CHARACTERIZATION AND MODELING OF NiZn AND Li-BASED BATTERIES

A Thesis

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Battery modeling helps to understand the battery behavior, as it adds a bridge between the chemical and the electrical worlds. The aim of this thesis is to study the characteristics of the battery and suggest models that can approximate the voltage profile curve and the energy characteristic curve of different battery chemistries. In order to achieve this goal, batteries of different chemistries are monitored throughout their lifetime and the role of all the identified parameters on battery performance are observed. An observation is made that a cell operates in both linear and nonlinear regions, and the models of these regions are split accordingly. An electric circuit model is suggested to represent all the battery dynamics for the linear region. In addition, a mathematical model is used to represent the cell behavior in the nonlinear region. This thesis also focuses on determining the best mathematical model to represent the energy characteristic curve for different chemistry cells. Simulation results obtained by using the electric circuit model and the energy characteristic curve model are validated with the experimental results for NiZn cells and Li-based cells. Further, the models are validated by performing some error calculations, and confirming that the error is below the tolerable level.
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A battery is an energy storage device that stores energy in the form of energized chemical species. Batteries can be categorized as primary (single use) and secondary (multiple use) battery. This thesis focuses on the modeling and characterization of secondary batteries. A secondary battery is often referred to as a rechargeable battery. Some rechargeable chemistries include NiCd, NiMH, NiZn and Li-Ion which are widely available. This thesis will focus on the modeling of the energy characteristic curve of a NiZn and Li-ion batteries and on determining the appropriate electric circuit model for different chemistry batteries. Different chemistry cells are cycled and monitored throughout their life, to study the characteristics of the cell. In addition to the modeling suggestions and cell characterizations, this thesis also gives some understanding for NiZn cell life based on experimental observations.

This thesis is organized in following manner. Chapter II gives the background information that is required to understand cell dynamics. In addition, Chapter II also gives the definition of different terms and terminology that are linked with a cell. Further, different popular models about the cell voltage are discussed. Chapter III presents the literature review of some of the useful electric circuit models that are used to represent the cell electrically. Chapter IV deals on the development of a
cell. In addition, this chapter also covers the procedures that are used to gather the experimental information from the charge-discharge cycle of different chemistry cells.

Chapter V discusses the procedures used to model the zero current curve which is often called energy characteristic curve of a cell. The first section of this chapter explains how the weighted-average-least-square technique is used to solve for the model parameters. This section also includes the algorithms that are implemented for the computation of the model. The second section of this chapter focuses on the electric circuit model of the cell. This section presents the circuit model that includes almost all important cell behavior. It also discusses the methods and techniques that are used to identify the circuit parameters from the experimental data. The last section of this chapter presents the experimental values of the identified parameters for different cell chemistries. Further, this section also shows some comparison plots of those parameters for different cell chemistries.

Chapter VI explains the simulation that is done to check the validity of the model, which is covered in Chapter V. Beside model validation, this chapter also presents the simulated responses and the real responses for the energy characteristic curves, the voltage profile curves and the charge profile curves for different cells of different chemistries. Finally, this chapter presents the error curves that are associated with the approximation. Lastly, Chapter VII provides some suggestions and conclusions.
CHAPTER II

BATTERY BACKGROUND

This chapter deals with the definition of the general terminology related to an electrochemical cell (cell characterization and cell modeling). The aim of this chapter is to introduce general electrochemical cell terminology, cell model approximation techniques and background theories that are necessary to follow the discussion.

2.1 Cell Voltage

A potential difference across a cell is the result of the chemical reaction occurring inside the cell. Energy is released during a chemical reaction as a result of the movement of charged particles. This available electrical energy in a cell is expressed as the cell potential. The electromotive force (EMF) of a cell is the available potential difference, and is related to the Gibbs Free energy as follow,

\[ \Delta G = nFE^0 \]

(2.1)

where, \( n \) is the number of moles of electrons participating in the reaction, \( F \) is Faraday’s constant, \( E^0 \) is the electromotive force of a cell and \( \Delta G \) is a Gibbs Free energy.
The theoretical voltage of cell can be determined from a table of potentials of standard electrodes [4]. The standard cell voltage (theoretical voltage) is the summation of the oxidation potential (i.e positive electrode) and the reduction potential (i.e negative electrode). The example below shows the calculation of the standard cell voltage of a NiZn cell at standard temperature, pressure and activities. The overall reaction of a NiZn cell is

\[ \text{Zn(OH)}_2 + 2\text{Ni(OH)}_2 \rightarrow 2\text{NiOOH} + \text{Zn} + 2\text{H}_2\text{O} \]

and can be split as:

**Negative Electrode:** \[ \text{Zn(OH)}_2 + 2e \rightarrow \text{Zn} + 2\text{OH}^- \quad 1.24 \text{ V} \]

**Positive Electrode:** \[ 2\text{Ni(OH)}_2 + 2\text{OH}^- \rightarrow 2\text{NiOOH} + 2\text{H}_2\text{O} \] \[ 0.49 \text{ V} \]

**Standard Cell Voltage** \( E^0 \) \[ 1.73 \text{ V} \]

The standard conditions are hard to have in reality, and the Nernst equation is often used to calculate the cell voltage under non-standard conditions [5]. The Nernst equation correlates a cell potential with the chemical energy of that cell. The chemical reaction [4] that occurs inside a cell can be generalized as,

\[ aA + bB \rightleftharpoons cC + dD \quad (2.2) \]

where \( a \) molecules of \( A \) and \( b \) molecules of \( B \) react to form \( c \) molecules of \( C \) and \( d \) molecules of \( D \). The Nernst equation for this cell voltage \( E \) is expressed as,

\[ E = E^0 - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (2.3) \]
where \( E^0 \) is the standard potential of the electrode reaction at 25° C [4], \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature in Kelvin, \( a_i \) is the activity of relevant species, and \( F \) is the Faraday constant (96485 C). By using Equation 2.3, the EMF of the cell can be determined if the activities of the reactants and electrolytes are known, and the amount of stored charge can be determined if the amount of reactants are known. The activities in the Nernst equation are often replaced by the concentrations for ionic species. The modified equation [4] consistent with the Nernst equation is,

\[
E = E^0 + \frac{RT}{nF} \ln \frac{C_0}{C_R} \quad (2.4)
\]

where \( C_0 \) is the concentration of oxidized species and \( C_R \) is the concentration of reduced species. Thus, the Nernst equation shows how the cell voltage changes with species activities and temperature, and is widely used.

When current effects are included, the Butler-Volmer equation [6] provides a more general relationship. The Butler-Volmer equation relates the electrical current of a cell to the concentration of the electroactive species of the cell,

\[
I = i_0 \left\{ \frac{C_0(0,t)}{C_0} \exp \left[ \frac{\alpha_a nF (E - E^0)}{RT} \right] - \frac{C_R(0,t)}{C_R} \exp \left[ -\frac{\alpha_c nF (E - E^0)}{RT} \right] \right\} \quad (2.5)
\]

where \( I \) is the electrode current density, \( C_0 \) and \( C_R \) are the concentration of the oxidized and the reduced form, respectively, \( C(0,t) \) refers to the time-dependent concentration at zero distance, \( \alpha_a \) is the anodic charge transfer coefficient, \( \alpha_c \) is the cathodic charge transfer coefficient, \( F \) is the Faraday constant, \( E \) is the electrode potential, \( E^0 \) is the standard potential, \( n \) is the number of electrons involved in the
electrode reaction, \( R \) is the universal gas constant and \( T \) is the absolute temperature. As the Butler-Volmer equation is generally impossible to solve for the voltage, many approximations have been presented, and these are reviewed here.

The Nernst equation that approximates the cell potential [7] can be modified to include internal resistance and state-of-charge. The modified Nernst equation is,

\[
E(t) = E_O - R\Omega i(t) - K_1 \ln(SOC_t)
\]  

(2.6)

where \( E_O \) is the initial voltage of the cell, \( R\Omega \) is the internal resistance of the cell, \( K_1 \) is a constant whose value is chosen to fit the model by representing the activities of the contributing species, and \( SOC \) is the state-of-charge of the cell. \( SOC \) is defined as the percent of possible energized species.

The Nernst model [7] has been further modified to more accurately determine the cell’s terminal voltage and is named the Modified Nernst Model. The modified Nernst model is expressed as,

\[
E(t) = E_O - R\Omega i(t) + K_2 \ln(SOC_t) + K_3 \ln(1 - SOC_t)
\]  

(2.7)

where \( K_3 \) is constant whose value is chosen to fit the model well.

Beside Nernst based models, other models have been derived to approximate a cell voltage. Some of them are discussed below. Another model named the Shepherd Model [8] relates a cell potential with its current. The voltage-current relations of a battery per Shepherd theory are given by following relation,

\[
E = E_S - K \left( \frac{Q}{Q - it} \right) i - Ni
\]  

(2.8)
where $E$ is the battery voltage, $E_S$ is a potential constant, $i$ is the apparent current density, $t$ is time, $N$ is the internal resistance per unit area, and $K$ is the coefficient of polarization per unit of current density. The Shepherd model 2.8 is further simplified as follows to approximate the cell voltage.

$$E(t) = E_O - R\Omega i(t) + \frac{K_i}{SOC_t}$$

(2.9)

where $E_O$ is the initial voltage of the battery, $R\Omega$ is the internal resistance of the battery, $K_i$ is the polarization resistance, $SOC_t$ is the state-of-charge of the battery with respect to time, and $t$ is time.

Another popular model to approximate the battery voltage is called Unnewehr Universal Model [8] and is

$$E(t) = E_O - R\Omega i(t) + K_iSOC_t$$

(2.10)

where $K_i$ is the polarization resistance.

The model obtained after combining 2.6, 2.7, 2.9 and 2.10 voltage approximation models, produces a more accurate estimation model [2]. The combined model is given by

$$E(t) = K_O - R\Omega i(t) - \frac{K_1}{SOC_t} - K_2SOC_t + K_3 \ln(SOC_t) + K_4 \ln(1 - SOC_t)$$

(2.11)

where $K_4$ is the polarization resistance and $K_1$, $K_2$, $K_3$ are constants whose value are chosen to make the simulated data model fit well to the actual data model.

Figure 2.1 shows the experimental voltage profile curve of a typical NiZn cell. The specific voltage and the voltage changing patterns depend on factors like cell
chemistries, charge rate, temperature etc. The standard potential of a NiZn cell is approximately 1.73 volts. A cell at rest is about 1.2 volts when it is mostly discharged. As soon as the cell is charged, the voltage jumps from 1.2 volts to about 1.5 volts. This jump seen in a cell voltage profile curve is primarily due to the nonlinearity of the voltage-charge relationship. Some of the jump is due to the internal resistance of the cell and the diffusion inside the cell.

2.2 Diffusion

Convection, electric potential drift and diffusion are the three mass-transfer processes which control the flow of ions in electrolyte. For a standard cell, diffusion is considered to be the dominant process for the flow of ions in an electrolyte. It explains
how particles are spread from a region of higher concentration to a region of lower concentration. It is one of the key dynamics for short-term cell transients.

Fick’s law gives the relation relating the mass and the concentration of ions within a cell with respect to time. Fick’s first law \[9\] gives the relation relating the mass that travels in a small interval of time through a small area. According to Fick’s first law, the diffusion within a cell for one dimension is given by,

\[ J(x, t) = -D \frac{\partial \phi}{\partial x} \]  

(2.12)

where \( J(x, t) \) is the diffusion flux in direction \( x \), \( D \) is the diffusion coefficient, \( \phi \) is the concentration, \( t \) is time and \( x \) is the position. Fick’s second law tells how the concentration of an electro-active material is changed by a diffusion process, and is expressed as

\[ \frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}, \]  

(2.13)

often called the diffusion equation. In order to solve Fick’s equations for the mass and the concentration inside a cell, a one dimensional diffusion system is designed, whose environment is similar to that of the cell. Figure 2.2 illustrates the cell environment, along with the respective boundary conditions. Hartley and Lorenzo (2002) solved the diffusion equation for the above designed boundary conditions, and suggested a solution. As the length of the diffusion channel increases, \( L \rightarrow \infty \), the solution of the diffusion equation in the Laplace domain, looking in from one terminal, is

\[ \phi(0, s) = \frac{1}{\sqrt{\beta s}} J_0(s) + \frac{\phi_{s0}}{s} \]
\[
J(0,t) = -D \frac{\partial \phi(L,0)}{\partial x}
\]

\[
J(L,t) = -D \frac{\partial \phi(L,t)}{\partial x}
\]

\[
\phi(x,0) = \phi_o
\]

Figure 2.2: Illustration of Diffusion Process with its Corresponding Boundary Conditions for a Cell

where the term \(1/\sqrt{\beta s}\) is often called the Warburg impedance \([4]\). In general, the Warburg impedance can be used to represent the diffusion process of a cell. Besides this, many low-order approximations to ionic diffusion can be derived \([4]\).

2.3 Cell Current

Current in a cell is the rate of exchange of charge particles between oxidized and reduced species. Faraday’s Law of Electrolysis \([10]\) explains how the electricity that passes through the cell is related to the mass of substance produced or consumed by the electrolysis process. Faraday’s 1\textsuperscript{st} Law of electrolysis states that the mass of substance produced by electrolysis at the electrode-electrolyte boundary is proportional to the quantity of the electricity used. Faraday’s 2\textsuperscript{nd} Law states that the mass of the substance altered by passing the same amount of electricity through an electrode is
proportional to their equivalent weights. Thus, the Faraday’s 1\textsuperscript{st} and 2\textsuperscript{nd} laws are summarized into single equation as,

\[ m = \left( \frac{Q}{F} \right) \left( \frac{M}{z} \right) \] (2.14)

where \( m \) is the mass of the substance liberated at an electrode, \( F \) is the Faraday constant (96,485 C mol\(^{-1}\)), \( M \) is the molar mass, \( z \) is the valency number of ions of the substance, and \( Q \) is the electric charge.

For constant-current electrolysis, \( Q = It \) and for variable electrical current, \( Q = \int_o^T Idt \). Thus, Faraday’s law says that the electric current controls the chemical reactions. For cell, the cell current is categorized as

- **Charging Current**: Charging current is the amount of current supplied to the battery in order to charge the battery. Different current profiles can be used to charge the battery. Battery chemistries should be considered when determining the charging current, in order to not harm the battery.

- **Discharging Current**: Discharging current is the amount of current withdrawn from the battery. Depending upon the need, one can change the discharge current rate. Choosing an inappropriate discharge current rate can impact the duration of battery discharge and the total life of the battery.

### 2.4 Capacity

Cell capacity is defined as the maximum amount of charge that is stored in a cell as energized species. In electrochemical form [11], battery capacity is defined as the
mass of active energizable material contained in the battery. Though capacity represents the maximum amount of energy that can be withdrawn from the battery, it depends on other conditions like state-of-charge (SOC), age and temperature. Figure 2.3 is an experimental result from a NiZn cell which shows the change in the capacity of a cell with respect to the age (cycle number). Some examples are discussed below to clarify the concept of capacity.

Example 1: If a fully charged cell has a capacity of 2.26 Ah (amp-hours), it means the cell is expected to produce 2.26 amperes of current for an hour. This relation will be true only if the cell is producing a constant current of 2.26 amperes. But if the cell is producing a different current, the time and current relation do not match perfectly.
Example 2: If a cell has a capacity of 2.26 A\text{Hr} and has a 75\% SOC, then the cell is expected to produce 2.26 A of current for 45 minutes.

The first example shows the nonlinear relation between the capacity, time and discharge rate, while the second example shows the importance of knowing the state-of-charge of a battery. In spite of the difficulties in deriving a simple relation to compute the capacity of a battery by considering all capacity effecting factors, these phenomena are expressed mathematically via the Peukert equation \[3\] which tells how the total discharge time varies with different discharge rates. The Peukert law is stated as:

\[ C_P = I^K t \]

where, \(C_P\) is the capacity at a one-ampere discharge rate, \(I\) is the discharge current, \(t\) is the time required to discharge the battery and \(K\) is the Peukert constant for a given cell. In practice, one cannot obtain the rated capacity of a battery. Therefore, the Peukert Law explains this phenomenon by giving a relationship to calculate the discharge time from the discharge rate.

2.5 Energy Curve

Figure 2.4 shows the ideal energy curve for a cell. As a result of different chemical processes \[12\] such as charge transfer, mass transfer, and intercalation of ions occurring inside a cell, the energy curve of a cell has a hysteresis effect. The internal resistance
of the cell, mostly due to the electrolyte diffusion, is the primary factor responsible for the hysteresis. The area inside a hysteresis curve gives total energy loss during the charging and discharging process. The area below the discharging curve gives the energy that is retrievable from a cell at the given discharge rate. The area below an charging curve gives total amount of energy delivered to a cell. Therefore, if the ideal energy characteristic curve of a battery can be well modelled, the prediction of the performance of the battery will be improved.

Experimental results show that if a sufficient rest period is allowed between the charge and discharge cycles, the voltage difference at the beginning and end of the energy curve will be reduced to some extent, as this rest period allows time for the chemical species to settle. The modeling of the hysteresis effects in the energy
curve is one of the major contributions of this thesis and is explained in detail in the following chapter.

2.6 State-of-Charge

State-of-Charge (SOC) is one way to express the available capacity of a cell. The state-of-charge is estimated in terms of the percentage of charge stored relative to the rated capacity [13]. An accurate approximation of the state-of-charge of a cell is important in ensuring a long cell cycle life. In addition, the SOC is monitored to maintain a cell in a safe operating range.

Many different experiments have been done to verify different theories behind the estimation of the state-of-charge of a cell. Among them, the most common and popular one is the Coulomb counting method, proposed by Hansen & Wang [14] and is an expression of Faraday’s law. The state-of-charge in an ideal cell is given by

\[ SOC(t) = SOC(0) + \int_0^t \frac{\dot{i}\tau}{Q} d\tau \quad (2.15) \]

where, \( Q \) is the capacity of the cell. This model is very simple, and it assumes all the charge entering the cell is converted to energized species. A more accurate approximation of the SOC is difficult, because the SOC of a cell is often determined from the cell voltage, which depends on factors like current, internal resistance, temperature, capacity, and the history of the cell usage.
2.7 Charge Acceptance Rate

The Charge Acceptance Rate [14] is the percentage of charge entering the cell that is converted to energized species. Figures 2.5 show the charge acceptance rate curve for an ideal cell, and a practical cell.

![Acceptance Rate versus Cell Life in Percentage for Ideal Case and Practical Case](image)

(a) Ideal Case  
(b) Practical Case

Figure 2.5: Acceptance Rate versus Cell Life in Percentage for Ideal Case and Practical Case

In the ideal case, a cell stores all the charge applied to it all the time, as it has unity charge acceptance rate. The charge acceptance rate is greatly influenced by the conditions inside a cell and the availability of the energized material for the reactions. The charge that is not accepted usually goes into secondary reactions, including electrolysis of water in the electrolyte. In practice, the acceptance rate
decreases slowly with an increase in the cell usage time, and it decays toward zero as the cell tends to die. In addition, the acceptance rate also depends upon the charging rate $I_R$ and $SOC$ of a cell.

2.8 Charge Efficiency

The charge efficiency of a cell is defined as the percentage of the ratio of the amount of charge out, to the amount of charge in, to the cell. Typical cell efficiencies for a NiZn cells are about 85%. Figure 2.6 shows the efficiency curve for a typical NiZn cell. The general expression for charge efficiency is,

$$\eta_Q = \frac{Q_{out}}{Q_{in}}$$  \hspace{1cm} (2.16)

where, $Q_{out}$ is the amount of charge delivered by the cell $Q_{in}$ is the amount of charge delivered to the cell.

2.9 Cycle Life

Cycle life is defined as the number of cycles up to which the performance of a cell is acceptable. For a typical NiZn cell, the published cycle life is about 500 cycles. Factors like charge-discharge rate, temperatures, secondary chemical reactions going inside a cell, and many other unknown factors are responsible for decreasing the cycle life. The cycle life for cells of all chemistries is nonlinear in nature and is hard to predict. Though, much research is going on, a relation with low error probability to approximate the cycle life is difficult to obtain.
2.10 Charge-Discharge Rate

The charge-discharge rate of a cell is directly related to its $IR$ loss. The $IR$ loss of a cell increases on increasing the current through a cell. In addition, increases in a cell charge-discharge rate also reduces the cell cycle life. If a cell is cycled with low charge-discharge rate, the cell can approach the theoretical Nernst voltage, and the theoretical capacity, resulting in an increase in cycle life. For higher charge-discharge rates, the slope of the charge-discharge curve becomes more sharp and there is higher probability for the reduction of cycle life and cell capacity. Figure 2.7 shows the change in the discharge times for different discharge rates of a typical NiZn cell. Different chemistry cells have their own charge-discharge rate limitations.
2.11 Cell Aging

Factors that indicate the cell aging process are capacity, charge acceptance rate, internal resistance, charge efficiency and self discharge rate. As the cell ages, the cell's ability to hold charge reduces, resulting in the decrease of the cell capacity and the cell acceptance rate. Generally, there will be a reduction in the activity of energizable materials inside the cell. There will also be an increase in the self discharge rate, as well as an increase in the $IR$ losses.
2.12 Charging Algorithm

Many charging algorithms are in practice depending upon specific cell chemistries and cell usages. A few popular charging methods are

- **Constant Current**: In constant current, a variable voltage source is used to charge a battery by maintaining a constant current flow. The charging process will be stopped as soon as the voltage at the cell reaches the full charge voltage level. This is the most simple and the most common charging algorithm.

- **Constant Voltage**: In the constant voltage charging algorithm, the voltage of the cell is maintained constant irrespective of current.

- **Pulsed Charge**: In a pulsed charging algorithm [17], current pulses of periods 20 to 30 milliseconds are used to charge the battery. This algorithm claims to equalize the chemical reactions which finally helps to reduce the gas formation, crystal growth, and temperature in a cell.

Other algorithms are used in different chemistries like Pb-acid, NiCad, NiMH [4].
CHAPTER III

BATTERY MODELING REVIEW

This chapter deals with the previous research in the field of battery development, modelling and management. A battery is a simple electrical energy storage device, but the electrochemical reaction that occurs inside the battery to transport electric charge makes it difficult to model it. Though extensive research has been done to represent chemistries of different batteries by their equivalent electrical models, the accuracy of the models is still not perfect.

A battery has been modelled in different ways. Electrochemical battery models, equivalent electrical circuit models, hydrodynamic models and many more models have been developed to predict the performance of the batteries. Unfortunately, none of these battery models are capable of accurately predicting all battery performance behavior. Modelling methods for these processes are discussed in this chapter. Some of these behavior controlling processes are:

- Charge-discharge Rate
- Self-discharge Rate
- State-of-Charge
- Cycle Life
- Aging
• Storage Capacity

Different electrical models have been proposed to represent the equivalent electrochemical activities of a battery. In theory, an electrical model should be capable of predicting the battery performance behavior. Though some of the models have represented many of the battery performance behaviors, most of the models suffer from some inaccuracy in predicting voltages, state-of-charges etc. Some of the simple and common battery models are discussed briefly in subsequent subsections.

3.1 Internal Resistance Model

The internal resistance model \([18, 3]\) uses an open-circuit voltage \(V_{OC}\), and a resistor \(R_{INT}\) to model a battery. This model accounts for the full voltage drop by a battery from its equilibrium open-circuit voltage to the terminal voltage. A schematic of the electrical model of the battery is shown in Figure 3.1.

The value of \(R_{INT}\) is approximated by monitoring the voltage response for a constant current pulse duration, and it also varies with the state-of-charge, temperature and current flow direction. The main limitation of this model is its sensitivity to load change. In addition, this model does not represent the transient diffusion process that occurs inside a battery.
3.2 Impedance Model

Diffusion is one of the key dynamics of a cell. The internal resistance model discussed above fails to address the diffusion. Based upon the diffusion process discussed in the Section 2.2, an electric circuit model called the Impedance Model is developed to represent a battery. The Figure 3.2 shows the impedance model. This circuit model represents both instantaneous charge transfer processes and diffusion processes [19]. The $R_{INT}$ term is used to represent instantaneous charge transfer processes and $R_D$, $C_D$, and $W$ are used to represent diffusion processes, where $W$ is called Warburg impedance, mentioned earlier.
3.3 Linear Electric Model

The Eveready Company (2001) described another electrical model to addresses the diffusion mechanism in the battery by adding parallel RC circuit. This model consists of an ideal open-circuit voltage $V_{OC}$ in series with a resistor $R_{INT}$, the effective instantaneous resistance and a parallel combination of an over-voltage resistance $R_D$ in parallel with a double layer capacitance $C_D$. Figure 3.3 shows the electrical circuit model proposed by Eveready Company.

The linear electric model a for battery considers the parameters to be constant irrespective of the state of the battery. In reality, all battery parameters depend on the state-of-charge of the battery. In addition, the storage capacity of the battery is
not addressed by these models.

3.4 Modified Linear Electric Model

In the modified linear electric model, a capacitor $C_S$ is added in series with the resistor $R_{INT}$, in order to address the charge storage in the battery. Figure 3.4 shows the modified electrical circuit model of the battery. Though this model addresses diffusion, instantaneous current, and storage capacitance, it has not addressed one of the important processes named, the self-discharge process that occurs inside a battery.
3.5 Complete Battery Model

The complete battery model addresses the self-discharge process to account for charge loss during the rest time. The self-discharge issue has been addressed by placing a resistor $R_{SD}$ in parallel with the storage capacitor $C_S$. This model is termed the complete battery model, as it addresses most of the battery performance measuring parameters. Figure 3.5 shows the complete battery model that models a battery. An alternative is later shown in Chapter V.

3.6 Modified Complete Battery Model

The models discussed so far are assumed to have the same resistance for both the charging and discharging cycle. Another model has been developed to offer different
internal resistance for the charging and discharging cycles. This model [20] is called the modified complete battery model. This model also models the nonlinear characteristic of the battery. The circuit diagram of the modified complete battery model is shown in Figure 3.5.

The internal resistance $R_C$ and $R_D$ are functions of temperature and depth of discharge. The diode is used to allow different internal resistances for charging and discharging. $R_{LC}$ is placed in series with the parallel $RC$ circuit in order to account for series internal resistance.
Battery Model

$V_{OC}$

$R_{LC}$

$R_C$ $D_1$

$R_D$ $D_2$

Figure 3.6: Modified Complete Battery Model
CHAPTER IV

EXPERIMENTAL SETUP

The research carried out in this thesis can be separated into two categories. The first category deals with the experimental part and the second category deals with the modeling and simulation part. This chapter explains what was done, and how, to gather the experimental data of different chemistry cells, which are further used for simulation and modeling.

The first part of the experiment is focused on the development of a NiZn cell. After sacrificing several NiZn cells, some useful techniques are learned. A NiZn cell is constructed by treating nickel and zinc electrodes with the KOH solution by thoroughly dipping the electrodes into 33% concentrated KOH solution and gently wiping it. Each electrode is placed inside a pouch formed by the separator. Three electrodes are used to create a cell, two nickels and one zinc. Each electrode is placed inside a separator pouch. The zinc electrode is then wrapped inside another pouch made of a separate electrolytically conducting membrane. The two nickel electrode in pouches are then placed on each side of the doubly wrapped zinc electrode. Finally this stack of electrodes are placed inside a fitting container, which contains 33% KOH solution. Figure 4.1 and Figure 4.2 illustrate the NiZn development process while Figure 4.3 shows a sketch of the cell that is developed by the above discussed
Figure 4.1: Battery Construction Steps [1]
Figure 4.2: Front View and Side View of a Cell [1]

Figure 4.3: Internal Diagram of a Cell
process. Based on those steps, eight different NiZn cells are developed in the Polymer Engineering Lab, of The University of Akron, for studying their characteristics. Among eight NiZn cells, five NiZn cells are developed by using the membrane developed in the Polymer Engineering Department of The University of Akron, one NiZn cell is developed by using the membrane developed by the Eagle-Picher Company and two NiZn cells are developed by using the membrane developed by the eVionyx Company.

A battery cycling machine from MACCOR (Model 4300) is used to cycle (charge-discharge) the cells and to extract and store all the important information from the charge-discharge cycles of all the cells throughout their life. Figure 4.4 shows the MACCOR machine that is used for the experiment. Figure 4.6 and Figure 4.7 show snapshots of the graphical user interface of the cycling machine.

This cycling machine is a programmable machine. The user has the flexibility to write an algorithm to charge-discharge the cell at different charge rates, different durations, and different states (i.e constant voltage state or constant current state). In addition, different sampling times can be assigned while extracting the information from the experiments. Figure 4.5 shows the snapshot of the program that is used by this cycling machine. This machine has large storage capacity, so one can cycle the cell for long durations of time without losing any important information.

In addition to the NiZn cells that are developed at The University of Akron, a commercial NiZn cell and a few other commercial Lithium-ion cells are also considered
for experiments for studying their characteristics. In total, eleven different cells are tested. Type I through Type VIII cells are cycled throughout their life, while the Type IX, Type X cells are cycled for few cycles and the Type XI cell is cycled for five hundred cycles which took about 5 months. Information on sampling time, voltage, current and stages (charge, discharge, rest) from every individual cycle are extracted and are stored for future analysis. The analysis of these data will be discussed in the next chapter. Table 4.1 shows the list of different cell chemistries that are tested along with their corresponding experimental specifications like: charge-discharge rate $I_R$, \[ \text{Table 4.1} \]
charge-discharge duration $T_D$, the sampling time $T_S$ and the rest period $T_R$. Figure 4.8, Figure 4.9, Figure 4.10, Figure 4.11, Figure 4.12, Figure 4.13 and Figure 4.16 show voltage profile of the first cycle, the $N_2$ cycle and the last few cycles of Type I, Type II, Type III, Type IV, Type V, Type VI and Type XI cells respectively. The $N_2$ cycle is the round up integer value of $N/2$, where $N$ is the cell life.

Figure 4.5: Sample Program
Figure 4.6: Outer GUI of Maccor Battery Testing Machine

Figure 4.7: Inner GUI of Maccor Battery Testing Machine
Table 4.1: Experimental Specifications for Different Chemistry Cells

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Cell Chemistry</th>
<th>$I_R$ (amp)</th>
<th>$T_D$ (hour)</th>
<th>$T_S$ (min)</th>
<th>$T_R$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>NiZn cell that used U Akron membrane I</td>
<td>0.55</td>
<td>7.02</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Type II</td>
<td>NiZn cell that used U Akron membrane II</td>
<td>0.55</td>
<td>7.93</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type III</td>
<td>NiZn cell that used U Akron membrane III</td>
<td>0.55</td>
<td>7.75</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type IV</td>
<td>NiZn cell that used U Akron membrane IV</td>
<td>0.55</td>
<td>8.04</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type V</td>
<td>NiZn cell that used U Akron membrane V</td>
<td>0.55</td>
<td>8.36</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type VI</td>
<td>NiZn cell that used Eagle-Picher membrane</td>
<td>0.35</td>
<td>12.68</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type VII</td>
<td>NiZn cell that used eVionyx membrane</td>
<td>0.35</td>
<td>12.20</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Type VIII</td>
<td>commercial NiZn cell</td>
<td>0.35</td>
<td>8.14</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type IX</td>
<td>commercial LiCo cell</td>
<td>0.50</td>
<td>6.33</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type X</td>
<td>commercial LiMn cell</td>
<td>0.80</td>
<td>9.58</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Type XI</td>
<td>commercial LiFePo4 cell</td>
<td>0.50</td>
<td>6.02</td>
<td>2</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 4.8: Illustration of first, $36^{th}$ and last few cycles of a Type I Cell
Figure 4.9: Illustration of first, 30th and last few cycles of a Type II Cell
Figure 4.10: Illustration of first, 40\textsuperscript{th} and last few cycles of a Type III Cell
Figure 4.11: Illustration of first, 27th and last few cycles of a Type IV Cell
Figure 4.12: Illustration of first, 64th and last few cycles of a Type V Cell
Figure 4.13: Illustration of first, 17th and last few cycles of a Type VI Cell
Figure 4.14: Illustration of first, 36th and last few cycles of a Type VII Cell
Figure 4.15: Illustration of first, 32\textsuperscript{nd} and last few cycles of a Type VIII Cell
Figure 4.16: Illustration of first, 250\textsuperscript{th} and 500\textsuperscript{th} cycles of a Type XI Cell
CHAPTER V

BATTERY MODELING APPROACH

This chapter covers the modeling of the energy characteristic curve of a cell. In addition, this chapter also deals with representing cell behavior by using the electric circuit model. Calculation procedures and experimental results of the electric circuit model parameters and other important cell behaviour predicting parameters are briefly discussed. Finally, results for different chemistries are summarized.

5.1 Modeling The Energy Characteristic Curve

The cell voltage versus the state-of-charge (SOC) for charging and discharging is plotted in Figure 5.1 for a typical NiZn cell. The curve obtained after averaging these two curves is named the Energy Characteristic Curve. This curve can be thought of as the zero-current curve, usually called the Nernst curve. Technically, this curve shows the cell potential under no current for various states-of-charge. Since we can never have zero-current when using the cell, the red line is the average of the voltages from charge and discharge. The significance of these curves has already been discussed in Section 2.5. In this section, we will discuss mathematical models that can be used to represent the energy characteristic curves for most cells. The energy characteristic curve has been modeled using different mathematical methods. These
include parabolic approximation, spline approximation, linear regression approximation and weighted-average-least-square approximation. Beside spline approximation, all other methods model the energy characteristic curve by breaking the curve into three different regions. Some of the model fitting approximations are discussed briefly in following sections.

The energy characteristic curve is first split into three regions, the lower nonlinear region, the linear region and the upper nonlinear region as shown in Figure 5.2. Cut-off points between the lower nonlinear region and the linear region, and cut-off points between the linear region and the upper nonlinear region are approximated by trial and error. The cut-off points are first guessed from the energy characteristic
curve of real experimental data. Then, the cut-off points are tested to verify the tolerable amount of error in all regions. In general, the first cut-off point $\alpha_1$ is at around 17% to 20% \textit{SOC} and the second cut-off point $\alpha_2$ is at around 80% to 85% \textit{SOC}. Values for the cut-off point have been tested and verified against different battery chemistries like NiZn and lithium-ion and are listed in Table 5.1.

![Energy Characteristic Curve](image)

**Figure 5.2: Different Regions of Energy Characteristic Curve**

Different models have been tried and tested to represent the lower nonlinear region and the upper nonlinear region of the energy characteristic curve. Some of them are discussed briefly in following sections.
Table 5.1: Cut-off Points for Different Cell Chemistries

<table>
<thead>
<tr>
<th>Battery Chemistries</th>
<th>Lower Cut-off point ($\alpha_1$)</th>
<th>Upper Cut-off point ($\alpha_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Zn</td>
<td>5% of (SOC)</td>
<td>70% of (SOC)</td>
</tr>
<tr>
<td>Lithium-ion</td>
<td>5% of (SOC)</td>
<td>85% of (SOC)</td>
</tr>
</tbody>
</table>

5.1.1 Model the Linear Region

To model the linear region of the energy characteristic curve, a straight line equation of the form $V = a(SOC) + b$ is used. A least-square regression technique is used to find the parameters $a$ and $b$, because all the data points of the linear region do not always fall on the best fit line. The straight line equation parameters, $a$ and $b$, are determined from a given set of data $(SOC_1, V_1), (SOC_2, V_2), ..., (SOC_n, V_n)$, where $n$ is the total data sets. The least-squared error solution [21] for the unknown coefficients $a$ and $b$ is obtained as,

$$b = \frac{\sum_{i=1}^{n} V \sum_{i=1}^{n} (SOC)^2 - \sum_{i=1}^{n} (SOC) \sum_{i=1}^{n} V (SOC)}{n \sum_{i=1}^{n} (SOC)^2 - (\sum_{i=1}^{n} (SOC))^2} \quad (5.1a)$$

$$a = \frac{n \sum_{i=1}^{n} V (SOC) - \sum_{i=1}^{n} V \sum_{i=1}^{n} (SOC)}{n \sum_{i=1}^{n} (SOC)^2 - (\sum (SOC))^2}. \quad (5.1b)$$

Thus, an approximation equation for the linear region of the energy characteristic is,

$$\hat{V} = a(SOC) + b. \quad (5.2)$$

Residual values and goodness-of-fit values are used to test the accuracy of approximated values $\hat{V}$. The residual error ($V - \hat{V}$) is the distance between the estimated values obtained from the model and the actual values. A goodness-of-fit
test tells how closely the predicted values match the actual values. The goodness of fit $R^2$ is given by,

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (V - \hat{V})}{\sum_{i=1}^{n} (V - \bar{V})}.$$  \hspace{1cm} (5.3)

5.1.2 Model the Nonlinear Region by Quadratic Form

A quadratic function can be used to model the lower nonlinear region and the upper nonlinear region of the energy characteristic curve and uses the form

$$V(t) = A(SOC)^2 + B(SOC) + C$$  \hspace{1cm} (5.4)

where, $V(t)$ and $(SOC)$ are an array of size $N$. This quadratic function should satisfy the points $[(SOC(0)), V(\beta_{nom})]$ and $[(SOC(\alpha_1)), V(\beta_1)]$, where $V(\beta_{nom})$ is equal to $V_{nom}$. Therefore, the Quadratic Equation 5.4 can also be expressed as,

$$V(\beta_{nom}) = A(SOC(0))^2 + B(SOC(0)) + C$$  \hspace{1cm} (5.5a)

$$V(\beta_1) = A(SOC(\alpha_1)^2) + B(SOC(\alpha_1)) + C$$  \hspace{1cm} (5.5b)

$$\frac{dV(t)}{d(SOC)}\bigg|_{V(t)=(SOC(\alpha_1))} = 2C(SOC(\alpha_1)) + B.$$  \hspace{1cm} (5.5c)

Subtracting Equation 5.5b from 5.5a, we have

$$V(\beta_1) - V(\beta_{nom}) = A \left[(SOC(\alpha_1)^2) - (SOC(0))^2\right] + B \left[(SOC(\alpha_1)) - (SOC(0))\right].$$  \hspace{1cm} (5.6)

Rearranging Equation 5.5c, we get

$$K_1 = 2C(SOC(\alpha_1)) + B.$$  \hspace{1cm} (5.7)
where, $K_1$ is the slope. On solving Equation 5.6 and Equation 5.7, the expressions for $A$, $B$ and $C$ become,

\[
A = \frac{[V(\beta_1) - V(\beta_{nom})] + K_1 [(SOC(\alpha_1)) - (SOC(0))]}{[(SOC(\alpha_1)) - (SOC(0))]^2} \quad (5.8a)
\]

\[
B = K_1 - 2C(SOC(\alpha_1)) \quad (5.8b)
\]

\[
C = V(\beta_1) - B(SOC(0)) - C(SOC(\alpha_1)^2). \quad (5.8c)
\]

An approximate value of $\hat{V}(t)$ is obtained by substituting the calculated values of $A$, $B$ and $C$ into Equation 5.4. The sum-of-squared error is computed by using an approximate value $\hat{V}(t)$ and real time data $V(t)$. The simulation result shows that this model gives satisfactory results for the upper nonlinear region, but it gives a significantly higher amount of error for the lower nonlinear region. Therefore, other techniques have been studied to accurately model the nonlinear regions of the energy characteristic curve.

5.1.3 Modeling the Nonlinear Region by an Exponential Form

To better represent the lower nonlinear region, an exponential expression in the following form is considered.

\[
V(t) = A \exp^{B(SOC)} + C \quad (5.9)
\]

where $A$, $B$ and $C$ are constant coefficients and $B$ is either negative or positive. The least-squares approach and the iteratively-reweighted-least-squares approach are used to solve Equation 5.9, which is used to predict the nonlinear regions of a cell.
5.1.4 Least-Squares-Approach to Solve Exponential Equation

The Equation 5.9 can be written in matrix form as,

\[
\begin{pmatrix}
V_1 \\
V_2 \\
\vdots \\
V_n
\end{pmatrix} =
\begin{pmatrix}
\exp^{B(SOC_1)} & 1 \\
\exp^{B(SOC_2)} & 1 \\
\vdots & \vdots \\
\exp^{B(SOC_n)} & 1
\end{pmatrix}
\begin{pmatrix}
A \\
C
\end{pmatrix}.
\]  

(5.10)

Let us consider

\[
\begin{pmatrix}
V_1 \\
V_2 \\
\vdots \\
V_n
\end{pmatrix} = \vec{V} \quad (5.11a)
\]

\[
\begin{pmatrix}
1 & \exp^{B(SOC_1)} \\
1 & \exp^{B(SOC_2)} \\
\vdots & \vdots \\
1 & \exp^{B(SOC_n)}
\end{pmatrix} = \phi \quad (5.11b)
\]

\[
\begin{pmatrix}
A \\
C
\end{pmatrix} = \vec{\theta} \quad (5.11c)
\]

where $\vec{V}$ is \( n \times 1 \) vector, $\phi$ is \( m \times n \) matrix and $\vec{\theta}$ is \( m \times 1 \) vector, and \( m = 2 \) here.

In vector form, the Equation 5.10 can be written as

\[
\vec{V} = \phi \vec{\theta} + \vec{\epsilon} \quad (5.12)
\]
where error $\vec{e}$ is an $n \times 1$ vector. If $B$ is known, then $\vec{\theta}$ becomes the least-squares solution for the Equation 5.9. Thus, the $\vec{\theta}$ that results in the smallest averaged squared error is found by letting,

$$\frac{\partial (R^2)}{\partial \vec{\theta}} = 0$$

where $R^2$ is the sum of the squares of the vertical deviations. So,

$$\frac{\partial (R^2)}{\partial \vec{\theta}} = \frac{\partial \left[ \frac{1}{2}(\vec{V} - \phi \vec{\theta})^T(\vec{V} - \phi \vec{\theta}) \right]}{\partial \vec{\theta}} = 0. \quad (5.13)$$

On simplifying, we get

$$(\phi^T \phi) \vec{\theta} = \phi^T \vec{V}. \quad$$

Solving for $\vec{\theta}$,

$$\vec{\theta} = (\phi^T \phi)^{-1} \phi^T \vec{V}. \quad (5.14)$$

The sum-of-squared error is defined as the sum of the square of the difference between the actual values to the approximated values from the model. This error is used to test how well the equation fits the real data. The sum-of-squared-error ($SSE$) is given by,

$$SSE = \sum_{i=1}^{i=n} (\vec{\phi} \vec{\theta} - \hat{V})^2 \quad (5.15)$$

where $\hat{V}$ is the experimental value and $\vec{V}$ is the approximated value.

Equation 5.9 can be solved by the least-squares method only if a pre-assumption about the coefficient $B$ is made. If the pre-assumed coefficient $B$ does not fit the model, a recalculation can be done for a new coefficient $B$. Thus an iteration method
is required to solve Equation 5.9 for the nonlinear region of a cell by the least-squares method, and the iteration method is explained in following steps:

- Step 1: Guess some value for $B$.
- Step 2: Find the value for $\phi$, by using Equation 5.11b.
- Step 3: Calculate the value of $\vec{\theta}$ from Equation 5.14.
- Step 4: Approximate $\hat{V}$, as $\hat{V} = \phi \vec{\theta}$
- Step 5: Find the value of $SSE$ for that approximated value $\hat{V}$.
- Step 6: Finally, compare $SSE$ value with the required criteria, and if $SSE$ is not acceptable, repeat the calculation from Step 1 by adjusting the coefficient $B$. The direction and magnitude of coefficient $B$ can be adjusted. Repeat these steps until the $SSE$ is acceptable.

The coefficient of the exponential equation obtained by the least squares approach to predict the nonlinear region of a cell has improved the approximation to some degree relative to the quadratic approach. In order to improve the accuracy level further, another technique for obtaining appropriate coefficients of the exponential equation for the nonlinear region has been studied.

5.1.5 Iteratively-Reweighted-Least-Square Approach to Solve Exponential Equation

The weighted-least-squares technique is better for those data sets where some points are considered as better controlled points than others. In the case of batteries, data
at the transition points between two regions are considered more important. Therefore, an approximation can be improved by assigning a weight on the error for those important data points.

Thus the Equation 5.12 is further modified as,

\[ WV = W \phi \bar{\theta} \]  \hspace{1cm} (5.16)

where \( W \) is the weight matrix,

\[
W = \begin{pmatrix}
  w_1 & 0 & \ldots & 0 \\
  0 & w_2 & \ldots & 0 \\
  \vdots & \vdots & \ddots & \vdots \\
  0 & 0 & \ldots & w_n \\
\end{pmatrix}
\]  \hspace{1cm} (5.17)

The values \( w_i \) of the diagonal matrix \( W \) are chosen in a way to add more weight on important data points and add less weight on less important data points. The additional weighting term modifies the parameter estimation Equation 5.14 as,

\[
\bar{\theta} = \left(\left(\phi^T W \phi\right)^{-1}\phi^T W V\right)
\]  \hspace{1cm} (5.18)

Based upon the error criteria, different values for the weight \( w_i \) can be used in a diagonal weight matrix \( W \). Some common examples for \( w_i \) are

- \( w_i = 1/(V_i - \hat{V}_i) \), where the value of the weight is the inverse of the residual error,
- \( w_i = 1/(V_i - \hat{V}_i)^2 \), where the value of the weight is the inverse of the sum of the square of error,
• \( w_i = 1/\sigma \), where the value of the weight is the inverse of the standard deviation,

• \( w_i = 1/\sigma^2 \), where the value of the weight is the inverse of the variance.

To clearly understand the application of the weighted-least-squares method to approximate an equation for the nonlinear region of the energy characteristic curve of a cell, similar dummy data has been taken and modeled by applying weights. Figure 5.3 shows how the weighted technique makes a difference in curve fitting. As a result of adding more weight on last three sample values, the weighted curve is more influenced toward those sample values compared to the unweighted curve.

![Figure 5.3: Comparison Between Weighted and Unweighted Curve Fitting Technique](image)

Figure 5.3: Comparison Between Weighted and Unweighted Curve Fitting Technique

Similar mathematics are required to determine appropriate coefficients of the equation which fits the energy characteristic curve of a cell. The energy characteristic curve is first split into three different regions and every region is modeled individually.
It is obvious that the starting and ending data points of the split regions have more influence for accurate recovery of the whole curve. After becoming deeply familiar with the nature of the energy characteristic curve of a cell, more weights are added at the starting and ending data points of those split regions.

For the lower nonlinear region, the value of weight for the diagonal matrix $W$ is

$$w_i = \begin{cases} 
1 & \text{if } 0\% \leq SOC \leq (SOC(\alpha_1) - 1)\% \\
k_1(n - i) & \text{if } (SOC(\alpha_1) - 1)\% < SOC \leq SOC(\alpha_1)\% 
\end{cases}$$

(5.19)

where, $k_1$ is a constant and $n$ is the number of diagonal elements of the weight matrix $W$. Similarly, for the upper nonlinear region, the value of weight for the diagonal matrix $W$ is

$$w_i = \begin{cases} 
k_2(m - i) & \text{if } SOC(\alpha_2)\% \leq SOC \leq (SOC(\alpha_2) + 3)\% \\
1 & \text{if } (SOC(\alpha_2) + 3)\% < SOC \leq 100\% 
\end{cases}$$

(5.20)

where, $k_2$ is a constant and $m$ is the number of diagonal elements of the weight matrix $W$. The parameters $k_1$ and $k_2$ are changed until the solution meets the required error criteria.

5.1.6 Algorithm to Model the Energy Characteristic Curve

Figure 5.4, Figure 5.5 and Figure 5.6 show the algorithms of the autonomous program designed to approximate the energy characteristic curve of a cell. The autonomous program implements the linear regression technique, the least-squares technique and the iteratively-reweighted-least-squares technique to estimate the unknown parameters of the system. In the first stage, the real data: cell voltage $V$, cell current $I$,
and time $t$ are loaded in the autonomous program. The data are then split into their respective regions based upon the criteria for the selecting regions. In addition, the linear region of a cell is modeled in this step by using the least-squares approximation technique. The procedures under the first stage of the autonomous program are illustrated by Figure 5.4.

In the second stage as shown by Figure 5.5, the real data that falls under the upper nonlinear region and the lower nonlinear region are processed individually. For both regions, the autonomous program computes all unknown parameters for their respective models. The least-squares approach is used to compute unknown parameters. Based upon the comparison, the best values for all unknown parameters are determined and stored. The stored parameters along with their respective real data are forwarded into the next stage, i.e third stage.

Figure 5.6 shows the third stage of the autonomous program. Based on the comparison results, the computed parameters are further refined to enhance the approximation. Here, the real data are weighted. The system parameters are recomputed by increasing the precision on the previously recomputed parameters, from the second stage. It uses an adaptive-reweighted-least-squares technique to compute the best parameters for the system. The recalculated parameters are checked with the error criteria. When the error criterion is not met, all the parameters are recomputed by changing weights. The magnitudes of the weights are changed in either direction depending upon the feedback signal. This iteration process is continued until all of these recomputed parameters offer the minimum possible error.
Start

Load experimental values \( I, T \) and \( V \)

Compute \( SOC \)

Check \( SOC \)

\( SOC > 88\% \)

\( SOC < 21\% \)

\( 21\% \leq SOC \leq 88\% \)

(Upper Exponential Region)
Approximate \( \hat{V} \)

(Linear Region)
Approximate \( \hat{V} \) and compute error \((e)\)

(Lower Exponential Region)
Approximate \( \hat{V} \)

Check error \((e)\)

\( e \leq \min \)

\( e > \min \)

Re-approximate \( \hat{V} \) by passing through neighbor points

Merge three regions

Stop

Figure 5.4: Algorithm for the First Stage
Load experimental values $I, T$ and $V$

Initialize $B = -20$ and $i = 1$

Approximate $\hat{V}$ and $SSE$

Is matrix $\phi$ Singular? 

If not, approximate $\hat{V}$ and $SSE$

If $SSE < 0.002$?

Store $B$ on $x_i$, $i = i + 1$

$B = B + 0.001$

Is $-20 \leq B \leq 20$ ?

Yes

No

Figure 5.5: Algorithm for the Second and the Third Stages
Figure 5.6: Algorithm for the Second and the Third Stages
5.2 Electric Circuit Battery Model

An accurate electrical circuit model is required to represent the dynamic relationship between the battery terminal voltage and current. This section deals with designing an accurate and simple circuit model by including the important cell dynamics. Figure 5.7 shows the simplest battery model that accounts for most of the cell behavior. A parallel $R_D C_D$ [24] circuit is used in series with the resistor and capacitor in order to account for the diffusion process that goes inside a cell to transfer the ions. The series resistor ($R_\Omega$) is used to model the instantaneous charge transfer process. The capacitor ($C_S$) is added in series with the resistor to account for the charge storage capability of a cell and is often termed as the effective storage capacitance of a cell.
Finally, a self discharge resistance \((R_{SD})\) is used to model the self discharge process (energy loss) of a cell. The following sections deal with the calculation of the circuit parameters from the experimental data.

5.3 Parameter Calculation for the Electric Circuit Model using Experimental Values

Following subsections explain the procedures used to generate the formulae to calculate the battery parameters.

5.3.1 Calculation of the Internal Resistance of a Cell

The internal resistance is a measure of how well the electrolyte diffuses inside a cell. The internal resistance also limits the available current and power from a cell. If the resistance of a cell changes with respect to the state-of-charge of a cell, it is termed Dynamic Resistance. The relation for dynamic resistance is,

\[
R(SOC_i) = \frac{V_{IN}(SOC_i) - V_{OUT}(SOC_i)}{I_{IN}(SOC_i) - I_{OUT}(SOC_i)}. \tag{5.21}
\]

Figure 5.8 is the experimental result of a NiZn cell, which shows how the internal resistance changes with respect to the state-of-charge of a cell. It can be obtained by using the above relation for dynamic resistance on experimental data of a cell for a one complete cycle. The total internal resistance \((R_T)\) of a cell for a cycle is taken as the mean value of the dynamic resistance \(R(SOC_i)\) for that cycle. Figure 5.9 shows the experimental results of the total internal resistance of a typical NiZn cell versus cell life. The following relation is used to calculate the total internal
Figure 5.8: Internal Resistance Versus SOC for a NiZn Cell

The resistance of a cell per cycle:

\[ R_T = \frac{\sum_{i=1}^{n} R(SOC_i)}{n} \]  

(5.22)

It should be noted that this calculation assumes that a constant charge or discharge current has been applied for enough time for the ionic diffusion to reach steady-state, thus giving the total resistance, \( R_T = R_\Omega + R_D \).

5.3.2 Calculation of the Diffusion Terms (\( R_D \) and \( C_D \)) and the Ohmic Resistance Term (\( R_\Omega \)) of the Electrical Circuit Model of a Cell

The \( C_D \) and \( R_D \) terms of Figure 5.7 represent the diffusion process that occurs inside a cell to transport the ions from one terminal to the another terminal. The short
transient seen in a cell voltage profile is the result of the diffusion. Thus, the parameters $C_D$ and $R_D$ are added in the electric circuit model to model the diffusion process which finally helps to predict the transient response of a cell.

As we know, the linear differential equation for any series $RC$ circuit is,

$$C \frac{dV}{dt} + \frac{V}{R} = 0. \quad (5.23)$$

Solving the linear differential equation for $V$ yields,

$$V(t) = V_0 \exp \left( -\frac{t}{RC} \right) \quad (5.24)$$

where, $V_0$ is the capacitor voltage at time $t = 0$. $RC = \tau$ is the time constant. The time constant is the time required for the voltage to fall to $V_0/e$ from the steady state.
To create an artificial voltage transition to extract the diffusion parameters, a short pulse of zero current is applied in the cell charging and discharging process for a short period of time. The short pulse of zero current allows the $RC$ components of a cell to show an exponential decay response as suggested by the Equation 5.24. Figure 5.10 is the experimental result of the voltage transient response obtained by the application of the zero current pulse. The phenomenon that is observed during the interval of the zero current pulse is utilized to estimate the diffusion parameters $C_D$ and $R_D$. For the exponential decay, the voltage response is assumed to be,

$$V(t) = V_0 \exp\left(-\alpha t\right).$$  \hspace{1cm} (5.25)

Figure 5.10: Observed Voltage Response for Short Pulse of Zero Current
This equation is rearranged to yield,

\[ \frac{V(t)}{V_0} = \exp(-\alpha t). \]

For \( x\% \) decay from its steady state, we can write

\[ \frac{V(t)}{V_0} = \exp(-\alpha T_{x\%}) = x\% \]

where \( T_{x\%} \) is the time required to decay to \( x\% \). Then

\[ -\alpha T_{x\%} = \ln(x\%) \]

\[ T_{x\%} = -\frac{\ln(x\%)}{\alpha}. \]

Therefore,

\[ \alpha = \frac{1}{\tau} = \frac{1}{R_D C_D} = -\frac{\ln(x\%)}{T_{x\%}}. \quad (5.26) \]

Figure 5.10 shows that the transient seen in the middle of the voltage profile curve does not reach the steady state before it resumes the normal charging process because of the insufficient rest period allowed, at the middle of the charging process. The exact time required for any cell voltage to reach the steady state is usually long. The steady state voltage level and the time required for the cell to reach the steady state voltage level is approximated by projecting the voltage decay curve toward the zero Nernst curve of the cell. The approximation procedures for the steady state voltage level \( V_A \) is explained in following steps.

- Step 1: First, voltage \( V_D \) and charge \( Q_D \) are extracted from the voltage-charge profile curve of the charging process, where \( V_D \) and \( Q_D \) are the voltage level and the charge level at the beginning of the rest period.
• Step 2: Secondly, voltage $V_X$ is extracted from the voltage-charge profile curve of the discharging process, where $V_X$ is the voltage level at the discharge curve for charge $Q_D$.

• Step 3: The steady state voltage level ($V_A$), the voltage level a cell could reach if a sufficient rest period is allowed, is approximated by averaging the voltage $V_D$, and the voltage $V_X$. Figure 5.11 shows the voltage levels $V_D$, $V_X$ and $V_A$ in the voltage-charge profile curve. Figure 5.12 shows the zoomed in version of the voltage transient response for the zero current pulse where the blue dotted line is the projected voltage response toward the steady state.

Figure 5.11: Illustration of Voltage Levels $V_D$, $V_A$ and $V_X$
Figure 5.12: Zoomed in Version of the Voltage Transient Caused by the Diffusion

In order to calculate the diffusion parameters from the experimental data, as referred by Figure 5.12, $\tau$ is calculated as,

$$
T_{V_B} = t_1 - t_0
$$

$$
V_B\% = \frac{V_B * 100}{V_C - V_A} \%
$$

$$
\tau = \frac{T_{V_B}}{-\ln(V_B\%)},
$$

(5.27)

The diffusion capacitance $C_D$ is,

$$
C_D = \frac{-T_{V_B}}{\ln(V_B\%)/R_D}
$$

(5.28)

and, the diffusion resistance ($R_D$) is,

$$
R_D = R_T - R_\Omega.
$$

(5.29)
The ohmic resistance term \( R_\Omega \) is responsible for the instantaneous voltage transient and can be approximated from the experimental data by using the following relation:

\[
R_\Omega = \frac{V_D - V_C}{I(t_0 + \Delta t) - I(t_0)}
\]  \hspace{1cm} (5.30)

where, \( \Delta t \) is the sampling time.

Hence, the \( R_\Omega \), \( R_D \) and \( C_D \) terms of the electric circuit model of a cell can be obtained from the experimental data by using the above discussed relations.

5.3.3 Calculation of the Self-discharge Resistance \( R_{SD} \) and Storage Capacitance \( C_S \) of the Electric Circuit Model

The self-discharge resistance \( R_{SD} \) is a measure of how much of the stored energy becomes unavailable for use due to charge transferring between the electrodes inside the cell. This can be due to secondary reactions or due to direct electrical connections between the electrodes. Therefore, a high self-discharge resistance is good as it prevents self-discharge. The self-discharge resistance is added in the electric circuit model in parallel to the storage capacitance and open circuit voltage to account for that lost energy. Based on the energy characteristic curve of a cell as shown by Figure 2.5, a relation is formed to calculate the self-discharge resistance of the cell and is derived as,

\[
Q_{LOSS} = Q_{in} - Q_{out}
\]
where, \( Q_{in} \) is the charge supplied to the cell and \( Q_{out} \) is the charge supplied by the cell. As,

\[
Q_{LOSS} = \int I_{LOSS} dt,
\]

assuming \( I_{LOSS} \) is constant, then\[
I_{LOSS} = \frac{Q_{LOSS}}{T}.
\]

Using Ohm's Law

\[
V = I_{LOSS}R_{SD}
\]

where, \( V \) is the rated voltage of a cell. Therefore, the self-discharge resistance \( (R_{SD}) \) is given as,

\[
R_{SD} = \frac{V}{I_{LOSS}}. \quad (5.31)
\]

The charge storage capacitance \( (C_S) \) of a cell is the effective capacitance of a cell as determined by the slope of the Nernst curve as discussed in the previous chapter. The instantaneous capacitance of a cell is the ratio of the change in charge stored to the change in voltage of a cell. Thus, for a cell, storage capacitance \( (C_S) \) is,

\[
C_S = \frac{\Delta q}{\Delta v} \quad (5.32)
\]

where \( \Delta q = \alpha_2 - \alpha_1 \) and \( \Delta v = \beta_2 - \beta_1 \) and \( \alpha_1, \alpha_2, \beta_1 \) and \( \beta_2 \) are determined from the linear region of voltage-charge profile curve as shown by Figure 5.2.

Figures 5.13 and 5.14 are the experimental results of storage capacitance and self-discharge resistance of a NiZn cells. These figures show the change of the
storage capacitance, and of the self-discharge resistance with respect to the cell cycle number. As shown in the figure, the self-discharge resistance eventually decreases to a point that the cells could no longer maintain a charge between the electrodes, which appears to be the primary cause of cell failure. Table 5.2 shows a list of all the average parameter values of the electric circuit model for different cells that were tested in the laboratory.
Table 5.2: Parameters Obtained from Experimental Results of Different Batteries

<table>
<thead>
<tr>
<th>Cells</th>
<th>$\bar{R}_\Omega$ (Ω)</th>
<th>$\bar{R}_D$ (Ω)</th>
<th>$\bar{C}_D$ (kF)</th>
<th>$\bar{C}_S$ (kF)</th>
<th>$\bar{R}_{SD}$ (Ω)</th>
<th>$\bar{R}_T$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>72</td>
<td>-</td>
<td>0.366</td>
</tr>
<tr>
<td>Type II</td>
<td>0.0145</td>
<td>0.22</td>
<td>17</td>
<td>63</td>
<td>75.60</td>
<td>0.234</td>
</tr>
<tr>
<td>Type III</td>
<td>0.021</td>
<td>0.24</td>
<td>13</td>
<td>71</td>
<td>41.09</td>
<td>0.225</td>
</tr>
<tr>
<td>Type IV</td>
<td>0.022</td>
<td>0.217</td>
<td>14</td>
<td>60</td>
<td>55.03</td>
<td>0.236</td>
</tr>
<tr>
<td>Type V</td>
<td>0.013</td>
<td>0.27</td>
<td>12</td>
<td>82</td>
<td>80.6</td>
<td>0.242</td>
</tr>
<tr>
<td>Type VI</td>
<td>0.017</td>
<td>0.233</td>
<td>16</td>
<td>73</td>
<td>550.53</td>
<td>0.250</td>
</tr>
<tr>
<td>Type VII(a)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>72</td>
<td>438.6</td>
<td>0.370</td>
</tr>
<tr>
<td>Type VII(b)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>-</td>
<td>0.362</td>
</tr>
<tr>
<td>Type VIII</td>
<td>0.19</td>
<td>0.27</td>
<td>17</td>
<td>64</td>
<td>847.5</td>
<td>0.46</td>
</tr>
<tr>
<td>Type IX</td>
<td>0.03</td>
<td>0.24</td>
<td>13</td>
<td>20</td>
<td>908.3</td>
<td>0.27</td>
</tr>
<tr>
<td>Type X</td>
<td>0.028</td>
<td>0.031</td>
<td>92</td>
<td>20</td>
<td>615.4</td>
<td>0.06</td>
</tr>
<tr>
<td>Type XI(a)</td>
<td>0.06</td>
<td>0.38</td>
<td>12</td>
<td>31</td>
<td>158.58</td>
<td>0.44</td>
</tr>
<tr>
<td>Type XI(b)</td>
<td>0.038</td>
<td>0.28</td>
<td>14</td>
<td>33</td>
<td>280.11</td>
<td>0.318</td>
</tr>
</tbody>
</table>

The Type VII(a), Type VII(b) are two similar NiZn cells that used same eVionyx membrane, Type XI(a) is a commercial LiFePO4 cell and Type XI(b) is a commercial LFP 18650P cell.
Figure 5.13: Self-discharge Resistance versus Cell Life for a NiZn Cell

Figure 5.14: Storage Capacitance versus Cell Life for a NiZn Cell
5.4 Important Parameters of the Cell with their Experimental Values

In addition to the electric circuit model, other parameters like energy loss, energy efficiency and capacity of a cell are equally important to understand the cell behavior. These additional parameters with their respective importance, are already discussed in the previous chapter. This section presents the experimental values for the energy loss ($E_{\text{LOSS}}$), the energy efficiency $\eta$ and the capacity versus cell numbers. Table 5.3 summarize these parameters values for different cell chemistries. The relations that are used to calculate the Energy $E$, Energy Loss ($E_{\text{LOSS}}$), the Charge $Q$, the Charge Efficiency ($\eta_Q$), the charge Loss ($Q_{\text{LOSS}}$) and the Energy Efficiency ($\eta_E$) are listed below:

**Energy:** $E = \int_{t=0}^{t=T} VIdt$, where $T$ is the time required for the cell to charge or discharge.

**Energy Loss:** $E_{\text{LOSS}} = E_{\text{in}} - E_{\text{out}}$ where, $E_{\text{in}}$ is the energy delivered to the cell and $E_{\text{out}}$ is the energy delivered by the cell.

**Charge:** $Q = \int_{t=0}^{t=T} Idt$

**Charge Efficiency:** $\eta_Q = \frac{Q_{\text{out}}}{Q_{\text{in}}} 100\%$

**Charge Loss:** $Q_{\text{LOSS}} = Q_{\text{in}} - Q_{\text{out}}$

**Energy Efficiency:** $\eta_E = \frac{E_{\text{out}}}{E_{\text{in}}} 100\%$

In order to characterize the battery well, the behavior of the above mention parameters with respect to cell life are observed for different cell chemistries. The figures
below show the change in the energy loss, cell capacity, cell efficiency and cell self-
discharge resistance for different Type cells. By observing those plots, it is clear that
the parameters like energy efficiency and capacity decrease with the increasing cell
usage.
Figure 5.15: Loss Energy Versus Cell Life of a Typical NiZn Cell

Figure 5.16: Capacity Versus Cell Life of a Typical NiZn
Figure 5.17: Self-discharge Resistance Versus Cell Life of a Typical NiZn Cell

Figure 5.18: Energy Efficiency Versus Cell Life of a Typical NiZn Cell
Table 5.3: List of Important Parameters obtained from the Experiments for Different Batteries

<table>
<thead>
<tr>
<th>Cells</th>
<th>Max. $C$</th>
<th>$\bar{C}$</th>
<th>Cell Life</th>
<th>$\eta_Q$</th>
<th>$E_{Loss}$</th>
<th>$\eta_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(amp-hours)</td>
<td>(amp-hours)</td>
<td>(cycles)</td>
<td></td>
<td>(amp-hours)</td>
<td></td>
</tr>
<tr>
<td>Type I</td>
<td>2.274</td>
<td>2.270</td>
<td>77</td>
<td>0.862</td>
<td>0.8595</td>
<td>0.78</td>
</tr>
<tr>
<td>Type II</td>
<td>2.05</td>
<td>1.94</td>
<td>60</td>
<td>0.86</td>
<td>0.87</td>
<td>0.818</td>
</tr>
<tr>
<td>Type III</td>
<td>1.87</td>
<td>1.53</td>
<td>80</td>
<td>0.70</td>
<td>1.518</td>
<td>0.78</td>
</tr>
<tr>
<td>Type IV</td>
<td>2.01</td>
<td>1.91</td>
<td>56</td>
<td>0.86</td>
<td>0.56</td>
<td>0.79</td>
</tr>
<tr>
<td>Type V</td>
<td>2.1535</td>
<td>1.9265</td>
<td>121</td>
<td>0.868</td>
<td>0.8945</td>
<td>0.7853</td>
</tr>
<tr>
<td>Type VI</td>
<td>2.11</td>
<td>2.06</td>
<td>37</td>
<td>0.89</td>
<td>0.75</td>
<td>0.85</td>
</tr>
<tr>
<td>Type VII(a)</td>
<td>2.173</td>
<td>1.752</td>
<td>64</td>
<td>0.77</td>
<td>1.274</td>
<td>0.69</td>
</tr>
<tr>
<td>Type VII(b)</td>
<td>2.2747</td>
<td>2.219</td>
<td>37</td>
<td>0.915</td>
<td>0.7133</td>
<td>0.8256</td>
</tr>
<tr>
<td>Type VIII</td>
<td>1.3</td>
<td>1.29</td>
<td>67</td>
<td>0.98</td>
<td>0.41</td>
<td>0.84</td>
</tr>
<tr>
<td>Type IX</td>
<td>3.7</td>
<td>3.68</td>
<td>42</td>
<td>0.99</td>
<td>0.16</td>
<td>0.99</td>
</tr>
<tr>
<td>Type X</td>
<td>3.7</td>
<td>3.66</td>
<td>78</td>
<td>0.98</td>
<td>0.35</td>
<td>0.98</td>
</tr>
<tr>
<td>Type XI(a)</td>
<td>1.4</td>
<td>1.4</td>
<td>500</td>
<td>0.99</td>
<td>0.31</td>
<td>0.94</td>
</tr>
<tr>
<td>Type XI(b)</td>
<td>1.1</td>
<td>1.1</td>
<td>500</td>
<td>0.99</td>
<td>0.17</td>
<td>0.96</td>
</tr>
</tbody>
</table>

The Type VII(a), Type VII(b) are two similar NiZn cells that used same eVionyx membrane, Type XI(a) is a commercial LiFePO4 cell and Type XI(b) is a commercial LFP 18650P cell.
Figure 5.19: Capacity versus Cell Age for Different Cell Chemistries

Figure 5.20: Charge Efficiency versus Cell Age for Different Cell Chemistries
Figure 5.21: Self-discharge Resistance versus Cell Age for Different Cell Chemistries

Figure 5.22: Energy Loss versus Cell Age for Different Cell Chemistries
The previous chapter discussed the method that are used model the energy characteristic curve (zero Nernst curve) and the electric circuit model of a cell. This chapter presents the results approximated by using the model discussed in the previous chapter. In addition this chapter also checks the validity of those models by comparing the approximated results with the experimental results.

6.1 Model validation for the Energy Characteristic Curve

To test the validity of the model for the energy characteristic curve, the model is tested against the cells of different chemistries such as NiZn, LiCo, LiMn and LiFePO₄. Different cell chemistries are chosen to test the model, as different cell chemistries offer different behaviors. Generally, different cell chemistries can have different ranges of open circuit voltages, battery power, self-discharge rates, cycle life and energy efficiencies. This section presents both the experimental results and the approximated results and their respective error curves for different cell chemistries such as NiZn, LiCo, LiMn and LiFePO₄.

In order to make a comparison between the real energy characteristic curve and the modeled energy characteristic curve, first the method that is used to calcu-
late the real energy characteristic curve from the experimental data is summarized. For the calculation of real energy characteristic curve, the information about the cell voltage, cell current and sampling time are required. Cell charge \( Q_r[n] \) and cell state-of-charge \( SOC[n] \) are calculated for every sampling time \( t_r[n] \) by utilizing that information. The information about charge, voltage and sampling times from every single cycle is split into two stages, namely the charging stage and the discharging stage. The charging stage information is \( Q_{rc}[n], V_{rc}[n], I_{rc}[n], SOC_{rc}[n] \) and \( t_{rc}[n] \), and the discharging stage information is \( Q_{rd}[n], V_{rd}[n], I_{rd}[n], SOC_{rd}[n] \) and \( t_{rd}[n] \). Then, the average values \( Q_{ra}[n], V_{ra}[n], SOC_{ra}[n] \) and \( t_{ra}[n] \) are calculated by using the information from the charging stage and the discharging stage. The curve obtained by plotting the average charge \( Q_{ra}[n] \) with respect to the sampling time \( t_{ra}[n] \) is the real energy characteristic curve and is often called zero Nernst curve of a cell.

The energy characteristic curves obtained by using the model explained in the Section 5.1 are presented here along with their real energy characteristic curves for comparison and model validation. Every first figure of the Figures 6.1, 6.2 and 6.3 show both the modeled and the real energy characteristic curves of a Type V (NiZn cell), Type IX (LiCo cell) and Type X (LiMn cell) respectively. For all the cases, the modeled energy characteristic curves appear to be almost the same as that of the real energy characteristic curves.

To check the accuracy of this model, the absolute error and the squared error are computed with respect to the sampling time. Every second and third figure of the
Figures 6.1, 6.2 and 6.3 reveal the absolute error and the sum-of-squared-error of a NiZn cell, a LiCo cell a LiMn cell respectively. For all cell chemistries, the comparison plot and the error plots demonstrate that the model produces accurate results for all regions (lower exponential region, linear region and upper exponential region) of the energy characteristic curve.

For a NiZn cell, the absolute error values are always less than 0.037 volts throughout the cycle. This implies that the approximated voltage for a NiZn cell does not deviate from the real value by more than ±0.037 volts. The \( SEE \) are almost zero for all the regions where the \( SOC \) is greater than 7%, and the \( SSE \) is less than 0.00015 for the remaining regions where the \( SOC \) is less than 7%. Thus, the model accuracy lies between (97.87% to 99%). For a LiCo cell, the absolute error values are always less than 0.029 volts. The SSE values are nearly zero for the regions where the \( SOC > 5\% \), and is less than 0.0001 for the \( SOC < 5\% \). For a LiCo cell, the model offers about 99.47% of accuracy. Finally, for LiMn cell, the absolute error values are always less than 0.04 volts and SSE is always less than 0.001. This model offers the accuracy of about 98.901% for LiCo cell.

The approximated values of the energy characteristic curve are close to the real values of the energy characteristic curve for all \( SOC \) values for all the cases. Similar results are observed on other different sets of experiments that are carried out on different cycle numbers and on different cells. Thus, by observing those results, it has been confirmed that the model approximation technique discussed in the previous chapter to model the energy characteristic curve is adequate.
Figure 6.1: Energy Characteristic Curve Comparison Between the Experimental Results and the Approximated Results, and their Error Curves for a Type V Cell
Figure 6.2: Energy Characteristic Curve Comparison Between the Experimental Results and the Approximated Results, and their Error Curves for a Type IX Cell
Figure 6.3: Energy Characteristic Curve Comparison Between the Experimental Results and the Approximated Results, and their Error Curves for a Type X Cell
6.2 Validity of the Electric Circuit Model

The determination of the parameters \((R_\Omega, C_S, R_D, C_D, R_{SD})\) of the electric circuit model was discussed in Section 5.3. This section is aimed to validate that electric circuit model by examining the response of the terminal voltage \(V_T(t)\). To analyze the circuit, the voltage equation for the electric circuit model shown by Figure 5.7 in the \(s\) domain is,

\[
V_T(s) = I(s)Z_{OUT} + V_{TH}.
\]  

(6.1)

The total impedance \(Z_{OUT}\) of the electric circuit model in the \(s\)-domain is,

\[
Z_{OUT} = \left[ R_D \left| \frac{1}{sC_D} \right| + R_\Omega + \left| \frac{1}{sC_S} \right| R_{SD} \right].
\]  

(6.2)

Thus,

\[
Z_{OUT} = \frac{R_D \cdot \frac{1}{sC_D}}{R_D + \frac{1}{sC_D}} + R_\Omega + \left( \frac{\frac{1}{sC_S}}{R_{SD}} \right) + R_{SD}.
\]

It is simplified as,

\[
Z_{OUT} = \frac{\frac{1}{sC_D}}{s + \frac{1}{R_D C_D}} + R_\Omega + \frac{\frac{1}{sC_S}}{s + \frac{1}{R_SD C_SD}}.
\]  

(6.3)

Now,

\[
V_{TH} = \left( \frac{R_{SD}}{R_{SD} + \frac{1}{sC_S}} \right) \frac{V_{OC}}{s}.
\]  

(6.4)

Therefore, the voltage response in the \(s\)-domain is

\[
V_T(s) = \left[ \frac{1}{s + \frac{1}{R_D C_D}} + R_\Omega + \frac{\frac{1}{sC_S}}{s + \frac{1}{R_SD C_SD}} \right] I(s) + \left( \frac{R_{SD}}{R_{SD} + \frac{1}{sC_S}} \right) \frac{V_{OC}}{s}.
\]  

(6.5)

As, the current \(I(s)\) is constant for the experimental setup, current in the \(s\)-domain \(I(s)\) becomes

\[
I(s) = \frac{I_K}{s}.
\]

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where $I_K$ is the constant current rate chooses to charge or discharge a cell. Thus, the voltage response $V_T(s)$ is further simplified as

$$V_T(s) = \left( \frac{\frac{1}{C_D}}{s + \frac{1}{R_D C_D}} \right) I_K + \frac{I_K}{s} + \left( \frac{\frac{1}{C_S}}{s + \frac{1}{C_S R_{SD}}} \right) I_K + \left( \frac{R_{SD}}{R_{SD} + \frac{1}{s C_S}} \right) \frac{V_{OC}}{s} \tag{6.6}$$

$$V_T(s) = I_K R_D \left\{ \frac{1}{s} - \frac{1}{s + \frac{1}{R_D C_D}} \right\} + R_\Omega I_K \left\{ \frac{1}{s} - \frac{1}{s + \frac{1}{C_S R_{SD}}} \right\} + V_{OC} \left( \frac{1}{s + \frac{1}{C_S R_{SD}}} \right) \tag{6.7}$$

Taking the inverse Laplace transform, the voltage response of the electric circuit model $V_T(t)$ is

$$V_T(t) = I_K R_D \left( 1 - e^{-\frac{t}{R_D C_D}} \right) + I_K R_\Omega + I_K R_{SD} \left( 1 - e^{-\frac{t}{C_S R_{SD}}} \right) + V_{OC} e^{-\frac{t}{C_S R_{SD}}} \tag{6.8}$$

Therefore,

$$V_T(t) = I_K R_D \left( 1 - e^{-\frac{t}{R_D C_D}} \right) + I_K (R_\Omega + R_{SD}) + (V_{OC} - I_K R_{SD}) e^{-\frac{t}{C_S R_{SD}}} \tag{6.9}$$

Hence this is the voltage response of the designed electric circuit model. This model is strictly applied on the middle of the operating window.

In order to test the validity of the derived voltage response of the electric circuit model, the voltage response is first simulated. During simulation, the coefficients $(R_\Omega, R_D, C_D, C_S$ and $R_{SD})$ of the voltage response of Equation 6.2 are calculated by extracting the information about time, voltage and current of a cell from the experimental setup. The calculation procedure of those coefficients is already discussed in Section 5.3. This section discusses how the voltage response $V_T(t)$ is implemented by utilizing those coefficients. For the ease of implementation of those equations in
computation, the continuous voltage signal $V_T(t)$ is converted as

$$V_T[n] = V_{OC} + V_S[n] + V_\Omega[n] + V_D[n]$$

(6.10)

where $n$ is the discrete-time subscript and $V_{OC}$ is the standard voltage of a cell. As we know,

$$V_\Omega[n] = I[n] R_\Omega$$

$$V_S = \frac{Q_s[n]}{C_S}$$

$$V_D = \frac{Q_D[n]}{C_D}.$$  

Thus, Equation 6.10 can be rewritten in the form

$$V_T[n] = V_{OC} + I[n] R_\Omega + \frac{Q_s[n]}{C_S} + \frac{Q_D[n]}{C_D}.$$  

(6.11)

where $Q_S[n]$ is the charge of the capacitance term and $Q_D[n]$ is the charge of the diffusion terms and $C_S$ and $C_D$ are the capacitance values that model the diffusion process and storage process respectively. These relations are used to simulate the voltage response for any cell. In order to implement the voltage response $V_T[n]$ on computer, an iteration method is used and is explained in following steps.

1. All coefficients of the voltage response equation are calculated for the cycle, one is interested in.

2. Initialize $Q_D[1] = 0$ and $Q_S[1] = 0$ and choose some value for sampling time $T$.

3. Perform following steps for $1 \leq n \leq N - 1$, where $N$ is the total sample number.

   (a) $\dot{Q}_D[n] = -\frac{1}{R_D C_D} Q_D[n] + I[n]$. 

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(b) $Q_D[n + 1] = Q_D[n] + T\dot{Q}_D[n]$.

(c) $\dot{Q}_S[n] = I[n] - \frac{V_{OC} + \frac{Q_S[n]}{V_S}}{R_{SD}}$.

(d) $Q_S[n + 1] = Q_S[n] + T\dot{Q}_S[n]$.

(e) For Linear Region: $V_S[n] = a * Q_S[n] + b$. 

For Nonlinear Region: $V_S[n] = A * \exp^{B*Q_S[n]} + C$.

(f) $V_D[n] = \frac{Q_D[n]}{C_D}$.

(g) $V_\Omega[n] = I[n]R_\Omega$.


4. Increment $n$ by 1 and go to step 3 until $n \leq N - 1$.

6.3 Results

The relations explained in Section 6.2 are implemented in MATLAB to simulate voltage and charge responses for different cell chemistries. Results obtained from the simulation are categorized into two parts, where the first part compares the simulated voltage response with the real voltage response, and the second part compares the simulated cell charge with the real cell charge.

Figure 6.4 and Figure 6.5 show simulated voltage values and real voltage values for the first six cycles, and for the first fifteen cycles of a Type V (NiZn) cell respectively. Similarly, Figure 6.6 and Figure 6.7 shows the simulated and real voltage of a Type X (LiMn) cell. The real voltage values are the recorded values from the experimental setup and simulated voltage values are the estimated values.
Figure 6.4: Simulated Voltage and Experimental Voltage of a Type V Cell

Figure 6.5: Simulated Voltage and Experimental Voltage of a Type V Cell
Figure 6.6: Single Cycle that Shows Simulated Voltage and Experimental Voltage of a Type X Battery

Figure 6.7: First Few Cycles of Simulated Voltage and Experimental Voltage of a Type X Battery

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Figure 6.8: Residual Error of the Simulated Voltage ($V_T$) for a Charging and Discharging process for a typical Type V Cell

Figure 6.9: Squared Error of the Simulated Voltage ($V_T$) for a Charging and Discharging process for a typical Type V Cell
Figure 6.10: Absolute Error of the Simulated Voltage ($V_T$) for a Charging and Discharging process for a Type X Battery

Figure 6.11: Squared Error of the Simulated Voltage ($V_T$) for a Charging and Discharging process for a Type X Battery
from the above discussed relations. It appears that the simulated voltage profile is similar to the real voltage profile. Thus, to check the accuracy level of the simulation, residual error and squared error are computed. Figure 6.8 and Figure 6.9 present the residual errors and squared errors of the simulated voltage response of a Type V cell respectively, and Figure 6.10 and Figure 6.11 show the residual error and squared error of the simulated result response of a Type X battery respectively.

These error plots and the voltage comparison plots clearly show that the simulated voltage is consistent to the real voltage level irrespective of the SOCl of the cell. The small wiggle that appears in the middle of every stage of every cycle is the result of the implementation of small rest period. The simulated voltage jumps seen at the beginning, middle (rest period) and ending of the every cycle is approximately same as that of the voltage jumps that occurred at the real voltage profile. Further, it is also noticed that the simulated voltage profile is excellent at the linear and upper nonlinear regions and is satisfactory at the lower nonlinear region.

For all the scenarios, the residual error and the squared error are nearly zero for the SOCl values that lies in between 10\% to 97\%. The lower part of the lower exponential region and the upper part of the upper exponential region suffer from some voltage degradation. The simulated voltage degrades from the real voltage by no more than 0.1 volts and the degradation occurs only at the transition stages. Beside the small degradation seen at the transition regions, the error is nearly zero for other regions. Similar results are observed while running the simulation on multiple different cells. By analyzing those results, it has been observed that the above
discussed simulation approach can offer the accuracy of about 98% at the transition regions and almost 99% at other regions while estimating the voltage response for most of the cells.

The second part of the simulation focuses on estimation of the charge of a cell. This remaining part of this section presents the simulation results and their corresponding errors. Figure 6.12 and 6.14 show the simulated charge and the real charge (integrated current) of the charging stage and discharging stage respectively, of a Type V (NiZn) cell for a randomly picked cycle number. Similarly Figure 6.16 and Figure 6.18 present the simulated charge for a Type X (LiMn) battery respectively. It has been noticed that the simulated charge has almost the same values as that of the real charge for almost all regions excluding the transition regions that occur at the beginning and ending of any cycle. The simulation results suffer from some fluctuations at the transitional regions. The small jumps seen at the middle of the operating window is the result of the rest period. The rest period at the middle of the charge-discharge process lets the cell to show its diffusion mechanism. As a result, the simulated charge responses also show some degradation at that artificial transition regions too.

In order to check the accuracy of the simulated charge responses of different cells, different errors are estimated and checked. Figure 6.13 and Figure 6.15 show the squared-errors for the charging stage and the discharging stage of the simulated charge responses of a NiZn cell respectively and Figure 6.17 and Figure 6.19 illustrate the squared-errors of the charge response of a LiMn cell respectively. The squared-error
Figure 6.12: Simulated and Experimental Charge for the Charging Stage of a Type V Cell

Figure 6.13: Squared Error of the Simulated Charge of a Type V Cell for the Charging Stage
Figure 6.14: Simulated and Experimental Charge of the Charging Stage of a Type X Battery

Figure 6.15: Squared Error of the Simulated Charge of a Type X Battery for Charging stage
Figure 6.16: Simulated and Experimental Charge for the Discharging Stage of a Type V Cell

Figure 6.17: Squared Error of the Simulated Charge of a Type V Cell for the Discharging Stage
Figure 6.18: Simulated and Experimental Charge of a Discharging Stage of a Type X Battery

Figure 6.19: Squared Error of the Simulated Charge of a Type X Battery for the Discharging Stage
of the simulation results for different cell chemistries are never greater than 0.003. Similar results were recorded while performing similar simulations for different data sets of different cells on different cycle numbers. The validity of the electric circuit model is unquestionable as the error level is sufficiently low.
Data are collected by cycling (charging-discharging) electrochemical cells of different chemistries such as NiZn, LiMn and LiCo until they reach the end of their life cycle. Batteries of different chemistries are monitored throughout their lifetime by varying charge-discharge rates to observe the role of these parameters on the battery life. Those collected data are used to identify the important parameters of a cell. Those parameters are used to characterize and model the specific cell.

A battery model suggested by this thesis includes all the cell dynamics and is applicable to most batteries. This thesis used different approach to model the battery performance. It uses the electric circuit model to model the linear region, and it uses an exponential form to model the nonlinear region of the battery. The model suggested by this thesis can approximate the energy characteristic curve, voltage profile curve and charge profile curve for different cell chemistries and is verified against experimental results. The approximate charge profile curve and voltage profile curve obtained by utilizing the model derived by this thesis exactly follows the same path as followed by the real voltage profile curve for all regions. It offers relative accuracy greater then 97% in every case studied. The model results are consistent and in an acceptable range for Li-based cell and NiZn cell.
This research can be extended for other chemistry cells. The parameter identification to model the energy loss due to the gas formation can be done to further improve the accuracy of the model. This model is tested at the temperature the cell has during the experiment. Reidentification of the parameters are needed if the temperature is changed.

Another idea to extend this research is to study the battery performance for specific applications, so that the performance may be optimized. The model is generally useful for most battery applications such as electric vehicles and autonomous robots.

The parameter identification algorithm can be adapted for use in real-time parameter identification, monitoring, and tracking. Doing this allows for determination of cell state-of-life and cell state-of-health.
BIBLIOGRAPHY


APPENDIX
SOFTWARE

This appendix includes all the programs that are used to extract and calculate battery parameters from experimental data and simulate the voltage profile curve based on those calculated parameters. The programs are separated into two parts. First part deals on the coefficients calculation and model identification. Second part presents the code for the model simulation.

Model Identification

This section includes the MATLAB programs that are used to identify, calculate and plot all the battery parameters.

```
clc; clf; clear all; close all;
filenameRawdata = 'LiMg.txt';
filenameOutput1 = 'LiMg-output1.txt';
filenameOutput2 = 'LiMg-output2.txt';
filenameOutput3 = 'LiMg-output3.txt';
filenameExponential = 'LiMg-exponential_opt.txt';
filenameLinear = 'LiMg-liner_opt.txt';
filenameOutput4 = 'LiMg-output4.txt';
C_pick_point = 75;  % pick the percentage value of the average capacitance for calculation of the capacitance of the battery.
L_limit = 20.97801241971359;  %Lower limit percentage
H_limit = 87.67855645421204;  %Higher limit percentage
low_limit = 0.4444;
upp_limit = 1.839;
```
%Load data and Refine them
format long;
fid = fopen(filenameRawdata);
y = textscan(fid, '%f %f %f %f %f %f %f %f %f %f %s %d %s %s %s');
fclose(fid);
sample = y{1}; sample = sample(2:length(sample));
cycleNo = y{3}; cycleNo = cycleNo(2:length(cycleNo));
testTime = y{5}; testTime = testTime(2:length(testTime));
step_time = y{6}; step_time = step_time(2:length(step_time));
step_time = step_time(2:length(step_time));
current = y{9}; current = current(2:length(current));
voltage = y{10}; voltage = voltage(2:length(voltage));
state = y{11}; state = state(2:length(state));

%Count Cycle number from the entire data file
cycle_count = 1;
count = 0;
for i = 1:length(cycleNo),
    if cycleNo(i) == cycle_count,
        count = count + 1;
        cycleIndex(cycle_count) = count;
    else
        cycle_count = cycle_count + 1;
        count = 1;
    end
end
count = [];
disp('cycle No =');
disp(cycleNo(length(cycleNo)));

%Extract index range for every cycle
countCycle = 1; c_index = 1; index = 1; d_index =1; total_count =0;
no = input('Prompt number of cycle');
if no <= cycleNo(length(cycleNo)) && (no ~= 0),
    for CountCycle = 1:no,
        if CountCycle == 1,
            InitialIndex(CountCycle) = 1;
            FinalIndex(CountCycle) = cycleIndex(CountCycle);
else
    InitialIndex(CountCycle) = FinalIndex(CountCycle -1) +1 ;
    FinalIndex(CountCycle) = InitialIndex(CountCycle) +...
    cycleIndex(CountCycle) -1;
end
end

figure;
plot(testTime, voltage, 'linewidth', 2);
axis([0 700 0.2 2.2]);
set(gca,'XTickLabel','','YTickLabel','')
set(gca,'XTick',0:200:700, 'fontsize', 16);
set(gca,'YTick',0.2:1:2.2, 'fontsize', 16);
xlabel('$Time (Seconds)$ ','interpreter','latex','FontSize',24);
ylabel('$Voltage (Volts)$ ','interpreter','latex','FontSize',24);
orient landscape
print -dpdf -r300 filename123
file_D = fopen('output0.5', 'w');
for i = 1: length(testTime),
    fprintf(file_D, '%f', testTime(i));
    fprintf(file_D, '		 %f 
', voltage(i));
end
fclose(file_D);
if no > 10,
    spacing = 1;
elseif no < 10 && no> 2,
    spacing = 1;
else
    spacing = 1;
end

%Main Program
for CountCycle = 1:no,
    State = state(InitialIndex(CountCycle):FinalIndex(CountCycle));
    Current = current(InitialIndex(CountCycle):FinalIndex(CountCycle));
    Voltage = voltage(InitialIndex(CountCycle):FinalIndex(CountCycle));
    Sample = sample(InitialIndex(CountCycle):FinalIndex(CountCycle));
    TestTime = testTime(InitialIndex(CountCycle):FinalIndex(CountCycle));
    CycleIndex = cycleIndex(CountCycle);
    [RCdata RDdata Cstate Dstate] = IndividualCycle( State, Current, Voltage, TestTime);
[Cdata Ddata] = ChargeCal(RCdata, RDdata, CountCycle, Cstate, Dstate);

[AvgVolt SiCQ ] = ChargeDischargeCurve(Cdata, Ddata);

[EnergyLoss, EnergyEff ] = Energy(Cdata, Ddata);

[R] = InternalR(Cdata, Ddata, CountCycle);

[Rd Cd Rohm TransientP T XTou VH VZ] = DiffusionRC(Cdata, Cstate, CountCycle, Ddata);

[Cs] = StorageCapacity(Cdata, Ddata);

[AccRate] = AcceptanceRate(Cdata, Ddata);

Eff(CountCycle) = EnergyEff;

[Rsd] = SelfDischargeR(Cdata, Cstate, CountCycle, Ddata, Eff(CountCycle));

ChargeAccRate(CountCycle) = AccRate;

CapacitanceS(CountCycle) = Cs;

TotalR(CountCycle) = R;

DiffResistance(CountCycle) = Rd;

DiffCapacity(CountCycle) = Cd;

OhmicResistance(CountCycle) = Rohm;

EnergyEfficiency(CountCycle) = EnergyEff;

LossEnergy(CountCycle) = EnergyLoss;

RChargeCal = Ddata(2,:);

RCharge(CountCycle) = max(RChargeCal);

RSD(CountCycle) = Rsd;

Transient(CountCycle) = TransientP;

TimeConstant(CountCycle) = T;

TimeTou(CountCycle) = XTou;

%Vhundred(CountCycle) = VH;

%Vsero(CountCycle) = VZ;

chargeee = Cdata(2,:);

voltageee = Cdata(3,:);

discharghee = Ddata(2,:);

disvoltageee = Ddata(3,:);

chargeee = chargeee ./max(discharghee) ./max(chargeee);

dischargeee = dischargeee ./max(disvoltageee) ./max(chargeee);

maxQ(CountCycle) = max(chargeee);

maxV(CountCycle) = max(voltageee);

[CPdata] = SignalProcessing(Cdata, Ddata);

[betal beta2 LStart LEnd thetal theta2 V0 VT Slope Yintercp checkX ...]

characteristicCurvePlot(Cdata, Ddata, FQ, FV) = CurveFitting(Cdata, Ddata, CPdata);

chargeee = Cdata(2,:);

voltageee = Cdata(3,:);

discharghee = Ddata(2,:);

disvoltageee = Ddata(3,:);

chargeee = chargeee .*max(discharghee) ./max(chargeee);

dischargeee = dischargeee .*max(disvoltageee) ./max(chargeee);

maxQ(CountCycle) = max(chargeee);

maxV(CountCycle) = max(voltageee);

[CPdata] = SignalProcessing(Cdata, Ddata);

[betal beta2 LStart LEnd thetal theta2 V0 VT Slope Yintercp checkX ...]

characteristicCurvePlot(Cdata, Ddata, FQ, FV) = CurveFitting(Cdata, Ddata, CPdata);

chargeee = Cdata(2,:);

voltageee = Cdata(3,:);

discharghee = Ddata(2,:);

disvoltageee = Ddata(3,:);

chargeee = chargeee .*max(discharghee) ./max(chargeee);

dischargeee = dischargeee .*max(disvoltageee) ./max(chargeee);

maxQ(CountCycle) = max(chargeee);

maxV(CountCycle) = max(voltageee);

[CPdata] = SignalProcessing(Cdata, Ddata);

[betal beta2 LStart LEnd thetal theta2 V0 VT Slope Yintercp checkX ...]

characteristicCurvePlot(Cdata, Ddata, FQ, FV) = CurveFitting(Cdata, Ddata, CPdata);

chargeee = Cdata(2,:);

voltageee = Cdata(3,:);

discharghee = Ddata(2,:);

disvoltageee = Ddata(3,:);

chargeee = chargeee .*max(discharghee) ./max(chargeee);

dischargeee = dischargeee .*max(disvoltageee) ./max(chargeee);

maxQ(CountCycle) = max(chargeee);

maxV(CountCycle) = max(voltageee);

[CPdata] = SignalProcessing(Cdata, Ddata);

[betal beta2 LStart LEnd thetal theta2 V0 VT Slope Yintercp checkX ...]

characteristicCurvePlot(Cdata, Ddata, FQ, FV) = CurveFitting(Cdata, Ddata, CPdata);
Beta1(CountCycle) = beta1;
Beta2(CountCycle) = beta2;
theta12(CountCycle) = theta1(1);
theta11(CountCycle) = theta1(length(theta1));
theta22(CountCycle) = theta2(1);
theta21(CountCycle) = theta2(length(theta2));
v0(CountCycle) = V0;
vT(CountCycle) = VT;
slope(CountCycle) = Slope;
yIntercp(CountCycle) = Yintercp;
avgVolt = AvgVolt;
avgQ = SiCQ;
fq = FQ;
fv = FV;

R = [] ; Cs =[] ; State = [] ; Current =[] ; Voltage = [] ; Capacity=[] ;
Sample =[] ; StepTime=[] ; TestTime=[] ; CycleIndex=[] ; TransIndex=[] ;
Cdata=[] ; Ddata=[] ; Cstate=[] ; Dstate=[] ; mCdata=[] ; mDdata=[] ;
end
count = 1 : length(TotalR);

%Storage Capacitance Curve
if length(CapacitanceS) > 1,
    figure;
    plot(1:length(CapacitanceS), CapacitanceS,'--rs','LineWidth',2,...
        'MarkerEdgeColor','k', 'MarkerFaceColor','g', 'MarkerSize',5)
    xlabel('Cycle number');
ylabel('Storage Capacitance (F)');
end

%Energy Loss curve
if length(LossEnergy) > 1,
    figure;
    plot(1:length(LossEnergy), LossEnergy,'--rs','LineWidth',2,...
        'MarkerEdgeColor','k', 'MarkerFaceColor','g', 'MarkerSize',5)
    xlabel('Cycle number');
ylabel('Energy Loss');
end
% Charge Acceptance Rate Curve
if length(ChargeAccRate) > 1,
    figure;
    plot(1:length(ChargeAccRate), ChargeAccRate, 'LineWidth', 2);
    axis([1 119 0 1]);
    set(gca,'YTick', 0.2:1:2.2, 'fontsize', 16);
    set(gca,'XTick', 0:20:100, 'fontsize', 16);
    xlabel('Number of Cycle ','interpreter','latex','FontSize',24);
    ylabel('Acceptance Rate ','interpreter','latex','FontSize', 24);
    orient landscape
    print -dpdf -r300 acceptancerate
end

% Total Resistance Curve
if length(TotalR) > 1,
    figure;
    plot(1:length(TotalR), TotalR, '--rs','LineWidth',2,...
        'MarkerEdgeColor','k','MarkerFaceColor','g','MarkerSize',5)
    xlabel('Cycle number');
    ylabel('Total Internal Resistance');
    axis([1 length(TotalR) 0 max(TotalR)+ 0.15 ]);}
end

% Capacity curve
figure;
plot( 1:length( RCharge), RCharge, 'k', 'linewidth', 2);
% p = set(p,'Color','red','LineWidth',2)
axis([1 119 0.2 2.4]);
%set(gca,'XTickLabel','','YTickLabel','')
set(gca,'YTick', 0.2:1:2.2, 'fontsize', 16);
set(gca,'XTick', 0:20:100, 'fontsize', 16);
xlabel('Number of Cycle (Seconds)','interpreter','latex','FontSize',24);
ylabel('Capacity (Amp-Hours) ','interpreter','latex','FontSize', 24);
orient landscape
print -dpdf -r300 capacity

% Energy Efficiency curve
figure;
plot( 1:length( EnergyEfficency), EnergyEfficency,'--rs','LineWidth',2,...
%Write on output file
write = 1;
if write == 1,
    file_1 = fopen(filenameOutput1, 'w');
    fprintf(file_1, 'EnergyLoss 		 CapctS 		 Effc ...
    \t	 ChargeRate 		 TotalR 		 Capacity\n');
    for i = 1: length(LossEnergy),
        fprintf(file_1, '%3.1E', LossEnergy(i));
        fprintf(file_1, ' %3.1E', CapacitanceS(i));
        fprintf(file_1, ' %3.1E', EnergyEfficency(i));
        fprintf(file_1, ' %3.1E', ChargeAccRate(i));
        fprintf(file_1, ' %3.1E', TotalR(i));
        fprintf(file_1, ' %3.1E', RCharge(i));
    end
    fclose(file_1);
    file_2 = fopen(filenameOutput2, 'w');
    fprintf(file_2, ' Cs 			 Rohm			 Rd 			 Cd 			 Rsd			 TrstP			 maxQ			 V0			 maxV			 VT\n');
    for i = 1: length(CapacitanceS),
        fprintf(file_2, '%3.1E ', CapacitanceS(i));
        fprintf(file_2, ' %3.1E ', OhmicResistance(i));
        fprintf(file_2, ' %3.1E ', DiffResistance(i));
        fprintf(file_2, ' %3.1E ', DiffCapacitance(i));
        fprintf(file_2, ' %3.1E ', RSD(i));
        fprintf(file_2, ' %3.1E ', Transient(i));
        fprintf(file_2, ' %3.1E ', maxQ(i));
        fprintf(file_2, ' %3.1E ', v0(i));
        fprintf(file_2, ' %3.1E ', maxV(i));
        fprintf(file_2, ' %3.1E ', vT(i));
    end
    fclose(file_2);
end
file_3 = fopen(filenameLinear, 'w');
fprintf(file_3, 'Lstart 			Lend 			 slope			 intercept \n');
for i = 1: length(CapacitanceS),
    fprintf(file_3, '%3.1E ', CapacitanceS(i));
    fprintf(file_3, ' %3.1E ', 0);
    fprintf(file_3, ' %3.1E ', 0);
    fprintf(file_3, ' %3.1E ', 0);
    fprintf(file_3, ' %3.1E ', 0);
    fprintf(file_3, ' %3.1E ', 0);
    fprintf(file_3, ' %3.1E ', 0);
end
fclose(file_3);
fprintf(file_3, '%1.6f ', Lstart(i));
fprintf(file_3, '	\t\t%1.6f ', Lend(i));
fprintf(file_3, '	\t\t%1.6f ', slope(i));
fprintf(file_3, '	\t\t%1.6f 
', yIntercp(i));
end
fclose(file_3);
file_4 = fopen(filenameExponential, 'w');
fprintf(file_4, 'beta1 \t\t\t theta11 \t\t\t ... 
theta12 \t\t\t beta2 \t\t\t theta21 \t\t\t theta22 
');
for i = 1: length(CapacitanceS),
   fprintf(file_4, '%1.6f ', Beta1(i));
   fprintf(file_4, '	\t\t%1.6f ', theta11(i));
   fprintf(file_4, '	\t\t%1.6f ', theta12(i));
   fprintf(file_4, '	\t\t%1.6f ', Beta2(i));
   fprintf(file_4, '	\t\t%1.6f ', theta21(i));
   fprintf(file_4, '	\t\t%1.6f ', theta22(i));
end
fclose(file_4);
file_5 = fopen(filenameOutput3, 'w');
fprintf(file_5, 'Q \t\t\t V
');
for i = 1:length(chargeee),
   fprintf(file_5, '%1.6f', chargeee(i));
   fprintf(file_5, '	\t\t%1.6f 
', voltageee(i));
end
fclose(file_5);
file_6 = fopen(filenameOutput4, 'w');
fprintf(file_6, 'DQ \t\t\t DV 
');
for i = 1:length(dischargeee),
   fprintf(file_6, '%1.6f', dischargeee(i));
   fprintf(file_6, '	\t\t%1.6f 
', disvoltageee(i));
end
fclose(file_6);
else
   Subroutine that extracts data for individual cycle from bulk data
   function [ RCdata RDdata Cstate Dstate] = IndividualCycle(State, Current, Voltage, TestTime)
   transition(1) = 1;
   end
Subroutine that extracts data for individual cycle from bulk data
function [ RCdata RDdata Cstate Dstate] = IndividualCycle(State, Current, Voltage, TestTime)
transition(1) = 1;
p=1; Dindex=1; Cindex = 1;

%%% 1 -CR, 2:-DR, 0 :-CD
flag = 4;

for i = 1 : length(TestTime) ,
C(i) = strcmp('C', State(i));
D(i) = strcmp('D', State(i));
R(i) = strcmp('R', State(i));
if i > 1,
    transition(i) = strcmp(State(i), State(i-1));
end
if transition(i) == 0,
    if ((C(i) - C(i-1)) ~= 0) &&((R(i) - R(i-1)) ~= 0),
        flag = 1;
        k(p) = i;
        p = p+1;
    end
    if ((C(i) - C(i-1)) ~= 0) &&((D(i) - D(i-1)) ~= 0),
        flag = 0;
        k(p) = i;
        p = p+1;
    end
    if ((D(i) - D(i-1)) ~= 0) &&((R(i) - R(i-1)) ~= 0),
        flag = 2;
        k(p) = i;
        p = p+1;
    end
end
if (C(i) == 1 ) || (flag == 1),
    Ccurrent(Cindex) = Current(i);
    Cvolt(Cindex) = Voltage(i);
    CtestTime(Cindex) = TestTime(i);
    Cstate(Cindex) = State (i) ;
    Cindex = Cindex +1;
end
if (D(i) == 1 )|| (flag == 2 ),
    Dcurrent(Dindex) = Current(i);
    Dvolt(Dindex) = Voltage(i);
    DtestTime(Dindex) = TestTime(i);
    Dstate(Dindex) = State(i);
Dindex = Dindex + 1;
end
end
RCdata = cat(1, CtestTime, Ccurrent, Cvolt);
RDdata = cat(1, DtestTime, Dcurrent, Dvolt);

Subroutine to calculate Charge per cycle

function[Cdata Ddata] = ChargeCal(RCdata, RDdata, CountCycle, Cstate, Dstate)
% RCdata =:
% R - Raw
% C - Charge
% D - Discharge
% data is array that contains CtestTime, Ccurrent, Cvolt, Csample);
Cno   = CountCycle;
CtestTime = RCdata(1, :);
Ccurrent = RCdata(2, :);
Cvolt   = RCdata(3, :);
DtestTime = RDdata(1, :);
Dcurrent = RDdata(2, :);
Dvolt   = RDdata(3, :);

% Charge Calculation for charging cycle
for i = 1:length(CtestTime),
    if i <= 1,
    CchargeCal(i) = 0;
    CsampleTime(i) = 0;
    else
    CsampleTime(i) = CtestTime(i) - CtestTime(1);
    CchargeCal(i) = CchargeCal(i-1) + (CsampleTime(i) - CsampleTime(i-1)).* Ccurrent(i);
    end
end
CchargeCal = CchargeCal./60; % Convert into AMP HR

% Charge Calculation for discharge cycle
for i = 1:length(DtestTime),
    if i <= 1,
    DchargeCal(i) = 0;
    DsampleTime(i) = 0;
    else
    DsampleTime(i) = DtestTime(i) - DtestTime(1);
    DchargeCal(i) = DchargeCal(i-1) + (DsampleTime(i) - DsampleTime(i-1)).* Dcurrent(i);
    end
end
DchargeCal = DchargeCal./60; % Convert into AMP HR
\text{RTDchargeCal}(i) = \max(\text{CchargeCal});

\text{else}

\text{DsampleTime}(i) = \text{DtestTime}(i) - \text{DtestTime}(1);
\text{DchargeCal}(i) = \text{DchargeCal}(i-1) + (\text{DsampleTime}(i) - \text{DsampleTime}(i-1)) \times \text{Dcurrent}(i);
\text{RTDchargeCal}(i) = \max(\text{CchargeCal}) - \text{DchargeCal}(i);

\text{end}
\text{end}

\text{RRDchargeCal} = -\min(\text{RTDchargeCal}) + \text{RTDchargeCal};
\text{DchargeCal} = \text{DchargeCal}./60; \textt{COnvert into AMP HR}
\text{RRDchargeCal} = \text{RRDchargeCal}./60;
\text{RDchargeCal} = \text{fliplr}(\text{DchargeCal});

%Refine discharge Cycle
\text{state} = \text{strcmp}('R', \text{Dstate}(1:length(\text{Dstate})));
\text{if sum(state) } \geqslant 1,
\text{flag1} = 0; \text{flag12} = 0; \text{countX} = 0;
\text{countX2} = 0; \text{countY} = 0; \text{countY2} = 0;
\text{flag2} = 0; \text{flag22} = 0;
\text{for } k = 1:length(\text{RDchargeCal}),
\text{if } k \leqslant 1,
\text{ADvolt}(k) = \text{Dvolt}(k);
\text{ADcharge}(k) = \text{RDchargeCal}(k);
\text{else}
\text{dx}(k) = \text{RDchargeCal}(k) - \text{RDchargeCal}(k-1);
\text{dy}(k) = \text{Dvolt}(k) - \text{Dvolt}(k - 1);
\text{if } \text{dy}(k) > 0,
\text{if } \text{dy}(k) \geqslant 0 \&\& \text{flag1} == 0,
\text{indexY} = k;
\text{flag1} = 1;
\end{if}
\text{countY} = \text{countY} + 1;
\end{if}
\text{if } \text{dy}(k) == 0,
\text{if } \text{dy}(k) == 0 \&\& \text{flag12} == 0
\text{indexY2} = k;
\text{flag2} = 1;
\end{if}
\text{countY2} = \text{countY2} + 1;
\end{if}
\text{end}
\text{end}
if dx(k) > 0,
    if dx(k) >= 0 && flag2 == 0,
        idxX = k;
        flag2 = 1;
    end
    countX = countX + 1;
end
if dx(k) == 0,
    if dx(k) == 0 && flag22 == 0,
        idxX2 = k;
        flag22 = 1;
    end
    countX2 = countX2 + 1;
end
end
end
Cdata = cat (1, CsampleTime, CchargeCal ,Cvolt, CtestTime, Ccurrent);
Ddata = cat (1, DsampleTime, RRDchargeCal ,Dvolt, DtestTime, Dcurrent);
else
    Cdata = cat (1, CsampleTime, CchargeCal ,Cvolt, CtestTime, Ccurrent);
    Ddata = cat (1, DsampleTime, fliplr(DchargeCal) ,Dvolt, DtestTime, Dcurrent);
end

% Subroutine that plot Charge Discharge Curve
function[AvgVolt SiCQ ] = ChargeDischargeCurve(Cdata, Ddata, Cstate, Dstate )
% Do interpolation on charge and discharge curve and then do the averaging
CchargeCal = Cdata(2,:);
DchargeCal = Ddata(2,:);
Cvolt = Cdata(3,:);
Dvolt = Ddata(3,:);
DtestTime = Ddata(4,:);
CtestTime = Cdata(4,:);
DstepTime = Ddata(1,:);
CstepTime = Cdata(1,:);

% Storage Capacitance Calculation from Scaled Data
if length(CchargeCal) >= 5 && length(DchargeCal) >= 5,
    CchargeCal = CchargeCal .*max(DchargeCal)./ max(CchargeCal);
    DchargeCal = DchargeCal .*max(DchargeCal)./ max(CchargeCal);

Cvolt = Cvolt.*max(Cvolt)./max(Dvolt);
Dvolt = Dvolt.*max(Cvolt)./max(Dvolt);

% interpolate Charge data
[ SiCQ, SiCV] = interpolation(CchargeCal, Cvolt, 0.002);
[ SiDQ, SiDV] = interpolation(DchargeCal, Dvolt, 0.002);

% Average Charge Discharge data
AvgVolt = (SiCV + SiDV)./2;
if length(DstepTime) <= 10 || length(CstepTime)<= 10,
else
    figure;
    subplot(221);
    hold on;
    plot(SiCQ, AvgVolt,'r');
    plot(SiCQ, SiCV, SiDQ, SiDV);
    xlabel('Charge');
    ylabel('Volt');
    hold off;
end
end

Subroutine to calculate energy of a cell

function [EnergyLoss EnergyEff] = Energy( Cdata, Ddata)
%% Extract data
CchargeCal = Cdata(2,:);
DchargeCal = Ddata(2,:);
Cvolt = Cdata(3,:);
Dvolt = Ddata(3,:);
DtestTime = Ddata(4,:);
CtestTime = Cdata(4,:);
Ccurrent = Cdata(5,:);
Dcurrent = Ddata(5,:);
if length(CchargeCal) >= 5 && length(DchargeCal) >= 5,
%% Energy loss calculation
    Cenergy = 0;
    for k = 1 : length(CchargeCal) - 1,
          delX(k) = abs(CchargeCal(k+1) - CchargeCal(k));
end
end

function [EnergyLoss EnergyEff] = Energy( Cdata, Ddata)
Cenergy = delX(k).*Cvolt(k) + Cenergy;
end
Denergy = 0;
for k = 1 : length(DchargeCal) - 1,
    delX(k) = abs(DchargeCal(k+1) - DchargeCal(k));
    Denergy = delX(k).*Dvolt(k) + Denergy;
end
EnergyLoss = Cenergy - Denergy;
EnergyEff = Denergy/Cenergy;
else
    EnergyLoss = Inf;
    EnergyEff = 0;
end

Subroutine to calculate internal resistance of a cell

function [R] = InternalR(Cdata, Ddata, CountCycle)
% Calculate internal Resistance form the interpolated charge discharge data
% points Cdata = cat (1, CsampleTime, CchargeCal ,Cvolt, CtestTime, Ccurrent);
CchargeCal = Cdata(2,:);
DchargeCal = Ddata(2,:);
Cvolt = Cdata(3,:);
Dvolt = Ddata(3,:);
DtestTime = Ddata(4,:);
CtestTime = Cdata(4,:);
Ccurrent = Cdata(5,:);
Dcurrent = Ddata(5,:);
if length(CchargeCal) >= 5 && length(DchargeCal) >= 5,
    % Storage Capacitance Calculation from Scaled Data
    CchargeCal = CchargeCal .*max(DchargeCal)/ max(CchargeCal);
    DchargeCal = DchargeCal .*max(DchargeCal)/ max(CchargeCal);
    %Dvolt = Dvolt.* max(Dvolt)/max(Cvolt);
    %Cvolt = Cvolt.* max(Dvolt)/max(Cvolt);
    % interpolate Charge data
    [ CscaleQ, CscaleV] = interpolation(CchargeCal, Cvolt, 0.002);
    [ DscaleQ, DscaleV] = interpolation(DchargeCal, Dvolt, 0.002);
    AscaleV = (CscaleV + DscaleV)./2;
    % Internal Resistance Calculation
    I = mean(Ccurrent);
for i = 1:length(CscaleV),
    diffVolt(i) = AscaleV(i) - DscaleV(i);
    InternalR(i) = diffVolt(i) ./ I;
end
Ctime = range(CtestTime);
Dtime = range(DtestTime);
if length(InternalR) == 1,
    time = 0;
else
    if Ctime >= Dtime,
        time = 0: max(Ctime)./(length(InternalR)-1):Ctime;
    else
        time = 0: max(Dtime)./(length(InternalR)-1):Dtime;
    end
end
if length(DtestTime)<= 5 || length(CtestTime) <= 5,
    else
    subplot(222);
    suptitle({’Cycle Count’; CountCycle});
    plot(time./60, InternalR);
    xlabel(’Time in Hour’);
    ylabel(’Internal Resistance’);
    figure;
    plot(time./60, InternalR,’k’, ’linewidth’, 2);
    set(gca,’YTick’, 0:1:2:9, ’fontsize’, 16);
    set(gca,’XTick’,[0 1.4 2.8 4.2 5.6 7], ’fontsize’, 16);
    set(gca,’XTickLabel’, ['$0.0$'; '$0.2$'; '$0.4$'; '$0.6$'; '$0.8$'; '$1.0$'], ’fontsize’, 16);
    xlabel(’State-of-Charge (SOC)’, ’interpreter’,’latex’,’FontSize’, 24);
    ylabel(’Resistance (R(SOC))’, ’interpreter’,’latex’,’FontSize’, 24);
    axis([0.01 6.5 0.1 0.9]);
    plotTickLatex2D(’xlabeldy’, 0.02, ’FontSize’, 16);
    plotTickLatex2D(’ylabeldx’, 0.02, ’FontSize’, 16);
    orient landscape
    print -dpdf -r300 internalResistance
end
%% Pick one Resistance value from the linear region
initialR = 45.* max(InternalR)./100;
finalR = 65.* max(InternalR)./100;
count = 1; summ = 0;
for $i = 1: \text{length}$(InternalR)$,$

if InternalR(i) $\geq$ initialR && InternalR(i)$\leq$ finalR,$$
\text{summ} = \text{InternalR}(i) + \text{summ};$$
\text{count} = \text{count} +1;$$
end$$
end$$
R = \text{summ}./\text{count};$$
else$$
R = \text{Inf};$$
end

Subroutine to calculate diffusion terms

function$$[\text{Rd}, \text{Cd}, \text{ROhm}, \text{PVR}, \text{T}, \text{XTou}, \text{Vhundred}, \text{Vzero}] = \text{DiffusionRC}(\text{Cdata}, \text{Cstate}, \text{CountCycle}, \text{Ddata})$$
\%\text{Rd} : \text{Resistance due to diffusion}$$
\%\text{Cd} : \text{Capacitance due to diffusion}$$
\%\text{ROhm} : \text{Ohmic resistance}$$
\text{Cno} = \text{CountCycle};$$
\text{CstepTime} = \text{Cdata}(1,:);$$
\text{Charge} = \text{Cdata}(2,:);$$
\text{Cvolt} = \text{Cdata}(3,:);$$
\text{CtestTime} = \text{Cdata}(4,:);$$
\text{Ccurrent} = \text{Cdata}(5,:);$$
\text{DstepTime} = \text{Ddata}(1,:);$$
\text{Dcharge} = \text{Ddata}(2,:);$$
\text{Dvolt} = \text{Ddata}(3,:);$$
\text{DtestTime} = \text{Ddata}(4,:);$$
\text{RestIndex} = 0;$$
\text{index} = 1;$$
for $i = 1: \text{length}(\text{Cstate})$$
R(i) = \text{strcmp('R', \text{Cstate}(i))};$$
if R(i) == 1,$$
\text{RestIndex}($\text{index}$) = i;$$
\text{index} = \text{index} +1;$$
end$$
end$$
if \text{sum}($\text{RestIndex}$) == 0,$$
\text{ROhm} = 0; \quad \text{Rd} = 0; \quad \text{Cd} = 0; \quad \text{PVR} = 0; \quad \text{T} = 0;$$
\text{XTou} = 0; \quad \text{Vhundred} = 0; \quad \text{Vzero} = 0;$$
else
for k = 1 : length(RestIndex),
  Rvolt(k) = Cvolt(RestIndex(k));
  RstepTime(k) = CstepTime(RestIndex(k));
  Rcharge(k) = Charge(RestIndex(k));
end

diff = abs(Dcharge(1:length(Dcharge)) - Rcharge(1));
flag = 1;
for k = 1:length(Dcharge),
  if abs(Dcharge(k) - Rcharge(1)) <= min(diff) & flag == 1,
    RDvolt = Dvolt(k);
    RDcharge = Dcharge(k);
    flag = 0;
  end
end

A = (Cvolt(RestIndex(1)) - RDvolt)/2;
ROhm = abs((Cvolt(RestIndex(1) - 1) - Cvolt(RestIndex(1)))./Ccurrent(RestIndex(1) - 1));
[TotalR] = InternalR(Cdata, Ddata, CountCycle);
Rd = TotalR - ROhm;
Vhundred = Cvolt(RestIndex(2));
Vzero = (Vhundred - A);
Vrange = A;
VR = Rvolt(length(RestIndex));
PVR = (Rvolt(length(RestIndex)) - Vzero)*100/ A;

% use interpolation to accurately calculate Tou among the rest data points
for k = 1 : length(RestIndex),
  Rvolt(k) = Cvolt(RestIndex(k));
  RstepTime(k) = CstepTime(RestIndex(k));
end
timeScale = RstepTime(1) : 0.00025 : RstepTime(length(RstepTime));
IntData = interp1(RstepTime, Rvolt, 'pchip', 'pp');
NewVolt = ppval(IntData, timeScale);
flag = 1;
for k = 1 : length(timeScale),
  if (NewVolt((k)) - VR <= 0.01) & flag == 1;
    Time = timeScale((k));
    flag = 0;
  end
end
end

T = RstepTime(length(RstepTime)) - RstepTime(1);

Alpha = (log(PVR/100)) / (-T*60);

Cd = 1./(Alpha *Rd);

XTou = T + CtestTime(RestIndex(1));

if length(CtestTime) <= 10 || length(DtestTime) <= 10,
else

subplot(224);

figure;

hold on;

plot(CtestTime, Cvolt, 'k', 'linewidth', 2);

line([CtestTime(RestIndex(1)) CtestTime(RestIndex(1))], [min(Cvolt) max(Cvolt)]), 'Color', 'r', 'LineStyle', '-

line([0 max(CtestTime)], [Cvolt(RestIndex(1)) Cvolt(RestIndex(1))], 'Color', 'b', 'LineStyle', '--');

line([0 max(CtestTime)], [ VR VR], 'Color', 'r', 'LineStyle', '--');

line([0 max(CtestTime)], [ Vzero Vzero], 'Color', 'b', 'LineStyle', '--');

line([0 max(CtestTime)], [Cvolt(RestIndex(1) -1) Cvolt(RestIndex(1)-1)], 'Color', 'b', 'LineStyle', '--');

xlabel('Time ', 'interpreter', 'latex', 'FontSize', 24);

ylabel('Voltage ', 'interpreter', 'latex', 'FontSize', 24);

set(gca, 'YTicklabel', '');

set(gca, 'XTicklabel', '');

set(gca, 'YTick', [1.818 1.85 1.859], 'fontsize', 16);

set(gca, 'XTick', [602 612], 'fontsize', 16);

set(gca, 'YTickLabel', ['$V_A$'; '$V_B$'; '$V_C$'], 'fontsize', 16);

set(gca, 'XTickLabel', ['$t_0$'; '$t_1$'], 'fontsize', 16);

%title({' Cycle number'; Cno});

axis ([512 720 1.7 1.899]);

plotTickLatex2D('xlabeldy', 0.02, 'FontSize', 16);

plotTickLatex2D('ylabeldx', 0.02, 'FontSize', 16);

box on;

hold off;

orient landscape

print -dpdf -r300 diffusionCalc

subplot(223);

figure;

plot(CstepTime, Cvolt, 'linewidth', 2);

plot(CstepTime, Cvolt-0.99, CstepTime, Ccurrent, 'plot

aa = CstepTime(RestIndex(1));

bb = (RstepTime(length(RstepTime)) + CstepTime(1));

cc = (Cvolt(RestIndex(1))) - PVR ;
Subroutine to calculate storage capacitance

function [Cs] = StorageCapacitance(Cdata, Ddata)

CchargeCal = Cdata(2,:);
DchargeCal = Ddata(2,:);
Cvolt = Cdata(3,:);
Dvolt = Ddata(3,:);
if length(CchargeCal) >= 5 && length(DchargeCal) >= 5,
Subroutine to calculate selfdischarge resistance

function [Rsd] = SelfDischargeR(Cdata, Cstate, CountCycle, Ddata, EnergyEff)

```matlab
[ iCQ, iCV] = interpolation(CchargeCal, Cvolt, 0.0002);
[ iDQ, iDV] = interpolation(DchargeCal, Dvolt, 0.0002);

%% Storage Capacitance Calculation from Scaled Data
CchargeCal = CchargeCal .* max(DchargeCal) ./ max(CchargeCal);
DchargeCal = DchargeCal .* max(DchargeCal) ./ max(CchargeCal);

%% Dvolt = Dvolt.* max(Dvolt)./max(Cvolt);
%% Cvolt = Cvolt.*max(Dvolt)./max(Cvolt);

[ SiCQ, SiCV] = interpolation(CchargeCal, Cvolt, 0.0002);
[ SiDQ, SiDV] = interpolation(DchargeCal, Dvolt, 0.0002);

AvgVolt = (SiCV + SiDV) ./ 2;
flagg = 0; flage = 0;
randomPoint1 = 0.35 * max(SiCQ);
randomPoint2 = 0.75 * max(SiCQ);

for k = 1 : length(SiCQ)
    if (SiCQ(k) >= randomPoint1) && (flagg == 0),
        capL = SiCQ(k);
        volL = AvgVolt(k);
        flagg = 1;
    end
    if (SiCQ(k) >= randomPoint2) && (flage == 0),
        capH = SiCQ(k);
        volH = AvgVolt(k);
        flage = 1;
    end
end

if (volH - volL) == 0,
    Cs = 0;
else
    capH = capH * 60 * 60;
    capL = capL * 60 * 60;
    Cs = abs((capH - capL) / (volH - volL));
end

else
    Cs = 0;
end
```

Subroutine to calculate selfdischarge resistance

function [Rsd] = SelfDischargeR(Cdata, Cstate, CountCycle, Ddata, EnergyEff)
Cno = CountCycle;
CstepTime = Cdata(1,:);
Charge = Cdata(2,:);
Cvolt = Cdata(3,:);
CtestTime = Cdata(4,:);
Ccurrent = Cdata(5,:);
DtestTime = Ddata(4,:);
DCharge = Ddata(2,:);
CtestTime = CtestTime./60;
Qloss = (Charge(length(Charge)) - EnergyEff* Charge(length(Charge)));
Qloss1 = (Charge(length(Charge)) - DCharge(1));
for i = 1:length(CtestTime),
    if i <= 1,
        LossChargeCal(i) = 0;
        sampleTime(i) = 0;
    else
        sampleTime(i) = CtestTime(i) - CtestTime(1);
        LossChargeCal(i) = LossChargeCal(i-1) + (sampleTime(i) - sampleTime(i-1));
    end
end
LossI1 = Qloss1./(2.*LossChargeCal(length(LossChargeCal)));
Rsd = max(Cvolt)/LossI1

Subroutine for data interpolation

function [x, y] = interpolation(xdata, ydata, spacing)
h = spacing;
%% erase redundant data parts
index = 1;
for i = 1:length(ydata),
    if i <= 1,
        Rydata(index) = ydata(i);
        Rxdata(index) = xdata(i);
        index = index + 1;
    else
        if ydata(i) == ydata(i - 1) || xdata(i) == xdata(i - 1),
            Rydata(index) = ydata(i);
            Rxdata(index) = xdata(i);
        else
            ....
Model Simulation

This section presents MATLAB codes that is used to simulate the voltage and charge profile curve of a cell for different cycles.

Main Program

close all; clear all;
filenameRawdata = 'Rawdata.txt';
filenameOutput1 = 'output.txt';
filenameOutput2 = 'UA6-output2.txt';
filenameOutput3 = 'UA6-output3.txt';
filenameOutput4 = 'UA6-output4.txt';
filenameExponential = 'UA6-exponential_opt.txt';
filenameLinear = 'UA6-liner_opt.txt';

fid = fopen(filenameRawdata);
y = textscan(fid, '%f %f %f %f %f %f %f %f %f %f %s %d %s %s %s');
close(fid);
testTime = y{5}; testTime = testTime(2:length(testTime));
current = y{9}; current = current(2:length(current));
cycleNo = y{3}; cycleNo = cycleNo(2:length(cycleNo));
voltage = y{10}; voltage = voltage(2:length(voltage));
state = y{11}; state = state(2:length(state));
cycle_count = 1;
count = 0;
for i = 1:length(cycleNo),
    if cycleNo(i) == cycle_count,
        count = count + 1;
        cycleIndex(cycle_count) = count;
    end
end

x = min(Rxdata) : h : max(Rxdata);
data1 = interp1(Rxdata, Rydata, 'pchip', 'pp');
y = ppval(data1, x);
else
    cycle_count = cycle_count +1;
    count = 1;
end

end
count = [];
disp('cycle No =');
disp(cycleNo(length(cycleNo)));
countCycle = 1;c_index = 1;index = 1;d_index =1;total_count =0;

%Extract Cycle Number
fid = fopen(filenameOutput2);
y = textscan(fid, '%s %s %s %s %s %s %s %s %s %s');
fclose(fid);
[Cs] = stringToNO(y{1});

% Ask user for cycle number
disp('Data Available cycle No =');
disp(length(Cs));
no = input('Prompt number of cycle');
if no <= length(Cs) && (no ~= 0),
    for CountCycle = 1:no,
        if CountCycle == 1,
            InitialIndex(CountCycle) = 1;
            FinalIndex(CountCycle) = cycleIndex(CountCycle);
        else
            InitialIndex(CountCycle) = FinalIndex(CountCycle -1) +1 ;
            FinalIndex(CountCycle) = InitialIndex(CountCycle) +
                cycleIndex(CountCycle) -1;
        end
    end
end
DiffusionVerif(1, filenameOutput2);

% simulation per cycle
for CountCycle = 1:no,
    %length(state)
    %InitialIndex
    %FinalIndex
    State = state(InitialIndex(CountCycle) : FinalIndex(CountCycle) );
Current = current(InitialIndex(CountCycle) : FinalIndex(CountCycle));
Voltage = voltage(InitialIndex(CountCycle) : FinalIndex(CountCycle));
TestTime = testTime(InitialIndex(CountCycle) : FinalIndex(CountCycle));
t = testTime(InitialIndex(CountCycle) : FinalIndex(CountCycle));
I = current(InitialIndex(CountCycle) : FinalIndex(CountCycle));
volt = voltage(InitialIndex(CountCycle) : FinalIndex(CountCycle));
Vo = voltage(InitialIndex(CountCycle));
CycleIndex= cycleIndex(CountCycle);

[RCdata RDdata Cstate Dstate] = IndividualCycleforSimulation
( State, Current, Voltage, TestTime);
CV = RCdata(3,:); CI = RCdata(2,:);
Ct = RCdata(1,:); DV = RDdata(3,:);
DI = RDdata(2,:); Dt = RDdata(1,:);

% storage charge simulation
if CountCycle <= 1,
    prevCQ(CountCycle) = 0;
else
    prevCQ(CountCycle) = dqs(length(dqs));
    prevCQ(CountCycle) = 0;
end
[cqs] = CQsCalc(CI, Ct, CountCycle, prevCQ(CountCycle), filenameOutput2, filenameOutput3);
prevDQ(CountCycle) = cqs(length(cqs));
[dqs] = DQsCalc(-DI, Dt, CountCycle,prevDQ(CountCycle), filenameOutput2, filenameOutput4);
[csV, csT] = VtCalc( CI, Ct, cqs, CountCycle, filenameOutput2, filenameLinear,filenameExponential);
[dsV, dsT] = VtCalc(-DI, Dt, dqs, CountCycle, filenameOutput2, filenameLinear, ilenameExponential);
rt{CountCycle} = [Ct Dt]; rv{CountCycle} = [CV DV];
st{CountCycle} = [csT dsT]; sv{CountCycle} = [csV dsV];
ct = Ct; cv = CV; dt = Dt; dv = DV;
[offset, MSV, MST] = offsetCalc(ct, cv, dt, dv, csT, csV, dsT, dsV);
msv{CountCycle} = [csV + offset dsV + offset];
msv1{CountCycle} = MSV;
msv1{CountCycle} = MST;
end
figure;
RT = []; RV = []; ST = []; SV = []; MSV = []; MSV1 = []; MST1 = [];
for k = 1:no,
    RT = [ RT rt(k)];
RV = [ RV rv{k}];
ST = [ ST st{k}];
SV = [ SV sv{k}];
MSV = [ MSV msv{k}];
MSV1 = [MSV1 msv1{k}];
MST1 = [MST1 mst1{k}];
end
plot(ST, SV, 'r', RT, RV);
figure;
plot(ST, MSV, 'r', RT, RV);
figure;
plot(MST1, MSV1, 'r', RT, RV);

Subroutine to extract data for individual cycle from the bulk of data

function [ RCdata RDdata Cstate Dstate] = IndividualCycleforSimulation(State, Current, Voltage, TestTime)
transition(1) = 1;
p=1; Dindex=1; Cindex = 1;
%%%% 1 -CR, 2:-DR, 0 :-CD
flag = 4;
for i = 1 : length(TestTime) ,
C(i) = strcmp('C', State(i));
D(i) = strcmp('D', State(i));
R(i) = strcmp('R', State(i));
if i > 1,
    transition(i) = strcmp(State(i), State(i-1));
end
if transition(i) == 0,
    if ((C(i) - C(i-1)) ~= 0) &&((R(i) - R(i-1)) ~= 0),
        flag = 1;
        k(p) = i;
        p = p+1;
    end
    if ((C(i) - C(i-1)) ~= 0) &&((D(i) - D(i-1)) ~= 0),
        flag = 0;
        k(p) = i;
        p = p+1;
    end
    if ((D(i) - D(i-1)) ~= 0) &&((R(i) - R(i-1)) ~= 0),
    end
end
end
flag = 2;
k(p) = i;
p = p+1;
end

if (C(i) == 1) || (flag == 1),
    Ccurrent(Cindex) = Current(i);
    Cvolt(Cindex) = Voltage(i);
    CtestTime(Cindex) = TestTime(i);
    Cstate(Cindex) = State(i);
    Cindex = Cindex +1;
end

if (D(i) == 1) || (flag == 2),
    Dcurrent(Dindex) = Current(i);
    Dvolt(Dindex) = Voltage(i);
    DtestTime(Dindex) = TestTime(i);
    Dstate(Dindex) = State(i);
    Dindex = Dindex +1;
end

RCdata = cat(1, CtestTime, Ccurrent, Cvolt);
RDdata = cat(1, DtestTime, Dcurrent, Dvolt);

Subroutine to simulate charge of charge cycle of a cell

function[mqs] = CQsCalc(I, t, CycleNO, offsetQ, filenameOutput2, filenameOutput4);
% I       ->  Current
% t       ->  time
% Rd      ->  Diffusion Resistance
% Cd      ->  Diffusion Capacitance
% Cs      ->  Storage Capacitance
% Rsd     ->  Self discharge Resistance
% V0      ->  Nominal Voltage
% LstartP ->  Linear region start percentage with respect to max charge
% LendP   ->  Linear region end percentage with respect to max charge
% beta1   ->  Exponential growth rate for first exponential region
% beta2   ->  Exponential growth rate for second exponential region
%% Extract Cs, Rd, Cd, Rohn, Rt from the output file
fid = fopen(filenameOutput2);
y = textscan(fid, '%s %s %s %s %s %s %s %s %s %s');
close(fid);
[Cs] = stringToNO(y{1});
[Rsd] = stringToNO(y{5});
[Local_V0] = stringToNO(y{8});
V0 = Local_V0;

fid1 = fopen(filenameOutput4);
x = textscan(fid, '%s %s ');
close(fid1);
Qreal = stringToNO(x{1});
Vreal = stringToNO(x{2});

T = 2*60;
qs(1) = 0;
Qs(1) = I(1) - (V0(CycleNO) + (qs(1)/Cs(CycleNO))) / Rsd(CycleNO);
qs(2) = qs(1) + T*Qs(1);
for k = 2 : length(I) - 1,
    if I(k) == 0,
        Qs(k) = 0;
    else
        Qs(k) = I(k) - (V0(CycleNO) + (qs(k)/Cs(CycleNO))) / Rsd(CycleNO);
    end
    qs(k+1) = qs(k) + T*Qs(k);
end
qs = qs ./ 3600; % now charge is in amp hr
mqs = qs(1:length(qs)) + offsetQ;
figure;
hold on;
plot( 1:length(mqs), mqs+0.0018, 'r', 1:length(Qreal), Qreal,'linewidth', 2)
hold off;

u = legend('Simulated Charge','Experimental Charge','FontSize', 16);
set(u,'interpreter','latex');
set(u,'Location','Northwest');
box on;
axis tight;
set(gca,'XTick',[0 50 100 150]);
set(gca,'XTickLabel', [0 ' 100' '200' '300'], 'fontsize', 16);
ylabel('Charge (Coulombs) ','interpreter','latex','FontSize', 24);
xlabel('Time (Minutes)', 'interpreter', 'latex', 'FontSize', 24);
plotTickLatex2D('xlabeldy', 0.02, 'FontSize', 16);
plotTickLatex2D('ylabeldx', 0.1, 'FontSize', 16);
orient landscape
print -dpdf -r300 simulateChargeResultC

%%Error Plot
RT = 1:length(Qreal);
RV = Qreal;
MST1 = 1:length(mqs);
MSV1 = mqs;
if max(RT) > max(MST1),
    for i = 1:length(MST1),
        if MST1(i) <= max(RT)
            MrT(i) = MST1(i);
            MrV(i) = MSV1(i);
        end
    end
    MrT = [MrT max(RT)];
    MrV = [MrV max(RV)];
    MrT = RT;
    MrV = RV;
else
    for i = 1:length(RT),
        if RT(i) <= max(MST1)
            MrT(i) = RT(i);
            MrV(i) = RV(i);
        end
    end
    MrT = [MrT max(MST1)];
    MrV = [MrV max(MSV1)];
    MrT = MST1;
    MrV = MSV1;
end
[ Ta, Va] = interpolation(MrT, MrV, 0.002);
[Tr, Vr] = interpolation(MrT, MrV, 0.002);
figure;
plot(Ta, (Va-Vr).^2, 'linewidth', 2);
box on;
axis([[0 150 0 0.025]]);
Subroutine to simulate charge for discharge cycle of a cell

```matlab
function [Rqs] = DQsCalc(I, t, CycleNO, maxQ, filenameOutput2, filenameOutput4);
    % I -> Current
    % t -> time
    % Rd -> Diffusion Resistance
    % Cd -> Diffusion Capacitance
    % Cs -> Storage Capacitance
    % Rs -> Self discharge Resistance
    % V0 -> Nominal Voltage
    % LstartP -> Linear region start percentage with respect to max charge
    % LendP -> Linear region end percentage with respect to max charge
    % beta1 -> Exponential growth rate for first exponential region
    % beta2 -> Exponential growth rate for second exponential region

    fid = fopen(filenameOutput2);
    y = textscan(fid, '%s %s %s %s %s %s %s %s %s %s');
    fclose(fid);
```
\[ [C_s] = \text{stringToNO}(y(1)); \]
\[ [R_{sd}] = \text{stringToNO}(y(5)); \]
\[ [V_{\text{local VT}}] = \text{stringToNO}(y(10)); \]
\[ V_T = V_{\text{local VT}}; \]
\[ \text{fid1} = \text{fopen}(\text{filenameOutput4}); \]
\[ x = \text{textscan}(\text{fid}, '%%s %%s '); \]
\[ \text{fclose}(\text{fid1}); \]
\[ Q_{\text{real}} = \text{stringToNO}(x(1)); \]
\[ V_{\text{real}} = \text{stringToNO}(x(2)); \]
\[ T = 2*60; \]
\[ q_{s}(1) = 0; \]
\[ Q_{s}(1) = I(1) - \frac{(V_T(CycleNO) + (q_{s}(1)/C_s(CycleNO)))}{R_{sd}(CycleNO)}; \]
\[ q_{s}(2) = q_{s}(1) + T*Q_{s}(1); \]
\[ \text{for} \ k = 2 : \text{length}(I), \]
\[ \quad Q_{s}(k) = I(k) - \frac{(V_T(CycleNO) + (q_{s}(k)/C_s(CycleNO)))}{R_{sd}(CycleNO)}; \]
\[ \quad q_{s}(k+1)= q_{s}(k) + T*Q_{s}(k); \]
\[ \text{end} \]
\[ q_{s} = q_{s} ./ 3600; \% \text{now charge is in amp hr} \]
\[ R_{qs}(1) = \text{max}(Q_{s}); \]
\[ R_{qs} = \text{max}(Q_{s}) + q_{s}(2:\text{length}(q_{s})); \]
\[ R_{qs} = -\text{min}(R_{qs}) + R_{qs} ; \]
\[ R_{qs} = R_{qs} * \text{max}(Q_{s}) ./ \text{max}(R_{qs}); \]
\[ \text{figure} ; \]
\[ \text{hold on} ; \]
\[ \text{plot}(1:\text{length}(R_{qs}),R_{qs},'r', 1:\text{length}(Q_{\text{real}}),Q_{\text{real}}, 'linewidth', 2); \]
\[ \text{hold off} ; \]
\[ u = \text{legend}('\text{Simulated Charge}', 'Experimental Charge', 'FontSize', 16); \]
\[ \text{set}(u, 'interpreter', 'latex'); \]
\[ \text{set}(u, 'Location', 'Southwest'); \]
\[ \text{box on} ; \]
\[ \text{axis tight} ; \]
\[ \text{set}(\text{gca}, 'XTick', [0 50 100 150]); \]
\[ \text{set}(\text{gca}, 'XTickLabel', ['0'; '100'; '200'; '300'], 'fontsize', 16); \]
\[ \text{ylabel}('\text{Charge (Coulombs)}', 'interpreter', 'latex', 'FontSize', 24); \]
\[ \text{xlabel}('\text{Time (Minutes)}', 'interpreter', 'latex', 'FontSize', 24); \]
\[ \text{plotTickLatex2D}('xlabeldy', 0.02, 'FontSize', 16); \]
\[ \text{plotTickLatex2D}('ylabeldx', 0.1, 'FontSize', 16); \]
\[ \text{orient landscape} \]
\[ \text{print} -dpdf -r300 simulateChargeResultD \]
RT = 1:length(Qreal);
RV = Qreal;
MST1 = 1:length(Rqs);
MSV1 = Rqs;
if max(RT) > max(MST1),
  for i = 1:length(MST1),
    if MST1(i) <= max(RT)
      MmT(i) = MST1(i);
      MmV(i) = MSV1(i);
    end
  end
  MmT = [MmT max(RT)];
  MmV = [MmV max(RV)];
  MrT = RT;
  MrV = RV;
else
  for i = 1:length(RT),
    if RT(i) <= max(MST1)
      MrT(i) = RT(i);
      MrV(i) = RV(i);
    end
  end
  MrT = [MrT max(MST1)];
  MrV = [MrV max(MSV1)];
  MmT = MST1;
  MmV = MSV1;
end
[ Ta, Va] = interpolation(MmT, MmV, 0.02);
[Tr , Vr] = interpolation(MrT, MrV, 0.02);
figure;
plot(Tr, (Va-Vr).^2, 'linewidth', 2);
box on;
axis([0 153.3 0 0.03]);
set(gca,'XTick', [0 50 100 153]);
set(gca,'XTickLabel', ['0'; '100'; '200'; '300'], 'fontsize', 16);
xlabel('Time ','interpreter','latex','FontSize', 23);
ylabel('Squared Error','interpreter','latex','FontSize', 23);
plotTickLatex2D('xlabeldy', 0.02, 'FontSize', 14);
Subroutine to simulate terminal voltage of a cell

```matlab
function [ Vt, time] = VtCalc(I, t, q, CycleNO, filenameOutput2, filenameLinear, filenameExponential)
    [Vohm] = VohmCalc(I, CycleNO, filenameOutput2);
    [Vs, time, qs] = VsCalc(I, t,q, CycleNO, filenameOutput2, filenameLinear, filenameExponential);
    [Vd, time] = VdCalc(I, t, CycleNO, filenameOutput2);
    Vt = Vohm + Vs + Vd + 3.47
%
%for NiZn 1.76  % for limn 3.46
    time = t;
    figure
    plot(time, Vs, 'r')
    figure
    plot(time, Vd)
```