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One Dimensional Computer Modeling of a Lithium-Ion Battery

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ONE DIMENSIONAL COMPUTER MODELING OF A LITHIUM-ION BATTERY

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

By

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2017
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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Ashwin S. Borakhadikar ENTITLED One Dimensional Computer Modeling of a Lithium-Ion Battery BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science in Mechanical Engineering.

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ABSTRACT

Borakhadikar, Ashwin S. M.S.M.E., Department of Mechanical and Materials Engineering, Wright State University, 2017. One Dimensional Computer Modeling of a Lithium-Ion Battery.

One Dimensional Computer Modeling of a Lithium-Ion Battery

Renewable energy storage is vitally important to many applications for which batteries are the finest choice. As energy storage technology may be applied to a number of areas that differ in power and energy requirements, modeling of battery performance is required. In recent years, a lot of research has been done in this area but, the earliest model was designed by Marc Doyle, T. F. Fuller, and J. Newman in 1993.

This work involves the development of a one-dimensional computer model of a lithium-ion battery which consists of three domains: the negative electrode, the separator, and the positive electrode. The solid electrodes are modeled based on porous electrode theory. A finite volume technique is used to solve four partial differential equations which simulate the dynamics of lithium-ion batteries. These equations are conservation of current in the solid electrodes, conservation of current in the electrolyte, conservation of species in the solid particles, and conservation of species in the electrolyte. Another important equation included in this model is the Butler–Volmer kinetic equation. In order to study the distributions of battery parameters, MATLAB computer routines were written to solve each partial differential equation and then were joined together sequentially in one computer code that simulates the performance of lithium-ion batteries during charging and discharging.

The developed model is capable of predicting the electrochemical behavior of the battery depending upon the input material properties. The results from the computer model developed as a part of this work are validated by comparing them with the available computational results for a 6 Ah battery with various current discharge rates (1C, 5C and 10C) from Smith et al. [26]. The effects of different charging and discharging conditions
on battery performance are presented as well. The distributions also show that battery voltage and concentration gradient in the electrolyte phase are found to vary with applied discharge current.
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Nomenclature

Letters

\( A \) Area of electrode
\( a_E \) Coefficient at grid point located in the east direction from the point of interest
\( a_p \) Coefficient at grid point located at the point of interest
\( a_s \) Active interfacial surface area to volume ratio in the active spherical particle
\( a_w \) Coefficient at grid point located in the west direction from the point of interest
\( C_e \) Concentration of lithium ions in electrolyte phase
\( C_s \) Concentration of lithium ions in solid phase
\( C_{s, \text{surface}} \) Concentration of lithium ions at surface of the active spherical particle
\( C_{s, \text{max}} \) Maximum solid phase concentration
\( D_s \) Diffusion coefficient of Li\(^+\) ions in solid phase
\( D_e \) Diffusion coefficient of Li\(^+\) ions in electrolyte phase
\( D_{e, \text{eff}} \) Effective diffusion coefficient of lithium ions in electrolyte phase
\( f \) Molar activity coefficient
\( F \) Faraday’s constant
\( i_o \) Exchange current density
\( I \) Applied current at the current collectors
\( j_{Li} \) Transfer current
\( k_{\text{eff}} \) Effective ionic conductivity
\( k_{d, \text{eff}} \) Effective diffusional conductivity
\( k_o \) Kinetic constant
\( L \) Location along the x-dimension
\( L_{\text{neg}} \) Thickness of negative electrode
\( L_{\text{sep}} \) Thickness of separator
\( L_{\text{pos}} \) Thickness of positive electrode
\( n_{\text{neg}} \) Number of control volumes in negative electrode
\( n_{\text{sep}} \) Number of control volumes in separator
\( n_{\text{pos}} \) Number of control volumes in positive electrode
\[ P \quad \text{Coefficients used in TDMA} \]
\[ Q \quad \text{Coefficients used in TDMA} \]
\[ r \quad \text{Radius of the spherical particle} \]
\[ R \quad \text{Universal gas constant} \]
\[ R_f \quad \text{Contact resistance between electrodes and the respective current collector} \]
\[ r_o \quad \text{Outer radius of the spherical particle} \]
\[ R_s \quad \text{Radius of electrode spherical particle} \]
\[ R_{SEI} \quad \text{Resistance due to irreversible film formation at solid-electrolyte interface} \]
\[ S \quad \text{Source term of differential equation} \]
\[ S_p \quad \text{Derivative of the source term w.r.t dependent variable} \]
\[ t \quad \text{Time of operation} \]
\[ t^+ \quad \text{Transference number} \]
\[ T \quad \text{Ambient Temperature} \]
\[ U \quad \text{Equilibrium Potential} \]
\[ U_n \quad \text{Equilibrium Potential at negative electrode} \]
\[ U_p \quad \text{Equilibrium Potential at positive electrode} \]
\[ x, y \quad \text{Stochiometric coefficients in negative and positive electrode} \]
\[ X_L \quad \text{Location of negative current collector} \]
\[ X_R \quad \text{Location of positive current collector} \]

**Greek Letters**

\[ \alpha_a, \alpha_c \quad \text{Anodic and cathodic charge transfer coefficients} \]
\[ \Delta x \quad \text{Distance between the edges of the control volume in Cartesian system} \]
\[ \delta x \quad \text{Distance between the computational grid points in Cartesian system} \]
\[ \varepsilon_e \quad \text{Electrolyte phase volume fraction} \]
\[ \varepsilon_f \quad \text{Conductive filler volume fraction} \]
\[ \varepsilon_p \quad \text{Polymer phase volume fraction} \]
\[ \varepsilon_s \quad \text{Active particle volume fraction} \]
\[ \eta \quad \text{Overpotential} \]
\[ \Gamma \quad \text{Diffusion coefficient related to field variables } (C_e, C_s, \varphi_e \text{ and } \varphi_s) \]
<table>
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<td>$\varphi_e$</td>
<td>Electrolyte phase potential</td>
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<tr>
<td>$\varphi_s$</td>
<td>Solid phase potential</td>
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<tr>
<td>$\sigma_{\text{eff}}$</td>
<td>Effective solid phase electrical conductivity</td>
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I would first like to thank my advisor, Dr. James Menart, for having faith in me and giving me the opportunity to do this thesis which started as an independent study, for which I am grateful. His knowledge and experience is enormous in this field which helped me a lot in completing my Master’s thesis. The discussions during our meetings were the main source for me to learn new concepts and become technically sound. While working on this project, every now and then I used to knock on his door with some doubts and he was always there to help and always guided me in the right direction. It was a great learning experience for me while working with him.

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Finally, I would like to express my very profound gratitude to my family back in India my Mom (Mrs. Anuradha Borakhadikar), Dad (Mr. Satish Borakhadikar), my Brother (Mr. Ashish Borakhadikar) and the new member in our family my sister in law (Mrs. Mrunalini Bhave) for being there for me. Also, my cousins in United States (Mrs. Priyanka Muley and Mrs. Pranjali Muley), who always stood behind me and boosted my confidence whenever I was in a deadlock. This accomplishment would not have been possible without all of them. Thank you.
Chapter 1. INTRODUCTION

The process of finding ways to generate energy is perhaps never-ending, so it is in the best interest to keep working on finding efficient ways to store energy. Renewable energy storage is vitally important to many applications for which batteries are the finest choice. As battery energy storage may be applied to a number of situations that differ in power and energy requirements, modeling of battery performance is required. In this chapter, we will briefly introduce the working principle of a lithium-ion battery and the modeling approach which can be considered while designing a battery.

After the commercialization of lithium-ion batteries by SONY in 1991, many models have been developed for different applications. The invention of an intercalation battery electrode was a landmark step in the development of batteries over the years. During the 1980s, Dr. John Goodenough and his co-workers invented the lithium-cobalt chemistry as an electrode material [1]; and until now, LiCoO2 is still the most used metal-oxide for the positive electrode of lithium-ion batteries for all kinds of electronic applications and portable devices [2].

Due to the amount of research and development done to improve the performance of lithium-ion batteries over last two decades, it now has higher specific power and higher specific energy as compared to other types of batteries. This comparison can be seen in the Figure 1. Also, the added advantages, of low self-discharge rate, long cycle life, and high average operating cell voltage, the demand for lithium ion batteries has gone up and they are gradually replacing previously developed Ni-MH batteries for many applications.
There are various types of lithium ion batteries which differ due to the materials used for the negative and positive electrodes. Some of the different types of lithium oxides used for the positive electrode are: lithium-cobalt-oxide (LiCoO$_2$), lithium-manganese-oxide (LiMn$_2$O$_4$), lithium-nickel-manganese-cobalt-oxide (LiNiMnCoO$_2$), lithium-iron-phosphate (LiFePO$_4$) and lithium-nickel-cobalt-aluminum-oxide (LiNiCoAlO$_2$). The material can be chosen based on specific energy, specific power, cost, safety, performance, and life span requirement.

Figure 2 depicts the comparison of characteristics of different lithium-ion chemistries plotted based on the important parameters. As is apparent from the figure below, no one material has perfect properties, therefore, the chemistry should be selected based on the application.

The commonly used electrolytes in lithium-ion batteries are solvent mixtures of alkyl carbonates together with a lithium salt. Ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC) and methyl propylene carbonate (MPC) are among the choices of solvents. Among these Ethylene carbonate (EC) is preferred.
Figure 2: Characteristic comparison of different types of lithium-ion chemistries [4].

1.1 Objectives of Project

Specific objectives of the project are:

- Develop an electrochemical, one-dimensional computer model of a lithium-ion battery.
- To simulate the discharging and charging processes of the battery.
- The developed model should be capable of predicting the electrochemical behaviour of the battery depending upon the input material properties and the kinetic parameters.
- Validate the numerical model against published results.
- To study the effect of charging / discharging rate on the performance of the battery.
### 1.2 Basic Principle of Lithium-Ion Battery

A basic lithium-ion battery consists of a negative electrode and a positive electrode which are immersed in an electrolyte and divided by a separator. It is constructed in such a way that; the electrodes can be solid or porous to allow the electrolyte to infiltrate throughout the electrode. The separator prevents electrons from flowing, but allows ions to travel through the electrolyte. The electrolyte acts as a good ionic conductor but poor electron conductor. This forces the electrons to travel through the external circuit.

The one-dimensional section from the negative current collector \((X_L = 0)\) to the positive current collector \((X_R = L)\) consists of three domains: the negative composite electrode (width \(L_{neg}\)), separator (width \(L_{sep}\)), and positive composite electrode (width \(L_{pos}\)). Figure 3 shows a schematic of the Lithium-ion cell.

At the macroscopic level, active solid material in the solid electrodes is assumed to be made up of tiny spherical particles as shown in Figure 3. These active particles are surrounded by electrolyte which infiltrates through the available spaces and provides a good medium for the diffused lithium ions to travel from one electrode towards the other during charging and discharging processes.

![Schematic of a lithium-ion cell](image)

**Figure 3: Schematic of a lithium-ion cell.**
1.2.1 Charging Process

During the charge process, the negative electrode acts as the cathode and the positive electrode acts as the anode. As shown in Figure 4, lithium ions move from the positive electrode (anode) to the negative electrode (cathode), while electrons move in the same direction from the anode to the cathode through an external circuit.

![Figure 4: Charging process.](image)

When a lithium ion cell is charged, an oxidation reaction process takes place at the positive electrode and a reduction reaction takes place at the negative electrode as shown by the chemical reactions:

Negative electrode:

\[ C + x\text{Li}^+ + xe^- \overset{\text{charging}}{\longrightarrow} \text{Li}_x\text{C} \]  \hspace{1cm} (1.1)

Positive electrode:

\[ \text{LiMO}_2 \overset{\text{charging}}{\longrightarrow} \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \]  \hspace{1cm} (1.2)

In these equations, LiMO\(_2\) represents the metal oxide as a positive material, such as LiCoO\(_2\), and C the carbonaceous negative material, such as graphite [5]. An oxidation process generates free electrons and lithium ions, where the ions travel through the separator and get deposited on the graphite electrode.
1.2.2 Discharging Process

During the discharge process, the negative electrode acts as an anode and the positive electrode as a cathode. As shown in Figure 5, positive ions move from the anode to the cathode through the separator, while electrons move in the same direction, from the anode to the cathode, through an external load. As the discharge process continues, negative charge builds up on the anode and the cathode builds up a positive charge.

![Figure 5: Discharging process.](image)

When it is being discharged, the process gets reversed from charging i.e. the oxidation process takes place at the negative electrode where the graphite electrode will lose an electron to produce a Li$^+$ ion. While, reduction process takes place at the positive electrode where lithium oxides are formed as mentioned in the following chemical reactions [5]

Negative electrode:

\[
\text{Li}_x\text{C} \overset{\text{discharging}}{\longrightarrow} \text{C} + x\text{Li}^+ + xe^- 
\]  

Positive electrode:

\[
\text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- \overset{\text{discharging}}{\longrightarrow} \text{LiMO}_2 
\]
1.3 Battery Modeling Approach

Battery modeling methods for lithium-ion batteries vary widely in terms of complexity, and computational requirements. Many researchers have also presented multi-dimensional models using different approaches and solving techniques, which will be covered in Chapter 2 of this thesis.

In this work, a numerical modeling approach has been used which is used to solve the fundamental, governing, partial differential equations. Battery modeling approaches can be categorized into the following three categories:

- Empirical modeling
- Circuit modeling
- Numerical modeling (electrochemical models)

and can be considered to compute the battery performance parameters.

1.3.1 Empirical Modeling

This modeling approach is based on empirical relationships and past experimental data to predict the characteristics of a battery. These models are not generalized enough to be applicable for design of new battery chemistries or materials. Though, the empirical modeling approach is relatively easy to compute compared to equivalent circuit and numerical models, these models only work for specific kinds of applications and typically offer very low accuracy.

1.3.2 Circuit Modeling

The circuit modeling approach is somewhat complex as compared to empirical models, and it is comprised of different electrical components, such as resistors and capacitive ladder like structures in order to simulate battery performance. Diffusion processes inside both electrodes are modeled by using a ladder network of capacitors and resistors. Circuit modeling, as compared to numerical modeling, takes less computational time but is less accurate.
1.3.3 Numerical Modeling

The numerical modeling approach depends upon the use of partial differential equations in order to predict battery performance. This approach is more complex and takes more computational time; but, the accuracy in predicting electrochemical behavior will be higher than circuit and empirical modeling. This model incorporates electrochemical kinetics and transport phenomena which govern the flow in a battery cell. This model requires inputs of geometric dimensions, physical constants, and material properties. For a given time-varying battery input current, the model predicts the battery time response, including output voltage.

The process of model validation includes testing the model under a variety of inputs and minimizing the error between the simulated and experimental responses. Once the model has been validated, the input parameters can be varied according to different battery designs and the desired results can be obtained. Thus, the numerical modeling approach can be used to optimize the performance of a battery.

1.4 Outline of Thesis

This thesis includes six chapters that discuss this project in detail. Chapter 1 provides a general introduction to lithium-ion batteries and its basic principles. Types of lithium-ion chemistries and, battery modeling approaches have also been discussed.

Chapter 2 of this thesis is the literature survey, which mainly consists of types of batteries, historical development of battery technology in general, and the current modeling work. Recent work in circuit modeling and modeling using partial differential equations of the lithium-ion batteries is reviewed in this chapter.

Chapter 3 deals with the analysis method used in this thesis work which includes the four-main governing partial differential equations and the boundary conditions, based on which the lithium battery model is developed. It also explains another important kinetic equation which couples these PDEs and the calculation of cell voltage.

Chapter 4 explains the numerical method used for this project and the geometry setup for the finite volume method. This chapter also explains the algorithm flow used in the developed MATLAB code in order to obtain satisfactory results.
Chapter 5 presents many results. At first, comparison results for the discharging condition with available computational data are presented. After that, results for the charging condition are presented, such as the solid and electrolyte phase potential, solid and electrolyte phase concentration. A few cases are also studied as part of this work which are explained in the last section of this chapter.

Finally, Chapter 6 presents the conclusions reached because of this work and any future work which can be done in order to improve the developed model.
Chapter 2. LITERATURE SURVEY

There has been a good deal of research in the area of modeling lithium-ion batteries. In this chapter, some of this research is discussed. This chapter is divided into three sections. In the first section of this chapter, a historical review of battery technology is presented and in the second section a few important types of batteries are covered. In the third section, research work carried out in last couple of decades is presented and it is categorized into circuit modeling and modeling using partial differential equations.

2.1 Historical Review

The earliest available battery was a Voltaic cell which was introduced in the early 1800’s. This battery had alternating discs of zinc and copper separated by cardboard and used a brine solution as the electrolyte [6] as shown in Figure 6.

Later in 1836, the Voltaic cell was modified into the Daniell cell which was comprised of two electrolytes to eliminate the hydrogen bubble problem found in the Voltaic cell. In the Daniell cell, hydrogen produced by the first electrolyte was absorbed by the second electrolyte [8]. In 1866, French scientist Georges Leclanchè invented and patented the Leclanchè cell which consists of a zinc anode and manganese dioxide with carbon mixed in it as cathode, dipped in an electrolyte. As shown in Figure 7, a carbon rod is placed in the mixture of carbon and manganese dioxide and placed, in a porous pot; the porous pot along with the zinc anode is placed in an ammonium chloride solution. Daniell came up with the idea of adding carbon in manganese dioxide to improve the conductivity and absorption. The above-mentioned batteries should be considered as primary batteries and for the most part they are not rechargeable.
Secondary or rechargeable batteries have been in use for over 100 years. The first rechargeable battery developed was a lead acid battery by Planté in 1859 which is still being used widely in an improved form such as the flooded or valve regulated lead acid battery depending upon the application. After lead acid batteries, researchers started experimenting by using different materials for anodes and cathodes which lead to the invention of the vented pocket-plate nickel cadmium battery in 1900. In the 1980s nickel-metal hydride batteries were introduced which uses
hydrogen absorbed in a metal alloy as the active negative material replacing cadmium in nickel-cadmium batteries due to the toxicity of the cadmium.

As with primary and secondary battery systems, significant performance improvements have been made in last few decades, and new battery types have been developed for commercial use.

There was a surge of interest in the 1970s and 1980s in developing new rechargeable lithium batteries when, it was discovered that intercalation reactions were ideal for energy storage. Before introducing the first commercial battery, Goodenough and co-workers patented the use of a lithium-cobalt chemistry as an intercalation electrode for the first time in 1981 [10]. Recharging a battery was possible because of the work done by Goodenough et al. on the intercalation electrodes. Later, Goodenough et al. was the source for the work done by R. Yazami and Ph. Touzain in 1983 [11]. These researchers presented battery cycling tests using lithium-graphite as a negative electrode and also calculated kinetic (diffusion coefficient) and thermodynamic (enthalpy) values.

Now, coming to the modeling of batteries using differential equations, John S. Newman and Charles W. Tobias [12] developed equations describing the behavior of porous electrodes in 1962. The presented model in their work, is an extension of conventional electrochemical systems which included transport phenomena and also modeled electrode kinetic reactions. They analyzed a one dimensional porous electrode by considering concentrations to be constant and a current collector on one side with the other side open to the electrolyte solution. The effect of variation of electrolyte concentration on the behavior of a porous electrode was also studied.

The galvanostatic charge and discharge of a lithium anode/solid polymer separator/insertion cathode cell was modeled by Doyle et al. in 1993 [13] using concentrated solution theory. The model in this paper is generalized in order to include a wide range of polymeric separator materials, lithium salts, and composite insertion cathodes as compared to Newman and Tobia’s model [12]. Numerical calculations for the cathode are simplified using the superposition principle. The partial differential equations are solved simultaneously using the subroutine BAND. The Crank-Nicolson method was used to evaluate the time derivatives. The designed model includes variable physical properties and at the end, results show the charge and discharge behavior of the lithium/polymer/insertion cell.

Then, Fuller et al. [14] modeled the galvanostatic charge and discharge of a dual lithium ion insertion cell instead of a single cell. Fuller et al’s work was derived from the work of Doyle et al.
[13] with a lithium anode. In this model, the presented results are for a Li$_x$C$_6$/propylene carbonate + LiClO$_4$/Li$_y$Mn$_2$O$_4$ cell. The optimum solvent used for this model is a mixed solvent system which improves the reversible insertion process at the carbon electrode. These investigators have proposed the use of lithium-ion dual insertion systems that exhibit large theoretical specific energy densities which have small losses over extended cycling periods.

Darling et al. [15] have developed a simplified model for the isothermal, galvanostatic discharge of a porous intercalation electrode. The main goal of this paper was to explore the behavior of porous electrodes when the exchange current density was very large. It was found that the reaction-rate distribution in the electrode was non-uniform. A solution to this problem was obtained by linearizing the governing differential equations.

### 2.2 Types of Batteries

In this section, the more important types of batteries which are commonly used for energy storage are discussed.

#### 2.2.1 Lead Acid Battery

The first practical lead acid battery was introduced by Raymond Plante in 1860. Because of its various applications, the lead-acid battery is manufactured in a variety of sizes and designs, ranging from less than 1 to over 10,000 Ah. The average operating range of a Pb-acid battery is around 2.0 V [16]. In the lead acid battery, lead oxide (PbO$_2$) is used as the active material for the positive electrode whereas, metallic lead (Pb) as the active material for the negative electrode, and sulphuric acid (H$_2$SO$_4$) as the electrolyte. VRLA (valve regulated lead acid) batteries are modern lead acid battery designs which were introduced in the 1980s [17]. Due to its limited energy density and relatively low cycle life as compared to other types of batteries, the use of lead-acid batteries has now dropped to 40-45% of the battery market.

#### 2.2.2 Nickel-MH battery

Nickel-MH batteries are an extended version of the nickel-cadmium batteries which were first introduced in the early 1970s [18]. The main difference between two batteries is only in the material used for the negative electrode. While charging, Ni-MH batteries have metal hydride
(MH) as its active material for the negative electrode which later reduces to a metal alloy. Similarly, in the positive electrode, during the charging state, nickel oxyhydroxide (NiOOH) is the active material at first and then this reduces to nickel hydroxide (Ni(OH)$_2$). The electrolyte contains a higher percentage of potassium hydroxide (KOH) and it has a ‘starved electrolyte’ design which helps during the diffusion of oxygen in the negative electrode at the end of the charging cycle. Even though a Ni-MH battery has better energy density and specific energy as compared to VRLA battery, nowadays Ni-MH batteries are getting replaced by lithium-ion batteries. This is occurring because of lithium-ion battery’s higher energy density, higher specific energy, and longer cycle life. The average operating range of Ni-MH battery is around 1.35 V [19].

### 2.2.3 Lithium-Ion Battery

After Ni-MH batteries, many different batteries were designed and proposed to increase the battery performance by altering anode and cathode materials. Similarly, the first commercial battery using a lithium anode was introduced by Sony in Japan in 1991. A basic lithium-ion battery consists of a layered structure graphitic carbon negative electrode and metal oxide (either layered or tunneled structure) positive electrode which are immersed in an electrolyte and separated by a separator. Most of the time, ethylene carbonate (EC) is used as the electrolyte. There are different types of lithium ion batteries as well, these differ in the lithium oxides used for the positive electrode and thus they have slight variations in the values of battery performance. Lithium-ion batteries have advantages such as a low-self discharge rate, higher energy density, higher specific power and long cycle life. However, these batteries may cause harm if they are overcharged or over-discharged. The typical operating range for lithium-ion batteries is 3.0 - 4.2 V/cell.

Figure 8 shows the sales comparison of various types of batteries over the last 15 years. During the early 2000s, nickel-cadmium batteries were in demand because they provided high power delivery and took a short time to recharge. This is a great advantage for power tool applications. When nickel-metal hydride batteries were introduced, they were preferred because of their higher energy density for same voltage operating range as Ni-Cd batteries. Later, experiments were done on the electrode materials of lithium-ion batteries in order to increase battery performance. The power provided and the energy density went up and thus, the boom in sales of lithium-ion batteries can be observed in Figure 8.
2.3 Current Modeling Work

In the current era, different types of modeling approaches are followed. In this section two approaches, and the recent mathematical modeling carried out by researchers using those approaches will be discussed.

2.3.1 Circuit Modeling

Notten et al. [21] mainly discusses the refined equivalent network circuits for both Ni-MH and lithium-ion battery systems. Their electronic network models describe the behaviour of batteries during normal operation and during over charging & discharging in case of the aqueous battery systems. Figure 9 depicts the electronic network of a lithium-ion battery, where LiCoO$_2$ is the positive electrode and LiC$_6$ is the negative electrode. The ladder network of capacitors and resistors in Figure 9, take care of diffusion processes inside both electrodes. They have also modeled the chemical domain which is represented by two double layer capacitances ($C_{dl}$), diodes ($D_{LiC6}$, $D_{LiCoO2}$), and ohmic resistances ($R_{LiC6}$, $R_{LiCoO2}$). The complicated transportation processes occurring inside the electrolyte are mathematically derived and are represented by the complex
ladder structure of resistors and capacitors (Li$^+$ and PF$_6^-$) in the middle region. The model was tested for the constant-current-constant-voltage (CCCV) charging regime.

![Figure 9: Electronic network model of lithium-ion battery [21].](image)

Shamsi et al. [4] also proposed a circuit model which was then used to predict battery behavior. The proposed model was designed by incorporating dynamic characteristics including non-linear open circuit voltage, discharge current, and capacity. The effect of temperature was also modeled using a cooling system. The equivalent circuit model (ECM) as shown in Figure 10 was studied and developed using MATLAB in such a way that it is applicable for all lithium-ion chemistries. The components of the above ECM are a voltage source representing the open circuit voltage of the battery, one internal resistance ($R_S$), two parallel circuits with one resistor ($R_1, R_2$) and one capacitor ($C_1, C_2$) each. For the parameter estimation of the circuit as well as to determine the OCV-SOC curve. Shamsi et al. carried out two tests, a pulse discharge test (PDT) and a continuous discharge test (CDT). The PDT was carried out by varying the pulse current levels to verify its effect of on the battery parameters and CDT was carried out by continuously discharging the
battery to verify its effect on the battery capacity. The model was validated by comparing the simulated profiles with those obtained experimentally.

![Equivalent circuit model of lithium-ion battery](image)

Figure 10: Equivalent circuit model of lithium-ion battery [4].

In the thesis by H. J. Bergveld [16] a general approach to model the equivalent circuit models of rechargeable batteries, including lead-acid, nickel-metal hydride and lithium-ion batteries, is discussed. His approach was based on the theory of physical system dynamics, so three domains – electrical, chemical and thermal, were distinguished and then coupled, which allowed the transfer of energy from one domain to the other.

Based on this approach, Bergveld constructed a network model of a lithium-ion battery by considering electrical and chemical domains, similar to the CGR17500 Li-ion battery developed by Panasonic and shown in Figure 11. This battery used LiCoO$_2$ for the positive electrode and graphite LiC$_6$ as the negative electrode. The model is almost entirely built up in the chemical domain and the only electrical domain components are a self-discharge resistor (R$_\text{leak}$) and electrode resistances (R$_{\text{LiCoO}_2}$, R$_{\text{LiC}_6}$).
Figure 11: Circuit representation of the electrical and chemical domains of a CGR17500 lithium-ion battery [16].

Yazdanpour et al. [22] developed a two-dimensional model of a lithium-ion battery which is an equivalent circuit model (ECM) with a coupled electrochemical-thermal (ECT) attributes. On the basis of following voltage behavior, which is measured during the relaxation phase, the number of RC networks required for a single cell is determined. As can be seen from Figure 12, two RC circuits can fit the measured data almost as well as 3 RC circuits resulting in computational complexity and cost. Thus, the authors have used six components in their design of the ECM which is similar in design as Figure 10 and consists of two parallel circuits of RC networks (1 capacitor and 1 resistor each), one internal resistance $R_0$ and $V_{oc}$ as the cell open circuit voltage. In the later
part of the work, Yazdanpour et al. have also developed an ECT model by using algorithms available in COMSOL MULTIPHYSICS, a finite element solver. The governing equations are solved simultaneously for two separated domains i.e. negative and the positive electrode in order to get the temperature profile in the cell and potentials across two electrodes.

![Figure 12: Voltage behavior of the different RC models compared with measured data [22].](image)

### 2.3.2 Modeling Using Partial Differential Equations

Lu and Mazumder [23] developed a one-dimensional model of lithium-ion battery based on the governing partial differential equations of current, species and energy conservation. The developed model is capable of predicting the electrochemical and thermal behaviour of the battery depending upon the input material properties, as well as thermal and kinetic parameters. They used a finite volume method to discretize the non-linear governing partial differential equations and linearized the source terms by using a suitable technique. The entire numerical procedure was executed using MATLAB. Their model was validated against the experimental measurements for charging and discharging of a Li$_x$C$_6$-Li$_y$Mn$_2$O$_4$ battery and with a standard load input of hybrid electric vehicle automotive drive cycle which was simulated by current pulses of 10C for a small period of 10 seconds.
Martinez-Rosas et al. [24] present dynamic, one-dimensional model and simulation of a lithium ion battery with chemistry \( \text{LiC}6 - \text{LiMn2O4} \). The presented model is a modified form of that used by Doyle et al. [13]. Martinez-Rosas et al. modify the boundary conditions to achieve better convergence of the solver. Analyzing the internal behavior of the battery was also included in this research. Discretization of the governing PDEs was performed by using a Taylor expansion. The resulting system of differential algebraic equations were solved by using the ode15i solver available in MATLAB. The method of lines (MOL) approach was used for solving the PDEs which proceeded by first discretizing the spatial derivatives and leaving the time variable continuous. The results were then validated against other published results and were proven to be more accurate. After validation, Martinez-Rosas et al. have presented a few case studies which were carried out by changing the design parameters, operating conditions of the battery, battery arrangement in order to achieve improved performance.

Golmon et al. [25] has presented a multi-scale finite element approach for lithium-polymer batteries to study the electrochemical, as well as mechanical interactions, by considering both macro and micro scales. For the macro-scale model, transport processes and deformations in the battery are modeled; and for the micro scale, a single active particle in the cathode is modeled. The macro-scale model presented in this work, is an extended version of Doyle and Newman’s [13] electrochemical porous electrode theory. While, at the micro-scale level they have accounted for differences in lithium-ion flux into the particles using the Butler–Volmer equation. The governing equations were solved in time by an implicit Euler backwards scheme and in space by a standard Galerkin finite element approach. As in the macro-scale, transport processes, the deformations in the battery are modeled in a one dimensional, Cartesian coordinate system while, single active particles are modeled by assuming a spherical configuration. Effects on the electrochemical-mechanical behavior of the battery is studied by varying important design parameters such as, cathode particle radius, electrochemical properties, current density and porosity of the electrodes. Some of Golmon et al.’s results are presented in Figure 13. This figure presents the battery potential plotted as a function of utilization of active material, which is the ratio of the actual over the maximum lithium concentration that can be inserted into active cathode material.

The effect of cathode particle size on battery potential was carried out by keeping the volume fraction, \( \epsilon \), constant at 0.3, and the particle size is varied from 1\( \mu \)m to 20\( \mu \)m and the results show a decrease in battery performance as shown in Figure 13-a. And Figure 13-b shows the effect of
current densities on battery potential, higher densities causes lower utilization of active material which results in lower battery capacity.

Figure 13: Effects on the potential of a lithium-polymer battery by varying: (a) cathode particle size (b) current densities [25].

Smith et al. [26] introduced a generalized method to numerically generate a control oriented 1D electrochemical model of a lithium ion battery. This model is derived from the electrochemical kinetics, conservation of species in the solid and liquid phase and conservation of current in the battery. The solid electrodes are modeled on the basis of porous electrode theory as in Doyle et al. [13]. The electrolyte diffusion and ionic conductivity are calculated by using Bruggeman’s relations. The one-dimensional domain is discretized into approximately 70 control volumes and each of the four governing PDEs are simultaneously solved for the x direction. The authors have used a model order reduction method to reduce the computational complexity thus, it is divided into sub models as: electrode submodel, electrolyte submodel and current/voltage submodel. This model was tested against a higher order nonlinear CFD model of a 6 Ah HEV cell with constant current profiles varying up to 50C between the discharge, charge, and rest cycles as shown in Figure 14.
Du et al. [27] introduced a surrogate modeling framework to plot the effect of design-related parameters on the performance of a lithium-ion cell. Surrogate based tools (such as kriging, polynomial response surface) were used to construct and validate models capable of predicting the specific energy and specific power. They studied the effect of cycling rate, particle size and transport properties on the specific energy and power of the cell. The focus of this study was on the positive electrode (cathode). After the simulations, global sensitivity analysis was also performed on the surrogate models to compare the relative important design variables and to identify and eliminate any unnecessary variables. Simulated results showed that available energy decreases with faster cycling rate and large particle size as shown in Figure 15.
Gu et al. [28] came up with a two-dimensional model to simulate the discharging of a lithium/thionyl chloride primary battery. This model incorporates the transport of species, current conservation, and electrode porosity variations as well as the electrolyte flow. Numerically it determined the electrolyte flow occurring inside the battery. Numerical simulations were performed using a finite volume method.

Ye et al. [29] designed a mathematical model by coupling electronic conduction, mass transfer, energy balance, and electrochemical mechanisms of a battery. Lithium ion diffusivity and chemical reaction rate in the cathode material are computed for different current charge and discharge rates for different operating temperature conditions. The computations for this model were performed using the finite element commercial software COMSOL MULTIPHYSICS. As lithium-ion diffusivity increases with operating temperature, the lithium-ion concentration gradient decreases which can be seen in Figure 16. The simulated results showed that the lithium ion concentration gradient in both liquid and solid phase are significantly affected by temperature variation; which per the authors, results in capacity losses and power loss during low temperatures. In the later part of the work, they studied reversible and irreversible heat generation during charging and discharging processes and suggested that a proper cooling system should be added to keep the battery temperature within the safety range.

Figure 15: Effect of cycling rate and cathode particle size on the specific energy of a lithium-ion cell [27].
Ji et al. [30] designed an electrochemical-thermal (ECT) coupled model, by considering concentration and temperature-dependent transport and kinetic properties. Their work studies lithium-ion cell behaviors at low temperatures by a combined experimental and modeling approach. To experimentally discover the electrochemical-thermal performance of the battery, 18,650 cylindrical cells of 2.2 Ah were used. Battery charging was achieved at a constant current of 0.7C followed by a constant voltage of 4.2 V. An ECT coupled model is developed on the basis of the four governing conservation equations mentioned in Wang et al. Calculations for given parameters and boundary conditions were done by using algorithms available in the commercial software ‘AutoLion’. Ji et al. have produced the results for three different situations, in the first situation, the C-rate was varied at room temperature to study its effects, in the second situation the C-rate was held constant and the temperature was varied, lastly the effects of C-rate on the performance of the battery at subzero temperatures was studied. To verify the results produced by this model, experiments were carried out for several days. The temperature range was varied from -20 °C to 45 °C and the discharge rates varied from 1C rate to 4.6C. Figure 17 depicts that the validation of the model by presenting the experimental data and model simulations to demonstrate the effect of temperature on the battery voltage for a discharge with 1C rate. It can be seen in the
above figure, as the temperature decreases, discharge capacity as well as battery voltage decreases. These results helped in optimizing the design of a lithium-ion cell operating at low temperatures.

Figure 17: Effect of temperature on the battery voltage for a discharge with a 1C rate [30].

Fang [31] designed an electrochemical-thermal coupled model to study lithium deposition on the negative electrodes while charging at subzero temperatures. The simulated results show that the lithium deposition on the negative electrode can be reduced either by reducing the negative electrode particle size or by improving the lithium diffusion coefficient. Fang’s model can predict the performance of individual electrodes of lithium-ion cells under hybrid electric vehicle conditions for different temperatures. In this work, the governing differential equations, except the solid phase concentration equation were solved by using the commercial software StarCD or FLUENT. The solid phase concentration was solved by discretizing the system of ordinary differential equations with respect to time and expressing the solution in explicit form. The solid phase concentration ($C_{se}$) is calculated explicitly using the previous time step values and the current value of the current density. In the later part of the Fang’s work, an aging mechanism was implemented into each electrode to study lithium-ion battery degradation during accelerated aging tests.
Subramanian et al. [32] presented a model of a lithium ion battery which is a mathematical reformulation of the physics-based battery models. This was done to improve the computational efficiency. The authors have presented an analytical approach which is similar to the Galerkin method. Each governing equation was solved separately by keeping the non-linear part of the equation on the right-hand side of the equation and linear part on left side. At first, a reduced 1D model was chosen for the reformulation with volume-averaged approximation for the solid-phase equations including the effects of porous electrodes.

Gu and Wang [33] developed a multi-dimensional, coupled, electrochemical and thermal (ECT) model for lithium-ion batteries. The purpose behind designing this ECT model was to demonstrate the need for a thermal and electrochemical coupled model to accurately predict behavior of the battery. The model can predict cell internal temperature distributions, as well as the average cell temperature evolution with time.

Kim et al. [34] demonstrated the thermal behavior of a lithium-ion battery during a charge cycle. In this work, the proposed two-dimensional model can calculate current density distributions and open circuit potential individually for each electrode only during a charging process. The solutions for the governing partial differential equations were obtained by using a finite element method. They validated the model by comparing the results from the simulations to experimental results for charging rates of 1C, 3C and 5C. Experiments were conducted using a 14.6Ah lithium-ion battery fabricated by LG Chemicals, at room temperature, 25°C. The thermal modeling was done by considering the two-dimensional transient equation of heat conduction and the temperature distribution presented shows that temperature near the current collector in the positive electrode is lower than on the negative electrode side.

Apart from above the mentioned models, Srinivasan and Wang [35] have developed a model to study the thermal behavior of the lithium-ion cells. The developed model includes the temperature dependence of various kinetic and mass-transfer properties and the reversible and irreversible processes. Using this model, the thermal and electrical energy and the active material utilization at each electrode were calculated. Also, the effects of temperature changes on the electrochemistry were studied.

Ramos [36] presented a complete mathematical model of lithium-ion batteries based on a macro-homogeneous approach developed by Neumann. The paper mainly focuses on the form of the Butler-Volmer equation. The Butler-Volmer kinetic equation simulates the force that drives
the lithium ions in and out of the solid particles in the battery electrodes. According to author, two common mistakes are found in the literature regarding a sign used in the boundary conditions and the use of the transfer coefficient which produce situations where the solution can turn out to be non-physical. He has proposed a corrected form of the equation for calculating the effective diffusion coefficient of lithium ions during charge conservation in electrolyte phase as:

\[ k_{d}^{\text{eff}} = \frac{\mu_{T}k_{e}^{\text{eff}}}{F} (2t_{+} - 1) \left( 1 + \frac{\partial\ln f}{\partial nC_{e}} \right) \] (2.1)

Modeling of secondary lithium batteries is reviewed in the paper presented by Botte et al. [37]. The models available to simulate the electrochemical and thermal behavior of a secondary lithium battery are discussed. They have proposed different methods of solving the governing partial differential equations including the finite difference method, the finite element method and the finite volume method. This paper gives a brief review of the mathematical techniques that have been used for solving the governing differential equations.

Gomadam et al. [38] have reviewed the research work done in the field of lithium-ion and nickel battery systems over the years at the University of South Carolina. In this work, various mathematical models which simulated the behavior of single electrodes, fuel cells, and batteries are presented. These models were simulated and tested for a variety of operating conditions, such as constant current discharge, pulse discharging, and cyclic voltammetry. Gomadam et al. made a few suggestions to extend previously developed models and to obtain better computational results.
Chapter 3. ANALYSIS

In this chapter, the details of the mathematical model used in this thesis to predict the operating performance of a lithium-ion battery are discussed. This is a one-dimensional model that is based on four partial differential equations that represent the behavior of the battery. In addition, an equation that represents the charge exchange between the solid particles and the liquid electrolyte, and an equation that contains the chemical potential of the active species are used. These six equations can be called the governing equations for the lithium-ion battery model presented in this thesis. First, the four governing differential equations will be presented, then the equation governing charge exchange between the solid particles and the liquid electrolyte will be discussed, and next the equation that contains the chemical potential of the active species is presented. Lastly, the equations used to determine the state of charge (SOC) and the cell electrical potential are presented.

3.1 Governing Equations

The governing differential equations for battery dynamics are derived from fundamental conservation laws. There is an insertion/de-insertion phenomenon occurring at the electrodes as the charge and discharge processes occur [24]. To explain these phenomena mathematically, the equations that govern mass conservation of lithium in the solid phases, mass conservation of lithium-ions in the electrolyte phase, current conservation in the solid phase and current conservation in the electrolyte phase need to be utilized.
3.1.1 Conservation of Species in Solid Phase

The solid electrodes are modeled based on the porous electrode theory [18] which states that the solid phase particles are assumed to be uniformly distributed throughout the negative and positive electrodes and that electrolyte permeates between these particles.

Per this theory, the lithium is considered to exist in two disjoint states: the solid phase in the electrode particles and the liquid phase in the electrolyte. In the model being used in this thesis work, the solid and electrolyte phases are treated as superimposed continua without regard to microstructure [12, 39].

The Cartesian electrochemical model depends upon the concentration of lithium-ions at the spherical particle’s surface. Thus, obtaining the lithium-ion concentration at the particle surfaces is important. This is mathematically represented as

\[ C_s(x, t) = c_s(x, r, t) \]  

where, \( x \) is the particle’s position relative to the beginning of the negative electrode (see Figure 3) and \( R \) is the radii of the solid particles. Only a single size of the solid particles in the negative electrode and a single size in the positive electrode are allowed in the model. Equation 3.1 means the concentration of lithium ions at a position \( x \) in the electrode is taken to be the concentration of the lithium ions at the surface of a representative spherical particle at that \( x \)-position. This means two coordinate systems need to be simulated simultaneously, a one dimensional Cartesian system and a one dimensional spherical system. The one-dimensional spherical system is required to get the solid surface lithium-ion concentration that can be delivered to the Cartesian equations. To obtain the lithium ion particle surface concentration, the concentration of lithium ions throughout the particle must be obtained. This is done by using the equation

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

where, \( C \) is the lithium concentration and subscript \( s \) represents the solid phase. The quantity \( r \) is the radial location in the spherical particle. Equation 3.2 is solved separately for the negative and the positive electrodes, and it does not have to be solved in the separator region.

The boundary condition for the solid spherical particles are

\[ \frac{\partial C_s}{\partial r} \bigg|_{r=r_i} = 0 \]  

(3.3)
and

\[-D_s \frac{\partial C_s}{\partial r}\bigg|_{r=r_0} = \frac{j_{\text{IL}}}{a_s F}\]  \hspace{1cm} (3.4)

where \(D_s\) is the solid phase diffusion coefficient, \(j_{\text{IL}}\) is the pore wall flux across the interface, and \(a_s\) is the active interfacial surface area.

\[a_s = \frac{3 \varepsilon_s}{R_s} = \frac{3}{R_s} (1 - \varepsilon_e - \varepsilon_p - \varepsilon_f)\]  \hspace{1cm} (3.5)

The active interfacial surface area is the area to volume ratio in the active spherical particles at a location \(x\).

Equation (3.3) represents the symmetry at the center of the active particle; whereas Equation (3.4) represents a flux balance at the solid particle surface.

### 3.1.2 Conservation of Species in Electrolyte Phase

The governing partial differential equation for conservation of species in the electrolyte phase is

\[\frac{\partial}{\partial t} (\varepsilon_e C_e) = \frac{\partial}{\partial x} \left(D_{e}^{\text{eff}} \nabla C_e\right) + \frac{1 - t_+}{F} j_{\text{IL}}\]  \hspace{1cm} (3.6)

where, \(C_e\) is the lithium concentration in the electrolyte phase, \(t_+\) is the transference number, \(\varepsilon_e\) is the electrolyte phase volume fraction, and \(D_{e}^{\text{eff}}\) is the effective lithium-ion diffusion coefficient in the electrolyte. The first term in Equation (3.6) is the unsteady term, the second term stands for the diffusion of lithium-ions in the electrolyte phase, and third term accounts for lithium-ions coming out from the solid phase and going into the electrolyte phase.

The transference number \(t_+\), electrolyte phase volume fraction \(\varepsilon_e\) and effective diffusion coefficient of lithium ions \(D_{e}^{\text{eff}}\) are assumed to be constant within the negative electrode, separator region, and positive electrode; but can have different values in these three regions. The effective diffusion coefficient is calculated using Bruggeman’s relation

\[D_{e}^{\text{eff}} = \varepsilon_e p D_e\]  \hspace{1cm} (3.7)

Equation (3.6) is solved for the entire battery domain (see Figure 3) with the zero flux boundary conditions at the current collectors.

\[\frac{\partial C_e}{\partial x}\bigg|_{x=0} = \frac{\partial C_e}{\partial x}\bigg|_{x=L} = 0\]  \hspace{1cm} (3.8)
3.1.3 Conservation of Charge in Solid Phase

Conservation of charge in the solid phase is described by the current conservation equation

\[
\frac{\partial}{\partial x} (\sigma_{\text{eff}} \nabla \varphi_s) = j_{li} \tag{3.9}
\]

where, \( \varphi \) is the electrical potential and subscript \( s \) represents the solid phase, \( \sigma_{\text{eff}} \) is the effective electrical conductivity of the electrodes, and \( j_{Li} \) is the transfer current. The electrical conductivity \( \sigma \) is assumed to be constant, but can be different values, in each electrode.

![Cartesian grid setup for charge conservation in solid phase.](image)

As shown in Figure 18, this differential equation, Equation 3.9 is solved separately for the negative and positive electrodes and not at all for the separator region. The boundary conditions at the two current collectors is proportional to the applied current density.

\[
-\sigma_{\text{eff}} \frac{\partial \varphi_s}{\partial x} \bigg|_{x=0} = \sigma_{\text{eff}}^+ \frac{\partial \varphi_s}{\partial x} \bigg|_{x=L} = \frac{I}{A} \tag{3.10}
\]

where, \( A \) is the electrode plate area and \( I \) is the applied current at the current collectors. If the applied current is positive, it signifies that the battery is discharging; and if the applied current is negative the battery is getting charged. The boundary conditions at the electrode-electrolyte interfaces are the no-current flow boundary conditions.

\[
\frac{\partial \varphi_s}{\partial x} \bigg|_{x=L_{neg}} = \frac{\partial \varphi_s}{\partial x} \bigg|_{x=L_{neg}+L_{pos}} = 0 \tag{3.11}
\]
3.1.4 Conservation of Charge in Electrolyte Phase

The governing partial differential equation for conservation of charge in the electrolyte phase is given by

$$\frac{\partial}{\partial x} \left( \kappa_e \frac{\partial \varphi}{\partial x} \right) + \frac{\partial}{\partial x} \left( \kappa_d \frac{\partial \ln C_e}{\partial x} \right) = -j_i \tag{3.12}$$

where, $\varphi$ is the electrical potential and the subscript $e$ represents the electrolyte phase, $C_e$ stands for the electrolyte phase lithium ion concentration, $\kappa^e$ is the effective ionic conductivity, and $\kappa_d^e$ is the effective diffusional coefficient. The first term in Equation (3.12) takes care of the drift of the lithium ions due to electrical conductivity, the second term takes care of the diffusion of the lithium ions due to the concentration gradient and the term on the right-hand side of this equation is the movement of lithium ions from the solid phase to the electrolyte phase.

The effective diffusional coefficient is calculated by using

$$\kappa_d^e = \frac{2RT\kappa^e}{F} (t_+ - 1) \left( 1 + \frac{\partial \ln \kappa}{\partial \ln C_e} \right) \tag{3.13}$$

and the effective ionic conductivity ($\kappa^e$) is calculated using Bruggeman’s relation,

$$\kappa^e = \kappa e^p_e \tag{3.14}$$

where electrolyte phase ionic conductivity, which is due to the drift of ions, is given by

$$\kappa = 15.8e^{-4}C_e\exp \left( 0.85 \left( \frac{C_e}{1000} \right)^{1.4} \right) \tag{3.15}$$

In Equation (3.15), the concentration needs to be inserted in units of moles/m$^3$ and the ionic conductivity is produced in S/m.

Equation (3.12) is solved for the entire cell domain that is in the electrolyte located in the negative electrode, in the electrolyte located in the separator, and the electrolyte located in the positive electrode. As the current collectors provide an impermeable wall to the electrolyte, zero flux boundary conditions are applied at these locations,

$$\left. \frac{\partial \varphi_e}{\partial x} \right|_{x=0} = \left. \frac{\partial \varphi_e}{\partial x} \right|_{x=L} = 0 \tag{3.16}$$
3.2 Butler-Volmer Kinetic Equation

The above discussed governing partial differential equations for $C_s, C_e, \phi_s & \phi_e$ are coupled to each other by the Butler-Volmer kinetic equation which is given by

$$j_{Li} = a_s i_o \left[ \exp \left( \frac{\alpha_a F}{RT} \left( \eta - \frac{R_{SEI}}{a_s} j_{Li} \right) \right) - \exp \left( - \frac{\alpha_e F}{RT} \left( \eta - \frac{R_{SEI}}{a_e} j_{Li} \right) \right) \right] \tag{3.17}$$

where $\eta$ is the overpotential, $i_o$ is the exchange current density and $R_{SEI}$ is the resistance due to film formation at the solid-electrolyte interface. The film formation resistance is taken as zero in this work.

The Butler Volmer kinetic equation primarily takes care of electro-chemical issues at the solid particle-electrolyte interface. An important parameter in this equation is overpotential $\eta$. This quantity accounts for the difference in the electrical potential between the solid and the electrolyte at a given x location in the battery cell and for the equilibrium potential of the solid at a given x location. The exponential terms in Equation (3.17) are non-linear and the overpotential is in both of these exponential terms. Figure 19 shows the transfer current as a function of overpotential. Very quickly the transfer current becomes a large negative or positive value as the magnitude of the overpotential increases.

The amount of current required for a lithium ion to travel from the active particle to the electrolyte surrounding it and again to travel through the electrolyte medium back to the active particle at positive electrode (during discharging) is equal to the transfer current ($j_{Li}$). Non-linearity in the transfer current mainly is due to the overpotential and values follow an exponential pattern as it can be seen in curve in Figure 19 which is for discharging condition. Value of overpotential should be closer to zero, as soon as it is increased even by a small factor the transfer current value changes exponentially and all calculations go out of range. During charging condition, the curve shown below will change axes. During charging/discharging condition, overpotential flips sign thus, the sign on the transfer current also changes which results in change in the flow direction of the lithium ions.

The exchange current density, $i_o$, in Equation (3.17), depends on the electrolyte concentration, $C_e$, and the difference between the maximum possible solid phase concentration, $C_{s, max}$, and the surface concentration, $C_{s,surface}$. The exchange current density is as

$$i_o = k_o C_e^{\alpha_a} (C_{s,max} - C_{s,surface})^{\alpha_a} C_{s,surface}^{\alpha_e} \tag{3.18}$$
where, $k_o$ is a kinetic rate constant, $\alpha_a$ and $\alpha_c$ are the anodic and cathodic transfer coefficients, and $C_{s,surface}$ is the concentration of lithium ions at the particle surface calculated using the spherical Equations (3.2), (3.3) and (3.4).

![Graph](image)

**Figure 19:** Effect of overpotential on transfer current.

### 3.3 Equilibrium Cell Potential

Overpotential ($\eta$) can be defined as the difference between the solid and electrolyte phase potential and the equilibrium potential ($U$) and is written as

$$\eta = \varphi_s - \varphi_e - U$$  \hspace{1cm} (3.19)

The solid potential used here comes from Equation (3.9) and the electrolyte potential comes from Equation (3.12). The equilibrium potential is evaluated as a function of the solid phase concentration at the particle surface. The equilibrium potential is the potential of the solid material at a particular $x$-location when no current is flowing inside the battery. The chemical potential of the solid particles is buried within the equilibrium potential.

Empirical relations are used to determine the equilibrium potential of a solid based on the concentration of lithium ions within the solid. A separate empirical correlation is obtained from
the literature for the negative and positive electrodes. The relation for the equilibrium potential for the negative electrode used in this work is [26]

\[
U_n = 8.0029 + 5.0647x - 12.578x^{\frac{1}{2}} - \frac{8.6322e - 4}{x} + (2.1765e - 5)x^{\frac{3}{2}}
- 0.46016\exp(15(0.06 - x)) - 0.55364\exp(-2.4326(x - 0.92))
\]  

(3.20)

and that for the positive electrode is [26]:

\[
U_p = 85.681y^6 - 357.7y^5 + 613.89y^4 - 555.65y^3 + 281.06y^2 - 76.648y
- 0.30987\exp(5.657y^{115}) + 13.1983
\]  

(3.21)

The \( x \) and \( y \) in these two equations are the stoichiometric coefficients, which are the ratios of the surface solid phase concentration to the maximum possible lithium-ion concentration in the solid phase,

\[
x = \frac{C_{s,e-}}{C_{s, max}}
\]

(3.22)

\[
y = \frac{C_{s,e+}}{C_{s, max}}
\]

Note that both electrodes are made of different materials and thus have different maximum possible concentrations of lithium ions.

### 3.4 State of Charge and Cell Potential

A couple of output parameters that should be determined after the governing equations have been solved are the state of change and the cell potential. The state of charge can be defined as the percentage of the amount of useful charge remaining inside a battery. This parameter indicates the remaining current producing capacity of the battery. The cell potential is the voltage that is produced between the two electrodes of the cell. This is the voltage available to drive current from the battery to the load. This quantity will drop as the cell is discharged.

The state of charge is a time dependent parameter and there are various mathematical methods available to calculate it. One of the methods is to calculate the average solid phase concentration and the stochiometric coefficients \( x \) and \( y \) (depending upon the electrode) at the 0% charge condition and the 100% charge condition. For the negative electrode, the SOC can be written as
\[ \text{SOC}(t) = \left( \frac{C_{s,\text{avg}}}{C_{s,\text{max}}} \right) \left( \frac{x_{100\%} - x_{0\%}}{x_{100\%} - x_{0\%}} \right) \]  \tag{3.23}

The average solid phase concentration, \( C_{s,\text{avg}} \), in this equation can be calculated by integrating the lithium-ion concentrations in the solid phase over the solid volume and dividing by the volume.

Sometimes the cell voltage distributions are plotted as a function of the depth of discharge, a term which is used to describe how deeply the battery is discharged and it can be calculated as

\[ \text{DOD} = 1 - \text{SOC}(t) \]  \tag{3.24}

The cell potential is defined as the difference between the potential at the positive current collector minus the electrical potential at the negative current collector. It is given by

\[ V(t) = \varphi_s(L,t) - \varphi_s(0,t) - \frac{R_f}{A} I(t) \]  \tag{3.25}

The solid potentials in this equation are obtained from Equation (3.9). The quantity \( R_f \) is a contact resistance between the electrode and the current collector for a unit area surface. For a good battery, this is a low number and is sometime ignored in the analysis. The area, \( A \), in Equation (3.25) is the electrode area and \( I \) is the applied current in amps.
Chapter 4. DISCRETIZATION TECHNIQUE

The governing partial differential equations discussed in the last chapter are discretized by the control-volume-based finite volume method mentioned in Patankar [40]. The resulting set of algebraic equations are iteratively solved by using a numerical solver. In this chapter, the numerical solution routine and the methodology of the computer program are discussed. First, the finite volume method will be looked at.

4.1 Finite Volume Method

For this work, Finite volume method was used to discretize the partial differential equations. The finite volume method is a discretization of the governing equation in an integral form. The net flux through the control volume boundary is the sum of integrals over the control volume faces in one dimension.

The total solution domain is divided into a finite number of small sub-domains which are called as control volumes. A typical internal control volume setup is shown in Figure 20. The grid defines boundaries of the control volumes while the computational grid points lie at the center of the control volume.

![Figure 20: Internal control volumes.](image-url)
For one-dimensional problems, the control volumes are subintervals of the problem domain and the grid points are at the mid-points of the sub-domains. These sub-domains for an entire cell can be seen in Figure 21. Numbering of grid points and edges (faces) of the control volumes is done such that the face numbering precedes grid point numbering.

Two geometries: Cartesian co-ordinate system and Spherical co-ordinate system are setup to solve the PDEs. The potentials in the solid phase (Equation 3.9) and electrolyte phase (Equation 3.11) are calculated at each grid point in the Cartesian co-ordinate system. Also, the concentration in electrolyte phase is calculated at each control volume grid point in the Figure 21.

Left portion of the control volume grid (denoted in red color in this case) is the negative electrode and middle portion is separator and rightmost portion of the grid (denoted in blue color in this case) is the positive electrode.

![Figure 21: Control volume grid for Cartesian system.](image)

The spherical co-ordinate system is a sub-grid to calculate surface concentration of spherical particle at the macroscopic level. This sub-grid is assumed to be located at all the control volume grid points. The innermost spherical grid point in the spherical system is assumed to be made up of zero volume and the distance of outermost point at the surface from the center is the radius of the active spherical particle. Figure 22 shows the Grid point setup in Spherical coordinate system.
4.1.1 Calculation of Coefficients of the Discretized System of Equations

Figure 23 represents the grid system used in this work. In this figure, the centroid of control volume, point ‘p’ is the point of interest at which the partial differential equation is discretized. The neighboring grid point in the west direction is denoted as point ‘W’, and grid point in the east direction is denoted as point ‘E’. Grid point spacing is given by ‘δx’ and the spacing between faces is given by ‘ΔX’.

For example, solution for a steady one dimensional equation:

\[
\frac{d}{dx} \left( k \frac{d\varphi}{dx} \right) + S = 0
\]  

(4.1)

results in a tridiagonal system of equations in 1D and can be written as –

\[
a_p \varphi_p = b_E \varphi_E + c_W \varphi_W + d
\]  

(4.2)

The coefficients \(a_e, a_w, a_p\) and \(d\) are calculated by:
\[ a_E = \frac{k_E}{\delta x_E} \]  \hspace{1cm} (4.2a)  
\[ a_W = \frac{k_W}{\delta x_W} \]  \hspace{1cm} (4.2b)  
\[ a_p = a_E + a_W - S_p \Delta x \]  \hspace{1cm} (4.2c)  
\[ d = S_c \Delta x \]  \hspace{1cm} (4.2d)

These calculated coefficients are then given as input to the TDMA solver.

Figure 23: Grid point setup in Cartesian coordinate system for one dimensional problem.

4.2 Thomas Algorithm

The Thomas algorithm is also known as Tri-Diagonal Matrix Algorithm (TDMA); it is a simplified form of Gaussian elimination that can be used to solve tridiagonal system of equations [40, 41]. Finite volume discretization gives a tridiagonal equation system in one-dimension. Tridiagonal system refers to the fact that when the matrix of the coefficients of these equations are written, all the non-zero coefficients align themselves among the diagonal and two off diagonals.
of the matrix as shown in Eq. (4.1). The TDMA is based on Gauss elimination technique and can be performed in two simple steps: forward elimination and backward substitution step.

We can re-write the Eqn. 4.2 as:

\[ a_i \varphi_i = b_i \varphi_{i+1} + c_i \varphi_{i-1} + d_i \]  \hspace{1cm} (4.3)

where, \[ a_i = a_p, \quad b_i = a_e, \quad c_i = a_w \] \hspace{1cm} (4.3a)

Let us suppose, there are ‘n’ number of grid points in the problem domain. So, the equation 4.3 is solved from \( i = 2 \) to \( i = n - 1 \), \( i = 1; i = n \) are the boundary grid points. To account for the special form of the boundary conditions, the coefficients at the grid points are set equal to zero, \[ a_w(1) = 0, \quad a_e(n) = 0 \]

After writing the Equation (4.2) in matrix form, gauss elimination technique should be used in order to compute the coefficients ‘\( P_i \)’ and ‘\( Q_i \)’. In the forward substitution process, we obtain the following relations:

\[ \varphi_{i-1} = P_{i-1} \varphi_i + Q_{i-1} \] \hspace{1cm} (4.4)

\[ \varphi_i = P_i \varphi_{i+1} + Q_i \] \hspace{1cm} (4.5)

By substituting the Equation (4.4) in (4.3) and rearranging the equations we obtain the following equations for ‘\( P_i \)’ and ‘\( Q_i \)’.

\[ P_i = \frac{b_i}{a_i - c_i \ast P_{i-1}} \] \hspace{1cm} (4.6)

\[ Q_i = \frac{d_i + c_i \ast Q_{i-1}}{a_i - c_i \ast P_{i-1}} \] \hspace{1cm} (4.7)

Solution for the equation system (\( \varphi \)) can be computed using backward substitution method from \( i = n - 1 \) to \( i = 1 \) by using Equation (4.5),

\[ \varphi_i = P_i + Q_i \varphi_{i+1} \] \hspace{1cm} (4.8)

while, \[ \varphi_n = Q_n \]
4.3 Source Term Linearization

All the governing differential equations discussed in chapter 3 can be generalized in the form of a diffusion equation:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot (\Gamma \nabla \phi) + S \tag{4.9}$$

where, ‘$\phi$’ represents a general conservable quantity, ‘$\Gamma$’ is diffusion coefficient related to $\phi$ and ‘$S$’ is the source term.

Source term ‘$S$’ in Equation (4.9) is often a non-linear function of the dependent variable ‘$\phi$’. So, the source term linearization procedure was carried out for conservation of charge in solid and electrolyte phase and conservation of species in electrolyte phase.

For these three PDEs, it is necessary to linearize the source term by using Equation (4.10):

$$S = S_c + S_p \phi_p \tag{4.10}$$

where, ‘$S_p$’ is the derivative of source term with respect to the dependent variable in each equation.

In case of conservation of charge in solid phase, the source term equals only the transfer current ($J_{li}$) which is given by butler-volmer kinetic equation (3.16) and it is dependent on solid phase potential ($\phi_s$) and electrolyte phase potential ($\phi_e$).

$$S_p = -\frac{dS}{d\phi_s} \tag{4.11}$$

While, the source term in conservation of charge in electrolyte phase, consists of transfer current ($J_{li}$) and the difference of logarithmic electrolyte concentration multiplied by effective diffusional conductivity ($\kappa_{D_{\text{eff}}}$).

$$S_p = \frac{dS}{d\phi_e} \tag{4.12}$$

Source term in conservation of species in electrolyte phase i.e. Equation (3.6), was linearized as,

$$S_p = \frac{dS}{dC_e} \tag{4.13}$$
### 4.4 Methodology

The flow chart shows how equations are used to design the one-dimensional model of lithium ion battery. Figure 24 shows there are seven steps in this program. At first the values of various parameters for Lithium-ion battery from Table (1) [26] are given as input to the program. Then, all the arrays of variables are initialized and few initial values of the important parameters that require an initial guess to start iterating are guessed. The next step includes setting up the control volume grid, which mainly consists the calculations of all the geometric parameters such as distance between the computational grid points, control volumes in Cartesian as well as spherical co-ordinate system.

Calculation of equilibrium potential (U) and transfer current \( j_{Li} \) are two intermediate steps before obtaining the discretized solution of the solid phase potential equation. In solid phase potential routine, the solution for the discretized system is obtained by using TDMA solver at each computational grid point in the negative electrode and then in the positive electrode separately. A convergence loop is set in this routine in order to obtain the converged values of the solid potentials and the overpotential (\( \eta \)). This loop was implemented to obtain the converged values. As many parameters are influenced by transfer current \( j_{Li} \) which are sensitive to overpotential variations, so with the help of convergence loop we try to get some reasonable overpotential values.

Next step is to solve the remaining three governing partial differential equations. Important step in the program is to discretize each partial differential equation individually and to obtain the solution for the discretized system using TDMA solver at each computational grid point in the control volume grid (see Figure 21). Conductivity and diffusion parameters are calculated in each routine depending on the use of the properties. All calculations are performed with an assumption that the battery is at 100% state of charge.

After solving the equations, values of the first iteration are checked for convergence. It is done by calculating the fractional differences between values obtained in that particular iteration and the previous iteration. If fractional change for each governing equation parameter \( (\varphi_s, \varphi_e, C_e & C_s) \) is smaller than the convergence factor which is equal to 1E-07, then the solution is converged, otherwise, the iteration loop will run continuously until the convergence is achieved. After obtaining the converged solution, the program will go the next time step. For each time step, once the solution reaches convergence, state of charge of the battery and the cell voltage is calculated.
and then, the results are post-processed to extract the necessary quantities and the distributions of these quantities are plotted against the position along one dimension and time.

Figure 24: Governing differential equation solution flow chart.
Table 1: Model parameters for a 6 Ah lithium-ion battery simulated in this work.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Negative electrode</th>
<th>Separator</th>
<th>Positive electrode</th>
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<tbody>
<tr>
<td><strong>Design specifications:</strong></td>
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<tr>
<td>Thickness (L) in μm</td>
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<td>Particle Radius (Rₚ) in μm</td>
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<td>Polymer phase volume fraction (εₚ)</td>
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<td>Conductive filler volume fraction (ε₇)</td>
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<td><strong>Li-ion concentrations:</strong></td>
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<td>Electrolyte concentration (Cₑ) in (mol/m³)</td>
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Chapter 5. RESULTS

In this chapter, a number of results from the MATLAB program developed as part of this thesis work, based on the mathematical model presented in Chapter 3 and the numerical routine presented in Chapter 4, are presented. These results include comparisons to published results and a number of other results that demonstrate the capabilities of this computer program. Results for both battery charging and discharging situations are presented as a function of time or DOD. DOD and time are related through Equations (3.24), (3.23) and the equations to find the solid particle concentrations. For parameters that depend on position, the computer program is capable of showing this dependence as well. All presented results are for a single cell, lithium-ion battery.

5.1 Program Validation Results for Discharge Condition

In this section, the results obtained by using the developed MATLAB program are compared against those published by Smith et al. [26] for different battery discharge rates. Since the battery considered is a 6 A-h, lithium-ion battery, the current flow at a discharge rate of 1C is 6 amps. These calculations were carried out for as long as the simulation indicated the battery had more current to deliver. The end of the simulation occurred when the solid electrode reached its saturation limit, i.e. it reached the maximum lithium-ion concentration that could be held within the solid of the positive electrode.

5.1.1 Cell Voltage

The voltages presented in this sub-section are those given by Equation (3.25). This is the voltage that is delivered to a load attached to the battery; and thus, shows how the battery output decays with DOD. While the relationships are not linear, the DOD can be used as a proxy for time.
For the first case, the battery is discharged at 1C until the battery is completely discharged, i.e. for a total duration of 3677 seconds. Values for electrode thickness are obtained from Table 1. The Simulated voltage profile for the 1C discharge rate is shown in Figure 25 where the orange line is the results from this work and the blue line is the results from Smith et al. [26].

At 100% charge, or zero DOD, the cell voltage from this work is 3.86 V and that from Smith et al. is only slightly less. As the cell is allowed to discharge with time or DOD, the cell voltage drops slowly until the DOD reaches about 0.85. At this point the voltage drops suddenly. The important observation from this figure is that this rapid drop occurs at a different DOD for the results from this work, than those of Smith et al. The simulation used in this work causes the cell to discharge quicker towards the end of its life than the simulation used by Smith et al. [26]. The results from this work show the end of the discharge process occurring at a DOD of 0.88 and Smith et al. show this occurring at a DOD of 1.05. Other than the differences in the two voltage profiles at the end of the discharge process, these two profiles show reasonable agreement.

![Cell Voltage comparison for a 1C discharge rate.](image)

Figure 25: Cell Voltage comparison for a 1C discharge rate.
The voltage profiles for a 5C discharge rate are as shown in Figure 26. The shapes of the two curves are more similar for this discharge rate, than they were for the 1C discharge rate. The biggest differences are once again seen at the higher DOD. For the results from this work, the battery is totally discharged at a DOD of 0.74. Since the DOD is less than one, this means there is still some charge available in the battery. If one were to wait while lithium-ions diffuse from the surface of the particles into the center, more useful power could be obtained from the battery. The end time shown in Figure 26 is the time when the surface of the particles that make up the positive electrode are saturated at their maximum value. Smith et al. [26] had their simulation stop at a DOD of 0.81 which is longer than this work’s value of 0.74.

![Figure 26: Cell voltage comparison for a 5C discharge rate.](image)

For an even higher discharge rate of 10C, the voltage profile comparison is as shown in Figure 27. In this case, the results from this work show the battery maintaining a higher voltage longer than the results of Smith et al. [26]. This is different than what happened for a 1C and 5C discharge rate. Obviously, the discharge rate has an effect on how the two results compare.
Results presented in Figure 25 represent the cell voltage distribution for the given values of electrode thickness in Table 1 for a 1C discharge rate. But, while going through Smith et al.’s results, it was found that their model uses different thickness for each region than the tabulated values. So, the cell voltage profile in Figure 28 was obtained by changing the electrode thickness to following values:

\[ L_{\text{neg}} = 46.80 \, \mu\text{m}; \quad L_{\text{sep}} = 23.70 \, \mu\text{m}; \quad L_{\text{pos}} = 41.30 \, \mu\text{m} \]

and a considerable amount of change was observed. In the voltage profile shown in Figure 28, the orange line (‘Using Dimensions-1’) is the result from this work using the tabulated values of electrode thickness; yellow line (‘Using Dimensions-2’) is the result from this work using above mentioned values of electrode thickness and the blue line is the results from Smith et al. [26]. Results for this case show that the end of the discharge process stops at almost exact DOD of 1.05 as Smith et al.’s model. Both the lines are following same trend and are in good agreement with each other as compared to Figure 25.
Similarly, the cell voltage profile in Figure 29 was obtained by changing the electrode thickness to above mentioned values, whereas, results presented in Figure 26 represent the cell voltage distribution for the given values of electrode thickness in Table 1 for a 5C discharge rate. Voltage drops smoothly as the discharge process continues and the biggest differences are once again seen at the higher DOD. For the results from this work, the end of discharge point goes beyond a DOD of 0.80, obtained by model presented in Smith [2007]. Since the DOD is less than one, this means there is still some charge available in the battery.

5.1.2 Solid Phase Surface Concentration

The comparison of the solid phase concentration profiles is depicted in Figure 30. The particle surface concentration of lithium ions in the solid is plotted in non-dimensional form as the ratio of the surface concentration in the solid particles to the maximum solid phase concentration possible in the solid. This ratio is plotted against the non-dimensional length of the cell. Concentration ratio profiles based on the data provided by Smith et al. [26] are plotted as dashed lines and those from
this work are plotted as solid lines. The solid surface concentrations shown in Figure 30 are divided into two regions, the left region is the concentrations in the negative electrode, and the right-side represents concentrations in the positive electrode. Since these are solid surface concentrations, they do not exist in the separator, and thus the reason for the blank region in Figure 30. The concentration ratio curves in Figure 30 are plotted for three different times, 0.1 seconds, 5 seconds, and 20 seconds. In this case, the starting point for the simulation was at a 50% DOD and the battery was discharged from this point.

![Figure 29: Cell voltage comparison for different widths of electrodes at 5C discharge rate.](image)

The results compare well for some regions, for some times, but noticeably differ at others. In particular, the concentration profiles from this work show higher concentrations in the negative electrode and lower concentrations in the positive electrode than Smith et al. [26]. Also, Smith et al.’s concentrations tend to bend more than those from this work. A first guess explanation for this behavior might be that Smith et al. used a different solid particle diffusion coefficient than what was used in this work. However, Smith et al. published in their paper [26] the exact same diffusion
coefficients used in this work. At this time, it is not known why these differences occur, but it is felt that these concentration differences have the cause of the voltage distribution differences shown in Figures 25, 26, and 27.

Figure 30: Comparison of concentration ratios with available data from Smith et al. [26] at a 5C discharge rate.

It is quite visible in Figure 30 that non-dimensional length for Smith et al.'s model in negative electrode is shorter and it is greater in positive electrode as compared to model presented in this work. The reason behind this can be explained as the electrode widths used in model presented by Smith et al. [26] uses different values than specified in the table. Thus, another case was simulated using those values for electrode thickness and change in concentration ratio was noticed. Figure 31 represents comparison of concentration ratios for three time steps at t = 0.1 second, 5 seconds and 20 seconds. Concentration ratio magnitudes for this case are almost constant at the specified time steps. Values obtained from published results in Smith et al. are represented as dashed lines and results obtained by this work are represented by circles. The concentration ratios match perfectly in the positive electrode with the published results obtained from Smith [2007], whereas,
concentration ratios in the negative electrode tend to dip more for Smith’s model as compared to ratios calculated by our model.

![Figure 31: Comparison of concentration ratios for a different set of electrode widths with available data from Smith et al. [26] at a 5C discharge rate.](image)

5.2 Additional Discharge Results

Additional results for the discharging condition discussed in the prior section are presented in this section. The simulation starts off at 100% state of charge and it approximately takes 3600 time steps with a time step of 1 second to reach the end of the discharge cycle. Within each time step, it took approximately 30-35 iterations to achieve convergence out to 0.001%. All the results are obtained at a constant temperature of 288 K and other necessary parameters are given in Table 1.

Distributions which are plotted as a function of position from the negative current collector to the positive current collector are divided into three parts: the left part of the plot represents the distribution in the negative electrode, the middle region is for the distribution in the separator, and the right-side is the distribution in the positive electrode.
5.2.1 Solid Phase Potential

Figure 32 shows the solid phase potential distribution for the discharging condition plotted against position in the solid electrodes. The electrical potential in each electrode is almost uniform at a specific time due to the high electrical conductivities of the solid electrodes. These potentials are calculated at a 1C discharge rate for various times such as 5 seconds, $t_f/4$, $t_f/2$, $3t_f/4$ and $t_f$ which equals 3600 seconds. Values at an initial time of 5 seconds are plotted instead of 0 seconds because they show a little change at early times in the discharge process. All the plots in this subsection have $t_0 = 5$ seconds as their initial time.

At the initial time $t_0$, the solid phase potential magnitude is 6.17 V in the positive electrode and 2.28 V in the negative electrode. Potentials in the positive electrode go down from the initial value and go up in the negative electrode. The gap between the magnitudes reduces as the discharge process continues. On an absolute basis, the electrical potentials in the positive electrode vary more with time than the electrical potentials in the negative electrode.

![Solid phase potential distribution for 1C discharge rate for different times.](image)
5.2.2 Electrolyte Potential

Figure 33 shows the electrolyte potential for the discharging condition plotted against location in the cell. It is calculated in all three regions. The absolute value of the electrolyte potential is unimportant because all these calculations allow the electric potentials to float. Thus, the calculation converges to an absolute voltage level based on the initial guesses. This floating of the potentials shows up in the electrolyte. What is important about the electrolyte potentials is the variations seen. The voltage throughout the electrolyte is relatively uniform for the entire domain. This flat electrical potential profile is due to the high ionic electrical conductivity in the electrolyte. The values of the electrolyte potentials change by millivolts or less until later times in the simulation. At the end of the simulation, time $t_f$, there is a visible deflection in the potentials which forms a negative slope. The electrical potential in the negative electrode are slightly higher than in the positive electrode. In a more magnified view of the electrical potentials in the electrolyte, it can be seen that the trend followed by the potentials will be similar to the electrolyte concentration distribution.

![Figure 33: Electrolyte potentials for a 1C discharge at different times.](image-url)
5.2.3 Electrolyte Concentration

Figure 34 shows smooth curves for the lithium-ion concentrations plotted against position in the cell for different times. During the start of the discharge process, the lithium-ion concentration in the electrolyte changes little from the initial value, but there are notable changes in the concentrations after 5 seconds. The initial profile starts flat around 1210 mol/m$^3$, until it reaches a peak value at 900 seconds. The concentrations throughout the cell go down after 900 seconds. The lithium-ion concentration is higher in the negative electrode because this is where lithium ions exit the solid and go into the electrolyte. The lithium-ion concentrations are lower in the positive electrode because this is where lithium ions are absorbed into the solid. The gradients in the lithium-ion concentration distributions drive lithium ions from the negative electrode to the positive electrode.

![Figure 34: Lithium-ion concentration in the electrolyte for a 1C discharge rate at different times.](image)
5.2.4 Surface Concentration

Figure 35 displays the surface concentrations plotted against position for a discharging condition. Surface concentration is the concentration at the surface of a spherical particle and these are calculated for each Cartesian control volume grid point (see Figure 21). Before discharging the battery, the concentration of lithium ions is higher in the negative electrode as compared to the positive electrode. The initial concentration starts off at the fully charged conditions. All the plots in this section are obtained by assuming the starting point for the discharge process is when the battery is at 100% SOC.

Figure 35 shows that the particle surface concentrations fall as a function of time in the negative electrode and rise as a function of time in the positive electrode. This is exactly what should be happening. Lithium-ions are released from the solid material that makes up the negative electrode and absorbed by the solid material that makes up the positive electrode. This is what causes the current in the battery. At 3600 seconds of discharging Figure 35 shows the positive electrode as being at its maximum lithium-ion concentration of 23,900 moles/m$^3$ denoted by the green color in Figure 35. When the positive electrode reaches the maximum value, it can be said that battery is fully discharged and there are no more active particles available to produce current.

![Figure 35: Solid surface lithium-ion concentrations for 1C discharge at different times.](image-url)
5.3 Results for Charging Condition

In this section, a few of the important battery quantities are presented at 1C charge rate. It takes almost 3840 seconds to completely charge this 6 A-h lithium-ion battery from the 0% SOC to the 100% SOC.

Few extended results for the charging condition will be presented in this section. The simulation starts off at 0% state of charge and it approximately takes 3840 time steps with a time step of 1 second for an entire charge cycle. Within each time step, it took approximately 20-23 iterations to achieve convergence by 6 orders of magnitude. Same number of control volumes is used for charging condition as used for discharging condition.

5.3.1 Cell Voltage

Simulated voltage profiles for several charging rates are as depicted in Figure 36. In order to compute the voltage characteristics of an entire charge cycle, the calculations were performed until they reach the point of maximum concentration in the negative electrode. For the charging results it was decided to plot the cell voltages versus SOC, instead of DOD, so the values go in an increasing order. Cell voltages are shown for charging rates from 1C to 30C.

In the voltage distribution shown, a maximum 92% SOC was attained when charging at 1C. It starts at initial voltage of 3.39 V and goes till it reaches 4.04 V after running for 3840 seconds. Even though the starting point for the solid and electrolyte electric potentials were the same for each case, the calculated cell voltages at higher charge rates started higher. For the 10C charge rate, 200 seconds of charging are required and a maximum cell voltage of 3.96 V at 47% SOC was obtained. For a 30C charge rate, only 32% SOC could be obtained. This is a short period of time because the current applied is very high and lithium-ions do not have time to diffuse all the way into the solid particles.

5.3.2 Solid Phase Potential

Figure 37 shows the solid phase potential distribution for the charging condition plotted against position in the solid electrodes. The electrical potential in each electrode is almost uniform at a specific time due to the high electrical conductivities of the solid electrodes. These potentials are
calculated at a 1C charge rate for various times such as 5 seconds, $t_f/4$, $t_f/2$, $3t_f/4$ and $t_f$ which equals 3840 seconds.

At the initial time $t_0$, the solid phase potential magnitude is 5.5 V in the positive electrode and 2.1 V in the negative electrode. Potentials in the positive electrode go up from the initial value and go down in the negative electrode. The gap between the magnitudes increases as the charge process continues. On an absolute basis, the electrical potentials in the positive electrode vary more with time than the electrical potentials in the negative electrode.

5.3.3 Electrolyte Potential

Figure 38 shows the electrolyte potential for the charging condition plotted against location in the cell. This flat electrical potential profile is due to the high ionic electrical conductivity in the electrolyte. Also for charging condition, the values of the electrolyte potentials change by millivolts or less until later times in the simulation. At the end of the simulation, time $t_f$, there is a visible deflection in the potentials which forms a positive slope. The electrical potential in the
positive electrode are slightly higher than in the negative electrode. In a more magnified view of the electrical potentials in the electrolyte, it can be seen that the trend followed by the potentials will be similar to the electrolyte concentration distribution for the charging condition.

![Graph showing solid phase potential distribution for 1C charging rate at different times.](image)

Figure 37: Solid phase potential distribution for 1C charging rate at different times.

### 5.3.4 Electrolyte Concentration

Figure 39 shows smooth curves for the lithium-ion concentrations plotted against position in the cell for different times. During the start of the charge process, the lithium-ion concentration in the electrolyte changes little from the initial value, but there are notable changes in the concentrations after 5 seconds. As the battery is further charged, the electrolyte concentrations get higher and higher till it reaches the end of charge cycle and follows a smooth curve as shown in distribution. While charging, the lithium-ion concentrations are lower in the negative electrode because this is where lithium ions are absorbed into the solid. The lithium-ion concentration is higher in the positive electrode because this is where lithium ions exit the solid and go into the
electrolyte. The gradients in the lithium-ion concentration distributions drive lithium ions from the positive electrode to the negative electrode.

![Figure 38: Electrolyte potential for a 1C charging rate at different times.](image)

5.3.5 Surface Concentration

Figure 40 displays the surface concentrations plotted against position for a charging condition. Before charging the battery, the concentration of lithium ions is lower in the negative electrode as compared to the positive electrode. The initial concentration starts off at the fully discharged conditions.

Figure 40 shows that the particle surface concentrations rise as a function of time in the negative electrode and fall as a function of time in the positive electrode. This is exactly what should be happening. As the battery is charged from a 0% SOC, lithium-ions are released from the solid material that makes up the positive electrode and absorbed by the solid material that makes up the negative electrode. This is what causes the current in the battery. Thus, concentration on the negative electrode increases as time proceeds and is denoted by green color when it is
maximum at 3840 seconds on the left portion of the concentration distribution. When it reaches that point, it can be said that battery is charged.

![Graph showing lithium-ion concentration in the electrolyte for a 1C charging rate at different times.](image)

**Figure 39:** Lithium-ion concentration in the electrolyte for a 1C charging rate at different times.

### 5.4 Effect of Discharge Rate

Once the results were validated by comparing them with available computational results from [26], few cases were studied. This was done to explore the performance of the lithium ion battery under different scenarios.

In a high-rate discharge, the surface composition of the electrodes can reach saturation before the full capacity of the electrodes is utilized, and that is why the capacity drawn from the cell will decrease with increasing discharge rate and decreasing temperature. This is not an irreversible process - if the next discharge is at a lower rate, the capacity may increase again [42]. This study
was carried at initial SOC = 100% and discharge rates were varied as 1C, 5C, 10C, 20C and 30C for a 6 Ah battery.

![Graph showing solid surface lithium-ion concentrations for a 1C charging rate at different times.](image)

**Figure 40:** Solid surface lithium-ion concentrations for a 1C charging rate at different times.

### 5.4.1 Cell Voltage

The battery is discharged at different C-rates to obtain the voltage discharge curve for each C-rate. The effect of varying discharge rate on cell voltage was that; it drops quickly which results in loss of power and does not use the maximum capacity of battery at higher rates as shown in Figure 41. If the current draw is too high, it reaches a point when there is no active material left to be drawn out of negative electrode thus, the concentration on positive side reaches the maximum solid phase concentration quickly.
5.4.2 Electrolyte Concentration

The effect of varying discharge rate was that the gradient of electrolyte Li concentration distribution increases as discharge rate increases. This behavior is shown in Figure 42. Initial concentration for this study was set equal to 1208 mol/m$^3$. This is done by varying discharge rates and keeping the initial salt concentration constant. All the profiles plotted in Figure 42 are at $t = t_f$ of that particular case depending upon the discharge rate.

At 1C discharge rate, change in the concentrations at both ends is only around 80 mol/m$^3$ whereas, at 10C and 20C rates the gradient is higher which results in significant change in the Li concentrations in electrolyte. If the applied current is increased, the slope will also increase resulting in high concentration at negative electrode and low concentration at positive electrode.

The reason behind this change in the electrolyte concentration gradient is that at low discharge rates, the diffusion of lithium ions is slower and thus there is a small change. When higher discharge rates are used, the diffusion of ions is really quick so the concentration shoots up and stays there as it can be seen in the case of 20C and 30C.
Figure 42: Effect of varying discharge rates on electrolyte concentration.
Chapter 6. CONCLUSIONS

The main objective of this work was to develop an electrochemical, one-dimensional computer model of lithium-ion batteries. This objective has been met by using a finite volume numerical technique to solve four highly coupled, partial differential equations which were obtained from fundamental conservation laws. On top of these four differential equations, two equations describing the chemical kinetics of the problem were solved. The developed model is capable of predicting the electrochemical behavior of a lithium-ion battery for a wide range of operating conditions.

Separate sections of MATLAB computer code were written for each of the four partial differential equations and then executed by a main calling program. To solve the algebraic equations that resulted from the discretization of the partial differential equations, a tri-diagonal matrix algorithm was used. This computer model is highly nonlinear and iteration was required to obtain a solution. A convergence criteria which computes the fractional difference of $C_s$, $C_e$, $\varphi_s$ and $\varphi_e$ between the current and previous iteration values was used to determine convergence of the simulation.

To validate the developed computer code, cell voltage and solid phase concentration results were compared to those published by Smith et al. [26] for different discharging rates. The comparisons are not perfect, but they are very close. It appears that Smith et al. used different thickness values of each region than the values published in a table in their paper. So, by obtaining a different set of electrode thickness from the results published in Smith [2007], few cases were simulated and results for those cases (presented in results section) show better agreement with published results as compared to previous case. It also appears that Smith et al. have the lithium ions diffusing out of the solid phase quicker than that predicted by the model produced in this work. At this time, it is not understood why this discrepancy exists.
A number of results for a lithium-ion battery have been produced by the developed computer code. Solid electric potentials, electrolyte electric potentials, solid lithium-ion concentrations, and electrolyte lithium-ion concentrations are calculated as a function of time and position. This can be done for both charging and discharging conditions in the battery. Results for both charging and discharging conditions have been presented in this thesis. Also presented are the effect of discharging rate on the battery voltage and electrolyte concentration. It was found that at higher rates of discharge, the high current draw results in the surface lithium-ion concentrations of the electrodes reaching saturation before the full capacity of the electrodes is utilized. In the case of electrolyte lithium-ion concentration at higher discharge rates, the gradient of the concentration is higher which aids in diffusing lithium ions across the separator.

In the future, additional checking of this developed computer model should be performed. A problem with making these comparisons is a number of sources do not present all of the required conditions for their simulation. In addition, some sources seem to have errors in the results that they present. Also, in the future a thermal model should be added to the MATLAB code developed here. The MATLAB code developed as part of this thesis work focuses on modeling the electrochemical behavior of the battery and does not include modeling of the thermal behavior. Lithium-ion batteries are sensitive to temperature variations, so it is desirable to model thermal behavior as well. Lastly, it would be desirable to integrate this battery computer model into the Wright State developed computer code called Solar_PVHFC. Storage is becoming an important issue in solar power systems, and this would provide Solar_PVHVC with some desirable functionality.
REFERENCES


[33] W. Gu and C. Wang, "Thermal-Electrochemical Coupled Modeling of a Lithium-ion cell".


[42] "How does charge rate and temperature affect capacity in lithium ion batteries," [Online]. [Accessed 20 April 2017].