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#### WASHINGTON UNIVERSITY IN ST. LOUIS

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Multiscale Modeling, Reformulation, and Efficient Simulation of Lithium-Ion Batteries

by

Paul Wesley Clairday Northrop

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

May 2014

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#### ABSTRACT OF THE DISSERTATION

#### Multiscale Modeling, Reformulation, and Efficient Simulation of Lithium-Ion Batteries

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Lithium-ion batteries are ubiquitous in modern society, ranging from relatively lowpower applications, such as cell phones, to very high demand applications such as electric vehicles and grid storage. The higher power and energy density of lithium-ion batteries compared to other forms of electrochemical energy storage makes them very popular in such a wide range of applications. In order to engineer improved battery design and develop better control schemes, it is important to understand internal and external battery behavior under a variety of possible operating conditions. This can be achieved using physical experiments, but those can be costly and time consuming, especially for life-studies which can take years to perform. Here using mathematical models based on porous electrode theory to study the internal behavior of lithium-ion batteries is examined. As the physical phenomena which govern battery performance are described using several nonlinear partial differential equations, simulating battery models can quickly become computationally expensive. Thus, much of this work focuses on reformulating the battery model to improve simulation efficiency, allowing for use to solve problems which require many iterations to converge (e.g. optimization), or in applications which have limited computational resources (e.g. control).

Computational time is improved while maintaining accuracy by using a coordinate transformation and orthogonal collocation to reduce the number of equations which must be solved using the method of lines. Orthogonal collocation is a spectral method which approximates all dependent variables as a series solution of trial functions. This approach discretizes the spatial derivatives with higher order accuracy than standard finite difference approach. The coefficients are determined by requiring the governing equation be satisfied at specified collocation points, resulting in a system of differential algebraic equations (DAEs) which must be solved with time as the only differential variable. The system of DAEs can be solved using standard time-adaptive integrating solvers. The error and simulation time of the battery model of orthogonal collocation is analyzed.

The improved computational efficiency allows for more physical phenomena to be considered in the reformulated model. Lithium-ion batteries exposed to high temperatures can lead to internal damage and capacity fade. In extreme cases this can lead to thermal runaway, a dangerous scenario in which energy is rapidly released. In the other end of the temperature spectrum, low temperatures can significantly impede performance by increasing diffusion resistance. Although accounting for thermal effects increases the computational cost, the model reformulation allows for these important phenomena to be considered in single cell as well as 2D and multicell stack battery models.

The growth of the solid electrolyte interface (SEI) layer contributes to capacity fade by means of a side reaction which removes lithium from the system irreversibly as well as increasing the resistance of the transfer lithium-ion from the electrolyte to the active material. As the reaction kinetics are not well understood, several proposed mechanisms are considered and implemented into the continuum reformulated model. The effects of SEI layer growth on a lithium-ion cell over 10,000 cycles is simulated and analyzed. Furthermore, a kinetic Monte Carlo model is developed and implemented to study the heterogeneous growth of the solid electrolyte layer. This is a stochastic approach which considers lithium-ion diffusion, intercalation, and side reactions. As millions of individual time steps may be performed for a single cycle, it is very computationally expensive, but allows for simulation of surface phenomena which are ignored in continuum models.

# **Chapter 1**

# Introduction

### **1.1 Lithium-Ion Batteries**

A growing awareness of the consequences of relying on fossil fuels has increased the demand for development of renewable sources of energy and alternative fuels for transportation. This has led to intense research of many technologies which directly and indirectly enable the transition to the wide-scale use of lithium-ion batteries can help facilitate the utilization of non-carbon based fuels. Many renewable energy sources are intermittent in nature and require an energy storage system in order to match energy production to demand. Alternative transportation fuels must have a high energy and power density to compete with petroleum based in terms of range and performance. Lithium-ion batteries operate at a higher voltage than other battery chemistries, which make them particularly useful in high energy and high power applications.

#### 1.1.1 Standard Lithium-Ion Battery Operation

Lithium-ion battery technology is fundamentally based on the reversible oxidation of lithium to lithium ions as given by the following electrochemical reaction:

$$Li \xrightarrow{\text{Discharge}} Li^+ + e^-$$
 (1.1)

Reaction (1.1) has a very high electrochemical potential ( $E^0 = -3.04V$  vs. the standard hydrogen electrode (SHE)). This property combined with the low molecular weight of lithium gives lithium-ion battery technology an advantage over other alternatives in terms of energy and power densities. The high energy density of lithium-ion batteries has led them to be popular in a variety

of electronic devices. These range from applications with small energy demands, such as implantable cardioverter-defibrillators, to very high energy and life demanding applications, such as in satellites, and now hybrid- and full-electric vehicles.



Figure 1-1: Schematic of lithium-ion cell being charged. The transport of lithium occurs in the opposite direction during discharge.

A lithium-ion battery consists of a positive electrode and a negative electrode separated by a porous membrane, as shown in Figure 1-1. During charge, lithium deintercalates from the positive electrode, diffuses in the electrolyte, and intercalates into the active material in the negative electrode. Note that in this work, and found commonly in the literature on the subject of batteries, the term "positive electrode" is used interchangeably with "cathode" and "negative electrode" is used interchangeably with "anode". This is done to avoid ambiguity by defining the terms "anode" and "cathode" based on whether oxidization or reduction occurs during discharge. Typically, a lithium metal oxide is used at the positive electrode, in which the metal in the metal oxide is reduced during discharge and oxidized during charging as given by the following reaction:

$$MO_y + Li^+ + e^- \xleftarrow{\text{Discharge}}_{\text{Charge}} LiMO_y$$
 (1.2)

The counter-reaction at the negative electrode is based on the oxidation of lithium shown in reaction (1.1). However, lithium metal is typically not used due to the formation of dendrites which can cross the separator region and short-circuit the cell. Such an occurrence can lead to dangerous thermal runaway reactions as all the stored energy in the cell is released as heat in a very short time. Therefore, a host material is employed when designing commercial cells in which the lithium metal is stored (though the use of lithium foil is popular for research purposes by minimizing the open circuit potential of the anode during cycling). Graphite is often used as the anodic active material due to its low cost and good cycling stability, leading to the following redox reaction to occur at the negative electrode:

$$LiC_6 \xrightarrow{\text{Discharge}} Li^+ + e^- + C_6$$
 (1.3)

This work focuses principally on graphitic anodes, though it should be mentioned that other materials, most notably silicon or Si/C composites are being researched with the aim to greatly improve energy density. Currently, such materials suffer from extreme volumetric changes that quickly lead to degradation after a few cycles, limiting their commercial use. Although simulating operations for materials which experience large stress strain effects will require the development of a model which considers these effects, the reformulation techniques developed in this thesis are applicable to other chemistries and materials which may be used. The versatility of the techniques developed here is explained in more detail in Chapter 2 and Chapter 3.

The electrodes in lithium-ion batteries are porous in nature and flooded with an electrolyte. The electrolyte and separator facilitate the transfer of lithium ions from the cathode to the anode during charging and vice versa during discharging. The porous nature of the electrodes increases the available surface area for lithium intercalation and reduces the diffusive

resistance, as lithium diffusion in the electrolyte is orders of magnitude greater than in the solid phase. This leads to designs which minimize the diffusion length of lithium in the solid phase, though at the expense of reduced energy density. This provides a trade off in which the optimal design must be determined based on the intended application.

Despite the great promise shown by lithium-ion batteries, several limitations still exist and are an active area of research. For example, concerns such SEI layer growth, side reactions, stress-strain, ohmic and diffusion resistance, etc can reduce capacity and overall performance.<sup>1,2</sup> Researchers have been trying to find novel anode and cathode materials with better physical, mechanical, and chemical properties to address these issues. Furthermore, the robustness and charge density can vary significantly among different chemistries.

### **1.2 Motivation of Li-ion Battery Simulation**

Modeling and simulation can provide insight that is either impractical or impossible to find using physical experiments. Physical experiments can be expensive in terms of money and time, and can practically test only a finite number of discrete conditions. In contrast, a computationally efficient model can perform simulation of many conditions in a short time, and the feasibility of using detailed physics based model has only increased as the cost of computer hardware has decreased while power has increased,. Furthermore, simulation can provide data on the internal states of the battery which cannot be measured *in situ*. Lithium-ion battery models can be used to enable better design and control and provide long term predictive capability.

Lithium-ion batteries have historically designed using an Edisonian trial-and-error approach, which can be expensive in terms of both money and time, as prototype batteries must be manufactured and cycled repeatedly, a process that can take years to complete. Furthermore, it is practical to only consider discrete values of the design parameters, with any conclusions for other designs based on interpolation and extrapolation of the data. In contrast, a well-developed optimization scheme can consider all parameters as continuous values, and modify them simultaneously.<sup>3</sup> This can lead to the development of an optimal design in a relatively short time. However, if there are many parameters which are being considered, the simulation may have to be run hundreds or thousands of times, increasing the need for efficient simulation techniques.

A well-defined physics based model can also be used to estimate the physical parameters in a system using experimental data.<sup>4</sup> Typically, only the voltage and current can be directly measured during battery operation, thus parameter estimation techniques can be used to determine internal parameters, such as transport coefficients and reaction rate constants. Once these parameters are found, the behavior of battery under different operating conditions can be predicted. Furthermore, parameter values can be tracked as a function of cycle number to provide predictions of capacity fade.

Similar to estimation of parameter values, a physics based model can be used to estimate the internal states of the battery based on experimental voltage and current data. This is particularly important in control applications and battery management systems (BMS), for example in large scale energy systems such as electric vehicles (EVs). When the battery is nearly depleted there are difficulties in the vehicle meeting high power demands, such as during high acceleration, which is aggravated as the battery ages. Furthermore, the present state of charge (SOC) is not precisely known. Thus, the battery is shut off while a significant amount of energy remains unused. A similar case exists when the battery is nearly completely charged. For this reason, Li-batteries for EVs are greatly overdesigned and carry a significant amount of extra weight and volume that is never used to propel the vehicle resulting in a corresponding increase in costs.<sup>5,6</sup> The BMS controls the flow of current into and out of the battery to maximize performance of the battery while maintaining safety. From this data, the BMS generally estimates SOC and state of health of the battery (SOH) of the battery, using a built-in model capable of predicting battery behavior. For reference, SOC refers to the fraction of charge that remains in the battery that can be used to provide power, while SOH refers to the maximum amount of charge that can be currently be stored, relative to the amount of charge that can be stored in a new battery. By using a validated physics based model in such control applications, the SOC can be more accurately determined and the amount of battery overdesign can be reduced to save money and minimize weight.

## **1.3 Models Used to Simulate Lithium-Ion Batteries**

In order to better understand lithium-ion battery operation and predict performance, several mathematical models have been developed.<sup>2</sup> These range from simple empirical-based models or circuit based models<sup>7,8</sup> to computationally expensive molecular dynamics simulators. These mathematical models for lithium-ion batteries vary widely in terms of complexity, computational requirements, and reliability of their predictions.<sup>2</sup> An ideal model would be perfectly predictive under all operating conditions and for the entire life of the battery. The SOC and SOH of the battery would be well known at all times. The temperature and charging/discharging under which the device is operating have a significant impact on output voltage and performance, which should be accounted for in a comprehensive model which considers the coupling of various physical phenomena. However this increases the computation demands of simulation. Ideally, a model would predict the internal behavior while maintaining minimal computational cost so that it can be solved instantaneously and with limited resources.

This is difficult in battery models, as many phenomena in batteries are best modeled using complex non-linear partial differential equations, while others are still not well understood. Furthermore, there is often a tradeoff between accuracy and computational costs for existing models.

#### 1.3.1 Empirical and circuit based models

Empirical models are minimally detailed and often provide the highest computational efficiency for lithium-ion batteries models by using polynomial, exponential, power law, logarithmic, and trigonometric function fits with past experimental data to predict the future behavior. However, these models use parameters that lack any physical meaning, and are not accurate outside of the operating conditions from which they were developed or as the battery grows older or as temperature changes occur, limiting the insight that can be gained from such models. Equivalent circuit models try to describe the underlying system using a representation that usually employs a combination of capacitors, resistors, voltage sources, and lookup tables,<sup>7</sup> while capacity fade is often represented by a capacitor with a linearly decreasing capacity and temperature dependence is modeled by a resistor-capacitor combination. Current research in this area includes adopting the parameters of the circuit based models to be more accurate by continuously updating the parameters using the current and voltage data.<sup>8</sup>

#### 1.3.2 Single Particle Model

The single particle model (SPM) is a simple model which represents each electrode as a single particle. The effects of mass transport in the solid phase of a lithium-ion cell are considered within the particle, but the concentration and potential effects in the solution phase between the particles are neglected.<sup>9-11</sup> The governing equations are based on Fick's Law in

spherical coordinates. The applied flux on the spherical surface is based on Butler-Volmer kinetics. The governing equation is shown in Table 1-1, which is identical for both electrodes. The SPM is a simplified physics based model which allows one to draw conclusions of battery performance for a range of conditions, although the assumptions are not valid for high rates or thick electrodes.<sup>9</sup> The limited computational requirements allow for fast simulation of battery performance making it popular as an initial attempt when considering additional physical phenomena, especially for life simulations.<sup>12,13</sup>

Governing Equation	<b>Boundary Conditions</b>			
$\frac{\partial c_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_i \frac{\partial c_i}{\partial r} \right]  i = p, n$	$\frac{\frac{\partial c_i}{\partial r}}{\frac{\partial c_i}{\partial r}}\Big _{r=0} = 0$ $\frac{\frac{\partial c_i}{\partial r}}{\frac{\partial c_i}{\partial r}}\Big _{r=0} = -j_i D_i$			
$\partial r$ $\partial r$ Additional Equation for Reaction Kinetics				
$j_{i} = 2k_{i}c_{e}^{0.5}(c_{i,max} - c_{i,surf})^{0.5}c_{i,surf}^{0.5}\sinh\left(0.5\frac{F(\Phi_{i} - U_{i}(\theta))}{RT}\right) = \frac{I_{app}}{a_{i}l_{i}F}$				

 Table 1-1:
 Governing Equation of the Single Particle Model

#### 1.3.3 Porous Electrode Pseudo Two-Dimensional Model

The pseudo-two-dimensional (P2D) model is a more detailed physics based model that considers several physically meaningful internal variables during simulation, including the electrochemical potentials within the solid phase and electrolyte along with lithium concentration in both the solid- and liquid-phases.<sup>14</sup> Doyle et al.<sup>14</sup> developed a general model based on concentrated solution theory to describe the internal behavior of a lithium-ion sandwich consisting of positive and negative porous electrodes, a separator, and current collectors.<sup>2</sup> Such a model allows researchers to quickly and cheaply study the effects of different operating conditions on battery performance without relying on costly physical experiments.

Governing Equations	Boundary Conditions	
Positive Electrode		
$\varepsilon_{\rm p} \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\rm eff,p} \frac{\partial c}{\partial x} \right] + a_{\rm p} \left( 1 - t_{+} \right) j_{\rm p}$	$\frac{\partial c}{\partial x}\Big _{x=0} = 0$	$-D_{\text{eff},p} \frac{\partial c}{\partial x} \Big _{x=l_p^-} = -D_{\text{eff},s} \frac{\partial c}{\partial x} \Big _{x=l_p^+}$
$\boxed{-\sigma_{eff,p} \frac{\partial \Phi_1}{\partial x} - \kappa_{eff,p} \frac{\partial \Phi_2}{\partial x} + \frac{2\kappa_{eff,p}RT}{F} (1 - t_+) \frac{\partial \ln c}{\partial x} = I}$	$\frac{\partial \Phi_2}{\partial x} _{x=0} = 0$	$-\kappa_{\text{eff,p}} \frac{\partial \Phi_2}{\partial x} \big _{x=l_p^-} = -\kappa_{\text{eff,s}} \frac{\partial \Phi_2}{\partial x} \big _{x=l_p^+}$
$\boxed{\frac{\partial}{\partial x} \left[ \sigma_{\text{eff,p}} \frac{\partial \Phi_{1}}{\partial x} \right] = a_{p} F j_{p}}$	$\frac{\partial \Phi_1}{\partial x} _{x=0} = -\frac{I}{\sigma_{eff,p}}$	$\frac{\partial \Phi_1}{\partial x}\big _{x=l_p^-} = 0$
$\left[\frac{\partial c_p^s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_p^s \frac{\partial c_p^s}{\partial r}\right]$	$\frac{\partial c_p^s}{\partial r} _{r=0} = 0$	$\frac{\partial c_p^s}{\partial r} _{r=R_p} = -j_p D_p^s$
Separator		
$\varepsilon_{s} \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff},s} \frac{\partial c}{\partial x} \right]$	$c\mid_{x=t_p^-}=c\mid_{x=t_p^+}$	$c \mid_{x=l_p+l_s^-} = c \mid_{x=l_p+l_s^+}$
$-\kappa_{\rm eff,s} \frac{\partial \Phi_2}{\partial x} + \frac{2\kappa_{\rm eff,s} RT}{F} (1 - t_+) \frac{\partial \ln c}{\partial x} = I$	$\Phi_2 \mid_{x=l_p^-} = \Phi_2 \mid_{x=l_p^+}$	$\Phi_2  _{x=l_p+l_s^-} = \Phi_2  _{x=l_p+l_s^+}$
Negative Electrode		
$\varepsilon_{n} \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff,n}} \frac{\partial c}{\partial x} \right] + a_{n} \left( 1 - t_{+} \right) j_{n}$	$\frac{\partial c}{\partial x}\Big _{x=l_p+l_x+l_n}=0$	$-D_{\text{eff,s}} \frac{\partial c}{\partial x} \big _{x=l_p+l_s} = -D_{\text{eff,n}} \frac{\partial c}{\partial x} \big _{x=l_p+l_s}$
$-\sigma_{\rm eff,n}\frac{\partial\Phi_1}{\partial x} - \kappa_{\rm eff,n}\frac{\partial\Phi_2}{\partial x} + \frac{2\kappa_{\rm eff,n}RT}{F}(1-t_+)\frac{\partial\ln c}{\partial x} = I$	$\Phi_2  _{x=l_p+l_s+l_n} = 0$	$-\kappa_{\mathrm{eff},s} \frac{\partial \Phi_2}{\partial x} \Big _{x=l_p+l_s^-} = -\kappa_{\mathrm{eff},p} \frac{\partial \Phi_2}{\partial x} \Big _{x=l_p+l_s^+}$
$\frac{\partial}{\partial x} \left[ \sigma_{\text{eff,n}} \frac{\partial \Phi_1}{\partial x} \right] = a_n F j_n$	$\frac{\partial \Phi_1}{\partial x}\Big _{x=l_p+l_s^-} = 0$	$\left \frac{\partial \Phi_1}{\partial x}\right _{x=l_p+l_s+l_n} = -\frac{I}{\sigma_{eff,n}}$
$\frac{\partial c_n^s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_n^s \frac{\partial c_n^s}{\partial r} \right]$	$\frac{\partial c_n^s}{\partial r}\big _{r=0} = 0$	$\frac{\partial c_n^s}{\partial r}\Big _{r=R_p} = -j_n D_n^s$

Table 1-2: Porous Electrode Pseudo 2D Model

The base P2D model is a detailed engineering model based on transport phenomena that describes the behavior of a 1-D battery subject to isothermal conditions consisting of a total of 10 governing partial differential equations (PDEs) in x, r, and t, across three regions which are given in Table 1-2 with appropriate boundary conditions. The boundary conditions at the electrode-separator interfaces are given to satisfy continuities and conservation of flux, while the electrode-current collector interfaces are insulating conditions for all variables except the solid phase

potential. The solid phase potential boundary conditions are dictated by the charging/discharge protocol considered and drives the ultimate evolution of the system. Note that the governing equations for the positive and negative electrodes are identical in form and differ only in the parameter values and correlations. The separator is void of active material, so all terms relating to the solid phase are absent. The first equation is derived from concentrated solution theory and material balances of lithium in the electrolyte phase. The second equation is the charge balance in the liquid phase while the third equation is the charge balance in the solid phase. The fourth equation is Fick's law of diffusion inside the solid particles (solid phase), which is analogous to governing equations of the single particle model discussed in Section 1.3.2. Thus the P2D model can be seen as an extension of the SPM which accounts for variation across the electrodes and effects of the electrolyte.

The auxiliary equations for the P2D model are given in Table 1-3. Butler-Volmer kinetics links the solid and electrolyte phases by describing the transfer of lithium (and charge) between the two domains. The open circuit potentials, denoted as  $U_n$  and  $U_p$ , are empirically determined functions of the local state of charge and are highly dependent on the active material used.

The validity of the P2D model over a wide range of conditions has led to it being very popular among battery researchers. Thus, much of the work presented in this thesis is based upon the P2D model. Specifically, Chapter 2 focuses on the reformulation of the P2D model to improve computational efficiency. This allows more detailed phenomena to be studied, as described in Chapter 3

 Table 1-3: Additional Expressions for Li-ion Battery Simulation

$$\begin{split} & \left| j_{p} = 2k_{p}c^{0.5}c^{s} \right|_{r=R_{p}}^{0.5} \left( c_{\max,p}^{s} - c^{s} \right|_{r=R_{p}} \right)^{0.5} \sinh\left[ \frac{0.5F}{RT} \left( \Phi_{1} - \Phi_{2} - U_{p} \right) \right] \\ & \left| j_{n} = 2k_{n}c^{0.5}c^{s} \right|_{r=R_{n}}^{0.5} \left( c_{\max,n}^{s} - c^{s} \right|_{r=R_{n}} \right)^{0.5} \sinh\left[ \frac{0.5F}{RT} \left( \Phi_{1} - \Phi_{2} - U_{n} \right) \right] \\ & \left| \kappa_{eff,i} = \varepsilon_{i}^{bragg_{i}} \left( \frac{4.1253 \times 10^{-2} + 5.007 \times 10^{-4}c - 4.7212 \times 10^{-7}c^{2}}{4.15094 \times 10^{-10}c^{3} - 1.6018 \times 10^{-14}c^{4}} \right), i = p, s, n \\ & \sigma_{eff,i} = \sigma_{i} \left( 1 - \varepsilon_{i} - \varepsilon_{f,i} \right), i = p, s, n \\ & D_{eff,i} = D\varepsilon_{i}^{bragg_{i}}, i = p, s, n \\ & a_{i} = \frac{3}{R_{i}} \left( 1 - \varepsilon_{i} - \varepsilon_{f,i} \right), i = p, s, n \\ & U_{p} = \frac{-4.656 + 88.669\theta_{p}^{2} - 401.119\theta_{p}^{4} + 342.909\theta_{p}^{6} - 462.471\theta_{p}^{8} + 433.434\theta_{p}^{10}}{-1.0 + 18.933\theta_{p}^{2} - 79.532\theta_{p}^{4} + 37.311\theta_{p}^{6} - 73.083\theta_{p}^{8} + 95.96\theta_{p}^{10} \\ & \theta_{p} = \frac{c^{s}}{c_{\max,p}^{s}} \\ & U_{n} = 0.7222 + 0.1387\theta_{n} + 0.029\theta_{n}^{0.5} - \frac{0.0172}{\theta_{n}} + \frac{0.0019}{\theta_{n}^{1.5}} + \\ & 0.2808 \exp(0.90 - 15\theta_{n}) - 0.7984 \exp(0.4465\theta_{n} - 0.4108) \\ & \theta_{n} = \frac{c^{s}}{c_{\max,n}^{s}} \end{array}$$

### 1.3.4Thermal Effects

The temperature at which a cell operates has a major impact on performance, safety, and life.<sup>15</sup> At low temperatures, high diffusive resistances reduce the amount of power that a battery is capable of providing, making operating battery powered devices difficult in cold weather. Conversely, a battery subjected to high temperature or extreme demands can be physically damaged or experience higher levels of capacity fade.<sup>15</sup> An overheated cell may ultimately undergo thermal runaway, a potentially explosive situation. A thermal runaway event can occur when a large release of energy from the cell, for example from a short circuit, causes a rapid

temperature rise. This can cause the solvent to vaporize and ultimately lead to rupture of the cell. As lithium is incredibly reactive, such a rupture can be disastrous.

Although thermal runaway is a severe event, high operating temperatures can also have other deleterious effects.<sup>15</sup> Side reactions which contribute to capacity fade may be more favorable under high temperatures. Stresses caused by thermal expansion can contribute to mechanical fracture.

Maintaining reasonable temperatures for cell operation is therefore important to ensure safety and longevity. However, temperature rises are a normal part of battery operations. The ohmic resistances directly contribute to heat generation, as does the lithium reaction themselves. The temperature rise can be rather pronounced (50°C or more) under adiabatic conditions, especially in high power applications. This must be taken into consideration when designing and operating lithium-ion batteries and thus considering the thermal effects in lithium-ion batteries has been a popular subject in the literature.<sup>16-20</sup> Further complications arise as the heat generation within a cell can vary with the temperature. Bandhauer, et al. examined the heat generation and capacity fade at different rates of charging and discharge, and applied their findings to study the effects when applied to electric vehicle applications.<sup>21</sup>

#### 1.3.5 Solid Electrolyte Interface

Along with Li-ion intercalation, side reactions can occur during battery operation, such as decomposition of the electrolyte and the formation of a surface layer, often referred to as the solid electrolyte interface (SEI) layer. The properties and chemical composition of the SEI layer have been a subject of intense research due to its importance in the safety, capacity fade, and the life cycle of Li-ion secondary batteries.

The SEI layer is a key element of Li-ion batteries and acts as a safety feature by maintaining a protective barrier between the negative electrode and the electrolyte. The SEI layer typically forms due to the reduction of the solvent (typically ethylene carbonate) and contributes to SEI layer thickness.<sup>22</sup> This model assumes that the solvent molecules, ethylene carbonate, must diffuse through the SEI layer to react with lithium at the active material surface to create a layer of lithium ethylene dicarbonate. The overall reaction by Safari, et al.<sup>22</sup> is

$$2EC+2Li \longrightarrow (CH_2OCO_2Li)_2 \tag{1.4}$$

These byproducts results in increasing the resistance to the intercalation/deintercalation of lithium ions and results in reducing the capacity of the battery. These phenomena can increase temperature and lead to thermal runaway. The SEI layer should be highly ion-conductive to reduce overvoltage, while being mechanically stable and flexible. These objectives require a *thin* but *stable* SEI layer that will not deteriorate or substantially change its composition or morphology with time and temperature during cycling and storage.

### **1.4 Scope of Thesis**

The work presented here generally focuses on the efficient simulation and model reformulation of lithium-ion batteries. Chapter 2 discusses the methods developed to improve simulation times and reduce computational costs to allow for the implementation of detailed models into more computationally limiting applications. Using a mathematical model for optimization, parameter estimation, or life studies requires the simulation to be run hundreds to thousands of times, necessitating efficient simulation techniques to be used. Similarly, on-line control applications, such as those found in electric vehicles, have limited computational resources available to do optimization calculations. These limitations have led to circuit-based or

single-particle models (see Sections 1.3.1 and 1.3.2) to be popular in such applications. However, the reformulated model developed in Chapter 2 becomes a viable option in applications that would otherwise be too computationally expensive for use of the P2D model. Using the more complicated P2D model can allow for predictions to be made over a wider range of conditions than is possible with simpler models.

The model reformulation also can be expanded to include additional physical phenomena to better predict battery behavior. Examples of this are shown in Chapter 3. Section 3.1 discusses the inclusion of thermal effects into the P2D model framework, including into multi-cell stack model, while Section 3.2 considers 2D effects. Inclusion of the growth of the SEI layer into the P2D model is also discussed in Section 3.3 to allow for the long term simulation of life and capacity fade. Stress and strain effects are also important for life studies as they also contribute to capacity fade, but that work is left to future generations of students.

Chapter 4 examines the growth of the SEI using a kinetic Monte Carlo (KMC) approach. A background on KMC is provided in Appendix C. This is significantly more computationally intensive simulation strategy that examines the growth of the SEI layer on the microscale and demonstrates the surface heterogeneity. The high computational cost makes the KMC model infeasible for use in online applications, but can provide insight to the conditions that ultimately lead to SEI layer growth and capacity fade. To analyze results for typical battery operation, the KMC model for growth of the SEI model is also coupled with the P2D model to give a multiscale model.

Background and examples on the mathematical techniques used in this work are provided in the Appendices. Specifically, the numerical method of lines can be used to solve partial differential equations as shown in Appendix A, which allows efficient time adaptive solvers to

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be used for integration. Appendix B discusses the method of weighted residuals: a way to determine the coefficients of spectral series to discretize spatial derivatives. A description of the kinetic Monte Carlo method is given in Appendix C. Appendix D shows how to solve a system of differential algebraic equations using the Euler method to numerically integrate, and the Newton-Raphson method to solve the algebraic equations. A perturbation approach building upon the method of lines and the method of false transients is given in Appendix E. Although the perturbation approach described in Appendix E is applied to elliptic partial differential equations, its development arose from the need to find consistent initial conditions for the battery models.

# Chapter 2

# Model Reformulation of the Porous Electrode Pseudo 2D

# Model

This chapter contains excerpts (specifically in Sections 2.2 and 2.3) from the following journal article reproduced here with permission from The Electrochemical Society:
P. W. C. Northrop, V. Ramadesigan, S. De, and V. R. Subramanian, "Coordinate Transformation, Orthogonal Collocation and Model Reformulation for Simulating Electrochemical-Thermal Behavior of Lithium-ion Battery Stacks," *Journal of the Electrochemical Society*, 158(12), A1461-A1477 (2011).

# 2.1 Background of Li-ion Battery Simulation

In order to obtain useful information from any mathematical model, a method must be used to solve the equations of that model. Ideally, an analytical solution is preferred, as it eliminates the error that arises when using numerical techniques and is usually computationally very cheap. An analytical solution provides insight into the behavior of the system while explicitly showing the effects of different parameters on the behavior. However, many engineering models, including most battery models, cannot be solved analytically due to nonlinearities in the equations and state dependent transport and kinetic parameters. The mathematical method used to solve the system of equations describing battery operation can have a significant impact on the computational cost of simulation.

#### 2.1.1 Traditional Simulation Approaches

Most standard solvers discretize an ODE or PDE using finite difference, finite volume, or finite element approaches. These schemes are well understood by most scientists and engineers and can be implemented in a straightforward manner. Thus, many commercial software packages, such as COMSOL,<sup>23</sup> Fluent,<sup>24</sup> etc. use these methods to numerically solve ODEs or

PDEs. However, many node points, control volumes, or elements are required for convergence. These methods are robust approaches for solving the problem, but the resulting set of algebraic or differential-algebraic equations can number into the thousands and is computationally expensive, even for linear problems, and is difficult to implement into a microcontroller or other resource-limited environment. Furthermore, many commercial solvers are over-designed in order to handle a wide variety of problems with minimal input from the user. They do not exploit the structure and unique characteristics of the underlying models, which can be used to improve the computational performance without compromising on the robustness.

Typically, the P2D model is simulated using finite difference schemes in x and taking a single time step, for example using the BANDJ solver.<sup>25</sup> To improve computational efficiency using adaptive solvers in time, the method of lines (MOL) is used which discretizes the spatial dimensions (x and r) using numerical techniques (often finite difference) to eliminate the spatial derivatives.<sup>26</sup> The method of lines converts the system of PDEs to a system of first order differential algebraic equations (DAEs) with time as the only differential independent variable, converting the system to an initial value problem (IVP).<sup>27-29</sup> The MOL allows for computationally efficient time stepping algorithms, such as DASSL and DASKR,<sup>30</sup> to be used to simulate the model. The method of discretization and refinement of the mesh determines the number of DAEs that are created. However, initial conditions can only be prescribed by the user for the variables which have explicit time derivatives in the system; the initial conditions for the algebraic variables must satisfy the algebraic equations and may not be accurately known a priori. Finding consistent initial conditions can be challenging and increases the difficulty of simulating battery models. Providing inconsistent initial conditions can cause many DAE solvers to fail. Thus, work has been done to better initialize the system so that simulation can be

performed.<sup>31,32</sup> Note that the initialization approach provided in Ref.<sup>31</sup> is used in the bulk of this work. As an aside, this initialization work prompted the development of a perturbation approach generalizable to elliptic partial differential equations. A detailed description of this perturbaion approach is given in Appendix E.

#### 2.1.2 Order Reduction and Efficient Simulation

Using traditional approaches to simulate the P2D model is computationally expensive, and has limited its use in applications which require the simulation to be performed dozens to hundreds of time to arrive at a solution, such as parameter estimation<sup>4</sup> and optimization,<sup>3</sup> or real-time control<sup>33</sup>. The high computational cost of simulation has motivated researchers to develop techniques to simplify the battery models and enable faster simulation and reduce memory requirements. For example, proper orthogonal decomposition has been used to reduce the total number of states simulated.<sup>34</sup> Quasi-linearization combined with a Padé approximation has also been used to simplify the model.<sup>35</sup> Previous reformulation work used Galerkin's method, but was unable to handle non-linear parameters.<sup>27</sup>

Order reduction methods can be used to decrease the number of equations that must be solved simultaneously, and enable faster computation when using limited resources.<sup>34</sup> However, there are disadvantages to using order reduction methods. The most obvious limitation of reduced order models (ROM) is that information contained in the model is often sacrificed to improve computational efficiency. A well-incorporated ROM is designed such that the loss of accuracy is minimized for the conditions of interest. However, the loss of information contained in the model can make the results invalid for cases significantly different from those for which the ROM was developed.<sup>37,40</sup>

Additionally, specific order reduction techniques are only useful for certain classes of problems. Many (though not all) methods can only be used on linear systems, and thus cannot be used for nonlinear models that describe many engineering systems, including battery models.<sup>36,37</sup> Nonlinear systems can be simplified by linearization around a reference point. However, this linearization is not valid at conditions that deviate significantly from the reference conditions. It is important to note that order reduction methodologies exist that can be performed directly on non-linear systems. For example, proper orthogonal decomposition (POD) fits a reduced set of eigenvalues to get a meaningful solution with fewer equations.<sup>34,38</sup> However, rigorous numerical solutions, or parameter values are changed, the POD model must be reconstructed, negating any computational advantage that it provides. In addition, while POD has been reported to be very useful for ODEs, for large number of ill conditioned DAEs arising from battery models, POD methods do not offer the same reduction in CPU time.<sup>34</sup>

#### 2.1.3 Solid Phase Reformulation

The P2D model considers two spatial dimensions: one across the thickness of the cells, denoted by x in this work, and another across the radius of the particle, denoted here by the variable r. This greatly increases the computational cost if a full order discretization is performed for both spatial dimensions, leading to alternative approaches to discretize the solid phase.<sup>14,28,39-42</sup> This has prompted researchers to develop numerous techniques to reduce the computational cost of simulating the radial dimension. One commonly used simplification is the parabolic profile approximation to eliminate the radial dependence of the governing equations by approximating the solid phase diffusion equation from Table 1-2:

$$\frac{\partial c_p^s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_i^s \frac{\partial c_i^s}{\partial r} \right] \qquad \qquad i = p, n \qquad (2.1)$$

By volume average the concentration and governing equation, Equation (2.1) can be split into the following two equations for the average concentration and the surface concentration:<sup>43,44</sup>

$$\frac{d}{dt}c_i^{s,avg} = -3\frac{j_i}{R_i} \qquad \qquad i = p,n \qquad (2.2)$$

$$\frac{D_{s,i}}{R_i}(c_i^{s,surf} - c_i^{s,avg}) = -\frac{j_i}{5} \qquad r = p,n$$
(2.3)

This reduces the dimensionality of the problem and reduces the overall computational cost of simulation. This has been shown to be valid at low rates and long times<sup>28,39,45</sup> and will be used for majority of the work in this thesis.

Ramadesigan, et al.<sup>39</sup> provides an alternative for simulation of discharge rates greater than 1C by using a mixed finite difference approach. The mixed finite difference approach uses 6 optimally spaced node points (with 6 corresponding governing equations) to describe the behavior of the lithium ion concentration in the radial direction within the solid phase particles. This is in contrast to the polynomial profile approximation, which relies on 2 governing equations to describe the solid phase concentration. This allows the mixed finite difference approach to better capture the dynamics within the electrode at high rates, though at the cost of additional computation time. Additionally, Section 2.5 relaxes the parabolic profile approximation by allowing for higher order polynomials to be used for the solid phase.

However, even if a parabolic profile approximation is used as given in Equations (2.2) and (2.3), the number of DAEs that are developed using a full order finite difference discretization is computationally prohibitive as nearly 1000 nonlinear DAEs must be solved. The

following sections discuss the application of spectral methods to discretize the P2D equations to improve computational efficiencies.

## **2.2 Coordinate Transformation**

It should be noted that the original formulation of the problem has the three regions defined sequentially. In other words, the equations for the positive electrode are defined on the region  $[0, l_p]$ , the equations for the separator are defined on the region  $[l_p, l_p+l_s]$ , and the negative electrode equations are defined on the region  $[l_p+l_s, l_p+l_s+l_n]$ . In order to decrease the required computation, each region is rescaled to a domain of [0, 1]. This effectively reduces the problem from three regions to a single region. This is shown graphically in Figure 2-1.



Figure 2-1: Coordinate transformation for a single 1-D cell—note that the final diagram is used to show that the cathode, separator, and anode are solved in the same coordinate domain. It does not indicate that a second linear dimension is considered.

As an example, this transformation is shown in detail for the electrolyte concentration in the cathode, separator, and anode. From Table 1-2, the governing equations for the electrolyte concentration are:

$$\varepsilon_{p} \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff},p} \frac{\partial c}{\partial x} \right] + a_{p} (1 - t_{+}) j_{p} \qquad 0 < x < l_{p}$$

$$\varepsilon_{s} \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff},s} \frac{\partial c}{\partial x} \right] \qquad l_{p} < x < l_{p} + l_{s}$$

$$(2.4)$$

$$\varepsilon_n \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff},n} \frac{\partial c}{\partial x} \right] + a_n \left( 1 - t_+ \right) j_n \qquad l_p + l_s < x < l_p + l_s + l_n \tag{2.6}$$

with the boundary conditions given as

$$\frac{\partial c}{\partial x}|_{x=0} = 0 \tag{2.7}$$

$$-D_{\text{eff,p}} \frac{\partial c}{\partial x} \Big|_{x=l_p^-} = -D_{\text{eff,s}} \frac{\partial c}{\partial x} \Big|_{x=l_p^+}$$
(2.8)

$$c|_{x=l_{p}^{-}}=c|_{x=l_{p}^{+}}$$
(2.9)

$$c|_{x=l_p+l_s^-} = c|_{x=l_p+l_s^+}$$
(2.10)

$$-D_{\text{eff,s}} \frac{\partial c}{\partial x} \Big|_{x=l_p+l_s^-} = -D_{\text{eff,n}} \frac{\partial c}{\partial x} \Big|_{x=l_p+l_s^+}$$
(2.11)

$$\frac{\partial c}{\partial x}|_{x=l_p+l_s+l_n} = 0 \tag{2.12}$$

In order to convert the three region cell to a single region, the spatial coordinate, x, must first be transformed to the dimensionless coordinates  $X_1$ ,  $X_2$ , and  $X_3$  in the anode, separator, and cathode, respectively. These transformations are achieved using the following equations:

$$X_1 = \frac{x}{l_p} \tag{2.13}$$

$$X_2 = \frac{x - l_p}{l_s} \tag{2.14}$$

$$X_{3} = \frac{x - l_{p} - l_{s}}{l_{n}}$$
(2.15)

Equations (2.13) to (2.15) can be applied to Equations (2.4) to (2.12) to arrive at the transformed governing equations for the concentration profiles:

$$\varepsilon_{\rm p} \frac{\partial c}{\partial t} = \frac{1}{l_p} \frac{\partial}{\partial X_1} \left[ \frac{D_{\rm eff,p}}{l_p} \frac{\partial c}{\partial X_1} \right] + a_{\rm p} \left( 1 - t_+ \right) j_{\rm p} \qquad 0 < X_1 < 1$$
(2.16)

$$\varepsilon_s \frac{\partial c}{\partial t} = \frac{1}{l_s} \frac{\partial}{\partial X_2} \left[ \frac{D_{\text{eff},s}}{l_s} \frac{\partial c}{\partial X_2} \right] \qquad \qquad 0 < X_2 < 1$$
(2.17)

$$\varepsilon_n \frac{\partial c}{\partial t} = \frac{1}{l_n} \frac{\partial}{\partial X_3} \left[ \frac{D_{\text{eff},n}}{l_n} \frac{\partial c}{\partial X_3} \right] + a_n \left( 1 - t_+ \right) j_n \qquad 0 < X_3 < 1$$
(2.18)

While the boundary conditions become

$$\frac{\partial c}{\partial X_1}\Big|_{X_1=0} = 0 \tag{2.19}$$

$$-\frac{D_{\text{eff,p}}}{l_p}\frac{\partial c}{\partial X_1}\Big|_{X_1=1} = -\frac{D_{\text{eff,s}}}{l_s}\frac{\partial c}{\partial X_2}\Big|_{X_2=0}$$
(2.20)

 $c|_{X_1=1} = c|_{X_2=0}$ (2.21)

$$c|_{X_2=1} = c|_{X_3=0}$$
(2.22)

$$-\frac{D_{\text{eff,s}}}{l_s}\frac{\partial c}{\partial X_2}\Big|_{X_2=1} = -\frac{D_{\text{eff,n}}}{l_n}\frac{\partial c}{\partial X_3}\Big|_{X_3=0}$$
(2.23)

$$\frac{\partial c}{\partial X_3}|_{X_3=1} = 0 \tag{2.24}$$

From Equations (2.16) to (2.24), it is clear that  $X_1$ ,  $X_2$ , and  $X_3$  are independent variables that can be replaced by a single dummy variable X, though we must differentiate between variables in the different regions (i.e. c is replaced by  $c_p$ ,  $c_s$ , or  $c_n$  for concentration in the positive electrode, separator and the negative electrode, respectively).

$$\varepsilon_{p} \frac{\partial c_{p}}{\partial t} = \frac{1}{l_{p}} \frac{\partial}{\partial X} \left[ \frac{D_{\text{eff},p}}{l_{p}} \frac{\partial c_{p}}{\partial X} \right] + a_{p} \left( 1 - t_{+} \right) j_{p} \qquad 0 < X < 1$$
(2.25)

$$\varepsilon_s \frac{\partial c_s}{\partial t} = \frac{1}{l_s} \frac{\partial}{\partial X} \left[ \frac{D_{\text{eff},s}}{l_s} \frac{\partial c_s}{\partial X} \right] \qquad \qquad 0 < X < 1$$
(2.26)

$$\varepsilon_{n} \frac{\partial c_{n}}{\partial t} = \frac{1}{l_{n}} \frac{\partial}{\partial X} \left[ \frac{D_{\text{eff,n}}}{l_{n}} \frac{\partial c_{n}}{\partial X} \right] + a_{n} \left( 1 - t_{+} \right) j_{n} \qquad 0 < X < 1$$
(2.27)

#### With the boundary conditions

$$\frac{\partial c_p}{\partial X}|_{X=0} = 0 \tag{2.28}$$

$$-\frac{D_{\text{eff,p}}}{l_p}\frac{\partial c_p}{\partial X}\Big|_{X=1} = -\frac{D_{\text{eff,s}}}{l_s}\frac{\partial c_s}{\partial X}\Big|_{X=0}$$
(2.29)

$$c_{p}|_{X=1} = c_{s}|_{X=0}$$
(2.30)

$$c_{s}|_{X=1} = c_{n}|_{X=0}$$
(2.31)

$$-\frac{D_{\text{eff,s}}}{l_s}\frac{\partial c_s}{\partial X}|_{X=1} = -\frac{D_{\text{eff,n}}}{l_n}\frac{\partial c_n}{\partial X}|_{X=0}$$
(2.32)

$$\frac{\partial c_n}{\partial X}|_{X=1} = 0 \tag{2.33}$$

A similar process is performed on the remaining variables and the resulting equations and boundary conditions are given in Table 2-1. Note that this coordinate transformation is used in the remainder of this thesis.

Governing Equations	Boundary Conditions				
Positive Electrode					
$\varepsilon_{p} \frac{\partial c_{p}}{\partial t} = \frac{1}{l_{p}} \frac{\partial}{\partial X} \left[ \frac{D_{\text{eff},p}}{l_{p}} \frac{\partial c_{p}}{\partial X} \right] + a_{p} \left( 1 - t_{+} \right) j_{p}$	$\frac{\partial c_p}{\partial X} _{X=0} = 0$	$\frac{-D_{\text{eff,p}}}{l_p}\frac{\partial c_p}{\partial X} _{X=1} = \frac{-D_{\text{eff,s}}}{l_s}\frac{\partial c_s}{\partial X} _{X=0}$			
$\frac{-\sigma_{\text{eff,p}}}{l_p} \frac{\partial \Phi_{2,p}}{\partial X} - \frac{\kappa_{\text{eff,p}}}{l_p} \frac{\partial \Phi_{2,p}}{\partial x} + \frac{2\kappa_{\text{eff,p}}RT}{F} \frac{(1-t_+)}{l_p} \frac{\partial \ln c_p}{\partial x} = I$	$\frac{\partial \Phi_{2,p}}{\partial X} _{X=0} = 0$	$\frac{-\kappa_{\text{eff,p}}}{l_p} \frac{\partial \Phi_{2,p}}{\partial X} \Big _{X=1} = \frac{-\kappa_{\text{eff,s}}}{l_s} \frac{\partial \Phi_{2,s}}{\partial X} \Big _{X=0}$			
$\left[\frac{1}{l_p}\frac{\partial}{\partial X}\left[\frac{\sigma_{\rm eff,p}}{l_p}\frac{\partial}{\partial X}\Phi_{1,p}\right]=a_{\rm p}Fj_{\rm p}$	$\frac{1}{l_p} \frac{\partial \Phi_{1,p}}{\partial X}  _{X=0} = -\frac{I}{\sigma_{eff,p}}$	$\frac{\partial \Phi_{1,p}}{\partial X} _{X=1} = 0$			
$\frac{d}{dt}c_p^{s,avg} = -3\frac{j_p}{R_p}$					
$\frac{D_p^s}{R_p} \left( c_p^{s,surf} - c_p^{s,avg} \right) = -\frac{j_p}{5}$					
Separator					
$\varepsilon_{s} \frac{\partial c_{s}}{\partial t} = \frac{1}{l_{s}} \frac{\partial}{\partial X} \left[ \frac{D_{\text{eff},s}}{l_{s}} \frac{\partial c_{s}}{\partial X} \right]$	$c_p \mid_{X=1} = c_s \mid_{X=0}$	$c_{s} _{X=1} = c_{n} _{X=0}$			
$\frac{-\kappa_{\rm eff,s}}{l_s}\frac{\partial\Phi_{2,s}}{\partial X} + \frac{2\kappa_{\rm eff,s}RT}{F}\frac{(1-t_{\star})}{l_s}\frac{\partial\ln c_s}{\partial X} = I$	$\Phi_{2,p} \mid_{X=1} = \Phi_{2,s} \mid_{X=0}$	$\Phi_{2,s} \mid_{X=1} = \Phi_{2,n} \mid_{X=0}$			
Negative Electrode					
$\varepsilon_n \frac{\partial c_n}{\partial t} = \frac{1}{l_n} \frac{\partial}{\partial X} \left[ \frac{D_{\text{eff,n}}}{l_n} \frac{\partial c_n}{\partial X} \right] + a_n \left( 1 - t_+ \right) j_n$	$\frac{\partial c_n}{\partial X} _{X=1} = 0$	$\frac{-D_{\text{eff,s}}}{l_s}\frac{\partial c_s}{\partial X}\Big _{X=1} = \frac{-D_{\text{eff,n}}}{l_n}\frac{\partial c_n}{\partial X}\Big _{X=0}$			
$\begin{bmatrix} \frac{-\sigma_{\text{eff,n}}}{l_n} \frac{\partial \Phi_{1,n}}{\partial X} - \frac{\kappa_{\text{eff,n}}}{l_n} \frac{\partial \Phi_{2,n}}{\partial X} + \\ \frac{2\kappa_{\text{eff,n}} RT}{F} \frac{(1-t_+)}{l_n} \frac{\partial \ln c_n}{\partial X} = I \end{bmatrix}$	$\Phi_{2,n} _{x=1}=0$	$\frac{-\kappa_{\text{eff,s}}}{l_s} \frac{\partial \Phi_{2,s}}{\partial X}  _{X=1} = \frac{-\kappa_{\text{eff,p}}}{l_n} \frac{\partial \Phi_{2,n}}{\partial X}  _{X=0}$			
$\frac{1}{l_n}\frac{\partial}{\partial X}\left[\frac{\sigma_{\rm eff,n}}{l_n}\frac{\partial}{\partial X}\Phi_{1,n}\right] = a_n F j_n$	$\frac{\partial \Phi_{1,n}}{\partial X} _{X=0} = 0$	$\frac{1}{l_n} \frac{\partial \Phi_{1,n}}{\partial X} \Big _{X=1} = -\frac{I}{\sigma_{eff,n}}$			
$\frac{d}{dt}c_n^{s,avg} = -3\frac{j_n}{R_n}$					
$\frac{D_n^s}{R_n} \left( c_n^{s, surf} - c_n^{s, avg} \right) = -\frac{j_n}{5}$					

 Table 2-1:
 Transformed governing equations for the P2D model

## 2.3 Model Reformulation Using Cosine Collocation

Here we focus on using spectral methods to discretize the spatial coordinates of the P2D model, specifically by using orthogonal collocation. The theory of orthogonal collocation is well established and stability theory has been discussed in the literature.<sup>46-48</sup> A brief background on orthogonal collocation is provided here while a more detailed description is provided in Appendix B.

#### 2.3.1 Development of DAEs Using Cosine Collocation

In order to set up a system of DAEs, the proposed reformulation discretizes the model in the *x*-direction while maintaining the time dependence to allow for the implementation of efficient time-adaptive solvers. Although this can be achieved using a variety of approaches, including finite difference, here each variable of interest is approximated by a summation of trial functions of the form:

$$u(X,t) = F(X,t) + \sum_{k=0}^{N} B_k(t) T_k(X)$$
(2.34)

Where u(X,t) is the variable of interest,  $T_k(X)$  are the chosen trial functions with homogenous boundary conditions, F(X,t) is a function chosen to satisfy the (time-dependent) boundary conditions, and  $B_k(t)$  are the coefficients of the trial functions. The only requirement of the trial functions is that they all be linearly independent. However, the choice of trial functions does affect the accuracy of the final solution, and a proper choice can improve convergence. For this model, the homogeneous trial functions are typically selected to be cosine functions while the boundary conditions are satisfied by linear and quadratic terms. The coordinate transformation discussed in Section 2.2 allows the cosine trial functions to be applied in a simple form of  $\cos(k\pi X)$  for each variable.

Positive Electrode
$c_{p}(X,t) = A_{p,c}(t)X^{2} + \sum_{k=0}^{N_{p}} B_{p,c,k}(t)\cos(k\pi X)$
$\Phi_{2,p}(X,t) = A_{p,\Phi_2}(t)X^2 + \sum_{k=0}^{N_p} B_{p,\Phi_2,k}(t)\cos(k\pi X)$
$\Phi_{1,p}(X,t) = \frac{i_{app}l_p}{\sigma_{eff,p}} \left[ \frac{1}{2} X^2 - X \right] + \sum_{k=0}^{N_p} B_{p,\Phi_1,k}(t) \cos(k\pi X)$
$c_{p}^{s,surf}(X,t) = \sum_{k=0}^{N_{p}} B_{p,c^{s,surf},k}(t) \cos(k\pi X)$
$c_{p}^{s,avg}(X,t) = \sum_{k=0}^{N_{p}} B_{p,c^{s,avg},k}(t) \cos(k\pi X)$
Separator
$c_{s}(X,t) = A_{s,c,1}(t)X + A_{s,c,2}(t)X^{2} + \sum_{k=0}^{N_{s}} B_{s,c,k}(t)\cos(k\pi X)$
$\Phi_{2,s}(X,t) = A_{s,\Phi_2,1}(t)X + A_{s,\Phi_2,2}(t)X^2 + \sum_{k=0}^{N_s} B_{s,\Phi_2,k}(t)\cos(k\pi X)$
Negative Electrode
$c_n(X,t) = A_{n,c}(t)(X-1)^2 + \sum_{k=0}^{N_n} B_{n,c,k}(t)\cos(k\pi X)$
$\Phi_{2,n}(X,t) = A_{n,\Phi_2}(t)(X-1)^2 + \sum_{k=0}^{N_n} B_{n,\Phi_2,k}(t) \cos\left[\left(k+\frac{1}{2}\right)\pi X\right]$
$\Phi_{1,n}(X,t) = -\frac{i_{app}l_n}{\sigma_{eff,n}} \left[\frac{1}{2}X^2\right] + \sum_{k=0}^{N_n} B_{n,\Phi_1,k}(t)\cos(k\pi X)$
$c_n^{s,surf}(X,t) = \sum_{k=0}^{N_n} B_{n,c^{s,surf},k}(t) \cos(k\pi X)$
$c_n^{s,avg}(X,t) = \sum_{k=0}^{N_p} B_{n,c^{s,avg},k}(t) \cos(k\pi X)$

Table 2-2: Approximate forms of equations using cosine collocation

The approximate form of each variable is given in Table 2-2. For the variables with nonhomogeneous boundary conditions, an additional linear and/or quadratic term is added to the approximate solution to satisfy the boundary conditions. This allows the boundary conditions to be applied analytically before applying the time-adaptive DAE solver. For example, the liquid phase concentration is approximated by the equations:

$$c_{p}(X,t) = A_{p,c}(t)X^{2} + \sum_{k=0}^{N_{p}} B_{p,c,k}(t)\cos(k\pi X)$$
(2.35)

$$c_{s}(X,t) = A_{s,c,1}(t)X + A_{s,c,2}(t)X^{2} + \sum_{k=0}^{N_{s}} B_{s,c,i}(t)\cos(k\pi X)$$
(2.36)

$$c_n(X,t) = A_{n,c}(t)(X-1)^2 + \sum_{k=0}^{N_n} B_{n,c,k}(t)\cos(k\pi X)$$
(2.37)

for the positive electrode, the separator, and the negative electrode, respectively. For the roughest approximation, let  $N_p = N_s = N_n = 1$ . In this case Equations (2.35) to (2.37) become

$$c_{p}(X,t) = A_{p,c}(t)X^{2} + B_{p,c,0}(t) + B_{p,c,1}(t)\cos(\pi X)$$
(2.38)

$$c_{s}(X,t) = A_{s,c,1}(t)X + A_{s,c,2}(t)X^{2} + B_{s,c,0}(t) + B_{s,c,1}(t)\cos(\pi X)$$
(2.39)

$$c_n(X,t) = A_{n,c}(t)(X-1)^2 + B_{n,c,0}(t) + B_{n,c,1}(t)\cos(\pi X)$$
(2.40)

It should be pointed out that there are no lithium ions leaving or entering the cell sandwich, so the flux at both ends of the cell is set to zero. These boundary conditions are included in the original form above by choosing the linear and quadratic terms appropriately. For example, in Equation (2.35) there is no linear term for the concentration of the electrolyte in the positive electrode so that the derivative,  $\frac{\partial}{\partial X}c_p(X,t)$ , is zero at the current collector located at X = 0, while holding no such restrictions at the positive electrode-separator interface. Similarly, the  $(X-1)^2$  term accomplishes the same effect in Equation (2.37) for the negative electrode. The equations given in Table 2-2 have been developed by considering the boundary conditions for each variable in the same manner as described above. The coefficients of the linear and quadratic terms,  $A_{r,v}(t)$ , are determined by requiring that each variable be continuous at both electrodeseparator interfaces, while also maintaining a continuous flux.

By applying continuity boundary conditions, it is possible to analytically solve for these coefficients simultaneously in terms of the coefficients of the trial functions. This is shown below for the positive electrode in which only a single cosine term is used, though this procedure can be applied for any number of trial functions used, for every region, and for every variable of interest. For example, it can be shown that the coefficient of the quadratic term from Equation (2.38) is related to the remaining coefficients by

$$A_{p,c}(t) = -B_{p,c,0}(t) + B_{p,c,1}(t) + B_{s,c,0}(t) + B_{s,c,1}(t)$$
(2.41)

Therefore the concentration equation for the positive electrode can be written as:

$$c_{p}(X,t) = (-B_{p,c,0}(t) + B_{p,c,1}(t) + B_{s,c,0}(t) + B_{s,c,1}(t))X^{2} + B_{p,c,0}(t) + B_{p,c,1}(t)\cos(\pi X)$$
(2.42)

This process is then repeated for each of the other unknowns  $(\Phi_1, \Phi_2, c^{s,avg})$  in each electrode, and the separator, when applicable. The final form of the approximated solutions (including solving for the  $A_{r,v,i}(t)$ 's in terms of the  $B_{r,v,i}(t)$ 's) are not shown due to the large number of terms present as each  $A_{r,v,i}(t)$  may be a function of up to six  $B_{r,v,i}(t)$ 's when using a single cosine term.

The coefficients of the trial function,  $B_{r,v,i}(t)$ , must be determined in order to give the best possible approximation of the solution to the twelve governing equations. This is done using the Method of Weighted Residuals (MWR).<sup>47</sup> This method solves for the coefficients,  $B_{r,v,i}(t)$ , by

setting the integral of the residual multiplied by a weight function to zero. By using an adequate number of independent weight functions, enough independent equations can be developed to solve for the unknown coefficients. Collocation is a specific version of the MWR in which the weight functions are Dirac delta functions, so that the governing equations are exactly satisfied as specified collocation points. Orthogonal collocation refers to the collocation method in which the collocation points are chosen as zeros of orthogonal polynomials, which has been shown to give better results.<sup>46-48</sup> A detailed discussion on the method of weighted residuals is given in Appendix B

It should be noted here that there is no requirement that the variables in different regions be approximated by the same number of terms. However, all the variables in a single region must be represented by the same number of terms. For example, if the concentration profile in the positive electrode is approximated using two cosine terms, the liquid and solid phase potentials must also be approximated by two cosine terms in the positive electrode with the same collocation points, but the concentration profile in the separator may be represented by any number of terms.

In development of the DAEs to be used to solve for the coefficients, each governing equation must be accounted for individually so that there are as many residual equations for each governing equation as there are coefficients to be solved in that region. For instance, if the variables in the positive electrode are represented by a single cosine term, the average solid phase concentration is approximated by

$$c_{p}^{s,avg}(X,t) = B_{p,c^{s,avg},0}(t) + B_{p,c^{s,avg},1}(t)\cos(\pi X)$$
(2.43)

Therefore, two collocation points are needed to solve for the two unknowns,  $B_{p,c^{s,avg},0}(t)$  &  $B_{p,c^{s,avg},1}(t)$ . The residuals are calculated using each of the five governing equations in the

positive electrode. Since each residual is defined to be zero at two node points from the orthogonal collocation method, we have now developed a system of 10 DAEs to solve for the 10 unknown coefficients in the positive electrode. This must be repeated for each of the other two regions as well. In the case that each variable in all three regions are approximated by a single cosine term, there are 10 DAEs in both the positive and negative electrodes, and four DAEs in the separator for a total of 24 coupled DAEs that must be solved simultaneously.

In general terms, the dependent variables in the positive electrode, the separator, and the negative electrodes are represented by  $N_p$ ,  $N_s$ , and  $N_n$  cosine terms respectively. Each variable thus has  $N_r$ +1 coefficients that must be determined in each region, where r denotes the region, and therefore  $N_r$ +1 residuals must be calculated. This results in  $N_r$ +1 DAEs for each variable. Since there are 5 governing equations (and 5 variables) for the positive and negative electrodes and 2 governing equations in the separator we have a total of  $5(N_p + 1) + 2(N_s + 1) + 5(N_n + 1)$  DAEs that must be solved simultaneously.

These equations are functions of time only, some of which are ordinary differential equations (ODEs) in time, while the remaining are algebraic equations. Solving this system of differential algebraic equations (DAEs) is not trivial, and the algebraic variables must be initialized prior to solving to ensure that the initial conditions are consistent with the governing algebraic equations, and is a reason numerical simulations often fail for battery models. Once initialization is complete, this system can be solved using FORTRAN with the help of time-adaptive solvers such as DASSL or DASKR.<sup>27,30</sup>

Once the coefficients are determined, the unknown variables are represented by continuous functions valid at any position in the cell. This is in contrast to a solution obtained using a finite difference approach in which the variable is only determined at discrete node points and would require interpolation methods to find the solution between two node points. Also, orthogonal collocation converges to a solution with an error on the order of  $h^{2N}$ , where *N* is the number of collocation points and *h* is the node spacing.<sup>46</sup> A typical finite difference solution that is typically used has error on the order of  $h^2$ , though higher order schemes are possible. Although the resulting equations are more complicated when using orthogonal collocation, fewer terms are required for a meaningful solution, resulting in fewer DAEs that must be solved and a net reduction in computation time. <sup>46</sup>

This reformulation makes no assumptions of the form of any parameter used in any of the equations. There are no requirements that neither the diffusion coefficients, nor the conductivities are constant or linear, and successful results have been obtained using diffusion coefficients which are functions of the electrolyte concentration and temperature. This model is also versatile enough to work under galvanostatic, potentiostatic, and constant power conditions, even for continuous cell charge-discharge cycles. This model also does not assume a particular chemistry and has proven to be robust for different chemistries involving a variety of open circuit potentials and battery design parameters. Importantly, as we have chosen the polynomials in the region 0 to 1, globally convergent profiles can be obtained for any condition by increasing the number of terms in the series.

#### 2.3.2 Model Reformulation

Further reformulations can be done to improve computation time by eliminating the need to numerically solve for the solid phase surface concentration while using the polynomial approximation for the solid phase. Once the remaining variables have been approximated by a series solution, it is possible to analytically solve for  $c_s^{surf}$  in terms of these variables. First, the pore wall flux,  $j_i$ , can be determined by rearranging Equation (2.3) above to give:

$$j_{i} = -5 \frac{D_{solid,i}}{R_{i}} \left( c_{i}^{s,surf} - c_{i}^{s,avg} \right) \qquad \qquad i = p,n$$
(2.44)

Consider the solid phase governing equation from Table 2-1

$$\frac{1}{l_i} \frac{\partial}{\partial X} \left[ \frac{\sigma_{eff,i}}{l_i} \frac{\partial}{\partial X} \Phi_{1,i} \right] = a_i F j_i \qquad i = p, n \qquad (2.45)$$

Equation (2.44) can be inserted into Equation (2.45) to give the following equation:

$$\frac{1}{l_i}\frac{\partial}{\partial X}\left[\frac{\sigma_{eff,i}}{l_i}\frac{\partial}{\partial X}\Phi_{1,i}\right] = -a_iF\frac{5D_i^s}{R_i}\left(c_i^{s,surf} - c_i^{s,avg}\right) \qquad \qquad i = p,n$$
(2.46)

From this the surface concentration can be solved in terms of the average solid phase concentration and the solid phase potential, assuming the solid phase conductivity,  $\sigma_{eff}$ , is a constant:

$$c_i^{s,surf} = c_i^{s,avg} - \frac{\sigma_{eff,i}R_i}{5a_iFD_i^s l_i^2} \frac{\partial^2 \Phi_1}{\partial X^2} \qquad \qquad i = p,n$$
(2.47)

At this point, the focus will be limited to the positive electrode for demonstration purposes. From Table 2-2, the solid phase potential,  $\Phi_{1,p}$  and solid phase average concentration,  $c_p^{s,avg}$ , have a series solution given by

$$\Phi_{1,p} = \frac{i_{app}l_p}{\sigma_{eff,p}} \left[ \frac{1}{2} X^2 - X \right] + \sum_{k=0}^{N_p} B_{p,\Phi_1,k} \left( t \right) \cos(k\pi X)$$
(2.48)

$$c_{p}^{s,avg} = \sum_{k=0}^{N_{p}} B_{p,c_{p}^{s,avg},k}(t) \cos(k\pi X)$$
(2.49)

By inserting Equations (2.48) and (2.49) into Equation (2.47), the solid phase surface concentration can be immediately written as

$$c_{p}^{s,surf} = -\frac{R_{p}i_{app}}{5a_{p}FD_{i}^{s}l_{p}} + B_{p,c^{s,avg},0}(t) + \sum_{k=1}^{N_{p}} \left\{ B_{p,c^{s,avg},k}(t) - \frac{\sigma_{eff,p}R_{p}R_{p}k^{2}\pi^{2}}{5a_{p}FD_{i}^{s}l_{p}^{2}} B_{p,\Phi_{1},k}(t) \right\} \cos(k\pi X)$$
(2.50)

By solving for the surface concentration analytically in terms of the other variables, we can eliminate the need to solve for two of the twelve unknowns (one from each electrode), resulting in fewer DAEs that must be solved. However, if the solid phase conductivity,  $\sigma_{eff}$ , is a function of *x* or is nonlinear, this reformulation cannot be performed.

#### 2.3.3 Results and Discussion

The model prediction obtained using a collocation reformulation using a varying number of terms is compared to a full-order finite difference solution based on 50 node points in x for the electrodes and 35 node points for the separator. The primary curve of interest is the discharge curve in Figure 2-2(a), which shows the full-order finite difference solution, as well as four solutions obtained using increasingly accurate orthogonal collocation approaches for a 1C rate of discharge. Figure 2-2(b) shows the residuals of the orthogonal collocation solutions relative to the finite difference solution, while Table 2-3 shows a comparison of the root mean squared error as well as computation time. The least accurate collocation solution is obtained by using only one cosine term for each region, as shown by the solid line in Figure 2-2. Progressively more accurate solutions can be obtained by using orthogonal collocation with a greater number of terms. Figure 2-2 also shows collocation solutions obtained using (3, 2, 3) terms (long dashed line), (5, 3, 5) terms (short dashed line), and (7,3,7) terms (dash-dot line). Note that the nomenclature,  $(N_p, N_s, N_n)$ , is used to represent the number of cosine terms used in the positive electrode, the separator, and the negative electrode, respectively. Experimental validation of the porous electrode pseudo-2D model can be found elsewhere in the literature.<sup>3-13</sup> Therefore an established solution method using finite difference was used to validate the reformulated model presented in this paper.



Figure 2-2: (a) Voltage-time curves for a 1C constant current discharge (b) Residual plot of collocation solutions vs. finite difference

Figure 2-3(a) and Figure 2-4 show that the electrolyte concentration at the end of discharge increases across the battery from the positive electrode to the negative electrode. These figures also show that the concentration in the positive electrode decreases during discharge, while it increases in the negative electrode, as lithium metal stored in the anode comes out of the active solid particle and reacts at the surface to produce lithium-ions causing an increase in local lithium salt concentration in the electrolyte. At higher rates of discharge, more lithium ions are released at the anode and absorbed in the cathode, increasing the concentration gradient.



Figure 2-3: Variable values at the current collector/cathode interface  $(\circ)$ , the cathode/separator interface  $(\Box)$ , the separator/anode interface  $(\Delta)$ , and the anode/current collector interface  $(\diamond)$  for (a) electrolyte concentration (b) liquid phase potential (c) solid phase potential (d) solid phase surface concentration and (e) solid phase average concentration. The markers represent the finite difference solution, the dash-dot line for (1, 1, 1) collocation, the short dashed line for the (3, 2, 3) collocation, and the long dash line for (5, 3, 5)

The primary advantage of this method is the speed of simulation, which arises because a relatively few number of terms are required to obtain a converged solution. Table 2-3 shows the simulation time when using various numbers of collocation points, as well as the root mean squared error relative to the finite difference solution. The times are presented using a FORTRAN based DASSL solver, as well as a Maple<sup>49</sup> solver for all simulations performed.



Figure 2-4: Electrolyte concentration across battery for (1, 1, 1) collocation (dashed line), (3, 2, 3) collocation (dotted line), and (5, 3, 5) collocation (solid line) in (a) transformed coordinates and (b) natural coordinates at 3500 seconds of discharge.

All simulations were performed using a 3.33. GHz, 24 GB RAM machine. Rates of discharge greater than a 1C rate were simulated using the mixed finite difference reformulation for the solid phase concentration in order to accurately track the battery behavior at high rates of discharge. However, the additional number of equations resulting from the mixed finite difference solution results in slower computation, as can be seen in Table 2-3. Note also that more terms were required to achieve a converged solution when analyzing greater rates. In order to quantify convergence of the series, the maximum magnitude of the coefficients of successive terms must be analyzed. This is shown in Figure 2-5Figure 2-5: Normalized maximum magnitude of coefficients for equations in Table 2-2 for (5,3,5) collocation for the cathode (long dash), separator (dash-dot), and anode (short dash)., indicating that the first terms are dominant and that the system converges. Interestingly, the later terms for describing the solid phase concentration carry more weight than for the other variables (although still significantly less than the first term).

Method	Number of Differential Algebraic Equations	Simulation Time (Maple) (ms)	Simulation Time (DASSL) (ms)	RSME (mV)
Finite Difference	590	$N/A^1$	4617	
(50,35,50)				
Orthogonal Collocation (1,1,1)	20	781	46	17.84
Orthogonal Collocation (3,2,3)	38	2355	78	5.46
Orthogonal Collocation (5,3,5)	56	6022	109	1.56
Orthogonal Collocation (7,3,7)	72	9812	156	0.57
1C Rate MFD	136	28361	530	0.91
(7,3,7) Collocation				
2C Rate MFD	136	24680	312	$6.18^2$
(7,3,7) Collocation				
5C Rate MFD	170	38548	250	$5.29^2$
(9,4,9) Collocation				
10C Rate MFD	204	64381	218	$9.42^2$
(11,4,11) Collocation				

Table 2-3: Simulation time and Root Mean Squared Error compared to FD

<sup>1</sup>The full order finite difference failed when using Maple solvers <sup>2</sup>The 2C, 5C, and 10C rates were compared to a full order MFD finite difference formulation which used 982 equations that took 2106 to 4040 ms to run using DASSL

The behavior of the coefficients for the liquid phase concentration and potential in the separator are nearly completely determined by the constant term alone. In fact, the weight of this term is in excess of 99.99%. This can be explained by analyzing the governing equations for the separator given in Table 1-2:

$$\varepsilon_s \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff},s} \frac{\partial c}{\partial x} \right]$$
(2.51)

$$-\kappa_{\rm eff,s} \frac{\partial \Phi_2}{\partial x} + \frac{2\kappa_{\rm eff,s} RT}{F} (1 - t_+) \frac{\partial \ln c}{\partial x} = I$$
(2.52)



Figure 2-5: Normalized maximum magnitude of coefficients for equations in Table 2-2 for (5,3,5) collocation for the cathode (long dash), separator (dash-dot), and anode (short dash).

If diffusion occurs quickly enough relative to the change in boundary conditions from the electrodes (which would be expected considering the small thickness of the region), the time derivative term in Equation (2.51) would approach 0. This leads to a linear concentration profile in the separator if the diffusivity is a constant. Therefore, the cosine terms of electrolyte concentration approximation from Table 2-2 would not contribute much to the final approximation. If the concentration is nearly linear and the reciprocal of concentration is nearly constant, the second term of Equation (2.52) will be nearly constant. Since the liquid phase conductivity,  $\kappa_{eff,s}$ , is only a weak function of concentration, and the concentration does not vary appreciably across the separator (see Figure 2-4), the conductivity will also remain nearly constant. This would lead to a linear profile for the liquid phase potential across the separator. This allows very good accuracy to be retained, even if no cosine terms are used in the separator.

A similar pattern emerges for the solid phase potential in the positive and negative electrodes, with the coefficient of the constant term dominating the cosine terms with a weight of

over 99.99%. This suggests that the solid phase potential could be approximated accurately with only the constant term, further reducing the computation required and improving computational speed. However, to implement this would require the procedure used to be adjusted, as it is required that the collocation points be identical for each variable in the current form. Preliminary attempts to limit the number of terms for the solid phase potential while maintaining a greater number of terms for the remaining variables have been unsuccessful. In our opinion, this is due to the fact that although  $\Phi_1$  has a nearly flat profile, the current density does have a significant profile across the electrode due to the relatively large conductivities



Figure 2-6: Current-Time and Voltage-Time curve for two continuous cycles consisting of constant power discharge followed by constant current charge and constant potential charge

The proposed approach has been used to estimate the values of internal parameters from experimental discharge curves. Also, this approach can simulate continuous battery cycling operation which undergoes constant current/power discharging followed by constant current charging and constant potential charging. This demonstrates the versatility of this method to simulate a wide variety of operating conditions. Figure 2-6 shows two such cycles which are subject to a constant power discharge of 120 W/m<sup>2</sup> a constant current charge of 25 A/m<sup>2</sup>,

followed by a constant potential charge at 4.1 V. For comparison, a 1C rate corresponds to ~30  $A/m^2$  using this chemistry. Note that the current state of the internal variables within the battery is carried over from the end of each cycle to the next cycle. Because the internal variables change with time, the behavior of the battery during these cycles is not necessarily identical, perhaps due to incomplete charging of the battery. Also, the internal parameters, such as porosity, etc. can be made to change with cycle number. Therefore, as developments continue in the understanding of capacity fade this continuous cycling procedure can predict the future behavior of the battery by the parameters already included, either changing or by introducing additional parameters/mechanisms specifically to address capacity fade. This may be achieved by modifying the continuum model directly, or by coupling the continuum model with microscopic models, such as Kinetic Monte Carlo<sup>50-54</sup> or Stress-Strain models<sup>55-57</sup> to create a true multiscale model.



Figure 2-7: Voltage-Time curves for higher rates of discharge

This method can also be used when higher rates of discharge are applied. However, in those circumstances, it is necessary to use the mixed finite difference approximation for the solid phase concentration,<sup>39</sup> rather than the parabolic profile used in the majority of this paper while

describing a 1C discharge. The basic method presented for reformulation in the *x*-direction, however, is valid for both parabolic profile approximation and for the mixed finite difference approach. The normalized discharge curves are given in Figure 2-7 for 2C, 5C, and 10C rates of discharge, with mixed-finite difference reformulation for the solid-phase concentration. Table 2-3 shows the computation time required to simulate the higher discharge conditions, as well as the RMSE of the voltage-time curve relative to a full finite difference. Also, more node points were required to accurately simulate a higher rate discharge when using collocation. However, even when a greater number of node points are used, the simulation time is reduced by increasing the rate of discharge because the battery reaches a fully discharged state in less time.

## 2.4 Model Reformulation Using Chebyshev Collocation

Using cosines as trial functions as described in Section 2.3 worked well in many cases, but several limitations arose under certain conditions. Primarily, oscillations in the approximate solutions became severe when many terms were used in Table 2-2, limiting the accuracy achievable during simulation when more than about 13 terms in the series were used. These limitations implicitly prevented the simulation of high charging and discharging rates, as higher rates of charge require greater accuracy due to the more complicated and non-linear profiles that arise. This motivated the desire to examine other approaches to take advantage of the properties of orthogonal collocation. Thus, the use of Chebyshev polynomials as the trial functions in the series solutions rather than trigonometric functions was attempted. It was found that the oscillations observed when using cosine collocation do not arise when using Chebyshev polynomials as more node points are used, allowing the numerical accuracy of the orthogonal collocation method to be fully realized.

Chebyshev polynomials are a set of orthogonal polynomials which can be defined from trigonometric functions:

$$T_n(x) = \cos\left(n \arccos\left(x\right)\right) \tag{2.53}$$

This gives Chebyshev polynomials many of the advantageous properties of Fourier series.<sup>48</sup> Practically, calculation of higher order Chebyshev polynomials can be performed using a recurrence relation. The first two Chebyshev polynomials are given as:

$$T_0(z) = 1$$
 (2.54)

$$T_1(z) = z \tag{2.55}$$

Higher order Chebyshev polynomials can be calculated from the recurrence relation:

$$T_{i}(z) = 2zT_{i-1}(z) - T_{i-2}(z)$$
(2.56)

As the Chebyshev polynomials are defined on the interval [-1,1], a change of variable is required to convert the domain to [0,1], as done in the previous work, where *X* is the dimensionless positions in the electrode or separator.<sup>29</sup>

$$z = 2X - 1 \tag{2.57}$$

Therefore, we use the following nomenclature to represent the rescaled Chebyshev polynomials

$$T'_{j}(X) = T_{j}(2X - 1)$$
(2.58)

#### 2.4.1 Development of DAEs Using Chebyshev Collocation

The fundamental idea of using orthogonal collocation with Chebyshev polynomials is the same as given in Section 2.3 and Appendix B. However, some differences do arise which must be addressed. Specifically, since Chebyshev polynomials do not inherently satisfy homogenous boundary conditions, the BCs must be handled in a slightly different way than described in Section 2.3.1, but can still be applied independently before the time solver is applied so that

additional equations do not need to be solved simultaneously. Extra linear and quadratic terms included in the series solutions would not be linearly independent, and are thus avoided. Therefore, additional Chebyshev polynomial terms are included to satisfy the BCs. The general series solution for the electrolyte potential and concentration, and solid phase potential (which require boundary conditions to be satisfied) takes the form of

$$u_{r,v}(X,t) = \sum_{i=0}^{N+2} B_{r,v,i}(t) T_i'(X)$$
(2.59)

where the subscripts r, v, i refer to the region (positive electrode, separator, or negative electrode), dependent variable (e.g. electrolyte concentration), and coefficient number, respectively, while  $u_{r,v}(X,t)$  refers to the profile of the specific dependent variable, v, in region r.

In this form, two of the coefficients  $(B_{r,v,i}(t))$  can be determined in terms of the remaining coefficients using the boundary conditions. The choice of which coefficients to solve for in this manner is somewhat arbitrary, provided that that the chosen ones can be used to satisfy the boundary conditions. For example,  $T_0(X)$  is a constant and cannot be used to specify flux boundary conditions, so  $B_{r,v,0}(t)$  cannot be reliably solved for because of the many flux conditions present in the P2D model. In the work presented here,  $B_{r,v,1}(t)$  and  $B_{r,v,2}(t)$  are determined directly using the BCs, but it should be noted that solving for other coefficients, such as  $B_{r,v,N+1}(t)$  and  $B_{r,v,N+2}(t)$ , does not significantly affect performance.

The variables which do not have spatial derivatives (and thus no boundary conditions), cannot use BC equations to increase the order of the series solution and thus are limited to using  $N^{\text{th}}$  order Chebyshev polynomials:

$$u(X,t) = \sum_{i=0}^{N} B_{r,v,i}(t) T_{i}'(X)$$
(2.60)

Equation (2.60) provides an applicable series approximation for the pore wall flux and the solid phase concentration. Using trial functions which are not homogeneous is advantageous for variables which do not have boundary conditions as it does not implicitly impose an artificial boundary condition on the numerical approximation. Imposing such a condition increases the difficulty of accurately representing the real solution and slows the rate of convergence. The series approximations used with Chebyshev trial functions are given in Table 2-4.

Table 2-4: Approximateformsofequationsusingcollocation	Chebyshev
$c_{r}(X,t) = \sum_{i=0}^{N_{r}+2} B_{r,c,i}(t)T_{i}(X)$	r = p, s, n
$\Phi_{2,r}(X,t) = \sum_{i=0}^{N_r+2} B_{r,\Phi_2,i}(t) T_i(X)$	r = p, s, n
$\Phi_{1,r}(X,t) = \sum_{i=0}^{N_p+2} B_{r,\Phi_1,i}(t) T_i(X)$	r = p, n
$j_{r}(X,t) = \sum_{i=0}^{N_{r}} B_{r,j_{r},i}(t) T_{i}(X)$	r = p, n
$c_{r}^{s,avg}(X,t) = \sum_{i=0}^{N_{r}} B_{r,c^{s,avg},i}(t)T_{i}(X)$	r = p, n

Unlike the reformulation given previously<sup>29</sup>, this modified version solves for the pore wall flux  $(j_p \text{ and } j_n)$  directly as series solution, rather than the surface solid phase concentration.

The choice of approach is largely a matter of preference. The parabolic profile approximation<sup>28</sup> for the solid phase concentration gives the surface concentration as:

$$c_r^{s,surf} = c_r^{s,avg} - \frac{j_r}{5} \frac{R_r}{D_{s,r}} \qquad r = p,n \qquad (2.61)$$

Recall that  $j_r$  and  $c_r^{s,avg}$  are series solutions, and thus  $c_r^{s,surf}$  is also a series solution. This approach is favored for several reasons. First, conceptually,  $c_r^{s,surf}$  and  $c_r^{s,avg}$  are clearly linked and often of similar value, so the second term in Equation (2.61) can be seen as a correction factor to calculate the surface concentration. Importantly, this shows that the variation between  $c_r^{s,surf}$  and  $c_r^{s,avg}$  is large at high rates, while at low rates  $c_r^{s,surf}$  and  $c_r^{s,avg}$  are nearly equal. Secondly, the profile of  $j_p$  and  $j_n$  varies significantly both in time and across the electrode. By having these variables be solved for directly as a series the solution is better able to track the moving front. Thirdly, when collocation is applied,  $j_p$  and  $j_n$  can be replaced as a single value in the resulting discretized equation (i.e. the value of  $j_p$  or  $j_n$  at the collocation point of interest).

#### 2.4.2 Results and Discussion

One of the principle flaws of the cosine collocation presented earlier was the oscillations which occurred when a high number of node points were used. These oscillations were especially prevalent in the estimate for the pore wall flux due to the particularly difficult profiles which arise. Such oscillations in the pore wall flux invariably leads to inaccuracies in the local SOC. Figure 2-8 shows the pore wall flux across the battery at four equispaced points in time (i.e. at 0% depth of discharge (DOD), 33% DOD, 67% DOD, and 100% DOD) during a 1C discharge as solved using a second-order finite difference with 75 interior node points in each electrode, and collocation with Chebyshev trial functions. Figure 2-9 shows the same results using cosine collocation. Note that the pore wall flux is negative in the cathode and positive in the anode during discharge. Cosine trial functions cause unacceptable oscillations in the numerical solution when many node points are used.



Figure 2-8: Pore wall flux profile across the cell for a 1C rate of discharge at 0%  $DOD(\Delta)$ , 33%  $DOD(\Box)$ , 67%  $DOD(\Diamond)$ , and 100%  $DOD(\circ)$  when using (1,1,1) Chebyshev collocation (dash-dotted line), (3,2,3) Chebyshev collocation (short dash line), (9,3,9) Chebyshev collocation (long dash line), (25,5,25) Chebyshev collocation (solid line). The converged finite difference approach is shown as markers.

Also note that using orthogonal collocation with cosine trial functions cannot capture the moving reaction zone exhibited by the pore wall flux, but Chebyshev polynomials can.

The increased diffusion resistances caused by the rapid depletion/saturation of lithium in the electrolyte at moderate to high rates cause a well-defined moving reaction zone to develop. Figure 2-10 demonstrates the moving front in the anode for a range of discharge rates using Chebyshev collocation. The reaction zone is more pronounced at high rates, while at low rates the variation across the electrode is relatively subdued. Additionally, at low rates, the majority of the electrode is can be utilized but only a small region is accessed at high rates, as the cutoff voltage is reached before much of the electrode is utilized.



Figure 2-9: Pore wall flux profile across the cell for a 1C rate of discharge at 0%  $DOD(\Delta)$ , 33%  $DOD(\Box)$ , 67%  $DOD(\langle \rangle)$ , and 100%  $DOD(\circ)$  when using (1,1,1) cosine collocation (dash-dotted line), (3,2,3) cosine collocation (short dash line), (9,3,9) cosine collocation (long dash line), (13,4,13) cosine collocation (solid line). The converged finite difference approach is shown as markers. Notice the severe oscillations that occur as more node points are used

During discharge, the rate of lithium ion production/consumption is greater than the rate of lithium-ion diffusion, creating a spatial variation of the electrolyte concentration, potential and solid phase concentration (which directly affects the local open circuit potential) across the electrode. Ultimately, these local effects affect the rate of the pore wall flux reaction across the electrode. At low rates diffusion plays a relatively minor role; the variation in reaction rates across the electrode is small and the system is primarily kinetically limited. At high rates, the diffusion resistance affects the behavior substantially and causes a large variation of the local reaction rates across the thickness of the electrode. This variation causes the regions of the electrodes nearest to the separator to become depleted or saturated to a greater extent than the regions near the current collectors, ultimately slowing the reaction and moving the reaction front deeper into the electrode. Thus, battery manufactures typically design batteries with thin electrodes for high power applications.



Figure 2-10: Pore wall flux for (a) 0.1C, (b) 0.5C, (c) 1C, (d) 3C, (e) 5C, and (f) 10C rates of discharge at 0% DOD ( $\Delta$ ), 33% DOD ( $\Box$ ), 67% DOD ( $\Diamond$ ), and 100% DOD ( $\circ$ ) using (25,5,25) Chebyshev collocation (update this figure to label the rates and times) Note that x=0 corresponds to the anode/separator interface. Note that the 10C solution uses a higher order approximation for the radial profile.

The profiles of the other dependent variables are shown in Figure 2-11 for a 1C rate of discharge and Figure 2-12 for a 5C rate of discharge. These tend to be smoother functions which tend to be easier to estimate using a series solution, and do not experience the same severe oscillations when cosine collocation is used. For example, the electrolyte concentration in each region can be estimated fairly well by a second order polynomial, as shown in Figure 2-11(a), despite the nonlinear generation term given by the pore wall flux (see Figure 2-8).



Figure 2-11: Profiles of internal variables for a 1C rate of discharge at 0% DOD ( $\Delta$ ), 33% DOD ( $\Box$ ), 67% DOD ( $\Diamond$ ), and 100% DOD ( $\circ$ ) when using (1,1,1) Chebyshev collocation (dash dot line), (3,2,3) Chebyshev collocation (short dash line), (9,3,9) Chebyshev collocation (long dash line), (25,5,25) Chebyshev collocation (solid line). The finite difference approach is shown as markers. The variables considered are the electrolyte concentration (a), electrolyte potential (b), solid phase potential (c), and local state of charge (d).


Figure 2-12: Profiles of internal variables for a 5C rate of discharge at 0% DOD ( $\Delta$ ), 33% DOD ( $\Box$ ), 67% DOD ( $\Diamond$ ), and 100% DOD ( $\circ$ ) when using (1,1,1) Chebyshev collocation (dash dot line), (3,2,3) Chebyshev collocation (short dash line), (9,3,9) Chebyshev collocation (long dash line), (25,5,25) Chebyshev collocation (solid line). The converged finite difference approach is shown as markers. The variables considered are the electrolyte concentration (a), electrolyte potential (b), solid phase potential (c), and local state of charge (d).

However, at high rates, the narrow reaction zone causes a more complicated profile to arise for the electrolyte concentration as the diffusion of lithium is not fast enough to completely smooth out the peak generation/consumption in the reaction zone as seen in Figure 2-12.The liquid phase potential shown in Figure 2-11(b) is quantitatively similar to the concentration. Figure 2-11(c) and Figure 2-12(c) give the solid phase potential and are nearly flat for all cases due to the relatively high conductivity and small thickness of the electrodes. Such flat profiles can be fairly easily approximated using numerical methods. Figure 2-11(d) and Figure 2-12(d) show the local SOC across the cell during discharge. The profile across the electrodes is essentially a time

integration the local pore wall flux. However, unlike the electrolyte concentration, the intercalated lithium cannot directly diffuse across the thickness of the electrode, leading to variations which do not dissipate. Also note that Figure 2-12(d) explicitly shows that a large fraction of the active material is not utilized when the cell is operated at a high rate of discharge.

#### 2.4.3 Error Analysis



Figure 2-13: Simulated discharge curves for 0.1C ( $\circ$ ), 0.5C ( $\Box$ ), 1C( $\diamond$ ), 3C ( $\Delta$ ) and 5C ( $\updownarrow$ )rates of discharge (1,1,1) Chebyshev collocation (dash-dot line), (3,2,3) Chebyshev collocation (short dash line), (9,3,9) Chebyshev collocation (long dash line), (25,5,25) Chebyshev collocation (solid line). The converged finite difference approach is shown as markers.

During battery operation, only the voltage difference can be experimentally measured easily; the internal variables cannot be directly measured. The convergence of the discharge curve is therefore considered important to quantify the accuracy of the solution. Figure 2-13 shows the discharge curves at five rates of discharge using an increasing number of collocation points while Figure 2-14 shows the root mean square error (RMSE) of the discharge curves as a function of average node spacing. Since an analytical solution does not exist, the RMSE must be

calculated relative to a solution of a higher order numerical solution which presumably has a negligible error compared the lower order models.

The RMSE values given in Figure 2-14 are calculated by comparison to both a full order finite difference solution with 75 node points in the electrodes and 35 points in the separator, and a collocation solution with 25 node points in the electrodes and 5 in the separator. Notice that the error converges continuously when compared to the collocation solution, but plateaus when compared to the finite difference solution. Since the solution is expected to get progressively more accurate as more terms are added (as we are not at machine precision, the existence of a plateau suggests that the error of the finite difference approximation is not negligible and is the primary contributing factor to the RMSE calculation for a high number of collocation points. Figure 2-15 shows the RMSE of both the finite difference solution and Chebyshev collocation as a function of the dimensionless node spacing on a log-log scale.



Figure 2-14: Root mean square error (RMSE) estimate for the discharge curve as a function of number of collocation terms used in the solution for 0.1C ( $\circ$ ), 0.5C ( $\Box$ ), 1C( $\diamond$ ), 3C ( $\Delta$ ) and 5C ( $\bigstar$ ). The short dash lines are the RMSEs as calculated by comparison with the full order finite difference solution while the long dashed lines are RMSEs as calculated by comparison with the highest order (25, 5, 25) collocation solution

Recall from Equation (B.8) that the collocation points are not equally spaced across the electrode, thus the "average node spacing" is calculated as simply the reciprocal of the number of node points. Figure 2-15 shows that the collocation approach is more accurate for a given node spacing, by at least an order of magnitude and often by several orders of magnitude. Notice that the error when using finite difference decreases linearly on a log-log scale as the node spacing is reduced, but the error from the collocation approach decreases superlinearly. This is established behavior when using Chebyshev collocation,<sup>48</sup> reflecting the  $h^{2N}$  order error (where *N* is the number of collocation points and *h* is the node spacing), that exists for orthogonal collocation.<sup>46</sup>



Figure 2-15: Root mean squared error of the discharge curves for a 1C rate as a function of average dimensionless node spacing using finite difference (long dash) and Chebyshev collocation (short dash). The RMSE was calculated relative to both the highest order Chebyshev solution ( $\Box$ ) and the finite difference solution with the smallest node spacing ( $\circ$ ).



Figure 2-16: Computational time to simulate a single 1C discharge as a function of number of node points using the finite difference approach ( $\circ$ ), cosine collocation ( $\Delta$ ), and Chebyshev collocation ( $\Box$ )

However, reducing the node spacing and improving the accuracy requires the calculation of the dependent variables at additional collocation points which increases the computational cost. The calculation time for simulating a 1C discharge is shown in Figure 2-16 using the FORTRAN solver DASKR<sup>58</sup> run on a 3.33. GHz, 24 GB RAM machine. Notice the simulation time is largely independent of rate of discharge, so the results given in Table 2-5 are for a 1C rate of discharge. The computation time increases exponentially as more node points are used, creating a tradeoff between the computational expense and the numerical accuracy.

The large number of node points required for an accurate finite difference solution reduces the feasibility of using such an approach where computational demand is limited. Figure 2-17 explicitly shows the tradeoff in computational cost and accuracy by comparing the simulation time on the abscissa and RMSE on the ordinate on a log-log scale. Importantly, the superlinear reduction of error seen when using Chebyshev collocation offsets the exponential increase in calculation time, showing a linear decrease (on a log-log scale) of the error as simulation time increases.

Table 2-5: Computation times and estimated errors for selected simulation runs for a 1C rate of discharge. (25,8,25) Chebyshev collocation is used for a baseline for calculating RMSE. The truncation and coefficient convergence errors are for the solid phase potential in the positive electrode.

Simulation	Simulation Time (ms)	RMSE (mV)	Truncation Error (mV)	Coefficient Convergence Error (mV)	Number of DAEs
Full Finite Difference	16857	0.0889	N/A	N/A	995
(1,1,1) Chebyshev	104	31.9	7.49e-4	14.1	25
(3,2,3) Chebyshev	123	6.99	9.91e-5	1.69	47
(5,3,5) Chebyshev	152	2.44	2.57e-5	0.156	69
(9,3,9) Chebyshev	214	0.328	2.74e-6	7.38e-4	109
(15,3,15) Chebyshev	417	0.0279	1.64e-7	5.81e-5	173
(25,5,25) Chebyshev	1190	N/A	1.53e-9	N/A	279

In contrast, the increase in computational costs when adding finite difference node points is greater than the reduction of error, giving a reduced marginal benefit as additional points are added. How many terms in the collocation solution should be used is heavily dependent on the application. Specifically, the acceptable error, computing resources, and operating conditions dictate the number of collocation points which are required.

The numerical source of error can be broadly divided into two categories. The first is the truncation error which arises when a finite number of terms in the series solution. The second source of error is the caused by the phenomenon that the calculated value of any coefficient,  $B_{r,v,i}(t)$  is dependent on the order of the series approximation and is referred to here as the coefficient convergence error. Estimates of both sources of error are given in Figure 2-18 for Chebyshev collocation and Figure 2-19 for cosine collocation.



Figure 2-17: Root mean squared error of the discharge curves as a function of simulation time using finite difference (long dash) and Chebyshev collocation (short dash). The RMSE was calculated relative to both the highest order Chebyshev solution and ( $\Box$ ) the finite difference solution with the smallest node spacing ( $\circ$ ).

The truncation error can be estimated by analyzing the coefficients of the series solutions. For Chebyshev polynomials and cosine functions, the function values are bounded on the interval [-1,1], so that the magnitude that each term contributes to the final solution can be estimated by directly comparing the coefficients. As the coefficients are time-dependent functions over the course of the charge or discharge cycle, the maximum absolute value is used so that the coefficients to be represented by a single value which can be directly compared.

For a converged solution, the magnitude of the series coefficients must decrease for each additional term. The dotted lines in Figure 2-18 shows the maximum magnitude of the coefficients of the series solution of (25,8,25) Chebyshev collocation. All coefficients are scaled by the maximum absolute value of the coefficient of the zero<sup>th</sup> trial function so that comparisons can be made among the different variables.

$$E_{trunct,i} = \frac{\max_{t=0.t_f} \left( \left| B_{r,v,i}(t) \right| \right)}{\max_{t=0.t_f} \left( \left| B_{r,v,0}(t) \right| \right)}$$
(2.62)



Figure 2-18: Comparison of truncation error as estimated as the final maximum value of the final coefficient value (short dash) and error due to the changing calculated value of the lowest order term (long dash) using up to (25, 8, 25) Chebyshev collocation for 0.1C ( $\circ$ ), 0.5C ( $\Box$ ), 1C( $\diamond$ ), 3C ( $\Delta$ ) and 5C ( $\Xi$ ) for the cathode variables. Note that the behavior of coefficients in the anode is similar.

For all the dependent variables, the series converges as more terms are included in the solution. The coefficients of the higher order terms decrease monotonically with coefficient number, with few exceptions. The solid phase potential converges rapidly, as expected due to the small spatial variation observed because of the relatively high electronic conductivity. The electrolyte concentration does not converge as rapidly in the electrodes because of the greater diffusion resistance requires higher order polynomials to estimate. Of all the variables solved for, the pore wall flux converges the slowest due to the highly nonlinear and complicated nature of incorporating Butler-Volmer kinetics. The moving front of the pore wall flux shown in Figure

2-8 cannot be well captured using low-order polynomials functions, and requires more terms to accurately track the behavior.

Convergence occurred more quickly for lower rates of discharge than for higher rates of discharge. Diffusion limited problems have larger gradients in the profiles of the all the variables which require higher order polynomials to approximate. The difficulty of calculating the variables at high rates is shown by the slower rates of convergence and shows the importance of using highly accurate methods for simulation of such conditions.

Similar qualitative trends can be observed for the truncation error when using cosine collocation as shown as the dash-dot lines in Figure 2-19. However, numerical errors limit the number of collocation terms that can be used. Furthermore, the maximum coefficient magnitudes do not reliably decrease monotonically as more terms are added. This lack of convergence limits the accuracy that can be achieved using cosine collocation.

The coefficient convergence error is more difficult to estimate directly, but contributes to the final error and cannot be ignored. The dashed lines of Figure 2-18 and Figure 2-19 estimate the variance error by comparing the maximum magnitude of the lowest order coefficient (which is the dominant term for all variables),  $B_{r,v,0}(t)$ , as calculated using (*N*, *M*, *N*) collocation compared to the largest order simulation performed ( i.e. (25,8,25) for Chebyshev collocation and (13,4,13) for cosine collocation):

$$\log_{10}\left(\frac{\left|\max_{t=0.t_{f}}\left(\left|B_{r,\nu,0}(t)\right||_{N}\right) - \max_{t=0.t_{f}}\left(\left|B_{r,\nu,0}(t)\right||_{N_{max}}\right)\right|}{\left|\max_{t=0.t_{f}}\left(\left|B_{r,\nu,0}(t)\right||_{N_{max}}\right)}\right|\right)$$
(2.63)

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Figure 2-19: Comparison of truncation error as estimated as the final maximum value of the final coefficient value (short dash) and error due to the changing calculated value of the lowest order term (long dash) using up to (13, 4, 13) cosine collocation for 0.1C ( $\circ$ ), 0.5C ( $\Box$ ), 1C( $\diamond$ ), 3C ( $\Delta$ ) and 5C ( $\Xi$ ) for the cathode variables. Note that the behavior of coefficients in the anode is similar.

In general, the coefficient convergence error is less significant than the truncation error. However, the coefficient convergence error does not decrease as rapidly as more terms are added, and tends to be less affected at increased C-rates. The exception is the solid phase potential, in which the coefficient convergence error dominates. This can be partially attributed to the very low truncation errors experienced in estimating the solid phase potential which arises from the very flat potential profile that exists in the solid phase.

#### 2.5 Extending the Parabolic Profile Approximation

![](_page_82_Figure_1.jpeg)

Figure 2-20: Simulated discharge curves when using spectral methods to discretize the radial direction when using collocation (long dash), Galerkin (short dash) and the hybrid method (dash-dot) for increasing levels of refinement for 5C, 10C, 15C, and 20C. The solid line is the discharge curve when using  $N_r = 7$  for comparison. Note that the 20C case cannot be simulated using  $N_r = 0$ .

In the work discussed in this section, the solid phase concentration profile was approximated as a second order polynomial in *r* across the radius of the particle. This has been shown to be valid at low rates and long times, but is not valid for high rates.<sup>28</sup> At high rates, a boundary layer forms near the particle surface where a rapid change in concentration exists while the interior concentration profile is fairly flat in the bulk of the particle. A parabolic profile approximation cannot capture such a profile and a higher order method is required to ensure accurate simulation. A mixed finite difference approach has been used to calculate the solid phase concentration at discrete points spaced unequally across the radius of the particle.<sup>39</sup> This can better capture the variation of the solid phase concentration across the radius, but developing higher or lower order approximations requires the location of the node points to be recalculated

to determine the optimal spacing. Spectral methods using Chebyshev series solutions can calculate the radial profile of the solid phase concentration with higher order accuracy to better approximate the concentration gradients and the solid phase diffusion resistances.

This is especially important at high rates of charge when diffusion resistances are significant. At time t=0, a non-constant concentration profile exists in the particle as a numerical artifact caused by finding consistent initial conditions to equate the flux at the particle surface with the reaction rate while using the prescribed initial conditions for the differential variables. A flat concentration profile would be expected at the beginning of charge/discharge, but that is not consistent with the flux boundary condition. Therefore, one degree of freedom must be modified to create a gradient at the particle surface to satisfy the boundary condition. Based on the concepts of transport phenomena, the transient gradient created by the application of the flux boundary condition would initially only exist in a thin boundary layer, with a flat profile seen in the interior of the particle. However, a parabolic profile which satisfies the flux condition at the particle surface is not flat, creating a significant effect near the center of the particle. The instantaneous development of such a profile also has the important effect of inaccurately estimating the surface concentration which directly affects the modeled voltage of the cell, leading to the discrepancies observed in Figure 2-20 at the beginning of discharge. Higher order approximations can maintain a flatter profile through most of the particle while satisfying the imposed gradient boundary conditions. However, as the system continues to evolve, the boundary layer extends to the center of the particle, at which point the parabolic profile becomes a much more appropriate approximation.

In order to estimate the radial concentration profile, a series solution in *r* is developed at each collocation point, *j*, across the electrode, where  $\rho = \frac{r}{R_r}$  is the dimensionless radial position:

$$c_{r,j}^{s}(X = X_{j,N_{\rho}}, \rho, t) = \sum_{i=0}^{N_{\rho}+1} B_{r,c^{s,avg},i,j}(t) Z_{\rho,j}(\rho) \qquad j = 0...N_{\rho}$$
(2.64)

With one of the  $N_r + 1$  terms used to account for the flux condition at  $\rho = 1$ . The radial trial functions,  $Z_{\rho,j}(\rho)$  are chosen as even Chebyshev polynomials

$$Z_{\rho,j}(\rho) = T_{2j}(\rho)$$
 (2.65)

Recall that Chebyshev polynomials are defined on the region [-1, 1]. By using only even polynomials on the interval [0, 1], the symmetry boundary condition at  $\rho = 0$  is automatically satisfied.

Note that a series solution is not explicitly required across the x-dimension for the solid phase equations. The solid phase concentration does not have a derivative with respect to x in the governing equations so discretization in x is not required. Interpolation can be performed during post processing if greater resolution is required. Using a double summation for the variation in both x and r simultaneously is possible, but increases the coupling of the problem and the computational cost of simulation. Furthermore, it is not physically meaningful that the spherical diffusion in one particle affects the diffusion in other particles so that the form of discretization given in (2.64) is preferred.

Several options to find the coefficients are considered here based on the method of weighted residuals discussed in Section B.2 in Appendix B. Orthogonal collocation can be used in the radial dimension in a manner in the same way as described previously for the *x*-direction. However, if the solid-phase diffusivity is constant across the active particles, the governing equation for the solid phase diffusion Table 1-2 is linear and Galerkin's method is feasible as analytical integrations can be performed. Here we discuss the merits of using orthogonal

collocation, Galerkin's method, and a hybrid collocation method which retains the advantages of the parabolic profile approximation used in the bulk of the work.

For the orthogonal collocation approach, the collocation points are again chosen as CGL points. However, since only even Chebyshev polynomials are used,  $2(N_r + 1)$  CGL points exist on the domain [-1,1]. Using the points which exist in the positive part of the domain (which are physically meaningful), the required number of nodes is developed. Since the CGL points are spaced more tightly near -1 and 1, using only half of the set results in more points clustered near the particle surface. This is advantageous as a boundary layer develops at the particle surface, especially during high rates of charge, thus having greater resolution near the boundary better captures the transient dynamics of the system.

Galerkin's method is an alternative to orthogonal collocation which uses the trial functions as the weight functions in the method of weighted residuals. Equation (B.4) from Appendix B thus becomes

$$\int_{0}^{\kappa_{r}} R\left(B_{r,c^{s,avg},i,j}\left(t\right),X\right) T_{2j}(\rho)d\rho = 0 \qquad \qquad j = 0...N_{\rho}$$
(2.66)

If the diffusion coefficient is constant across the radius of the particle, the governing equation for radial diffusion is linear and the integration can be performed analytically. Gelerkin's method is an ideal choice because this weight function minimizes the square of the residual across the domain.<sup>47</sup> However, needing to perform the integral in (2.66) is prohibitive in many nonlinear systems.

The final case considered builds upon the parabolic profile approximation by using collocation to achieve higher order solutions when large gradients exist in the solid phase that are difficult to approximate with low order polynomials. One of the advantages of the parabolic profile approximation is that it directly tracks the average concentration in the solid particles,

which is useful for determining the state of charge of the battery, and ensures that mass is conserved in the solid particles. The average concentration in a spherical particle is given as

$$c_{s,r,j}^{avg}(X,t) = \frac{1}{3} \int_{0}^{1} c_{r,j}^{s}(X,\rho,t) \rho^{2} d\rho \ j = 0...N_{\rho}$$
(2.67)

By using a mass balance on the particle, the evolution of the average concentration is given by

$$\frac{d}{dt}c_{s,r}^{avg}(x,t) = -3\frac{j_r(x,t)}{R_r}$$
(2.68)

Equation (2.68) is identical to Equation (2.2) for the parabolic profile and, importantly, is the same regardless of the number of terms used in (2.64). This hybrid approach aims to maintain the mass conservation built into the parabolic profile, but allows for higher order approximations to be used. At high rates, the boundary condition at the particle surface requires a steep profile to meet the flux demand. In order to satisfy the specified gradient while maintaining the specified average concentration, a change in the initial surface concentration is required numerically.

![](_page_87_Figure_0.jpeg)

Figure 2-21: Root mean square error of the discharge curve for 5C ( $\Delta$ ), 10C( $\Box$ ), 15C( $\Diamond$ ) and 20C ( $\circ$ ) an increasing number of terms in the radial direction using collocation (long dash), Galerkin (dash dot), and hybrid approach (short dash).

This large jump in concentration at the surface directly affects the calculated open circuit potential, and can cause the parabolic profile approximation to give negative concentrations in the interior of the particle, which is not physically feasible. Using higher order approximations avoid this problem. Furthermore, the integration in (2.67) can be performed analytically if a polynomial is used to approximate the solid phase concentration, independent of the governing equation. This is important as this hybrid approach can be used even in the case of nonlinear diffusion coefficients, which is important when concentration dependent diffusivities are considered.

![](_page_88_Figure_0.jpeg)

Figure 2-22: Concentration profiles in the radial direction for a 15C discharge at the cathode-separator interface at four equispaced times during discharge for the hybrid method with for  $N_r = 0$  ( $\Delta$ ),  $N_r = 1$  ( $\Box$ ),  $N_r = 2$  ( $\diamond$ ) and  $N_r = 3$  ( $\bigstar$ ). The solid line is the solution for  $N_r = 7$ .

Here the three approaches (collocation, Galerkin, and hybrid) are compared using (15,5,15) Chebyshev collocation across the thickness of the electrode, as this was shown to be a converged solution in the previous section. The value of  $N_{\rho}$  was varied from 0 to 7 for a 5C, 10C, 15C, and 20C rate of discharge. The discharge curves are shown in Figure 2-20 for the three cases using  $N_{\rho} = 0,1,2,3$  terms. The  $N_{\rho} = 7$  case is a converged solution and used as for comparison, and the results achieved with  $N_{\rho} = 7$  are indistinguishable for the three different methods considered here. Notice that the solution found with  $N_{\rho} = 3$  is nearly identical to the  $N_{\rho} = 7$  solution. Figure 2-21 shows the root mean square error of the estimated discharge curve using an increasing number of terms compared to the  $N_{\rho} = 7$  solution. Notice that the error

steadily decreases monotonically and additional terms are expected to further reduce the error, but even for  $N_{\rho} = 3$  the observed RMSE is less than a millivolt error for a 5C rate of discharge, though the error is larger when greater discharge rates are applied. The reason for this is twofold. First, larger gradients occur at higher rates, which require more terms to capture the dynamics. Secondly, we can see in Figure 2-20 that the error is greatest early during discharge, so that the error for the lower rates of charge gets averaged out more so than the high rates. Notice that there is not a substantial difference in the errors for the different methods used except for the  $N_{\rho} = 0$  case. For the  $N_{\rho} = 0$  solid phase approximations, the hybrid case corresponding to the parabolic profile approximation gives the best results. However, the error is substantial and has the additional problem of predicting a negative concentration as seen in Figure 2-22 which gives the predicted concentration profiles for the different methods for an increasing number of node points at the anode-separator interface at 4 discharge times for a 15C rate of discharge. However, the hybrid approach does ensure that total mass is conserved, which is not guaranteed in the other approaches. This is improved for  $N_{\rho} = 1$ , which is a fourth order solution similar to the result found in a previous work.<sup>28</sup> In all cases, the low-order approximations do not capture the flat profile in the interior of the particle. However, the profile converges fairly rapidly for all cases, and by  $N_r = 2$  most oscillations have died out except at the very beginning of discharge. At the at the beginning of discharge, the profile should be flat with an infinitesimal gradient at the particle surface corresponding to the pore wall flux, but such a profile cannot be captured with a finite number of terms.

### **2.6 Conclusions**

The porous electrode P2D model is a physically meaningful model that can be used to simulate lithium ion battery operation. However, the computational cost of simulating the P2D model using standard techniques is too high to be utilized in computationally expensive operations, such as optimization and real time control. In order to increase the feasibility of using the P2D model in such applications, an improved reformulated model was developed to reduce the number of equations that must be solved to simulate battery operation.

The reformulation presented is robust enough to be used for a variety of conditions with limited assumptions to maintain the most accurate physics of the model. Although only a single battery chemistry is shown here, this method has been used successfully for a number of different chemistries across a wide range of physical parameters. This model thus allows an efficient battery model simulation for use in control and optimization routines, as well as for parameter estimation.

In order to reduce the computational cost of simulation each dependent variable was approximated as series solution, either using trigonometric functions or Chebyshev polynomials. Although discretizing the system using orthogonal collocation is more computationally intense than an equivalent number of finite difference equations, many fewer terms are required for convergence so the net simulation time can be reduced while improving accuracy. Using Chebyshev polynomials minimizes oscillations which allows for more node points to be used for higher rates.

For higher rates of discharge, the parabolic profile approximation for the solid phase concentration is not satisfactory so higher order spectral methods were used. In order to develop the higher order approximation, three approaches were tried: a collocation approach, a Galerkin approach, and a hybrid approach combining collocation with the volume averaging of the parabolic profile approximation. It was found that the 3 different approaches were not substantially different for most cases. For the lowest order approximations (which were generally considered unsatisfactory for rates greater than 5C) the hybrid approach gave the best approximation of the voltage-time curve, but calculates a negative concentration in the interior of the particle, which is not physically meaningful. This is avoided using more terms. Even using a single additional term (corresponding to a 4<sup>th</sup> order polynomial) greatly reduces the error and eliminates the problem of giving non-physical solutions. Higher rates of discharge are more difficult to calculate accurately, but using  $N_r = 3$  provides a converged solution for the cases considered here.

The number of terms to use in the simulation of the P2D is dictated by the application being considered, as there is a tradeoff between accuracy and computational cost. The use of spectral methods, such as Chebyshev collocation, shifts the tradeoff to improve the accuracy for a given computational cost. The number of collocation points used is dependent on the computational resources available, required accuracy, computational time, and operating conditions. Furthermore, the design and materials used in the manufacture of the battery can affect the accuracy of simulation. In general, conditions which increase the diffusion resistance cause more variation in the dependent variables across the electrode or particles. For example, thicker electrodes or larger particles increase the diffusion length that the lithium must travel and require more terms to accurately simulate. A material or electrolyte with a large diffusion coefficient would allow lithium to travel quickly and would maintain a flatter profile (i.e. smaller derivatives) which is easier to capture using fewer terms in a series solution. The simulation of a single discharge curve can use a highly accurate formulation as the difference between milliseconds and seconds is relatively minor. However, design optimization requires the simulation of hundreds of discharge curves. These can be performed in a desktop computer with significant computational resources without strict time constraints. Thus, a moderate number of terms can be used to give reasonable accuracy. To achieve the same level of accuracy in a finite different formulation, the computational cost would be prohibitively expense.

The reformulated model described in this chapter has been used by others to maximize the energy density of a lithium-ion battery by modifying design parameters, specifically electrode thicknesses and porosities.<sup>3</sup> The work presented in ref.<sup>3</sup> maximized energy density while ensuring that the cell provided power for a specified amount of time for a given discharge output. For high rates of charge, the energy density was maximized by minimizing the diffusion restance; increasing the porosity and decreasing thickness. Conversely, when the application had a low demand, lower porosities could be used to increase the energy density, as having a high power density is not required.

In contrast to design optimization, online control requires quick simulation to optimize the charging/discharging protocol on the order of milliseconds. Furthermore, mobile applications, such as electric vehicles, the computational resources are limited in order to minimize cost and weight. Thus, using low order Chebyshev series solutions are necessary in such applications. This shows that such a reformulated model can be solved when computational resources are limited and provides promise for use in online BMS systems to maximize performance and reduce cost.

Work is being done in the MAPLE lab to incorporate the reformulated model into microcontrollers with the ultimate of developing a model predicative control (MPC) scheme for

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use in battery management systems (BMS) in online applications. Incorporating the reformulated P2D model into MPC schemes can improve the useable capacity of batteries by allowing a greater amount of the physical battery capacity to be safely and reliably used. By better understanding the internal behavior of the battery, the conditions that lead to detrimental behavior can be predicted so that the safety margins can be reduced. Using reformulated models and improved simulation techniques,<sup>27-29,39</sup> advanced control schemes can be developed leading to better utilization of any battery chemistry.

Using information on the state of charge and state of health of the battery determined from a physics-based model, the BMS will modify the inputs to optimize present and future performance while ensuring safety. Therefore, a BMS which utilizes a detailed physics-based model can better control the battery to optimize performance as opposed to a BMS that relies solely on empirical models or tables. Electrochemistry, physics and chemical engineering principles determine the model's accuracy in predicting the internal states, as well as the significance of those states. The physics of the system dictate what is predictable and controllable, however, the mathematics enable *real-time* prediction and control.

Recognizing this opportunity to improve the efficiency and utilization battery systems and to increase the viability and cost-effectiveness of existing technologies for EVs., the US Department of Energy (DOE) recently invested \$30M to develop smarter battery management systems and advanced sensing technologies to circumvent potential problems due to capacity fade and safety concerns through its Advanced Management and Protection of Energy Storage Devices (AMPED) program under Advanced Research Projects Agency – Energy (ARPA-E). A major goal of APRA-E aims to take technical achievements from the lab and into commercial applications. Washington University's MAPLE Lab is a recipient of one of the AMPED grants to improve Li-ion battery performance in electric vehicles by using the reformulated model presented in this thesis.

## Chapter 3

# Extending the Porous Electrode Pseudo 2D Model Using

### Reformulation

This chapter contains excerpts (specifically in Section 3.1) from the following journal article reproduced here with permission from The Electrochemical Society: P. W. C. Northrop, V. Ramadesigan, S. De, and V. R. Subramanian, "Coordinate Transformation, Orthogonal Collocation and Model Reformulation for Simulating Electrochemical-Thermal Behavior of

Lithium-ion Battery Stacks," Journal of the Electrochemical Society, 158(12), A1461-A1477 (2011).

Chapter 2 discussed a model reformulation of the porous electrode P2D which significantly reduced the computational cost of lithium ion battery simulation, while maintaining high accuracy. This reformulation enables the use of the P2D model into applications that would otherwise be too computationally expensive to justify its use, such as online control, optimization, and parameter estimation. Furthermore, the P2D model has proven to be robust enough to allow for the inclusion of additional physical phenomena as understanding improves.<sup>10,25,59-68</sup> In this chapter, the reformulated model is used to allow for more complicated physical phenomena to be considered for study, including thermal effects and capacity fade.

# 3.1 Thermal Modeling and Reformulation of Lithium-Ion Battery Stacks

Accurately predicting temperature effects is essential to ensure safety, especially in applications where a significant temperature rise is expected.<sup>20,69</sup> Including thermal effects increase the complexity and fidelity of the model by including more physical phenomena but also increases the computational costs of simulation, both directly and indirectly. In addition to the costs associated with increasing the number unknowns, the equations in the thermal model

are more nonlinear and more tightly coupled because of the existence of thermal dependent parameters which can further increase stiffness. The additional equations which govern the thermal behavior are given in Table 3-1 with supplemental equations given in Table 3-2.

Governing Equation	Boundary Conditions		
Positive Electrode			
$\rho_p C_{p,p} \frac{dT_p}{dt} = \frac{\partial}{\partial x} \left[ \lambda_p \frac{\partial T_p}{\partial x} \right] + Q_{\text{rxn,p}} + Q_{\text{rev,p}} + Q_{\text{ohm,p}}$	$ \left. \begin{array}{c} \lambda_{p} \left. \frac{\partial T_{p}}{\partial x} \right _{x=l_{p}} = h \Big( T_{p} \Big _{x=0} - T_{\infty} \Big) \\ -\lambda_{p} \left. \frac{\partial T_{p}}{\partial x} \right _{x=l_{p}} = -\lambda_{s} \left. \frac{\partial T_{s}}{\partial x} \right _{x=0} \end{array} \right. $		
Separator			
$\rho_{s}C_{p,s}\frac{dT_{s}}{dt} = \frac{\partial}{\partial x}\left[\lambda_{s}\frac{\partial T_{s}}{\partial x}\right] + Q_{\text{ohm,s}}$	$ \begin{array}{c c} T_p \mid_{x=l_p} = T_s \mid_{x=l_p} \\ T_s \mid_{x=l_p+l_s} = T_n \mid_{x=l_p+l_s} \end{array} $		
Negative Electrode			
$\rho_n C_{p,n} \frac{dT_n}{dt} = \frac{\partial}{\partial x} \left[ \lambda_n \frac{\partial T_n}{\partial x} \right] + Q_{\text{rxn,n}} + Q_{\text{rev,n}} + Q_{\text{ohm,n}}$	$ \begin{aligned} -\lambda_s \frac{\partial T_s}{\partial x} \Big _{x=l_p+l_s} &= -\lambda_n \frac{\partial T_n}{\partial x} \Big _{x=l_p+l_s} \\ -\lambda_n \frac{\partial T_n}{\partial x} \Big _{x=l_p+l_s+l_n} &= h \Big( T_n \Big _{x=l_p+l_s+l_n} - T_\infty \Big) \end{aligned} $		

Table 3-1:	Governing	Equations	for 1	Femperature
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In order to meet power and energy demands, lithium-ion cells are often arranged in a stack configuration. These stacks can be rather large and can consist of hundreds of cells in series or in parallel. Here an 8-cell stack is presented as a proof of concept which maintains the coupling between all the cells within the stack and the full physics based model with temperature varying properties, and heat generation and discharge for each cell are calculated simultaneously. The electrochemical equations used for the thermal model are identical to those given in Table 1-2 with the addition of three more governing equations to model the temperature in three regions, as well as nonlinear electrolyte diffusion and electrolyte conductivity coefficients which are functions of concentration and temperature, based on work done by Valøen et al.<sup>73</sup> These additional equations are shown in Table 3-1 and Table 3-2. This is computationally difficult and

an efficient method is required for simulation, and we believe this has slowed the development of such a stack model.

Bernardi et al.<sup>16</sup> used an energy balance to develop a general thermal model for battery operation by considering the various modes of heat generation within the cell. Other researchers have built upon this model by incorporating heat generation effects during battery discharge for specific systems and conditions<sup>17-20</sup> Kumaresan et al.<sup>70</sup> used the model developed by Gu and Wang<sup>20</sup> to couple temperature to other variables for a single cell and validated the model with the results obtained experimentally.

Pals and Newman<sup>17,69</sup> modeled the temperature profile of a multi-cell stack by simulating the behavior of a single cell, with lithium foil as the anode, to determine the rate of heat generation and different temperatures and states of charge. They then modeled a full stack by considering the effect of heat transfer between cells in the stack by using an approximation for the heat generation in each cell. In this way, the individual cells were decoupled and the calculations for an individual cell were performed independently of the temperature calculation for the entire stack.<sup>69</sup> Chen and Evens<sup>71,72</sup> performed a thermal analysis of a lithium-ion battery stack in the context of preventing thermal runaway reactions. However, they simplified the model by incorporating empirical discharge data and constant physical parameters into the model.

Further complications also arise due to the presence of current collectors located between each pair of cell sandwiches, as well as at both ends of the battery stack. These current collectors provide additional thermal mass to the system which can slow the heating of the battery and should be considered in any comprehensive thermal stack model.

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$$\begin{split} & \mathcal{Q}_{\text{strul}} = Fa_{i}j_{i}\left(\Phi_{1,i} - \Phi_{2,i} - U_{i}\right), i = p, n \\ & \mathcal{Q}_{\text{strul}} = Fa_{i}j_{i}T_{i}\frac{\partial U_{i}}{\partial T}, i = p, n \\ & \mathcal{Q}_{\text{strul}} = \sigma_{\text{eff}_{i}}\left(\frac{1}{l_{i}}\frac{\partial \Phi_{1,i}}{\partial X}\right)^{2} + \kappa_{\text{eff}_{i}}\left(\frac{1}{l_{i}}\frac{\partial \Phi_{2,i}}{\partial X}\right)^{2} + \frac{2\kappa_{\text{eff}_{i}}RT_{i}}{F}\left(1 - l_{+}^{0}\right)\frac{1}{l_{i}^{2}}\frac{1}{c_{i}}\frac{\partial c_{i}}{\partial X}\frac{\partial \Phi_{2,i}}{\partial X}, i = p, n \\ & \mathcal{Q}_{\text{ohms}} = \kappa_{\text{eff}_{s}}\left(\frac{1}{l_{i}}\frac{\partial \Phi_{2,s}}{\partial X}\right)^{2} + \frac{2\kappa_{\text{eff}_{s}}RT_{s}}{F}\left(1 - l_{+}^{0}\right)\frac{1}{c_{s}}\frac{1}{l_{s}^{2}}\frac{\partial c_{s}}{\partial X}\frac{\partial \Phi_{2,i}}{\partial X} \\ & D_{g',i} = \varepsilon_{i}^{\text{lenge}_{i}} 1.0 \times 10^{-4} \times 10^{-443} \frac{54}{r^{-29-5.040^{3}c_{0}}} \frac{022540^{3}c_{0}}{r^{0}}, i = p, s, n \\ & \kappa_{i} = \varepsilon_{i}^{\text{lenge}_{i}} 1.0 \times 10^{-4} \times c_{s'}\left(\frac{-10.5 + 0.668 \times 10^{-3}c_{i} + 0.494 \times 10^{-6}c_{i}^{2} + 0.074T_{i} - 1}{1.78 \times 10^{-5}c_{i}T_{i} - 8.86 \times 10^{-10}c_{i}^{2}T_{i} - 6.96 \times 10^{-3}T_{i}^{2} + 2.80 \times 10^{-8}c_{i}T_{i}^{2}}\right)^{2} \\ & U_{i}(T_{i}, \theta_{i}) = U_{ixef}\left(T_{ref}, \theta_{i}\right) + \left(T_{i} - T_{ref}\right)\left[\frac{dU_{i}}{dT}\right]_{r_{ref}}, i = p, n \\ \\ & \frac{dU_{p}}{dT} = -0.001 \frac{\left[0.199521039 - 0.928373822\theta_{p} + 1}{1.36455068900003\theta_{p}^{2} - 0.611544893999998\theta_{p}^{3}}\right]}{\left[(1 - 5.661479886999997\theta_{p} + 11.47636191\theta_{p}^{2} - 9}{9.82431213599998\theta_{p}^{3} + 3.048755063\theta_{p}^{4}}\right) \right] \\ & \frac{dU_{s}}}{dT} = \frac{0.001}{\left[\frac{0.005269056 + 3.299265709\theta_{s} - 91.79325798\theta_{s}^{2} + 1004.911008\theta_{s}^{1} - 5812.278127\theta_{s}^{4} + 1}{193881.6488\theta_{s}^{3} + 374577.3152\theta_{s}^{2} - 385821.1607\theta_{s}^{2} + 16575.8597\theta_{s}^{3}}\right] \\ & D_{i,egf} = D_{i}^{*} \exp\left(-\frac{E_{s}^{D_{i}}}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}}\right], i = p, n \\ & k_{i,eff} = k_{i} \exp\left(-\frac{E_{s}^{A_{i}}}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}}\right], i = p, n \end{array} \right] \end{split}$$

The same orthogonal collocation reformulation and solution method presented in Chapter 2 for the isothermal battery simulation was used for reformulation of the thermal model for a battery stack. The coordinate transformation can be extended to add multiple cells to a stack. The inclusion of current collectors in the model increases the number of regions which are considered without a significant increase in the number of variables.

![](_page_99_Figure_0.jpeg)

Figure 3-1: Schematic for a multi-cell battery stack

A challenge in the transformation occurs because there is one more current collector than there are cells; there is not a one-to-one correspondence between the current collectors and cell sandwiches. The transformation is achieved by considering the current collectors as additional regions in which only the temperature variable is considered. The only other variable which is applicable in the current collector is the solid phase potential, which is assumed to be constant and equal to the end point potentials of the adjacent electrodes. The primary challenge arises in formulating the equations and boundary conditions in a consistent manner in the battery stack.

The approximate expressions for temperature were developed with cosine collocation in the same way as discussed in Section 2.3.1 for the other variables. Both linear and quadratic terms are included in these approximate expressions in order to maintain generality so that various thermal boundary conditions can be used, such as constant temperature, constant flux, or convection, as well as continuity of temperature and of heat flux between the regions. The current collectors are approximated in a similar manner. Since the current collectors are constructed of highly conductive materials, the temperature does not vary significantly across the current collectors, and no cosine terms are needed for an accurate approximation. A single constant term is adequate and must be solved for using the governing heat equation. The inclusion of the current collectors minimally increases the computational load, as only a small number of variables are added. For example, an eight-cell stack has 298 DAEs that must be solved for if current collectors are ignored. That increases to 307 DAEs when the temperature within the current collectors is considered.

Model simulation of full battery stacks provides additional challenges which can be addressed by using this reformulation and orthogonal collocation followed by a numerical solution to solve the time dependence. It is necessary to consider a full multi-cell battery stack when thermal effects are included, as a temperature profile across the battery can affect cell performance. In the case of isothermal operation, each cell is exposed to the exact same conditions which cause each individual cell to behave identically. If this symmetry is broken, for instance by forcing a temperature gradient across the cell stack, the cells may behave differently from each other.

![](_page_100_Figure_2.jpeg)

Figure 3-2: Temperature at the center of an 8-cell stack during a 1C rate of discharge subject insulated conditions (solid line), a heat transfer coefficient of 1W/m2 (long dash), a heat transfer coefficient of 10W/m2 (short dash), and fixed temperature (dash-dot) boundary conditions

A schematic of an *N*-cell stack is given in Figure 3-1, where each anode-separatorcathode group constitutes a single cell, with aluminum current collectors located between adjacent cathodes and copper current collectors located between adjacent anodes. Note that both electrodes at the end of the stack are anodes, and each successive cell reverses the order of the electrodes. In the configuration studied here, the cells are connected in parallel so that the same voltage is applied at each cell. Therefore, if a constant current discharge is applied to the entire battery stack, the current provided by each individual cell may vary with time. At the boundaries between the electrodes and current collectors, the electrolyte concentration is considered to have zero flux, whereas the temperature and heat flux are continuous. Additionally, the solid phase potential drop between the anode/current collector interface and the cathode/current collector interface is the same across all cells. This couples the behavior of each cell, so that all cells in the stack must be solved simultaneously. Because of the large number of equations that arise from the coupled thermal electrochemical multi-cell stack model, reformulation was performed to reduce the number of DAEs for efficient simulation.

In order to perform the stated transformation on an *N*-cell stack with current collectors, it was necessary to mathematically treat alternating cell sandwiches differently. For the odd numbered cells, the entire sandwich consisted of a total of five regions: a copper current collector, the anode, the separator, the cathode, and an aluminum current collector. The even numbered cells only consisted of the cathode, the separator, and the anode. Additionally, the odd numbered cells were flipped so that they were orientated in a cathode-separator-anode configuration so that all cells are consistent. A final copper current collector (which is present regardless of the size of the stack) was considered independently of the individual cells. This results in a system in which the positive electrode for each cell is defined on the region  $[0, l_p]$ , the separator on the region  $[l_p, l_p+l_s]$ , and the negative electrode on the region  $[l_p+l_s, l_p+l_s+l_n]$ (the current collectors, where applicable, are considered outside of this range). This simplifies the problem by eliminating the need to keep track of the location and orientation of each cell in the entire stack during simulation. For the interior cells, the boundary conditions at each end of each cell are determined by continuity. It must be noted that the application of the continuity of flux requires the direction of the flux to be reversed in adjacent cell to account for flipping every other cell to achieve a consistent orientation. Once this is done, each cell is transformed to a single region, as described in Section 2.2 for a single cell. This reduces the entire stack to a single region defined from [0, 1], and the stack can be solved in the same way as described previously.

![](_page_102_Figure_1.jpeg)

Figure 3-3: Temperature profile across an 8-cell lithium ion battery at the end of discharge when the ends (a) are maintained to be a fixed temperature difference of 10 K and (b) are exposed to a heat transfer coefficient of 1 W/m<sup>2</sup>K and an ambient temperature of 298 K

Extending the model to include the effects of temperature in a multiple cell stack can allow for more detailed simulation, albeit at an increased computational cost. Figure 3-2 shows the temperature rise at the center of the battery with varying values of the heat transfer coefficients at the end of the stack. For the insulated (h=0) case, there is a 55 K temperature rise within the battery, whereas there in no discernible temperature rise when the battery ends are held at fixed temperature ( $h=\infty$ ). In this case, the battery is sufficiently thin (on the order of approximately a millimeter) that there is not a significant temperature profile within the battery. Figure 3-3(b) shows the temperature profile of an 8-cell stack when the ends are exposed to a heat transfer coefficient of 1  $W/m^2K$ . Notice that the observed variation in the battery is a small fraction of a degree. However, for large batteries, or in two and three dimensions, the possibility of creating a hotspot becomes more significant.

![](_page_103_Figure_1.jpeg)

Figure 3-4: Current-Time curves for the first cell (solid line) and last cell (dashed line) within an 8-cell stack with an applied temperature gradient undergoing constant current discharge (1C) using the coupled thermal electrochemical model.

Figure 3-3 (a) shows the temperature profile within an 8-cell stack when the temperature of each end of the multi-cell stack is fixed to create temperature decrease of 10 K across the battery. The discharge current for the first and last cell in an 8-cell series stack under these conditions is shown in Figure 3-4. Notice that the current provided by the individual cells are not identical throughout discharge. while each individual cell is at the same voltage. This causes the individual cells to behave differently, resulting in the subtlety different current curves observed in Figure 11. The higher temperature of the first cell causes it to initially discharge at a faster rate than the last cell. However, by the end of discharge, the cooler cell provides a greater

current because it exists at a greater state of charge. Figure 3-5(a) shows the concentration profile across the entire battery in the transformed coordinates for each individual cell, which further demonstrates how temperature can affect internal battery characteristics. Figure 3-5(b) shows the concentration profile across the entire stack in natural coordinates at the end of discharge. Note that there is no electrolyte in the region of the current collectors, leading to a discontinuity at those points. In this example, the stack is sufficiently small that internal heat generation effects do not significantly alter the temperature profile when the ends are held at a fixed temperature.

![](_page_104_Figure_1.jpeg)

Figure 3-5: Concentration profile across an 8-cell stack at the end of discharge for transformed coordinates (left) and natural coordinates (right). ( $\circ$ ) denotes the first cell and ( $\diamond$ ) denotes the last cell in the series

However, for larger stacks, higher applied current and/or different boundary conditions, the temperature profile may be significantly affected by internal heat generation leading to greater behavior variations among the individual cells without an arbitrarily forced condition. The other spatial directions, y and z, are important for thermal models at high rates, and the coordinate transformation and the orthogonal collocation approach is still valid. A detailed pseudo 4D model (x, y, z and r) in stack environment can be reduced to a unit cell of X, Y, Z varying from 0

to 1 in dimensionless transformed coordinates as explained earlier. The proposed approach is also useful for developing models for optimization of graded electrodes or materials wherein control vector parameterization converts a given single region to *N* regions to represent discrete functions of porosity, particle size or shape.

### 3.2 Simulating a Two-Dimensional Lithium-Ion Cell

In addition for allowing the simulation of multi-cell stacks, the reformulated model can also be used to study two-dimensional cells. The standard P2D model only models variation in the direction perpendicular to the electrodes, as that is the primary direction of ion transport under ideal conditions. However, a variation in the direction parallel to the electrodes can occur, for example, due to manufacturing defects, or difference thermal characteristics at the top and bottom of the cell. A pseudo 3D model can be used to account for these occurrences. However, including an additional dimension greatly increases the computational cost. A finite difference approach with 50 node points in each electrode and 35 node points in separator in the *x*-direction and 25 node points in the *y*-direction results in a system of nearly 15,000 DAEs that must be solved for a single cell, *if* the parabolic profile is used in the solid phase. If a more detailed discretization is used for the solid-phase diffusion, the number of equations will be even greater. Thus, much of the work done by researchers modeling thermal behavior in batteries have used a 1D model<sup>15</sup> or decoupled the thermal profile from the electrochemical reactions.<sup>19,20,35,69-71</sup>

For example, Evans et al.<sup>71</sup> modeled heat generation in cylindrical cells using local current density which was decoupled from the overall thermal effects. Kim et al.<sup>74</sup> simulated a large format lithium-ion polymer battery using parameters from small cells, but maintained a one-way coupling between the thermal and electrochemical effects (i.e. the electrochemical

reactions and current flow contributed to the thermal calculation, but the temperature did not affect electrochemical behavior). They extended this model for electric vehicle applications using constant power charge/discharge protocols.<sup>75</sup> Inui et al.<sup>76</sup> studied heat generation in prismatic and cylindrical cells using a finite element analysis with resistive heating in each element. Kim, et al.<sup>77</sup> developed a Multi-Scale Multi-Dimensional (MSMD) model to study large format lithium-ion batteries. This MSMD model simulated the electrochemical behavior at the particle, electrode, and cell domains, with appropriate coupling between the scales. This allowed multiple cell designs to be tested, while only using a 1D model for the electrode domain (analogous to cell sandwich level), but being able to model the temperature in 3D.<sup>77</sup>

Gerver and Meyers <sup>78</sup> performed 3D thermal simulation of lithium batteries in planar configurations by arranging several 1D porous electrode models in series and a grid configuration. Thus, all current flow in the cell sandwich was in the direction perpendicular to the electrode, and lithium-ion transport in the direction parallel to the electrodes was neglected. The different 1D nodes were coupled at the current collectors, which were modeled as a system of temperature varying resistors.<sup>78</sup> This improves the computational efficiency as solving several 1D models is simpler than solving a full 2- or 3-dimensional model, while allowing for some effects of a temperature profile to be analyzed. McCleary, et al.<sup>79</sup> extended the work of Gerver and Meyers by applying a similar approach of using a series of 1D porous electrode models to spirally and prismatically wound cells, which are standard configurations for commercially made lithium-ion cells, by accounting for the effects of curvature and increasing electrode surface areas in the outer layers. They were able to model the effect of the number and positions of tabs on heat generation but again neglected ion transport and current density in the direction parallel to the electrodes.<sup>79</sup>. Christensen et al.<sup>80</sup> coupled the 1D dualfoil model<sup>18</sup> in a Fluent

environment<sup>24</sup>, allowing a fine mesh grid to be used for the temperature simulation while using a coarser mesh for the electrochemical reactions. At each time step, the local temperature was used to determine the behavior of each electrochemical element, by using a Newton-Raphson approach to solve for the voltage to achieve the total specified current (with voltage and temperature being the only variable to couple the 1D electrochemical elements). Once the electrochemical elements reached a converged solution, the heat generation was calculated from the current density and fed into the thermal mesh.<sup>80</sup> This approach allowed parallelization of a multi-core processor performed to solve the system improve computational speed of the entire system.<sup>80</sup> Tourani et al.<sup>81</sup> coupled a series of 1D porous electrochemical reaction and electrical resistances and experimentally verified their results for a lithium polymer cell, and a lithium iron phosphate cell. Xu et al.<sup>82</sup> performed a two-dimensional modeling using COMSOL<sup>23</sup> which accounted for mass and charge conservation in both dimensions and examined the effect that tab position had on the temperature profiles.

Governing Equations
$\varepsilon_{i} \frac{\partial c}{\partial t} = \nabla \cdot D_{eff,i} \nabla c + a_{p} \left( 1 - t_{+} \right) j_{i}$
$-\nabla \cdot \left[\sigma_{\rm eff} \nabla \Phi_1\right] - \nabla \cdot \left[\kappa_{\rm eff} \nabla \Phi_2\right] + \nabla \cdot \left[\frac{2\kappa_{\rm eff} RT}{F} \left(1 - t_{\rm +}\right) \nabla \ln c\right] = 0$
$\sigma_{eff,i} \nabla^2 \Phi_1 = a_i F j_i$
$\frac{\partial c_p^s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_p^s \frac{\partial c_p^s}{\partial r} \right]$

 Table 3-3: Governing equations of the porous electrode model in higher dimensions
Table 3-3 shows how including additional dimensions make simulation more complicated and is a generalization of the governing equations of the porous electrode model given in Table 1-2 to higher dimensions. Specifically, the charge balance must be represented as a 2<sup>nd</sup> order PDE in the 2D formulation. When only a single dimension is considered, the charge balance equation can be simply integrated to give the total current flowing through the cell, resulting in the equation given in Table 1-2. Further difficulties arise when applying the boundary conditions of the solid phase potential,  $\Phi_1$ , at the current collector/electrode interface. Note that the current flowing out of the cell is based on the derivative of  $\Phi_1$ , in a manner analogous to heat transfer. In a one dimensional model, the flux of  $\Phi_1$  can thus be specified at the boundary. However, in a multidimensional model, such an approach neglects the possible variation parallel to the electrodes. For example, more current may flow out of the top of the cell than out of the bottom.

### 3.2.1 Two-Dimensional Stack with Simplified Boundary Conditions

The reformulation strategies discussed in Chapter 2 for a one dimensional case can be applied to the two dimensional case presented here. More details on performing collocation in two dimensions is given in Appendix B. In this subsection we consider a two-dimensional 2-cell stack with a height of 1mm. The small height improves the stability and provides an initial proof of concept for a 2D cell, but limits the variation which can occur in the *y*-direction. The boundary conditions used are given in Figure 3-6, with the realization that the solid phase boundary conditions neglects the possible variation of current in the *y*-direction, but is used as initial approximation of a 2D model. Relaxations of this assumption are discussed later. Note that continuity boundary conditions are applied at the electrode/separator interfaces.



Figure 3-6: Boundary conditions used as an initial approximation of the 2D model



Figure 3-7: Discharge curve simulated using the 2D model (solid line), a 1D model with applied temperature conditions (long dash line), and a 1D model with adiabatic conditions (short dash line)

Note that the boundary conditions for temperature are not identical at the top and bottom of the cell, with the bottom being at a specified temperature while the top is insulated. This breaks the symmetry in the *y*-direction and forces variations to exist in *y*. The simulated discharge curve for a 1C discharge curve of a 2-cell battery stack is given in Figure 3-7. For comparison, Figure 3-7 also shows the predicted discharge curves using a 1D model.

As the 1D model cannot account for temperature variation in the *y*-direction, two cases were considered: insulated conditions and applied temperature conditions. For a single 1C discharge, the effect of the temperature profile (given in Figure 3-8) is rather small. However, even in this case, there is a clear difference in the performance between the two 1D simulations, with the insulated case experiencing a slightly higher voltage due to the decreased resistance that occurs at higher temperatures. Furthermore, the 2D model predicts a discharge curve between the two extremes, as would be expected since the 2D model is not completely insulated, but there is enough thermal resistance to allow for a temperature profile.



Figure 3-8: Temperature profile (left) and concentration profile (right) at the end of discharge of a two-cell 2D stack

Additionally, the temperature profile can induce a variation in y-direction of the other variables, albeit a minor variation. Figure 3-9 shows the solid phase potentials in the anode and cathode. Note that Figure 3-8 and Figure 3-9 use dimensionless values for the position in x and y. Though the magnitude is small under these conditions, under more extreme conditions or for

larger cells these variations could significantly affect performance by increasing or decreasing resistance.



Figure 3-9: Solid phase potential profile in the anode (left) and cathode (right) at the end of discharge of a two-cell 2D stack (note that the anode exists from [0,1] and [5,6], the plotting algorithm automatically connects the two regions)

### 3.2.2Two-Dimensional Thermal Lithium-Ion Cell with y-variation of Current

#### Density

The 2D model presented in Figure 3-6 does not consider the possible variation in the ydirection for current density, instead specifying a constant flux at the current collector. Under most conditions the variation is likely to be minor, but under certain circumstances, specifically those which result in a thermal gradient across the height of the battery, the current density may not be constant, which can occur in large format cells. As an initial approach at relaxing the constant current density assumption, a constant current charge (or discharge) is simulated by requiring that the *integral* of the current density across the current collector is a constant, as demonstrated in Figure 3-10 and given by

$$\int_{0}^{l_{y}} \sigma \frac{\partial \Phi_{1}}{\partial x} = -I_{app}$$
(3.1)

Thus, although the current density may vary at different points in *y*, the total current flowing through the cell is constant. However, the boundary condition given in Equation (3.1) is not adequate to fully characterize the system, as an infinite number of profiles can satisfy the condition. Therefore, the assumption is made the solid phase potential at the current collector interface does not vary across the height of the cell, although it is allowed to vary with time. Mathematically this can be expressed as:

$$\Phi_1(x=0, y, t) = f(t)$$
(3.2)

This assumption is considered valid for most conditions as the high conductivities of the current collectors (typically constructed of aluminum and copper) which ensure that any variation in voltage potentials is minimal. Thus, the assumption of a constant (in *y*) is a better assumption to use than the constant current density assumption in most applications.



Figure 3-10: Alternate boundary conditions for the 2D battery model



Figure 3-11: Temperature (left) and current density at the cathode- $(\Box)$  and anode- $(\circ)$  current collector interfaces (right) for a 1C discharge at 0% DOD (solid line), 33% DOD (long dash), 67% DOD (short dash), and 100% DOD (dash dot)

The boundary conditions given in Equations (3.1) and (3.2) have been used to solve for the 2D battery model using reformulation techniques. This approach is robust and allows for implementation of porous electrode models for application in which variation across the height of the cell is expected to play a major role in battery life and performance. The boundary conditions shown in Figure 3-10 can result in large temperature increases within a sufficiently large cell lithium-ion cell, even when only a 1C discharge is applied. Note, importantly, that the current collectors and battery casing, etc. are neglected in this model. Including those would likely reduce the magnitude of the temperature increase by increasing the thermal mass of the system. Also, the current collector, being thermally conductive, would facilitate improved heat transfer across the height of the cell. The temperature increase is shown in Figure 3-11, as is the current density at both electrode-current collector interfaces, for a cell with a height of 5cm (in contrast to the 1mm height used in the previous subsection). The temperature variation across the thickness of the electrode was negligible, as has been observed in the 1D model (Section 3.1).

Here, the temperature profile in y has a small but noticeable effect on current density for most of the discharge time. Specifically, areas of the cell which are at a higher temperature have a slightly higher current density. A higher temperature facilitates improved diffusion by reducing resistance, and directly increases the rate of reaction. However, at the end of discharge, the current density is provided principally near the applied temperature boundary, and at a much higher rate. This shows that even though the cell as a whole undergoes only a 1C discharge, the local current density can reach well over 2C in certain regions of the cell. This relatively rapid discharge in small region of the cell can cause increased SEI growth as well as increasing the local heat generation which in turn causes a more complicated thermal profile to arise and possibly causing hot spots and further damage the cell. This localized heat generation is partially responsible for the oscillations which are observed for the final temperature curve in Figure 3-11, though the limited ability to use a large number of collocation points also contributed to the inaccuracy. Here, (4,1,4,3) collocation was used for simulation (that is, using up to a 4<sup>th</sup> order Chebyshev polynomial in the electrodes, 1<sup>st</sup> order in the separator, and 3<sup>rd</sup> order in the ydirection). The changing reaction zone is shown explicitly in Figure 3-12 which shows the local pore wall flux as contour plots. At the beginning of discharge there is no appreciable variation in the y-direction, only across the thickness of the electrode, as expected from Figure 2-8 for the 1D model. However, as a greater temperature gradient is established, the variation of the pore wall flux across the height of the cell is more significant that across the thickness, as shown in Figure 3-12 (b) and (c). By the end of discharge, only a small fraction of the electrode volume (near the cold plate and separator) provides the majority of current demand. The spike in local current density at the end of the discharge can be attributed to the saturation (or depletion, at the anode) of lithium in the warmer areas of the cell. Thus, regions which would not otherwise be favored

due to the thermal conditions become favorable sites for reaction for thermodynamic reasons. Figure 3-13 shows the local SOC in the cathode.



Figure 3-12: Contour plots of the pore wall flux in the cathode at 0% DOD (a), 33% DOD (b), 67% DOD (c), and 100% DOD (d). Note that the contour lines are in units of  $\frac{\mu mol}{m^2 s}$ . x = 0 corresponds to the cathode-current collector interface and y = 5 corresponds to the fixed temperature boundary condition.

Figure 3-13 (b) and (c) show that in the midst of discharge, the SOC varies significantly in both the *x*- and *y*- directions, and that the variation across the height mirrors the gradient of temperature seen in Figure 3-11. Ultimately, Figure 3-13 (d) shows that there is a region of the cell adjacent to the current collector and near the cold plate which is significantly underutilized. In this region, the diffusion and ohmic resistance is at its highest point in the electrode. It is both cooler, directly limiting lithium diffusion, and furthest from the separator, requiring more current to be carried in the electrolyte.



Figure 3-13: Contour plots of the local SOC in the cathode at (a) 0% DOD, (b) 33% DOD, (c) 67% DOD, and (d) 100% DOD. x = 0 corresponds to the cathode-current collector interface and y = 5 corresponds to the fixed temperature boundary condition.

Although these give good results, the battery model given by Figure 3-10 is not fully inclusive as the variation of potential across the battery height is neglected. A natural extension would be the inclusion of the current flow through the current collectors in the model, as shown in Figure 3-14. Continuity of the solid phase potential and flux would have to be applied at the current collector/electrode interfaces. This would allow for variation of both potential and current density at the current collector-electrode interface. The current out of the current

collector could be approximated as having a constant flux at the tab. This formulation would neglect the possible variation in current density across the thickness of the current collector, but that variation is expected to be negligible due to the high conductivity and small thickness of the current collectors.



Figure 3-14: Proposed boundary conditions for the solid phase potential in a 2D model with current collectors included.

## **3.3 Capacity Fade Due to Growth of the SEI Layer**

As batteries are repeatedly cycled, the overall capacity is reduced. One mechanism of capacity fade is the growth of the solid electrolyte interface (SEI) layer on the graphite surface. Having capacity fade mechanisms is essential for the long term life simulations. As life studies of batteries require many cycles to be simulated, reformulation can be a useful tool for performing such studies.

### 3.3.1 Development of an SEI Reformulated Model

Here we develop a reformulated model for SEI growth by considering reduction of the solvent (typically ethylene carbonate) to be responsible for increasing SEI layer thickness.<sup>22</sup> This model assumes that the solvent molecules, ethylene carbonate, must diffuse through the SEI layer to react with lithium at the active material surface to create a layer of lithium ethylene dicarbonate. The overall rate expression is given by Safari, et al.<sup>22</sup> is

$$2\text{EC}+2\text{Li}\longrightarrow(\text{CH}_2\text{OCO}_2\text{Li})_2 \tag{3.3}$$

There is not a clear consensus in the literature concerning the rate expression of the SEI growth, although most are variations on Butler-Volmer kinetics, with different prexponential dependences on the lithium and solvent concentration.<sup>13,22,66</sup> This allows for comparisons to be made among the different mechanisms. The first kinetic expression examined from the work of Pinson, et al.<sup>13</sup>:

$$j_{SEI} = -k_{SEI} c_{sol}^{0.5} c_{LI^+}^{0.5} \exp\left(\frac{\alpha}{FRT} \left(\Phi_1 - \Phi_2 - U_{SEI} - \frac{\delta}{\kappa_{SEI}} (j_n + j_{SEI})\right)\right)$$
(3.4)

Equation (3.4) results in a diffusion limited reaction for the parameters provided in Pinson, et al.<sup>13</sup>. The equilibrium potential value,  $U_{SEI}$  is not well known and values of 0.4 V<sup>66,83</sup> and 0.8 V<sup>13,84</sup> can be found in the literature. Another model considered here was developed by Ramadass, et al.<sup>66</sup> and postulates kinetically limited SEI growth:

$$j_{SEI} = -k_{SEI} \exp\left(\frac{\alpha}{FRT} \left(\Phi_1 - \Phi_2 - U_{SEI} - \frac{\delta}{\kappa_{SEI}} (j_n + j_{SEI})\right)\right)$$
(3.5)

Safari et al.<sup>22</sup> gives another kinetic expression based on the assumption that the reduction of the solvent if the rate limiting step in the mechanism. This results in the following rate expression for the SEI layer growth.

$$j_{SEI} = -k_{SEI}c_{sol} \exp\left(\frac{\alpha}{FRT} \left(\Phi_1 - \Phi_2 - \frac{\delta}{\kappa_{SEI}} (j_n + j_{SEI})\right)\right)$$
(3.6)

Note that Safari, et al.<sup>22</sup> neglected  $U_{SEI}$  and rather choose to incorporate its value into the rate constant.

The pore wall flux given in Table 1-2 must also be modified to account for the resistance caused by the SEI layer. This resistance is captured in the final term in Equation (3.7).

$$j_{n} = 2k_{n}c^{0.5}c^{s}|_{r=R_{n}}^{0.5}\left(c_{\max,n}^{s} - c^{s}|_{r=R_{n}}\right)^{0.5}\sinh\left[\frac{0.5F}{RT}\left(\Phi_{1} - \Phi_{2} - U_{n} - \frac{\delta}{\kappa_{SEI}}\left(j_{n} + j_{SEI}\right)\right)\right]$$
(3.7)

Although Safari, et al.<sup>22</sup> and Ramadass, et al.<sup>66</sup> applied their fade mechanisms to the single particle model, reformulation makes it feasible to use these models in the P2D model. Including the growth of the SEI layer into the P2D model necessitates the addition of more dependent variables and governing equations, as well as affecting existing governing equations. Note that this only directly affects the conditions in the anode, and is not considered on the cathode. Regardless of the mechanism chosen, the growth to the SEI layer is given by

$$\frac{\partial \delta}{\partial t} = -\frac{j_{SEI}M_{SEI}}{\rho_{SEI}}$$
(3.8)

Equation (3.8) is valid for cases in which  $\delta \ll R_{p,n}$ . A more accurate formulation which accounts for the spherical nature can be used, but is generally not necessary as other assumptions of the model are likely to fail for cases in which  $\delta \ll R_{p,n}$  does not hold.

Developing a reformulated model with SEI growth can be done by using series solutions to represent the rate of the side reaction and thickness of the SEI layer across the electrode in a manner similar to the other variables as given in Chapter 2. This allows the variation of the SEI layer to be studied across the electrode. The method of weighted residuals can be applied to Equations (3.4)-(3.5) and Equation (3.8) to determine to coefficients of the series solution to be found. Thus, considering SEI layer growth increases the number of governing equations by two and the total number of DAEs by  $2(N_n + 1)$  over the base P2D model.

Importantly, it is the concentration of lithium and solvent at the active material surface that determine the rate of reaction for both lithium intercalation. As both the solvent molecules and lithium ions diffuse through the SEI layer, the SEI layer provides a resistance between the active material and the electrolyte. This resistance causes a variation to exist between the concentration at the active material surface and at the electrolyte interface. This is important to consider when modeling the system as the electrolyte concentration external to the SEI does not directly dictate the rate of reaction. Therefore, the concentration profile for each species must be calculated in some form.

The diffusion of both species can be modeled using Fick's law. Again using Cartesian coordinates as  $\delta \ll R_{p,n}$  this is given as

$$\frac{\partial c_{SEI}}{\partial t} = D \frac{\partial^2 c_{SEI}}{\partial x^2} + \frac{\partial \delta}{\partial t} \frac{\partial c_{SEI}}{\partial x}$$
(3.9)

Where the final term of Equation (3.9) accounts for any convective effects due to the outward growth of the SEI layer. Note that the convective term can be directly rewritten using Equation (3.8) for the SEI layer growth. Boundary conditions at the particle surface and the electrolyte interface are required to model the transport of the species across the SEI layer. At the SEI-electrolyte interface the concentrations within the SEI layer are specified as equal to the electrolyte values. At the active material surface, the rate of reaction of both species must equal the rate of diffusion to the surface. For the solvent this is given as

$$D_{SEI,sol} \frac{\partial c_{sol}}{\partial r}|_{r=R_{p,n}} = j_{SEI}$$
(3.10)

Since lithium is consumed in both the intercalation reaction and the SEI formation reaction, the diffusion of lithium at the active material surface must satisfy both reactions:

$$D_{SEI,LI^+} \frac{\partial c_{LI^+}}{\partial r} \Big|_{r=R_{p,n}} = j_{SEI} + j_n$$
(3.11)

Importantly,  $j_{SEI}$  does not contribute to the intercalation of lithium in the graphite, and the boundary conditions for the solid phase (see Table 1-2) remain unchanged. Rather,  $j_{SEI}$  represents lithium that is irreversibly removed from the system.

If a linear profile is used to estimate the variation of the lithium and solvent species within the SEI, no additional equations are needed, as the boundary conditions described above are sufficient to provide the concentration at the surface. This gives the solvent concentration at the surface to be given by

$$c_{sol,SEI} = c_{sol,elec} - \frac{\dot{j}_{SEI}}{D_{SEI,sol}}\delta$$
(3.12)

Where  $c_{sol,elec}$  is the concentration of solvent in the bulk electrolyte. Similarly, the concentration of lithium ions at the active material surface can be given by

$$c_{Li^{+},SEI} = c_{Li^{+},elec} - \frac{j_{SEI} + j_{n}}{D_{SEI,Li^{+}}}\delta$$
(3.13)

Appling Equations (3.12) and (3.13) to the reaction rate equations increases the complexity of the resulting DAEs and increases the coupling of the system by directly considering diffusion resistances.

Equations (3.12) and (3.13) assume a linear profile of the respective species across the SEI layer. This is valid in a pseudo-steady state situation, for example if the rate of diffusion is faster than the growth of the SEI layer and any change in reaction rates. If a more detailed parabolic

profile is used to track transients, a volume averaged approach can be applied to Equation (3.9) to track the average concentration within the SEI. Such an approach better captures the behavior within the SEI layer. However, including a term for concentration in the SEI layer increases overall computational costs, even in ways that would not at first be apparent. For example, the governing equation for the electrolyte concentration must be modified. Rather than the removal of lithium from the solvent (given by the generation term of the lithium-ion mass balance equation in Table 1-2) being directly equal to the pore wall flux, it must be equated to the diffusion of lithium into the SEI layer. In this work, a linear profile is used exclusively for the sake of computational efficiency and stability.

### 3.3.2 Effects of SEI Layer Growth



Figure 3-15: SEI layer growth over 10,000 cycles for Mechanisms  $A(\circ)$ ,  $B(\Box)$ , and  $C(\Delta)$ . The upper lines represent the area of the electrode nearest to the separator while the lower lines are the area nearest to the current collector.

The growth of the SEI layer is studied by simulating a lithium ion cell over multiple cycles. Here a single cycle consists of a constant current charge to a specified cutoff, constant potential charge at the same voltage (with the total charging time is constrained to 7200

seconds), followed by a 1000 second relaxation phase before undergoing a constant power discharge. In this analysis, the diffusion limited case (Equation (3.4)) will be referred to as Mechanism A, the kinetically limited case (Equation (3.5)) will referred to as Mechanism B, and the solvent limiting case (Equation (3.6)) will be referred to as Mechanism C. The parameters were chosen to be consistent with the source data where possible while providing results that can be directly compared by ensuring that the SEI layer thickness between the simulations where within an order of magnitude.

Figure 3-15 shows the growth of the SEI layer for 10,000 cycles (a bit over three years of continuous cycling) for the three different reaction mechanisms at the first and last collocation points. Importantly, note that the growth of the SEI layer is self-limiting; the rate of growth is greatest at the beginning of life, but decreases as the battery ages, especially for the diffusion limited case given as Mechanism A.



Figure 3-16: SEI thickness across the anode at the end of 10,000 cycles for Mechanisms  $A(\circ)$ ,  $B(\Box)$ , and  $C(\Delta)$ .



Figure 3-17: Discharge curves for Mechanisms A(a), B(b), and C(c) at cycle 1 (solid line), cycle 2500 (long dash), cycle 5000 (short dash), cycle 7500 (dash dot), and cycle 10000 (dash double dot). Subplot (d) shows the discharge curve at cycle 10000 for Mechanisms A(solid line), B(long dash), and C(short dash) compared to the initial discharge curve (dash dot)

A thicker SEI layer increases the diffusive resistance of the solvent molecules to the active material surface, which directly slows the reaction. A thick SEI also increases the electrical resistance between the solid and electrolyte which affects the overpotential which arises in the exponential term of the kinetic expression. Figure 3-16 explicitly shows the final profile of the SEI thickness at the end of 10,000 cycles across the anode. There is very little variation in Mechanism A as the diffusion of solvent is the limiting factor in that case, which does not vary significantly. However, for the more kinetically limited cases, the variation across the electrode is rather large. During cycling, the portion of the electrode nearest to the separator is most reactive (see Figure 2-8) due to the greater overpotentials which exist. This leads to greater SEI formation near the separator when compared to deep in the electrode. This suggests

that designing and operating lithium-ion cells to mitigate the overpotential could minimize SEI layer growth.

The discharge curves for each mechanism are shown in Figure 3-17, which shows both a reduction in capacity and a reduction in voltage. The SEI layer has a two-fold effect on the battery performance. Any lithium that is bound in the SEI layer as lithium dicarbonate cannot be recovered in a later cycle. Thus, the growth of the SEI layer directly contributes to a reduction in available lithium and thus capacity. The SEI layer also increases the resistance of transfer of lithium from the electrolyte to the electrode (and vice versa) as well as increases the electrical resistance by reducing the overpotential. This has the effect of reducing the voltage available during discharge.



Figure 3-18: Cell capacity (upper lines) and total capacity lost (lower lines) for Mechanisms  $A(\circ)$ ,  $B(\Box)$ , and  $C(\Delta)$ .

Figure 3-18 shows the cell capacity as a function of cycle number. Note that the charge and discharge capacities are indistinguishable on this scale as the columbic efficiency of any single cycle is over 99.99%. The cumulative capacity lost is also shown, which is significant after a few thousand cycles.

## **3.4 Conclusions**

The versatility of the porous electrode model allows for the inclusion of additional physical phenomena, which is critical for safety and life considerations. However, the inclusion of additional physical phenomena can greatly increase computational costs, both by requiring more equations, and by increasing the coupling among existing equations. Thus, a reformulated model can be used to simulate such models. Here we discussed the inclusion of temperature, which has important safety consequences, and the inclusion of the growth of the SEI layer, which directly affects the life performance of the cell.

The addition of Arrhenius type dependence of diffusion coefficients and reaction rate constants on temperature was also included in the thermal model. This increases the fidelity of the model at the expense of increased complexity and computation time. This approach is robust enough to solve these equations faster than if a finite difference approach were used. This is especially pronounced when a coupled thermal electrochemical multi-cell stack model is used due to the large number of equations that must be solved. However, such a stack model better describes how individual cells operate in the context of a full battery stack. This is important when thermal or other effects cause the individual cells to not operate identically from each other. Since it is often not practical or possible to measure each cell individually in a stack, these differences can lead to potentially dangerous or damaging conditions such as overcharging or overdischarging certain cells within the battery causing thermal runaway or explosions. The ability to efficiently simulate battery stacks facilitates monitoring of individual cell behavior during charging and discharging operations and thereby reducing the chances of temperature buildup causing thermal runaway making the use of stacks safer. The growth of the SEI layer allowed for a lithium-ion cell to be studied over the course of the life of the battery. The effect of the SEI side reaction is clearly pronounced in reducing the capacity over 10,000 cycles for the cases examined here. Critically, the reformulated model using a (15,3,15) Chebyshev collocation was able to simulate 10,000 cycles in only a few hours. This ultimately allows for long term simulations to be run for a range of conditions and cycling protocols.

The capacity fade due to SEI layer growth can be attributed to both removal of lithium from the system and increased resistance between the solid and liquid phases, though the lithium removal seems to be the dominant effect for the parameters presented in this work. As the mechanism of SEI layer growth is not well understood, three different mechanisms were considered, including diffusion limited and kinetically limited cases. In diffusion limited cases the thickness of the SEI layer was predicted to be nearly uniform within the electrode, while kinetically limited cases showed a larger variation. Whether the SEI layer growth is kinetically or diffusion limited will have an effect on any strategies used to mitigate fade. A kinetically limited cell can control the growth somewhat directly by using more conservative charging protocols which limit the overpotentials in the cell. In contrast, diffusion limited cells will be less sensitive to the charging protocol. Rather, in a diffusion limited cell, factors which affect diffusivity of the solvent in the SEI layer are likely to have a more significant effect. This immediately suggests that a SEI layer model described in Section 3.3 should be combined with the thermal model in Section 3.1 with temperature dependent diffusivities to allow for a comprehensive model to study capacity fade. Combining the thermal model with the SEI layer growth in the reformulated framework presented here has already been done as a proof of concept. However, at the time of this writing, a thorough analysis has not been completed for that effort.

Other mechanisms relating to capacity fade, most notably due to stress and strain effects, are currently being explored for simulation in the MAPLE lab. Incorporating those mechanisms into the reformulated model is left for future students.

# Chapter 4

# Kinetic Monte Carlo Simulation of the Growth of the SEI

## Layer

This chapter contains excerpts (specifically in Section 4.1.1) from the following journal article reproduced here with permission from The Electrochemical Society:

R. N. Methekar, P. W. C. Northrop, K. Chen, R. D. Braatz, and V. R. Subramanian, "Kinetic Monte Carlo Simulation of Surface Heterogeneity in Graphite Anodes for Lithium-ion Batteries: Passive Layer Formation," *Journal of the Electrochemical Society*, 158(4), A363-A370 (2011).

The work discussed in the previous chapters focused exclusively on continuum models of lithium-ion batteries. Continuum models based on chemical engineering fundamentals can offer great insight into battery performance over the course of many cycles, but are limited in their ability to capture many phenomena, especially events on the microscale as shown in Figure 4-1. For example, the growth of the solid electrolyte interface (SEI) layer was discussed in Section 3.3 from a continuum perspective. The SEI layer is created by a side reaction of the solvent with the lithium. This irreversibly removes lithium from the system and reduces capacity. A thick SEI also increases the resistance between the solid and liquid, which slows reaction and reduces the output voltage. However, the continuum model assumes the SEI layer grows uniformly across the surface of the particle.

This is not necessarily the case, and significant heterogeneities in the thickness of the SEI layer. A very heterogeneous surface will have areas in which a thin SEI layer provides areas of relatively short paths for lithium ions to travel from the electrolyte to the active material. A more homogeneous surface will not allow "shortcuts" to lithium intercalation. A kinetic Monte Carlo (KMC) approach is presented here in an attempt to model the surface heterogeneity on a lithium cell. KMC is a computationally expensive stochastic approach which considers discrete events within a system.

A general background on the KMC algorithm is given in Appendix C. The first part of this chapter discusses a simplified 2D model for the particle surface. This is done first independently of any external model, and then coupled with the P2D model. Later a three dimensional model which explicitly considers the thickness of the SEI layer is developed and studied.

$$\frac{\partial c_n^s}{\partial t} = D_{s,n} \left( \frac{\partial^2 c_n^s}{\partial r^2} + \frac{2}{r} \frac{\partial c_n^s}{\partial r} \right)$$
Li Intercalation into the graphite
  
Reactions at the electrode electrody interface –KMC
  
Li
Transport in the Electrolyte
  
Li<sup>+</sup>

$$\sigma_{cff,n} \frac{\partial^2 \Phi_1}{\partial x^2} = a_n F j_n$$

$$-\sigma_{eff,n} \frac{\partial \Phi_1}{\partial x} - \kappa_{eff,n} \frac{\partial \Phi_2}{\partial x} + \frac{2\kappa_{eff,n} RT}{F} (1 - t_+) \frac{\partial \ln c}{\partial x} = I$$

$$\varepsilon_n \frac{\partial c}{\partial t} = D_{eff,n} \frac{\partial^2 c}{\partial x^2} + a_n (1 - t_+) j_n$$

Figure 4-1: The reactions which occur on the electrode surface a often glossed over when using continuum models, necessitating a more detailed approach

## 4.1Two Dimensional KMC Model

The first attempt at developing a KMC model was based on a greatly simplified view of the SEI layer. This considers a electrode surface as a two dimensional plane modeled as a 25 by 25 rectangular lattice. The growth of the SEI layer is considered in a binary sense: the SEI layer either allows for lithium passage or it does not. Thus, the surface is considered to be comprised of active sites with lithium reversibly adsorbed and passivated sites due to the SEI layer. This model considers for generals classes of events that can occur at each KMC transition: adsorption of lithium-ion onto an empty site and intercalating into the cell, desorption of a lithium-ion from the surface, surface diffusion of lithium from a filled site to an adjacent empty site, or an irreversible passivation of a site on the surface. A schematic of the possible transitions is given in Figure 4-2.



Figure 4-2: Transitions in the 2D KMC model for SEI layer growth. White represents empty sites, gray are active sites, and black are passivated sites.

Formation and growth of the passive SEI layer is considered as a side reaction represented by using the Bulter-Volmer equation.<sup>66</sup> The intercalation of  $Li^+$  from electrolyte to the electrode can be described by<sup>85</sup>

$$K_1 C_{I_1^{+}}^{0.5} \exp(-\alpha F \eta/RT) \tag{4.1}$$

The adsorbed Li (see Figure 4-2) can intercalate inside or diffuse on the electrode surface or form a passive layer. The liberation of Li from the electrode particle is described by<sup>83</sup>

$$K_2 C_{Li^+}^{0.5} \exp(\alpha F \eta/RT) \tag{4.2}$$

where the nonlinear reaction rate constants  $K_1$  and  $K_2$  are functions of the active surface coverage  $\theta$ , and are given by:

$$K_1 = \frac{3}{R_{pn}} k_n (1 - \theta)$$
(4.3)

$$K_2 = \frac{3}{R_{pn}} k_n \theta \tag{4.4}$$

The value of  $k_n$  (electrochemical rate constant typically used in the continuum model) is given in Table 4-1 and  $\eta$  is the overpotential given by

$$\eta = V - U_n \tag{4.5}$$

with *V* being the applied voltage with respect to graphite (lower voltages results in a faster rate of charge), and the open-circuit potential  $U_n$  given by

$$U_n = 0.7222 + 0.1387\theta + 0.029\theta^{0.5} - \frac{0.0172}{\theta} + \frac{1.9 \times 10^{-3}}{\theta^{1.5}} + 0.2808 \exp(0.9 - 15\theta) - 0.7984 \exp(0.4465\theta - 0.4108)$$
(4.6)

The surface diffusion rate is given by<sup>83</sup>

$$\frac{1}{2}\gamma_D\theta(1-\theta) \tag{4.7}$$

And the passive SEI layer formation rate is given by

$$K_{3} \exp\left(-0.5F(V-U_{n_{SEI}})/RT\right)$$
 (4.8)

where  $K_3$  is a function of the exchange current density typically used in the continuum model and is given by:

$$K_3 = \frac{3}{R_{pn}F} i_{0,P}$$
(4.9)

The formation of the passive SEI layer is assumed to be governed by Bulter-Volmer kinetics, as shown in Equation (4.8). The term  $(V-U_{n_{SEI}})$  indicates the overpotential for SEI layer.

	Parameters	Values
$a_n$	Specific surface area of the negative electrode, $m^2/m^3$	723,600
$Ct_n$	Electrolyte concentration, mol/m <sup>3</sup>	30,555
$D_{sn}$	Lithium-ion diffusion coefficient in the intercalation of negative electrode, $m^2/s$	3.9×10 <sup>-14</sup>
F	Faraday's constant, C/mol	96,487
$\dot{i}_{0,P}$	Exchange current density, $A/m^2$	1.5×10 <sup>-9</sup>
k <sub>n</sub>	Intercalation/deintercalation reaction rate constant, $(mol/m)^{0.5}/s$	5.0307×10 <sup>-11</sup>
$l_n$	Thickness of negative electrode, m	8.8×10 <sup>-5</sup>
R	Universal gas constant, J/(mol K)	8.314
R <sub>pn</sub>	Radius of intercalation of negative electrode, m	2×10 <sup>-6</sup>
Т	Operating temperature, K	303.15
$U_n$	Open-circuit potential of the negative electrode, V	
$U_{n_{SEI}}$	Open-circuit potential of the SEI layer, V	0.4
V	Applied potential with respect to graphite (equivalent to	0.001
	4.2 - 0.001 = 4.199 V for a lithium-ion battery with the	
	cathode operating at 4.2 V with no limitations)	
$\gamma_{\rm D}$	Diffusion frequency, 1/s	$1 \times 10^{-10}$

 Table 4-1: Parameter values used in the 2D KMC simulation

A surface KMC simulation was implemented in which the transition rates from one configuration of the lattice sites to other configurations were computed from Equations (4.1)-(4.9), where the probability of event i occurring is given by

$$P_j = \frac{r_j}{\sum_i r_i} \tag{4.10}$$

and the length of each time step is calculated from

$$\Delta t = -\frac{\ln(\chi)}{\sum_{i} r_{i}}$$
(4.11)

Where  $\chi$  is a uniformly distributed pseudorandom variable chosen on the domain (0,1]. The general KMC algorithm is described in detail in Appendix C. <sup>52</sup>

#### 4.1.1 Isolated Model

As a first look, the 2D KMC model was applied to a simple system which only considered the electrode surface and neglected many of the other phenomena present in a lithium-ion cell. This requires many of the parameters present in Equations (4.1)-(4.9) to be held constant, despite normally varying in a standard cell. For example, variations in overpotentials and electrolyte concentration can vary substantially during a single charging cycle or across the electrodes. The effects of variables external to the surface are neglected in the first part of the work discussed here.

As this work only examined a constant overpotential charging protocol, a much higher charging rate during the initial seconds of any charging cycle is observed, which tapers to zero as the battery becomes fully charged. Due to the high rates of charging, the time required for charging and the simulation time was reduced, however, the electrode fails in nearly 100 cycles. Low rates of charging would make the KMC simulations highly computationally expensive. High rates of charging will enhance the rate of intercalation as well as deintercalation, which result in high rate of byproduct formation. If the byproduct formation rate is high, then the surface coverage of the passive SEI layer will be high and capacity fade will occur at a faster rate causing the life cycle of the to be reduced significantly. To make the simulations efficient, some of the important aspects like mass transfer in the electrolyte and Ohmic limitations were ignored, which are important at high rates of charging. In the next section, the KMC model will be coupled with reduced order models for the continuum phases to perform multiscale simulations for a wide range of operating conditions.



Figure 4-3: End of cycle active surface coverage for various applied potentials with respect to graphite (this is roughly equivalent to a charging voltage of 4.2-V so larger voltages have a lower charge)

Additionally, the effect of charging potential on the surface coverage composition was examined. Figure 4-3 shows the end-of-charge active surface coverage for various applied potentials. This represents the equilibrium concentration of lithium at the specified overpotential. The simulations predict that the life of a battery increases for a higher applied potential versus graphite, which is equivalent to a lower charging voltage. For all charging potentials, no change in active surface coverage is observed for the first several cycles. The number of cycles that are run before a change in the active surface coverage is observed depends on the rate of charge. This ranges from about 10 cycles for high rates of charging to hundreds or thousands for lower rates of charging. For lower charging rates, the active surface coverage is predicted to be much less in the initial cycles than with the higher rates. This is expected if we are charging a constant low potential, since the battery is not charged to 4.2 V, as is typical for Li-ion batteries. If the battery is charged only to 4 V or less, the battery has a large amount of unused capacity that is reflected in the maximum active surface coverage.



Figure 4-4: End of cycle passive surface coverage for various applied potentials with respect to graphite (charging potential = 4.2-V so larger voltages have a lower charge)

Similarly, the growth of the passive layer with cycle number is shown in Figure 4-4. The KMC results indicate that the rate of increase of the passive layer is approximately linear during the first charge cycles. This linear region corresponds to the cycles in which the active surface coverage does not change (Figure 4-3). Once the passive surface coverage reaches a critical value, the KMC results indicate that the maximum active surface coverage begins to decrease while the passive layer grows at an increased rate. The growth of the passive layer then begins to taper until the battery fails. As would be expected, lower rates of charging results in a lower initial growth rate of the passive layer, which allows the battery to be operated for more cycles. An interesting observation is that, once the critical passive layer coverage is reached, the rate of the passive layer growth is similar for all applied potentials. Another interesting observation is that the lower changing rates can actually reach a higher surface coverage of the passive layer sites when charging to a lower battery voltage (higher applied potential versus graphite), more sites

can be disabled before an effect is noticed on the steady-state active surface coverage at the end of each cycle.

### 4.1.2 KMC P2D Coupled Model

The KMC model presented in Section 4.1.1 does not accurately consider the conditions which exist under normal battery operation. Specifically, the constant overpotential and constant electrolyte assumptions are typically not valid under normal operating conditions. Furthermore, although the above model does predict SEI passive layer growth, it does not predict how such growth will reduce the capacity of the cell. One solution to both shortcomings is to couple the KMC model with the reformulated P2D model described in previous chapters. This allows the SEI layer growth to be studied across the thickness of the electrode as well as to perform life studies on the lithium ion battery for various rates of charging.

Conventional charging typically dictates that a battery is charged by supplying a constant current until a specified voltage is reached at which point the battery is charged at a constant potential until the current drops below a minimum value (during constant potential charging the applied current decreases exponentially). Coupling of the KMC model with the continuum P2D model is necessary to analyze the effect of the passive layer growth on the battery behavior. The KMC model has limited predictive capabilities when applied in isolation, and gives limited information on the battery system as a whole, but can provide useful information involving the growth of the passive layer. Conversely, the P2D model can predict the behavior of a single charge/discharge cycle with reasonable accuracy, but the base model does not consider any mechanism for capacity fade. This means that behavioral changes of the battery does not vary from cycle to cycle, although some work has been done to use the continuum model to predict capacity fade, as described in Section 3.3.



Figure 4-5: Flowchart showing the intermittent coupling of the 2D KMC model with the continuum P2D model

The two models were coupled intermittently. That is, the continuum porous electrode simulation was initially run to simulate a constant current charging condition to a specified cutoff of 4.1V, followed by a constant potential charge at the same voltage. This was constrained to simulate one hour of charging time. If the cutoff potential was not reached in one hour of charging, no constant potential charging was performed. For the first cycle, the anode surface was assumed to be in a virgin state, and no modifications were made to base model. This assumption was relaxed for later cycles. This simulation provides information on the overpotential and electrolyte concentration (among other variables) at all positions and times which can be incorporated into the KMC simulation.

Following the continuum simulation, the KMC simulation can be run. At each time step the probability of each event occurring, as well as the characteristic time, is dependent on the lithium ion concentration in the electrolyte as well as the overpotential between the solid and liquid phases, as described in Equations (4.1)-(4.9) in Section 4.1.1. The values for the electrolyte concentration and overpotentials can be obtained from the continuum model. Since these variables are not constant across the thickness of the electrode, it is reasonable to assume that the KMC simulations will predict different amounts of passive layer growth at different points across the electrode. Ideally, the KMC simulation would be performed continuously across the thickness of the electrodes. Since this is computationally very demanding, the KMC simulation has been performed at three representative points in the electrode: the electrolyteelectrode interface, the center of the electrode, and the electrode-current collector interface. A flowchart depicting the coupled algorithm is given in Figure 4-5.

The KMC simulation can be run time step to time step by incorporating the calculated values from the continuum model at each simulation time and position. All three planes of the

SEI layer are considered simultaneously. That is, the at each time step, an event may occur at any planes. The probabilities of an event occurring on each plane are, of course, dependent on the conditions at that location at that time. Having more possible outcomes that can occur at each time step reduces the length of each time step as given in Equation (4.11).



Figure 4-6: Growth of the passive SEI layer from the coupled KMC-P2D model for (a) 0.5C, (b) 1C, and (c) 2C at the anode-separator interface ( $\Box$ ), the middle of the anode ( $\circ$ ), and anode-current-collector interface ( $\Diamond$ )

The growth of the passive layer can thus be tracked throughout the cycle, as well as the active layer coverage. The passivation level at the end of the charge cycle can then be incorporated into the continuum model as a reduction in anode capacity for simulation of the next cycle. Since three points were simulated using KMC, the entire electrode capacity was assumed to follow a parabolic profile. This allows the discrete data obtained from the KMC simulation to be incorporated into the continuum P2D model. This can be repeated for a number of cycles and capacity fade can be studied.



Figure 4-7: Active layer coverage from the coupled KMC-P2D model for 0.5C (top row), 1C (middle row), and 2C (bottom row) at the anode-separator interface ( $\Box$ ), the middle of the anode ( $\circ$ ), and anode-current-collector interface ( $\Diamond$ ), at cycle 1 (left column), cycle 25 (center column), and cycle 50 (right column). Importantly note that a 1 hour charge is applied in a CC-CV manner, if applicable.

The results have been consistent with observed trends that higher rates of charge are more detrimental to battery performance. Furthermore, these data have shown that the SEI layer formation can vary significantly across the position of the electrode, which can be seen in Figure 4-6. Specifically, the KMC predicts the region nearest to the separator experiences the most severe passivation. This is expected due to the lower overpotential near the separator increasing the rate of reaction for both lithium intercalation and SEI layer formation. Also, the rate of charge affects the SEI layer coverage across the electrode. Figure 4-6 shows that the growth of the SEI passivation is more severe for high rates of charge. The lower overpotentials required to

meet the higher charging demand also lead to a higher incidence of the side reaction which leads to capacity fade. Interestingly, the passive layer coverage at the separator/anode interface for a 1C rate of charge surpasses that of the 2C rate after about 30 cycles. It is conjectured that this is caused by the shorter time that the region near the separator is electrochemically active. It was shown in Section 2.4.2 (Figure 2-8) that lithium intercalation occurs within a moving reaction zone during discharge. It is likely that the reaction zone from the higher rate of charge moves quickly past the plane being studied. This would be exacerbated by the existence of the passive layer which would be unable to supply much capacity before the reaction zone moved deeper in the electrode, thereby reducing further passivation at the anode/separator interface. This growth of the passive layer near the anode/separator interface reduces the available active material present in this region. This effectively increases the utilization of the electrode closer to the current collector as the lithium must migrate deeper into the electrode to intercalate. This also increases the internal resistance of the battery.

The active layer coverage also tends to be high at the plane adjacent to the separator, as can be seen in Figure 4-7, especially for high rates of charge, which reach an equilibrium concentration. This is logical, as this is the region nearest to the positive electrode (the source of the lithium ions during charge) it would be expected that lithium would intercalate there first. Furthermore, this is consistent with the solid phase concentrations predicted by the P2D continuum model. As cycling continues, and passivation becomes more significant, the equilibrium concentration of lithium decreases. This is expected as more sites become passivated, it is not possible for lithium to intercalate. This results in the planes deeper in the electrode contributing more to the capacity of the cell, even though this is not favored due to the increased resistance.

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Figure 4-8: Voltage time curves for constant current charging for 0.5C (a), 1C (b), and 2C (c) for cycle 1 (solid line), cycle 10 (long dash), cycle 20 (short dash), cycle 30 (dash dot), cycle 40 (dash double dot), and cycle 50 (dash triple dot)

The reduction in the amount of charge which can be stored is shown explicitly in Figure 4-8, which compares the constant current charging protocols for 2C, 1C, and 0.5C rates of charge. Note that for the parameters and conditions considered here, a substantial fade was observed within 50 cycles. The high computational cost associated with the KMC model makes simulations of thousands of cycles prohibitive. Although the direct loss of active material contributes largely to the observed decline in capacity, the non-uniform nature of lithium intercalation also contributes. The passivation of the SEI in this model occurs most prominently near the anode/separator interface, which coincides with where lithium intercalation occurs most prevalently. During later cycles, lithium must intercalate deeper within the electrode which increases the diffusive resistance. This can be seen in Figure 4-7 where the active material utilization near the separator decreases with increasing cycle number, while the other planes of interest increase in utilization.
Figure 4-9 shows the discharge curves for the systems considered in this work. Here the capacity fade is noticeable after 50 cycles for the 1C and 2C rates of discharge Very little fade is observed for the 0.5C rate as shown in Figure 4-9(a). This can be attributed to the fact that the full capacity of the cell is not required in that application, so the effects of reduced capacity are not visible. The 1C rate maintains voltage fairly well for all cycles, but the total capacity decreases by almost 50%. The 2C condition shows a similar degree of fade, but also shows a decrease in voltage output which directly reduces the power that could be retrieved from the cell.



Figure 4-9: Voltage time curves for constant current discharging for 0.5C (a), 1C (b), and 2C (c) for cycle 2 (solid line), cycle 10 (long dash), cycle 20 (short dash), cycle 30 (dash dot), cycle 40 (dash double dot), and cycle 50 (dash triple dot). Note that cycle 1 was excluded as it began from a fully charged state, whereas all later cycles began after a 1 hour CC-CV charge.

These results suggest that more significant capacity fade is observed during high rates of charge. This observation is present for two primary reasons. The large applied current causes a lower overpotential to be applied during the charging, which increases the rate of passive layer formation. Also, the active material utilization is more skewed toward the separator interface at higher rates of charge. That, coupled with the higher passivation, forces even more lithium to

diffuse even deeper into the electrolyte, causing the diffusive resistances to have a significant impact on performance.

#### 4.2 Extending the KMC Model to Study SEI Layer Thickness

The two dimensional KMC described in Section 4.1 neglects many of the important phenomena concerning the effect and behavior of the SEI layer. Specifically, it considered the SEI layer to either allow for unlimited transfer of lithium to the active material surface, or it completely prevented the intercalation of lithium into the active material. This ignores the physical behavior of the SEI layer as a barrier between the active material and the electrolyte. Rather, it is believed that the SEI layer allows diffusion of lithium, but that a thicker SEI layer increases that resistance which contributes to capacity fade as the lithium ions must diffuse further to reach the electrolyte surface. Thus, here a 2+1D KMC model is developed to study the growth of the SEI layer by considering the thickness.

The particle surface is represented by a two dimensional plane divided in a Cartesian grid. The domain of this simulation is the section of the SEI layer on the particle surface. Above the SEI layer exists the electrolyte and below exists the active material, neither of which are directly simulated in the KMC model. This model considers several physical phenomena occurring within the SEI layer:

- 1) Diffusion of lithium ions from the electrolyte into the SEI layer
- 2) Diffusion of solvent molecules from the electrolyte into the SEI layer
- 3) Diffusion of lithium ions within the SEI layer
- 4) Diffusion of solvent molecules within the SEI layer
- 5) Reaction of lithium ions to intercalate into the active material
- 6) Deintercalation of lithium from the active material into SEI
- 7) Reaction of lithium ions with solvent molecules to cause SEI layer growth

The possibility of each event occurring is dependent on the geometry of the site being observed. Event classes 1 and 2 can only occur in vacant SEI sites adjacent to the electrolyte. Note that the thickness of the SEI layer is not uniform, and grows during simulation (see event #7) so which sites are adjacent changes as the simulation progresses. Also, diffusion from the electrolyte need not be from above the SEI layer, if electrolyte exists laterally from the SEI site. Similarly, diffusion of lithium and of solvent can only occur from a filled site to an adjacent empty site at any single time step. Additionally, the electrochemical reactions (events #5, #6, and #7) only occur at the interface with the active material. Figure 4-10 depicts the events considered in this model. The lithium intercalation rates are based on Butler-Volmer kinetics. The growth of the SEI layer is based on the kinetics given by Pinson, et al.<sup>13</sup> and were used in Section 3.3. The rate of each event is given in Table 4-2.



Figure 4-10: Depictions of the KMC transitions considered in the 2+1D model. The slanted lines are sites where lithium-ions are present, vertical lines are where solvent is present, and the crosshatch represents sites filled by both lithium-ions and solvent. The arrows are to aid the reader to where the example transition occurred. Note that the 3<sup>rd</sup> dimension modeled is in the direction into the page.

Note that Table 4-2 shows the rates of each *individual* event. For example, if there are no lithium ions adjacent to the active material, intercalation cannot occur. The relative probabilities of each event occurring are dependent on the rate of reaction as described in 5.2Appendix C

based on the reaction rates given in Table 4-2. This model allows variation in thickness of the SEI layer to be studied throughout the life of the cell. This heterogeneity can have significant impacts on overall performance and is an attribute which is typically ignored in continuum models.

Transition Number	Transition Event Description	Rate	Notes
(1)	Transfer of $Li^+$ to SEI from electrolyte	$\gamma^*_{Li^+ \to SEI}$	Requires empty site adjacent to electrolyte
(2)	Transfer of solvent to SEI from electrolyte	$\gamma^*_{Solvent \to SEI}$	Requires empty site adjacent to electrolyte
(3)	Diffusion of $Li^+$ in SEI	$D^*_{L^+}$	Requires filled site adjacent to empty site
(4)	Diffusion of solvent in SEI	$D^*_{Solvent}$	Requires filled site adjacent to empty site
(5)	Intercalation of $Li^+$ from SEI to graphite	$k_n c_{Li^+}^{0.5} c_{s,max} \left(1-\theta\right)^{0.5} \theta^{0.5} \exp\left(-\alpha \frac{F}{RT}\eta\right)$ $\eta = \phi_1 - \phi_2 - U_n(\theta) - \frac{\delta_{SEI}}{\kappa_{SEI}} (j_n + j_{n,SEI})F$	Requires filled site adjacent to active material
(6)	Deintercalation of $Li^+$ from graphite to SEI	$k_n c_{Li^+}^{0.5} c_{s,max} \left(1 - \theta\right)^{0.5} \theta^{0.5} \exp\left(\alpha \frac{F}{RT} \eta\right)$ $\eta = \phi_1 - \phi_2 - U_n(\theta) - \frac{\delta_{SEI}}{\kappa_{SEI}} (j_n + j_{n,SEI})F$	Requires empty site adjacent to active material
(7)	Growth of SEI layer	$i_{0,SEI} c_{Solvent}^{0.5} \left( c_{s,max} \theta \right)^{0.5} \exp \left( \alpha \frac{F}{RT} \eta \right)$ $\eta = \phi_1 - \phi_2 - U_n(\theta) - \frac{\delta_{SEI}}{\kappa_{SEI}} (j_n + j_{n,SEI})F$	Requires both $Li^+$ and solvent to be present and adjacent to active material

 Table 4-2:
 Transition events and rates in the 2+1D KMC model

The computational cost of this 2+1D model is much greater than the simple 2D model described in Section 4.1. Several reasons exist for this. The most obvious is the addition of the third dimension, which increases the number of sites which must be accounted for. Specifically, whereas the 2D model has  $N^2$  sites, the 2+1D is closer to  $N^3$ , although the exact number is

dependent on the thickness of SEI layer across the surface. Thus, in the 2+1D model, the everincreasing SEI thickness requires that more sites are considered, causing the computational cost to increase with cycle number. In addition to the larger number of sites which must be accounted for, diffusion plays a much more significant role. For the 2D model from Section 4.1, lithium intercalation and passivation can immediately occur on the surface. Although diffusion can occur on the surface, it does not affect the predictions much. Conversely, the 2+1D model requires that diffusion of lithium occurs through the SEI layer before intercalation can occur. As diffusion is a "random-walk" process, with no preferential direction, many individual transitions often must be performed to intercalate any lithium, even for a relatively thin SEI. Furthermore, a three dimensional geometry allows for any individual species to diffuse in up to six direction during any transition events, which increases the total number of transitions which must be accounted for (as each site can have both, either, or neither of lithium and solvent present), as well as the transitions, as solvent diffuses in the same way as lithium ions, though much slower.

The total number of transition events which may occur is also increased by the inclusion of more physical phenomena. Lithium intercalation into the active material is considered a separate from lithium-ion diffusion from the electrolyte. Also, the diffusion of lithium from the electrolyte to the SEI layer can occur anywhere in which the SEI layer interfaces with the electrolyte. For a very heterogeneous SEI, this can be much larger than  $N^2$ , which further contributes to the computational cost.

The existence of such a large number of transitions has the side effect of reducing the length of each time step due to Equation (4.11). Thus, not only is more memory required to store all the transition events, more events must be simulated during a charging cycle. These

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challenges motivated a move from Maple to MATLAB as a platform of simulation. MATLAB is much faster at manipulating the vectors and matrices which are used to store the states of the system as well as to store the transition events. Importantly, the updating the states and transitions events is difficult and requires elements to be found and removed in matrices. For large systems, this is computationally significant and MATLAB fares better for this type of work. The ability to write MATLAB functions to update the system can also increase readability by splitting hundreds to thousands lines of codes into more manageable segments. This also makes debugging easier as each transition can be tested individually. It is likely that a true programming language, such as C++, FORTRAN, or Python would have better computational gains.

#### 4.2.1 2+1D KMC Model in Isolation

Initially, the 2+1D model was applied in isolation analogously to the system in Section 4.1.1. For example, the potential distribution, electrolyte concentration, and solid phase lithium concentration are not directly incorporated into the model. Thus, this model can use very rough approximations to study SEI layer growth. For example, a constant overpotential can be used for calculation of the reaction rates throughout the charging cycle, while the solid phase concentration can be estimated by the considering the maximum lithium concentration, the size of the domain being simulated, and the number of lithium ions which have intercalated during charge. This simplified approach can be used to draw conclusions on the general conditions that lead to SEI layer growth.

Each charge cycle is simulated from an initial state of charge in the anode of 10% and continues until the state of charge (SOC) reaches 90%. At each time step, an event is chosen

based on the state of the system corresponding to the physical phenomena described in Table 4-2. Should a lithium intercalation event occur, the SOC is updated by the equation:

$$\theta = \theta + \frac{1}{N_{bulk}} \tag{4.12}$$

Where  $\theta$  is the SOC and  $N_{hdk}$  is the total number of lithium "sites" in the active material which are to be considered as a surrogate for the total concentration. The value of  $N_{hdk}$  is chosen based on the size of the domain being simulated, the radius of the active material particles, and to allow for reasonable computational time. The simulation is allowed to continue until the cutoff SOC is reached. A single charging cycle of a 5x5 site surface can consist of millions of individual transition events.



Figure 4-11: Charging profiles calculated from the 2+1D KMC model for Cycle 1 (solid line), Cycle 10 (long dash), and Cycle 19 (short dash)

At the end of the charge cycle, the profile of the SEI layer is saved and the cell undergoes discharge, which is not directly simulated and it is assumed that SEI growth is minimal during discharge. The SOC is reset to the initial condition and another charge cycle is performed. This can be repeated indefinitely. However, the increasing SEI thickness also increases size of the

domain which is simulated. Thus, the real time of simulation increases with cycle number, limiting the number of cycles which can realistically be modeled.

Figure 4-11 shows the charging results using the only the 2+1D KMC model described in this section for the first, middle and last cycle considered. For this example a 5x5 site representative surface was used to establish the domain and the applied overpotential was held constant at 0.1V. Although the potential difference between the electrolyte and solid material was held constant in this model, the equilibrium potential of the anode was calculated based on the fractional coverage of lithium in the active particle. The change in the equilibrium potential throughout charging causes the rate of charging to be maximal at the beginning of charge and taper off near the end. Figure 4-11 also shows that the time required to reach a fully charged state increases at later cycles. This is expected as the thicker SEI layer which exists at later cycles requires that any lithium which is to be intercalated must diffuse a greater distance to react with the active material.

The growth of the SEI layer over the cycles simulated is depicted in Figure 4-12. Figure 4-12 shows the maximum, minimum, and mean height of the SEI layer on a 5x5 grid for two different random number seed values. There is good agreement between simulations run identically, except for different pseudorandom numbers being generated. The mean height of the SEI layer follows a fairly smooth progression throughout life, as the effects of the random nature of the system get averaged out over the course of simulation.



Figure 4-12: Maximum ( $\Delta$ ), minimum ( $\circ$ ), and mean ( $\Box$ ) SEI thicknesses over 20 cycles of simulation. The different line styles represent solutions from using different seed values for the pseudorandom numbers.

Conversely, the maximum and minimum values show a more apparent stepwise progression, because the minimum and maximum values do not change as frequently, and change by a full integer unit when they do. The general trend for all metrics of measuring the SEI thickness is the same: the rate of SEI growth continuously decreases with increased cycle time. The decrease in the observed reaction rate is due to the same reasons that the charging time increases: the diffusion length is greater. There is a rapid growth of SEI layer for the first couple of cycles which greatly slows after this initial formation phase. As diffusion of the solvent in the SEI is orders of magnitude slower than the diffusion of lithium ions, the rate of side reaction is slowed at a more pronounced rate than the main reaction. While Figure 4-12 analyzes the aggregate data of the SEI layer growth, Figure 4-13 shows the heterogeneous profiles of the SEI layer at the end of three charging cycle. This gives a more visual depiction of the growth of the SEI layer from cycle to cycle.



Figure 4-13: SEI thickness on a 5x5 grid at (a) Cycle 1, (b) Cycle 10, and (c) Cycle 20

The thicker SEI layer also increases the simulation time when using the KMC model. This is partially due to the greater diffusion length, which means more steps are required for a lithium ion to transport through the SEI layer from the electrolyte to the active material. Recall that in this model, there is no directional preference for diffusion; diffusing from the electrolyte to the active material is done in a strictly random walk fashion. Thus, the average number of steps for a lithium ion to successfully intercalate can increase much more than one would expect from considering a direct path. The thicker SEI layer also increases the domain which must be simulated and accounted for. As more lithium and solvent molecules are considered, the number of possible events increase, causing a decrease in the time step at each transition. Thus, more KMC transitions are required. This is shown in Figure 4-14 which depicts the simulation time for each cycle for both a 5x5 grid and a 10x10 grid. The much higher computation cost associated with a larger grid demonstrates why the analysis in the work is primarily limited to a 5x5 grid.



Figure 4-14: Simulation time of the 2+1D KMC model for a 5x5 grid (°) and a 10x10 grid (□)

It is important to note that although quantitative analysis is not appropriate due to the limitations of the model and knowledge of the parameters, some qualitative analysis can be readily performed. Using a 2+1D KMC model is computationally very expensive and is not viable to be used in studies which require numerous simulations to be run. This work serves as a demonstration of the detail that can be achieved by using KMC simulations, but is limited to merely 20 cycles due to the high computational cost. We also limited our analysis to a 5x5 surface grid. Using a larger grid does not have a major effect on the conclusions which are drawn from the data and gives similar results for the average thicknesses and charging profiles. However, a larger grid does show higher maximum and lower minimum thicknesses of the SEI layer as would be expected by virtue of having a larger population being drawn from. A more informative statistic would be the standard deviation of the SEI thicknesses over the surface of interest, but that further increases the computational cost.

4.2.2 KMC P2D Coupled Model



Figure 4-15: Flowchart showing the more intimate coupling used between the 2+1D KMC and P2D models

In order to improve the meaningfulness of the KMC results and to study variation of the SEI layer across the electrode, the KMC model was coupled with the reformulated P2D model. This was done more intimately than the work describe in Section 4.1.2. Rather than running the full P2D charging simulation prior to performing the KMC analysis, the P2D model was simulated as the KMC model was run. This was accomplished using the lowest order reformulated model described in Chapter 2 with the SEI layer growth as described in Section 3.3.

The reformulated equations were developed using Maple with (1,1,1) Chebyshev collocation. The resulting system of differential algebraic equations and its analytical Jacobian were translated into MATLAB to allow for incorporation of the reformulated P2D model with the KMC model. At each KMC step the P2D DAE system was advanced by the time step calculated from the KMC analysis using an Euler forward approach. In this work the time steps are small enough that the potential instabilities of the Euler forward (or other explicit scheme for integration) were not considered a problem. Higher-order integration schemes were considered unnecessary because of the very short  $\Delta t$ 's involved in the KMC simulation (on the order of milliseconds).

The very short times involved ensure that high accuracy can be retained and it may not be necessary to perform a Newton-Raphson iteration at each time step. This is very desirable as inverting the Jacobian of the system of equations is computationally expensive and should be avoided if at all possible. To reduce the need for Newton-Raphson iteration, an initial guess for the algebraic equations at the current time step is extrapolated from the previous two time steps using linear extrapolation. If these guesses satisfy the residual equations within a specified tolerance, Newton-Raphson is not performed at that time step. The short times in this simulation combined with the intelligent (and cheaply obtained) initial guesses greatly reduce the number of

matrix inversions which are required, as even when Newton-Raphson is required, a single iteration is often sufficient to achieve convergence. An overview of using Euler approaches with Newton-Raphson methods is given in 5.2Appendix D.



Figure 4-16: Charge-discharge cycles used in the P2D/2+1D KMC coupled model.

Coupling of the P2D model with the KMC simulation allows for the SEI layer to be modeled across the thickness of the electrode. This can provide valuable insight as an SEI thickness which is not uniform across the anode thickness can exacerbate capacity and power fade. However, this requires that the KMC be run at multiple planes simultaneously. This further increases the computational costs of the coupled simulation. If two planes are considered, the number of domain sites is doubled, resulting an increase in the number of simulation events that must be accounted for at each KMC time step. As a consequence, the length of each time step is reduced proportionally. Thus, many more time steps are performed during simulation, as well as a similar increase in the number of Newton-Raphson steps that are required. Due to the large number of events that occur during a charge cycle, considerations must be made to conserve memory. Importantly, it is not necessary that all the states be recorded at each time step.

A preliminary study was performed for coupling the P2D model with the KMC algorithm. This was made very challenging due to the high computational cost of simulation, which made debugging a slow procedure, as running the first cycle took over a day, and subsequent cycles often took longer. Here we discuss the results of four consecutive charge-discharge cycles simulated using the algorithm described in Figure 4-15. For simplicity, only constant current charging and discharging at a 1C rate was considered, as shown in Figure 4-16.



Figure 4-17: Maximum ( $\Delta$ ), minimum ( $\circ$ ), and mean ( $\Box$ ) SEI thicknesses over 4 cycles of simulation for 1<sup>st</sup> collocation point (long dash) and 2<sup>nd</sup> collocation points.

The minimum, maximum, and average thicknesses of the SEI layer at the two collocation points are given in Figure 4-17. For these, the majority of the SEI layer growth occurs during the first cycle. Note that both charge and discharge conditions are represented on this graph. As the electrochemical conditions during discharge are not conducive for SEI layer growth (and was neglected in the KMC model), there is no increase in SEI thickness during those times. Note that there is also little variation in the SEI profiles at the two different collocation points studied here. This is consistent for diffusion limited cases as was shown in the continuum model in Section 3.3. The SEI profiles at the end of the  $1^{st}$ ,  $3^{rd}$ , and  $4^{th}$  cycles are shown in Figure 4-18 for the two collocation points.



Figure 4-18: SEI profiles using 2+1D KMC coupled with the P2D model for the 1<sup>st</sup> collocation point (a, b, & c) and the 2<sup>nd</sup> collocation point (d, e, & f) at the end of the 1<sup>st</sup> cycle (a & d), 3<sup>rd</sup> cycle (b & e), and 4<sup>th</sup> cycle (c & f)

The coupled model presented here is primarily a one-way coupling and should be considered as a preliminary work for a two-way coupled model to be developed. The P2D model calculates the overpotentials and other variables which are used to determine the rate constants of the KMC model, but the events that occur in the KMC model are not fed directly back to the P2D model. Specifically, events which are determined to occur from the KMC model can be used to change the continuum variables. For example, if lithium-ion diffusion from the electrolyte to the SEI layer occurs in the KMC model, the lithium-ion concentration in the continuum model can be reduced. This would replace the generation term in the P2D model. Thus, the continuum model would be limited to simulating phenomena which do not explicitly occur in the KMC model. Thus, the KMC model would provide the linkage between the electrolyte and solid phase in the continuum model, and allow for the pseudorandom nature to propagate into the P2D model.

## Chapter 5

# **Conclusions and Future Directions**

### 5.1 The Reformulated Porous Electrode Model

#### 5.1.1 Improving Computational Efficiency

The reformulation of the porous electrode pseudo two dimensional model presented in Chapter 2 was successful in substantially reducing the computational cost of simulation and may have a significant continuing impact in battery modeling efforts. Although this dissertation largely focused on the parameters and chemistry given by Doyle, et al.,<sup>14</sup> it must be stated that this model has been used for other applications with different chemistries. The reduction in computational costs has enabled other members of the MAPLE lab to use the physics based P2D model in applications that were considered to computationally expensive to use such a detailed model. De, et al.<sup>3</sup> used the reformulated to perform model based optimal design studies to maximize energy densities of the lithium-ion cell by simultaneously considering up to four design parameters. Such optimization requires the P2D model to be run thousands of times to find an optimal solution. Thus a computationally efficient and accurate model is highly desirable and allows for more parameters to be considered and optimized in a reasonable time.

Suthar, et al.<sup>33</sup> used the reformulated model to perform optimal control and state estimation. Like design optimization, this requires fast and efficient simulation. However, unlike design optimization, state estimation and control require real-time simulation. Thus, while the reformulated model was a significant convenience in the optimal design study, for control the reformulated model is essential if a detailed model is desired. Furthermore, in cases in which

simulation is to be performed on-line in resource limited conditions (e.g. microcontrollers), a simulation strategy which requires fewer equations enables the use of high-level models to be used. Ultimately, the DOE's ARPA-E AMPED program has provided significant funding to the MAPLE lab to develop a battery management system using model predictive control based on the reformulated model described in this work. The hope of that project is to improve the usable energy density and safety of lithium-ion batteries in electric vehicles.

Both collocation using trigonometric function and Chebyshev polynomials were considered as trial functions in Chapter 2. It was found that for a low number of node points, both approaches were similar. However, as more node points were used, trigonometric functions led to large oscillations and reduced accuracy, while oscillations died out and accuracy continuously improved when using Chebyshev polynomials. This is especially critical at high rates, which are more difficult to accurately simulate due to the large gradients that exist in the cell. A higher order collocation approach was also applied to the solid phase, which is necessary when simulating higher rates or when short time behavior is critical, as the parabolic profile can lead to profiles which are not physically meaningful at high rates. Ultimately, the final base reformulation code developed in this thesis allows for a variable number of collocation terms across the cell thickness and across the particle radius, though mass conservation in the particles is forced in the same manner as done with the parabolic profile approximation.

Although the work presented in this thesis represents a major improvement over standard numerical techniques, it would be naive to believe that further improvements will not be continued to be made. Work continues in the MAPLE group to reformulate the solid phase to retain accuracy and conserve mass while reducing the number of equations which can be incorporated into the P2D model. Higher order schemes are being examined as an alternative to collocation. Furthermore, improvements in the integration of the resulting differential algebraic equations in time will have a direct impact on simulation efficiency. As hardware and software improves, numerical techniques must evolve to fully utilize the available resources. Nearly the entirety of the work presented here would not be possible without a well developed computer algebra system to perform the symbolic math necessary to perform orthogonal collocation with more than a few terms, especially considering the highly nonlinear and coupled nature of the battery models. Furthermore, developing solving techniques which can parallelize the simulation steps will fully utilize the processing power available, as even the cheapest computing platforms have multiple cores, which can be further improved using hyperthreading.

The price of computational power has dropped over the years following Moore's law, creating an attitude the computational limitations do not exists. For many simple models that engineers use on a regular basis this may be true. Thus, researchers and engineers tend to be somewhat unconcerned with the computational requirements of simulation, as an inefficient (but easily applied) method can be used to arise at a seemingly satisfactory solution. However, the computational resources available for a given application are always finite. There is always a tradeoff between the detail of the model (e.g. the physical phenomena considered), the accuracy of simulation (e.g. from the number of terms or fineness of a simulation mesh), and time required to perform a simulation. Improved computational resources allow for improvements in all three areas, and thus the ever-increasing availability of computational power should be seen as a very exciting prospect for the future of simulation. However, this is not the only way in which the trade-off can be improved. The underlying mathematical techniques can also improve simulation time and accuracy, as shown in Chapter 2, and allows for more detail to be incorporated into the

model, as shown in Chapter 3. Thus, any researcher or engineer should strive to use an accurate and efficient simulation whenever performing modeling studies.

#### 5.1.2 Extending the Reformulated Model

Chapter 3 focused on the inclusion of additional physical phenomena into the reformulated model developed in Chapter 2, allowing for more comprehensive studies to be performed. Thermal analysis is essential to ensure that safe limits are maintained. This is particually important in large format cell in which thermal gradients can develop, possibly leading to localized hotspots which cannot be detected using surface temperature measurements.

Although simulation of an 8-cell stack was performed in Section 3.1, commercially made cells can have upwards of 150 cells connected in series and parallel. The reformulated model increases the feasibility of performing a fully coupled simulation of a large stack, but further work needs to be done to address the high memory requirements of such a configuration, especially if more collocation terms are to be used to improve accuracy at high rates. It is important to realize that only voltage (for cells connected in parallel) or current (for cells connected in series) and temperature are coupled between cells in a stack. Thus, simulation efficiency could likely be improved by decoupling the cells at each time step and iterating to find a converged solution. This approach would also facilitate the use of multiple processing cores if parallel processing is used.

The two dimensional model developed in Section 3.2 showed that temperature variations which are significant in the direction parallel to the electrode can lead to major variations in the local electrochemical behavior. The amount at which a variation exists in the *y*-direction is highly dependent on the specific application considered and the surrounding environment. As the computation costs of simulating a thermal-electrochemical model in two dimensions is large, the number of collocation points that could be achieved was limited. This challenge could be at least partially alleviated by translating the system of DAEs to FORTRAN or C for improved efficiency. Furthermore, the effect of current flow within the current collectors should also be considered in a future work.

A one-dimensional model was also developed which provided the framework for inclusion of SEI layer growth into the P2D model. As the kinetics which govern the growth of the SEI layer are not well understood, three different mechanisms from the literature<sup>13,22,83</sup> were used. Thus, the model developed here can be easily modified as understanding of the SEI layer improves.

As the diffusion of solvent through the SEI layer is necessary for additional growth to occur, operating the cell at a higher temperature will likely increase the rate of capacity fade by reducing the diffusion resistance. Thus, a comprehensive model which includes thermal effects and SEI layer growth (with temperature varying parameters) can provide the opportunity to perform life analysis and develop optimal strategies which ultimately minimize fade. A preliminary effort has been performed by the author as a proof of concept, but the model stiffness made simulating more than a couple thousand cycles difficult, and time constraints prevented a thorough analysis to be performed.

As other mechanisms of capacity fade are better understood, they should be incorporated into the reformulated model. The MAPLE group has done some work analyzing the stress and strain effects in a single particle model,<sup>12</sup> and it is expected that the reformulated model could be used to study the variation of the stress across the electrode thickness. A stress-strain model should be combined with the SEI layer growth model as fracture of the SEI layer can expose the active material and accelerate capacity fade. A more ambitious work would involve considering

the particle size distribution within the electrodes, and performing a population balance analysis to track the changes with cycle number. This can have a significant impact in long term battery performance and will be a significant challenge to accurately model.

#### **5.2 Kinetic Monte Carlo Simulations**

The kinetic Monte Carlo simulation described in Chapter 4 was a much more fundamental work which examined the heterogeneous growth of the SEI layer. The 2D model in Section 4.1 greatly simplified the mechanics of the solid electrolyte interface layer by ignoring the effects of SEI thickness and just assuming complete passivation of the electrode surface. However, useful analysis was able to be performed, especially when coupled with the P2D model. This allowed the SEI layer to vary across the thickness of the electrode, and showed that regions nearest the separator interface tended to be most passivated due to the lower overpotentials applied in that region.

The 2+1D KMC model improved the accuracy of the model by including the SEI layer thickness in the simulation, which is more in line with SEI behavior. The sheer number of possible events in a three dimensional domain encourages the development of efficient simulation techniques. Much of the work in developing the 2+1D KMC model focused on the reducing the cost of each time step and optimizing performance. Ultimately the growth of the SEI layer was successfully simulated using this approach, and a three dimensional profile was developed. A one-way P2D coupling was performed in which the porous electrode model was solved at each time step. This considerably increased the computational costs, especially as the domain increased due to the SEI layer growth. Further work will be needed to improve the coupling between the P2D model and KMC simulation to give a true two-way coupling. Such a

work will not be trivial, but the framework developed with the one-way coupling will provide a good starting point. Additionally, determination of physically meaningful parameters will be necessary to fully complete the model.

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## **Appendix A**

## The Numerical Method of Lines

### A.1 Background and Motivation

The method of lines is an efficient routine in which the spatial dimensions are discretized using any of a number of techniques, such as finite difference, finite element, finite volume, or collocation methods.<sup>26,86-95</sup> This converts the partial differential equation (PDE) to an initial value problem (IVP) system of ordinary differential equations (ODE) or differential algebraic equations (DAEs), which allows for either explicit or implicit time stepping algorithms to be used. Software packages have been developed to specifically solve problems using the method of lines.<sup>86</sup> Alternatively, the resulting DAEs can be solved using standard efficient time integrators,<sup>96</sup> including FORTRAN solvers such as DASKR or DASSL or in a computer algebra system such as Matlab<sup>97</sup> (dsolve), Maple<sup>49</sup>(dsolve), Mathematica<sup>98</sup> (ndsolve), etc. The versatility and simplicity of the method of lines has led to its use in a wide range of engineering applications, including fracture problems,<sup>99</sup> heat transfer,<sup>100</sup> solving Navier-Stokes equations,<sup>101</sup> and electromagnetic.<sup>95,102</sup> Furthermore, Pregla and Cietzorreck used the method of lines in conjunction with the source method to handle inhomogeneous boundary conditions and discontinuities in microstrip lines and antennas.<sup>102</sup>

# A.2 Mathematical Example

Consider a simple reaction diffusion process modeled by the following application of Fick's law with a first order reaction as a second order partial differential equation:

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - k_A c_A \tag{A.1}$$

Using a finite difference scheme, the second derivative term can be discretized as

$$\frac{\partial^2 c_A}{\partial x^2} \Big|_j \approx \frac{c_{A,j+1} - 2c_{A,j} + c_{A,j-1}}{\left(\Delta x\right)^2} \qquad \qquad j = 1..N$$
(A.2)

Equation (A.2) can be applied to Equation (A.1) to yield the following system of ordinary differential equations:

$$\frac{\partial c_{A,j}}{\partial t} = D_A \frac{c_{A,j+1} - 2c_{A,j} + c_{A,j-1}}{\left(\Delta x\right)^2} - k_A c_{A,j} \qquad j = 1..N$$
(A.3)

The system of ODEs given by Equation (A.3) can be solved using a choice of implicit or explicit IVP solver, including Eular's forward and backward methods, the Crank-Nicolson method, or a Runge-Kutta approach, for example.

The method of lines eliminates the need to directly solve the partial differential equation. The method described in Equations (A.1) to (A.3) can be extended to higher dimensional problems, for example for diffusion in two dimensions. More importantly for the work presented in this thesis, the method of lines can be applied to algebraic equations, i.e. those without a time derivative. This results in a system of differential algebraic equations (DAEs) that must be solved via efficient time-stepping algorithms.

Although a finite difference discretization is provided here, other methods can be used to eliminate the spatial derivatives to enable the method of lines approach. The model reformulation discussed in Chapter 2 uses the orthogonal collocation method described in Appendix B.

## **Appendix B**

## Method of Weighted Residuals and Orthogonal Collocation

This appendix contains excerpts from the following journal article reproduced here with permission from The Electrochemical Society:

P. W. C. Northrop, V. Ramadesigan, S. De, and V. R. Subramanian, "Coordinate Transformation, Orthogonal Collocation and Model Reformulation for Simulating Electrochemical-Thermal Behavior of Lithium-ion Battery Stacks," *Journal of the Electrochemical Society*, 158(12), A1461-A1477 (2011).

#### **B.1** Motivation

Although finite differences can be easily applied to discretize differential equations, many node points are required to achieve high accuracy. Alternatively, spectral methods can be used for discretization by approximating the dependent variables as a series solution of trial functions:

$$u_{approx}(x,t) = \sum B_k(t) Z_k(x)$$
(B.1)

Where  $Z_i(x)$  are pre-chosen trial functions, and the coefficients,  $B_i(t)$  are to be determined numerically. This represents all dependent variables as continuous functions of x, rather than at discrete node points. Also, orthogonal collocation converges to a solution with an error on the order of  $h^{2N}$ , where N is the number of collocation points and h is the node spacing.<sup>32</sup> The finite difference solution that is typically used has error on the order of  $h^2$ . Although the resulting equations are more complicated when using orthogonal collocation, fewer terms are required for a meaningful solution, resulting in fewer DAEs that must be solved and a net reduction in computation time.<sup>32</sup>

The boundary conditions can be satisfied by including the necessary number of additional functions to Equation (B.1). These may be additional trial functions of the same form of  $Z_k(x)$ , or they may be of different forms, for example, by using polynomials to solve for the boundary

conditions and trigonometric functions for the main solution, as done in Section 2.3. In either case, it is possible to determine the coefficients of the additional terms directly by application of the boundary conditions to Equation (B.1). This generally holds true for any type of boundary condition (i.e. Direclet, Neumann, or Robin), provided one does not try something terribly silly like use a constant term to satisfy flux conditions.

### **B.2** The Method of Weighted Residuals

#### **B.2.1** Development of Equations

The coefficients,  $B_i(t)$ , of the series approximation from equation (B.1) are determined by using the method of weighted residuals (MWR) which aims to find the coefficients which minimize the error.<sup>47</sup> Consider a general differential equation of the form:

$$D[u(x)] = 0 \tag{B.2}$$

Define the residual of an approximate solution

$$R(x) = D\left[u_{approx}(x)\right]$$
(B.3)

If the residual, R(x), is identically zero for all *x*, the approximate solution is the exact solution, but this is not generally the case in numerical solutions. The MWR aims to minimize the residual across the domain in some average way:

$$\int R\left(B_k(t), x\right) W_j(x) dx = 0 \qquad \qquad j = 0...N$$
(B.4)

Where N+1 weight functions,  $W_j(x)$ , are used to generate enough equations to solve for the unknown coefficients. Some options for the weight functions are given in Table B-1.

 Table B-1: Choices of weight functions

Method	Weight Function, $W_j(x)$	Notes
Moments	$x^{j}$	Conceptually simple, but better options
Galerkin	$Z_j(x)$	Same as trial function; minimizes sum of squared error
Subdomain	$\begin{cases} 1 & x_{j-1} < x < x_j \\ 0 & \text{otherwise} \end{cases}$	
Collocation	$\delta(x-x_j)$	Dirac delta function; choice of points affect accuracy; eliminates need to perform integration

In the case of highly non-linear governing equations, as those found in battery models, the integration in Equation (B.4) must be done numerically with significant computational cost. For collocation, the Dirac delta function is used as the weight function,  $W_j(x) = \delta(x - x_j)$ , to eliminate the need to perform the integration and reduces to

$$R\left(B_k(t), x = x_j\right) = 0 \qquad \qquad j = 0...N \tag{B.5}$$

Importantly, the error is minimized when the collocation points are chosen specifically as zeros of orthogonal polynomials. This is referred to as orthogonal collocation.<sup>46</sup>

#### **B.2.2** Choosing Collocation Points

In this work, the zeros of Jacobi polynomials are used when trigonometric trial functions are used, and Chebyshev-Gauss-Lobatto (CGL) points are used when Chebyshev polynomials are used as trial functions.

In Section 2.3 the collocation points are determined using the zeros of a specific class of orthogonal polynomials called the Jacobi polynomials when using trigonometric functions. The Jacobi polynomials are given by the relation:
$$P_{N}^{(\alpha,\beta)}(x) = \sum_{k=0}^{N} (-1)^{N-k} \gamma_{k} x^{k}$$
(B.6)

Where  $\gamma_0 = 1$  and  $\gamma_i$  is given by the recurrence relation:

$$\gamma_{k} = \frac{N-k+1}{k} \frac{N+k+\alpha+\beta}{k+\beta} \gamma_{k-1}$$
(B.7)

For a Jacobi polynomial of order *M*, there are *M* zeros in the interval [0,1]. Since there are  $N_r + 1$  coefficients for each variable in each region, a Jacobi polynomial of order  $N_r + 1$  must be used to develop enough collocation equations.  $\alpha \& \beta$  are characteristic parameters of the Jacobi polynomial. A trial and error approach found that  $\alpha = \beta = 0$  minimized the error of the discharge curve relative to the finite difference approach for most simulations. However, at high rates of charge and high node points, oscillations were observed as a result of numerical instabilities. This instability was eliminated by using  $\alpha = \beta = 1$  for a 5C discharge and  $\alpha = \beta = 2$  for a 10C discharge.

When Chebyshev polynomial trial functions are used, as in Section 2.4, Chebyshev-Gauss-Lobatto (CGL) points are used.<sup>48</sup> When N trial functions are used, the  $k^{th}$  zero is given as

$$X_{k,N} = -\frac{1}{2} \cos\left(\frac{\left(k + \frac{1}{2}\right)\pi}{N+1}\right) + \frac{1}{2}$$
(B.8)

These are the N zeros of the  $N^{th}$  +1 Chebyshev polynomial rescaled to the [0,1] domain.<sup>48</sup>

Both choices of collocation points place more collocation points near the boundaries and fewer near the center. This is favored as spectral methods inherently have a lower order of accuracy near the edge of the domain than near the center so that an equal spacing scheme results in better accuracy far from the edge.<sup>48</sup> Unequal node spacing addresses this issue. Additionally,

in many engineering systems modeled using transport equations, the region near the boundaries display a steep change in the dependent variables in relatively small region. Thus, accuracy in the boundary layer is critical for overall accurate simulation.

#### **B.2.3** Collocation in two dimensions

The application of orthogonal collocation to higher dimensions is a fairly straightforward extension of the one-dimensional case. The series approximation must consist of a double summation which can generally be given as

$$u_{approx}(x, y, t) = \sum_{j} \sum_{k} B_{j,k}(t) Z_{j}(y) Z_{k}(x)$$
(B.9)

The coefficients,  $B_{j,k}(t)$ , are solved in the same way as in the 1D problem: the residual is set to be zero at specified collocation points. The points are chosen as zeros of orthogonal polynomials as described in Equations (B.6) or (B.8) for both x and y. Furthermore, the boundary conditions can be applied *a priori* as with the one-dimensional case. However, this requires many more terms. For example, if N collocation points are considered in the *x*-direction, the boundary conditions at y = 0 and y = 1 require N functions to satisfy the constraints. In other words, the collocation point must be considered on boundaries in addition to the interior. This essentially applies orthogonal collocation to the boundary conditions in the same way that orthogonal collocation is applied to the governing differential equations. This is required as the boundaries in a two-dimensional domain are lines, rather than points. Thus, in general, it is not possible to satisfy the boundary conditions at all points using a series solution consisting of a finite number of terms. The method of weighted residuals is therefore applied at the boundary to develop enough equations to find a solution.

#### **B.3 Incorporating Orthogonal Collocation**

To maximize computational efficiency, it is important to note that it is most efficient to solve for the values of the dependent variables at the collocation points, rather than directly solving for the coefficients. The advantage of such an approach is best shown by the following example. Consider the reaction-diffusion problem example from Appendix A:

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - k_A c_A \tag{B.10}$$

Approximate the concentration of A by a series solution

$$c_{A,approx}(x,t) = \sum_{i=0}^{N} B_i(t) Z_i(x)$$
 (B.11)

Note that here we are neglecting the inclusion of boundary conditions, but those can be satisfied by adding two additional equations to Equation (B.11). The collocation points,  $x_k$ , can be applied to the series approximation, Equation (B.11) to develop N+1 equations:

$$c_{A}(x_{k},t) = C_{k}(t) = \sum_{i=0}^{N} B_{i}(t) Z_{i}(x_{k}) \qquad k = 0...N$$
(B.12)

Where  $C_k(t)$  is the value of the concentration at the  $k^{th}$  collocation point. Solving the linear system of equations in Equation (B.12) (noting that  $T_i(x_k)$  are calculable numerical values) for  $B_i(t)$  in terms of  $C_k(t)$  results in a modified series solution:

$$c_{A}(x,t) = \sum_{i=0}^{N} C_{i}(t) Z_{i}^{*}(x)$$
(B.13)

 $Z_i^*(x)$  is the linear combination of the trial functions which satisfies the system of equations in (B.12) so that the variable values at the collocation can be considered as coefficients. Applying Equation (B.13) to the governing equation results in a computational advantage over using Equation (B.11). Applying Equation (B.11) directly to Equation (B.10) results in the following convoluted system of equations

$$\sum_{i=0}^{N} Z_{i}(x_{j}) \frac{\partial B_{i}(t)}{\partial t} = D_{A} \sum_{i=0}^{N} B_{i}(t) \frac{\partial^{2} Z_{i}(x)}{\partial x^{2}} \Big|_{x_{j}} - k_{A} \sum_{i=0}^{N} B_{i}(t) Z_{i}(x_{j}) \qquad j = 0...N$$
(B.14)

However, if equation (B.13) is used, the discretized system of equations simply become

$$\frac{\partial C_{A,j}(t)}{\partial t} = D_A \sum_{i=0}^N C_{A,i}(t) \frac{\partial^2 Z_i^*(x)}{\partial x^2} \Big|_{x_j} - k_A C_{A,j}(t) \qquad \qquad j = 0...N$$
(B.15)

Equation (B.15) is simpler and is easier to solve as each equation only has a single time derivative and single forcing term. The form of equation (B.15) also reduces the numerical coupling of the system of equations and reduces the size of the system of equations. Using this approach, only spatial derivatives must be replaced as a series summation, as the non-derivative terms can be directly replaced by the  $C_{A,j}(t)$  term. Note that the numerical complexity of the derivative approximations are unaffected by this approach. The advantage is especially pronounced in the more complicated nonlinear governing equations which are seen in the battery model, and as more series terms are used. Furthermore this approach increases the overall sparsity of the resulting system of equations reducing the computational demands of simulation.

# **Appendix C**

# **Kinetic Monte Carlo**

This appendix contains excerpts from the following journal article reproduced with permission from The Electrochemical Society: R. N. Methekar, P. W. C. Northrop, K. Chen, R. D. Braatz, and V. R. Subramanian, "Kinetic Monte Carlo Simulation of Surface Heterogeneity in Graphite Anodes for Lithium-ion Batteries: Passive Layer Formation," *Journal of the Electrochemical Society*, 158(4), A363-A370 (2011).

Kinetic Monte Carlo (KMC) is a stochastic approach which considers discrete events to occur in a step-by-step manner in a microscale system. At each time step, an event is randomly chosen to be executed and the states of the system updated. The probability of each specific event occurring in a given time step is determined from the rates of each phenomena being simulated. Thus, those events which have faster rates are more likely to occur at any given time step. Mathematically, this is given as

$$P_j = \frac{r_j}{\sum_i r_i}$$
(C.1)

Where the reaction rates are given in  $s^{-1}$ . A uniform random number,  $\chi_1$ , is then chosen on the domain [0,1] to choose the specific event,  $r_i$  such that

$$\frac{\sum_{i=0}^{j-1} r_i}{\sum_{i=0}^{N} r_i} \le \chi_1 < \frac{\sum_{i=0}^{j} r_i}{\sum_{i=0}^{N} r_i}$$
(C.2)

Note that the rates are given for each *specific* event, rather than each class of event. For example, consider a simplified system with a single particle where only diffusion is considered. Although diffusion is the only physical phenomena being studied, there are multiple discrete events considered. A diffusion hop in the +x direction must be treated as a separate event from a

diffusion hop in the -y direction, for instance. Because each individual event must be accounted for, there can be hundreds or thousands of possible KMC moves to be chosen from, even though only a handful of physical phenomena may be considered. In practice, the computational costs of calculating the probabilities can be reduced by considering the class of events (e.g. diffusion of species A) as group, assuming all individual events within a class have the same probability. In this way, the probability of an event occurring within class *C*, can be given by

$$P_c^* = \frac{N_c r_c}{\sum_{i}^{M} N_i r_i}$$
(C.3)

where  $N_c$  is the number of discrete events possible in class *C* and *M* is the number of classes considered. Thus, a random number is first chosen to decide the class of event which will occur, analogous to equation (C.2)

$$\frac{\sum_{i=0}^{j-1} N_i r_i}{\sum_{i=0}^{M} N_i r_i} \le \chi_1 < \frac{\sum_{i=0}^{j} N_i r_i}{\sum_{i=0}^{M} N_i r_i}$$
(C.4)

Once the class of event is determined, the specific event (i.e. diffusion of molecule #ifrom point (x, y) to point (x', y')) can be randomly chosen from the subset of events within a chosen class using a uniform distribution. Simultaneously considering hundreds or thousands of events in Equation (C.2) is computationally very expensive because of the number of summations (up to  $N_{tot}$ ) that must be performed to determine the specific event. Equation (C.4) requires many fewer (up to M) summations to be performed and sorted, providing significant computational cost savings. Since each specific event within a given class has equal probabilities, selection of which event can be done be simply using a random number to pick an event out of a list, rather than using the form of Equation (C.2).



Figure C-1: Flowchart depicting general kinetic Monte Carlo algorithm with the individual events subdivided by class. All pseudorandom variables are chosen on the domain (0,1]

After a specific event is determined, the simulation progresses to the next time step. The length of time between KMC events is also not deterministic, but also found probabilistically. Another uniformly distributed pseudorandom variable,  $\chi_2$ , is chosen on the domain (0,1] to calculate the elapsed time between steps using equation<sup>103</sup>

$$\Delta t = -\frac{\ln \chi_3}{\sum_{i=1}^M N_i r_i} \tag{C.5}$$

Equation (C.5) is convenient as any time step from 0 to  $\infty$  is possible (though very long time steps are very, very unlikely). Furthermore, the expected value of (C.5) is equal to the characteristic time of the system, giving it a physically meaningful interpretation and allows the simulation to progress at an expected rate without forcing a specific time step.

When an event is chosen, the system advances to the next step based on the outcome of that event. Thus the possible events must be updated, and the probabilities recalculated. For a large system, it is likely that most of the possible events are identical for the new state as for the old state. For example, if the chosen event involved element #i in one area of the domain, events involving element #j in a spatially separate area are not affected. Thus, only the events involving ion #i, or events involving the either the previous or current location must be updated. This is much more computationally efficient than recalculating all possible events at every time step.

The simulation can be continued indefinitely, or until a certain termination condition is met. Analysis can be performed by considering the final state of the system, or the events which occurred during simulation, depending on the system being studied.

# **Appendix D**

# Numerically Integrating a System of DAEs Using Euler's Method and Newton-Raphson

Wherever appropriate and possible, this thesis utilized efficient numerical simulation of large scale DAEs using DASKR. For clarity and to provide a simple and robust method of solving DAEs, this appendix is provided. Consider a system of differential algebraic equations of the form

$$\frac{d\mathbf{y}}{dt} = \mathbf{f}(t, \mathbf{y}, \mathbf{z})$$
(D.1)  
$$0 = \mathbf{g}(t, \mathbf{y}, \mathbf{z})$$

Where **y** is the vector of differential variables, z is the vector of algebraic variables, **f** is the vector of differential equations, and **g** is the vector of algebraic equations. Several options exist for the discretization of the differential equations in Equation (D.1) to advance the system to the next time step. The Euler forward method, an explicit method gives

$$\mathbf{y}^{i+1} = \mathbf{y}^i + \mathbf{f}(t, \mathbf{y}^i, \mathbf{z}^i) \Delta t$$
 (D.2)

Euler forward is computationally simple but can be unstable. Furthermore, the algerbraic equations cannot be integrated directly and must be solve simultaneously. Euler backward is an implicit method which is unconditionally stable:

$$\mathbf{y}^{i+1} = \mathbf{y}^i + \mathbf{f}(t, \mathbf{y}^{i+1}, \mathbf{z}^{i+1}) \Delta t$$
 (D.3)

Equation (D.3) is a system of equations which must be solved simultaneously to arrive at a solution, unlike Equation (D.2), which can be evaluated directly. Both the Euler backward and Euler forward methods are of order  $\Delta t$  error, which is less than ideal. The Crank-Nicholson

method is an alternative method which is accurate to the order  $\Delta t^2$ , without greatly increasing the computational complexity

$$\mathbf{y}^{i+1} = \mathbf{y}^{i} + \frac{\Delta t}{2} \left( \mathbf{f}(t, \mathbf{y}^{i+1}, \mathbf{z}^{i+1}) + \mathbf{f}(t, \mathbf{y}^{i}, \mathbf{z}^{i}) \right)$$
(D.4)

The Crank-Nicholson method is also implicit and unconditionally stable, but can experience spurious oscillations, making the less accurate Euler backward preferred in stiff applications.

Regardless of the specific discretization used in time, Equation (D.2), (D.3), or (D.4) can be applied to Equation (D.1) to give the following general system of strictly algebraic equations:

$$0 = \mathbf{f}^{*}(t, \Delta t, \mathbf{y}^{i}, \mathbf{y}^{i+1}, \mathbf{z}^{i}, \mathbf{z}^{i+1})$$
  

$$0 = \mathbf{g}(t, \mathbf{y}^{i+1}, \mathbf{z}^{i+1})$$
(D.5)

As both parts of Equation (D.5) are now algebraic we can combine the two parts for simplicity

$$0 = \mathbf{h}(t, \Delta t, \mathbf{y}^{i}, \mathbf{y}^{i+1}, \mathbf{z}^{i}, \mathbf{z}^{i+1})$$
(D.6)

Where the superscript, i, refers to the current time step, of which all values are known. Note that if an explicit scheme is used, the  $\mathbf{f}^*$  equation in Equations (D.5) can be solved independently, and  $\mathbf{h}$  is identical to  $\mathbf{g}$ , otherwise  $\mathbf{f}^*$  must be included in  $\mathbf{h}$  and a simultaneous solution is required. Finding a solution to Equation (D.6) can be done using the Newton-Raphson approach, which requires the calculation of the Jacobian. If  $\mathbf{h}$  consists of N equations with N unknowns, the Jacobian is an  $N \times N$  matrix defined as

$$\mathbf{J}_{j,k} = \frac{d\mathbf{h}_j}{d\mathbf{x}_k} \tag{D.7}$$

Where  $\mathbf{x}$  is the union of  $\mathbf{y}^{i+1}$  and  $\mathbf{z}^{i+1}$ . The Newton-Raphson approach is an iterative procedure which finds the solution to Equation (D.6) using the following formula

$$\mathbf{x}^{l+1} = \mathbf{x}^l + \gamma \mathbf{J}^{-1} \mathbf{h} \tag{D.8}$$

Where  $\mathbf{x}^{l+1}$  is the refined approximation from  $\mathbf{x}^{l}$  and  $\gamma$  is a relaxation parameter which can take on values from (0,1]. A smaller relaxation parameter can prevent overshooting of the solution (which can cause the method to fail in some cases), but may slow convergence. Equation (D.8) is repeated until the error (as defined as the maximum absolute value of either  $\mathbf{J}^{-1}\mathbf{h}$  or  $\mathbf{h}$ ) is less than a prescribed tolerance. In general, the Newton-Raphson procedure must be used at the beginning of simulation to find consistent initial conditions for the algebraic variables.

The convergence of the Newton-Raphson approach is highly dependent on the initial guess provided,  $\mathbf{x}^0$ , at each time step. A good initial guess can reduce the number of iterations which must be performed in Equation (D.8), while a poor initial guess may not converge at all. As the Jacobian calculation and matrix inversion in Equation (D.8) is computationally expensive, any reduction in the number of iterations which are performed is usually advantageous. For the algebraic variables, the converged values from the previous two time steps can be used to estimate the value at the current time step using linear extrapolation:

$$\mathbf{z}^{i+1,0} = \mathbf{z}^{i} + \frac{\Delta t^{i}}{\Delta t^{i-1}} \left( \mathbf{z}^{i} - \mathbf{z}^{i-1} \right)$$
(D.9)

The differential variables can be estimated using linear extrapolation as well, or can use the Euler forward method to give a good initial guess:

$$\mathbf{y}^{i+1,0} = \mathbf{y}^{i} + \mathbf{f}(t, \mathbf{y}^{i}, \mathbf{z}^{i})\Delta t$$
 (D.10)

A flowchart depicting the algorithm described here using the Newton-Raphson approach with the Euler backward method is given in Figure D-1.

It must be noted that other numerical approaches can be incorporated into this framework. For example, Richardson extrapoloation solves the system using time steps of  $\Delta t$  and  $\frac{\Delta t}{2}$ . Based on the difference between the two solutions, the final approximation is achieved

by extrapolating the error down to a time step of zero length. This improves the order of accuracy in time. Furthermore, it can be determined whether a smaller time step is required, or a larger time step can be used, allowing for adaptive schemes to be used.



Figure D-1: Using Euler backward and Newton Raphson to solve a system of DAEs

The Newton-Raphson iteration can also be improved upon by using tearing algorithms. Tearing algorithms divide the full system of algebraic in multiple smaller systems. Each subsystem can be iterated upon independently, using variable values from the other subsystems. This requires an iterative procedure to be performed over the subsystems. As the Jacobian is smaller in each subsystem is much small than the full system, the inversion is much simpler. For systems which are largely decoupled, or have certain variables which are only weakly coupled with the remainder of the system, tearing algorithms can greatly improve speed. However, for tightly coupled systems, many iterations between the subsystems are required, negating any benefit of the smaller size of the Jacobian.

## **Appendix E**

## **A Robust False Transient Method of Lines for Elliptic**

### **Partial Differential Equations**

This pppendix is reproduced with permission in accordance with the author rights from the following article: P. W. C. Northrop, P. A. Ramachandran, W. E. Schiesser, and V. R. Subramanian, "A Robust False Transient Method of Lines for Elliptic Partial Differential Equations," *Chemical Engineering Science*, 90; 32–39 (2013).

Available online at http://www.sciencedirect.com/science/article/pii/S0009250912006835

#### **E.1 Background**

Simulation of lithium-ion battery behavior often requires solving a nonlinear system of differential algebraic equations (DAEs), as described in Chapter 2 and Appendix B. One challenge in solving this system of DAEs is the initialization problem. That is, finding initial conditions which satisfy the algebraic equations. If consistent initial conditions are not provided, many DAE solvers fail. This has led to the development of a perturbation approach to initialize the algebraic variables in battery models.<sup>31</sup> Here we extend that approach to solve generic elliptic partial differential equations by building upon the method of false transients<sup>26,88,89,93,104,105</sup> with a similar perturbation approach.

A wide variety of partial differential equations arise when describing engineering systems. For examples, variations on Laplace's equation arise frequently in problems of transport phenomena.<sup>106</sup> In order to solve such a wide range of problems, several numerical methods exist to solve partial differential equations. The choice of method is dependent on the desired accuracy, as well as concerns about the stability and robustness of the system, while maintaining computational efficiency. Furthermore, these characteristics are dependent on the form of the partial differential equation to be solved, i.e. elliptic, parabolic, or hyperbolic. For parabolic

equations such as the heat equation, several numerical methods exist that can be used to find a solution.<sup>90</sup> For example, the method of lines is one such efficient routine in which the spatial dimensions are discretized using any of a number of techniques, such as finite difference, finite element, finite volume, or collocation methods, as shown in Appendix B.<sup>26,86-95</sup> This converts the partial differential equation (PDE) to an initial value problem (IVP) system of ordinary differential equations (ODE) or differential algebraic equations (DAEs). Software packages have been developed to specifically to solve problems using the method of lines.<sup>86</sup> Alternatively, the resulting DAEs can be solved using standard efficient time integrators,<sup>96</sup> including FORTRAN solvers such as DASKR or DASSL or in a computer algebra system such as Matlab<sup>97</sup> (dsolve), Maple<sup>49</sup>(dsolve), Mathematica<sup>98</sup> (ndsolve), etc. The versatility and simplicity of the method of lines has led to its use in a wide range of engineering applications, including fracture problems,<sup>99</sup> heat transfer,<sup>100</sup> solving Navier-Stokes equations,<sup>101</sup> and electromagnetic.<sup>95,102</sup> Furthermore, Pregla and Cietzorreck used the method of lines in conjunction with the source method to handle inhomogeneous boundary conditions and discontinuities in microstrip lines and antennas.<sup>102</sup>

The solution of elliptic partial differential equations, such as Laplace's equation, is more difficult because there is not a simple way to convert the equations to an initial value problem to allow the use of the method of lines. A Newton-Raphson method, or another approach to solving a system of nonlinear equations, can be used if the system of algebraic equations resulting from the discretization is sufficiently well behaved and a reasonable initial guess is available. A semianalytical method of lines, valid for linear elliptic PDEs and certain quasilinear elliptic PDEs has been presented previously.<sup>107</sup> However, a more popular choice has been the method of false transients, partially due to its ability to handle some nonlinear problems, and ease of implementation. In the false transient method the variables are discretized in the spatial or

boundary value independent variables (*x* and *y*), and a pseudo time derivative is arbitrarily added to the problem statement.<sup>26,88,89,93,104,105</sup> The addition of this fictitious time derivative converts the elliptic PDE to a parabolic PDE and allows the solution to be determined by marching in pseudo time to a steady state condition, in a manner analogous to the standard method of lines. By doing this, the efficient IVP/DAE solvers can be applied in a matter analogous to the method of lines.<sup>93</sup>

Like the method of lines, the method of false transients is used to solve a variety of engineering problems. For example, Xu, et al., used the false transient method to describe the concentration and temperature profiles of catalyst particles.<sup>108</sup> This approach has also been used to numerically solve for three dimensional velocity profiles by solving the Navier-Stokes equation,<sup>109</sup> as well as solving the convective diffusion equation for axial-diffusion problems in laminar-flow reactors.<sup>110</sup> Other researchers have used the false transient method for analyzing mass transfer in porous media<sup>111</sup> or laminar film boiling.<sup>112</sup>

However, as shown in this section, the system of ODE/DAEs resulting from the use of the false transient method can be unstable and may not converge to the desired (or any) solution. This problem can sometimes be rectified by modifying the form of the equations or boundary conditions using intuition and trial and error. In other cases, the system cannot be made to converge, regardless of how the problem is presented. An alternative, Jacobian-based perturbation approach is shown here, which is robust and does not suffer from the same stability issues which befall the false transient method. A similar approach has been used as a superior method for the initialization of the algebraic variables in systems of DAEs.<sup>31</sup>

# E.2 Generic Formulation of the False Transient Method and the Perturbation Method

Consider a general PDE of the form

$$D(\phi(\mathbf{x})) = 0 \tag{E.1}$$

Where  $\phi(\mathbf{x})$  is the (continuous) dependent variable of interest,  $\mathbf{x}$  is the vector of independent variables, and D is a generic linear differential operator with the form:

$$D = \sum_{i} \sum_{j} a_{ij} \frac{\partial^{i}}{\partial x_{j}^{i}}$$
(E.2)

Equation (E.1) can be discretized using any of a number of techniques, such as finite difference, finite element, finite volume, or collocation, among others. This results in a system of algebraic equations of the form

$$\mathbf{g}(\mathbf{\Phi}) = 0 \tag{E.3}$$

where  $\Phi$  is the vector of the discretized dependent variables. In linear systems, Equation (E.3) can be solved directly, though this is generally not the case in nonlinear problems. Both the method of false transients and the perturbation method introduce a pseudo time variable,  $\tau$ , such that Equation (E.3) is represented as:

$$\mathbf{g}(\mathbf{\Phi}(\tau)) = 0 \tag{E.4}$$

When using the method of false transients, this is done by introducing a first order pseudo-time derivative into Equation (E.4) such that it becomes:

$$\mathbf{g}\left(\mathbf{\Phi}\left(\tau\right)\right) = \frac{d\mathbf{\Phi}}{d\tau} \tag{E.5}$$

This allows the use of efficient time adaptive ODE solvers to be used. In order for convergence to occur, the right hand side must go to zero as  $\tau_{goes}$  to infinity:

$$\lim_{\tau \to \infty} \frac{d\Phi}{d\tau} = 0 \tag{E.6}$$

This reduces Equation (E.5) to Equation (E.3) and ensures that the original problem is satisfied. However, the method of false transients can fail if Equation (E.6) does not hold, as can occur in an unstable system. Therefore, an alternative perturbation approach is shown here. A small perturbation parameter,  $\delta$ , can be applied in time to Equation (E.4) such that

$$\lim_{\delta \to 0} \mathbf{g}(\boldsymbol{\Phi}(\tau + \delta)) = 0 \tag{E.7}$$

Equation (E.7) can be expanded using a Taylor series to give

$$\mathbf{g}(\mathbf{\Phi}(\tau)) + \mathbf{\delta} \frac{d\mathbf{g}(\mathbf{\Phi}(\tau))}{d\tau} + O(\mathbf{\delta}^2) = 0$$
 (E.8)

Assuming that  $\delta$  is sufficiently small that the higher order terms can be neglected, Equation (E.8) reduces to

$$\mathbf{g}(\mathbf{\Phi}(\tau)) + \grave{\mathbf{o}} \frac{d\mathbf{g}(\mathbf{\Phi}(\tau))}{d\tau} = 0$$
(E.9)

The total derivative in Equation (E.9) can be rewritten using the chain rule with partial derivatives

$$\mathbf{g}(\mathbf{\Phi}(\tau)) + \delta \left[ \frac{\partial \mathbf{g}}{\partial \mathbf{\Phi}} \frac{\partial \mathbf{\Phi}}{\partial \tau} + \frac{\partial \mathbf{g}}{\partial \tau} \right] = 0$$
(E.10)

Noting that  $\frac{\partial g}{\partial \Phi} = J$ , where **J** is the Jacobian representing the algebraic system. Also, note that

from Equation (E.3),  $\mathbf{g}$  is not a function of pseudo time directly; only indirectly as the dependent

variables,  $\mathbf{\Phi}$ , are functions of pseudo time. Therefore,  $\frac{\partial \mathbf{g}}{\partial \tau} = 0$  above and Equation (E.10), can be rearranged to give

$$\mathbf{g}\left(\mathbf{\Phi}\left(\tau\right)\right) = -\mathbf{\hat{o}}\mathbf{J}\frac{\partial\mathbf{\Phi}}{\partial\tau} \tag{E.11}$$

Equation (E.11) can be considered as an application of Davidenko's Method.<sup>89</sup> Note that the choice of  $\delta$  is somewhat arbitrary, and must be chosen with consideration to the system. Ideally b must be sufficiently small that the assumption that the higher order terms in Equation (E.8) can be neglected is valid. Here,  $\delta = 10^{-3}$  is used throughout the remainder of this work. This choice is somewhat arbitrary as changing  $\delta = 10^{-3}$  by an order of magnitude in either direction does not affect the steady state results. Equation (E.11) is similar to Equation (E.5)given above for the method of false transients, and similarly allows for the use of efficient DAE solvers, although the right hand side consists of a linear combination of time derivatives of several of the dependent variables,  $\Phi$ . The use of the Jacobian ensures that Equation (E.11) is stable and more robust than Equation (E.5). This will be shown for linear models using matrix algebra and considering the exponential matrix solution that Equation (E.6) is always valid and Equation (E.11) converges to Equation (E.3) at infinite times irrespective of the initial conditions. The concepts can then be extended to nonlinear models by considering the eigenvalues of the resulting system of equations. In contrast, the false transient method may or may not converge to Equation (E.3) depending on the eigenvalues of the Jacobian. This will be explained in more detail in a later section.

# E.3 Implementation and Comparison of the False Transient Method and the Perturbation Method

Several examples will be shown to compare the performance of the false transient method with the proposed Jacobian approach, as well as to note the conditions which cause failure of the method of false transients. The examples will be explored in 2-dimensional space in Cartesian coordinates, although extensions to other coordinate systems and to 3-dimensional space are appropriate and can be applied analogously. In this paper, the system of ODEs given in Equations (E.5) and (E.11) were written to a FORTRAN file and simulated using DASKR for computational efficiency. Furthermore, all symbolic calculations for the calculation of the Jacobian when using the perturbation approach were performed in Maple.<sup>49</sup>

#### E.3.1 Solving Laplace's Equation

The simplest example to be considered is Laplace's equation, which is given in 2 dimensional rectangular coordinates as:

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = 0$$
 (E.12)

Laplace's equation is used in numerous engineering disciplines such as steady state heat/mass transfer or when calculating potential fields. The following boundary conditions are considered, as shown in Figure E-1.

$$\frac{\partial \phi(0, y)}{\partial x} = 0 \tag{E.13}$$

$$\frac{\partial \phi(x,0)}{\partial y} = 0 \tag{E.14}$$

$$\phi(1, y) = 0$$
 (E.15)



Figure E-1: Boundary conditions used for solving Example 1 (Laplace's equation) and Example 2 (Helmholtz's Equation)

Notice that Equation (E.16) is made to be non-homogeneous in order to avoid the trivial solution. This problem can be solved analytically using the standard separation of variables technique to yield:

$$\phi = \sum_{n=0}^{\infty} \frac{(-1)^n 4\cos\left(\frac{2n+1}{2}\pi x\right) \cosh\left(\frac{2n+1}{2}\pi y\right)}{\pi (2n+1) \cosh\left(\frac{2n+1}{2}\pi\right)}$$
(E.17)

Since an analytical solution can be found only for limited cases (e.g. linear problems), Equation (E.17) is used to benchmark the accuracy of the proposed approach.

A numerical solution can be found by discretizing Equation (E.12) into M interior node points in x and N interior node points in y. This discretizes the domain into  $(N+2) \times (M+2)$  node points when the surface points are considered. The following finite difference schemes of order  $h^2$  are used:

$$\frac{\partial^2 \phi(x, y)}{\partial x^2} \approx \frac{\phi_{m-1}^n - 2\phi_m^n + \phi_{m+1}^n}{\left(\Delta x\right)^2}$$
(E.18)

$$\frac{\partial^2 \phi(x, y)}{\partial y^2} \approx \frac{\phi_m^{n-1} - 2\phi_m^n + \phi_m^{n+1}}{\left(\Delta y\right)^2}$$
(E.19)

with *m* as the node index in the *x*-direction and *n* as the node index in the *y*-direction. When these approximations are applied to Equation (E.12), the following equation is obtained for each interior node point, (m,n):

$$\frac{\phi_{m-1}^{n} - 2\phi_{m}^{n} + \phi_{m+1}^{n}}{\left(\Delta x\right)^{2}} + \frac{\phi_{m}^{n-1} - 2\phi_{m}^{n} + \phi_{m}^{n+1}}{\left(\Delta y\right)^{2}} = 0 \text{ for } m = 1...M, n = 1...N$$
(E.20)

A second order forward finite difference is applied for the Neumann boundary conditions given in Equations (E.13) and (E.14):

$$\frac{\partial \phi(0, y)}{\partial x} \approx \frac{-\phi_2^n + 4\phi_1^n - 3\phi_0^n}{2\Delta x} = 0 \text{ for } n = 0...N + 1$$
(E.21)

$$\frac{\partial \phi(x,0)}{\partial y} \approx \frac{-\phi_m^2 + 4\phi_m^1 - 3\phi_m^0}{2\Delta y} = 0 \text{ for } m = 0...M + 1$$
 (E.22)

The Dirichlet boundary conditions from Equations (E.15) and (E.16) can be expressed simply as

$$\phi_{M+1}^n = 0$$
 for  $n = 0...N + 1$  (E.23)

$$\phi_m^{N+1} = 1$$
 for  $m = 0...M + 1$  (E.24)

Equations (E.20) to (E.24) are a system of linear algebraic equations which can be solved trivially using a variety of solvers. However, for nonlinear systems which cannot be solved so simply, other methods can be utilized to arrive at a solution, and thus this is used as a verifiable test problem. When the method of false transients is applied to Equations (E.20)-(E.24) the following ordinary differential equations (ODEs) are obtained.

$$\frac{d\phi_n^m}{d\tau} = \frac{\phi_{m-1}^n - 2\phi_m^n + \phi_{m+1}^n}{\left(\Delta x\right)^2} + \frac{\phi_m^{n-1} - 2\phi_m^n + \phi_m^{n+1}}{\left(\Delta y\right)^2} \text{ for } m = 1...M, n = 1...N$$
(E.25)

$$\frac{d\phi_0^n}{d\tau} = \frac{-\phi_2^n + 4\phi_1^n - 3\phi_0^n}{2\Delta x} \text{ for } n = 0...N + 1$$
(E.26)

$$\frac{d\phi_m^0}{d\tau} = \frac{-\phi_m^2 + 4\phi_m^1 - 3\phi_m^0}{2\Delta y} \text{ for } m = 0...M + 1$$
(E.27)

$$\frac{d\phi_{M+1}^n}{d\tau} = -\phi_{M+1}^n \text{ for } n = 0...N + 1$$
 (E.28)

$$\frac{d\phi_m^{N+1}}{d\tau} = 1 - \phi_m^{N+1} \text{ for } m = 0...M + 1$$
(E.29)

Note that the formulation of Equations (E.28) and (E.29) required a rearrangement of Equations (E.23) and (E.24) in order to develop stable ODEs which converge to the solution. In order to explain why such a rearrangement is necessary, recall that the following condition must be satisfied for convergence to occur:

$$\lim_{\tau \to \infty} \frac{d\phi_m^n}{d\tau} = 0 \tag{E.30}$$

Thus, Equations (E.25)-(E.29) reduce to Equations (E.20)-(E.24) at long psuedo times. However, if the method of false transients were applied directly to Equation (E.23) to give:

$$\frac{d\phi_{M+1}^n}{d\tau} = \phi_{M+1}^n \tag{E.31}$$

The solution to the eigenfunction problem in Equation (E.31) is an exponentially increasing function. Therefore, the resulting system of ordinary differential equations (ODEs) is unstable and Equation (E.30) will not be satisfied. In this relatively simple example, the sign of Equation (E.31) could simply be changed to ensure stability, as it can be determined to be unstable a priori. However, the instability may not be so obvious for more complicated problems, or the stability issue may not be fixed by simply changing the sign.

When the perturbation approach described above in Equation (E.11) is applied to the system given in Equations (E.20) to (E.24) the following system of linearly coupled ODEs results

$$-\frac{\grave{o}}{(\Delta y)^{2}} \left( \frac{d\phi_{m-1}^{n}}{d\tau} - 2\frac{d\phi_{m}^{n}}{d\tau} + \frac{d\phi_{m+1}^{n}}{d\tau} \right) - \frac{\grave{o}}{(\Delta x)^{2}} \left( \frac{d\phi_{m}^{n-1}}{d\tau} - 2\frac{d\phi_{m}^{n}}{d\tau} + \frac{d\phi_{m}^{n+1}}{d\tau} \right) = \frac{1}{(\Delta y)^{2}} \left( \phi_{m-1}^{n} - 2\phi_{m}^{n} + \phi_{m+1}^{n} \right) + \frac{1}{(\Delta x)^{2}} \left( \phi_{m}^{n-1} - 2\phi_{m}^{n} + \phi_{m}^{n+1} \right)$$
(E.32)

$$\frac{-\grave{o}}{2\Delta x} \left( -\frac{d\phi_2^n}{d\tau} + 4\frac{d\phi_1^n}{d\tau} - 3\frac{d\phi_0^n}{d\tau} \right) = \frac{-\phi_2^n + 4\phi_1^n - 3\phi_0^n}{2\Delta x}$$
(E.33)

$$\frac{-\grave{o}}{2\Delta y} \left( -\frac{d\phi_m^2}{d\tau} + 4\frac{d\phi_m^1}{d\tau} - 3\frac{d\phi_m^0}{d\tau} \right) = \frac{-\phi_m^2 + 4\phi_m^1 - 3\phi_m^0}{2\Delta y}$$
(E.34)

$$-\dot{\mathbf{o}}\frac{\phi_{M+1}^n}{d\tau} = \phi_{M+1}^n \tag{E.35}$$

$$-\dot{o}\frac{\phi_m^{N+1}}{d\tau} = \phi_m^{N+1} - 1$$
 (E.36)



Figure E-2: Converged solution of Laplace's Equation

Equations (E.35) and (E.36) demonstrate the robustness of the perturbation method. Regardless of whether the boundary conditions are applied as Equations (E.23) & (E.24) or in the form required for the false transient solution, Equations (E.35) and (E.36) will converge to the expected solution. Considering Equations (E.32)-(E.36) in matrix form, as shown in Equation (E.11) above, we have

$$-\partial \mathbf{J} \frac{d\mathbf{\Phi}}{d\tau} = \mathbf{J}\mathbf{\Phi} + \mathbf{b} \tag{E.37}$$

for a linear system of equations. Equation (E.37) can be explicitly solved for in the time derivatives to yield

$$\frac{d\mathbf{\Phi}}{d\tau} = -\dot{\mathbf{o}}^{-1}\mathbf{I}\mathbf{\Phi} - \dot{\mathbf{o}}^{-1}\mathbf{J}^{-1}\mathbf{b}$$
(E.38)

which is unconditionally stable and will always converge to a solution.



Figure E-3: Convergence of the perturbation method (solid line) and false transient method (dashed line) for Laplace's Equation (Inset shows the graph at very short pseudo time)

Figure E-2 shows the converged 2-D numerical solution, as determined using 50 interior node points in *x* and *y* (for a total of 2704 points). Figure E-3 compares the solution found with a perturbation of  $\partial = 0.001$  with the traditional method of false transients by showing the value of  $\phi$  at *x*=0 and *y*=0 as a function of the pseudo time variable used in both methods. The proposed approach is superior because (1) steady state is achieved at shorter values of the dummy variable and (2) the method is robust, and is inherently stable as shown by Equation (E.38).

#### E.3.2 Solving Helmholtz's Equation

As a slightly more complicated example, Laplace's equation will be expanded to Helmholtz's equation by including a linear term to Equation (E.12):

$$\frac{\partial^2 \phi(x, y)}{\partial x^2} + \frac{\partial^2 \phi(x, y)}{\partial y^2} + k^2 \phi(x, y) = 0$$
(E.39)

In order to examine a non-trivial case, the boundary conditions used are nonhomogeneous and identical to Equations (E.13) to (E.16). Once again an analytical solution can be found using the separation of variables technique:

$$\phi(x,y) = \sum_{n=0}^{\infty} \frac{(-1)^n 4\cos\left(\frac{2n+1}{2}\pi x\right)\cosh\left(\sqrt{-k^2 + \left(\frac{2n+1}{2}\right)^2 \pi^2}y\right)}{\pi (2n+1)\cosh\left(\sqrt{-k^2 + \left(\frac{2n+1}{2}\right)^2 \pi^2}\right)}$$
(E.40)

which reduces to Equation (E.17) when  $k^2 = 0$ . Note also that for values of  $k^2 > \left(\frac{2n+1}{2}\right)^2 \pi^2$ , a negative value exists under the radical in Equation (E.40), leaving an imaginary argument for the

hyperbolic cosine terms. It can be shown using Euler's formula that:

$$\cosh(zi) = \cos(z) \tag{E.41}$$

Therefore, as  $k^2$  increases, the behavior of the denominator of Equation (E.40) changes from hyperbolic cosine to standard cosine. Thus, singularities exist in the system for certain values of  $k^2$  in which no solution exists. Also, there is a sign change which occurs across these values. This is worth noting, as it can increase the difficulties in finding a solution when using numerical methods. Equation (E.39) can be discretized using a finite difference scheme given in Equations (E.18) and (E.19) as done previously for Laplace's equation.



Figure E-4: Convergence of  $\phi$  for the Helmholtz Equation with  $k^2 = 1$  using the perturbation method (solid line) and the false transient method (dashed line). The inset shows the convergence at very short pseudo time.

The resulting equation is similar to Equation (E.20) with an additional linear term included:

$$\frac{\phi_{m-1}^{n} - 2\phi_{m}^{n} + \phi_{m+1}^{n}}{\left(\Delta x\right)^{2}} + \frac{\phi_{m}^{n-1} - 2\phi_{m}^{n} + \phi_{m}^{n+1}}{\left(\Delta y\right)^{2}} + k^{2}\phi_{m}^{n} = 0 \text{ for } m = 1...M, n = 1...N$$
(E.42)

The boundary conditions are unchanged from before and can be applied in the same manner as before and are identical to Equations (E.21) to (E.24). Again, this is a linear system which can be solved using standard solvers, but we will examine solutions obtain via the method of false transients and the perturbation approach. The method of false transients results in the following system of ODEs to be solved:

$$\frac{d\phi_n^m}{d\tau} = \frac{\phi_{m-1}^n - 2\phi_m^n + \phi_{m+1}^n}{\left(\Delta x\right)^2} + \frac{\phi_m^{n-1} - 2\phi_m^n + \phi_m^{n+1}}{\left(\Delta y\right)^2} + k^2 \phi_n^m \text{ for } m = 1...M, n = 1...N$$
(E.43)

with Equations (E.26) to (E.29) still directly applicable for the boundary conditions. In contrast, the perturbation method gives the following system of linearly coupled ODEs:

$$-\frac{\grave{o}}{\left(\Delta y\right)^{2}} \left(\frac{d\phi_{m-1}^{n}}{d\tau} - 2\frac{d\phi_{m}^{n}}{d\tau} + \frac{d\phi_{m+1}^{n}}{d\tau}\right) - \frac{\grave{o}}{\left(\Delta x\right)^{2}} \left(\frac{d\phi_{m}^{n-1}}{d\tau} - 2\frac{d\phi_{m}^{n}}{d\tau} + \frac{d\phi_{m}^{n+1}}{d\tau}\right) - \grave{o}k^{2}\frac{d\phi_{m}^{n}}{d\tau} = \frac{1}{\left(\Delta y\right)^{2}} \left(\phi_{m-1}^{n} - 2\phi_{m}^{n} + \phi_{m+1}^{n}\right) + \frac{1}{\left(\Delta x\right)^{2}} \left(\phi_{m}^{n-1} - 2\phi_{m}^{n} + \phi_{m}^{n+1}\right) + k^{2}\phi_{m}^{n}$$
(E.44)

with Equations (E.33) to (E.36) still applicable for the boundary conditions. For small values of  $k^2$ , this system will converge to the analytical solution using either approach. Figure E-4 shows the convergence of the false transient method and the perturbation approach at the origin for a value of  $k^2 = 1$ , while Figure E-5 shows the overall 3-D solution profile.



Figure E-5: Solution profile of Helmholtz's equation for  $k^2 = 1$ .

Notice that the perturbation method converges faster than the false transient method. However, if a larger value of  $k^2$  is used, the system does not converge when using the standard method of false transients. For example, Figure E-6 shows the value of  $\phi$  in the domain for a value of  $k^2 = 6$ . Figure E-7 shows the convegence. In this case, the method of false transients does not converge, whereas the perturbation method does. In fact, the method of false transients does not converge for any  $k^2 > \frac{\pi^2}{2}$ . This is in fact, the location of the first singularity in the solution as

can be seen from the analytical expression in Equation (E.40).



Figure E-6: Convergence of  $\phi$  for the Helmholtz Equation with  $k^2 = 6$  using the perturbation method (solid line) and the false transient method (dashed line). The inset shows the convergence at very short pseudo time.

This can also be analyzed by considering Equations (E.43) as developed from the false transient method in matrix form for linear problems:

$$\frac{d\mathbf{\Phi}}{d\tau} = \mathbf{A}\mathbf{\Phi} + \mathbf{b} \tag{E.45}$$

Where  $\Phi$  is the variable vector, **A** is the coefficient matrix (which is equivalent to the Jacobian of the system for a linear problem), and **b** is a vector of nonhomogeneous terms arising from the boundary conditions. The solution to such a system of linear ODEs can be directly solved using exponential matrices and is the following form:<sup>113,114</sup>

$$\Phi = \exp(\mathbf{A}\tau)\mathbf{c} + \Phi_{\mathbf{n}} \tag{E.46}$$

Where **C** is a vector of constants chosen to satisfy the initial conditions and  $\Phi_p$  is the particular solution to Equation (E.45).



Figure E-7: Solution profile of Helmholtz's equation for  $k^2 = 6$ 

The exponential matrix,  $\exp(\mathbf{A}\tau)$ , is analogous to the standard scalar exponential in terms of behavior. Importantly, the eigenvalues of  $\mathbf{A}$  determine whether the solution will converge to zero or diverge to infinity. Therefore, if all the eigenvalues are negative, the false transient method will converge to a meaningful solution. Conversely, if *any* of the eigenvalues are positive, the method of false transients will diverge. Since the eigenvalues are dependent on the parameter  $k^2$  for the system of equations considered here, we can predict how fast the false transient method will converge, or if it will fail. Figure E-8 shows that all eigenvalues are

negative for 
$$k^2 < \frac{\pi^2}{2}$$
 for this system and positive otherwise.



Figure E-8: Effect of  $k^2$  on the maximum eigenvalue of the false transient system, notice that the eigenvalues increase with increasing  $k^2$  indicating the instability of the false transient method.

However, compare this with the proposed perturbation method by converting Equations (E.44) into matrix form by using Equation (E.11) above and considering that the right hand side of Equations (E.43) and (E.44) are equivalent we arrive at the following equation:

$$-\partial \mathbf{J}\frac{d\mathbf{\Phi}}{d\tau} = \mathbf{A}\mathbf{\Phi} + \mathbf{b} \tag{E.47}$$

which is similar to Equation (E.37) above for Laplace's equation. Equation (E.47) can be converted to explicit form by left multiplying both sides by  $-\delta^{-1}\mathbf{J}^{-1}$  to arrive at the following (recognizing that  $\mathbf{A} = \mathbf{J}$ ):

$$\frac{d\mathbf{\Phi}}{d\tau} = -\dot{\mathbf{o}}^{-1}\mathbf{I}\mathbf{\Phi} - \dot{\mathbf{o}}^{-1}\mathbf{J}^{-1}\mathbf{b}$$
(E.48)

where **I** is the identity matrix. Equation (E.48) can also be solved using exponential matrices in a manner analogous to Equation (E.46) to give

$$\boldsymbol{\Phi} = \exp(-\tilde{\mathbf{o}}^{-1}\mathbf{I}\tau)\mathbf{c} + \boldsymbol{\Phi}_{\mathbf{p}}$$
(E.49)

where **C** is a vector of constants chosen to satisfy the initial conditions and  $\Phi_p$  is the particular solution, and are not necessarily equal to those in Equation (E.46) above. Importantly, the eigenvalues of  $-\dot{o}^{-1}\mathbf{I}$  are all equal to  $-\dot{o}^{-1}$  and always negative regardless of the value of the parameter  $k^2$  under consideration. This ensures the stability of the perturbation approach and encourages fast convergence.

#### E.3.3 Solving the Frank-Kamenetskii Equation



Figure E-9: Boundary conditions used for solving Example 2 (Frank-Kamenetskii equation)

The advantage of the proposed perturbation approach arises from its ability to handle nonlinearities, and to solve problems with multiple steady stats. It is worth noting that this method can handle nonlinear source terms as well as nonlinearities in the state additive terms. However for demonstration purposes, only the Frank-Kamenetskii equation is considered, which has an exponential source term and exhibits multiple solutions. This is given by the following non-dimensional equation<sup>115</sup>:

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \delta \exp(\phi) = 0$$
 (E.50)

where  $\delta$  is referred to as the Frank-Kamenetskii parameter.<sup>115</sup> This represents the dimensionless temperature when a zeroth order exothermic reaction occurs, while implicitly assuming that the reactant is being continuously fed. Note that the source term in Equation (E.50) is derived from

zeroth order Arrhenius kinetics for a reaction with sufficiently large activation energy such that some terms can be neglected. A more thorough derivation can be found in the literature.<sup>115</sup>. The following boundary conditions are used, and also shown in Figure E-9.

$$\frac{\partial \phi(0, y)}{\partial x} = 0 \tag{E.51}$$

$$\frac{\partial \phi(x,0)}{\partial y} = 0 \tag{E.52}$$

$$\phi(1, y) = 0$$
 (E.53)

$$\phi(x,1) = 0 \tag{E.54}$$

Note that it is not necessary to apply non-homogeneous boundary conditions for this case to analyze a non-trivial solution due to the nonlinear source term. Still, Equation (E.50) cannot be solved analytically because of the nonlinearity. When the finite difference scheme used above is applied to this problem, the following system of non-linear algebraic equations is obtained:

$$\frac{\phi_{m-1}^{n} - 2\phi_{m}^{n} + \phi_{m+1}^{n}}{\left(\Delta x\right)^{2}} + \frac{\phi_{m}^{n-1} - 2\phi_{m}^{n} + \phi_{m}^{n+1}}{\left(\Delta y\right)^{2}} + \delta \exp(\phi_{m}^{n}) = 0 \text{ for } m = 1...M, n = 1...N$$
(E.55)

$$\frac{\partial \phi(0, y)}{\partial x} \approx \frac{-\phi_2^n + 4\phi_1^n - 3\phi_0^n}{2\Delta x} = 0 \text{ for } n = 0...N + 1$$
(E.56)

$$\frac{\partial \phi(x,0)}{\partial y} \approx \frac{-\phi_m^2 + 4\phi_m^1 - 3\phi_m^0}{2\Delta y} = 0 \text{ for } m = 0...M + 1$$
(E.57)

$$\phi_{M+1}^n = 0 \text{ for } n = 0...N + 1$$
 (E.58)

$$\phi_m^{N+1} = 0$$
 for  $m = 0...M + 1$  (E.59)

Unlike the first two cases considered, this example results in a system of non-linear equations and cannot be solved using basic linear or non-linear solvers, such as Maple's built-in fsolve command. Standard numeric based solvers can also have trouble solving this system.

Therefore, the method of false transients or the perturbation method is a good choice for finding the solution to this problem. Application of the false transient method gives the following system of ODEs:

$$\frac{d\phi_n^m}{d\tau} = \frac{\phi_{m-1}^n - 2\phi_m^n + \phi_{m+1}^n}{\left(\Delta x\right)^2} + \frac{\phi_m^{n-1} - 2\phi_m^n + \phi_m^{n+1}}{\left(\Delta y\right)^2} + \delta \exp(\phi_n^m) \text{ for } m = 1...M, n = 1...N \quad (E.60)$$

With the boundary conditions similar to in the previous cases. Conversely, the perturbation method gives:

$$-\frac{\grave{\mathrm{o}}}{\left(\Delta y\right)^{2}}\left(\frac{d\phi_{m-1}^{n}}{d\tau}-2\frac{d\phi_{m}^{n}}{d\tau}+\frac{d\phi_{m+1}^{n}}{d\tau}\right)-\frac{\grave{\mathrm{o}}}{\left(\Delta x\right)^{2}}\left(\frac{d\phi_{m}^{n-1}}{d\tau}-2\frac{d\phi_{m}^{n}}{d\tau}+\frac{d\phi_{m}^{n+1}}{d\tau}\right)-\grave{\mathrm{o}}\delta\exp\left(\phi_{m}^{n}\right)\frac{d\phi_{m}^{n}}{d\tau}=$$
$$\frac{1}{\left(\Delta y\right)^{2}}\left(\phi_{m-1}^{n}-2\phi_{m}^{n}+\phi_{m+1}^{n}\right)+\frac{1}{\left(\Delta x\right)^{2}}\left(\phi_{m}^{n-1}-2\phi_{m}^{n}+\phi_{m}^{n+1}\right)+\delta\exp\left(\phi_{m}^{n}\right)$$

for 
$$m = 1...M$$
,  $n = 1...N$  (E.61)



Figure E-10: Converged solution for  $\phi$  located at the origin for various values of  $\delta$  determined using the perturbation approach.

This problem exhibits some interesting behavior. For example, for  $\delta > \delta_{crit}$ , there is no solution, while for  $\delta < \delta_{crit}$  there exists two solutions. Figure E-10 shows the solution value(s) of

 $\phi$  at the origin for various values of  $\delta$  as determined using the perturbation approach, demonstrating the multiple solutions of the problem. Note that the lower branch solution is a stable equilibrium point, while the upper branch solution is an unstable equilibrium point. When using the proposed approach, both stable and unstable solutions can be found depending upon the initial guesses used. However, it is not possible to find the upper branch solution using the method of false transients. If the initial guess provided is less than the upper branch solution, the false transient method will always converge to the stable lower branch solution. Conversely, if an initial guess is provided which is greater than the upper branch solution, the false transient method will diverge to infinity.



Figure E-11: Maximum eigenvalue of the Jacobian for the equilibrium solutions of the nonlinear problem. This indicates the stability of the lower branch solution, and the instability of the upper branch solution.

This instability makes it impossible to track the upper branch solution by continuing from small values of  $\delta$  using standard solving methods. An arc length approach can be used to trace the solution given in Figure E-10, by integrating all unknowns and all parameters across the arc length of the solution curve. However, that cannot be used to directly determine the solution profile for a given value of the parameter  $\delta$ , as the parameter is solved as a function of arc
length. Furthermore, such a method requires a two step predictor/corrector approach due to the nonlinearities, which increases complexity and computational cost.



Figure E-12: Condition number of the Jacobian at various values of the parameter  $\delta$  for the upper and lower branch solutions. The bifurcation point as  $\delta$  approaches  $\delta_{crit}$  is particularly ill-conditioned.

The difficulty observed in the convergence of the false transient method to the upper branch solution can be predicted by considering the Jacobian of the problem. For the lower branch solution, all the eigenvalues of the Jacobian are negative, indicating a stable equilibrium solution. In other words, the system of ODEs developed using the method of false transients will converge to the lower branch solution, even if the system is slightly perturbed from the steady state solution. In contrast, the upper branch solutions represent an unstable equilibrium point, as evidenced by the positive eigenvalues observed at those points. Graphically, this is shown in Figure E-11 which shows the maximum eigenvalue of the Jacobian for the various equilibrium points. Even though the upper branch solution does satisfy  $\frac{d\Phi}{d\tau} = 0$ , any deviation from equilibrium will cause the solution to diverge from the upper branch. If the deviation is above the upper branch solution, the instability will cause the solution to diverge to infinity. However, if the deviation is below the upper branch solution, the system will converge to the lower branch solution, a stable equilibrium point.



Figure E-13: Solution profiles when  $\delta = 0.5$  for (a) upper branch and (b) lower branch. Notice the qualitative and quantitative differences

It is also worth noting the difficulty of finding the solution near the bifurcation point, when  $\delta = \delta_{crit}$ . At this point, the condition number of the Jacobian increases significantly at the solution points, indicating the system is particularly ill-conditioned as the parameter  $\delta$ approaches its critical value. Interestingly, however, the Jacobian as computed from the upper branch solution is not significantly more ill-conditioned than the lower branch solution. This is shown graphically in Figure E-12. It is worth noting that other techniques, such as the arc-length tracking method can be used to better track the bifurcation of multiple steady states.



Figure E-14: Convergence of proposed method (solid line) and false transient (dashed line) for a value of  $\delta$  =0.5, using (Inset shows the graph at very short pseudo time) using  $\phi = 0$  as an initial condition (top). Same system with initial guesses near the upper branch solution—the perturbation method converges to the upper branch solution while the false transient still converges to the lower branch solution (bottom left). Same system using  $\phi = 3$  as an initial condition (bottom right); the false transient method diverges.

Figure E-13(a) shows the surface plot for the lower branch solution for the case that  $\delta = 0.5$ , while Figure E-13(b) shows the profile for the upper branch solution. In order to show the importance of providing an initial guess as well as to compare convergence, Figure E-14 shows the value of  $\phi_0^0$  as a function of pseudo-time for the false transient method and the perturbation approach when  $\delta = 0.5$ . The top figure of Figure E-14 uses an initial guess of

 $\phi_n^m = 0$  for all *m* and *n*, while the bottom left figure of Figure E-14 uses the upper branch solution for  $\delta = 0.6$  as an initial guess for  $\delta = 0.5$ . This is to show that the perturbation approach and the method of false transients will not necessarily converge to the same solution, even when identical initial conditions are applied. Furthermore, the bottom right figure of Figure E-14 shows the convergence when an initial guess of  $\phi_n^m = 3$  for all *m* and *n*. In this case, the perturbation approach converges to the upper branch, while the false transient method fails after a few pseudo-seconds of simulation. This further demonstrates the advantages of the purposed approach.

It also must be stated that the perturbation method will also not converge for certain initial conditions, such as for profiles significantly above the values in the upper branch solution. This is due to the presence of the exponential term which becomes unstable for large values of  $\Phi$ . However, the proposed method is much more forgiving in that it will converge for a wider range of initial conditions than the false transient method.

# **E.4 Conclusions**

A Jacobian-based perturbation approach was presented as an alternative to the method of false transients when solving elliptic PDEs. Both methods discretize the spatial variables using standard finite different schemes and introducing a pseudo time variable, although other discretization schemes, such as collocation, could be used. However, the perturbation approach is shown to converge to a meaningful solution for a wider range of problems and initial guesses than the method of false transients. Furthermore, when using the method of false transients, the equations must be carefully applied in such a way to ensure that the DAEs are stable and converge to the expected solution if possible. The proposed perturbation approach is much more robust and the equations can be applied in any logically consistent manner. Also, in cases where multiple solutions exist, the Jacobian-based perturbation approach is more capable of finding the multiple solutions, specifically those which represent unstable equilibrium points. In contrast, the false transient method may only converge to a stable solution regardless of the initial guesses used. It is important to note that there are many methods to solve elliptic PDEs. The objective of this paper is to make the false transient method more robust. Comparing other numerical approaches to solve such problems is beyond the scope of this work.

The primary difficulty of the proposed approach arises from the calculation of the Jacobian of the system of equations. This requires symbolic calculations that are not trivial and require the use of a computer algebra system. In contrast, the method of false transients can be applied relatively easily to any system of equations. We believe that this has contributed to the popularity of the method of false transients in the past, despite some of the shortcomings of the method, some of which have been discussed above. Additionally, the resulting system of ODEs is not necessarily in an explicit form (one derivative in each ODE), which may be difficult for standard or library solvers to handle. As DAE solvers and computer algebra systems like Maple<sup>49</sup> or Mathematica<sup>98</sup> are becoming more common and more efficient, the perturbation approach is a viable alternative for solving elliptic PDEs in a robust manner.

# **Curriculum Vitae**

# Paul W. C. Northrop

### PROFESSIONAL PROFILE

Ph.D. Chemical Engineer with experience in modeling and efficient simulation using fundamental chemical engineering principles including transport phenomena and reaction kinetics applied to engineering problems. Developed more computationally efficient methodologies of simulating lithium ion batteries to allow for better control and optimization of design, which is applicable regardless of material used. Filed United States Provisional Patent App. No. 61/725,572 for developing a battery management system to improve performance of electric vehicles.

#### **RESEARCH HIGHLIGHTS**

- Developed improved numerical techniques based on orthogonal collocation and model reformulation to reduce the computational cost of simulating lithium ion batteries.
- Funded in part by DOE ARPA-E award #DE-AR0000275 to develop a BMS for electric vehicles to improve performance using reformulated models.
- Improved model of supercapacitors for a novel design using a chitosan based hydrogel. Used this model to estimate physical parameters using experimental data and study life.
- Refined a numerical method to solve elliptic partial differential equations based on a perturbation approach to the method of false transients.
- Used a kinetic Monte Carlo algorithm to study the growth of the solid electrolyte interface layer to show the surface heterogeneity of the anode surface.

#### EDUCATION

Ph.D. Chemical Engineering, Washington University, St. Louis, MO	May 2014
B.S. Chemical Engineering (Summa cum Laude), Washington University, St. Louis, MO	May 2009

# **RESEARCH EXPERIENCE**

# Graduate Research Assistant, Washington University in St. Louis

**Ph.D. Thesis.** "Multiscale Modeling, Reformulation, and Efficient Simulation of Lithium Ion Batteries." Advisor: Venkat Subramanian

- Improved simulation efficiency of lithium ion batteries leading to better design and control
- Modeled and tested chitosan based supercapacitors for performance and life
- Modeled heat regenerator reactor for carbon dioxide reformulation for production of SynGas

# INDUSTRIAL EXPERIENCE

Intern, Baker Petrolite

2007; 2008

2012

Participated in Process Hazard Analysis reporting, wrote Standard Operating Procedures, and aided in plant layout for safety and maintenance concerns

#### Patents

United States Provisional Patent App. No. 61/725,572

Filed provisional patent "Reformulated model based prediction, monitoring and control of rechargeable electrochemical batteries" to improve performance, life, and safety of lithium-ion batteries in electric vehicles

### HONORS AND AWARDS

IEEE Student Achievement Award of the Industrial Electrochemistry and Electrochemical Engineering Division of the Electrochemical Society (2014)

Student Travel Grant from the Battery Division of the Electrochemical Society to the 219<sup>th</sup>/221<sup>st</sup>/223<sup>rd</sup> ECS Meeting (2011, 2012, 2013)

Student Travel Grant from the Energy Technology Division of the Electrochemical Society to the 222<sup>nd</sup> ECS Meeting (2012)

Procter & Gamble Senior Scholar Award – Energy, Environmental, and Chemical Engineering (2009)

#### **MEMBERSHIPS**

American Institute for Chemical Engineers (AIChE) (2007-Present) Electrochemical Society (2010-Present) Tau Beta Pi—Engineering Honor Society

#### PUBLICATIONS

**P. W. C. Northrop**, B. Suthar, and V. R. Subramanian, "Improved Reformulation for the Simulation of Lithium-Ion Battery Operation Using Chebyshev Based Spectral Methods," in preparation.

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R. N. Methekar, **P. W. C. Northrop**, K. Chen, R. D. Braatz and V. R. Subramanian, "Kinetic Monte Carlo Simulation of Surface Heterogeneity in Graphite Anodes for Lithium-Ion Batteries: Passive Layer Formation," *Journal of the Electrochemical Society*, 158(4), A363-A370 (2011).

# **ABSTRACTS AND PRESENTATIONS**

**P. W. C. Northrop**, B. Suthar, and V. R. Subramanian, Model Reformulation for Lithium-ion Battery Simulation and Control, Annual Meeting of the American Institute of Chemical Engineers, San Francisco, California, November 7, 2013

**P. W. C. Northrop**, B. Suthar, and V. R. Subramanian, Model Reformulation for Lithium-ion Battery Simulation, 224<sup>th</sup> Meeting of the Electrochemical Society, San Francisco, California, October 28, 2013

**P. W. C. Northrop**, V. R. Subramanian, and R. D. Braatz, Integration of a Kinetic Monte Carlo Algorithm with Continuum Models to Examine Capacity Fade, 223<sup>rd</sup> Meeting of the Electrochemical Society, Toronto, Ontario, Canada, May 14, 2013

**P. W. C. Northrop**, R. D. Braatz, and V. R. Subramanian, Simultaneous Coupling of Kinetic Monte-Carlo Simulation with Continuum Models to Examine Capacity Fade, 222<sup>nd</sup> Meeting of the Electrochemical Society, Honolulu, Hawaii, October 8, 2012

**P. W. C. Northrop**, S. De, V. Ramadesigan, V. R. Subramanian, and S. Santhanagopalan, Efficient Simulation of Two Dimensional Thermal Electrochemical Models of Lithium Ion Battery Stacks, 221<sup>st</sup> Meeting of the Electrochemical Society, Seattle, Washington, May 10, 2012

**P. W. C. Northrop**, N. Choudhury, and V. R. Subramanian, Modeling and Parameter Estimation of Chitosan-Based Electrode Binder, 221<sup>st</sup> Meeting of the Electrochemical Society, Seattle, Washington, May 9, 2012

**P. W. C. Northrop**, V. R. Subramanian, and R. D. Braatz, Coupling of Kinetic Monte-Carlo Simulation with Continuum Level Models to Examine Capacity Fade, 220<sup>th</sup> Meeting of the Electrochemical Society, Boston, Massachusetts, October 13, 2011

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**P. W. C. Northrop**, V. Ramadesigan, and V. R. Subramanian, Optimal Design and Capacity Fade Analysis of Lithium Ion Batteries Using Efficient Simulation and Modeling, Lithium Innovation Center, De Las Nubes Al Cristal, Santiago, Chile, May 5, 2011

**P. W. C. Northrop**, R. Methekar, V. R. Subramanian, Kejia Chen, and R. D. Braatz, Kinetic Monte Carlo Simulation of Surface Heterogeneity for Lithium-Ion Batteries: Passive Layer Formation and Simulation of Capacity Fade, 219<sup>th</sup> Meeting of the Electrochemical Society, Montreal, Quebec, Canada, May 3, 2011