B T}{e} \operatorname{arcsinh}\left(-\frac{i_{\text{cell}}}{2i_{0,\text{wall}}}\right), \qquad x = 0, \quad t \in \mathcal{T}.$$
 (3.1.78)

The overall cell voltage is defined by Smith and Bazant [22] as the difference in electrochemical potential between current collectors. Using the $x = L_s + L_c$ collector in the graphite electrode as reference of zero, the overpotential at the counter electrode in (3.1.78) is analogous to (3.1.65) as being the difference between the electrochemical potential of the reduced state and the oxidized state at x = 0. At the counter electrode, $\mu_R = 0$ giving the expression

$$\eta_{\text{wall}} = -\frac{\mu_O}{e} - \frac{\mu_e}{e}, \qquad x = 0, \quad t \in \mathcal{T}.$$
(3.1.79)

Substituting in the dilute Nernst-Planck chemical potential from (3.1.36) for the oxidized state, solving for the cell potential $\phi_{\text{cell}} = -\mu_e/e$ gives,

$$\phi_{\text{cell}}^{\text{NP}} = \eta_{\text{wall}} + \frac{k_B T}{e} \ln \left(\nu_+ \frac{c_l}{c_{l,\text{ref}}} \right) + z_+ \phi_l, \qquad x = 0, \quad t \in \mathcal{T}.$$
(3.1.80)

Conversely for the Stefan-Maxwell formulation like in (3.1.68),

$$\phi_{\text{cell}}^{\text{SM}} = \eta_{\text{wall}} + z_+ \phi_l, \qquad x = 0, \quad t \in \mathcal{T}.$$
(3.1.81)

These are then able to be compared to the experimentally collected data in Figure 2.3 for the voltage fitting optimization later in (4.2.1).

3.1.2.4 Solid Electrode Current

Ohm's law is applied in Smith and Bazant [22] using an electrode conductivity σ_s to relate the solid electrode current density \mathbf{i}_s and solid electric potential ϕ_s ,

$$\mathbf{i}_s = -\frac{(1-\epsilon)}{\tau_s} \sigma_s \nabla \phi_s, \qquad x \in \mathcal{L}_c, \qquad t \in \mathcal{T}, \qquad (3.1.82a)$$

$$\mathbf{n} \cdot \mathbf{i}_s = 0, \qquad \qquad x = L_s, \qquad t \in \mathcal{T}, \qquad (3.1.82b)$$

$$\mathbf{n} \cdot \mathbf{i}_s = i_{\text{cell}}, \qquad \qquad x = L_s + L_c, \quad t \in \mathcal{T}, \qquad (3.1.82c)$$

where for the solid, tortuosity is again given by the Bruggeman relation $\tau_s = (1 - \epsilon)^{-1/2}$. The boundary condition (3.1.82b) exists at the interface of the electrically insulating separator.

Similar as to imposing conservation of charge on the electrolyte in (3.1.17), the electrode as per Smith and Bazant [22] is also constrained to follow conservation of charge with local electroneutrality,

$$-\nabla \cdot \mathbf{i}_s - z_+ e R_V = 0, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T}.$$
(3.1.83)

Here, the divergence of solid phase current density \mathbf{i}_s has a volumetric sink/source term R_V term equal and opposite to that in the analogous electrolyte equation (3.1.17).

The total macroscopic current I is equal to the current density $\mathbf{n} \cdot \mathbf{i}_s$ integrated over the surface of all particles in the length of the electrode. Consider now the divergence theorem,

$$\int_{A_p} \mathbf{n} \cdot \mathbf{i}_s \, dA = \int_{V_p} \boldsymbol{\nabla} \cdot \mathbf{i}_s \, dV, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T}, \tag{3.1.84}$$

where the volume integral of the divergence of current density gives the surface integral of current into the particle $\mathbf{n} \cdot \mathbf{i}_s$. The expression for total current using (3.1.84) and expanding the volume integral is then,

$$I = \int_{L_s}^{L_s + L_c} \int_{A_p} \nabla \cdot \mathbf{i}_s \, dA \, dx, \qquad t \in \mathcal{T}.$$
(3.1.85)

Using the conservation of charge equation (3.1.83) then allows current to be expressed in terms of the volume-averaged reaction rate R_V as given in (3.1.88a). The interior integral is constant and simplifies as the surface area A_p . Dividing area out of the total current as $i_{cell} = I/A_p$, the final form of the galvanostatic constraint is expressed as the total cell current density per unit cross-sectional area,

$$i_{\text{cell}} = \int_{L_s}^{L_s + L_c} z_+ e R_V \, dx, \qquad t \in \mathcal{T}.$$
 (3.1.86)

For a galvanostatic experiment with a charge rate of $C_r = 1/44$ hours to obtain the maximum concentration $c_{s,\max}$ in the absence of the SEI layer, total cell current is prescribed to be

$$i_{\text{cell}} = (1 - \epsilon_l) P_L L_c e c_{s, \max} \frac{C_r}{3600} \qquad t \in \mathcal{T}, \qquad (3.1.87)$$

where the prefactors serve to account for volume of electrolyte in the porous electrode. The loading percent of active material is $P_L = 1$ in the absence of an inert conducting matrix. The reaction rate can be defined as per the average solid electrode lithium \bar{c}_s change over time from (3.2.28) in addition to the change in SEI layer c_{side} from (3.1.72),

$$R_V = -(1-\epsilon)P_L V_j \left(\frac{\partial \bar{c}_s}{\partial t} + \frac{\partial c_{\text{side}}}{\partial t}\right), \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T},$$
(3.1.88a)

$$R_V = 0, \qquad x \in \mathcal{L}_s, \quad t \in \mathcal{T}.$$
 (3.1.88b)

Each consecutive particle has a fraction of volume $V_j = 1$ since there are none being modeled in parallel here in terms of electrolyte access. When multiple particles exist at each battery position, variation in radii is required to avoid wasted computational effort by duplicating results.

The model equations for electrolyte transport and reaction rates can now be presented as the Newman model. It is used to simulate dynamics on the macroscopic scale with volume-averaged sink/source terms representing electrode particles. A simplified variant of the model uses a homogenized, solid-state electrode with thermodynamics account for by using only a fit OCV to determine the amount of lithium leaving the electrolyte. In the following sections, the interior microscopic dynamics are also addressed and subsequently volume-averaged to capture the staging or phase-separation known to occur in graphite.

3.2 Phase-Separating Electrode Model

Consider now the microscopic scale dynamics modeled within the particles $r \in \mathcal{R}$. The boundary conditions explored in Section 3.1.2.1 serve to couple the macroscopic electrolyte dynamics to volume-averaged quantities here. Many of the same thermodynamic arguments found in Section 3.1.1 can be made again in the context of lithiated solid graphite particles to find the inward flux of intercalated ions. The dynamics in the solid evolves for any given Li concentration c_s to minimize the Gibbs free energy. Typical diffusion treatments are characterized by parabolic free energies with just one stable minimum. Morales Escalante *et al.* [15] gives a brief historical context on staging, the particular arrangements of lithium particles and empty lattice sites. The concept of staging was first explored by Rüdorff and Hofmann [20] to describe the observed staggering of graphite layers with intercalated components. A more realistic staging model by Daumas and Herold [5] uses defects to describe the transition in a sequence of stages as the concentration increases during the intercalation process. In this section, the formulation of a free energy with two or more stable phases is done through enthalpy and entropy considerations. The later introduction of the periodic bilayer model captures the higher staging observed in experimental observations as discussed in Ferguson and Bazant [8].

3.2.1 Cahn-Hilliard Model

The generalized continuum model formulated by Cahn and Hilliard [3] is introduced as a particular form of free energy such that there are two stable minima and the free energy can be reduced through phase separation within the binodal region. A smaller subsection of that as will be discussed is the unstable spinodal region where a homogenous concentration undergoes spinodal decomposition into two separate phases of high and low concentration. This phenomenon in the context of electrochemistry is discussed in depth in Bazant [2] and appears as a "shrinking core". The interface between a high concentration shell and a dilute core moves inward as the particle becomes fully lithiated.

3.2.1.1 Linear Irreversible Thermodynamics

In the interest of determining the set of equations governing system evolution in the solid electrode, the phenomenological relations between fluxes and forces must again be considered as was the case for electrolyte in (3.1.37). The thermodynamic treatment of transport in Latz and Zausch [14] demonstrates that independent thermodynamic fluxes for ionic transport, heat transfer, and current are coupled through constitutive equations involving driving forces in the form of potential gradients. As an example, electrical current can occur not only as expected through a electric potential gradient, but also from inhomogeneities in density and temperature. To name a few cross-interaction responses, the Peltier effect describes heat flow as a result of voltage difference while the converse Seebeck effect describes electrical current caused by a temperature difference. Similarly, the direct piezoelectric effect shows electrical current from mechanical stress with a corresponding reverse piezoelectric effect for deformation from voltage difference.

The constitutive equations in the linear approximation near equilibrium known as Onsager's reciprocal relations are consequences of microscopic reversibility and the principle of detailed balance. The rate of entropy production is derived in Latz and Zausch [14] in terms of the phenomenological coefficients of the Onsager matrix using the fundamental thermodynamic relation and continuity equations. Applying the second law of thermodynamics for positive entropy production, the Onsager matrix is
found to be necessarily symmetric such that paired converse effects like mentioned before have equivalent ratios. Furthermore, entropy growth requires a positive-definite Onsager matrix such that the heat conductivity, electrical conductivity, and interdiffusion coefficient are restricted to positive values.

To begin modeling the diffusion of Li in the solid-phase electrode, it is most simple to assume a diagonal Onsager's matrix such that there are no coupled fluxes. Following the approach outlined in Novick-Cohen and Segel [19], consider the interdiffusion in a binary mixture between components A and B. In the context of a lithiated graphite electrode, the corresponding designations are for vacancies A and lithium particles B configured on a lattice. Ionic fluxes evolve in accordance with thermodynamic driving forces in the constitutive relations,

$$\mathbf{F}_{A} = -M_{AA} \nabla \mu_{A} - M_{AB} \nabla \mu_{B}$$

$$\mathbf{F}_{B} = -M_{BA} \nabla \mu_{A} - M_{BB} \nabla \mu_{B},$$
(3.2.1)

where components of the mobility tensor \mathbb{M} relate gradients in the chemical potentials $\mu_{A,B}$ to fluxes $\mathbf{F}_{A,B}$. Since the evolution of lithium particles is of interest, a simplified coordinate system can be chosen for lithium flux relative to that of vacancies $\mathbf{F} = \mathbf{F}_B - \mathbf{F}_A$. The sum of concentrations of both Li and vacancies is the total amount the lattice can hold $c_A + c_B = c_{s,\max}$. This constraint allows vacancy concentration to be post-calculated with a concentration of lithium in the solid electrode $c_s = c_B = c_{s,\max} - c_A$.

Still following Novick-Cohen and Segel [19], the isothermal and isobaric Gibbs-Duhem relationship demonstrates the chemical potentials $\mu_{A,B}$ are not independent,

$$(c_{s,\max} - c_s)\boldsymbol{\nabla}\mu_A + c_s\boldsymbol{\nabla}\mu_B = 0.$$
(3.2.2)

Further simplification of the net ionic flux ${f F}$ is now possible as

$$\mathbf{F} = -M\boldsymbol{\nabla}(\mu_B - \mu_A),\tag{3.2.3}$$

where the net mobility M is related to the mobility tensor components by

$$M = (c_{s,\max} - c_s)(M_{BB} - M_{AB}) + c_s(M_{AA} - M_{BA}).$$
(3.2.4)

In an orthorhombic crystal lattice, the mobility tensor is diagonal such that the off-diagonal components are $M_{AB} = M_{BA} = 0$, but is generally not isotropic. In this context however, the further assumption of having a cubic crystal is made such that $M_{AA} = M_{BB} = M(c_s)$. The net mobility M in (3.2.4) simplifies to $M(c_s)$ and is furthermore related to the diffusivity $D(c_s)$ through the standard Einstein relation $D(c_s) = M(c_s)k_BT$ with k_B being Boltzmann's constant and T being temperature. As an aside, the Einstein relation can be obtained through the fluctuation-dissipation theorem and Green-Kubo relation as per Kubo [12]. An alternative form is the Stokes-Einstein equation which replaces mobility to demonstrate the inverse proportionality between the diffusion coefficient and viscosity. The functional dependence of diffusivity on concentration is found in Smith and Bazant [22] and relates to the activity coefficients of the diffusing state and the diffusing transition state,

$$M(c_s) = \frac{D_0}{k_B T} \left(1 - \frac{c_s}{c_{s,\max}} \right) \frac{c_s}{c_{s,\max}},\tag{3.2.5}$$

where D_0 is the dimensional diffusivity prefactor. With the constitutive relation between species flux and the thermodynamic driving force established, considerations of the particular form of free energy the system seeks to minimize gives the evolution equations required in the next section to model interior dynamics of a lithiated graphite particle.

3.2.1.2 Gibbs Free Energy

Returning once again to Novick-Cohen and Segel [19], by definition the difference in chemical potential between lithium particles and vacancies is the change in Gibbs free energy $g(c_s)$ with respect to a change in amount of component,

$$\mu_B - \mu_A = \frac{\partial g}{\partial c_s}.\tag{3.2.6}$$

The notation is hereafter simplified to no longer require designations A and B with the net flux in (3.2.3) becoming,

$$\mathbf{F} = -\frac{D_0}{k_B T} \left(1 - \frac{c_s}{c_{s,\max}} \right) \frac{c_s}{c_{s,\max}} \nabla \frac{\partial g}{\partial c_s}.$$
(3.2.7)

The evolution of concentration profiles then follows a continuity equation obtained by imposing mass conservation. In the absence of sink or source terms, the rate of change of concentration is equivalent to the negative divergence of the flux (3.2.7),

$$\frac{\partial c_s}{\partial t} = \boldsymbol{\nabla} \cdot \left[\frac{D_0}{T} \left(1 - \frac{c_s}{c_{s,\max}} \right) \frac{c_s}{c_{s,\max}} \boldsymbol{\nabla} \frac{\partial g}{\partial c_s} \right], \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$
(3.2.8)

For the simplified case of a free energy dependent only on concentration and not its

derivatives, the total free energy in a volume V_p is

$$G = \int_{V_p} g(c_s(x, r; t)) \, dV.$$
 (3.2.9)

The system will evolve in such a way that total Gibbs free energy is minimized. As such, the energy extremal configurations must satisfy the Euler-Lagrange equation with a conservation of composition constraint imposed over the whole volume. The contraint is expressed in Novick-Cohen and Segel [19] by ignoring the flux through the particle surface as

$$\int_{V_p} c_{s,0} dV = \int_{V_p} c_s(x,r;t) \, dV, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$
(3.2.10)

where $c_{s,0}$ is some initial concentration. Using calculus of variations to find extrema gives the result

$$\frac{\partial g}{\partial c_s} = \text{constant}, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$
 (3.2.11)

where the constant depends on the constraint (3.2.10).

Before moving on to address the case of free energy with dependence on gradient terms, some additional work is required such that parallels can later be drawn between the two formulations. Consider a generic configuration c_s as compared to an equilibrium configuration $c_{s,e}$. A measure of "distance" from equilibrium is then expressed as

$$G(c_s) - G(c_{s,e}) = \int_{V_p} \left[g(c_s) - g(c_{s,e}) \right] dV$$

=
$$\int_{V_p} \left[\frac{\partial g}{\partial c_s} (c_{s,e}) (c_s - c_{s,e}) + \mathcal{O}(c_s - c_{s,e})^2 \right] dV, \qquad (3.2.12)$$

$$x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}$$

where $g(c_s)$ has been expanded as a Taylor series about $c_{s,e}$. It is then observed in Novick-Cohen and Segel [19] that near equilibrium, $\partial g/\partial c_s$ is approximately proportional to the distance $g(c_s) - g(c_{s,e})$. The chemical potential (3.2.6) is then considered the thermodynamic driving force for flow.

In the case that $g(c_s)$ is a concave up parabola (i.e. $g = b_0 + b_1c_s + b_2c_s^2$ with $b_2 > 0$) and mobility M is constant, then (3.2.8) reduces to the standard diffusion equation with qualitatively similar behavior as a special case seen later in Figure 3.2. A parabolic free energy has just one stable minimum that prevents separation between phases. More advanced formulations of the free energy will contain multiple minima causing the system to separate into multiple phases.

3.2.1.3 Cahn-Hilliard Gradient Energy

Given a solution of concentration c_s , the original work of Cahn and Hilliard [3] provides the first few terms of the Taylor series expansion of local Gibbs free energy gabout the free energy per molecule g_0 as,

$$g(c_s, \nabla c_s, \nabla^2 c_s) = g_0(c_s) + \sum_j P_j \frac{\partial c_s}{\partial x_j} + \sum_{jk} \kappa_{jk}^{(1)} \frac{\partial^2 c_s}{\partial x_j \partial x_k} + \frac{1}{2} \sum_{jk} \kappa_{jk}^{(2)} \frac{\partial c_s}{\partial x_j} \frac{\partial c_s}{\partial x_k}$$
(3.2.13)

where the series coefficients are

$$P_{j} = \left[\frac{\partial g}{\partial(\partial c_{s}/\partial x_{j})}\right]_{0},$$

$$\kappa_{jk}^{(1)} = \left[\frac{\partial g}{\partial(\partial^{2} c_{s}/\partial x_{j}\partial x_{k})}\right]_{0},$$

$$\kappa_{jk}^{(2)} = \left[\frac{\partial^{2} g}{\partial(\partial c_{s}/\partial x_{j})\partial(\partial c_{s}/\partial x_{k})}\right]_{0}.$$

(3.2.14)

The author describes $\kappa_{jk}^{(1)}$ and $\kappa_{jk}^{(2)}$ as tensors related to crystal symmetry. The polarization vector components are P_j in a polar crystal where indices j, k represent dimensions in a coordinate system.

Assuming the binary solution in question is isotropic such that it has no preferred direction, expansion coefficients (3.2.14) reduce to

$$P_{j} = 0$$

$$\kappa_{jk}^{(1)} = \delta_{jk} \frac{\partial g}{\partial \nabla^{2} c_{s}}$$

$$\kappa_{jk}^{(2)} = \delta_{jk} \frac{\partial^{2} g}{(\partial |\nabla c_{s}|)^{2}}.$$
(3.2.15)

Note the appearance of Kronecker deltas leave only diagonal components hereafter denoted κ_1 and κ_2 . Here, the coordinates x_j are dropped in favor of generic gradients where spherical coordinates can be implemented later given the geometry of the particle. The isotropic result of (3.2.13) is then simplified as,

$$g(c_s, \nabla c_s, \nabla^2 c_s) = g_0(c_s) + \kappa_1 \nabla^2 c_s + \kappa_2 (\nabla c_s)^2,$$

$$x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T},$$
(3.2.16)

where $g_0(c_s)$ is referred to as the homogeneous free energy as it would be the only

nonzero term in a solution with no inhomogeneities or concentration gradients. Here it is important to assert the reciprocal of intermolecular distance be large compared to concentration gradient such that truncating the series expansion gives good approximation.

It is now possible to integrate (3.2.16) over the whole volume to obtain a total Gibbs free energy G,

$$G = \int_{V_p} g_0(c_s) + \kappa_1 \nabla^2 c_s + \kappa_2 (\nabla c_s)^2 \, dV, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}, \quad (3.2.17)$$

where the dependence on number of particles per unit volume is absorbed into the coefficients.

To simplify further, Cahn and Hilliard [3] then apply the divergence theorem to the middle term. The term is expanded as

$$\int_{V_p} (\kappa_1 \nabla^2 c_s) dV = \int_{A_p} (\kappa_1 \nabla c_s \cdot \mathbf{n}) dA - \int_{V_p} \frac{d\kappa_1}{dc_s} (\nabla c_s)^2 dV,$$

$$x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}$$
(3.2.18)

It is now necessary to impose the natural boundary condition $(\nabla c_s \cdot \mathbf{n} = 0)$ which assumes effects of surface wetting are negligible. This assertion will also be seen to assist in obtaining the variational Euler-Lagrange equation to determine system evolution. It is worth noting that Smith and Bazant [22] allow for an optional consideration of wetting and dewetting through a change in surface energy with respect to concentration.

Upon substitution of (3.2.18), the simplified form of expression (3.2.17) is of particular relevance and is known as the Landau-Ginzburg free energy, valid in the continuum limit. Also known as the coarse-grained free energy, molecular detail is "washed-out" in the rewritten total Gibbs free energy

$$G = \int_{V_p} g_0 + \frac{1}{2} \kappa (\boldsymbol{\nabla} c_s)^2 \, dV, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T},$$
(3.2.19)

where the 1/2 is optionally pulled from the substitution

$$\frac{1}{2}\kappa = \kappa_2 - \frac{d\kappa_1}{dc_s}
= \left[\frac{\partial^2 g}{(\partial |\boldsymbol{\nabla} c_s|)^2}\right]_0 - \left[\frac{\partial^2 g}{\partial c_s \partial \boldsymbol{\nabla}^2 c_s}\right]_0.$$
(3.2.20)

The parameter κ is known as the gradient penalty and functionally serves as an energetic cost to concentration gradients. The regular solution approach will later be used to establish a functional form of the homogeneous free energy $g_0(c_s)$. In doing so, the sharpness of the phase boundary between low and high concentrations will be shown to have direct dependence on the magnitude of κ .

3.2.1.4 Generalized Potential

Consider again (3.2.19) as is shown in the Landau-Ginzburg free energy form. Notable here is that κ is assumed to be positive such that formation of spatial inhomogeneities is not without an energetic price. Novick-Cohen and Segel [19] uses the natural boundary condition mentioned in (3.2.18) and the conservation of composition constraint (3.2.10) as Lagrange multipliers in the variational problem. The new Euler-Lagrange equation becomes

$$\frac{\partial g_0}{\partial c_s} - \kappa \nabla^2 \tilde{c}_s = \text{constant}, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$
(3.2.21)

In the same treatment as before in (3.2.12), the "distance" from equilibrium is

$$G(c_s) - G(c_{s,e}) = \int_{V_p} g(c_s) - g(c_{s,e}) dV$$

$$= \int_{V_p} \left[\frac{\partial g_0(c_s)}{\partial c_s} - \kappa \nabla^2 \tilde{c}_s \right] (c_s - c_{s,e}) + \mathcal{O}[(c_s - c_{s,e})^2] dV.$$
(3.2.22)

Note that in addition to expanding in a Taylor series, integration by parts and an additional application of the natural boundary condition were required by Novick-Cohen and Segel [19] to obtain the result. Parallels between (3.2.12) and the new forcing term proportional to distance from equilibrium in (3.2.22) suggests the equation for a new generalized potential equivalent to the variational derivative of total Gibbs free energy,

$$\mu = \frac{\delta G}{\delta c_s} = \frac{\partial g_0(c_s)}{\partial c_s} - \kappa \nabla^2 \tilde{c}_s. \tag{3.2.23}$$

To obtain the new evolution equation, the net flux is treated the same as in (3.2.7)where it is set to be proportional to the forcing term. In full, the net flux is

$$\mathbf{F} = -\frac{D_0}{k_B T} \left(1 - \frac{c_s}{c_{s,\max}} \right) \frac{c_s}{c_{s,\max}} \boldsymbol{\nabla} \left[\frac{\partial g_0}{\partial c_s} (c_s) - \kappa \boldsymbol{\nabla}^2 \tilde{c}_s \right], \qquad r \in \mathcal{R}, \quad (3.2.24a)$$

$$\mathbf{n} \cdot \mathbf{F} = 0, \qquad (3.2.24b)$$

$$\mathbf{n} \cdot \mathbf{F} = -\omega \frac{i}{e}, \qquad (3.2.24c)$$

where $x \in \mathcal{L}_c$ and $t \in \mathcal{T}$. The boundary conditions on flux at the surface of the particle depend on the net reduction current from the Butler-Volmer reaction in (3.1.63) as well as the fraction ω not diverted to the side reaction in (3.1.74). The zero flux at the center comes from the assumption the particle is spherically symmetric with no sink or source both at r = 0 and for $r \in \mathcal{R}$. By mass conservation, the generalized continuum model is now found as the negative divergence of flux (3.2.24),

$$\frac{\partial c_s}{\partial t} = \boldsymbol{\nabla} \cdot \left[\frac{D_0}{k_B T} \left(1 - \frac{c_s}{c_{s,\max}} \right) \frac{c_s}{c_{s,\max}} \boldsymbol{\nabla} \left(\frac{\partial g_0}{\partial c_s} (c_s) - \kappa \boldsymbol{\nabla}^2 \tilde{c}_s \right) \right],$$

$$t \in \mathcal{T}, \quad x \in \mathcal{L}_c, \quad r \in \mathcal{R}.$$
(3.2.25)

The average concentration \bar{c}_s in a whole particle is expressed as,

$$\frac{\partial \bar{c}}{\partial t} = \frac{1}{V_p} \int_{V_p} \frac{\partial c_s}{\partial t} \, dV, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T}.$$
(3.2.26)

The conservation equation (3.2.25) with the divergence theorem,

$$\int_{V_p} \boldsymbol{\nabla} \cdot \mathbf{F} dV = \int_{A_p} \mathbf{n} \cdot \mathbf{F} \, dA, \qquad (3.2.27)$$

allows the flux boundary condition (3.2.24c) to give the average concentration rate of change in terms of the Butler-Volmer net reduction current density i,

$$\frac{\partial \bar{c}}{\partial t} = \frac{1}{V_p} \int_{A_p} -\mathbf{n} \cdot \mathbf{F} \, dA = \frac{A_p}{V_p} \omega \frac{i}{e}, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T}.$$
(3.2.28)

Note that this is the compliment of the reaction lithium diverted through the side reaction in (3.1.72). The Cahn-Hilliard model is then defined by boundary conditions in (3.2.24) and conservation equation (3.2.25) which differs from the standard diffusion models in its inclusion of the gradient penalty term and use of homogeneous free energy $g_0(c_s)$ from regular solution theory. The following section will find the Gibbs free energy through consideration of the thermodynamic potentials in the fundamental thermodynamic equation.

3.2.1.5 Regular Solution Theory

The Gibbs free energy g found in Carter [4] as the fundamental thermodynamic relation is,

$$g = h - sT, \tag{3.2.29}$$

where h is molar enthalpy and s is molar entropy. A number of statistical mechanical arguments made in Cahn and Hilliard [3] are required to separately treat the enthalpic contribution and the entropic contribution to obtain a particular concentration dependence of free energy.

To determine the configuration entropy per particle, the lattice is assumed to be comprised of P equicomposition layers. The Boltzmann expression $S = k_B \ln W$ relates the total configuration entropy S to the total number of ways W the particles on the lattice can be arranged. For number of ways that layer P can be arranged W_P , the total number of ways for all layers is the product of that in each individual layer such that the Boltzmann expression becomes,

$$S = k_B \ln \left(\prod_P W_P\right) = k_B \sum_P \ln W_P. \tag{3.2.30}$$

In each layer P containing N_P particles, the number of ways W_P is a function of composition \tilde{c}_P for a binary mixture of particles and vacancies given by Cahn and Hilliard [3] as,

$$W_P = \frac{N_P!}{(\tilde{c}_P N_P)! \left[(1 - \tilde{c}_P) N_P \right]!}.$$
(3.2.31)

Finally, applying Stirling's approximation $\ln N_P! = N_P \ln N_P - N_P + \mathcal{O}(\ln N_P)$ to the

Boltzmann expression (3.2.30) gives the configuration entropy per particle to be,

$$s = -k_B \left[c_s \ln \left(\frac{c_s}{c_{s,\max}} \right) + \left(c_{s,\max} - c_s \right) \ln \left(1 - \frac{c_s}{c_{s,\max}} \right) \right], \qquad (3.2.32)$$

Important to note is that s, the entropic contribution to the Gibbs free energy, has no dependence on concentration gradient and is contained within the homogeneous free energy $g_0(c_s)$ from (3.2.19).

Consider now the treatment of h, the enthalpic contribution to Gibbs free energy, for a two-component cubic lattice as given by Cahn and Hilliard [3]. Let $C(S_1)$ and $C(S_2)$ be probabilities of finding a lithium particle at sites S_1 and S_2 respectively. The probability that an AB bond will be formed by a particle B at site S_1 and a vacancy A at site S_2 is then $P_{AB} = C(S_1)(1 - C(S_2))$. Given a radius vector \mathbf{r} of site S_2 relative to S_1 , expanding $C(S_2)$ about S_1 to obtain as a function of $C(S_1)$ yields after truncating,

$$C(S_2) = C(S_1) + (\mathbf{r} \cdot \nabla)C(S_1) + \frac{1}{2!}(\mathbf{r} \cdot \nabla)^2 C(S_1) + \frac{1}{3!}(\mathbf{r} \cdot \nabla)^3 C(S_1).$$
(3.2.33)

Consider the coordination number Z_n (also known as ligancy) denoting the quantity of molecules in the *n*th coordination shell at a radius r_n from site S_1 . Coordination spheres and shells are used in crystallography to describe the number of other particles that each particle in a crystalline solid contacts as a first-, second-, ..., or *n*th-nearestneighbor. The probable number of AB bonds between a particle B at S_1 and the vacancies A in its *n*th coordination shell is then given in Cahn and Hilliard [3] by the product,

$$Z_n P_{AB} = Z_n C(S_1) \bigg[1 - C(S_1) - \bigg(\sum (\mathbf{r} \cdot \boldsymbol{\nabla}) C(S_1) + \frac{1}{2!} \sum (\mathbf{r} \cdot \boldsymbol{\nabla})^2 C(S_1) \bigg) \bigg],$$
(3.2.34)

where summations are over all the sites in the *n*th shell and the third and higher derivatives are neglected $\mathcal{O}((\mathbf{r} \cdot \nabla)^3 C(S_1)) = 0$. Expressing (3.2.34) in terms of vector components and performing the summations gives the reduced result,

$$Z_n P_{AB} = Z_n \tilde{c}_s(S_1) [1 - \tilde{c}_s(S_1)] - \frac{1}{6} Z_n \tilde{c}_s(S_1) \nabla^2 \tilde{c}_s(S_1), \qquad (3.2.35)$$

where the probability C has been replaced by the corresponding mol fraction $\tilde{c}_s = c_s/c_{s,\text{max}}$ of the lithium particles B.

If $\nu_n = E_{AB} - (1/2)(E_{AA} + E_{BB})$, where E's are the intermolecular potentials for the *n*th coordination shell, then total energy per molecule at S_1 is

$$U(S_1) = \tilde{c}_s(S_1)[1 - \tilde{c}_s(S_1)] \sum_n Z_n \nu_n - \frac{1}{6} \tilde{c}_s(S_1) \nabla^2 \tilde{c}_s(S_1) \sum_n Z_n r_n^2 \nu_n.$$
(3.2.36)

Simplifications can now be made by introducing two new parameters to encapsulate the effect of the summations over all coordination shells. The regular solution parameter is defined to be,

$$\Omega_a \coloneqq \sum_n Z_n \nu_n, \tag{3.2.37}$$

representing a mean interaction energy. The characteristic interface width is then defined as,

$$\lambda^2 \coloneqq \frac{\sum_n Z_n r_n^2 \nu_n}{3 \sum_n Z_n \nu_n},\tag{3.2.38}$$

representing a root-mean-squared effective "interaction distance" for energy in a concentration gradient. The expression for the enthalpic contribution to Gibbs free energy can then be written,

$$h = \Omega_a c_s \left(1 - \frac{c_s}{c_{s,\max}} \right) - \frac{1}{2} \Omega_a \lambda^2 c_s \frac{\boldsymbol{\nabla}^2 c_s}{c_{s,\max}}.$$
 (3.2.39)

It is now possible to express the Gibbs free energy as the regular solution model with both entropic and enthalpic contributions,

$$g = k_B T \left[c_s \ln \left(\frac{c_s}{c_{s,\max}} \right) + (c_{s,\max} - c_s) \ln \left(1 - \frac{c_s}{c_{s,\max}} \right) \right] + \Omega_a c_s \left(1 - \frac{c_s}{c_{s,\max}} \right) - \frac{1}{2} \Omega_a \lambda^2 c_s \frac{\boldsymbol{\nabla}^2 c_s}{c_{s,\max}}, \qquad (3.2.40)$$
$$x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$

Recall the Gibbs free energy obtained in (3.2.17) which predicted a homogeneous free energy term in addition to a gradient penalty. In comparing to the newly obtained (3.2.40), all of the entropic contribution and the first term of the enthalpic contribution are without gradient dependence and hence contained within the homogeneous free energy g_0 . The second term of the enthalpy however can be directly compared as,

$$\kappa_1 \nabla^2 c_s + \kappa_2 (\nabla c_s)^2 = \frac{1}{2} \Omega_a \lambda^2 c_s \frac{\nabla^2 c_s}{c_{s,\max}}, \qquad (3.2.41)$$

to give the relations $\kappa_1 = -c_s \Omega_a \lambda^2$ and $\kappa_2 = 0$ such the relation (3.2.20) gives a gradient penalty coefficient of $\kappa = 2\Omega_a \lambda^2$. Solving, an expression may then be obtained for characteristic interface width,

$$\lambda = \sqrt{\frac{\kappa}{2\Omega_a}}.\tag{3.2.42}$$

The relative magnitude of gradient penalty κ to regular solution parameter Ω_a is found to have a direct impact on the thickness of phase separating boundaries between regions of high and low concentrations.

The now complete total Gibbs free energy is of the form,

$$G = \int_{V_p} \frac{1}{2} \kappa \frac{(\boldsymbol{\nabla} c_s)^2}{c_{s,\max}} + g_0(c_s) \, dV, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$
(3.2.43)

Expanding in full,

$$G = \int_{V_p} \frac{1}{2} \kappa \frac{(\nabla c_s)^2}{c_{s,\max}} + \Omega_a c_s \left(1 - \frac{c_s}{c_{s,\max}} \right) + k_B T \left(c_s \ln \left(\frac{c_s}{c_{s,\max}} \right) + (c_{s,\max} - c_s) \ln \left(1 - \frac{c_s}{c_{s,\max}} \right) \right) dV \qquad (3.2.44)$$
$$x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$

Finally, taking the variational derivative from (3.2.23) of the total free energy yields the expression for chemical potential,

$$\mu = k_B T \ln \frac{c_s}{c_{s,\max} - c_s} + \Omega_a \left(1 - 2\frac{c_s}{c_{s,\max}} \right) - \kappa \frac{\boldsymbol{\nabla}^2 c_s}{c_{s,\max}}.$$
 (3.2.45)

It is now possible to examine the second derivative of the Gibbs free energy with respect to concentration to obtain a condition on convexity of the curve and hence number of minima. It is found that for small enough regular solution parameters $\Omega_a < 2k_BT$, the behavior of the evolution is similar to that of a parabolic Gibbs free energy found in standard diffusion models. In such a case there is only one global minimum as demonstrated in Figure 3.2 that prevents separation into two stable phases.



Figure 3.2: Homogeneous Gibbs free energy g_0 and chemical potential μ_0 curves for $\Omega_a < 2k_BT$ where there is only one stable equilibrium such that no phase separation occurs.

If instead $\Omega_a > 2k_BT$ as in Figure C.2, the Gibbs free energy forms a central, concave-down bump that produces two local minima at low and high concentrations. The "miscibility gap" is described by Bazant [2] as the region between two minima where the mixture of Li and lattice sites is not completely miscible or homogeneous. The Maxwell or common tangent construction is a simple geometrical approach allowing for the determination of a coexistence or binodal region where it is energetically favorable to separate into a linear combination of two stable states with the same average concentration. This region can be found using the common tangent to find the binodal points corresponding to $\partial g_0/\partial c_s = \mu_0 = 0$. Upon entering this region, the free energy can be reduced to the corresponding point on the common tangent with ratios of each stable phase determined through the lever rule. The "chemical spinodal" corresponds to the region where convexity is lost within the spinodal points where $\partial^2 g_0/\partial c_s^2 = \partial \mu_0/\partial c_s = 0$. Inside this unstable region, infinitesimal fluctuations can trigger spinodal decomposition into two stable phases. Outside the chemical spinodal but still within the binodal region is referred to as metastable and requires large perturbations away from a homogenized state to trigger phase separation through nucleation.

3.2.2 Extension to Multiple Phases

It was shown previously in Section 3.2.2 that the coexistence of two stable phases near the extreme filling fractions (nearly empty and nearly full) is possible within the miscibility gap in the Gibbs free energy of the solid graphite electrode. With unstable homogenous compositions, recall the result is a "shrinking core" model with a higher concentration shell that moves inwards to replace a lower concentration, dilute center as the particle becomes lithiated. Given lithium concentration also affects the coloring of graphite, staging or pattern formation in the lattice is directly observable through imaging of the electrode. Experimental results from Ferguson and Bazant [8] motivate the need for a more advanced formulation that is able to capture three distinct phases. They propose an extension to the Cahn-Hilliard model that features additional enthapic contributions to the Gibbs free energy.

Recall that in finding the entropic and enthalpic contributions to Gibbs free energy, it was assumed the graphite volume lattice was comprised of a number of repeating, equicomposition layers to comprise the entire graphite volume. The simplest proposed adaptation introduces an additional layer that periodically repeats such that individual concentrations c_j for j = 1, 2 evolve with the same intra-layer Cahn-Hilliard dynamics as before. Additional coupling terms are introduced here to represent the new inter-layer forces that produce a Gibbs free energy surface with more than two minima. The new formulation is called the periodic bilayer model as it features two interacting layers that repeat instead of layered identical slices from the original model.



Figure 3.3: Staging diagrams for the periodic bilayer model of a graphite lattice with intercalated lithium.

The three stable phases possible in the new formulation are referred to as stages and shown in Figure 3.3 with a particular numbering scheme to identify each. Stage 1' and stage 1 are analogous to both layers being in the original two phases that existed for low and high concentrations respectively seen at the binodal points in Figure C.2. Stage 1' represents the two repeating layers being both nearly empty while conversely, stage 1 represents the two being both nearly full. With the periodic bilayer model, an additional stage 2 is considered to be half-full with one layer having high concentration while the other is dilute. Since the layers are indistinguishable, the labeling of each is interchangeable and stage 2 also exists in the symmetrical case when concentrations are swapped. Recall in the original Cahn-Hilliard model that the ratio of phase separation between stable equilibria in the Gibbs free energy was determined by the lever rule with free energy being reduced to a point on the common tangent. The common tangent construction now gives up to two planes that are tangent to the surface of the Gibbs free energy as a function of the two layer concentrations. Stage 1' and stage 1 are found at tangent points in the diagonal corners while the two possibilities for stage 2 are in the off-diagonal corners of the Gibbs free energy illustrated in Figures C.4 and C.5.

It was previously discussed that the generalized potential is the variational derivative of free energy such that the tangent points in a particular tangent plane will have equivalent effective chemical potentials. With two possible common tangent planes, a phase-separating system reducing its free energy can produce two flat voltage plateaus. While "staircase" voltages are commonly seen in experimental opencircuit potentials, Smith *et al.* [23] describes how additional repeating layers with a greater number of dilute stages are required to capture the high voltage plateaus for low-filling fractions seen in the C/100 cell voltage from Figure 2.3. Furthermore, Ferguson and Bazant [8] remarks there are at least five distinct phases in graphite during lithium insertion. The periodic bilayer model as a first approximation however has the ability to capture the large voltage drop occurring at a filling fraction of one half discussed in the next section.

3.2.2.1 Cross-Layer Interaction Energy

Within each individual layer j, a local free energy of the form (3.2.44) still applies with a total concentration now determined by a sum of local concentrations $c_1 + c_2$. The free energy is replicated here with a subscript j to denote intralayer configuration,

$$g_{j}(c_{j}, \boldsymbol{\nabla} c_{j}) = \Omega_{a}c_{j}\left(1 - \frac{c_{j}}{c_{s, \text{ref}}}\right) + c_{j}\ln\left(\frac{c_{j}}{c_{s, \text{ref}}}\right) + (c_{s, \text{ref}} - c_{j})\ln\left(1 - \frac{c_{j}}{c_{s, \text{ref}}}\right) + \frac{1}{2}\kappa\frac{(\boldsymbol{\nabla}\tilde{c}_{j})^{2}}{c_{s, \text{ref}}}, \qquad (3.2.46)$$
$$x \in \mathcal{L}_{c}, \quad r \in \mathcal{R}, \quad t \in \mathcal{T},$$

where $c_{s,ref} = c_{s,max}/2$ is the maximum capacity in a layer occupying half the volume. The extension explored by Smith *et al.* [23] and Ferguson and Bazant [8] now becomes relevant as the total free energy will not only be the sum of the intralayer configurations but also require extra cross-interaction terms to account for the mixing enthalpies between layers.

The Gibbs free energy for the periodic bilayer model is a combination of intralayer effects (3.2.46) with the addition of an interaction free energy g_{int} that depends on compositions in both layers,

$$g = g_1(c_1, \nabla c_1) + g_2(c_2, \nabla c_2) + g_{\text{int}}(c_1, c_2).$$
(3.2.47)

The intralayer free energies are again double-welled and are able to phase-separate into low concentration stage 1' and high concentration stage 1. Stage 2 phases with every other layer full are stabilized by a repulsive interaction free energy that penalizes the proximity of lithium in adjacent layers. The reference Ferguson and Bazant [8] gives the particular polynomial form of additional terms as an extension to that found in the enthalpic considerations of (3.2.39),

$$g_{\rm int}(c_1, c_2) = \Omega_b \frac{c_1 c_2}{c_{s,\rm ref}} + \Omega_c c_1 \left(1 - \frac{c_1}{c_{s,\rm ref}}\right) \frac{c_2}{c_{s,\rm ref}} \left(1 - \frac{c_2}{c_{s,\rm ref}}\right).$$
(3.2.48)

Two new parameters are introduced in the additional enthalpic terms that have physical implications. Common to experimental results is a "staircase" voltage plateau in near-equilibrium charge or discharge curves occuring at the half filling fraction depicted in Figure C.6. The difference between the plateaus is set by the $\Omega_b > 0$ term which represents the repulsive interaction between cross-plane particles and increases the free energy of the nearly full stage 1 relative to the more sparse stage 1' and 2. The other $\Omega_c > 0$ term, as discussed in Ferguson and Bazant [8], represents a particle-vacancy cross-plane mixing enthalpy that penalizes partially filled layers and further stabilizes stage 2 phases. Functionally this term has a similar effect as Ω_a in that there is increased energenic penalty to homogenous states $c_1 \approx c_2$. Though not done here, Smith *et al.* [23] suggests setting $\Omega_c = 0$ to save on computational cost given its effect overlaps with an existing enthalpic term. The system evolution then traces out a path g^* on the Gibbs free energy.

The generalized chemical potential for each layer is analogous to (3.2.45) for the one layer model,

$$\mu_j = \frac{\delta G}{\delta c_j} = \frac{\partial g}{\partial c_j} - \kappa \nabla^2 \tilde{c}_j, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$
(3.2.49)

Expanding in full gives,

$$\mu_{j} = k_{B}T \ln \frac{\tilde{c}_{j}}{1 - \tilde{c}_{j}} + \Omega_{a}(1 - 2\tilde{c}_{j}) - \kappa \nabla^{2}\tilde{c}_{j}$$
$$+ \Omega_{b}\tilde{c}_{k} + \Omega_{c}\tilde{c}_{k}(1 - \tilde{c}_{k})(1 - 2\tilde{c}_{j})$$
$$x \in \mathcal{L}_{c}, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}.$$
$$(3.2.50)$$

where j, k = 1, 2 and $j \neq k$. The flux of lithium within each graphite layer is then similar to before in (3.2.24) as they relate to the gradient in chemical potentials μ_j for j = 1, 2,

$$\mathbf{F}_{j} = -\frac{D_{0}}{k_{B}T} \left(1 - \tilde{c}_{j}\right) \tilde{c}_{j} \nabla \frac{\delta G}{\delta c_{j}}, \qquad r \in \mathcal{R}, \qquad (3.2.51a)$$

$$\mathbf{n} \cdot \mathbf{F}_j = 0, \qquad \qquad r = 0, \qquad (3.2.51b)$$

$$\mathbf{n} \cdot \mathbf{F}_j = -\frac{1}{2}\omega \frac{i_j}{e}, \qquad r = a, \qquad (3.2.51c)$$

where $x \in \mathcal{L}_c$ and $t \in \mathcal{T}$. Applying the conservation of mass continuity equation in each layer gives

$$\frac{\partial c_j}{\partial t} = \boldsymbol{\nabla} \cdot \left[\frac{D_0}{k_B T} \left(1 - \tilde{c}_j \right) \tilde{c}_j \boldsymbol{\nabla} \frac{\delta G}{\delta c_j} \right], \qquad t \in \mathcal{T},$$
(3.2.52)

where $x \in \mathcal{L}_c$ and $r \in \mathcal{R}$. Here, if lithium particles were physically moving between layers it could be captured by a sink/source term. Note that intercalation reactions at the surface are stated by Ferguson and Bazant [8] to proceed independently as if they were separate reactants. As such, many of the reaction equations in Section 3.1.2 are duplicated and made local to each of the two layers. Accordingly, the boundary condition (3.2.51c) differs from (3.2.24c) by a factor of 1/2 given each layer occupies half the surface area receiving their respective net reduction currents i_j expressed in the next section.

3.2.2.2 Multilayer Reaction Rates

The average concentration \bar{c}_s change in a whole particle is analogous to (3.2.26),

$$\frac{\partial \bar{c}}{\partial t} = \frac{1}{V_p} \int_{V_p} \frac{\partial c_1}{\partial t} + \frac{\partial c_2}{\partial t} \, dV = \frac{A_p}{V_p} \omega \frac{i_1 + i_2}{2e}, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T}, \tag{3.2.53}$$

such that the Butler-Volumer net reduction current is still recovered as in (3.2.28) though with an altered fraction of Li accepted into particle,

$$\omega = \tanh\left(\gamma\left[1 - \frac{\tilde{c}_1 + \tilde{c}_2}{2}\right]\right), \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
 (3.2.54)

Here, it was decided to use the average surface composition in the calculation of fraction ω as opposed to defining two separate parameters ω_j , j = 1, 2. This is in line with the assumption the macroscopic quantities such as $c_{\text{side}}(x,t)$ and $\bar{c}_s(x,t)$ are blind to the individual layers within the particles.

The remaining extensions from the one layer model pertain to the coupling equations through the Butler-Volmer net reduction current (3.1.63) and side reactions (3.1.72). The side reaction rate and compliment to (3.2.51c) is then the average of the reduction currents,

$$\frac{\partial c_{\text{side}}}{\partial t} = \frac{A_p}{V_p} (1 - \omega) \left(\frac{i_1 + i_2}{2} \right), \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.2.55)

Here, reduction currents are presented expanded already with the exchange rate,

$$i_j = k_0 \left(\frac{c_l}{c_{l,\text{ref}}}\right)^{1/2} (1 - \tilde{c}_j)^{1/2} (\tilde{c}_j)^{1/2} \left[\exp\left(\frac{-e\eta_j}{2k_BT}\right) - \exp\left(\frac{e\eta_j}{2k_BT}\right)\right], \quad (3.2.56)$$
$$x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$

Surface overpotentials for each layer j = 1, 2 are analogous to before in (3.1.66),

$$\eta_j = \frac{\mu_j}{e} - E_\theta - \left(\frac{\mu_O}{e} - \phi_s\right) \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.2.57)

Note that the diffusional chemical potential of the oxidized state μ_O is able to be replaced as before with the chosen Nernst-Planck from (3.1.36) or Stefan-Maxwell formulation as in (3.1.68).

In this extended periodic bilayer model, the chemical potential in each layer can be simplified by collecting the common terms that appear in both equations from symmetry,

$$\mu_j = \mu_{\text{eff}} - \kappa \boldsymbol{\nabla}^2 \tilde{c}_j. \tag{3.2.58}$$

The reference Smith et al. [23] finds the effective chemical potential to be,

$$\mu_{\text{eff}} = \frac{\partial g^*}{\partial (c_1 + c_2)},\tag{3.2.59}$$

where g^* is the particular free energy path the system evolves along with the sum $c_1 + c_2$ constrained to the charge rate. In keeping with Morales Escalante *et al.* [15], the Nernst voltage $V_{eq} = E_{\theta} - \mu_{eff}/e$ can be replaced with the function fit to C/100

experimental data given in (3.1.71) in the equation for surface overpotential,

$$\eta_j = -U_{\text{eq}}\left(\frac{\tilde{c}_1 + \tilde{c}_2}{2}\right) - \frac{\kappa \nabla^2 \tilde{c}_j}{e} - \frac{\mu_O}{e} \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.2.60)

As a final note, any relevant equations from macroscopic electrolyte dynamics not reproduced here in Section 3.2.2 are equivalent to those covered in Section 3.1 that do not have dependence on the solid concentration c_s .

3.3 Summary of Model Equations

Disparities in length scales allows for an assumption of translational symmetry and homogenization in the coordinate plane orthogonal to battery length x and spherical symmetry in the graphite particles. Model equations can then be expressed less generally in terms of the pseudo two-dimensional x-r domain. Accordingly, vector quantities are reduced to being their components only along the relevant coordinates. Particular initial conditions are also given in the equations here that are replicated from earlier and condensed into the relevant PDE's to solve.

3.3.1 Stefan-Maxwell Concentrated Electrolyte

The evolution equations from Section 3.1.1 for transport in a concentrated liquidphase binary electrolyte for a Li-ion battery come from the conservation of anions (3.1.13a) using flux boundary conditions (3.1.25) with the particular form of Stefan-Maxwell (SM) flux (3.1.56),

$$\epsilon \frac{\partial c_l}{\partial t} = -\frac{\partial F_l}{\partial x}, \qquad x \in \mathcal{L}, \qquad t \in \mathcal{T}, \qquad (3.3.1a)$$

$$F_l = -\left(\frac{\epsilon}{\tau} \mathcal{D}\frac{\partial c_l}{\partial x} + \frac{1-\iota_+}{e}i_l\right), \qquad x \in \mathcal{L}, \qquad t \in \mathcal{T}, \qquad (3.3.1b)$$

$$F_l = 0, \qquad x = 0, L_s + L_c, \quad t \in \mathcal{T}, \qquad (3.3.1c)$$

$$c_l = c_{l,\text{ref}}, \qquad x \in \mathcal{L}, \qquad t = 0, \qquad (3.3.1d)$$

where $c_{l,\text{ref}}$ is the initial homogeneous lithium concentration in the electrolyte. The current density has boundary conditions discussed in (3.1.26) with the particular form for the (SM) model (3.1.58),

$$i_{l} = -\frac{\epsilon}{\tau} \sigma_{l}^{\text{SM}} \left(\frac{\partial \phi_{l}}{\partial x} + 2 \frac{k_{B}T}{ec_{l}} \left(t_{+}^{0} - 1 \right) \frac{\partial c_{l}}{\partial x} \right), \qquad x \in \mathcal{L}, \qquad t \in \mathcal{T}, \qquad (3.3.2a)$$

$$i_l = i_{\text{cell}}, \qquad x = 0, \qquad t \in \mathcal{T}, \quad (3.3.2b)$$

$$i_l = 0, \qquad x = L_s + L_c, \quad t \in \mathcal{T}.$$
(3.3.2c)

The electric potential at the current collector in the porous electrode is chosen as the reference and cell voltage is measured at the counter electrode from (3.1.81),

$$\phi_{\text{cell}} = \frac{2k_B T}{e} \operatorname{arcsinh} \left(-\frac{i_{\text{cell}}}{2k_{0,\text{foil}}\tilde{c_l}^{1/2}} \right) + \phi_l, \qquad x = 0, \qquad t \in \mathcal{T}, \qquad (3.3.3a)$$
$$\phi_s = 0, \qquad \qquad x = L_s + L_c, \quad t \in \mathcal{T}. \qquad (3.3.3b)$$

Ohm's law from (3.1.82) gives a current density in the solid-phase electrode to be

related to the solid electric potential,

$$i_s = -\frac{(1-\epsilon)}{\tau_s} \sigma_s \frac{\partial \phi_s}{\partial x}, \qquad x \in \mathcal{L}_c, \qquad t \in \mathcal{T}, \qquad (3.3.4a)$$

$$i_s = 0,$$
 $x = L_s,$ $t \in \mathcal{T},$ (3.3.4b)

$$i_s = i_{\text{cell}}, \qquad x = L_s + L_c, \quad t \in \mathcal{T}.$$
 (3.3.4c)

Each of the above equations are applicable on the macroscopic scale and appear in both phase-separating electrode models. The following sections will detail the particular coupling equations and electrode evolution equations as they pertain to the original Cahn-Hilliard model and then the periodic bilayer model.

3.3.2 Cahn-Hilliard Model (CHR)

The conservation of liquid electrolyte current density (3.1.17) and the conservation of solid electrode current density (3.1.83) have equal and opposite sink/source terms (3.1.88) from Section 3.1.2,

$$\frac{\partial i_l}{\partial x} = 0, \qquad x \in \mathcal{L}_s, \quad t \in \mathcal{T},$$
(3.3.5a)

$$\frac{\partial i_l}{\partial x} = \frac{3}{a}(1-\epsilon)i, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T},$$
(3.3.5b)

$$\frac{\partial i_s}{\partial x} = -\frac{3}{a}(1-\epsilon)i, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T},$$
(3.3.5c)

(3.3.5d)

The net reduction current from (3.1.63) for (CHR) serves to couple volume-averaged transport on macroscopic scales to the microscopic transport dynamics within the

solid-phase electrode particles,

$$i = k_0 \tilde{c}_l^{1/2} \left(1 - \tilde{c}_s\right)^{1/2} \tilde{c}_s^{1/2} \left[\exp\left(\frac{-e\eta_s}{2k_B T}\right) - \exp\left(\frac{e\eta_s}{2k_B T}\right) \right]$$

$$x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
 (3.3.6)

Furthermore, the surface overpotential from (3.1.70) as the reaction driving force is,

$$\eta_s = -U_{\rm eq}(\tilde{c}_s) - \kappa \nabla^2 \tilde{c}_s - \phi_l + \phi_s, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.3.7)

The side reaction fraction from (3.1.74) then controls the amount of flux actually entering the electrode versus being diverted to the SEI layer,

$$\omega(c_s) = \tanh\left(\gamma\left[1 - \frac{c_s}{c_{s,\max}}\right]\right), \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
 (3.3.8)

The dynamics of lithium transport in each solid-phase electrode particle in the (CHR) model from Section 3.2.1 follow the evolution equation (3.2.25). For a homogeneous initial lithium concentration $c_{s,0}$,

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 M(c_s) \frac{\partial}{\partial r} \frac{\delta G}{\delta c_s} \right], \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}, \quad (3.3.9a)$$

$$M(c_s)\frac{\partial}{\partial r}\frac{\partial G}{\delta c_s} = 0 \qquad x \in \mathcal{L}_c, \quad r = 0, \quad t \in \mathcal{T}, \quad (3.3.9b)$$

$$M(c_s)\frac{\partial}{\partial r}\frac{\partial G}{\delta c_s} = -\omega \frac{i}{e} \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}, \quad (3.3.9c)$$
$$\frac{\partial c_s}{\partial r} = 0, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}, \quad (3.3.9d)$$
$$\frac{\partial c_s}{\partial r} = 0, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}, \quad (3.3.9e)$$

$$c_s(r,0) = c_{s,0}, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t = 0.$$
(3.3.9f)

Here, boundary conditions come from flux considerations in (3.2.24). The initial condition is a homogeneous concentration $c_{s,0}$ that begins very small for a depleted electrode. The mobility from (3.2.5) is,

$$M(c_s) = \frac{D_0}{k_B T} \left(1 - \frac{c_s}{c_{s,\max}} \right) \frac{c_s}{c_{s,\max}}.$$
(3.3.10)

The variational derivative of the total Gibbs free energy is the chemical potential from (3.2.45),

$$\frac{\delta G}{\delta c_s} = k_B T \ln \frac{\tilde{c}_s}{1 - \tilde{c}_s} + \Omega_a \left(1 - 2\tilde{c}_s\right) - \kappa \frac{1}{r^2} \frac{\partial^2}{\partial r^2} \left(r^2 \tilde{c}_s\right).$$
(3.3.11)

The solid electrode evolution equations are then simulated for each and every particle placed in the electrochemical cell.

3.3.3 Periodic Bilayer Model (CHR2)

The conservation of liquid electrolyte current density (3.1.17) and the conservation of solid electrode current density (3.1.83) have equal and opposite sink/source terms (3.1.88) from Section 3.1.2,

$$\frac{\partial i_l}{\partial x} = 0, \qquad x \in \mathcal{L}_s, \quad t \in \mathcal{T}, \qquad (3.3.12a)$$

$$\frac{\partial i_l}{\partial x} = \frac{3}{a}(1-\epsilon)\frac{i_1+i_2}{2}, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T},$$
(3.3.12b)

$$\frac{\partial i_s}{\partial x} = -\frac{3}{a}(1-\epsilon)\frac{i_1+i_2}{2}, \qquad x \in \mathcal{L}_c, \quad t \in \mathcal{T}.$$
(3.3.12c)

The net reduction currents (3.2.56) for (CHR2) serve to couple volume-averaged transport on macroscopic scales to the microscopic transport dynamics within the solid-phase electrode particles,

$$i_j = k_0 \tilde{c}_l^{1/2} \left(1 - \tilde{c}_j\right)^{1/2} \left(\tilde{c}_j\right)^{1/2} \left[\exp\left(\frac{-e\eta_j}{2k_B T}\right) - \exp\left(\frac{e\eta_j}{2k_B T}\right) \right],$$

$$x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
 (3.3.13)

Surface overpotentials for each layer j = 1, 2 are from (3.2.57),

$$\eta_j = -U_{\text{eq}}\left(\frac{\tilde{c}_1 + \tilde{c}_2}{2}\right) - \frac{\kappa \nabla^2 \tilde{c}_j}{e} - \phi_l + \phi_s, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
(3.3.14)

The side reaction fraction from (3.2.54) then controls the amount of flux actually entering each electrode particle layer versus that being diverted to the SEI layer,

$$\omega = \tanh\left(\gamma\left[1 - \frac{\tilde{c}_1 + \tilde{c}_2}{2}\right]\right), \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}.$$
 (3.3.15)

The (CHR2) model from Section 3.2.2 then has evolution equations for each layer j = 1, 2 from (3.2.52) with flux boundary conditions (3.2.51),

$$\frac{\partial c_j}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 M(c_j) \frac{\partial}{\partial r} \frac{\delta G}{\delta c_j} \right], \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t \in \mathcal{T}, \quad (3.3.16a)$$

$$M(c_j)\frac{\partial}{\partial r}\frac{\delta G}{\delta c_j} = 0 \qquad \qquad x \in \mathcal{L}_c, \quad r = 0, \quad t \in \mathcal{T}, \quad (3.3.16b)$$

$$M(c_j)\frac{\partial}{\partial r}\frac{\delta G}{\delta c_j} = -\omega \frac{i_j}{2e} \qquad \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}, \quad (3.3.16c)$$
$$\frac{\partial c_j}{\partial r} = 0, \qquad \qquad x \in \mathcal{L}_c, \quad r = 0, \quad t \in \mathcal{T}, \quad (3.3.16d)$$

$$\frac{\partial c_j}{\partial r} = 0, \qquad x \in \mathcal{L}_c, \quad r = a, \quad t \in \mathcal{T}, \quad (3.3.16e)$$
$$c_j = \frac{c_{s,0}}{2}, \qquad x \in \mathcal{L}_c, \quad r \in \mathcal{R}, \quad t = 0. \quad (3.3.16f)$$

The mobility from (3.2.5) is,

$$M(c_j) = \frac{D_0}{k_B T} \left(1 - \frac{c_j}{c_{s,\text{ref}}}\right) \frac{c_j}{c_{s,\text{ref}}}.$$
(3.3.17)

The chemical potential for the (CHR2) model comes from (3.2.50),

$$\frac{\delta G}{\delta c_j} = k_B T \ln \frac{\tilde{c}_j}{1 - \tilde{c}_j} + \Omega_a (1 - 2\tilde{c}_j) - \kappa \frac{1}{r^2} \frac{\partial^2}{\partial r^2} \left(r^2 \tilde{c}_j \right) + \Omega_b \tilde{c}_k + \Omega_c \tilde{c}_k (1 - \tilde{c}_k) (1 - 2\tilde{c}_j).$$
(3.3.18)

The sets of PDE's in this section summarizing the mathematical models would then need to be discretized and nondimensionalized in order to simulate battery dynamics computationally. These aspects however are beyond the scope of this work which requires only a working level understanding of the simulation software MPET to solve the inverse problem discussed in the following chapters.

Chapter 4

Inverse Modeling

In this chapter, an optimization problem is formulated as one way to solve the inverse problem. The goal is to infer a set of optimal parameters that characterize the modeled system. The optimal solution corresponds to a minimized error functional quantifying the discrepancy between experimental data from Chapter 2 and simulation data of the various models from Chapter 3. Available data for comparison at a given time collected during the C/44 experiment includes lithium concentration profiles in the solid-phase electrode discussed in Section 4.1, as well as the overall cell voltage in Section 4.2. Many of the thermodynamic properties, mainly those that pertain to the electrolyte, are obtained from the literature and are not subject to variation in seeking an optimal solution. Refer to Appendix A for these tabulated values. The remaining p unknown parameters are denoted with vector $\mathbf{m} \in \mathbb{R}^p$ and inferred from the solution of an optimization problem. The accuracy of the final reconstructed properties allowing the model to match the experimental data most closely will then depend on the correctness of fixed parameters, in addition to the ability of the model to capture the physics of the system. Any approximations or concessions made in

these two regards instead produce an optimal solution with effective parameters that may differ from actual physical values by way of compensating for those inadequacies.

It was shown in Chapter 3, there are a number of different options in selecting components of the multi-scale model. The macroscopic, volume-averaged electrolyte equations from Section 3.1.1 can be that of the dilute Nernst-Planck model (NP) or instead the concentrated Stefan-Maxwell model (SM). While multiple options also exist for reaction rates (e.g., Marcus kinetics from Bazant [2]), all cases here will be that of the Butler-Volmer reaction type (BV) from Section 3.1.2. On the microscopic scale within the graphite particles, two variants of the Cahn-Hilliard reaction model are introduced in Section 3.2: the original one layer (CHR) and the extended periodic bilayer model (CHR2). The main focus of this work is in assessing the relative fidelity of the following combined two formulations for solid-phase electrode,

- model (SM)-(BV)-(CHR), denoted (CHR) for brevity, features 6 unknown parameters $\mathbf{m} = \{k_{0,\text{foil}}, k_0, \gamma, \sigma_s, D_0, \Omega_a\},\$
- model (SM)-(BV)-(CHR2), denoted (CHR2), features 8 unknown parameters $\mathbf{m} = \{k_{0,\text{foil}}, k_0, \gamma, \sigma_s, D_0, \Omega_a, \Omega_b, \Omega_c\}.$

It is notable that parameters applicable on the microscopic scale are inferred from comparison of macroscopic quantities. Such inference across scales is made possible through the strong coupling between the solid electrode and liquid electrolyte from the reaction rate at the surface of graphite particles. The net reduction current scales with the exchange rate constant k_0 through (3.1.64). The analogous reaction occurs at the counter electrode with foil rate constant $k_{0,\text{foil}}$ which serves predominantly to shift cell voltage up and down by changing the overpotential in (3.1.81). The fraction of lithium reacted into a graphite particle instead of the SEI layer depends on the side reaction parameter γ from (3.1.72). The conductivity σ_s enters in the solid current density (3.1.82) through Ohm's law. The regular solution parameter Ω_a in (3.2.40) and secondary interaction parameters Ω_b , Ω_c unique to (CHR2) in (3.2.48) determine the shape of the free energy and control the phase-separating behavior within the electrode. The diffusivity coefficient D_0 in (3.2.25) and (3.2.52) then affects the propagation of lithium within the electrode particles. All other parameters are inherited from the work by Morales Escalante *et al.* [15] and held constant throughout the duration of an optimization that looks to minimize the problems in the following sections.

4.1 Concentration Error Functional

Experimentally obtained profiles $\hat{c}_s(x, t_k)$, $k = 1, \ldots, N$, from Figure 2.1 are spatially resolved over the length of the battery and measure the concentration of intercalated lithium. The corresponding model variable is the averaged concentration $\bar{c}_s(x, t)$ obtained through a normalized integral of solid-phase concentration $c_s(x, r; t)$ over the volume of particles at a given position, as was the case in (3.2.26). The error functional as found in Morales Escalante *et al.* [15] is formulated as the least-squares difference between the model-based prediction and the measured quantity,

$$\mathcal{J}_{c_s}(\mathbf{m}) = \frac{1}{2NL_c} \sum_{k=1}^N \int_{L_s}^{L_s + L_c} \left[\frac{\bar{c}_s(x, t_k)}{c_{s, \max}} - \frac{\hat{c}_s(x, t_k)}{c_{s, \max}} \right]^2 \, dx. \tag{4.1.1}$$

The prefactor here serves to average the error over the domain of integration. Note again the "snapshot" approximation is applied to the simulation data at each of the discrete times when the experimental profiles are defined. Another limiting factor is the spatial resolution of the MRI measurements over the length of the electrode. To reduce computational work while retaining some benefit of higher model resolution, for each of the six battery positions available in the experimental data, two cell volumes are averaged such that twelve total graphite particles are placed along the length of the battery. More intensive simulations may choose to average even higher multiples of the experimental resolution. Multiple particles may also be placed at a single cell volume in parallel with regards to electrolyte access to capture the effect of particle size distribution.

4.2 Cell Voltage Error Functional

The other optimization problem of interest differs from that found in Morales Escalante *et al.* [15] due an overall cell voltage $\phi_{\text{cell}}(t)$ expressed in (3.1.81) that includes the effects of a Li-metal counter electrode. For C/44 experimental cell voltage data $\hat{\Phi}(t)$, the error functional is,

$$\mathcal{J}_{\Phi}(\mathbf{m}) = \frac{1}{2t_f} \int_0^{t_f} \left[(\phi_{\text{cell}}(t) - IR_{\text{ser}}) - \hat{\Phi}(t) \right]^2 dt.$$
(4.2.1)

where R_{ser} is the series resistance that modifies cell voltage through Ohm's law. Since the voltage data is collected continuously over the course of the experiment, the leastsquares error is able to be compared at a greater number of times than concentration profiles.

4.3 Multiobjective Optimization

In keeping with Morales Escalante *et al.* [15], a weighted average of errors is proposed as,

$$\mathcal{J}_{\rho}(\mathbf{m}) = (1-\rho)\mathcal{J}_{c_s}(\mathbf{m}) + \rho\mathcal{J}_{\Phi}(\mathbf{m}), \qquad 0 \le \rho \le 1.$$
(4.3.1)

Accordingly, the optimization problem becomes for a given ρ ,

$$\min_{\mathbf{m}\in\mathbb{R}^p}\mathcal{J}_{\rho}(\mathbf{m}).$$
(4.3.2)

It is noted in attempting a multi-objective optimization to minimize both \mathcal{J}_{c_s} and \mathcal{J}_{Φ} that the particular weight relative to each other is unknown. By solving the optimization problem over a range of ρ values, the so-called Pareto front is obtained as the parametrized curve in a plot of \mathcal{J}_{Φ} versus \mathcal{J}_{c_s} . In visualizing all of the potentially optimal solutions, a particular value of ρ and the corresponding optimal parameters can be selected depending on the trade-off between the two errors deemed most appropriate.
Chapter 5

Computational Models

In this chapter, the software MPET is used to simulate the mathematical models detailed in Chapter 3. The results of simulating the battery dynamics of both Cahn-Hilliard models enables comparison with experimental results. Configuring the solver to run the particular formulation in this work requires a number of modifications to the original source code Smith, Raymond B. [24] in Python. The use of a MAT-LAB optimization routine to find a solution to the problem (4.3.2) then uses MPET as a black box program to reconstruct the unknown parameters of the model that produce approximate laboratory data.

5.1 Multiphase Porous Electrode Theory (MPET)

The Newman model, as decribed in Section 3.1 with fundamental theory discussed in Fuller *et al.* [10], is a widely popular, multiscale model of an electrochemical cell that predicts macroscopic battery behavior from microscopic physical models. The accompanying software Dualfoil from Newman, J. [18] is written in Fortran and is what the software Multiphase Porous Electrode Theory (MPET) from Smith, Raymond B. [24] written in Python replaces. The most basic formulation is to homogenize the battery in directions parallel to the current collectors and within the particle to obtain a one-dimensional model along the battery length x. The typical treatment of porous electrode theory (PET) then uses solid-state electrode particles as determined from surface reactions and concentration field driven transport in the electrolyte. In such a case, accounting for the thermodynamics of the system requires fitting of the opencircuit voltage to act as a reaction driving force.

More complex, phase separating materials are discussed in Smith and Bazant [22] where inhomogeneous concentration profiles within particles instead give voltage as an emergent property. These particles are positioned in the electrode domain as volumetric sink/source terms for ions and electrons. In addition to having much of the same functionality as Dualfoil, MPET allows for the use of a Cahn-Hilliard phase-field models (3.3.9a) and (3.3.16a) based on nonequilibrium thermodynamics in the pseudo two-dimensional x-r domain. Validation of the open-source MPET was done by the authors against the popular commercial software COMSOL using a finite element method.

In Smith and Bazant [22], the PDE's outlined in Section 3.3 are chosen to be represented and evaluated in the form of differential algebraic equations (DAE) using a type of finite volume method (FVM). Since this spatial discretization does not use a finite difference method, MPET does well to handle the sharp interface that characterizes strong phase separation. The method is additionally credited with a precision of numerical accuracy in assuring conservation of species. Given the large variation in the dynamical system's time rate of change, MPET uses a variable-order adaptive time stepper. The integration method used in the implicit IDAS time stepper from SUNDIALS (Suite of Nonlinear and Differential/Algebraic Equation Solvers) applies the backward differentiation formula (BDF) to the DAE system.

Smith and Bazant [22] discusses the use of the ADOL-C automatic differentiation library to form the analytical-accuracy Jacobian matrix to help solve the nonlinear equations. Modifications and additions to the model are made easier by not requiring manual input of analytical derivatives or relying on approximations of the Jacobian. DAE Tools from Dragan D. [6] wraps IDAS with ADOL-C such that a high-level modeling language environment in Python handles the interactions with low-level software packages. Smith and Bazant [22] use the object oriented framework of the Python environment to separately define the overall cell model from the active material models. The use of DAE Tools allows for easy definition of a simulation setup that initializes model instances with starting configurations. Any number of electrode particles may be simulated and communicate only the necessary information to the electrolytic cell. The next section details the necessary code injections to successfully implement the particular mathematical model of interest.

5.1.1 Modifications

Customizing MPET to match the experimental setup in Chapter 2 and mathematical models in Chapter 3 is primarily done through the input configuration files with entries tabulated in Appendix A. Each option chosen was available in the vanilla version of Smith, Raymond B. [24], with detailed descriptions found in their sample configuration file. Further modification was then required for certain hard-coded aspects of MPET with changes made to the source code:

- mpetrun.py as the starting function that calls main.
 - Attempting too small of discretization may result in runaway memory consumption leading to an unresponsive computer. The solution by the user "Ulises CT" on Stack Overflow allowed for the memory use to be limited on Linux systems through Python.
- io_utils.py as the module for creating data structures from input files.
 - The added side reaction parameter γ needed to be retrieved from the input electrode configuration file and stored in the dictionary for electrode particle parameters.
 - Treating γ like the other configurable model parameters, it is also duplicated in a dictionary of nondimensionalized parameters, though without any scaling.
- mod_electrode.py for options CHR and CHR2.
 - A DAE variable is first created for later use in either the (CHR) or (CHR2) model to track the time rate of change in the concentration of the side reaction.
 - The analytical function $U_{eq}(c_s)$ from (3.1.71) is added with an input of (CHR) surface filling fraction or a (CHR2) average of the two layer surface fractions. Coefficients for the fit function are given in Table C.1 from Appendix C.
 - The function $U_{eq}(c_s)$ and the nonhomogeneous gradient penalty term of the chemical potential at the particle surface are then used to replace μ/e in

(3.1.68) for (CHR) and (3.2.60) for (CHR2) to calculate the overpotential in the Butler-Volmer net reduction current.

- The side reaction fraction ω from (3.1.74) as a function of (CHR) surface filling fraction or (3.2.54) with averaged (CHR2) fractions are calculated using the additionally imported parameter γ .
- The flux boundary conditions are multiplied by side reaction fraction ω for consistency with (3.3.9c) and (3.3.16c).
- The DAE equations for calculating variable $\partial c_{\text{side}}/\partial t$ from (3.1.72) for (CHR) and (3.2.55) for (CHR2) are implemented using the compliment $(1 - \omega)$ and the calculated net reduction currents.
- mod_cell.py for assuring conservation of charge (3.1.83) and calculating total current (3.1.86) from reaction rates.
 - The volumetric sink/source term (3.1.88) must be modified to add the rate of lithium entering the SEI layer from DAE variable $\partial c_{\text{side}}/\partial t$ to the change in average $\partial \bar{c}_s/\partial t$ for each instance of an electrode particle.
- props_elyte.py for the (SM) model with the property set valoen_reimers.
 - The transference number t^0_+ from (3.1.42) is made to be that from Appendix A.
 - The diffusivity $\mathcal{D}(c_l)$ must be made to be the expression (3.1.60) with the appropriate constants from Appendix A.
 - The thermal factor is not used in this model and is made to be unity such that there is no further dependence on concentrations.

- The conductivity in the electrolyte $\sigma_l^{\text{SM}}(c_l)$ chooses temperature dependent terms to have coefficients of zero for consistency with (3.1.61). See Appendix A for the particular nonzero constants used.
- props_am.py for (CHR) option LiFePO4 and (CHR2) option LiC6.
 - The reference chemical potential μ_{Θ} for each of the two options needs to be set to that from Appendix A.

5.2 Numerical Approaches to Optimization

The simplest approach to optimizing a multivariable function is by breaking the problem into two parts such that linear programming (LP) can be used. For some initial set of unknown parameters \mathbf{m}_0 , first a suitable search direction is found. Using the line search strategy to minimize along that direction, a new point is found to then repeat the process on. Edgar *et al.* [7] describes how these two steps can be iterated until some convergence criteria for termination is met and the approximate optimal solution is obtained. Speed of convergence will depend on how sophisticated the methods are for choosing a search direction and finding the appropriate step size from the line search during each iteration. Alternatively, a nonlinear programming (NLP) method is better suited to solve an optimization problem where the objective function is nonlinear. As discussed in Edgar *et al.* [7], generating search directions sometimes involves evaluating partial derivatives either analytically or with usually less accuracy using finite difference methods. In the case here, the governing system is too complicated to obtain analytical derivatives.

There is also a family of optimization methods known as direct search that do not

require information about the gradient of the objective function with respect to the unknown parameters and rely on direct evaluations only. They have the advantage of being able to handle discontinuities or sharp changes in slope otherwise causing errant behavior in derivative calculations requiring some degree of smoothness. Similarly, direct search methods often naturally handle return values of NaN and Inf from the objective function that require special consideration in algorithms based on gradient information. The drawback of derivative-free searching is they often rely on trial and error approaches to finding an optimal solution that are in general more inefficient for certain well-behaved problems able to take advantage of gradients in determining search directions.

The number of iterations in an optimization depends on a solver's stopping criteria which are in general set tolerances that halt progression when some threshold is achieved. One such termination condition is a step tolerance that characterizes the change in magnitude of input parameters used in the objective function from the previous iterative step. This value is chosen depending on the desired precision of the parameters yielding an approximate optimal solution. Another common criterion is a function value tolerance which represents the lower bound on the change in value of the objective function during a step. Meeting this threshold is an indication the algorithm has achieved sufficient flatness in the objective function that it can be considered an extremal value. Certain implementations of optimization algorithms also make use of an optimality tolerance that depends on a first-order optimality measure of how close the solution is to optimal. Each unique optimization method may require any one or more stopping criteria be achieved before ending the iterations. Tolerances used as stopping criteria are specified as either absolute values or instead relative to the previous step values. Relative tolerances have the advantage of handling poorly scaled problems which can have unknown parameters with different orders of magnitude. Trying to use an absolute step tolerance would cause numerical difficulties in that contributions of larger magnitude variables would dominate smaller magnitude ones and lead to loss of information. Certain algorithms allow for specification of typical parameter values such that differing orders of magnitude can be accounted for. In general, it is safest to properly scale both the input parameters as well as output of the objective function so the algorithm only deals with values of order unity. Characteristic scales can be obtained for the physical parameters through dimensional analysis. Alternatively, scaling input parameters by the initial point \mathbf{m}_0 and corresponding objective function evaluation $\mathcal{J}_{\rho}(\mathbf{m}_0)$ guarantees that the optimization algorithm begins with well scaled variables provided they do not end up changing drastically as the routine proceeds.

In solving the optimization problems in Chapter 4, central to choosing an appropriate algorithm is a distinction made between a constrained or unconstrained problem. For each of the unknown parameters **m**, thermodynamic arguments made previously require simple inequality constraints of being nonnegative. In MATLAB, the routine fmincon is a constrained nonlinear multivariable optimization algorithm that can handle inequality constraints on unknown parameters. Depending on the problem being solved, the particular constrained algorithm used may be one of: interior-point, trust-region-reflective, sqp, or active-set.

The positivity of the thermodynamic properties can instead be addressed by expressing such parameters in terms of squares of auxiliary real variables. Within the objective function, each application of input parameter is subsequently squared such that any attempts by the optimization algorithm to make them negative are reflected about zero. Unconstrained multivariable solvers can be used with this approach such as MATLAB's fminsearch as a derivative-free, direct search Nelder-Mead simplex method applied to find the minimum of the objective function (4.3.1).

5.2.1 Nelder-Mead Simplex Method

The Nelder-Mead technique, also known as the downhill simplex method, is based on function comparison rather than gradient evaluations and is commonly used on nonlinear problems where derivatives are unknown. Geometrically, a simplex for any number of dimensions is a generalization of a triangle or tetrahedron. A p-simplex is made up of p+1 vertices with edges connecting each such that a 0-simplex is a point, a 1-simplex is a line, a 2-simplex is a triangle, a 3-simplex is a tetrahedron, and so forth. The authors Nelder and Mead [16] found that evaluating an objective function output at a set of points in the input parameter space could allow for optimization by adapting the corresponding simplex to the local landscape of the objective function. Continually updating the simplex with particular new vertices to replace the old ones in search of a minimum allows for the polytope to elongate down slopes, follow the direction of angled valleys, and contract in the neighborhood of the solution.

It should be noted however that the downhill simplex method is a heuristic search method with the potential to converge to non-stationary solutions. As such, it can be useful to perform one or more restarts that use the returned solution of a completed optimization as the initial value for another attempt. If subsequent optimizations also return the same result, it may be regarded as a local minimum. Additionally, this method is not a global optimizer and benefits from sampling initial points from various regions of the parameter-space that may be otherwise inaccessible in hopes of finding a global solution.

While there are a number of modern improvements to the Nelder-Mead algorithm, the particular variation used in fminsearch is as described in Lagarias *et al.* [13]. To begin, an initial simplex must be formed with p + 1 points where p is the number of unknown parameters. A specified initial point $\mathbf{m}_0 \in \mathbb{R}^p$ is used as one of the vertices in the initial simplex. The remaining p points of the simplex are each found by adding 5% to one of the p unknown parameters in the initial guess. Note that by optimizing with respect to the square-root of the original parameters, the initial simplex becomes 10.25% in each direction. More sophisticated choices may be more appropriate given an initial simplex too small causes the algorithm to perform a local search such that a non-optimal solution is returned. An initial simplex too large could have difficulties finding the most optimal result given the method works best when the objective function is unimodal and varies smoothly. This aspect however is not something that can be modified in fminsearch natively and again emphasizes the importance of trying a variety of initial guesses.

A single, generic iteration will typically replace the worst point in the simplex with a new, better vertex from an objective function standpoint. In the event a shrink is performed however, only the vertex with the lowest error is kept while p new points replace the remaining ones in the simplex. Lagarias *et al.* [13] describes how a complete Nelder-Mead method is defined by four scaler coefficients that modify the particular operation being performed at each iteration. The standard choice is that the coefficient of *reflection* be 1, *expansion* be 2, *contraction* be 1/2, and *shrinkage* also be 1/2. These operations shown in Figure 5.1 are in order of attempt to locate a point with a value of error functional smaller than any of those in the current simplex:

- Reflect the worst point \mathbf{m}_{p+1} about the centroid $\bar{\mathbf{m}}$ in the hyperspace of the other points to get reflection point \mathbf{m}_r .
- Expand in the direction beyond \mathbf{m}_r by calculating the expansion point \mathbf{m}_e .
- Contract outside the current simplex by doing a contraction between centroid $\bar{\mathbf{m}}$ and reflection \mathbf{m}_r .
- Contract inside by doing a contraction between centroid m
 m and worst point
 *m*_{p+1}.
- Shrink as a last resort by keeping only the best point \mathbf{m}_1 and halving the distance between all of the others.

Algorithm 1 describes the full fminsearch optimization routine as implemented by MATLAB.

The stopping criteria in fminsearch differs from other methods in that it depends on both an absolute step tolerance and an absolute function tolerance instead of just one. This condition is found to be too strong in some cases, preventing termination when the simplex becomes too small with a wide distribution of objective function values. Also problematic is the opposite case when objective function values in a large simplex are too similar. This can be addressed by manually tracking the simplex using MATLAB's output function, called after successful completion of an iteration. Custom stopping criteria may then be specified to require only one tolerance be met, though analysis of results should take into consideration the implications of which threshold was met. It is also notable that unlike other methods, tolerances are calculated based on the distribution of points in the simplex rather than from some difference between iterations. Given they are not relative, good scaling is important to achieve termination before reaching the set number of maximum iterations. The optimal solution is then the best point in the simplex after the final iteration.



Figure 5.1: All the operations from Lagarias *et al.* [13] illustrated using a two-dimensional simplex analogy including: original simplex (solid black), reflection (dotted black), expansion (solid red), contraction outside (solid blue), contraction inside (dashed blue), and shrinkage (dashed red).

Algorithm 1 Nedler-Mead simplex method as used in fminsearch

Input: Initial guess of unknown parameters \mathbf{m}_0 , objective function $\mathcal{J}_{\rho}(\mathbf{m})$, step tolerance T_m^* , and function value tolerance T_F^* **Output**: Optimal solution set m[1, :]

 \triangleright %comment: First step is to create initial simplex *m* around the starting point

 \mathbf{m}_0 with p parameters and evaluate the objective function at each%

$$m[1,:] \leftarrow \mathbf{m}_0$$

$$F[1] \leftarrow \mathcal{J}_{\rho}(m[1,:])$$
for $j = 2$ to $p + 1$ **do**

$$m[j,:] \leftarrow \mathbf{m}_0$$

$$m[j,j-1] \leftarrow 1.05 \times m[j,j-1]$$

$$F[j] \leftarrow \mathcal{J}_{\rho}(m[j,:])$$

end for

repeat

- ▷ %comment: Order the p + 1 vertices to satisfy $F[1] \le F[2] \le \cdots \le F[p+1]\%$ $[F, I] \leftarrow \text{sort}(F)$ $m \leftarrow m[I, :]$
- \triangleright %comment: **Reflect** the worst point about the centroid of the better points%

 $\bar{m} \leftarrow \sum_{j=1}^{p} m[j,:]/p$ $m_r \leftarrow 2 \times \bar{m} - m[p+1,:]$ $F_r \leftarrow \mathcal{J}_{\rho}(m_r)$ $\text{if } F[1] \le F_r < F[p] \text{ then}$ $m[p+1,:] \leftarrow m_r$

else if $F_r < F[1]$ then

 $\succ \ \% \text{comment: Expand by calculating the expansion point\%}$ $m_e \leftarrow 2 \times m_r - \bar{m}$ $F_e \leftarrow \mathcal{J}_{\rho}(m_e)$ if $F_e < F_r$ then $m[p+1,:] \leftarrow m_e$

else

$$m[p+1,:] \leftarrow m_r$$

end if

 \mathbf{else}

flag
 $\leftarrow 0$
 $\label{eq:flag} \mathbf{f}[p] \leq F_r < F[p+1] \ \mathbf{then}$

 \triangleright %comment: Contract outside between \bar{m} and m_r %

$$m_c \leftarrow (\bar{m} + m_r)/2$$

 $F_c \leftarrow \mathcal{J}_{\rho}(m_c)$
if $F_c < F_r$ then

 $m[p+1,:] \leftarrow m_c$

else

```
flag \leftarrow 1
```

end if

 \mathbf{else}

 $\triangleright~\% \text{comment:}~\mathbf{Contract~inside}$ between \bar{m} and m[p+1]%

 $m_{cc} \leftarrow (\bar{m} + m[p+1])/2$ $F_{cc} \leftarrow \mathcal{J}_{\rho}(m_{cc})$ if $F_{cc} < F[p+1]$ then $m[p+1,:] \leftarrow m_{cc}$ else flag $\leftarrow 1$ end if

end if

if flag = 1 then

 \triangleright %comment: Shrink by keeping the best point and moving the others closer%

for j = 2 to p + 1 do $m[j,:] \leftarrow (m[1,:] + m[j,:])/2$ $F[j] \leftarrow \mathcal{J}_{\rho}(m[j,:])$

end for

end if

end if

for j = 1 to p do

$$T_m[j] \leftarrow |\max(m[:,j]) - \min(m[:,j])|$$

end for

$$T_m \leftarrow \max(T_m)$$

 $T_F \leftarrow |\max(F) - \min(F)|$

 $\triangleright \ \ \% \text{comment: Terminate with step tolerance } T_m^* \text{ and error tolerance } T_F^*\%$ until $T_m < T_m^*$ and $T_F < T_F^*$

Chapter 6

Results & Discussion

In this chapter, analysis is conducted on inverse modeling results from using both the classical approach based on a single-objective optimization and an extended multi-objective optimization approach discussed in Chapter 4. Evaluating the error functionals (4.1.1) and (4.2.1) requires solving the system of PDE's summarized in Section 3.3 with computational methods discussed in Chapter 5. Comparisons are made between the (CHR) model and the (CHR2) model to determine the relative benefit of extending the Cahn-Hilliard formulation to the periodic bilayer model. The optimization algorithm is shown to work as desired through the validation performed in Appendix B.

When fitting model data, it is important to only take seriously the differences in quality of fit which are discernible, given limitations from the error present in experimental data. The original work of Krachkovskiy *et al.* [11] estimates the error in total intercalated lithium to be about 3% such that any improvement achieved between the two models in the concentration fitting must be substantially higher to

be conclusive. An additional consequence of measurement error is obtaining "effective" reconstructed optimal parameters that possess a certain degree of uncertainty. Analysis in this regard is left for future work where a full accounting of the statistical implications of this study can be addressed.

6.1 Single-objective Optimization

Optimization of only one of the two error functionals corresponds to the extremal cases in the weighted average (4.3.1) where $\rho = 0$ gives the concentration error (4.1.1) and $\rho = 1$ gives the cell voltage error (4.2.1). The focus of this section will be on examining the optimal solution after fitting concentration profiles only. The values of error functionals obtained after optimization are presented in Table 6.1 with corresponding reconstructed unknown parameters in Table 6.2. An improvement in concentration profile fit of 19.71% is found when extending the Cahn-Hilliard formulation (CHR) to the periodic bilayer model (CHR2). Note again the fitting is not being performed on voltage measurements here so analysis in that regard is left for the next section. Multiple restarts were done to eliminate the possibility of terminating at a non-stationary value rather than a local minimum. In both models, termination occurred upon satis fying a function value tolerance of 1×10^{-3} while a step tolerance of 1×10^{-2} was unmet (noting that optimization is done with respect to square-rooted parameters and scaled by the initial starting point). This indicates the landscape of the error functional is flat near the local minimum which typically occurs for ill-posed inverse problems where a distribution of parameter combinations produce similar concentration profiles.

| | (CHR) | (CHR2) | Δ |
|----------------------|-----------------------|-----------------------|---------|
| \mathcal{J}_{c_s} | 1.664×10^{-4} | 1.336×10^{-4} | 19.71% |
| \mathcal{J}_{Φ} | 2.136×10^{-3} | 2.120×10^{-3} | 0.7491% |

Table 6.1: Error functional values for the two models that result from solving the optimization problem (4.3.2) with $\rho = 0$ for fitting only concentration profiles.

| $k_{0,\text{foil}}$ | k_0 | $\gamma_{\rm side}$ | σ_s | D_0 | Ω_a | Ω_b | Ω_c |
|---------------------|-------|---------------------|------------|-------------------------|-------------------------|------------------------|-------------------------|
| 10.59 | 4.690 | 6.990 | 1.045 | 2.001×10^{-14} | 1.052×10^{-20} | _ | _ |
| 8.993 | 4.216 | 5.679 | 2.212 | 1.497×10^{-14} | 1.020×10^{-20} | 2.022×10^{-22} | 4.242×10^{-24} |

Table 6.2: (CHR) model (top) and (CHR2) model (bottom) optimal reconstructions of parameters based on single-objective optimization (4.3.2) with $\rho = 0$.

The optimal regular solution parameter Ω_a is almost the same in both models where they are larger than the threshold $2k_BT$ at which phase separation becomes energenically favorable. Smith *et al.* [23] mentions that the concentration profiles are relatively insensitive to gradient penalty κ which would otherwise seem like good candidate for reconstruction. This was found to be especially true for the (CHR) model which gives the same objective function result over varying magnitudes of gradient penalty, provided the corresponding characteristic interface widths from (3.2.42) both represent a small fraction of the particle radii $\lambda \ll a$. Recall the size of spatial discretization is set to be half of the characteristic interface width in order to resolve phase boundaries. Hence, there is a significant impact on computational cost where too small κ can take a prohibitively large amount of effort to simulate. When the optimization algorithm attempts such a configuration, MPET may fail to initialize or otherwise stall indefinitely. These cases and certain combinations of other parameter values can produce a return value of Inf from the error functional and underscores the importance of selecting an optimization routine that can handle such discontinuities. Here, κ is held at a constant value big enough to give reasonably quick simulation times and chosen to be that which produces optimal concentration profile results in the (CHR2) model.

Characteristic scalings as they relate to the electrode particles are displayed in Table 6.3 and are discussed in Smith *et al.* [23] to provide insight on how the reconstructed parameters influence the system's behavior. A characteristic time scale for reactions can be expressed as,

$$\tau_R = \frac{ec_{l,ref}a}{k_0},\tag{6.1.1}$$

and for diffusivity in the graphite particles,

$$\tau_D = \frac{a^2}{D_0}.$$
 (6.1.2)

The Damköhler number is then taken as the ratio,

$$D_a = \frac{\tau_D}{\tau_R},\tag{6.1.3}$$

as discussed in Bazant [2] to capture which the limiting factor is in the balance between lithium entering through reactions and being carried away from the surface by diffusion. The longer time scales for the (CHR2) model corresponds to the reconstructed parameters in Table 6.2 where the Butler-Volmer exchange rate constant k_0 and diffusion coefficient D_0 are both larger in magnitude for (CHR1).

| | (CHR) | (CHR2) |
|----------------------------------|---------------------------------|---------------------------------|
| Interface width, λ | $2.726\times 10^{-8}\mathrm{m}$ | $2.768\times 10^{-8}\mathrm{m}$ |
| Reaction time, τ_R | $1.208\mathrm{h}$ | $1.344\mathrm{h}$ |
| Species transport time, τ_D | $1.152\mathrm{h}$ | $1.540\mathrm{h}$ |
| Damköhler number, D_a | 0.954 | 1.146 |

Table 6.3: Characteristic scalings for the two models based on parameters obtained from Table 6.2.

The concentration profiles predicted by the two different models to best match experimental data are shown in Figure 6.1. The improvement in fit can be noticed in comparing the fifth time slice $\hat{c}_s(x, t_5)$ and later. The (CHR2) model is found to allow the first spatial position to accelerate its filling rate and increase the gap between the subsequent particles in the battery. Compare this to the (CHR) model where a smoother transition across the battery does not capture the jump between the first and second position quite as well. It is possible there exists a better choice of an initial guess or set of unknown parameters that would further allow the (CHR2) model to capture the jump seen in the second battery position occurring for $\hat{c}_s(x, t_8)$ and later.

Recall that the error functional (4.1.1) and the concentration profiles use the average in each particle $\bar{c}_s(x, t_k)$ from (3.2.26). The electrode volumes placed at each battery position contain a single graphite particle to be simulated with no others in parallel with regards to electrolyte access. Since the experimental data is discretized into six partitions along the length of electrode, the number of volumes chosen to be simulated across the battery cell is twelve such that the model has double the spatial

resolution with reasonable computational cost. Hence, two particles are averaged together for each experimental data segment along the battery length.

Within each simulated spherically symmetric particle, concentrations $c_s(x,r;t)$ for (CHR) and $c_1(x,r;t) + c_2(x,r;t)$ for (CHR2) depend on the radial position. This pseudo two-dimensional domain (x,r) is presented for the two models in Figure 6.2 where distinct phase separation between high and low concentrations is clearly evident. Again examining volumes closest to the separator, there is a noticeable difference between the models. The improvement in fit for the (CHR2) model is attributable to a different phase-separating behavior in the first few particles that does not occur in the (CHR) model. The emergence of a half-full stage 2 is discernible in the heatmap at later times in the (CHR2) model as an annulus with intermediate concentration between the dilute core and the high concentration shell. Time snapshots for only the first particle closest to the separator where this effect is strongest are overlaid in Figure 6.3. There, it is clearly evident the effect of the periodic bilayer model as phase separation shows the three stable phases of both layers being nearly empty, one layer being full with the other dilute, and finally both layers being nearly full approaching the particle surface at later times.

The concentration profiles can be integrated over the length of the battery and normalized to produce the totaled quantities displayed in Figure 6.4. This corresponds to the total amount of lithium intercalated into the graphite electrode particle which is then normalized by the total lattice site capacity $c_{s,\max}$ to become a filling fraction comparable to the state of charge predicted by the C-rate. Both (CHR) and (CHR2) are nearly identical here and closely match the behavior of the experimental data. The growth of the SEI layer is seen to occur instantaneously at some critical time and proceeds at a constant rate for the remaining duration. The shape of these curves are influenced by γ which plays a significant role in the fraction ω from (3.1.74) in determining the amount of lithium diverted from the graphite and into the SEI layer. The sum of this and the lithium entering the graphite gives a linear relation with time, characteristic of a galvanostatic experiment with a constant current and C-rate of C/44. It is notable that at early times in the experiment, the amount of intercalated lithium is lesser than the idealized charge rate. This is not attributable to lithium being in the SEI layer as the physical picture of the phenomenon is that deposition begins at some critical moment and monotonically increases thereafter. The early discrepancy could however be because the NMR imaging used to collect the experimental data is not measuring the lithium in the dilute higher stages.

Though voltage is not being fitted here, the comparison of model results to experimental results are still shown in Figure 6.5. In both models, a distinct drop in cell voltage is seen at about a 1/4 state of charge corresponding to the point at which the SEI layer begins to grow. This is also the time at which particles across the length of the battery simultaneously undergo phase separation into a high concentration outer shell and a low concentration inner core. Given the concentration on the surfaces suddenly jump from a small to a large quantity, equations referencing these values like the OCV from (3.1.71) and the SEI layer fraction from (3.1.74) respond accordingly.

Smith *et al.* [23] discusses how an ensemble of particles at each battery position with a distribution of radii will phase-separate at different times and act to smooth out the instantaneous jump seen in the macroscopic quantity of cell voltage. Due to the computational cost of simulating a number of particles at each cell volume however, the model here simulates only one particle per volume with a set radius. Note however the voltage drop from the (CHR2) model is slightly less than that of the (CHR) model and produces marginally better fit voltages as a result.

Another output from the model that gives insight into the system's dynamics is the volumetric sink/source term of ions (3.1.88). On clear display in Figure 6.6 is the galvanostatic constraint from (3.1.86) that necessitates the reaction rate integrated over the length of the battery be equal to a constant total cell current density. This is evident when the first few particles spike in the amount of lithium they accept while the remaining particles have reaction rates that languish as a result. Both models are similar in this regard with only slight variation between the two plots. The solid electric potentials are also displayed in Figure 6.7.

Finally, the electrolyte concentration and electric potential are shown respectively in Figures 6.8 and 6.9 to gain an understanding of the macroscopic dynamics in the model. At any given time, electrolyte concentration monotonically decreases across the length of the battery. This is consistent with the counter electrode supplying Liions at x = 0 to replace those removed by the particles along $x \in \mathcal{L}_c$. The steepness of the declining slopes corresponds to the magnitude of the volumetric sink/source term at that position and time, balanced with the influx of lithium diffusing across the cell. A characteristic time for electrolyte diffusion can also be found as,

$$t_{\rm ref} = \frac{L_c^2}{\mathcal{D}(c_{l,\rm ref})} = 309.45 \,\mathrm{s.}$$
 (6.1.4)

Given the timescale here is much faster than those in Table 6.3 and the overall length of experiment, the electrolyte profiles equilibrate rapidly away from the homogeneous initial state at the reference concentration.

Since experimental data did not measure the quantity of lithium in the electrolyte,

the properties pertaining to the macroscopic transport processes are inherited from Morales Escalante *et al.* [15] and not subject to optimization. Note that for brevity, only the (CHR) model is plotted for these quantities since they are indistinguishable from those produced by the (CHR2) model. The electric potential in the electrolyte takes on an identical shape as its concentration at each time. The electrolyte potential at the counter electrode is used as a reference to compare relative potential drops across the cell at different times. These reference values notably produce shape of the cell voltage through (3.1.81). Animations of the following figures can be viewed for the (CHR) model at https://youtu.be/HOISrjiad6s and for the (CHR2) model at https://youtu.be/neFwizATsDU.



Figure 6.1: Green bars are normalized experimentally obtained concentration profiles $\hat{c}_s(x, t_k)$ versus the spatial coordinate x at time levels $t_k = 2.5, 5, \ldots, 25$ h. Blue circles are $\bar{c}_s(x, t_k)$ for (CHR) model (top) and (CHR2) model (bottom) with parameters obtained from Table 6.2. Red stars are the residuals.



Figure 6.2: Heat map of filling fraction $\tilde{c}_s(x,r;t_k)$ from the (CHR) model (top) and $(\tilde{c}_1(x,r;t_k) + \tilde{c}_2(x,r;t_k))/2$ from the (CHR2) model (bottom) as a function of solid electrode length x and radial position r over a series of time slices for k = 1...10. Parameters used are from Table 6.2.



Figure 6.3: Normalized concentration profile $\tilde{c}_s(2.125 \times 10^{-4}, r; t_k)$ for (CHR) model (top) and $\tilde{c}_i(2.125 \times 10^{-4}, r; t_k)$, i = 1, 2 (solid/dotted) for (CHR2) model (bottom) as a function of radial position r colored based on times t_k , $k = 1 \dots 10$ within the first electrode particle, closest to the separator. Parameters used are from Table 6.2.



Figure 6.4: The red line is normalized experimentally obtained total lithium $\Delta x \sum \hat{c}_s(x, t_k)$. The blue line is normalized total $\Delta x \sum \bar{c}_s(x, t_k)$ and black line is normalized total $\Delta x \sum \tilde{c}_{side}(x, t_k)$ in SEI layer for (CHR) model (top) and (CHR2) model (bottom) using parameters from Table 6.2. Green is sum of blue and black.



Figure 6.5: Cell voltage ϕ_{cell} versus state of charge. The solid red line is the C/44 experimentally obtained profile and blue line with circles is from the (CHR) model (top) and (CHR2) model (bottom) with parameters used from Table 6.2.



Figure 6.6: Reaction rate from (3.1.88) at the surface of solid electrode particles as a function of battery position x with color based on times t_k , k = 1...10. Displayed here is the (CHR) model (top) and (CHR2) model (bottom) with parameters obtained from Table 6.2.



Figure 6.7: Solid electrode particle potential $\phi_s(x, t_k)$ as a function of battery position x with color based on times t_k , k = 1...10. Displayed here is the (CHR) model (top) and (CHR2) model (bottom) with parameters obtained from Table 6.2.



Figure 6.8: Normalized concentration in the electrolyte $\tilde{c}_l(x, t_k)$ with contours colored based on their times t_k , k = 1...10 for the (CHR) model results with parameters obtained from Table 6.2.



Figure 6.9: Electrical potential in the electrolyte $\phi_l(x, t_k) - \phi_l(0, t_k)$ with contours colored based on their times t_k , k = 1...10. Each individual curve uses a reference potential as that measured at the counter electrode for the (CHR) model results with parameters obtained from Table 6.2.

6.2 Multi-objective Optimization

The goal of solving the multi-objective optimization problem (4.3.1) is to find a set of reconstructed unknown parameters that produce simultaneously good fits for both concentration profiles and cell voltage. A "Pareto front" is obtained by solving the family of optimization problems in a sweep over various weights between error functionals for the two datasets. This Pareto front allows for the user to then decide on an appropriate trade-off between fitting concentration or voltage to obtain the reconstructed parameters corresponding to that particular value of ρ . Since the magnitudes of each individual error functional can differ wildly, the ideal range of ρ values is not inherently known. Finer resolution sweeps are required when large jumps are observed in initial findings, though this is not found to be necessary here.

Since the optimization algorithm used is a local minimizer, the initial guess of parameters for each weight is very important in determining the optimal result. Hence, a continuation approach is warranted where each successive value of ρ in the sweep uses the optimal result of the previous weight as an initial guess. With greater emphasis placed on concentration fitting in this work, the optimal reconstructed parameters from the single-objective optimization in Table 6.2 are used as the initial point for a sweep beginning at $\rho = 0$. Stepping by increments of 0.1, the optimization problem (4.3.1) is solved at each weight to produce the culminating results of this work displayed in Figure 6.10.

Since the goal is to reduce both error functionals, the better results will appear near the bottom-left of the plot. Both Pareto fronts for the two models feature a cluster a tight-knit data points that indicate both models can simultaneously fit both sets of measurements rather well. In particular, variation is on a scale two orders of magnitude smaller for voltage error functional values and the discrepancy seen in Figure 6.5 is not reduced without further suppressing phase separation by decreasing Ω_a . Finally, the reconstructed unknown parameters that were obtained through solving an optimization problem at each ρ are shown in Figure 6.11 for those common to both models. Those unique to the (CHR2) model only are displayed in Figure 6.12. Refer to Tables 6.4 and 6.5 for the error functionals and optimal reconstructed parameters corresponding to a weight $\rho = 0.4$ found to achieve simultaneously good agreement with both datasets.



Figure 6.10: Pareto fronts for the (CHR) model in black and the (CHR2) model in blue from multi-objective optimization over a sweep of weights. On the vertical axis is the error functional for the concentration profiles while the horizontal axis is the error functional for the cell voltage profiles. Points are colored based on their value of ρ . Note if a point is not visible it is behind a later value of ρ that did not improve upon the error functional $\mathcal{J}_{\rho}(\mathbf{m}_0)$.



Figure 6.11: Optimal reconstructed parameters obtained by solving the optimization problem (4.3.1) over the range of ρ values corresponding to the Pareto front results in Figure 6.10. The (CHR) model is black and the (CHR2) model is blue.


Figure 6.12: Optimal reconstructed parameters unique to the (CHR2) model obtained by solving the optimization problem (4.3.1) over the range of ρ values corresponding to the Pareto front results in Figure 6.10.

| | (CHR) | (CHR2) | Δ |
|----------------------|-----------------------|-----------------------|----------|
| \mathcal{J}_{c_s} | 1.664×10^{-4} | 1.347×10^{-4} | 19.05% |
| \mathcal{J}_{Φ} | 2.136×10^{-3} | 2.099×10^{-3} | 1.732% |

Table 6.4: Error functional values for the two models that result from solving the optimization problem (4.3.2) with $\rho = 0.4$ where concentration profiles and voltage profiles are simultaneously small.

| $k_{0,\mathrm{foil}}$ | k_0 | $\gamma_{ m side}$ | σ_s | D_0 | Ω_a | Ω_b | Ω_c |
|-----------------------|-------|--------------------|------------|-----------------------|-------------------------|-----------------------|-------------------------|
| 11.68 | 4.690 | 6.990 | 1.045 | 2.001×10^{-14} | 1.052×10^{-20} | _ | _ |
| 9.122 | 4.276 | 5.803 | 2.244 | 1.518×10^{-14} | 1.027×10^{-20} | 2.045×10^{-22} | 4.303×10^{-24} |

Table 6.5: (CHR) model (top) and (CHR2) model (bottom) optimal reconstructions of parameters based on multi-objective optimization (4.3.2) with $\rho = 0.4$.

Chapter 7

Conclusions & Outlook

In this study, models for lithium transport in the solid electrode graphite particles were considered based on the original Cahn-Hilliard model and extended periodic bilayer model to solve the inverse problem by inferring material properties from experimental data. In particular, error functionals quantifying the difference between simulated model data and laboratory measurements of concentration and voltage profiles allowed for the determination of which Gibbs free energy formulation could more accurately capture certain physical phenomena. The hypothesis of this work was proven to be correct in that the more complex periodic bilayer model (CHR2) is found to outperform the original Cahn-Hilliard model (CHR) by both metrics. Accordingly, the optimal set of unknown parameters obtained by the periodic bilayer model corresponding to intermediate values of ρ may be considered more accurate reconstructions of actual, physical material properties.

It is worth noting that the majority of improvement over the original model was obtained through capturing specific features in the concentration profile fitting while the change to the voltage error functional was only marginal. Using the standard diffusion equation may rectify discrepancy in voltages but at too much of a penalty to the concentration fitting. Furthermore, the increased computational cost of simulating the more complex (CHR2) model was manageable and did not represent a significant barrier to obtaining results. Accordingly, the (CHR2) model is more advantageous to use as it represents a better description of the true physics of cross-plane lithium interaction and stability of additional stable phases. These results were not directly compared to the findings of Morales Escalante *et al.* [15] due to differences in the treatment of counter electrode leading to mismatching electrolyte concentration profiles and overall cell voltage.

Overall, MPET was found to be a very powerful tool that had most of the mathematics and physics needed here accounted for already. The most challenging aspect was addressing the multitude of configurable options for the software to be consistent with the experimental setup and previous work by Morales Escalante *et al.* [15]. By requiring close scrutiny for each aspect of the full multi-scale model, a greater understanding of battery operation as a whole was gained than if electrode dynamics alone were considered. The results shown here, while collected over a period of a few short days, represent the culmination of a long and hard-fought process of iterative discovery. Thousands of hours were sunk into simulating precursor setups that lacked one feature or another of the present study while gradually understanding and exploring each component of the complicated multi-scale model.

While the main research question of this work was answered, the successful reproduction of experimental results using MPET opens a number of potential future avenues of research in the area of predicting material properties by modeling the transport processes in a Li-ion battery:

- Expand the list of parameters to be reconstructed during inverse modeling to include any more of those that are unknown and may impact results.
- Infer state-dependent material properties such as is done in Morales Escalante et al. [15] as functions of concentration instead of being made constant.
- Conduct sensitivity analysis on the input parameters to determine which are more likely to influence the fitting to experimental data.
- Perform inverse modeling on other experimental datasets using the techniques developed here.
- Redo this work's results for other electrolyte models (e.g., Nernst-Planck) and other reaction types (e.g., Marcus).
- Incorporate neglected aspects of the model like electrical resistances, surface wetting, and stress.
- Extend the mathematical theory for the Cahn-Hilliard model to feature three or more periodic layers.
- Formulate a physics-based model to replace the ad-hoc, contrived accounting of the side reaction rate and SEI layer formation.
- Use other particle shapes than a sphere such as an ellipsoid or cylinder.
- Simulate many graphite particles in parallel with regard to electrolyte access at each volume with a distribution of radii as shown in Figure 7.1 at a significantly increased computational cost.

- Increase the number of volumes and hence discretization along the length of the battery x at an increased computational cost.
- Recreate the optimization algorithm and data handling wrapper in Python instead of MATLAB for more seamless integration with original MPET code.
- Switch to a global optimizer or test an array of initial guesses for further improvement of profile fitting.
- Perform the validation by perturbing the parameters that produce the manufactured dataset a sufficient number of different ways to assess the optimizer's ability to approach a solution from any direction.



Figure 7.1: Battery schematic of multiple particles per volume.

Appendix A

Parameter Values

| Parameter | Units | Value | | | | | | | |
|-------------------------------------|----------|--------------------|--|--|--|--|--|--|--|
| MPET configuration file | | | | | | | | | |
| Profile type | _ | CC | | | | | | | |
| Charge rate, C_r | h^{-1} | 1/44 | | | | | | | |
| Fraction of full charge to simulate | _ | 26/44 | | | | | | | |
| Current ramp time | S | 1×10^{-3} | | | | | | | |
| Number of discretization in time | _ | 52 | | | | | | | |
| Relative tolerance | _ | 1×10^{-6} | | | | | | | |
| Absolute tolerance | _ | 1×10^{-6} | | | | | | | |
| Temperature, T | Κ | 298 | | | | | | | |
| Random seed | _ | true | | | | | | | |
| Random seed value | _ | 652761 | | | | | | | |

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| 0 I | 1 0 | |
|---|---------------------|---------------|
| Parameter | Units | Value |
| Series resistance, $R_{\rm ser}$ | Ω | 0 |
| Number of electrode volumes | _ | 12 |
| Number of separator volumes | _ | 8 |
| Particles per electrode volume | _ | 1 |
| Li foil exchange rate constant, $k_{0,\text{foil}}$ | ${\rm Am^{-2}}$ | See Table 6.2 |
| Li foil film resistance, $R_{\rm foil}$ | Ω | 0 |
| Particle radius, a | μm | 9.11 |
| Standard deviation of radii | — | 0 |
| Initial electrode filling fraction, $\tilde{c}_{s,0}$ | — | 0.001 |
| Simulate bulk electrode conductivity | _ | true |
| Conductivity, σ_s | ${ m S}{ m m}^{-1}$ | See Table 6.2 |
| Simulate particle conductivity losses | _ | false |
| Electrode length, L_c | μm | 300 |
| Separator length, L_s | μm | 200 |
| Active material loading percent, P_L | _ | 1 |
| Electrolyte liquid volume fraction, ϵ_l | _ | 0.1624 |
| Separator liquid volume fraction, $\epsilon_{l,s}$ | _ | 0.55 |
| Bruggeman exponent | _ | -1/2 |
| Initial electrolyte concentration, $c_{l,\text{ref}}$ | $ m molm^{-3}$ | 1000 |
| Cation/anion charge number, z_{\pm} | _ | ± 1 |

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| | 1 0 | |
|--|-------------------------------|--|
| Parameter | Units | Value |
| Cation/anion dissociation number, ν_\pm | _ | 1 |
| Electrolyte model | — | SM |
| Stefan-Maxwell property set | _ | valoen_reimers |
| Number of electrons in reaction, n | _ | 1 |
| Cation stoichiometric coefficient, s_+ | _ | -1 |
| Type of solid particles | _ | CHR or CHR2 |
| Discretization of solid | m | $\frac{1}{2}\sqrt{\frac{\kappa}{2\Omega_a}}$ |
| Particle shape | _ | sphere |
| Chemical potential of reduced state | _ | LiFePO4 or LiC6 |
| Log pad | _ | false |
| Noise | _ | false |
| Regular solution parameter, Ω_a | J | See Table 6.2 |
| Secondary interaction terms, $\Omega_{b,c}$ | J | See Table 6.2 |
| Gradient penalty, κ | ${ m J}{ m m}^{-1}$ | 1.092939×10^{-7} |
| Stress coefficient | Pa | 0 |
| Van der Waals-like interaction energy | - | 0 |
| Total Li site density within solid, ρ_s | m^{-3} | 1.397345×10^{28} |
| Dimensional diffusivity prefactor, D_0 | $\mathrm{m}^2\mathrm{s}^{-1}$ | See Table 6.2 |
| Diffusivity function | _ | lattice |

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| v 1 | 1 0 | | | | | | | |
|--|-------------------------------|---------------------------|--|--|--|--|--|--|
| Parameter | Units | Value | | | | | | |
| Surface wetting | Jm | 0 | | | | | | |
| Reaction type | _ | BV_mod01 | | | | | | |
| Exchange rate constant, k_0 | ${\rm Am^{-2}}$ | See Table 6.2 | | | | | | |
| Charge transfer coefficient | _ | 1/2 | | | | | | |
| Film resistance | _ | 0 | | | | | | |
| Other MPET properties | | | | | | | | |
| Side reaction fraction, γ | _ | See Table 6.2 | | | | | | |
| Reference chemical potential, μ_{θ} | _ | $0.08847 \frac{e}{k_B T}$ | | | | | | |
| Transference number, t^0_+ | _ | 0.33 | | | | | | |
| Electrolyte conductivity prefactor, σ_0 | ${ m S}{ m m}^{-1}$ | 0.0014492 | | | | | | |
| Electrolyte conductivity coefficient, a_0 | _ | -41.5292 | | | | | | |
| Electrolyte conductivity coefficient, a_1 | _ | -9.626 | | | | | | |
| Electrolyte conductivity coefficient, a_2 | _ | 1.518 | | | | | | |
| Electrolyte diffusivity prefactor, \mathcal{D}_0 | $\mathrm{m}^2\mathrm{s}^{-1}$ | 6.9864×10^{-10} | | | | | | |
| Electrolyte diffusivity coefficient b | _ | -0.87637 | | | | | | |
| Open-circuit voltage coefficients $b_{j,k}$ | _ | See Table C.1 | | | | | | |

Continued from previous page

Appendix B

Inverse Modeling Validation

The goal in this section is to determine the overall ability of the optimization algorithm to obtain an accurate reconstruction of unknown parameters. Recall in Chapter 4 that the least-squares difference between model data and experimental data is used in the error functional. Consider instead the experimental data replaced with a manufactured dataset also generated using the mathematical model, though now by a set of known parameters. By knowing ahead of time the exact optimal solution that produces an objective function value of zero, beginning the optimization routine at some other initial point will determine its ability to reconstruct that correct result.

Both the initial set of parameters and the set of parameters generating the target dataset must be chosen to appropriately reflect what a typical optimization using experimental data would look like. Hence, a good choice for the target data is the optimal result from a previously completed optimization, most resembling experimental data. To select an initial point, the target set of parameters can then be perturbed by normally distributed random numbers. A number of initial points should be tried to gain a complete understanding of the algorithm's ability to converge from all directions. A standard deviation for the perturbations is chosen such that the initial objective function evaluation is at least as large as the optimal result using experimental data.

Success can be measured by not only how similar an optimal solution is to the target set of parameters, but also by how close to zero the objective function can achieve. A large final cost error functional would indicate the optimization routine is stuck on a local minimum or non-stationary point and otherwise unable to reach the target parameter set. A small final cost error functional with an optimal solution that differs from the targeted parameters would demonstrate the problem is degenerate in that the same result is obtainable through various parameter sets. For some parameters accurately reconstructed and others not, insight is gained on which are sensitive or insensitive for producing change in the model data.

The results of validation are displayed for the (CHR) model in Table B.1 and for the (CHR2) model in Table B.2. Parameter values for the initial and final points are shown as being relative to those in Table 6.2 used to produce the manufactured datasets. The concentration error functional is seen in Figures B.1 and B.2 to be greatly reduced by several orders of magnitude over the optimization iterations. This result alone shows the validation is successful in achieving excellent agreement with the manufactured data. It is important to note however that while some parameters such as γ and Ω_a were able to be reconstructed almost perfectly by having a strong, well-defined effect on results, others like k_0 and σ_s did not recover the original target values. This is further evidence the objective function has many local minima that produce similar error functional values despite using largely varying parameters. Note also that $k_{0,\text{foil}}$ is known to affect only voltage profiles such that it would have no possibility of being recovered in fitting of the concentration profile. The resulting simplex for each optimization is given in Tables B.3 and B.4. Like most optimizations ran for this work, the termination criteria met was that for function value tolerance instead of for parameter step tolerance. This is consistent with the depiction of the objective function being considerably flat near the optimal solution.

| $\bar{\Delta}$ | k_0 | D_0 | $k_{0,\text{foil}}$ | Ω_a | $\gamma_{\rm side}$ | σ_s | \mathcal{J}_{c_s} | \mathcal{J}_{Φ} |
|----------------|-------|-------|---------------------|------------|---------------------|------------|----------------------------|------------------------|
| 11.5 | 0.870 | 0.852 | 1.104 | 1.012 | 0.742 | 1.037 | 3.718×10^{-4} | 5.619×10^{-5} |
| 9.3 | 1.092 | 0.894 | 0.794 | 0.995 | 0.976 | 1.122 | $ $ 8.556 $\times 10^{-7}$ | 2.755×10^{-6} |

Table B.1: Validation is done based on single-objective optimization (4.3.2) with $\rho = 0$ to a manufactured dataset from the (CHR) model with parameters from Table 6.2. This target set of parameters is used to scale those shown here where the initial point (top) is perturbed by some random amount. The final point (bottom) in the case of a perfect reconstruction would give all 1s with 0% average difference from target ($\overline{\Delta}$) and error functionals of 0.

| $\bar{\Delta}$ | k_0 | D_0 | $k_{0,\text{foil}}$ | Ω_a | Ω_b | Ω_c | $\gamma_{\rm side}$ | σ_s | \mathcal{J}_{c_s} | \mathcal{J}_{Φ} |
|----------------|-------|-------|---------------------|------------|------------|------------|---------------------|------------|-----------------------|------------------------|
| 11.5 | 1.174 | 1.099 | 1.036 | 1.137 | 0.925 | 0.782 | 1.066 | 1.114 | 9.225×10^{-4} | 3.671×10^{-4} |
| 6.1 | 1.085 | 1.027 | 1.107 | 0.998 | 0.852 | 0.958 | 0.995 | 1.075 | 1.368×10^{-6} | 9.123×10^{-7} |

Table B.2: Validation is done based on single-objective optimization (4.3.2) with $\rho = 0$ to a manufactured dataset from the (CHR2) model with parameters from Table 6.2. This target set of parameters is used to scale those shown here where the initial point (top) is perturbed by some random amount. The final point (bottom) in the case of a perfect reconstruction would give all 1s with 0% average difference from target ($\bar{\Delta}$) and error functionals of 0.



Figure B.1: Semi-log plot of the objective function evaluation of the best vertex in the simplex at each iteration of the optimization algorithm. Validation is performed against the manufactured dataset from the (CHR) model with parameters from Table 6.2.



Figure B.2: Semi-log plot of the objective function evaluation of the best vertex in the simplex at each iteration of the optimization algorithm. Validation is performed against the manufactured dataset from the (CHR2) model with parameters from Table 6.2.

| _ | k_0 | D_0 | $k_{0,\mathrm{foil}}$ | Ω_a | $\gamma_{ m side}$ | σ_s | $\mathcal{J}_{ ho}$ |
|----------------|-------|-------|-----------------------|------------|--------------------|------------|---------------------|
| \mathbf{m}_1 | 1.121 | 1.024 | 0.848 | 0.991 | 1.147 | 1.041 | 0.002 |
| \mathbf{m}_2 | 1.115 | 1.022 | 0.853 | 0.988 | 1.136 | 1.046 | 0.002 |
| \mathbf{m}_3 | 1.116 | 1.018 | 0.859 | 0.990 | 1.146 | 1.043 | 0.003 |
| \mathbf{m}_4 | 1.113 | 1.018 | 0.850 | 0.990 | 1.139 | 1.047 | 0.003 |
| \mathbf{m}_5 | 1.112 | 1.018 | 0.863 | 0.990 | 1.139 | 1.047 | 0.003 |
| \mathbf{m}_6 | 1.109 | 1.022 | 0.856 | 0.987 | 1.132 | 1.039 | 0.003 |
| \mathbf{m}_7 | 1.104 | 1.023 | 0.859 | 0.989 | 1.131 | 1.046 | 0.003 |
| | | | | | | | |

Maximum function value difference -0.8×10^{-3}

Maximum step difference 0.017

Table B.3: Final simplex for validation performed on the original (CHR) model to a manufactured dataset. Parameters here are scaled by the initial point and square-rooted while the error functional is scaled only by the initial value.

| _ | k_0 | D_0 | $k_{0,\text{foil}}$ | Ω_a | Ω_b | Ω_c | $\gamma_{\rm side}$ | σ_s | $\mathcal{J}_{ ho}$ |
|----------------|-------|-------|---------------------|------------|------------|------------|---------------------|------------|---------------------|
| \mathbf{m}_1 | 0.961 | 0.967 | 1.034 | 0.937 | 0.960 | 1.106 | 0.966 | 0.983 | 0.001 |
| \mathbf{m}_2 | 0.969 | 0.978 | 1.029 | 0.935 | 0.956 | 1.106 | 0.960 | 0.974 | 0.002 |
| \mathbf{m}_3 | 0.976 | 0.988 | 1.027 | 0.936 | 0.958 | 1.097 | 0.962 | 0.973 | 0.002 |
| \mathbf{m}_4 | 0.977 | 0.989 | 1.027 | 0.938 | 0.960 | 1.094 | 0.966 | 0.978 | 0.002 |
| \mathbf{m}_5 | 0.969 | 0.988 | 1.029 | 0.935 | 0.948 | 1.112 | 0.954 | 0.963 | 0.002 |
| \mathbf{m}_6 | 0.972 | 0.988 | 1.027 | 0.939 | 0.960 | 1.094 | 0.968 | 0.976 | 0.002 |
| \mathbf{m}_7 | 0.972 | 0.991 | 1.028 | 0.936 | 0.950 | 1.099 | 0.965 | 0.973 | 0.002 |
| \mathbf{m}_8 | 0.980 | 0.976 | 1.027 | 0.935 | 0.963 | 1.100 | 0.962 | 0.977 | 0.002 |
| \mathbf{m}_9 | 0.971 | 0.978 | 1.029 | 0.936 | 0.953 | 1.106 | 0.953 | 0.973 | 0.002 |
| | | | | | Maximun | n function | n value d | ifference | 0.001 |
| | | | | | | Maximu | m step d | ifference | 0.024 |

Table B.4: Final simplex for validation performed on the extended (CHR2) model to a manufactured dataset. Parameters here are scaled by the initial point and square-rooted while the error functional is scaled only by the initial value.

Appendix C

Open-Circuit Voltage Fitting

Cell voltage data $\hat{U}_{eq}(\tilde{c})$ that approximates the open-circuit voltage of the battery as a function of state of charge \tilde{c} is also available from an equivalent experiment using a slower C/100 charge rate. For use of this OCV in the Butler-Volmer surface overpotential, the analytical function $U_{eq}(\tilde{c})$ from (3.1.71) must be fit to the tabulated experimental data for compatibility with the MPET solver (see, Section 5). An optimal solution $\mathbf{b} = \{b_0, b_{1,1}, b_{1,2}, b_{j,k}\}, j = 2, 3, \dots, 8, k = 1, 2, 3$, is given in Table C.1 from using MATLAB's fit function with a sufficiently close initial guess. The agreement between the fitting and the dataset is shown in Figure C.1.

| | k = 1 | k = 2 | k = 3 |
|-----------|----------|----------|-----------|
| $b_{0,k}$ | 5.638 | _ | _ |
| $b_{1,k}$ | 1.09 | -13.23 | _ |
| $b_{2,k}$ | 0.003622 | -0.2905 | -0.0152 |
| $b_{3,k}$ | -2.022 | -1.376 | 0.1839 |
| $b_{4,k}$ | -12.12 | 0.007597 | 0.005092 |
| $b_{5,k}$ | -0.01253 | -0.5646 | 0.05742 |
| $b_{6,k}$ | -0.02946 | -0.1779 | -0.02292 |
| $b_{7,k}$ | -0.0368 | -0.02385 | -0.005836 |
| $b_{8,k}$ | -4.478 | 0.3037 | -0.002818 |

Table C.1: Coefficients for the open-circuit voltage function $U_{eq}(\tilde{c}_s)$ from (3.1.71), fit to C/100 experimental data.



Figure C.1: Comparing cell voltage from the C/100 experiment to the function approximating OCV $U_{eq}(\tilde{c})$ with a set of fit parameters from Table C.1.

The chemical potential in (3.2.45) also relates to the open-circuit voltage through the Nernstian relationship (3.1.69), detailed in Smith *et al.* [23]. The optimal value from Table 6.2 for regular solution parameter Ω_a from the (CHR) model can be used to generate Figure C.2 of the local homogeneous Gibbs free energy density from (3.2.40) and chemical potential from (3.2.45). The common tangent construction is applied to find the binodal region where the free energy may be reduced through phase separation. Recall that outside the spinodal region, sufficient perturbation from the homogenized state is required to trigger phase separation through nucleation. Inside the region defined by the points located at extrema of μ_0 , spinodal decomposition can trigger separation from infinitesimal perturbations.

In Figure C.3, the chemical potential is used with the reference chemical potential μ_{Θ} in the Nernstian expression (3.1.69) for open-circuit voltage. This is qualitatively compared against the experimentally measured C/100 cell voltage that approximates the OCV. Characteristic of the (CHR) model is only one flat voltage plateau that fails to capture any of the voltage drops in the OCV observed experimentally.

In a similar treatment, the optimal values from Table 6.2 for regular solution parameters $\Omega_a, \Omega_b, \Omega_c$ from the (CHR2) model can be used to generate Figure C.4 of the local homogeneous Gibbs free energy density surface from (3.2.47). For a given state of charge $\tilde{c} = (\tilde{c}_1 + \tilde{c}_2)/2$, the Gibbs free energy surface in the absence of gradient terms $g_0(\tilde{c}_1, \tilde{c}_2)$ has a minimum energy found by solving,

$$\min_{\tilde{c}_1} g_0(\tilde{c}_1, 2\tilde{c} - \tilde{c}_1). \tag{C.0.1}$$

Since the free energy is symmetric with respect to \tilde{c}_1 and \tilde{c}_2 , there exists two equivalent minimal energy trajectories. Just one is isolated when the above is made a constrained optimization problem by imposing $2\tilde{c} - 1 < \tilde{c}_1 < \tilde{c}$ and $0 < \tilde{c}_1 < 1$. Solving (C.0.1) for each of $0 < \tilde{c} < 1$ gives a particular \tilde{c}_1 and $\tilde{c}_2 = 2\tilde{c} - \tilde{c}_1$ that are used in (3.2.59) to obtain the path dependent effective chemical potential as a function of state of charge $\mu_{\text{eff}}(\tilde{c})$.

As discussed in Section 3.2.2, the free energy may be further reduced through phase separation when common tangent planes are able to be constructed. Since the lower tangent plane is known to be parallel to the $\tilde{c}_1\tilde{c}_2$ -plane, it will exist when there are three values within $0 < \tilde{c} < 0.5$ that satisfy $\mu_{\text{eff}}(\tilde{c}) = 0$. The zeros corresponding to where μ_{eff} goes from negative to positive are the binodal points. Within the binodal region, the free energy can be reduced through phase separation to the common tangent plane such that the effective chemical potential is zero. By exploiting the symmetry of the problem, the upper common tangent plane is found by reflecting the first binodal region about $\tilde{c} = 0.5$. This second plateau will then feature some constant effective chemical potential $\mu_{\text{eff}} > 0$.

A subset of the binodal region is the spinodal region defined within the points at which $d\mu/d\tilde{c} = 0$ (i.e. inflection points of g_0). There, spinodal decomposition triggers separation into two distinct phases from infinitesimal perturbations in the homogenized state. Outside this subset however, the system would typically require sufficient perturbation that phase-separation happens through nucleation. In Smith *et al.* [23], the metastable region is demonstrated to cause an "overshoot" before falling to the stable-equilibrium plateau.

The Gibbs free energy surface can alternatively be presented as a contour plot where the minimal energy trajectory is easier to discern. This and the corresponding chemical potential from (3.2.50) are shown in Figure C.5. Again applying the Nernstian expression (3.1.69) gives an open-circuit voltage able to be compared to the experimental approximation in Figure C.6. One of the crowning features of the (CHR2) model is in being able to capture the half filling fraction open-circuit voltage drop. This is attributable to parameter Ω_b which increases the free energy of the nearly full stage 1. However, the optimal result of the concentration profile fitting is a value of Ω_b just large enough to produce a very small drop. The experimentally obtained OCV is observed to contain a pronounced voltage drop though closer to 0.6 than a filling fraction of 1/2. Several other voltage plateaus are also observed at low filling fractions that represent dilute higher staging and are not captured by the chemical potential. It is noted that these plateaus are seen to still possess a partial slope indicating the mathematical model is still not accounting for some effect in that regard.



Figure C.2: Homogeneous Gibbs free energy \tilde{g}_0 versus filling fraction \tilde{c}_s (top) and corresponding chemical potential $\tilde{\mu}_0$ versus filling fraction (bottom) for the (CHR) model with Ω_a obtained from Table 6.2. The solid blue lines are the sections of the curves outside the binodal region defined by the binodal points (open circles). The dotted blue line represents the section of curve inside the spinodal region defined by the spinodal points (green circles). The dashed blue lines are the sections within the binodal region but outside the spinodal region. The red line represents the path followed upon phase separation.



Figure C.3: C/100 cell voltage versus state of charge for experiment (solid black) and Nernstian voltage from (3.1.69) for the (CHR) model using the chemical potential displayed in Figure C.2.



Figure C.4: Homogeneous Gibbs free energy surface \tilde{g}_0 versus filling fractions \tilde{c}_i , i = 1, 2 for the (CHR2) model with $\Omega_a, \Omega_b, \Omega_c$ obtained from Table 6.2. The solid blue lines are the sections of the minimal energy trajectory outside the binodal region defined by the binodal points (open circles) while the dashed blue lines are inside this region. The red line represents the path followed upon phase separation which lie along the common tangent planes in green.



Figure C.5: Contour plot of the homogeneous Gibbs free energy \tilde{g}_0 versus filling fractions \tilde{c}_i , i = 1, 2 (top) and corresponding effective chemical potential $\tilde{\mu}_{\text{eff}}$ versus the average filling fraction of the two layers (bottom) for the (CHR2) model with $\Omega_a, \Omega_b, \Omega_c$ obtained from Table 6.2. The solid blue lines are the sections of the minimal energy trajectory outside the binodal region defined by the binodal points (open circles) while the dashed blue lines are inside this region. The red line represents the path followed upon phase separation.



Figure C.6: C/100 cell voltage versus state of charge for experiment (solid black) and Nernstian voltage from (3.1.69) for the (CHR2) model using the chemical potential displayed in Figure C.5.

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