An Analysis of Lithium-ion Battery State-of-Health through Physical Experiments and Mathematical Modeling

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Abstract

Lithium-ion batteries are ubiquitous in modern society. The high power and energy density of lithium-ion batteries compared to other forms of electrochemical energy storage make them very popular in a wide range of applications, most notably electric vehicles (EVs) and portable devices such as mobile phones and laptop computers. However, despite the numerous advantages of lithium-ion batteries over other forms of energy sources, their performance and durability still suffer from aging and degradation. The purpose of the work presented in this thesis is to investigate how different load cycle properties affect the cycle life and aging processes of lithium-ion cells. To do so, two approaches are taken: physical experiments and mathematical modeling.

In the first approach, the cycle life of commercial lithium-ion cells of LiNiCoAlO₂ chemistry was tested using three different current rates to simulate low-, medium-, and high-power consuming applications. The batteries are discharged/charged repeatedly under the three conditions, all while temperature, voltage, current, and capacity are recorded. Data arising from the experiments are then analyzed, with the goal of quantifying battery degradation based on capacity fade and voltage drop. The results are then used to build two predictive models to estimate lithium-ion battery state-
of-health (SoH): the decreasing battery $V_{0+}$ model and the increasing CV charge capacity model. Furthermore, a simple thermal model fitted from the battery temperature profiles is able to predict peak temperature under different working conditions, which may be the solution to temperature sensitive applications such as cellphones.

The limitation to physical experiments is that they can be costly and extremely time-consuming. On the other hand, mathematical modeling and simulation can provide insight, such as the internal states of the battery, that is either impractical or impossible to find using physical experiments. Examples include lithium-ion intercalation and diffusion in electrodes and electrolytes, various side-reactions, double-layer effects, and lithium concentration variations across the electrode layer. Thus, in the second approach, work focuses on implementing the pseudo-two-dimensional (P2D) model, the most widely accepted electrochemical model on lithium-ion batteries. The P2D model comprises highly-nonlinear, tightly-coupled partial differential equations that calculate lithium concentration, ionic flux, battery temperature and potential to significant accuracy. The unparalleled prediction abilities of the P2D model, however, are shadowed by the low computational efficiency. Thus, much of this work focuses on reducing model complexity to shorten effective simulation time, allowing for use in applications, such as a battery management system, that have limited computational resources. In the end, four model reductions have been identified and successfully implemented, with each one achieving a certain standard of accuracy.
Preface

This thesis is original work by the author, XiangRong Kong.

A version of Chapter 2 has been published [Kong X.R., Wetton B., Wilkinson D., Bonakdarpour A., and Gopaluni, B. Advanced Control of Chemical Processes, 2018]. I was the lead investigator, responsible for literary research, experiment design, data analysis, as well as manuscript composition. Dr. Wilkinson and Dr. Gopaluni from the chemical engineering department provided the necessary laboratory and equipment to conduct experiments. Dr. Bonakdarpour executed all experiments and managed data collection. Dr. Wetton was the supervisory author on this project and was involved throughout the project in concept formation and manuscript edits.

The content of Chapter 3 is based on [18] by the author’s co-supervisor, Dr. Bhushan Gopaluni. However, the author adopted a different approach in solving the original problem, which led to higher efficiency and better robustness. Therefore, the content of Chapter 3 is independent of [18] and hence original work by the author.
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Dedication

To my wonderful parents, who stood by me and supported all my ideas and dreams. I love you dearly. To my best friends in all aspects of my life, who have been by my side through difficult times. Your constant support and encouragement continue to help me reaching my goals. I am forever thankful to have you in my life.
With rapidly growing energy consumption, there is a large increase in demand for more efficient and sustainable energy resources. Today, we rely on fossil fuels for most of our energy needs. Combustion of fossil fuels leads to the emission of greenhouse gases into the atmosphere [7]. Global warming is a direct consequence of the accumulation of greenhouse gases. Renewable sources such as solar and wind energy are “green” but intermittent energy sources. Meanwhile batteries are electrochemical storage devices with which we can store energy in the form of chemical potential difference and use it whenever and wherever needed [6]. During the many decades of research, different chemistries of batteries have been developed, such as nickel cadmium (NiCd), nickel metal hydride (NiMH), lead acid, lithium ion (Li-ion), and lithium ion polymer (Li-Poly). Among these, lithium-ion batteries provide one of the best tradeoffs in terms of power density, low weight, cell voltage, and low self-discharge. With these attractive features, lithium-ion batteries are becoming the ubiquitous power sources for portable consumer electronics such as mobile phones, as well as large battery packs used in hybrid-electric and plug-in hybrid-electric vehicles (HEVs and PHEVs) [11].
1.1 Lithium-ion Batteries

A lithium-ion battery comprises four main sections including a positive electrode (cathode), a negative electrode (anode), an electrolyte, and a porous membrane separator, as shown in Fig. 1.1. The potential difference between the two electrodes drives the lithium ions from one to the other. The current collectors transfer the electrons through the external circuit [6].

![Figure 1.1: Schematic of lithium-ion battery being discharged](image-url)
1.1. Lithium-ion Batteries

1.1.1 Standard lithium-ion battery operation

The functioning of a lithium-ion battery is based on the reversible oxidation of atomic lithium to lithium ion as given by the following electrochemical reaction,

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

Before discharge, the positive and negative electrodes, which store lithium salts as numerous solid particle grains, are at different chemical potentials. During the discharge process, electrons ($e^-$) are released from the negative electrode to the positive electrode through the external circuit. This generates an electrical current to power desired applications. As a result, an electrical potential difference is developed between the two electrodes. The lithium-ions ($\text{Li}^+$) then detach from the anode solid particles and travel from the anode to the cathode through an electrolyte. Finally, the Li-ions intercalate as atomic lithium in cathode solid particles. The electrolyte, where lithium-ion migration occurs, is crucial in satisfying the electro-neutrality condition. The rate at which lithium-ions flow across the interface between solid particles and electrolyte is described by the ionic flux $j$. The transfer process is reversed when the battery is charging, which is carried out by providing an external power source to the cell [7].

Overall, this redox reaction shown in Eq. 1.1 has a very high electrochemical potential ($E^0 = -3.04V$ compared to the standard hydrogen cell). This property combined with the low molecular weight gives lithium-ion battery technology an advantage over other alternatives in term of energy
1.2 Battery Degradation

density [11]. The high energy density characteristic has led lithium-ion batteries to be popular in a variety of electronic devices. These range from applications with very small energy demand such as implantable cardioverter-defibrillators, to extremely high energy demand such as satellites, and now hybrid (HEV) and plug-in hybrid (PHEV) electric vehicles [7].

1.1.2 Common lithium-ion battery materials

The commercially available lithium-ion batteries commonly contain graphite as a negative electrode material, and lithium iron phosphate, lithium cobalt oxide, spinel or their derivatives as a positive electrode material. A typical electrolyte is 1:1 by volume mixture of ethylene-carbonate (EC) and dimethyl-carbonate (DMC) with 1M LiPF$_6$ salt. Poly-olefins have proven stable over time and are universally used in lithium-ion batteries as separators [6].

1.2 Battery Degradation

Despite the great promise shown by lithium-ion batteries, their performance suffers from aging and degradation that should be recognized and accounted for. The degradation of a battery compares to the aging of a vehicle fuel tank. A new fuel tank can hold its full capacity and may easily provide the engine with all the energy stored at a desired rate. As the tank is refilled, the bottom of the tank may accumulate sediments which slowly decrease its capacity. These sediments could clog the fuel tank filters which would limit the rate at which fuel could be extracted. To make matters
worse, the fuel tank may develop small holes through which fuel would be lost [6]. In the same manner, a battery loses capacity with use throughout its lifetime, decreasing the total amount of energy it can store and deliver. As the battery degrades, the internal resistance increases resulting in a more difficult extraction of the stored energy, in addition to the loss of part of this energy in the form of heat during charging and discharging. In the following subsections some of the causes that may contribute to battery degradation are briefly summarized.

1.2.1 Battery use

SEI (solid electrolyte interface) protects the negative electrode from aggressive solvents in the electrolyte. This film forms during every charge/discharge cycle, however it captures some amount of electrochemically active lithium, increasing the internal resistance and decreasing the capacity.

1.2.2 Rate of charge/discharge

High rates of charge and discharge are the main contributor for lithium deposition, caused when the flow of lithium ions is greater than the one which can be intercalated in the electrode. When this occurs, lithium ions deposit as metallic lithium which captures active lithium and may even cause a short-circuit between the electrodes.

1.2.3 Temperature

High temperature accelerate unwanted chemical reactions which degrade and reduce the capacity of the battery. With higher temperature, the chem-
1.3. The Two Approaches

Physical reaction of reduction on the surface of the carbon electrode will occur at a faster rate, causing gas. With this increased pressure and temperature, the surface film on the electrode can be stretched or damaged. This forms cracks through which electrolyte can react with the lithiated carbon particles from the electrode, forming more SEI and therefore capturing more active lithium particles.

1.2.4 Depth of charge/discharge

A cell which is cycled with high depth-of-discharge (DOD) deteriorates quickly due to a constant stripping and re-depositing of the solid electrodes. A battery will last significantly more cycles with small DODs rather than with large DODs. Battery life can be maintained in an acceptable range for plug-in hybrid electric vehicles if very deep cycles, (> 0.6 DOD) are avoided.

1.3 The Two Approaches

Significant research has been focused on trying to understand the aging mechanisms in lithium-ion cells and connect them with measurable and identifiable features in an effort to improve their utilization and reliability. Understanding why the battery degrades helps to focus efforts where the battery suffers most. Equally important is the understanding of how much it degrades [6]. It is crucial for any kind of energy storage to be able to estimate the battery degradation as a function of specific charge/discharge regimes and conditions. To answer the two questions, there are two popular approaches: physical experiments and mathematical modeling. This work
1.3. The Two Approaches

1.3.1 First Approach: Physical Experiments

Lithium-ion battery degradation and aging are mainly characterized by irreversible capacity loss (capacity fade) and voltage loss, coupled to changes in kinetic and thermodynamic properties of involved materials and their interfaces. In this approach, work centres on the experimental testing of lithium-ion batteries in a laboratory. The batteries are cycled under different conditions, all while measurements of temperature, voltage, current, depth of discharge, and cell capacity are performed. Data arising from the experiments are then scrutinized to form a broad understanding of the cell’s aging process, with particular emphasis on quantifying the ability of the cells to store charge as a function of their working life as well as the heat generated under different discharge rates. The results are then used to build two predictive models to estimate lithium-ion battery state-of-health (SoH).

1.3.2 Second Approach: Mathematical Modelling

Modelling and simulation can provide insight, such as the internal states (e.g., ionic flux, electrolyte lithium concentration) of the battery that is either impractical or impossible to find using physical experiments. This approach is particularly important in control applications and battery management systems (BMS). According to [18], mathematical models for lithium-ion battery dynamics fall within two main categories: Equivalent Circuit Models (ECMs) and Electrochemical Models (EMs). ECMs use only electrical components, e.g. inductors, resistors, and capacitors, to represent
1.4 Thesis Structure

Battery dynamics. While this type of model is structurally simple and computationally efficient, cumulative measurement errors, capacity degradation through usage life, environmental parameter variation, and device sensitivity to initial conditions heavily affect performance. In contrast, EMs are more accurate due to their ability to describe detailed physical phenomena, including lithium-ion intercalation and diffusion in electrodes and electrolyte, various side-reactions, double-layer effects, and lithium concentration variations. The most widely used EM today is the pseudo-two-dimensional (P2D) model, which is described by a set of tightly coupled and highly nonlinear partial differential-algebraic equations (PDAEs) [18]. In this approach, we first provide a robust implementation of the full P2D model, then discuss potential model reductions to improve simulation efficiency which allows for the more computationally limiting applications.

1.4 Thesis Structure

This thesis is structured into two chapters based on the two approaches discussed above.

Chapter 2 focuses on the first approach: physical experiments. We first explain the type of battery being experimented, the equipment used to perform discharge/charge cycles, and the tools employed for battery status measurements. We then discuss the three treatments (C/2, 1C, and 2C current rates) used to simulate low-, medium-, and high-power demanding real-life applications as well as the experimental procedures. Next we show battery aging by providing results on the voltage vs. capacity profiles and also the
1.4. Thesis Structure

temperature profiles. Based on the results, two SoH prediction models, the decreasing $V_{0+}$ model and the increasing CV charging capacity model, are proposed. Lastly, we take a closer look at the temperature profiles and fit parameters to a simple thermal model, with Newton’s law of cooling as the underlying theory. Future work to this chapter involves two projects. First, robustness of the two SoH prediction models can be verified by testing them on different batteries under different conditions. Second, battery aging due to cycling (discharge/charge) can be distinguished from pure temperature variation by dividing batteries into two batches: one is discharged/charged with different current rates under room temperature, whereas the other is thermocycled using the temperature profile generated from batch one but not discharged/charged.

Chapter 3 focuses on the second approach: mathematical modeling. The first half of the chapter revolves around the implementation of the full P2D model. We first provide a general overview of the different sections of a battery, then discuss in detail every of the governing P2D equations, as well as the boundary and interface conditions. Next we define the grid structure and proceed to discretize the entire model using the finite difference method. Lastly we implement the model on MATLAB, show results, and analyze numerical convergence. Although the full P2D model is currently the most accurate lithium-ion battery model, it requires an extreme amount of computing resource. However, using a mathematical model for optimization, parameter estimation, controller design, or life studies requires the simulation to be run hundreds to thousands of times within a short period, necessitating efficient simulation techniques to be used. Similarly, online
1.4. Thesis Structure

applications, such as those found in electric vehicles, have limited computational resources available to do the complex calculations [3]. Therefore, in the second half of the chapter, we discuss potential model reductions toward a fast-solver. The four reduced models developed in this chapter, with each one achieving a different standard of accuracy, become viable options in applications that would otherwise be too computationally expensive for the use of the full P2D model. Future work to this chapter includes code migration into a compiled language (e.g. C#, Java) for even higher computational efficiency, and also implementation of the reduced P2D models on actual battery controllers. In addition, parallel computing through multicore CPU, as well as cloud computing on memory-optimized instances can be experimented to further reduce simulation time.
Chapter 2

State-of-Health Estimation of Li-ion Batteries

Lithium-ion battery packs are a source of major or supplementary power for portable electronics such as cellphones, and laptop computers, mobile applications such as electric vehicles and electric scooters, and also back-up power systems of several scales. A key aspect of the technology is their proprietary Battery Management Systems (BMS) that monitor the battery to maintain safe operation during charging and use, and allow some performance optimization. Such systems have a component that estimates the pack State-of-Charge (SoC), that is, the amount of charge still in the pack to deliver power to the application. The simplest SoC indicators rely on an invariant model of the cell’s performance to yield their output and do not take into account how a pack is changing over time. However, in reality the performance of batteries decreases over time and with use, described as a change in the battery’s State-of-Health (SoH). Specifically, the battery SoH is defined by a lower battery capacity and an increased internal resistance.

In recent years, a lot of attention has been focused on the diagnosis of lithium-ion battery SoH. Nearly all literature regard discharge/charge cur-
rent rate and operation temperature as top factors affecting SoH. However, a concrete mathematical model which can connect these two factors to battery’s SoH is still not available.

This chapter introduces experiments that involve discharging and charging lithium-ion batteries over many cycles, while their voltage, capacity, current, and temperature profiles are recorded. Based on the data analysis, two predictive lithium-ion battery SoH models are presented.

2.1 Experimental

Cylindrical 18650 lithium-ion rechargeable cells (Panasonic NCR18650B, Fig. 2.1) of Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO$_2$) chemistry are tested in this work. The nominal cell voltage and capacity are 3.6V and 3.2Ah, respectively. The manufacturer recommended charge/discharge voltage boundaries are between 2.5 and 4.2V.

Figure 2.1: Panasonics NCR18650B Lithium-ion Batteries
2.1 Experimental

2.1.1 Galvanostatic cycling of lithium-ion batteries

Galvanostatic cycling refers to the discharge and charge of batteries with “static”, or constant, current rates. It is performed under room temperature within the manufacturer specified voltage range of 2.5-4.2V. Each cycle consists of six stages,

1. Constant current discharge (CCD) at a chosen C-rate until 2.5V
2. Open circuit voltage (OCV) for 30 minutes
3. Constant current charge (CCC) at 1C until voltage reaches 4.2V
4. OCV for 30 minutes
5. Constant voltage charge (CVC) at 4.2V for 4 hours
6. OCV for 30 minutes

Here, the C-rate is the current rate required to discharge the battery within 1 hour to the manufacturer specified voltage cutoff. In our case, the voltage cutoff is 2.5V and 1C=3.2A. Meanwhile, the open circuit voltage (OCV) in steps (2), (4) and (6) refers to disconnecting any external circuit so that voltage and electrolyte inside the battery equilibrate. In this work, the chosen C-rates for step (1) are C/2, 1C, and 2C, in order to simulate low-, medium-, and high-power demanding applications. Note that all cycles were performed under room temperature, \( \sim 22^\circ \text{Celsius} \).

A 10A, VMP3 multi-channel potentiostat from BioLogic Science Instruments was used to perform the discharge/charge cycles, with 30 minutes of OCV between each discharge/charge step, all while voltage, current, and
2.2. Results

capacity are recorded in 30 second intervals. Temperature of the cell during cycling was recorded by self-adhesive, silicon based cement, K-type thermocouple temperature sensors (SA1K-72, Omega Engineering Inc.) with better than 0.3s response time. Two thermocouples were used: one attached to the main body of the cell and one attached to the anode tip. The cover of the cell was carefully removed where the self-adhesive thermocouple was attached. Temperature data were recorded by a high-speed 8-channel TCIC thermocouple interface card (TCIC-USB-ENC, Omega Engineering Inc.).

Fig. 2.2 shows a typical 1C current and voltage profile of the battery for one discharge/charge cycle. During constant current discharge, the current is denoted as a negative value (-3.2A) and the voltage decreases nonlinearly until it reaches the cutoff voltage of 2.5V. During constant current charge, the current is held constant at 3.2A with a rising voltage until the voltage reaches the maximum voltage of 4.2 V, at which point constant voltage charge begins. The profiles for C/2 and 2C follow the same pattern except the current rates are 1.6A and 6.4V, respectively.

2.2 Results

Recall that each discharge cycle completes in approximately i) 2hrs for C/2, ii) 1hr for 1C, and iii) 0.5hr for 2C, excluding the constant current and constant voltage charge processes and the OCVs in between. Therefore, due to the limitation of time and equipment, 200 cycles of 2C, 100 cycles of 1C, and 25 cycles of C/2 are performed.
2.2. Results

2.2.1 Voltage vs. Capacity Plots

Voltage vs. capacity curves give crude estimation of battery degradation. As a battery is cycled, its maximum capacity decreases. This is indicated by a leftward shift of the curves.

Fig. 2.3 shows voltage vs. capacity curves. From top to bottom, each row represents C/2, 1C, and 2C current rate, respectively. The left column represents constant current discharge whereas the right column represents constant current charge. Notice that both discharge and charge curves of all three current rates illustrate a similar pattern: they move to the left over time, indicating that the capacity, or the amount of charge the battery is able to hold, decreases as it is cycled. Going down the rows, we observe that as C-rate increases, the capacity drop is on average larger every cycle, and
2.2. Results

also the starting voltage of the discharge is lower. Both of these illustrate that higher current rates cause faster battery aging.

2.2.2 Temperature Plots

Fig. 2.4 shows the battery temperature vs. time of each cycle for C/2, 1C, and 2C. As labeled on the plots, the first, second, and third peak each represents the constant current discharge, constant current charge, and constant voltage charge, respectively, while the three temperature drops rep-
2.2. Results

resent the OCVs. Notice that there are relatively large room temperature fluctuations during the cycling process. Going from top to bottom, we observe that higher current rates cause faster and larger rise in battery temperature. However, there is no clear association between battery temperature and cycle number.

![Figure 2.4: Battery Temperature vs. Cycles](image-url)
2.3 SoH Prediction Model

Present models of lithium-ion battery SoH prediction are based on large amounts of battery operation data. However, even the most advanced battery management system (BMS) nowadays has very limited data storage. Based on the assumption that voltage vs. capacity curves follow a similar pattern for varying discharge rates, the models presented in this section attempt to predict SoH through only a short history of battery operation, which makes BMS implementation highly feasible. Specifically, given merely the voltage and charge drawn, the two models predict the number of discharge/charge cycles the battery has performed through, a natural indicator of battery SoH.

2.3.1 SoH prediction model based on decreasing $V_{0+}$

Recall that as the battery is cycled, the amount of charge it is able to store decreases, resulting in a loss of power output. Let $\gamma$ denote the cycle number a battery has been discharged/charged through. Let $V_{0+}$ be the voltage at the beginning of discharge (see Fig. 2.2), with it a function of cycle number,

$$V_{0+} = V_{0+}(\gamma) \quad (2.1)$$

We expect $V_{0+}$ to decrease as battery ages. This property alone can be an indicator of battery SoH. Fig. 2.5 shows the plot of $V_{0+}$ vs. $\gamma$ for the three C-rates.

Notice that the vertical axis for the three plots are intentionally left un-normalized for the best visual inspection. All three plots show that $V_{0+}$ and
2.3. SoH Prediction Model

Figure 2.5: $V_{0+}$ vs. Cycle Number - with Linear Fit, for a) C/2, b) 1C, and c) 2C

$\gamma$ is linearly related. Performing linear regression, we obtain the function,

$$V_{0+}(\gamma) = \beta_0 + \beta_1 \gamma$$  \hspace{1cm} (2.2)

The linear fit superimposed on the data points is shown on the same figure. The values of $\beta_0$ and $\beta_1$ for the three C-rates are listed in the table below.
2.3. SoH Prediction Model

<table>
<thead>
<tr>
<th></th>
<th>C/2</th>
<th>1C</th>
<th>2C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\beta_0)</td>
<td>4.0062</td>
<td>3.7831</td>
<td>3.4928</td>
</tr>
<tr>
<td>(\beta_1)</td>
<td>-0.00056</td>
<td>-0.00068</td>
<td>-0.0013</td>
</tr>
</tbody>
</table>

We can interpret \(\beta_0\) as the \(V_0^+\), in Volts, of a new battery which has not gone through any discharge/charge cycles, and \(\beta_1\) as the rate of decrease in \(V_0^+\), in Volts per cycle. Since the batteries were new and never used prior to the experiments, we observe that \(\beta_0\) decreases with increased current rate as expected, while \(\beta_1\) drops. This makes sense as higher current rate results in faster battery aging, indicated by a faster rate of decrease in \(V_0^+\) per cycle.

With \(\beta_0\) and \(\beta_1\) found for the three C-rates, to predict lithium-ion battery SoH using this model, simply determine the C-rate of the application, and then evaluate cycle number \(\gamma\) using Eq. 2.2, with the battery’s \(V_0^+\) measured. A small \(\gamma\) implies a relatively healthy battery whereas a large \(\gamma\) implies the opposite. The limitations to this model are that it assumes a strictly constant current rate of the battery’s application, and also it requires the battery to be fully charged to access \(V_0^+\).

2.3.2 SoH prediction based on increasing CV charging capacity

The previous SoH prediction model assumes the current rate of discharge/charge process is constant, which is usually not the case in real applications. For example, the driver of an electric vehicle may accelerate for a few seconds, drawing a large current, followed by an immediate deceleration, drawing a small current. However, the constant voltage charge after
the constant current charge is relatively much more consistent, since it does not depend on the previous discharge/charge current rates. Hence, measuring the change in capacity during constant voltage charge as a function of cycle number is another way to assess the SoH of the battery.

Figure 2.6: Capacity vs. Cycle Number for Constant Voltage Charge - with Linear Fit, for a) C/2, b) 1C, and c) 2C
2.3. SoH Prediction Model

Fig. 2.6 shows the capacity vs. cycle number of constant voltage charge for the three C-rates. A linear fit of the data points is superimposed on the same figure, with the equation,

\[
\text{capacity}(\gamma) = \delta_0 + \delta_1 \gamma
\]  

(2.3)

We observe that, independent of the C-rate, the amount of charge needed to complete the constant voltage charge process is positively related to the cycle number. This is expected since as battery ages, its internal resistance increases due to SEI formation, so charging is more difficult and takes longer. Going down the rows, as C-rate increases, the slopes of capacity vs. cycle number plots become steeper, implying faster battery aging. The values of \( \delta_0 \) and \( \delta_1 \) for the three C-rates are listed in the table below.

<table>
<thead>
<tr>
<th></th>
<th>C/2</th>
<th>1C</th>
<th>2C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_0 )</td>
<td>1.1652</td>
<td>1.1691</td>
<td>1.1723</td>
</tr>
<tr>
<td>( \delta_1 )</td>
<td>0.0002</td>
<td>0.0014</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

To predict lithium-ion battery SoH using this model, simply measure the battery capacity during constant voltage charge and then evaluate cycle number \( \gamma \) using Eq. 2.3. Compared to the previous model, this one has the advantage that it does not require the application of the battery to draw a strictly constant current. The downside is that measuring \( V_{0+} \) for the previous model takes a single data point whereas measuring capacity takes many, depending on the granularity of measurement. Therefore this model requires the BMS to have a more advanced data storage. Furthermore, notice that the parameters \( \delta_0 \) and \( \delta_1 \) for 1C and 2C are close in magnitude,
implying that SoH prediction may have a lower accuracy for high current rates.

## 2.4 Temperature Profile Modelling

We now analyze the temperature profile recorded and fit parameters to a simple thermal model.

### 2.4.1 Temperature profile revisited

The column on the left on Fig. 2.7 shows the close-up of the constant current discharge and OCV of the temperature profile of each cycle for the three C-rates. Here the rising temperature is caused by constant current discharge, while the temperature drop to ambient represents the OCV. The linear trend in temperature has been removed to reduce the effect of room temperature variations.

The temperature profiles for all cycles are averaged and plotted in the right column of Fig. 2.7. The decrease of the temperature is in an exponential decay form, suggesting Newton’s law of cooling, which can be modelled by,

\[
\frac{\partial T}{\partial t} = -k(T - T_{\text{room}})
\]

(2.4)

where \(k\) is a constant to be fitted, and \(T_{\text{room}}\) is the room temperature.

The rising temperature for every C-rate, on the other hand, begins to show a plateau after midway (expected if the heat generation was constant in time), but experiences an inflection point, as labeled on the plots, and then increases sharply until constant current charge is over. This phenomenon
2.4. Temperature Profile Modelling

is obvious for C/2 and 1C, and can also be observed for 2C under a more careful scrutiny. This suggests that there is an increasing volumetric heat generation term, \( g(t) \), during discharge,

\[
\frac{\partial T}{\partial t} = -k(T - T_{\text{room}}) + cg(t)
\]  

(2.5)

where \( k \) is the same constant as in Eq. 2.4, and \( c \) is another constant to be fitted. The inverse of \( c \) is the average thermal capacity of the cell.

Figure 2.7: Temperature (normalized) vs. Time of CCD and OCV for C/2, 1C, and 2C
2.4. Temperature Profile Modelling

According to [18], this volumetric heat generation term has the form,

\[ g(t) = \frac{I(IR + \eta)}{\pi r^2 H} \]  

(2.6)

where \( I \) is the current, \( R \) is the effective resistance, \( \eta \) is the overpotential, and \( r \) and \( H \) are radius and height of the cell, respectively. The denominator represents the volume of the cylindrical cell.

Decoupling the resistance from the overpotential is challenging from this set of data. We consider the average of the voltage difference between charge and discharge for C/2, 1C, and 2C in Fig. 2.8. The difference, divided by 2, is relatively constant in discharge capacity initially. Thus we consider the initial \((V_{cc} - V_d)/2I\) as the effective "resistance" \( R \). Note that in Fig. 2.8, the discharge capacity for 1C begins at 0.4: as the cell charges, constant voltage charge begins when the cell voltage reaches 4.2V and the remaining charge is added in a way that is not directly comparable to discharge. The same pattern applies to the other two C-rates.

Although there is an overpotential for both charge and discharge, we ascribe the overpotential \( \eta \) in Eq. 2.5 to predominantly the discharge, thus,

\[ IR + \eta = \begin{cases} 
(V_{cc} - V_d)_*/2 & \theta < \theta_* \\
V_{cc} - V_d - (V_{cc} - V_d)_*/2 & \theta > \theta_* 
\end{cases} \]

where \( \theta_* \) is the capacity at which constant current charge changes to constant voltage charge (\( \theta_* \approx 1.2\text{Ah} \) for 1C as shown in Fig. 2.8), and \((V_{cc} - V_d)_*/2\) is the value of the voltage difference at this capacity (\( \approx 0.40\text{V} \) in this case).
2.4. Temperature Profile Modelling

2.4.2 Temperature fitting

The analytical solution to Eq. 2.4 is,

\[ T(t) = T_i + (T_m - T_i)e^{k(t_m - t)} \]  \hspace{1cm} (2.7)

and the solution to Eq. 2.5 is,

\[ T(t) = T_i + e \int_0^t g(s)e^{k(s-t)}ds \]  \hspace{1cm} (2.8)

where \( t_i \) and \( T_i \) are respectively starting time and starting temperature of the temperature rise, and \( t_m \) and \( T_m \) are respectively starting time and
starting temperature of the temperature drop.

By fitting numerical solutions of Eq. 2.7 and 2.8 to experimental data and then minimizing residuals, the values of \( k \) and the inverse of \( c \) for each C-rate are obtained as,

\[
\begin{array}{c|ccc}
 & C/2 & 1C & 2C \\
k & 0.0180 & 0.0204 & 0.0194 \\
1/c & 760.17 & 731.31 & 735.04 \\
\end{array}
\]

The quality of the fit for the three C-rates is shown in Fig. 2.9. By dimensional analysis, \( k \) has units of \( \frac{1}{s} \) and \( c \) has units of \( \frac{J}{m^3K} \). From the results, \( k \) is simply the constant in Newton’s law of cooling while \( c \) is the inverse of average thermal capacity [18].

From Eq. 2.7, we notice that the term \((t_m - t)\) in the exponent is always negative. Therefore, the value of \( k \) determines the rate in which battery temperature equalizes with room temperature: a larger \( k \) implies a faster rate and a smaller \( k \) implies the opposite. Therefore, \( k \) represents temperature insulation with the outside, an intrinsic property of the battery material. Since the batteries tested in the experiments are of the exact same type and thus of the exact same material, we observe from the table that the \( k \) are similar in value and independent of the current rate. On the other hand, the \( 1/c \) term represents the amount of energy in joules needed to increase the battery temperature by \( 1^\circ \). This is also an intrinsic property of the battery and is independent of the current rate applied. Hence, we observe that the values of \( 1/c \) are similar across C/2, 1C, and 2C, as shown in the table.
2.4. Temperature Profile Modelling

An useful application the simple thermal model in this section provides is a predictive algorithm of battery temperature. With voltage, current, and temperature profiles measured, this thermal model can provide information on intrinsic properties of the battery as represented by $k$ and $1/c$. This information can then be used to answer questions on the peak temperature certain applications will reach under given environmental temperature and current rate. The answers to these questions ultimately concerns the most crucial problem of battery usage: is the battery safe within the predicted temperature range.

Figure 2.9: Temperature Fitting for CCD and CCC a) C/2 b) 1C c) 2C
2.5 Conclusion

In this study, Panasonic NCR18650B lithium-ion batteries were cycled under room temperature with current rates of C/2, 1C, and 2C while their current, voltage, capacity, and temperature profiles were recorded. Battery degradation and aging is clear from the drop of $V_{0+}$ and the leftward shift of voltage vs. capacity curves. Two models were proposed to predict lithium-ion battery state-of-health: 1) the decreasing battery $V_{0+}$ model and 2) the increasing CV charge capacity model. Each has its advantage and limitations. Additionally, we derived a fitted thermal model that can be used to predict cell temperature under different current rates, which is useful if the container of the battery is temperature sensitive, for example, a mobile phone. Future work that may yield interesting results includes distinguishing battery aging due to cycling (discharge/charge) from purely temperature variation. This can be done by setting up two treatments: the first treatment involves discharging/charging batteries with different current rates under room temperature, while the second treatment involves no discharge/charge but thermocycles batteries using the temperature profile generated from the first treatment.
Chapter 3

Numerical Modelling of Lithium-Ion Batteries

3.1 The P2D Model

3.1.1 Model Overview

The pseudo-two-dimensional (P2D) model consists of coupled nonlinear PDAEs for the conservation of mass and charge in the three sections of the battery - cathode, separator, and anode - denoted respectively by the indexes $p$, $s$, and $n$. The positive and negative current collectors are denoted by $a$ and $z$. The index $i \in S$ is used to refer to a particular section of the battery, where $S := \{a,p,s,n,z\}$. The governing equations of the P2D model are taken from [18]. The objectives of this work are to (i) provide a robust implementation, (ii) identify model reductions, and (iii) make progress towards a fast-solver. Fig. 3.1 depicts the five domains inside of the battery cell as well as the virtualization of solid particles inside the two electrodes.
3.1. The P2D Model

3.1.2 Positive and Negative Electrodes

Solid-particle concentration

Diffusion inside solid spherical particles with radius $R_p$ is described by Fick's law,

$$\frac{\partial c_s(r,t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_s \frac{\partial c_s(r,t)}{\partial r} \right]$$  \hspace{1cm} (3.1)
3.1. The P2D Model

with boundary conditions,

$$\frac{\partial c_s(r,t)}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial c_s(r,t)}{\partial r} \bigg|_{r=R_p} = -\frac{j(x,t)}{D_{\text{eff}}}$$

where \( r \) is the radial direction, or the pseudo-second-dimension, along which the ions intercalate within the active particles. Here \( j \) represents the ionic flux across the solid particles and the electrolyte.

**Solid-particle potential**

Solid-particle potential in the two electrodes, \( \Phi_s(x,t) \in \mathbb{R} \), is described by the equation,

$$\frac{\partial}{\partial x} \left[ \sigma_{\text{eff},i} \frac{\partial \Phi_s(x,t)}{\partial x} \right] = a_i F j(x,t)$$

Due to physical constraints, it is necessary to impose zero-flux boundary conditions for \( \Phi_s \) at the interface between electrodes and the separator, as well as the enforcement of Ohm’s law at the cathode and anode ends,

$$\sigma_{\text{eff},i} \frac{\partial \Phi_s(x,t)}{\partial x} \bigg|_{x=\hat{x}_0,\hat{x}_n} = -I_{\text{app}}(t)$$

$$\sigma_{\text{eff},i} \frac{\partial \Phi_s(x,t)}{\partial x} \bigg|_{x=\hat{x}_p,\hat{x}_s} = 0$$

Here \( I_{\text{app}}(t) \) is the applied current density given as an operating condition.
3.1. The P2D Model

Electrolyte concentration

In the positive and negative electrodes, the electrolyte concentration \( c_e(x, t) \in \mathbb{R}^+ \) is described by the equation,

\[
\epsilon_i \frac{\partial c_e(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff},i} \frac{\partial c_e(x, t)}{\partial x} \right] + a_i (1 - t_+) j(x, t) \tag{3.6}
\]

where \( t \in \mathbb{R}^+ \) is the time and \( x \in \mathbb{R} \) is the spatial direction through electrodes and separator along which the ions are transported. The first term on the right represents diffusion of the electrolyte while the second term represents ionic flux from the solid particles.

At the cathode and anode ends, we impose zero-flux boundary conditions,

\[
\left. \frac{\partial c_e}{\partial x} \right|_{x=x_0,x_n} = 0 \tag{3.7}
\]

Meanwhile at the two electrode-separator interfaces, we enforced the continuity of electrolyte concentration,

\[
c_e(x, t) \bigg|_{x=x_p^-} = c_e(x, t) \bigg|_{x=x_p^+} \tag{3.8}
\]

\[
c_e(x, t) \bigg|_{x=x_s^-} = c_e(x, t) \bigg|_{x=x_s^+} \tag{3.9}
\]

Similarly, continuity of fluxes is also enforced. Due to changes in material properties along the length of the battery, the values of different coefficients (e.g., \( D_{\text{eff},i}, \kappa_{\text{eff},i}, \lambda_i \)) need to be evaluated at the interface between two different materials. For the flux of electrolyte at the two electrode-separator
3.1. The P2D Model

interfaces, we have

\[ -D_{\text{eff},p} \frac{\partial c_e(x,t)}{\partial x} \bigg|_{x=\hat{x}_p^-} = -D_{\text{eff},s} \frac{\partial c_e(x,t)}{\partial x} \bigg|_{x=\hat{x}_p^+} \quad (3.10) \]

\[ -D_{\text{eff},s} \frac{\partial c_e(x,t)}{\partial x} \bigg|_{x=\hat{x}_s^-} = -D_{\text{eff},n} \frac{\partial c_e(x,t)}{\partial x} \bigg|_{x=\hat{x}_n^+} \quad (3.11) \]

Electrolyte potential

Electrolyte potential in the two electrodes, \( \Phi_e(x,t) \), is described by the equation,

\[ a_i F j(x,t) = -\frac{\partial}{\partial x} \left[ \kappa_{\text{eff},i} \frac{\partial \Phi_e(x,t)}{\partial x} \right] + \frac{\partial}{\partial x} \left[ \kappa_{\text{eff},i} \Upsilon T(x,t) \frac{\partial \ln c_e(x,t)}{\partial x} \right] \quad (3.12) \]

Given that only potential differences are measurable, without loss of generality, \( \Phi_e \) can be set to zero at the end of the anode. On the cathode side, zero-flux conditions are imposed,

\[ \frac{\partial \Phi_e}{\partial x} \bigg|_{x=x_0} = 0, \quad \Phi_e \bigg|_{x=x_n} = 0 \quad (3.13) \]

At the two electrode-separator interfaces, similar to the electrolyte concentration, continuity of potential,

\[ \Phi_e(x,t) \bigg|_{x=x_p^-} = \Phi_e(x,t) \bigg|_{x=x_p^+} \quad (3.14) \]

\[ \Phi_e(x,t) \bigg|_{x=x_s^-} = \Phi_e(x,t) \bigg|_{x=x_s^+} \quad (3.15) \]
as well as continuity of fluxes,

\[ -\kappa_{\text{eff},p} \frac{\partial \Phi_e(x,t)}{\partial x} \bigg|_{x=x_p^-} = -\kappa_{\text{eff},s} \frac{\partial \Phi_e(x,t)}{\partial x} \bigg|_{x=x_p^+} \]  \hspace{1cm} (3.16)

\[ -\kappa_{\text{eff},s} \frac{\partial \Phi_e(x,t)}{\partial x} \bigg|_{x=x_s^-} = -\kappa_{\text{eff},n} \frac{\partial \Phi_e(x,t)}{\partial x} \bigg|_{x=x_s^+} \]  \hspace{1cm} (3.17)

are enforced.

**Temperature**

Temperature variations are also included with the set of equations describing the system. The thermal equations include different source terms, which are the ohmic, reversible, and reaction generation rates \( Q_{\text{ohm}} \), \( Q_{\text{rev}} \), and \( Q_{\text{rxn}} \), respectively,

\[ \rho_i C_{p,i} \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( \lambda_i \frac{\partial T(x,t)}{\partial x} \right) + Q_{\text{ohm}} + Q_{\text{rxn}} + Q_{\text{rev}} \]  \hspace{1cm} (3.18)

The ohmic generation rate takes into account heat generated as a consequence of the motion of lithium-ions in the solid/liquid phase. The reaction generation rate accounts for heat generated due to ionic flux and over-potentials, and the reversible generation rate takes into account the heat rise due to the entropy change in the electrodes’ structure [18].

At all section interfaces, boundary conditions include both continuity of solution and continuity of flux. For example, at the cathode-separator
3.1. The P2D Model

interface,

\[-\lambda_p \frac{\partial T(x,t)}{\partial x} \bigg|_{x=x_p^-} = - \lambda_s \frac{\partial T(x,t)}{\partial x} \bigg|_{x=x_p^+}\]

(3.19)

\[T(x,t) \bigg|_{x=x_p^-} = T(x,t) \bigg|_{x=x_p^+}\]

(3.20)

Boundary conditions at other interfaces are of similar form.

Ionic Flux

Intertwining temperature, electrolyte concentration, electrolyte potential, solid-particle concentration, and solid-particle potential is \(j(x,t)\). \(j(x,t)\) is the flux of lithium ions across the surface of the solid-particles into the electrolyte at position \(x\) and time \(t\), and is given by Butler-Volmer kinetics,

\[j(x,t) = 2k_{\text{eff},i} \sqrt{c_e(x,t)(c_{s,i}^{\text{max}} - c_s^*(x,t))c_s^*(x,t)} \sinh \left[ \frac{0.5F}{RT(x,t)} \eta_i(x,t) \right]\]

(3.21)

where

\[\eta_i(x,t) = \Phi_s(x,t) - \Phi_e(x,t) - U_i\]

(3.22)

represents the overpotential. Note that \(i = \{p,n\}\), indicating the ionic flux is present in only the positive and negative electrodes but not the separator.

3.1.3 Separator

Since the separator is absent of any solid particles, the dynamics in the separator is simplified as equations of solid-particle concentration and
potential, $c_s(r,t)$ and $\Phi_s(x,t)$, as well as the ionic flux, $j(x,t)$, are eliminated.

**Electrolyte concentration**

The $c_e$ equation of the separator, in contrast to that of the electrodes, consists of purely diffusion and no ionic flux,

$$\epsilon_i \frac{\partial c_e(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D_{\text{eff},i} \frac{\partial c_e(x,t)}{\partial x} \right] \quad (3.23)$$

Similarly, the electrolyte potential is also independent of the ionic flux,

$$0 = -\frac{\partial}{\partial x} \left[ \kappa_{\text{eff},i} \frac{\partial \Phi_e(x,t)}{\partial x} \right] + \frac{\partial}{\partial x} \left[ \kappa_{\text{eff},i} \Upsilon T(x,t) \frac{\partial \ln c_e(x,t)}{\partial x} \right] \quad (3.24)$$

**3.1.4 Current Collectors**

The two current collectors span the two ends of the battery. Absent of both electrolyte and solid particles, temperature rise in the current collectors is caused solely by the applied current density,

$$\rho_i C_{p,i} \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ \lambda_i \frac{\partial T(x,t)}{\partial x} \right] + \frac{P_{\text{app}}(t)}{\sigma_{\text{eff},i}}, \quad i \in a, z \quad (3.25)$$

and Newton’s law of cooling with the outside,

$$-\lambda_a \frac{\partial T(x,t)}{\partial x} \bigg|_{x=0} = h(T_{\text{ref}} - T(x,t)) \quad (3.26)$$

$$-\lambda_z \frac{\partial T(x,t)}{\partial x} \bigg|_{x=L} = h(T(x,t) - T_{\text{ref}}) \quad (3.27)$$
The heat exchange coefficient $h$ is proportional to the reciprocal of temperature insulation: a low $h$ indicates high insulation and faster increase of battery temperature, and the opposite for high $h$.

### 3.1.5 Constants and Additional Equations

All experimentally measured parameters and additional equations used in the implementation are reported in Table I and II in the Appendix. The open circuit voltage (OCV) is denoted by $U$ while the entropic variation of the OCV is denoted by $\frac{\partial U}{\partial T}$. Since the cathode, anode, and the separator are composed of different materials, for a given section $i$, different electrolyte diffusion coefficients $D_i$, solid-phase diffusion coefficients $D_i^s$, electrolyte conductivities $\kappa_i$, porosities $\epsilon_i$, thermal capacities $C_{p,i}$, thermal conductivities $\lambda_i$, densities $\rho_i$, solid-phase conductivities $\sigma_i$, particle surface area to volumes $a_i$, maximum solid phase concentrations $c_{s,i}^{\text{max}}$, overpotentials $\eta_i$, and particle radiuses $R_{p,i}$, can be defined. The terms $R$ and $F$ are the universal gas constant and the Faraday constant, respectively, with $t_+$ representing the transference number and $T_{\text{ref}}$ the environment temperature.

Within the battery, continuous interface conditions are imposed across the different materials. In order to get a more detailed description of the conductivity ($\kappa_{\text{eff,}i}$) and diffusion phenomena ($D_{\text{eff,}i}$) inside the electrolyte, all the related coefficients are determined as a function of $c_e$ and $T$. In order to take into account the properties of different materials used in the battery, effective diffusion and conductivity coefficients are evaluated according to the Bruggeman’s theory, with “eff” suffixes representing effective values of each coefficients.
3.2 Numerical Implementation

3.1.6 Summary

In this section, all governing equations, interface and boundary conditions of the P2D model are explained. Mathematically, the system is mixed of second-order boundary value and parabolic type. This is a typical structure of models coming from electrochemical systems [9]. We are now ready to proceed to the model implementation.

3.2 Numerical Implementation

3.2.1 Discretization of Governing Equations

Recall that the battery is composed of five sections: positive current collector (a), cathode (p), separator (s), anode (n), and negative current collector (z). The cathode and the anode each further contains solid spherical particles with radius $R_p$, resulting in the pseudo-second dimension $r$.

The overall picture of the model is depicted in Fig. 3.2.

Figure 3.2: Model discretization using the finite difference method

Dimension $x$ and pseudo-second-dimension $r$ are both discretized on a staggered grid using the finite difference method. The grid structure in the $x$-direction is defined by subdividing the spatial domain $x \in \mathbb{R}$ into
3.2. Numerical Implementation

\( N_a + N_p + N_s + N_n + N_z \) non-overlapping segments with geometrically centered nodes (as depicted in Fig. 3.3). Every segment is associated with a centre \( x_n \) and spans the interval \([x_{n-\frac{1}{2}}, x_{n+\frac{1}{2}}]\). The unknown variable at \( x_n \) is denoted by \( \Omega_n \).

![Figure 3.3: One-dimensional finite difference grid structure](image)

To facilitate the treatment of boundary and interface conditions, the ends of each segment are aligned with the domain boundaries and internal interfaces. The number of segments in each section, \( N_i \) for \( i \in \{a, p, s, n, z\} \), is chosen so that the width of every segment is uniform across all five sections and is defined as

\[
\Delta x = \frac{\sum_i l_i}{\sum_i N_i} \quad (3.28)
\]

where \( l_i \) represents the length of a particular section of the battery and is listed in Table IV.

At each \( x_n \), the pseudo-second-dimension \( r \) is discretized using the same approach except it is only present in the cathode and anode and has a different segment width \( \Delta r \).

Once the discretization grid is structured, the governing equations are discretized with finite difference. The central difference scheme is used for both first and second derivatives. A few key discretizations are shown in this
sections. All the interface conditions used to enforce continuity between adjacent materials are discussed in Implementation of Boundary and Interface Conditions section.

**Solid-particle concentration**

The solid-particle concentration equation is discretized as follows

\[
\frac{\partial c_{s,n}(r,t)}{\partial t} = \frac{D_s r_m^2 (c_{s,n,m+1} - c_{s,n,m})}{r_m^2 (c_{s,n,m} - c_{s,n,m-1})} - \frac{r_m^2}{2} \left( c_{s,n,m} + c_{s,n,m-1} \right) \Delta r^2
\]

(3.29)

where \(r_m\) is the coordinate of dimension \(r\) measured from the center of the particle. The solid-particle surface concentration, \(c_s^*\), which is needed in the ionic flux equation, can be obtained using the ghost point technique,

\[
c_s^* = \frac{c_{s,n,M} + c_{s,n,M+1}}{2}
\]

(3.30)

where suffixes \(s,n,M\) and \(s,n,M+1\) represent the last and the ghost point of the solid particle at a particular \(x\).

**Solid potential**

The solid potential equation of the electrodes is discretized as follows,

\[
\sigma_{eff,j} \Phi_{s,n-1} - 2 \Phi_{s,n} + \Phi_{s,n+1} = a_i F j_n \Delta x
\]

(3.31)

In the separator, since there is no solid particles, this equation does not apply.
3.2. Numerical Implementation

Temperature

For the temperature equation in the electrodes, the reversible and reactive heat sources can be discretized as

\[ Q_{\text{rxn},n} = F a_i j_n \eta_{i,n} \quad (3.32) \]
\[ Q_{\text{rev},n} = F a_i j_n T_n \frac{\partial U_{i,n}}{\partial T} \quad (3.33) \]

whereas the derivatives present in the ohmic source are numerically approximated as

\[ \frac{\partial \Phi_s(x,t)}{\partial x} \bigg|_{x_n} \approx \frac{\Phi_{s,n+1}(t) - \Phi_{s,n-1}(t)}{2\Delta x} \quad (3.34) \]
\[ \frac{\partial \Phi_e(x,t)}{\partial x} \bigg|_{x_n} \approx \frac{\Phi_{e,n+1}(t) - \Phi_{e,n-1}(t)}{2\Delta x} \quad (3.35) \]
\[ \frac{\partial \ln c_e(x,t)}{\partial x} \bigg|_{x_n} \approx \frac{\ln c_{e,n+1}(t) - \ln c_{e,n-1}(t)}{2\Delta x} \quad (3.36) \]

using a central differencing scheme. Together, the temperature equation in the electrodes can be discretized as,

\[ \rho_i C_{p,i} \frac{\partial T(x,t)}{\partial t} = \lambda_i T_{n-1} - 2T_n + T_n + 1 \frac{T_n}{\Delta x} + Q_{\text{ohm},n} + Q_{\text{rxn},n} + Q_{\text{rev},n} \quad (3.37) \]

3.2.2 Implementation of Boundary and Interface Conditions

Boundary conditions require certain variables being evaluated at the ends of segments. For example, consider the electrolyte potential \( \Phi_e \) at the
interface between the anode and the negative current collector,

\[ \Phi_e(x, t) \bigg|_{x=x_n} = 0 \]  

(3.38)

In order to recover such value, the ghost point technique is used, as shown in Fig. 3.4.

Figure 3.4: Interpolation technique to recover interface values

The discretized equation is thus,

\[ \frac{\Phi_{e,N} + \Phi_{e,N+1}}{2} = 0 \]  

(3.39)

We can apply the same approach to continuity and interface conditions. Consider the electrolyte concentration \( c_e \). Since electrolyte is present in all of cathode, separator, and anode, continuity of the solution for both the concentration \( c_e \) and the potential \( \Phi_e \) have to be enforced at the cathode-separator and the separator-anode junctions. The easiest way would be to use the ghost point technique. For example, at the cathode-separator
3.2. Numerical Implementation

junction, the continuity condition for the electrolyte concentration is,

\[ c_e(x, t) \bigg|_{x = \hat{x}^- p} = c_e(x, t) \bigg|_{x = \hat{x}^+ p} \]  \hspace{1cm} (3.40)

which can be discretized as,

\[ \frac{c_{e,pN} + c_{e,pN+1}}{2} = \frac{c_{e,s0} + c_{e,s1}}{2} \]  \hspace{1cm} (3.41)

where suffixes \( p_N \) and \( p_{N+1} \) represent the last and the ghost point of the cathode, and \( s_1 \) and \( s_0 \) represent the first and the ghost point of the separator. Fig. 3.5 is a pictorial description of this interface.

![Electrolyte continuity across the cathode and the separator](image)

Figure 3.5: Electrolyte continuity across the cathode and the separator

Similarly, continuity of fluxes across interfaces is also enforced. Consider the equation of diffusion coefficient \( D_{\text{eff}} \) at the same cathode-separator junction,

\[ - D_{\text{eff},p} \frac{\partial c_e(x, t)}{\partial x} \bigg|_{x = \hat{x}^- p} = - D_{\text{eff},s} \frac{\partial c_e(x, t)}{\partial x} \bigg|_{x = \hat{x}^+ p} \]  \hspace{1cm} (3.42)

which can be discretized as,

\[ - \frac{D_{\text{eff},pN} + D_{\text{eff},pN+1}}{2} \frac{c_{e,pN} - c_{e,pN}}{\Delta x} = - \frac{D_{\text{eff},s0} + D_{\text{eff},s1}}{2} \frac{c_{e,s1} - c_{e,s0}}{\Delta x} \]  \hspace{1cm} (3.43)

Again, suffixes \( p_N \) and \( p_{N+1} \) represent the last and the ghost point of the
3.2. Numerical Implementation

cathode, and $s_1$ and $s_0$ represent the first and the ghost point of the separator. Notice that all boundary conditions discretized using the ghost point technique retains second-order accuracy.

3.2.3 Time Discretization and Newton’s Method

With spatial discretization completed, we now proceed to discretize time. Backward Euler (BE) time-stepping is chosen in order to maintain stability at each time-step while keeping an appropriate size of $\Delta t$. The example below shows a fully discretized solid particle concentration equation,

$$
\frac{c_{s,n}^{k+1} - c_{s,n}^k}{\Delta t} = \frac{D_s r_{m+1/2}^2 (c_{s,n,m+1}^{k+1} - c_{s,n,m}^{k+1}) - r_{m-1/2}^2 (c_{s,n,m}^{k+1} - c_{s,n,m-1}^{k+1})}{\Delta r^2}
$$

(3.44)

where $k$ indicates the current time-step and $k=0$ refers to the initial condition.

With every of the P2D equations discretized in space and time, we can arrange all the variables into a vector $u^{k+1}$,

$$
u^{k+1} = \begin{bmatrix} c_{e,p}^{k+1} & c_{e,s}^{k+1} & c_{e,n}^{k+1} & c_{s,p}^{k+1} & c_{s,n}^{k+1} & J_p^{k+1} & J_n^{k+1} & \Phi_{s,p}^{k+1} & \Phi_{s,n}^{k+1} \\
\Phi_{e,p}^{k+1} & \Phi_{e,s}^{k+1} & \Phi_{e,n}^{k+1} & T_a^{k+1} & T_p^{k+1} & T_s^{k+1} & T_n^{k+1} & T_z^{k+1} \end{bmatrix}^T
$$

where $k$ represents time-step. The goal is that, with known initial condition $u^0$, we want to find $u^{k+1}$ for $k = 0, 1, 2, ..., K$, which is described by the matrix equation,

$$
A \cdot u^{k+1} + v - u_{\text{cur}} = 0
$$

(3.45)
3.2. Numerical Implementation

where $A$ is a constant coefficient matrix that takes into account all linear part of every P2D equation, $v$ is a vector consisting all nonlinear part, and $u_{\text{cur}}$ is a vector containing information about the current time-step,

\[
    u_{\text{cur}} = \begin{bmatrix}
        c^k_{e,p} & c^k_{e,s} & c^k_{e,n} & c^k_{s,p} & c^k_{s,n} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
    \end{bmatrix}^T
\]

Since the majority of the P2D equations are nonlinear, matrix Newton’s method is used to find the root. To use Newton’s method, let

\[
    F = A \cdot u^{k+1} + v - u_{\text{cur}} \tag{3.46}
\]

We compute matrix $J$, the derivative of $F$ with respect to $u^{k+1}$,

\[
    J = A + Dv \tag{3.47}
\]

where $Dv$ is the Jacobian matrix of vector $v$, namely, $Dv_{ij} = \frac{\partial v_i}{\partial u_j}$. Approximation of the P2D equations is now possible with the following algorithm,

**Algorithm:** Backward Euler Approximation to P2D equations

1. construct matrix $A$
2. construct vector $u_{\text{cur}}$
3. for time-steps $k = 0, 1, 2, ..., T_f$ do
   1. construct vector $v$ and matrix $Dv$
   2. construct matrix $J$
   3. calculate residual $= A \cdot u^{k+1} + v - u_{\text{cur}}$
5. while residual $< tol$ do


3.2. Numerical Implementation

find solution $y$ to $J \cdot y = \text{residual}$
update $u^{k+1} = u^{k+1} - y$
update vector $v$ and matrix $Dv$
update matrix $J$
update residual $= A \cdot u^{k+1} + v - u_{cur}$

end while

update $u_{cur}$ with values of $u_{k+1}$

end for

The residual here is calculated using the formula,

$$\text{residual} = ||A \cdot u^{k+1} + v - u_{cur}||_{\infty} \quad (3.48)$$

where we are using the maximum norm. Numerically, Newton iteration will continue until the residual is smaller than a specified tolerance $tol$. Note that Newton iteration can fail to converge or find a different root to the one sought after if the function has many inflection points or if the initial guess is not close enough. For our purposes, we will not run into these situations as our initial guess computed explicitly using the initial condition given in Table II will be sufficiently close in our BE solution.

3.2.4 Implementation Results

Simulation results were obtained using MATLAB R2018a on a Windows 10@1.8GHz PC with 16GB of RAM for the experimental battery parameters in Table IV with a cutoff voltage of 2.5V and environmental temperature
3.2. Numerical Implementation

of 298.15K. For the proposed chemistry, the 1C value is ≈ 30 A/m². The default discretization sets \( \Delta x = 1 \times 10^{-6} \) and \( \Delta r = 0.5 \times 10^{-6} \) unless specified otherwise. The battery voltage is calculated by taking the difference between the solid partial potential of the first segment of the cathode and that of the last segment of the anode,

\[
V = \Phi_{s,p_1} - \Phi_{s,n_N}
\]

In the first scenario shown in Fig. 3.6, a 1C discharge simulation with a fixed value of \( h = 1\text{W}/(\text{m}^2\text{K}) \) is performed and the average temperature for each section is plotted. Since the thermal conductivity coefficients are extremely high (\( \lambda_a = 237, \lambda_p = 2.1, \lambda_s = 0.16, \lambda_n = 1.7, \) and \( \lambda_z = 401 \)) with respect to the length scale of each section (\( O(10^{-5}) \)), heat diffusion is sufficiently fast through the entire battery so that the temperature is virtually the same across all five sections. Therefore, in subsequent discussions, the battery temperature simply refers to the average temperature across all five sections.

In the second scenario shown in Fig. 3.7, 1C discharge simulations are compared for a wide range of heat exchange coefficient \( h \). As expected, decreasing the value of the heat exchange coefficient \( h \) leads to a more insulated battery and thus a faster increase of the cell temperature. Moreover, due to the coupling of all of the governing equations, it is possible to note the influence of different temperatures on the cell voltage.

In the third scenario shown in Fig. 3.8, for a fixed value of \( h = 1\text{W}/(\text{m}^2\text{K}) \), different discharge cycles are compared at 1C, 2C, and 5C. According to the
3.2. Numerical Implementation

Figure 3.6: Average temperature of each battery section in 1C discharge with $h = 1\text{W/(m}^2\text{K)}$

different applied currents, the temperature rises in different ways. It is interesting to note the high slope of the temperature during the 5C discharge, mainly due to the electrolyte concentration $c_e$ being driven to zero in the positive electrolyte by the high discharge rate.
3.2. Numerical Implementation

![Graph showing temperature and voltage over time for different heat exchange coefficients]

Figure 3.7: 1C discharge cycle run under different heat exchange coefficients: $h = 0.01$, $h = 1$, and $h = 100$

3.2.5 Verification of Implementation Results

From Taylor series, we observe that our discretization of time using BE is first-order accurate,

$$\frac{\partial f}{\partial t} \bigg|_{t_{k+1}} \approx \frac{f_{k+1} - f_k}{\Delta t} + O(\Delta t) \quad (3.49)$$
3.2. Numerical Implementation

Figure 3.8: Discharge cycle run under 1C, 2C, and 5C

and our discretization of space for both first and second derivatives using central-difference is second-order accurate,

\[
\frac{\partial f}{\partial x} \approx \frac{f_{n+1} - f_n}{2\Delta x} + O(\Delta x^2) \quad (3.50)
\]

\[
\frac{\partial^2 f}{\partial x^2} \approx \frac{f_{n-1} - 2f_n + f_{n+1}}{\Delta x^2} + O(\Delta x^2) \quad (3.51)
\]

We can now verify the implementation results by explicitly calculating the order of convergence.
3.2. Numerical Implementation

Suppose we had an exact solution $u_{\text{exact}}$ to the P2D equations and let $u_{\text{approx}}$ denote our approximation to the exact solution. Without the loss of generality, the global error $E$ is calculated by the absolute value of the difference between the cell voltage vs. time profile from the exact solution and that from the approximate solution, averaged over the length of simulation time,

$$E = \frac{\int_{t_i}^{t_f} ||V_{\text{exact}}(t) - V_{\text{approx}}(t)|| dt}{t_f - t_i}$$

(3.52)

Since we have $O(\Delta t)$ error from Backward Euler and $O(\Delta x^2)$ error from finite difference, the order of the total error in our implementation is,

$$E = O(\Delta t) + O(\Delta x^2)$$

(3.53)

Our method is said to converge if this error vanishes as $\Delta x \to 0$ and $\Delta t \to 0$.

We now use our simulation results to illustrate that our implementation is indeed first-order in time and second-order in space. To confirm that it is first-order in time, we fix the number of grid points in both $x$ and $r$, so that the spatial error $O(\Delta x^2)$ remains constant and will not affect convergence. We then divide the time-step size $\Delta t$ by 2 successively. The error from time-stepping $E_{\text{time}}$ is calculated by taking the maximum norm of each successive approximation normalized over total simulation time,

$$E_{\text{time}} = \frac{\int_{t_i}^{t_f} ||V_{\Delta t/2} - V_{\Delta td}|| dt}{t_f - t_i}$$

(3.54)
3.2. Numerical Implementation

and the estimated convergence rate can then be written as,

\[ C_R = \log_2 \left( \frac{\int_{t_i}^{t_f} ||V_{\Delta t/4} - V_{\Delta t/2}dt||}{\int_{t_i}^{t_f} ||V_{\Delta t/2} - V_{\Delta t}dt||} \right) \]  

(3.55)

with \( C_R = 1 \) for first-order and \( C_R = 2 \) for second-order. First-order convergence in time is clearly seen in Table 3.1

<table>
<thead>
<tr>
<th>( \Delta t )</th>
<th>( E_{time} )</th>
<th>( C_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.1959 \times 10^{-2}</td>
<td>1.0325</td>
</tr>
<tr>
<td>10</td>
<td>5.8463 \times 10^{-3}</td>
<td>1.0192</td>
</tr>
<tr>
<td>5</td>
<td>2.8845 \times 10^{-3}</td>
<td>1.0192</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: First-order convergence in time for Backward Euler method

The situation is more complicated when comes to checking the convergence rate in space, as there are two dimensions \( x \) and \( r \) with \( \Delta x \neq \Delta r \). Therefore, we will need to check each one individually. First, we fix \( \Delta t \) and \( \Delta r \) so that convergence is dependent solely on \( \Delta x \). We then half \( \Delta x \) successively. The error \( E_x \) from discretizing \( x \) is calculated by taking the maximum norm of each successive approximation normalized over total simulation time,

\[ E_x = \frac{\int_{t_i}^{t_f} ||V_{\Delta x/2} - V_{\Delta x}dt||}{t_f - t_i} \]  

(3.56)

and the estimated convergence rate can then be written as,

\[ C_R = \log_2 \left( \frac{\int_{t_i}^{t_f} ||V_{\Delta x/4} - V_{\Delta x/2}dt||}{\int_{t_i}^{t_f} ||V_{\Delta x/2} - V_{\Delta x}dt||} \right) \]  

(3.57)
3.2. Numerical Implementation

<table>
<thead>
<tr>
<th>$\Delta x$</th>
<th>$E_x$</th>
<th>$C_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-6}$</td>
<td>$6.1631 \times 10^{-7}$</td>
<td>1.3619</td>
</tr>
<tr>
<td>$0.5 \times 10^{-6}$</td>
<td>$2.3979 \times 10^{-7}$</td>
<td></td>
</tr>
<tr>
<td>$0.25 \times 10^{-6}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: Error and convergence for discretization in $x$

The results are shown in Table 3.2. Different from our expectation, the $C_R$ here is less than 2, which may be due to the extremely small magnitude of error that interferes with MATLAB’s intrinsic machine precision.

Lastly, we fix $\Delta t$ and $\Delta x$ so that convergence is dependent solely on $\Delta r$. We then half $\Delta r$ successively. Similarly, the error $E_r$ from discretizing $r$ is calculated by taking the maximum norm of each successive approximation over total simulation time,

$$E_r = \frac{\int_{t_i}^{t_f} ||V_{\Delta r/2} - V_{\Delta r}dt||}{t_f - t_i}$$

and the estimated convergence rate can then be written as,

$$C_R = \log_2 \left( \frac{\int_{t_i}^{t_f} ||V_{\Delta r/4} - V_{\Delta r/2}dt||}{\int_{t_i}^{t_f} ||V_{\Delta r/2} - V_{\Delta r}dt||} \right)$$

The results are shown in Table 3.3. Here, $C_R$ is asymptotically approaching the expected second-order convergence rate as we half $\Delta r$. Notice that, of $\Delta t$, $\Delta x$, and $\Delta r$, it is $\Delta r$ which has the most impact on the accuracy of our implementation.
3.3. Model Reduction

The ultimate goal of P2D model simulation is to implement it on advanced battery management systems (ABMS). ABMS anticipate problems through online fault diagnosis which can prevent damage, ensure safety, minimize charging time, and slow down battery aging. These are possible only if model simulations are extremely fast. The full P2D model is currently the most accurate electrochemical model but the computational time is too long to be implemented on ABMS. To achieve a better trade-off between accuracy and computational time, four different model reductions are proposed: the two-parameters approximation model, the temperature-reduction model, the $\Phi_s$-reduction model, and the mixed-reduction model. The ideal reduced model can achieve less than 1% error when compared with the full model at any discharge rate. The convergence of each approximate model is assessed by comparing its cell potential vs. time profiles under different applied current rates $I_{\text{app}}(t)$ with that of the full P2D model, as shown in Fig. 3.9.

<table>
<thead>
<tr>
<th>$\Delta r$</th>
<th>$E_r$</th>
<th>$C_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.5 \times 10^{-6}$</td>
<td>$1.8701 \times 10^{-2}$</td>
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</tr>
<tr>
<td>$0.25 \times 10^{-6}$</td>
<td>$2.2434 \times 10^{-3}$</td>
<td>2.0960</td>
</tr>
<tr>
<td>$0.125 \times 10^{-6}$</td>
<td>$5.2474 \times 10^{-4}$</td>
<td>2.0960</td>
</tr>
<tr>
<td>$0.0625 \times 10^{-6}$</td>
<td>$5.2474 \times 10^{-4}$</td>
<td>2.0960</td>
</tr>
</tbody>
</table>

Table 3.3: Error and convergence for discretization in $r$
3.3. Model Reduction

The improved efficiency of the four reduced models is demonstrated in Table 3.4 by comparing their individual effective simulation time with that of the full model.
### 3.3. Model Reduction

<table>
<thead>
<tr>
<th></th>
<th>Simulation Duration</th>
<th>Effective Simulation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full model</td>
<td>3590s</td>
<td>341.016s</td>
</tr>
<tr>
<td>Two-parameters approximation model</td>
<td>3540s</td>
<td>203.716s</td>
</tr>
<tr>
<td>Reduced temperature model</td>
<td>3580s</td>
<td>161.194s</td>
</tr>
<tr>
<td>Reduced $\Phi_s$ model</td>
<td>3600s</td>
<td>261.079s</td>
</tr>
<tr>
<td>Mixed reduction model</td>
<td>3600s</td>
<td>123.921s</td>
</tr>
</tbody>
</table>

Table 3.4: Timing comparisons of different models running under 1C, with $\Delta t = 10$, $\Delta x = 1 \times 10^{-6}$, $\Delta r = 0.5 \times 10^{-6}$, and $h = 1$

### 3.3.1 Two-Parameters Approximation Model

**Model overview**

Recall that diffusion inside solid spherical particles is described by Fick’s law,

$$\frac{\partial c_s(r, t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 D_s p \frac{\partial c_s(r, t)}{\partial r} \right]$$  \hspace{1cm} (3.60)

with boundary conditions,

$$\left. \frac{\partial c_s(r, t)}{\partial r} \right|_{r=0} = 0, \quad \left. \frac{\partial c_s(r, t)}{\partial r} \right|_{r=R_p} = -\frac{j(x, t)}{D_{\text{eff}}^s}$$ \hspace{1cm} (3.61)

In this model, a major source of computational burden comes from the pseudo-second-dimension ($r$).

In the two-parameters approximation model, concentration profiles inside the particle are assumed to be quadratic in $r$,

$$c_s(r, t) = a(t) + b(t) \frac{r^2}{R_p^2}$$ \hspace{1cm} (3.62)

where $a(t)$ and $b(t)$ are to be determined. Substituting Eq. 3.62 into Eq.
3.3. Model Reduction

3.60, we obtain,

\[ \frac{\partial a(t)}{\partial t} + \frac{r^2}{R_p^2} \frac{\partial b(t)}{\partial t} - \frac{6D_{\text{eff}}^* b(t)}{R_p^2} \]  \hspace{1cm} (3.63)

The boundary condition at \( r = 0 \) is automatically satisfied. The boundary condition at \( r = R_p \) becomes,

\[ 2 \frac{D_{\text{eff}}^* b(t)}{R_p} = -j \]  \hspace{1cm} (3.64)

We are interested in the average concentration and surface concentration. Thus, \( a(t) \) and \( b(t) \) are expressed in terms of volume-average concentration \( c_{\text{avg}}^s(x,t) \) and surface concentration \( c_{\text{s}}^s(x,t) \). The volume-averaged concentration is given by,

\[ c_{\text{avg}}^s(x,t) = \int_{r=0}^{R_p} \frac{3r^2}{R_p^2} c_s(r,t) d\left( \frac{r}{R_p} \right) \]  \hspace{1cm} (3.65)

Applying Eq. 3.62 in Eq. 3.65, we get,

\[ c_{\text{avg}}^s(x,t) = a(t) + \frac{3}{5} b(t) \]  \hspace{1cm} (3.66)

The surface concentration \( c_{\text{s}}^s(x,t) \) is obtained by substituting \( r = R_p \) in Eq. 3.62,

\[ c_{\text{s}}^s(x,t) = a(t) + b(t) \]  \hspace{1cm} (3.67)
3.3. Model Reduction

Eq. 3.66 and 3.67 are solved to obtain,

\[ a(t) = -\frac{3}{2}c_s^*(x,t) + \frac{5}{2}c_{avg}^s(x,t) \]  \hfill (3.68)

\[ b(t) = -\frac{5}{2}c_{avg}^s(x,t) + \frac{5}{2}c_s^*(x,t) \]  \hfill (3.69)

Now we can substitute \( a(t) \) and \( b(t) \) into Eq. 3.62,

\[ c_s(r,t) = -\frac{3}{2}c_s^*(x,t) + \frac{5}{2}c_{avg}^s(x,t) + \left( -\frac{5}{2}c_{avg}^s(x,t) + \frac{5}{2}c_s^*(x,t) \right) \frac{r^2}{R_p^2} \]  \hfill (3.70)

We need two equations to evaluate the average concentration \( c_{avg}^s(x,t) \) and the surface concentration \( c_s^*(x,t) \). The former can be evaluated by volume averaging the entire governing Eq. 3.60,

\[ \int_{r=0}^{R_p} 3 \frac{r^2}{R_p^2} \frac{\partial c_s}{\partial t} - D_{eff}^s \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_s}{\partial r} \right) d\left( \frac{r}{R_p} \right) = 0 \]  \hfill (3.71)

Substituting Eq. 7 and 13, and evaluating, we have,

\[ \frac{\partial c_{avg}^s(x,t)}{\partial t} = -\frac{3}{R_p} j(x,t) \]  \hfill (3.72)

The surface concentration is obtained by evaluating the boundary condition at \( r = R_p \). Applying Eq. 3.92 to Eq. 3.62, we have,

\[ c_s^*(x,t) - c_{avg}^s(x,t) = -\frac{R_p}{D_p^s} \frac{j(x,t)}{5} \]  \hfill (3.73)

In summary, the original diffusion inside solid-particles is now approxi-
3.3. Model Reduction

... by means of average and surface concentration,\n\[
\frac{\partial c_{\text{avg}}^{s}(x,t)}{\partial t} = -3j(x,t) \frac{R_p}{R_p^s} c^{s}(x,t) - c_{\text{avg}}^{s}(x,t) = -\frac{R_p j(x,t)}{D_p^s} \frac{R_p}{5}
\]

This reduction leads to a one-dimensional problem in \( x \) by removing the pseudo-second-dimension \( r \). In terms of computation, 47.63\% of variables are eliminated for any specified \( \Delta x \) and \( \Delta r \).

Results analysis

From Fig. 3.9 we observe that for medium (2C) and high (5C) discharge rates, the model simulation ends prematurely, primarily because the electrolyte concentration \( c_e \) being driven to zero in the positive electrode by the high discharge rate.

The performance of the model is evaluated by the absolute difference of cell potential profile averaged over total simulation time with the full model,
\[
E_{tp} = \frac{\int_{t_i}^{t_f} ||V_{\text{reduced}} - V_{\text{full}}|| dt}{t_f - t_i} \tag{3.74}
\]

Note that since the reduced model ends prematurely, \( t_f \) is normalized by extending the earlier ending model with \( V = 0 \) until it has the same length of time as the full model. The performance of the two-parameters approximation model can be seen in Table 3.5,

In terms of accuracy, the two-parameters approximation model meets our criterion of less than 1\% error only for discharge rate < 1C. In terms
### 3.3 Model Reduction

<table>
<thead>
<tr>
<th></th>
<th>$E_{tp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1C</td>
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</tr>
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<td>2C</td>
<td>0.058324</td>
</tr>
<tr>
<td>5C</td>
<td>0.28877</td>
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</table>

Table 3.5: Performance of the two-parameters approximation model

of effective simulation time (Table 3.4), this model improves computational efficiency by 40%.

#### 3.3.2 Temperature-Reduction Model

**Model overview**

From Fig. 3.6, the temperature is shown to be constant in all sections, in other words $T$ is constant in $x$. Thus, we can reduce computation time by simply having one single global temperature variable $T$ instead of a different $T$ variable on each grid point. This model reduction eliminates 8.99% of variables for any specified $\Delta x$ and $\Delta r$.

**Results analysis**

Similar to the two-parameters approximation, the temperature-reduction model ends prematurely at 2C and 5C, as seen in Fig. 3.9. However at 5C, its potential vs. time profile is clearly closer to the full model. To confirm model performance, we use the same metric,

$$E_{tr} = \int_{t_i}^{t_f} ||V_{reduced} - V_{full}|| dt$$

(3.75)
3.3. Model Reduction

Again, $t_f$ is normalized by extending the earlier ending model with $V = 0$ until it has the same length of time as the full model. The performance of the temperature-reduction model can be seen in Table 3.6,

<table>
<thead>
<tr>
<th>$E_{tr}$</th>
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<tbody>
<tr>
<td>1C</td>
</tr>
<tr>
<td>2C</td>
</tr>
<tr>
<td>5C</td>
</tr>
</tbody>
</table>

Table 3.6: Performance of the temperature-reduction model

In terms of accuracy, the temperature-reduction model meets our criterion of less than 1% error only for discharge rate $< 1$C. In terms of effective simulation time (Table 3.4), although this model eliminates less variables than the previous reduced model, it achieves the highest computational efficiency. This is because temperature is embedded in every of the P2D equations. Reducing all temperature into one single variable converts many vector and matrix operations into scalar calculations, and thus greatly shortens simulation time.

3.3.3 $\Phi_s$-Reduction Model

Model overview

The effective diffusivity of electrolyte and solid particles, $D_{eff}$ and $D_{eff}^s$, are of the same magnitude. However, because the length of electrolyte ($8 \times 10^{-5}$m for cathode and $8.8 \times 10^{-5}$m for anode) is $\sim 20$ times of that of the solid particles ($4 \times 10^{-6}$m in diameter), actual diffusion is much faster in the latter. Consequently, the solid concentration $c_s$ is nearly uniform in
3.3. Model Reduction

both cathode and anode, and thus there is little solid potential ($\Phi_s$) variation in each section. Therefore, instead of having $N_p$ and $N_n$ identical values of $\Phi_s$ in the cathode and anode, respectively, we can reduce the model to have only two $\Phi_s$, one for each section. This eliminates 6.75% of variables for any specified $\Delta x$ and $\Delta r$.

Results analysis

From Fig. 3.9, we observe that the $\Phi_s$-reduction model overlaps the full model almost completely for all three discharge rates. To confirm model performance, we again use the standard,

$$E_{spr} = \frac{\int_{t_i}^{t_f} ||V_{\text{reduced}} - V_{\text{full}}|| dt}{t_f - t_i}$$

(3.76)

where $t_f$ is normalized similar to the previous two reduced models by extending the earlier ending model with $V = 0$ until it has the same length of time as the full model. The performance of the $\Phi_s$-reduction model can be seen in Table 3.7,

<table>
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</thead>
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<tr>
<td>1C 0.0014062</td>
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<tr>
<td>2C 0.0024186</td>
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<td>5C 0.004695</td>
</tr>
</tbody>
</table>

Table 3.7: Performance of the $\Phi_s$-reduction model

In terms of accuracy, the $\Phi_s$-reduction model exceeds our criterion of less than 1% error for all of low (1C), medium (2C), and high (5C) discharge rates. In terms of effective simulation time (Table 3.4), this model improves
3.3. Model Reduction

computational efficiency by 23%.

3.3.4 Mixed-Reduction Model

Model overview

Lastly we try to combine all model reductions into a single model. That is, the mixed-reduction model incorporates the above three model reductions: the two parameter approximation model, the temperature-reduction model, and the $\Phi_s$-reduction model. In terms of computation, 63% of variables are eliminated for any specified $\Delta x$ and $\Delta r$.

Results analysis

From Fig. 3.9 we observe that the mixed-reduction model simulation ends much prematurely and produces results with the largest offset when compared to the full model. The performance deteriorates quickly at higher current rates.

To confirm model performance, we again use the standard,

$$E_{mr} = \frac{\int_{t_i}^{t_f} ||V_{reduced} - V_{full}|| dt}{t_f - t_i}$$  \hspace{1cm} (3.77)

Same as before, $t_f$ is normalized by extending the earlier ending model with $V = 0$ until it has the same length of time as the full model. The performance of the mixed-reduction model can be seen in Table 3.,

In terms of accuracy, the mixed-reduction model meets our criterion of less than 1% error only for discharge rate $< 1C$. At 2C and 5C, this model yields errors of 10% and 39%. This large error is expected as this model
3.4 Conclusion

Table 3.8: Performance of the mixed-reduction model

| $E_{mr}$ | 1C    | 0.0092687 | 2C    | 0.10125 | 5C    | 0.3893 |

eliminates a high percentage of fundamental variables. In terms of effective simulation time (Table 3.4), this model improves computational efficiency by 64%, the largest efficiency increase of all. Applications that require only low current rates but fast response time on battery monitoring may incorporate this model into their BMS.

3.4 Conclusion

This chapter describes a detailed procedure for the numerical implementation of the pseudo-two-dimensional (P2D) model. The treatment of boundary conditions is addressed with particular attention to the interface conditions across the different sections of the battery. The simulations demonstrate high numerical stability for different operating scenarios.

Four model reductions with elimination of different variables to reduce computational complexity are implemented and tested. All reduced models have effective simulation time shorter than that of the full model, with mixed-reduction model being the fastest, followed by reduced-temperature model, two-parameters approximation model, and lastly reduced $\Phi_s$ model.

The results of this work show the promise of the proposed framework as a reliable and efficient MATLAB-based program for the P2D model simula-
3.4. Conclusion

tion. Further developments such as code migration into a compiled language (e.g. C#, Java) can only improve the current performance. As the proposed simulations are written in standard serial mode, the computation time could be reduced by at least a factor of ten by using a multicore CPU using parallel DAE solvers. Modern versions of MATLAB have easy-to-implement built-in options for distributing calculations among multiple cores on a single CPU, and among multiple CPUs.
Chapter 4

Summary and Future Work

Here we provide a summary for each of the two approaches taken and discuss future extensions to the work done.

4.1 First Approach: Physical Experiments

In this approach, lithium-ion batteries are cycled under different current rates, while their temperature, voltage, current, and cell capacity are measured. Battery aging, which is accelerated by high current rates, is illustrated with plotting and analysis. Two predictive models that can estimate lithium-ion battery state-of-health are built from the data generated. Future work that may be interesting includes distinguishing battery aging due to cycling (discharge/charge) from purely temperature variation. This can be done by setting up two treatments: the first treatment involves cycling batteries with different current rates while recording their temperature, and the second treatment involves no discharge/charge but thermocycles batteries using the temperature profile generated from the first treatment. A necessary equipment needed for this work is heating tape with a custom programmed controller.
4.2 Second Approach: Mathematical Modelling

In this approach, we provided a robust implementation of the pseudo-two-dimensional (P2D) model and discussed four potential model reductions that greatly shorten simulation time. Each model reduction achieves a different standard of accuracy, which can be programmed onto battery management system of different applications. An interesting future work that may further improve computational efficiency includes developing a split-step solver. In this split-step solver, with \( a \) and \( c \) given by the initial condition, first update the nonlinear parts \( j, s, \Phi, \) and \( \phi \) with Newton’s method, then update \( T \) and \( a \) explicitly using the forward Euler method. Lastly, with \( j \) and \( T \) known from the previous two steps, update \( c \) using the IMEX (implicit-explicit) method. Overall, this split-step solver tailors the most efficient method to each equation: implicit method for the nonlinear equations and explicit method for the linear equations. The simulation time is thus expected to further shorten.
Bibliography


[14] Ramadesigan, V. et. al., Efficient Reformulation of Solid-Phase Diffu-


Appendix A

Table I. Additional equations

Open circuit potential (thermal dependence)

\[ U_p = U_{p,\text{ref}} + (T(x, t) - T_{\text{ref}}) \frac{\partial U_p}{\partial T} \bigg|_{T_{\text{ref}}} \]

\[ U_n = U_{n,\text{ref}} + (T(x, t) - T_{\text{ref}}) \frac{\partial U_n}{\partial T} \bigg|_{T_{\text{ref}}} \]

Entropy change

\[ \frac{\partial U_p}{\partial T} \bigg|_{T_{\text{ref}}} = -0.001 \left( \frac{0.199521039 - 0.9283738229 \theta_p + 1.3645506890000362^2}{1 - 5.66147988999997 \theta_p + 11.4763191 \theta_p^2} \right) \]

\[ \frac{\partial U_n}{\partial T} \bigg|_{T_{\text{ref}}} = \left( \frac{0.001(0.005269056 + 3.29926579696 - 91.793257986^2 + 1004.911099 \theta_n^3)}{1 - 48.99287227 \theta_n + 1017.234804 \theta_n^2} \right) \]

\[-5812.278127 \theta_n^3 + 19329.754067 - 37147.89478 \theta_n^2 + 38379.18127 \theta_n - 10481.85209 \theta_n^2 \]

\[-16515.05309 \theta_n^2 \]

Open circuit potential (reference value)

\[ U_{p,\text{ref}} = -4.656 + 88.669^2 - 401.119 \theta_n^3 + 342.909 \theta_n^2 - 462.471 \theta_n^2 + 433.434 \theta_n^3 \]

\[ U_{n,\text{ref}} = \left( 0.7222 + 0.1387 \theta_n + 0.029 \theta_n^5 - 0.0172 \theta_n - 0.0019 \theta_n^2 \right) \]

\[ + 0.2808 e^{0.9 - 15 \theta_n} - 0.7984 e^{0.4465 \theta_n - 0.4108} \]

\[ \theta_p = \frac{c_{s,p}^*(x,t)}{c_{s,p}^\infty} \]

\[ \theta_n = \frac{c_{s,n}^*(x,t)}{c_{s,n}^\infty} \]

Heat source terms (anode and cathode)

\[ Q_{\text{ohm}} = \sigma_{\text{eff},i} \left( \frac{\partial \Phi_s(x,t)}{\partial x} \right)^2 + \kappa_{\text{eff},i} \left( \frac{\partial \Phi_e(x,t)}{\partial x} \right)^2 \]

\[ + 2 \kappa_{\text{eff},i} \frac{RT(x,t)}{P} \left( 1 - t_+ \right) \frac{\partial \ln c_e(x,t)}{\partial x} \frac{\partial \Phi_e(x,t)}{\partial x} \]

\[ Q_{\text{rxn}} = F a_i j(x,t) \eta_i(x,t) \]

\[ Q_{\text{rev}} = F a_i j(x,t) T(x,t) \frac{\partial U_i}{\partial T} \bigg|_{T_{\text{ref}}} \]
Table I. Additional equations (continued)

Heat source terms (separator)

\[ Q_{\text{ohm}} = \kappa_{\text{eff},i} \left( \frac{\partial \Phi_e(x,t)}{\partial x} \right)^2 + \frac{2\kappa_{\text{eff},i} RT(x,t)}{F} (1 - t_e) \frac{\partial \ln c_e(x,t)}{\partial x} \frac{\partial \Phi_e(x,t)}{\partial x} \]

Various coefficients

\[ D_{\text{eff},i} = \epsilon_i^{\text{brugg}} \times 10^{-4} \times 10^{-4.43 - \frac{54}{T(x,t) - 229 - 5 \times 10^{-3} c_e(x,t)} - 0.22 \times 10^{-3} c_e(x,t)} \]

\[ \kappa_{\text{eff},i} = \epsilon_i^{\text{brugg}} \times 10^{-4} \times c_e(x,t) \left( -10.5 + 0.668 \times 10^{-3} c_e(x,t) \right) + 0.494 \times 10^{-6} c_e^2(x,t) + (0.074 - 1.78 \times 10^{-5} c_e(x,t) \right) - 8.86 \times 10^{-10} c_e^2(x,t)) T(x,t) + (-6.96 \times 10^{-5} \right) + 2.8 \times 10^{-8} c_e(x,t)) T^2(x,t) \right)^2 \]

\[ k_{\text{eff},i} = k_i e^{-\frac{k_i}{R}} \left( \frac{1}{T(x,t)} - \frac{1}{T_{\text{ref}}} \right) \]

\[ D_{\text{eff},i}^s = D_i e^{-\frac{D_i}{R}} \left( \frac{1}{T(x,t)} - \frac{1}{T_{\text{ref}}} \right) \]

\[ \sigma_{\text{eff},i} = \sigma_i (1 - \epsilon_i - \epsilon_{f,i}) \]

\[ \Upsilon := \frac{2(1 - t_e)}{F} \]
### Table II. List of parameters used in simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
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<tr>
<td>$c_{e}^{\text{init}}$ [mol/m$^3$]</td>
<td>Initial concentration in the electrolyte</td>
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<td>Initial solid-phase concentration</td>
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<td>$c_{s}^{\text{max}}$ [mol/m$^3$]</td>
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### Table II. List of parameters used in simulation (continued)

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