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Modeling, Hybridization, and Optimal Charging of Electrical Energy Storage Systems

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MODELING, HYBRIDIZATION, AND OPTIMAL CHARGING
OF ELECTRICAL ENERGY STORAGE SYSTEMS

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Yasha Parvini
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Accepted by:
Dr. Ardalan Vahidi, Committee Chair
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Abstract

The rising rate of global energy demand alongside the dwindling fossil fuel resources has motivated research for alternative and sustainable solutions. Within this area of research, electrical energy storage systems are pivotal in applications including electrified vehicles, renewable power generation, and electronic devices. The approach of this dissertation is to elucidate the bottlenecks of integrating supercapacitors and batteries in energy systems and propose solutions by the means of modeling, control, and experimental techniques.

In the first step, the supercapacitor cell is modeled in order to gain fundamental understanding of its electrical and thermal dynamics. The dependence of electrical parameters on state of charge (SOC), current direction and magnitude (20-200 A), and temperatures ranging from -40 °C to 60 °C was embedded in this computationally efficient model. The coupled electro-thermal model was parameterized using specifically designed temporal experiments and then validated by the application of real world duty cycles.

Driving range is one of the major challenges of electric vehicles compared to combustion vehicles. In order to shed light on the benefits of hybridizing a lead-acid driven electric vehicle via supercapacitors, a model was parameterized for the lead-acid battery and combined with the model already developed for the supercapacitor, to build the hybrid battery-supercapacitor model. A hardware in the loop (HIL) setup consisting of a custom built DC/DC converter, micro-controller (µC) to implement the power management strategy, 12 V lead-acid battery, and a 16.2 V supercapacitor module was built to perform the validation experiments.

Charging electrical energy storage systems in an efficient and quick manner, motivated to solve an optimal control problem with the objective of maximizing the charging efficiency for
supercapacitors, lead-acid, and lithium ion batteries. Pontryagins minimum principle was used to solve the problems analytically. Efficiency analysis for constant power (CP) and optimal charging strategies under different charging times (slow and fast) was performed. In case of the lithium ion battery, the model included the electronic as well as polarization resistance. Furthermore, in order to investigate the influence of temperature on the internal resistance of the lithium ion battery, the optimal charging problem for a three state electro-thermal model was solved using dynamic programming (DP).

The ability to charge electric vehicles is a pace equivalent to fueling a gasoline car will be a game changer in the widespread acceptability and feasibility of the electric vehicles. Motivated by the knowledge gained from the optimal charging study, the challenges facing the fast charging of lithium ion batteries are investigated. In this context, the suitable models for the study of fast charging, high rate anode materials, and different charging strategies are studied. The side effects of fast charging such as lithium plating and mechanical failure are also discussed.

This dissertation has targeted some of the most challenging questions in the field of electrical energy storage systems and the reported results are applicable to a wide range of applications such as in electronic gadgets, medical devices, electricity grid, and electric vehicles.
Dedication

I dedicate this dissertation to my beloved family. Thanks for your endless love and support in all stages of my life, including my Ph.D. studies.
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In the course of my Ph.D. studies, I had the privilege to interact, collaborate, and learn from top notch scientists, researchers, and engineers. This indeed is the true value of my spectacular Clemson experience.

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Chapter 1

Introduction

1.1 Overview

The focus of this dissertation is on modeling, hybridization, and optimal charging of electrical energy storage systems. The electrical energy storage systems studied are supercapacitors as the prominent storage devices in terms of power density, Lithium-ion batteries as the superior battery chemistry in terms of energy density, and last but not least lead-acid batteries with the noticeable cost advantages. Energy Storage devices play an important role in our everyday life through facilitating the development of areas such as renewable power generation [1–5], transportation electrification [2, 3], and portable medical and consumer electronic devices. In order to facilitate the integration of these devices in power applications, we model the electrical and thermal dynamics of them in a wide range of temperature and loads. Increasing the degree of freedom by integrating the supercapacitor and lead-acid battery in a hybrid configuration, motivates the study of extending the vehicle’s driving range which is a well known challenge for electric vehicle commercialization. Charging accounts for half the life span of storage systems and is an important factor in determining the lifetime and recharging speeds. Utilizing optimal control theory we shed light on the achievable charging efficiencies while considering long and short charging times. The above-mentioned three projects are the building blocks of the completed research in the dissertation.

In the first study a validated lumped and computationally efficient electrical and thermal
model for a cylindrical supercapacitor cell is developed. The electrical model is a two state equivalent electric circuit model with three parameters that are identified using temporal experiments. The dependence of parameters on state of charge (SOC), current direction and magnitude (20-200 A), and temperatures ranging from -40 °C to 60 °C is incorporated in the model. The thermal model is a linear 1-D model with two states. The reversible heat generation which is significant in double layer capacitors is included in the thermal model. The coupling of the two models enables tuning of the temperature dependent parameters of the electrical model in real time. The coupled electro-thermal model is validated using real world duty cycles at sub-zero and room temperatures with root mean square error of (20-87 mV) and (0.17-0.21 °C) for terminal voltage and temperature, respectively.

The second project evolves around studying the circumstances under which, the hybridization of a lead-acid powered vehicle using supercapacitors will result in extended range. In the first step the lead-acid battery equivalent electric circuit model was parameterized using experimental data and validation was performed. The second step was to integrate the battery model with a DC/DC converter and an existing supercapacitor model to build the hybrid energy storage (HES) model. In the hybrid topology the supercapacitor is responsible for providing the power during traction and capturing the regenerative energy during braking. The battery which is decoupled from the high frequency and high power dynamics of the load functions as an on-board charger for the supercapacitor module. The custom built full-bridge DC/DC converter is located between the battery and supercapacitor in order to regulate the charging current from the battery to the supercapacitor according to the power management strategy. Simulations were performed based on a 48 V electric scooter using city driving cycle and the results were compared with experiments using a hardware in the loop (HIL) setup specifically built for this study. The hardware in the HIL setup consists of a 12 volt lead-acid battery, DC/DC converter, micro-controller (µC), and a 16 V supercapacitor module. The load which includes the vehicle dynamics and the driving cycle is simulated for the HIL experiments. The results show that by regenerating 20% of the available braking energy the range will be improved by 10%.

The third research emphasizes on different charging strategies for stand-alone supercapacitors (SC), lithium-ion (Li-ion), and lead-acid batteries. Constant power (CP) and optimal charging
strategies are formulated and the corresponding charging currents are obtained. Efficiency analysis for different charging strategies and charging times (slow and fast) is performed. The identical objective function for all modules is to minimize the resistive losses during a given charging time by utilizing Pontryagin’s minimum principle. An analytical solution exists for the SC case which is constant current (CC) charging. In case of the Li-ion battery the model includes the electronic as well as polarization resistance. The variation of the total internal resistance with SOC in lead-acid chemistry is considerable and the optimal charging problem results in a two point boundary value problem with an initial and a final condition to be satisfied. Furthermore, a thermal model is coupled with the electrical model of the Li-ion battery to study the effect of voltage, current, and temperature constraints on the charging process.

The fourth study focuses on fast charging challenges and bottlenecks in lithium ion batteries. Suitable models for fast charging, high rate anode materials, and control strategies that emphasize on reducing the charging time are discussed. The side effects of high current charging such as lithium plating and mechanical failure are specifically summarized.

Further details of the mentioned research directions are described in the following sections.

1.1.1 Electro-Thermal Modeling of Cylindrical Supercapacitors

High power density and long cycle life beside other features such as wide temperature operation range, durability in harsh environments, fast and efficient cycling due to low internal resistance, and low maintenance costs makes supercapacitors an attractive electrical energy storage system for various applications [6]. A model of a supercapacitor is required for any application in order to simulate the performance of the system while satisfying electrical and thermal constraints. An equivalent electric circuit model was proposed for the electrical model of the supercapacitor. The model was parameterized using pulse-relaxation data collected from the experiments conducted on the cell. The model is valid from -40 °C to 60 °C considering the dependency of the parameters on temperature, SOC, current direction, and current magnitude. Electrochemical impedance spectroscopy (EIS) measurements were used to study the frequency response of the supercapacitor and to compare it with the electrical model obtained using pulse-relaxation experiments. The thermal
model included the reversible (entropic) as well as the irreversible heat generation. The thermal model consisted of four parameters which were identified as constants using actual current profiles. The coupling between the electrical and the thermal model was done by feeding the total heat generation calculated from the electrical model into the thermal model and tuning the temperature dependent electrical model parameters according to temperature variation obtained from the thermal model. Finally the electro-thermal model was validated using real world driving cycles. The comprehensive and validated electrical model developed in this study is used to build the hybrid supercapacitor-battery model in the next research.

1.1.2 Hybridization of Lead-Acid Battery using Supercapacitors for Range Extension of a Battery Driven Vehicle

Achieving satisfactory driving range in battery electric vehicles has been a challenge for scientists and engineers from its early days in nineteenth century. Efforts on improving the energy density of batteries has led to various secondary type of batteries for traction purposes in electric vehicles (EV) and hybrid electric vehicles (HEV). Lead-acid, nickel metal hydride, and lithium-ion batteries are the major chemistries that have been commercialized. The following challenges limit the wider consumer acceptance of EVs:

- Accelerated battery aging when used in power applications
- Limited charging rate which curtails the amount of regenerative braking energy that can be captured
- Battery packs for EV and HEVs typically need to be oversized to satisfy the power requirements
- Limited vehicle driving range for EVs

In this research, firstly the lead-acid battery’s equivalent electric circuit model is parameterized and validated using experimental data. In the second step the battery model is integrated with the SC model from the above-mentioned research, to build the hybrid energy storage (HES)
model. In the HES topology, the SC is responsible for providing all the power during traction and also capture the regenerated energy from braking. The battery which is decoupled from the high power dynamics of the load, functions as an on-board charger for the SC module. The full-bridge DC/DC converter regulates the charging current according to the power management strategy. Simulations are performed based on a duty cycle derived using an electric scooter platform and a city driving cycle and the results are compared with experiments using a hardware in the loop (HIL) setup specifically built for this study. The HIL setup consists of a 12 V lead-acid battery, DC/DC converter, micro-controller (µC), and a 16.2 V SC module. The results show that by regenerating 20% of the available braking energy the range will improve by 10%.

Regenerative braking as a charging event and the importance of charging efficiency motivates the third research direction. The developed models from the first and second studies are directly used in the third project.

1.1.3 Achievable Charging Efficiencies in Supercapacitors and Batteries using Analytical and Numerical Methods in Optimal Control

Much research and development is spurred towards monitoring and control of the cell charging method, current rate (C-rate) [7,8], temperature [9–11], number of charging/discharging that are important factors in studying the efficiency and cycle life of batteries and supercapacitors [12–18]. In the third research the objective is to maximize the charging efficiency by minimizing the resistive losses in a given charging time and a specified range of SOC. A major performance bottleneck is the heat generated due to resistive losses, during charge and discharge cycles, reducing the overall efficiency and shortening the life span [19–21]. Studies that investigate the optimization of efficiency over the entire driving cycle, mask the fundamental efficiency bottlenecks of stand-alone components such a the electrical energy storage module. This research evaluates different charging strategies for stand-alone supercapacitors (SC), lithium-ion (Li-ion), and lead-acid batteries. Constant power (CP) and optimal charging strategies are formulated and the corresponding charging currents are obtained. Efficiency analysis for different charging strategies and charging times (slow and fast) is performed. The identical objective function for all modules is to minimize the resistive
losses during a given charging time by utilizing Pontryagin’s minimum principle. An analytical solution exists for the SC case which is constant current (CC) charging. The variation of the total internal resistance with SOC in lead-acid chemistry is considerable and the optimal charging problem results in a two point boundary value problem. In case of the Li-ion battery the model includes the electronic as well as polarization resistance. Furthermore, in order to investigate the influence of temperature on the internal resistance of the Li-ion battery, the optimal charging problem for a three state electro-thermal model is solved using dynamic programming (DP).

1.1.4 Fast Charging Challenges in Lithium-Ion Batteries

Among the wide variety of energy storage systems the lithium ion battery in the transportation sector and the pumped hydro storage (PHS) in the electricity grid are the dominant technologies. In 2014, the rated capacity of the U.S. grid-scale energy storage was 29 GW, where the cumulative share of all kind of battery storage systems was 542 MW, accounting for only 2% of the total operational capacity (Source: The U.S. Department of Energy’s Global Energy Storage Database). Within the battery technologies lithium ion is a promising storage system for use in grid-scale applications due to its unique technical advantages such as high energy density, high cycling efficiency, low self-discharge, relatively good cycle life as well as the projected decrease in its cost [22]. However, the challenges facing the deployment of electrical energy storage technologies such as lithium ion batteries in various applications, has motivated research and development in both academia and industry. A number of these barriers are the accelerated aging of lithium ion batteries in high power applications, low temperature performance limitations, low energy density for applications such as electric vehicles which results in range anxiety, and finally the limited charging rate that results in prolonged charging times. The problem of faster charging times is an imperative factor in feasibility of the technology and user acceptability. This chapter encompasses the research that has focused on increasing the charging rate of lithium-ion batteries by investigating the pros of using detailed electrochemical models, various control strategies, and high rate electrode materials. The negative side effects of rapid charging such as lithium plating and mechanical failure are also discussed. Models consisting of electrode, electrolyte and thermal dynamics, anode materials with nanostructure
morphologies, and control strategies based on detailed models and subject to electrical and thermal constraints; are promising approaches in addressing the fast charging problem.

1.2 Dissertation Outline

The remainder of this dissertation is organized in the following order. In Chapter 2, the electrothermal modeling, identification, and experimental validation of the SC is presented. Chapter 3 covers the driving range extension study, by introducing the hybrid battery/supercapacitor model, configuration, power management strategy, and HIL experiments. Chapter 4, presents the research on optimal charging of SC, lead-acid, and lithium ion batteries using analytical and numerical methods. Chapter 5 includes the review on the fast charging of lithium ion batteries. Chapter 6, summarizes this dissertation with the conclusion remarks.
Chapter 2

Supercapacitor Electrical and Thermal Modeling, Identification, and Validation for a Wide Range of Temperature and Power Applications

2.1 Literature Review

Within different electrical energy storage technologies capacitors and supercapacitors are interesting because of their unique characteristics and broad application spectrum. Conventional capacitors are constructed by separating two metallic electrodes by an insulating material called dielectric. In order to keep these capacitors small for electronic devices the only practical way to increase the energy density is to use an electrical insulator (dry or electrolytic) with a higher dielectric constant [23–25]. However the capacitance of these capacitors remain in the order of pico to milli Farads which is not suitable for high energy and power applications. The key to achieve higher energy density is by increasing the surface area using porous electrodes with an extremely large internal effective surface [26]. These efforts led to the development of supercapacitors also known
as “ultracapacitors” or “electric double layer capacitors” (EDLC). The first EDLC was patented by H.I. Becker of General Electric [27]. The first commercialized supercapacitor working with double layer principle was based on the efforts of Robert A. Rightmire and his fellow researcher Donald L. Boos from the Standard Oil Company of Ohio (SOHIO) [28, 29]. The capacitance of these devices can be orders of magnitude larger than those of conventional dry and electrolytic capacitors [30]. Carbon is one of the materials of choice for electrode as it combines unique properties such as high surface-area, conductivity, and temperature stability as well as corrosion resistance with relatively low cost [31]. Metal oxides and polymers are also used as electrode materials [32–34]. The electrodes are immersed inside the electrolyte which is a liquid providing pure ionic conductivity between the positive and negative electrodes. The electrolyte could be either aqueous or non-aqueous depending on the materials and application. Aqueous H$_2$SO$_4$ or KOH electrolytes are common in supercapacitors because of their higher electrical conductivity. Organic electrolyte such as tetraethylammonium tetrafluoroborate (TEA-BF$_4$) in acetonitrile (AN) or propylene carbonate (PC) are also used which allows higher cell voltage up to 2.7 V compared to the 1 V in aqueous electrolytes [35]. Separators are used to prevent electric shorting between electrodes. Separators must be porous so that the ions can pass through them and also stay inert in the supercapacitor cell environment [30]. Supercapacitors are manufactured in cylindrical or prismatic shapes. In the cylindrical design the positive electrode, negative electrode, and the separator are packed in a spiral wound shape. The supercapacitor used in this research is a cylindrical cell with activated carbon electrodes and acetonitrile based electrolyte and the charge storage mechanism is based on the electric double layer established at the electrode-electrolyte interface. Electric double layer capacitors are characterized by high power density and exceptional cycle life. The high power capability arises from the low internal resistance as a result of high electrolyte conductivity, low electronic resistance of the electrode, and the interface between electrodes and current collectors [31]. Formation of electric double layers is due to electrostatic forces and as minimum redox reactions or phase changes occur, the process is highly reversible providing virtually unlimited cycle life [36].

High power density and long cycle life beside other features such as wide temperature operation range, durability in harsh environments, fast and efficient cycling due to low internal re-
sistance, and low maintenance costs makes supercapacitors an attractive electrical energy storage system for various applications [6]. Supercapacitors have been utilized in wind power generation for smoothing fast wind-induced power variations, power leveling of wind farms, and facilitating low voltage operation of doubly fed induction generator (DFIG) [37–44]. Examples of utilizing supercapacitors as energy buffers in solar power generation via photovoltaic panels and Stirling engines are studied in the literature [45–47]. The application of supercapacitors in power system protection as uninterruptible power supply (UPS) in different fields such as telecommunications is also reported [48–52]. In [53], Bakhoum et al. introduce a tunable supercapacitor with variable capacitance suitable for applications such as ultra-wide-band radio transceivers and electro-mechanical transducers with high sensitivity. Luo et al. presents supercapacitors as a promising energy storage for applications in power systems such as transmission and distribution stabilization, voltage regulation and control and motor starting [54]. In bioengineering and medical devices supercapacitors are utilized as energy storage units in devices including magnetic resonance imaging (MRI) and as power supply for laser-based breast cancer detector [55, 56]. In cars, aircraft, and railway vehicles supercapacitors have been studied as stand-alone storage modules or in combination with batteries or fuel cells [18, 57–69]. Improvement in fuel economy up to 15% is reported for a full-size SUV where the internal combustion engine is integrated with supercapacitors in a mild hybrid electric configuration [70]. Having the high efficiency and fast charging capability of supercapacitors in mind, an optimal charging current is obtained considering the dynamics of the vehicle and the electric motor during regenerative braking [71]. Utilizing supercapacitors in a hybrid supercapacitor/battery configuration and with the goal of increasing battery lifetime, a decrease in life cycle cost of 23-50% is reported compared to the battery-only electric city bus [72]. Another interesting application of supercapacitors is boosting the poor low temperature performance of batteries and also helping the cold start of diesel engines [73–75].

A model of supercapacitor is required in all the above-mentioned applications in order to simulate the performance of the system while satisfying electrical and thermal constraints. Electrical models of supercapacitors can be categorized in two groups: (i) models that attempt to mimic all the physical and chemical phenomenon of charging and discharging which are accurate but not
computationally efficient. Continuum models based on Poisson-Nernst-Planck equations, atomistic models based on molecular dynamics, and quantum models based on electron density functional theory (DFT) are in this category [76], (ii) models that are suitable for system level studies which are accurate enough and also suitable for on board and real time applications. Equivalent electric circuit models that mainly capture the terminal voltage dynamics is an example for this group. In this study we are interested in introducing a validated model appropriate for real time integration in a system level. A number of studies have focused on modeling the electrical behavior of supercapacitors in time and frequency domains by proposing equivalent electric circuit models and their identification procedure [77–81]. Musolino et al. propose a full frequency range model that captures the self-discharge and redistribution phenomena [82]. Torregrossa et al. improves the model presented in [77] that captures the diffusion of the SC residual charges during charging/discharging and rest phases [83]. In [13], Rizoug et al. use frequency analysis to identify the resistive parameters and a time domain approach for capacitance characterization. These proposed models are accurate for fixed temperature operations as the dependence of model parameters on temperature are not taken into account. The importance of the variation of electrical model parameters with temperature is studied in [84–86]. Buller et al. uses electrochemical impedance spectroscopy to identify model parameters considering dependence on four voltage levels and temperatures from -30 °C to 50 °C [87].

The proposed equivalent circuit model in this dissertation has the following characteristics:

- Terminal voltage dynamics is captured with high accuracy (20-87 mV) suitable for all power system applications.

- Computationally efficient with only 3 parameters to be identified.

- Carefully designed temporal experiments (pulse-relaxation) are utilized for identification purposes.

- The dependence of model parameters on temperature (range:-40 °C to 60 °C), state of charge (SOC) (range:0-100), current direction (charge/discharge), and also for the first time, current magnitude (range: 20-200 A) is investigated.
• EIS measurements in the frequency domain at -20 °C and 25 °C are used to validate the model parameterized in time domain.

• A second validation method is performed by tracking the model performance under dynamically rich and real-world duty cycles rather than simple pulse tests often utilized in the literature.

On the other hand having the knowledge of how the temperature of a supercapacitor cell varies helps predict thermal run-aways and its aging behavior [88]. It also enables obtaining models for cooling management purposes at the stack level [89] and real time tuning of the temperature dependent parameters of the electrical model [90–93]. The thermal dynamics can be predicted by numerically solving the governing partial differential equations (PDE) as investigated in [94, 95]. However these complex first principle based thermodynamic models are computationally expensive and therefore not suitable for real time applications. Utilizing a reduced order model with sufficient accuracy for power applications is of interest in this study. In [96], Berrueta et al. propose reduced order electrical and thermal models for a 48 V supercapacitor module and the application of the electrical model is shown in a micro-grid case study. However the thermal model is over simplified by neglecting the reversible heat generation effect which is significant in EDLCs [97] and considering the pack as a whole body (zero-dimensional model) which results in a high reported RMS error for the thermal model (2.229 °C) [96]. In [98, 99] electrical and thermal models are proposed and efforts have been made on including the reversible heat generation according to [97], however clear results on capturing the exothermic effect during charging and endothermic behavior during discharging are not observable in the papers.

The proposed reduced order thermal model in this study has the following characteristics:

• The thermal model is a linear 1-D model with 2 states.

• Temperature dynamics is captured with high accuracy (0.17-0.21 °C) suitable for thermal management systems.

• Computationally efficient with only 4 parameters to be identified.
• Both the reversible (entropic effect) and irreversible heat generation (joule heating) are integrated in the model.

• Real world duty cycles are used to parametrize the model.

• The thermal model is coupled with the electrical model to capture the changes in the parameters of the electrical model that depend on temperature.

• The coupled electro-thermal model is validated using a practical driving cycle rather than simple constant current cycles often used in the literature.

This chapter is organized in the following order. In section 2.2 the experimental setup which the parameterization and validation experiments are performed and also the EIS equipment is described. In section 2.3 the electrical model of the supercapacitor and its parameterization is presented. Section 2.4 covers the frequency domain analysis using EIS measurements. Section 2.5 describes the thermal model, integration of the reversible heat generation in the model, coupling of the electrical and thermal models, identification results of the model, and the experimental validation. Finally, section 2.6 concludes the chapter.

2.2 Experimental Setup

Experiments have been conducted on a cylindrical Maxwell BCAP3000 cell with activated carbon as electrodes. The cell contains non-aqueous electrolyte allowing the maximum rated voltage of 2.7 V. The specifications of the cell are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Voltage (V)</td>
<td>2.7</td>
</tr>
<tr>
<td>Nominal Capacitance (F)</td>
<td>3000</td>
</tr>
<tr>
<td>Mass (kg)</td>
<td>0.5</td>
</tr>
<tr>
<td>Specific Power (Wkg(^{-1}))</td>
<td>5900</td>
</tr>
<tr>
<td>Specific Energy (Whkg(^{-1}))</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2.1: Supercapacitor cell specification
All the pulse-relaxation experiments related to parametrization and validation of both the electrical and thermal models are conducted using the following set of equipments:

- Power supply: Bitrode FTV1-200/50/2-60 cycler which is capable of supplying up to 200 A suitable for running the pulse-relaxation and also the driving cycle validation tests.

- Thermal chamber: Cincinnati sub-zero ZPHS16-3.5-SCT/AC capable of controlling the ambient temperatures as low as -40 °C and up to 150 °C.

- Temperature sensor: OMEGA T-type thermocouple which its accuracy is the maximum of 0.5 °C or 0.4% according to technical information provided by the manufacturer.

Fig. 2.1 shows the cell connected to the power supply and placed in the thermal chamber with the thermocouple attached to the surface of the cell. The cell is suspended to allow uniform airflow around the cell for a better identification of the convective heat coefficient.

The EIS measurements are obtained using Gamry series G-750 potentiostat/galvanostat equipment along with the thermal chamber where the cell was located for controlled ambient temperature.

![Figure 2.1](image)

**Figure 2.1:** The supercapacitor cell connected to the power supply with the thermocouple attached to the surface and placed in the thermal chamber.
2.3 Electrical Model of the Supercapacitor

The equivalent electric circuit model, identifying cell capacitance and open circuit voltage ($OCV$), and also electric model parameter estimation results are presented in this section.

2.3.1 Equivalent Electric Circuit Model

In this study the galvanostatic approach is used in the whole modeling procedure where current is the input to the system and the output of interest is the terminal voltage. This approach is also widely used in the battery literature for parameterizing equivalent electric circuit model parameters [100–102] and using the model in control oriented research such as optimal charging of lithium-ion and lead-acid batteries [103]. Fig. 2.2 shows the schematic of the proposed equivalent electric circuit model. It consists of a resistance $R_s$ connected in series to the $RC$ branches. Considering positive sign for the charging and negative sign for discharging and applying Kirchhoff’s voltage law (KVL) to the circuit shown in Fig. 2.2, the equation governing the terminal voltage $V_T$, could be written as follows:

$$V_T = OCV(SOC) + IR_s + \sum_{j=1}^{n} V_{RC,j} \quad (2.1)$$

In equation (3.1), $OCV$ is a linear function of $SOC$ for an ideal capacitor. The $SOC$ is
determined by coulomb counting by the following state equation:

\[ \frac{dSOC}{dt} = \frac{I}{CV_{\text{max}}} \]  \hspace{1cm} (2.2)

where \( C \) and \( V_{\text{max}} \) are the nominal capacitance in Farads and the maximum voltage across the cell at full charge. The second term in (3.1), is the voltage drop over the series resistance and the last part is the sum of voltage drops across \( RC \) branches. Dynamics of each \( RC \) pair is described as:

\[ \frac{dV_{RC,j}}{dt} = -\frac{1}{R_jC_j}V_{RC,j} + \frac{I}{C_j} \]  \hspace{1cm} (2.3)

where \( R_j \) and \( C_j \) are the corresponding resistance and capacitance of each \( RC \) branch, respectively.

### 2.3.2 Cell Capacitance and Open Circuit Voltage

The \( OCV \) and capacitance (\( C \)), are the primary modeling parameters to be identified. Capacitance and capacity are the terms used to determine the amount of electric charge stored in electrical energy storage systems. Capacitance is the term used for supercapacitors with the unit of Farads. Equivalently the term capacity is used in the battery literature with the unit of ampere hours (Ah). The relationship between capacity in Ah and capacitance (\( C \)) in Farads is:

\[ \text{capacity} = \frac{CV_{\text{max}}}{3600} \]  \hspace{1cm} (2.4)

The capacitance of the cell used in this study is 3000 F which is equivalent to 2.25 Ah. The term C-rate is the rate at which charging (discharging) is performed. For example charging a cell with a capacity of 2.25 Ah from zero to full charge with a C-rate of one means, supplying a current of 2.25 A that results in a charging time of one hour. Similarly the charging current values used in this study which are 22.5 A, 67.5 A, 135 A, and 191 A are equivalent to C-rates of 10C, 30C, 60C, and 85C respectively. The power supply utilized in this research has a current limit of 200 A, which is the reason of choosing 191 A as the maximum pulse current applied in the experiments. The capacitance is obtained by charging the cell from zero to maximum voltage applying a small
constant current. The reason for using small current is to minimize the effect of resistive losses and measure the capacitance more accurately. Constant current assumption allows to integrate (3.2) using the boundary conditions \( SOC(0) = SOC_i \) and \( SOC(t_f) = SOC_f \) and to find the capacitance:

\[
C = \frac{t_f I(t)}{V_{\text{max}}(SOC_f - SOC_i)}
\]  

(2.5)

where \( t_f \) is the charging time. \( SOC_f \) and \( SOC_i \) are not measured and by definition are one at full charge \((V_T = V_{\text{max}} = 2.7 \text{ V})\) and zero at the empty state \((V_T = V_{\text{min}} = 0 \text{ V})\). The charging current used in the experiment was 0.112 A (equivalent to a C-rate of \( \frac{C}{20} \)) and the time recorded to fully charge the empty cell was 21.05 hours which according to (3.4) results in a capacitance of 3143 F. Similarly a constant current of 0.1178 A was applied to discharge the fully charged cell to zero. The recorded time was 18.73 hours resulting in a capacitance of 2934 F. The reported nominal capacitance by the manufacturer is 3000 F which is almost the average of the measured capacitance for charging and discharging. The \( OCV \) as a function of \( SOC \) is obtained by charging the cell from \( V_0 = 0 \text{ V} \) to \( V_{\text{max}} = 2.7 \text{ V} \) with a small constant current of 0.45 A (equivalent to a C-rate of \( \frac{C}{5} \)). By applying a small constant current, the recorded terminal voltage at each time corresponds to the \( OCV \) at that time. The obtained \( OCV \) profile is almost identical for a C-rate equal to \( \frac{C}{5} \) compared to \( \frac{C}{20} \), so we present the results based on the \( \frac{C}{5} \) rate, which is a shorter test to run. Using the coulomb counting method governed by (3.2), \( SOC \) is obtained at each time. This provides a profile for \( OCV \) as a function of \( SOC \) to be integrated in the supercapacitor model. The difference between charging and discharging \( OCV \) is small due to low current and small equivalent series resistance.

The \( OCV \) as a function of \( SOC \) is shown in Fig. 2.3. In this figure the ideal linear \( OCV \), the measured terminal voltage with a high constant current of 140 A, and the \( OCV \) used in this study are shown. The effect of high current is shown to compare it with the low current measurements. As it can be observed, the high current results in a loss of capacity of 6% as the cell reaches its maximum allowed voltage in a shorter time. This is the reason of using low current for identifying the capacity and the \( OCV \) of the cell. The \( OCV \) of the supercapacitor under investigation has a nonlinear relationship with \( SOC \) as shown in experiment-2 in Fig. 2.3. A fourth order polynomial
is fitted to the $OCV$ versus $SOC$ data and integrated in the model as follows:

$$OCV(SOC) = -0.18(SOC)^4 + 0.59(SOC)^3 - 1.2(SOC)^2$$
$$+ 3.5(SOC) - 1.9 \times 10^{-4}$$

(2.6)

The nonlinearity in the $OCV$ profile is due to the small pseudo-capacity behavior of the cell [104].

![Figure 2.3: Ideal and real $OCV$ for low and high currents versus $SOC$.](image)

2.3.3 Equivalent Electric Circuit Model Identification

The unknown parameters of the equivalent circuit are $R_s$, $R_j$, and $C_j$. In order to record a rich set of data for identification and also to investigate the dependence of parameters on $SOC$, current magnitude and direction and also temperature, the following set of pulse-relaxation experiments are performed:

- Experiments are conducted at six temperature levels (-40, -20, 0, 25, 40, 60 °C). The lower and upper limits for the temperature are the actual limits reported by the manufacturer.

- At each temperature level four pulse current rates (191, 135, 67.5 and 22.5 A) are applied.

- Starting at a fully discharged state the cell is charged by the pulse current to 5% $SOC$ then
followed by a 20 second relaxation period. This procedure is repeated for each 5% $SOC$ interval until the cell is fully charged.

- Similar pulse-relaxation procedure is repeated for discharging immediately at the end of the charging process.

Fig. 2.4 is one example of the total of 24 different pulse relaxation tests. This test will be called the “sample test” throughout the dissertation and will be used to present the identification process and model accuracy investigation. In this specific test the temperature is 25 °C and the current is 191 A.

![Figure 2.4: Sample pulse-relaxation test at 25 °C and 191 A current.](image)

The relaxation period at each $SOC$ level contains the information needed to estimate the equivalent electric circuit model parameters. The relaxation or rest phase consists of two segments as depicted by the insets in Fig. 2.4. The first part is a sudden change in terminal voltage at the moment the current is set to zero. This change is observed by an instant drop in voltage while charging and a jump in voltage during discharge and is captured by $R_s$ in the model. The second part in the relaxation stage is the exponential behavior in voltage and is modeled by the $RC$ branches. $R_s$ is obtained by dividing the instant voltage change by the pulse current at each 5% $SOC$ level. Fig. 2.5 illustrates the variation of $R_s$ during discharge with respect to $SOC$ and temperature at 19 °C.
each current level. This figure shows that as the temperature increases $R_s$ decreases regardless of the current magnitude except for 60 °C. In supercapacitors, the electronic resistance of the electrode and electrolyte and also interfacial resistance between the electrode and the current-collector contribute to the amount of $R_s$ [105, 106]. An increase in electrolyte resistance or an increase in the interface resistance between the electrode and the current collector could contribute to the increase in $R_s$ at 60 °C. The dependence of $R_s$ on $SOC$ is small according to Fig. 2.5 for all temperatures and currents except the high current case (191 A). The dependence in this case can be approximated by fitting a second order polynomial to the data in the following general form:

$$R_s(SOC) = a(SOC)^2 + b(SOC) + c$$ (2.7)

Table 2.2 shows the coefficients for the fitted second order polynomials to the data at different temperatures and current of 191 A.

**Table 2.2:** The coefficients of the fitted second order polynomial for different temperatures and current of 191 A

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>-40</td>
<td>6.7E-5</td>
<td>-6.5E-5</td>
<td>4.4E-4</td>
</tr>
<tr>
<td>-20</td>
<td>1.9E-4</td>
<td>-1.8E-4</td>
<td>4.1E-4</td>
</tr>
<tr>
<td>0</td>
<td>1.1E-4</td>
<td>-1.2E-4</td>
<td>3.8E-4</td>
</tr>
<tr>
<td>25</td>
<td>1.2E-4</td>
<td>-1.3E-4</td>
<td>3.7E-4</td>
</tr>
<tr>
<td>40</td>
<td>5.7E-5</td>
<td>-6.1E-5</td>
<td>3.6E-4</td>
</tr>
<tr>
<td>60</td>
<td>4.9E-5</td>
<td>-6.4E-5</td>
<td>4.2E-4</td>
</tr>
</tbody>
</table>

Another representation of Fig. 2.5 is plotted in Fig. 2.6 to be able to observe the dependence of $R_s$ with respect to the magnitude of pulse current at different temperatures and during discharge period. The figure indicates that the variation of $R_s$ with the current magnitude is negligible regardless of the ambient temperature.

The temperature measurements form the thermocouple attached to the surface of the cell for all 24 set of pulse-relaxation tests are depicted in Fig. 2.7. This figure shows that applying higher
Figure 2.5: $R_s$ as a function of $SOC$ for all temperatures at each pulse current level during discharging.

Figure 2.6: $R_s$ as a function of $SOC$ for all currents at each temperature during discharging.
pulse current results in a higher surface temperature at the end of the charging period regardless of the ambient temperature. The highest observed increase in surface temperature is 1.5 °C at the highest ambient temperature of 60 °C and at the highest current. According to Fig. 2.5 a 23-30 % increase in $R_s$ occurs from 40 to -40 °C. This indicates that the effect of a small change in temperature during the pulse-relaxation tests on $R_s$ is negligible. Another interesting observation from Fig. 2.7 is that during discharging the surface temperature of the cell decreases. This phenomena and the reasoning will be addressed in the thermal modeling section of the dissertation.

![Figure 2.7: Supercapacitor cell surface temperature at different ambient temperatures and pulse current rates.](image)

At this point the knowledge of small variation of $R_s$ with $SOC$ and negligible temperature effect during each pulse-relaxation test allows to consider a constant value for $R_s$ at each temperature and current level. This is done by taking the average of the $R_s$ with respect to $SOC$ for the charging and discharging sections separately. The final $R_s$ is obtained by averaging the values obtained from the charging and discharging sections for each pulse relaxation test. Fig. 2.8 shows the variation of the constant averaged $R_s$ with temperature and current magnitude. This figure indicates that $R_s$ is highest at -40 °C and that the change of the average $R_s$ with respect to temperature is higher than that due to current magnitude.

The next step is to identify the values of resistance and capacitance of the $RC$ branches with the assumption that the parameters are constant and not a function of $SOC$. Identification of $R_j$ and $C_j$ is performed by minimizing the square error between the measured and simulated terminal
voltages for each pulse-relaxation experiment to obtain the estimated values for each temperature level and current magnitude. The cost function to be minimized is:

\[ J = \sum_k (V_m(k) - V_T(k))^2 \]  

(2.8)

where \( V_m \) and \( V_T \) are the measured and simulated terminal voltages, respectively. The number of \( RC \) branches will be determined based on the accuracy of the estimation results.

Firstly a simple first order model named \( OCV - R_s \) which consists of resistance \( R_s \) connected in series to the terminals of the supercapacitor is considered. The single parameter in this model is \( R_s \) which is already identified. The root mean square error (RMSE) between the terminal voltage from the model and sample test experiment considering the ideal versus the real \( OCV \) is obtained. The RMSE numbers in Table 2.3 show that the real nonlinear \( OCV \) profile should be integrated in the model as the results for the sample test indicate a 50% decrease in RMS error. The drop in RMSE is also significant for other tests using the nonlinear \( OCV \) profile.

In the next step a single \( RC \) branch is added in series to the \( OCV - R_s \) to build the \( OCV - R_s - RC \) model. Fig. 2.9 compares the terminal voltage results from the \( OCV - R_s - RC \) model and the experimental data from the sample test.
The result shows that the electrical model with the estimated $R_1$ and $C_1$ accurately predicts the dynamics of the terminal voltage with a RMSE of 20 mV as listed in Table 2.3. This result shows that the $OCV - R_s - RC$ model is accurate enough and will be used as the final electrical model.

**Table 2.3:** RMS error between model and experiment

<table>
<thead>
<tr>
<th>Model</th>
<th>RMSE (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear-$OCV-R_s$</td>
<td>100</td>
</tr>
<tr>
<td>Nonlinear-$OCV-R_s$</td>
<td>50</td>
</tr>
<tr>
<td>$OCV-R_s-RC$</td>
<td>20</td>
</tr>
</tbody>
</table>

By performing a similar procedure used to estimate the electric model parameters for the sample test, $R_1$ and $C_1$ parameters were identified for the other 23 pulse-relaxation experiments. Fig. 2.10 and 2.11 summarize the estimated parameters $R_1$ and $C_1$ as a function of all temperature and current levels, respectively. Similar to $R_s$ that reaches its maximum value at low temperatures, $R_1$ also shows such a behavior. The resistance in the $RC$ branch represents the polarization resistance which in general is due to kinetic reactions and also diffusion process. In the case of a double layer supercapacitor with carbon electrodes and organic electrolyte the kinetic reactions are
minimum. The charge transfer is mostly based on electrostatic diffusion of ions in the pores of the electrode material. Similar to $R_s$ that reaches its maximum value at low temperatures, $R_1$ also shows such a behavior. The $C_1$ value corresponds to the double layer capacitance of the supercapacitor. The value of $C_1$ depends on the surface area of the activated carbon, electrical conductivity of the electrolyte, and the double-layer effective thickness [84, 107]. The variation of any of the mentioned parameters contribute to the observed higher value of $C_1$ at the current of 135 A. One direction for future work is to use a more complicated model and also in situ measurements to explain the current dependency of model parameters in detail.

![Figure 2.10: Estimated $R_1$ as a function of temperature and current.](image)

### 2.4 Frequency Analysis Using Electrochemical Impedance Spectroscopy Measurements

Fig. 2.12 shows the electric model proposed and identified using pulse-relaxation experiments in the previous section. Considering a linear relationship for the OCV as a function of SOC, (3.1) can be re-written for the final electrical model as follows:

$$V_T = \frac{\int I dt}{C} + IR_s + V_1$$  \hspace{1cm} (2.9)
By taking Laplace transform of both sides of (2.9) and obtaining the ratio of terminal voltage ($V_T$) as the output to current ($I$) as the input, the transfer function of the electrical model of the supercapacitor is derived as follows:

$$Z(S) = \frac{1}{CS} + \frac{R_s}{R_1C_1S + 1}$$  \hspace{1cm} (2.10)

Substituting $S = j\omega$ in (2.10), the impedance of the supercapacitor is obtained as a function of the current frequency ($\omega$). An informative way of representing the impedance dynamics is the so-called Nyquist diagram which is the imaginary part of the impedance plotted versus the real part, for a known range of frequencies. The intersection of the Nyquist plot with the real axis represents $R_s$ in the model. The resistances contributing to the amount of $R_s$ are the electronic resistance of the electrode material, resistance between the electrode and the current-collector, electrolyte resistance and the ionic resistance of ions moving through the separator [31]. The dependence of $R_s$ on the electrode and electrolyte resistance is investigated in [105] showing that the lower amount of active carbon material used in the electrode and also higher electrolyte conductivity will result in a smaller $R_s$. The effect of resistance between the electrode material and the current collector is studied in [106] illustrating that treating the current collector before applying the coating of active carbon
will result is a smaller $R_s$. The resistance in the $RC$ branch represents the polarization resistance which in general is due to kinetic reactions and also diffusion process. In the case of a double layer supercapacitor with carbon electrodes and organic electrolyte the kinetic reactions are minimum. The charge transfer is mostly based on electrostatic diffusion of ions in the pores of the electrode material. The $C_1$ value corresponds to the double layer capacitance of the supercapacitor.

**Figure 2.12:** Identified single $RC$ electrical model.

In order to study the frequency response of the supercapacitor electrochemical impedance spectroscopy (EIS) experiments were performed. Using the Gamry series G-750 potentiostat/galvanostat equipment, experiments with the following specifications were conducted:

- Two temperature levels of -20 °C and 25 °C.
- Small input currents of 0.4 A for -20 °C and 0.2 A for 25 °C.
- Frequency window of 50 mHz to 100 kHz.
- The sampling rate is 20 points per each decade of frequency.
- Data is gathered at 0, 20, 40, 50, 60, 80, and 100% $SOC$ at each temperature level.

Fig. 2.13 shows the Nyquist plot for two temperature levels. It shows that $R_s$ is less at higher temperatures. Also in average the value for $R_s$ from EIS measurements is higher than the values from pulse-relaxation experiments which is consistent with [13]. The figure also shows that
at high frequencies (points closer to the origin) supercapacitor has a pure resistive behavior and at very low frequencies a mostly capacitive behavior.

In order to depict the dependency of the magnitude and phase of the complex impedance on frequency explicitly, the Bode plots are presented. Fig. 2.14 compares the magnitude and phase between the single $RC$ model and the EIS measurements at 25 °C.

Considering the estimated values for $R_s$, $R_1$, and $C_1$ from the pulse-relaxation sample test the transfer function for the supercapacitor is:

$$Z(S) = \frac{(S + 0.0005)(S + 0.9989)}{S(S + 0.00056)} \quad (2.11)$$

As it can be observed from the phase plot of the model the system begins from a -90 degree of phase at low frequencies which represents the integrator term in the transfer function. The term $(S + 0.9989)$ in the numerator of the transfer function affects the system at the corner frequency of about $(\omega = 1)$ causing the phase to approach to zero degree. The effect of the other two terms in the numerator and denominator of the transfer function is not observable in the bode plot as they almost cancel out each other and do not effect the impedance. The Bode plots for the EIS measurements differ from the model at frequencies above 100 rad/s. The increase of the phase angle from zero
degrees at 100 rad/s to +90 degrees at higher frequencies indicates an inductive behavior. This behavior is not captured by the model as the frequency of the pulse-relaxation experiments is less than 100 rad/s. This is acceptable, as in practical applications the frequency of the current as the input to the system is much lower than 100 rad/s.

![Bode plot](image)

**Figure 2.14:** Bode plot of the single RC electrical model versus EIS measurements.

After developing the electrical model and analyzing it in the frequency domain the next steps are to develop the thermal model of the supercapacitor and to validate the coupled electro-thermal model.

### 2.5 Thermal Model of the Supercapacitor

A computationally efficient thermal model developed for cylindrical batteries [108] is modified and adopted for the thermal modeling of the supercapacitor. In the beginning of this section the two-state thermal model will be described. In the consecutive sections entropic heat generation
and electro-thermal coupling will be introduced. Finally parameterization results are presented.

### 2.5.0.1 Two State Thermal Model

The model is based on one dimensional heat transfer along the radial direction of a cylinder with convective heat transfer boundary conditions as illustrated in Fig. 2.15.

![Figure 2.15](image_url)

**Figure 2.15:** Given the assumption of uniform heat generation with a convective cooling boundary condition at the surface, the radial temperature distribution can be approximated as a 4th order polynomial.

A cylindrical supercapacitor, so-called a jelly-roll, is fabricated by rolling a stack of cathode/seperator/anode layers. Assuming a symmetric cylinder, constant lumped thermal properties such as cell density, conduction heat transfer, and specific heat coefficient are used [108]. Uniform heat generation along the radial direction is a reasonable assumption according to [109]. The temperature distribution in the axial direction is more uniform than the radial due to higher thermal conductivity [110]. The radial 1-D temperature distribution is governed by the following PDE:

$$\rho c_p \frac{\partial T(r, t)}{\partial t} = k_t \frac{\partial^2 T(r, t)}{\partial r^2} + \frac{k_t}{r} \frac{\partial T(r, t)}{\partial r} + \frac{Q(t)}{V_{cell}}$$  \hspace{1cm} (2.12)

with boundary conditions:

$$\frac{\partial T(r, t)}{\partial r} \bigg|_{r=0} = 0$$  \hspace{1cm} (2.13)
\[ \frac{\partial T(r, t)}{\partial r} \bigg|_{r=R} = -\frac{h}{k_t} (T(R, t) - T_\infty) \] (2.14)

where \( t, \rho, c_p \) and \( k_t \) are time, volume-averaged density, specific heat, and conduction heat transfer coefficients, respectively. The heat generation rate inside the cell is \( Q \), the cell volume is \( V_{\text{cell}} \) and \( R \) is the radius of the cell. The first boundary condition in (2.13) is to satisfy the symmetric structure of the cell around the core. Convective heat transfer at the surface of the cell forms the boundary condition in (2.14). Here \( T_\infty \) is the ambient air temperature and \( h \) is the heat transfer coefficient for convective cooling.

With uniform heat generation distribution, the solution to (2.12) is assumed to satisfy the following polynomial temperature distribution as proposed in [111]:

\[ T(r, t) = \alpha_1(t) + \alpha_2(t) \left( \frac{r}{R} \right)^2 + \alpha_3(t) \left( \frac{r}{R} \right)^4 \] (2.15)

The volume-averaged temperature \( \bar{T} \), and volume averaged temperature gradient \( \bar{\gamma} \) are chosen as the states of the thermal model. These quantities can be related to the temperature distribution as follows:

\[ \bar{T} = \frac{2}{R^2} \left[ \int_0^R r T \, dr \right] \] (2.16)

\[ \bar{\gamma} = \frac{2}{R^2} \left[ \int_0^R r \left( \frac{\partial T}{\partial r} \right) \, dr \right] \] (2.17)

Using (2.15) the surface \( T_s \) and core \( T_c \) temperature of the cell are expressed by:

\[ T_s = \alpha_1(t) + \alpha_2(t) + \alpha_3(t), \quad T_c = \alpha_1(t) \] (2.18)

The temperature distribution \( T(r, t) \) can be written as a function of \( T_s, \bar{T}, \) and \( \bar{\gamma} \) after some algebraic manipulation. The original PDE (2.12), can be reduced to a set of two linear ordinary
differential equations (ODE) with the state space representation of:

\[
\dot{x} = Ax + Bu, \quad y = Cx + Du
\]  

(2.19)

where \( x = [\bar{T} \quad \bar{\gamma}]^T \), \( u = [Q \quad T_\infty]^T \), and \( y = [T_c \quad T_h]^T \) are state, input, and output vectors respectively. The parameter \( \beta = \frac{k_t}{\rho c_p} \) is the thermal diffusivity. Finally the linear system matrices A, B, C, and D are:

\[
A = \begin{bmatrix}
-48\beta h / (24k_t + rh) & -15\beta h / (24k_t + rh) \\
-320\beta h / r^2(24k_t + rh) & -120\beta(4k_t + rh) / r^2(24k_t + rh)
\end{bmatrix}
\]

\[
B = \begin{bmatrix}
\beta / k_n \text{cell} & 48\beta h / r(24k_t + rh) \\
0 & 320\beta h / r^2(24k_t + rh)
\end{bmatrix}
\]

\[
C = \begin{bmatrix}
24k_t - 3rh / 24k_t + rh & -120rh / r(24k_t + rh) \\
24k_t / 24k_t + rh & 15rh / 48k_t + 2rh
\end{bmatrix}
\]

\[
D = \begin{bmatrix}
0 & 4rh / 24k_t + rh \\
0 & rh / 24k_t + rh
\end{bmatrix}
\]

This linear two state model is relatively easier to parameterize compared to the detailed PDE models, as shown in the following sections.
2.5.0.2 Thermal Test Procedure

In order to investigate the dependence of temperature dynamics on current magnitude, depth of discharge (SOC range) and also relaxation period (rest time), the following set of repeated cycling experiments are performed:

- Experiments are conducted at two temperature levels (-20 and 25 °C).
- At each temperature level three current levels (140, 100, and 50 A) are applied.
- Two SOC ranges (0-100% and 50-100%) and two resting times (90 and zero seconds) are studied.
- In each set of experiments a fully discharged or a half charged cell undergoes cycles of charge-rest-discharge until the surface temperature of the cell reaches steady state, followed by a long rest period till the surface temperature relaxes to its initial value.

Fig. 2.16 shows the surface temperature and voltage evolution under a pulse test with current of 140 A. In this test, the cell is cycled in the upper half of the voltage range (50-100% SOC) with an ambient temperature of -20 °C and 90 seconds of rest between every charge and discharge period. The surface temperature reaches steady state after approximately 1 hour.

2.5.1 Irreversible and Reversible Heat Generation

The total heat generation consists of two parts. The first contributor to the total heat generation is the ohmic losses. These losses are due to the internal resistance of the cell. This irreversible joule heating effect is associated with the losses in $R_s$ and $R_1$ as follows:

$$Q_{\text{joule}} = R_s I^2 + \frac{V_1^2}{R_1}$$

(2.20)

where $V_1$ is the voltage across $R_1$ in the single RC branch.

The inclusion of reversible heat generation in the model which is the second contributor to the total heat generation is required to accurately predict the dynamic temperature response for
Figure 2.16: Sample test for the study of temperature dynamics of the supercapacitor.

cycling over different SOC ranges at both low and high currents and temperatures. The reversible (entropic) heat generation rate is governed by [97]:

\[ Q_{\text{rev}} = \delta \bar{T} I(t) \]  

(2.21)

The reversible heat generation rate is proportional to current and the volume average temperature \( \bar{T} \) with the unit of Kelvin (K) [97]. The constant of proportionality \( \delta \) is related to the physical properties of the cell and will be estimated from the temperature measurements. As an example, Fig. 2.17 shows the reversible and irreversible heat generation profiles for the specific test at 140 A, 25 °C with a 90 second rest period and charging the cell from zero to full charge. The first two subplots show the applied current profiles and the measured surface temperature. The inset in the heat generation plot at the steady state region shows that the reversible heat generation rate is proportional to the magnitude and direction of the current while the irreversible heat generation rate is always positive and almost a linear function of time. Integrating the heat generation rates during charging and discharging at the steady state region, the reversible heat generation is calculated to be 616 joules compared to the 392 joules of the irreversible heat generation.
Figure 2.17: Reversible and irreversible heat generation rates for a test at 25 °C, 140 A, 90 second rest, and full SOC range.

Figure 2.18: Thermal pulse tests at -20 °C and 140 A for different SOC ranges and rest periods.
Fig. 2.18 shows a set of four experiments at -20 °C and pulse current of 140 A that highlights the effect of rest period between the charge and discharge cycle and depth of discharge on the dynamics of temperature rise. All profiles show an overall increase in the cell temperature during the test which is due to the irreversible heat generation. The effect of entropy on the temperature rise is only observable when there is a rest. In this case the RMS current is lower and therefore $Q_{\text{joule}}$ is smaller. While in the case without any rest between charging and discharging the average steady state temperature is not a function of $SOC$ range. A closer look at the inset in Fig. 2.18 will also reveal that there is an obvious non-linearity in the temperature ripple. This is due to the reversible heat generation which is a result of entropy change during charge and discharge period. Considering the ions in the supercapacitor as the system of interest, the change of entropy of this system from state 1 to state 2 is [112]:

$$\Delta S = -\int_{1}^{2} \frac{dQ_{\text{rev}}}{T} = -C_{p}ln\left(\frac{T_{2}}{T_{1}}\right)$$

(2.22)

where $C_{p}$ is the heat capacitance of the double layer supercapacitor. Entropy can be interpreted as a measure for disorder in a system. This means that the higher the level of disorder in a system, the higher the entropy. During charging as the ions move to the surface of the electrodes the disorder of the system of ions is decreasing, therefore the entropy decreases. According to (2.22), for $\Delta S$ to be negative (decreasing entropy) $T_{2}$ should be greater that $T_{1}$ which explains the increase in temperature during charging. While discharging, the disorder level of ions is increasing as they spread out in the electrolyte randomly similar to an ideal gas [97]. This results in an increase in the entropy ($\Delta S > 0$) which dictates a decrease in temperature ($T_{2} < T_{1}$) according to (2.22) clarifying the observed cooling effect during discharge.

### 2.5.2 Coupling of the Electrical and Thermal Models

The electrical and thermal models are coupled to form the complete system model. The total heat generation rate is calculated from the equivalent circuit model, and the temperature (which is the output of the thermal model) feeds back into the resistance of the equivalent circuit. Fig. 2.19 is
the schematic of the coupled electro-thermal model.

![Schematic of the coupled electro-thermal model](image)

**Figure 2.19:** Coupling of the electrical and thermal models.

### 2.5.3 Parameterization Results for the Thermal Model

The convective \( h \) and conductive \( k_t \) heat coefficients, specific heat coefficient \( C_p \), and the parameter in (2.21) associated with reversible heat generation (\( \delta \)) are the parameters to be identified for the thermal model. The urban assault cycle (UAC) which is used to generate the battery current profile [113] for a heavy vehicle (13.4 ton) and also utilized in parametrization of battery thermal models in [108] and [100] was scaled up by a factor of six to generate an input current profile with sufficient excitation for supercapacitor applications. Also a relaxation period of one hour is added to the data set which results in useful temperature relaxation data for parameterizing the heat capacity and coefficient of convective cooling in the model. The physical parameters of the cell that are measurable are summarized in Table 3.3.

**Table 2.4:** Physical parameters of the cell

<table>
<thead>
<tr>
<th>Mass (kg)</th>
<th>Length (m)</th>
<th>Radius (m)</th>
<th>Volume (m(^3))</th>
<th>Density (kgm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>0.138</td>
<td>0.0304</td>
<td>4E-4</td>
<td>1277</td>
</tr>
</tbody>
</table>

Parameter estimation is performed by minimizing the square error between the measured
$(T_m)$ and simulated $(T_s)$ surface temperatures. The cost function to be minimized is:

$$J = \sum_k (T_m(k) - T_s(k))^2$$  \hspace{1cm} (2.23)

Fig. 2.20 compares the modeled surface temperature with experimental measurements performed on the cell using the UAC at $25 \, ^\circ C$ and sub-zero temperature of $-20 \, ^\circ C$. The histogram of the temperature error is also shown for both temperatures. The RMS error is 0.13 $^\circ C$ and 0.11 $^\circ C$ for $25 \, ^\circ C$, and -20 $^\circ C$ respectively, which is an indicator of the estimation accuracy.

![Figure 2.20: Thermal model parameterization result using the urban assault driving cycle (UAC) at (a) 25 $^\circ C$ and (b) -20 $^\circ C$.](image)

Table 3.4 shows the values of the identified thermal model parameters for both $25 \, ^\circ C$ and $-20 \, ^\circ C$. The value estimated for $h$ is in the range of forced convective heat transfer coefficient for air which is between 10 to 200 W/(m$^2$K). The thermal chamber consists of a fan inside it which helps regulate the temperature to the preset value. The estimated value of $h$ will depend on the fan being on or off during the experiment which is the reason for different values for $h$ at two temperatures of $25 \, ^\circ C$ and $-20 \, ^\circ C$. The specific heat coefficient values is close to the amount of the cell’s organic based electrolyte (Acetonitrile $c_p$=1863 J/kgK at $25 \, ^\circ C$). The thermal conductivity values are a result of the combined thermal conductivity of activated carbon, electrolyte, separator and the aluminum current collectors formed in a jelly roll shape. The value of 0.0004 for $\delta$ at $25 \, ^\circ C$ is comparable to

38
0.00033 J·Coulomb⁻¹·K⁻¹ reported in [97] for a 2.7 V, 5000 F prismatic cell with organic electrolyte at room temperature.

Table 2.5: Identified thermal parameters at 25 °C and -20 °C using UAC

<table>
<thead>
<tr>
<th>T</th>
<th>h</th>
<th>c_p</th>
<th>( k_t )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>157</td>
<td>1259</td>
<td>0.49</td>
<td>4E–4</td>
</tr>
<tr>
<td>-20</td>
<td>26</td>
<td>1480</td>
<td>0.74</td>
<td>2.3E–4</td>
</tr>
</tbody>
</table>

2.5.4 Electro-Thermal Model Validation

The supercapacitor was tested under a different current profile, the escort convoy cycle (ECC). ECC which is a current profile for batteries [108], was scaled up by a factor of four and used as the second driving cycle to validate the thermal model and also the electrical model. Under this current profile at 25 °C and -20 °C the terminal voltage and the surface temperature of the cell are measured. The identified parameters obtained from the parameterization procedures are fixed and the terminal voltage and surface temperature from the model are compared to the actual measurements. Fig. 2.21 shows that both the electrical and thermal models mimic the actual measurements of voltage and temperature with good accuracy at both 25 °C and -20 °C. The histogram of the voltage and temperature errors are also shown. The RMS error for the terminal voltage are 82 mV and 87 mV for 25 °C and -20 °C, respectively. The surface temperature RMS error is 0.17 °C for 25 °C and 0.21 °C for -20 °C.

2.6 Conclusions

In this dissertation an equivalent electric circuit model was proposed for the electrical model of a supercapacitor. The model was parameterized using pulse-relaxation data from the experiments conducted on the cell. The model is valid from -40 °C to 60 °C considering the dependency of the parameters on temperature, \( SOC \), current direction, and current magnitude. The final electrical
The electro-thermal model consists of three parameters and the analysis shows that the parameters are more a function of temperature than $SOC$ or current magnitude and direction. EIS measurements were used to study the frequency response of the supercapacitor and to compare it with the electrical model obtained using pulse-relaxation experiments. The thermal model included the reversible (entropic) as well as the irreversible heat generation. The thermal model consisted of four parameters which were identified as constants using actual current profiles. The coupling between the electrical and the thermal model was done by feeding the total heat generation calculated from the electrical model into the thermal model and tuning the temperature dependent electrical model parameters according to temperature variation obtained from the thermal model. Finally the electro-thermal model was validated using real world driving cycles. The validation results show the high accuracy of the proposed electro-thermal model which is suitable for real time implementations in all kinds of power systems and also thermal management of supercapacitor packs.

Figure 2.21: Electro-thermal model validation using scaled ECC current profile at (a) 25 °C and (b) -20 °C.
Chapter 3

Range Extension of a Lead-Acid Battery Driven Vehicle using Supercapacitors: Modeling and Hardware In the Loop Validation

3.1 Literature Review

There is an extensive body of literature discussing battery-SC hybrids in different applications [41, 64, 114]. The added degree of freedom via hybridizing has its own pros and cons. The main advantage is the possibility of combining the high energy density batteries with the superior power density of SCs. The high power density of the SC allows shaving the peak load on the battery and increases the specific power of the electrical energy storage system [62, 115, 116]. Other research shows the benefits of the battery-SC hybrids in terms of battery life extension [117–121]. Hybrid battery-SCs are also used in stationary applications such as microgrid and uninterruptible power supplies (UPS) [49, 122]. In [123], SCs are utilized to capture the regenerative braking energy in a race car. The inclusion of SCs resulted in a smaller battery pack, lower resistive losses,
and lower peak current which extends the service life of the electronic components.

The two basic challenges of hybridizing are choosing the configuration and developing a power management strategy. On the configuration side, the topologies are divided into two major categories, passive and active. Passive hybrid configurations include direct parallel connection of the battery and SC, or connection with diodes [124]. In passive designs the power split is primarily controlled by the internal resistance of the modules and voltage of the battery. In the active structure power electronic devices are utilized as the hardware that facilitates the power split between the battery and the SC [125–128]. The design with two bi-directional converters allows full control of the power flow between battery, SC, and to the load. However, using one converter is cheaper, easier to control, and most importantly has smaller losses compared to two converters [129–131]. Two potential single converter architectures for HES are shown in Fig. 3.1. In Fig. 3.1(a), the battery is directly connected to the load which has the advantage of less voltage fluctuation compared to SCs. In this topology however the battery suffers from high currents during high power traction and braking events. The internal resistance of SCs is less than batteries so connecting the SC directly to the load as in Fig. 3.1(b), increases the traction efficiency. Also SCs can undergo high charging currents and are much more efficient during charging compared to batteries, which increases the regenerative braking efficiency. The problem with this topology is that SCs terminal voltage varies in a larger range than batteries and such a large voltage window is not favorable on the load side [132]. One solution is to add a second converter between the SC and the load to regulate the voltage to the DC bus voltage [133].

On the other hand, there are studies focusing on different control strategies to split the power demand between the battery and the SC [61, 134, 135]. These studies are successful in controlling the power flow in the HES while considering the limits on battery and SC current, voltage, and state of charge ($SOC$). However most of them ignore one or more of the following real world scenarios: (i) component efficiency (specifically converter efficiency), (ii) battery and SC model accuracy, (iii) experimental validation using real world duty cycles, and (iv) comparison with a battery-only platform considering some kind of performance metric.

The objective of increasing the mileage of EVs, has been of interest to many researchers
Fujimoto et al. in [138], optimizes the front and rear driving-braking force distributions considering the motor losses and the slip ratio of the wheels, to improve the cruise range of EVs. In a similar study, Wang et al. in [139], report improvement in range of an EV by effective torque distribution between the wheels and no other additional hardware. Efforts have been made to improve EV’s range by adding range extender modules such a fuel cell to the battery driven vehicles [140, 141]. Hybrid battery-SC energy storage systems have also been considered in range improvement studies. Yang et al. in [142], improve the range of a scooter by 20% utilizing regenerative braking and electronic gearshifting between the battery and SC. Moreno et al., show that a range improvement of 3.3-28.7% in a hybrid electric vehicle with lead-acid battery and SC energy storage is achieved, depending on whether if the battery can or cannot capture regenerative braking [143]. However this study does not compare the range results to the battery-only case which masks the efficiency of added components such as the converters. Carter et al., report small improvement in range for a lead-acid electric kit car equipped with SC for practical regeneration rates and a 6.6-9.4% higher range for high regeneration rates (70-76%), depending on the driving cycle. In the aforementioned study, the component models are based on commercial software and the results are not validated by experiments [144].

In this research we present the simulated and experimentally validated range extension results based on a new HES topology combined with a widely applicable control strategy. The highlights of this study are:

- Models for lead-acid and SC modules are parameterized, validated, and used to build the HES model.
- In the proposed topology the battery is completely decoupled from the load and functions as an on-board charger for the SC.
- The topology includes only one uni-directional DC/DC converter which is placed between the battery and the SC as shown in Fig. 3.1(b). The voltage variation on the SC side is kept small by an appropriate power management strategy instead of using a second converter.
• The simplicity of the control strategy allows it to be implemented using inexpensive commercial micro controllers.

• The converter is specifically built for this study which enables monitoring the real world efficiency bottlenecks of the HES.

• The HES model is fully scalable. However for simulation and experimental implementation, an electric scooter platform is used along with the New York City driving cycle to derive a real world duty cycle.

• A 12 V HIL setup is used to implement the control strategy and extract the range results.

• The range results for the HES is compared to the battery-only platform.

The Remainder of this chapter is organized in the following order. In Section 3.2 the battery and SC models are described. In Section 3.3 the HES topology, converter design, and the power management strategy are described. Section 3.4 presents the HIL setup and the simulation and experimental results for the stand-alone battery platform and the HES system. Finally Section 3.5 presents the concluding remarks.

3.2 Energy Storage Modeling

In this section the electric models for both the battery and SC are presented. Equivalent electric circuit models are proposed and parameterized for both the battery and SC with the following characteristics:

• Fewer parameters to be identified compared to the electrochemical models.

• Computationally efficient and appropriate for control oriented studies.

• Accurate terminal voltage prediction.

These validated models will be used to build the HES model.
3.2.1 Equivalent Electric Circuit Model

Fig. 3.2 shows the schematic of the equivalent electric circuit model. It consists of an equivalent series resistance which represents the internal resistance of the cell and also RC branches that capture the voltage behavior during relaxation. The current is the input to the model and the output is the terminal voltage. Positive current is chosen to represent charging and the terminal voltage is obtained by applying the Kirchhoff’s voltage law (KVL) to the circuit shown in Fig. 3.2:

\[ V_T = V_{ocv}(SOC) + IR_s + \sum_{j=1}^{n} V_{RC,j} \]  \hspace{1cm} (3.1)

In (3.1), \( V_{ocv} \) is the open circuit voltage (OCV) which is a nonlinear function of \( SOC \) for both lead-acid battery and the double layer SC. The \( SOC \) is determined using coulomb counting, governed by the following state equation:

\[ \frac{dSOC}{dt} = \frac{I}{q_{max}} \]  \hspace{1cm} (3.2)
where \( q_{\text{max}} \) is the nominal capacity in Coulombs. The second part in (3.1), is the voltage drop over the ohmic resistance and the last part is the sum of voltage drops across parallel RC branches connected in series. The voltage dynamics of each RC pair is described as:

\[
\frac{dV_{\text{RC},j}}{dt} = -\frac{1}{R_jC_j} V_{\text{RC},j} + \frac{I}{C_j}
\]

(3.3)

where \( R_j \) and \( C_j \) are the equivalent resistance in Ohms and capacitance in Farads for each branch, respectively.

![Schematic of the equivalent electric circuit model with “n” number of RC branches.](image)

**Figure 3.2:** Schematic of the equivalent electric circuit model with “n” number of RC branches.

### 3.2.2 Battery Capacity and Open Circuit Voltage Identification

The battery used in this study is an AP-12220EV lead-acid module with the specifications listed in Table 3.1.

The first step in modeling is to measure the capacity and also obtain the OCV as a function

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (V)</td>
<td>12</td>
</tr>
<tr>
<td>Upper Voltage Limit (V)</td>
<td>14.7</td>
</tr>
<tr>
<td>Lower Voltage Limit (V)</td>
<td>10.5(at 1.1A)</td>
</tr>
<tr>
<td>Nominal Capacity (Ah)</td>
<td>22</td>
</tr>
<tr>
<td>Specific Power (W/kg(^{-1}))</td>
<td>180</td>
</tr>
<tr>
<td>Specific Energy (Wh/kg(^{-1}))</td>
<td>42</td>
</tr>
</tbody>
</table>

**Table 3.1:** Lead acid battery specification

46
of $SOC$. The actual capacity is measured by discharging the battery from its upper voltage limit to its lower voltage limit under a small constant current. Knowing that the applied current is constant one can integrate (3.2) and use the boundary conditions $SOC(0) = SOC_i$ and $SOC(t_f) = SOC_f$ to find the discharging (charging) time:

$$t_f = \frac{q_{\text{max}}(SOC_f - SOC_i)}{I(t)}$$  \hspace{1cm} (3.4)

The current fed into the module for capacity test is 0.55 A. This current according to (3.4) will discharge the battery with nominal capacity of 22 Ah from $SOC_i = 1$ to $SOC_f = 0$ in 40 hours. Such a small current minimizes the Peukert’s effect and hence, the measured capacity is more accurate. The actual capacity measured for the module is 19.7 Ah at 100% depth of discharge (DOD). In lead-acid batteries with an increase in DOD during cycling, positive active mass degradation is accelerated which reduces the cycle life of the battery [145]. In order to decelerate the aging process the battery is limited to 35% DOD (or to keep it above 65% $SOC$) as recommended by the battery manufacturer. The model developed for the lead-acid battery in this study is only applicable for discharging cycles.

The $OCV$ as a function of $SOC$ is obtained by running the following experiment similar to the method used in [146]:

- Fully charge the battery using the constant current-constant voltage (CC-CV) protocol recommended by the manufacturer, then allow the module to relax for at least 3 hours. The relaxed voltage for the fully charge module is 13.04 V.

- Discharge the fully charged module at a low current of 0.55 A for 2 hours which is equivalent to a 5% change in $SOC$ according to (3.4) followed by a relaxation period of 3 hours.

- Repeat this 5% pulse-relaxation until the battery reaches 65% state of charge.

Fig. 3.3 illustrates the mentioned experiment to obtain the $OCV$ profile. The measured terminal voltage at the end of every relaxation period at every 5% $SOC$ level, corresponds to the $OCV$ at that $SOC$ level. Using the coulomb counting method shown in (3.2) the $SOC$ of the
Figure 3.3: Experimental current applied to the module and the corresponding terminal voltage for obtaining the OCV.
battery is obtained at each time. This provides a look-up table for $OCV$ as a function of $SOC$ to be integrated in the battery model. Fig. 3.4 shows the $OCV$ obtained as a function of the $SOC$ from 65% to 100%.

![Figure 3.4: OCV versus SOC for the lead-acid battery.](image)

### 3.2.3 Lead-Acid Battery Modeling and Parameterization

The choice of the equivalent electric circuit in this study is a first order model with a single $RC$ branch connected in series to $R_s$. The parameters to be identified are $R_s$, $R_1$, and $C_1$. In order to gather a rich data set for identification purposes the following pulse-relaxation experiment is performed:

- Constant current-constant voltage (CC-CV) charging to 100% $SOC$, with 0.05C cut-off.

- Discharge the fully charged module by applying a 22 A of current for 180 seconds. This will result in a 5% drop in $SOC$ from 100% to 95% according to (3.4), then allow the battery to relax for 3 hours.

- Repeat step 2 until the battery reaches 65% state of charge.

Fig. 3.5 illustrates the mentioned pulse relaxation experiment. The free response of the system (i.e zero input) is when the pulse current indicated in Fig. 3.5 is cut off. This corresponds
to the so called relaxation period. The voltage response during relaxation consists of two parts as follows:

- The first part is the instant voltage jump as shown in Fig. 3.5 which occurs right at the moment the discharging current is cut off. This behavior is due to the internal resistance of the module.
- The second part is the exponential behavior in voltage which is captured by the $RC$ branches in the model.

![Figure 3.5: Experimental current applied to the lead-acid module and the corresponding terminal voltage for model parameterization.](image)

The series resistance $R_s$, is calculated by dividing the instant voltage jump by the pulse current. $R_s$ as a function of $SOC$ is obtained by repeating this calculation for each $SOC$ level. Using this data, a $2^{nd}$ order polynomial in the range of 65% to 100% $SOC$, is fitted to $R_s$ values as follows:

$$R_s = 8.8(SOC)^2 - 17(SOC) + 19 \quad (3.5)$$

The second part of the relaxation period contains the dynamics to identify $R_1$ and $C_1$. The identification is performed by minimizing the square error between the measured and simulated
terminal voltages at each time instant. The cost function is:

$$J = \sum_{k} (V_m(k) - V_T(k))^2 \quad (3.6)$$

where $V_m$ and $V_T$ are the measured and simulated terminal voltages, respectively. The parameterization results are shown in Fig. 3.6. The root mean square (RMS) error between the model and the experimental terminal voltage is 83 mV. The estimated $C_1$ has a constant value of 5086 F. The identified values for $R_1$ is used to fit a 2$^{nd}$ order polynomial as a function of $SOC$ in the range of 65% to 100%:

$$R_1 = 16(SOC)^2 - 1.3(SOC) + 8.2 \quad (3.7)$$

![Figure 3.6: Parameterization results for the lead-acid battery.](image)

### 3.2.4 Supercapacitor Modeling and Parameterization

The SC utilized in this research is a Maxwell BCAP3000 cylindrical cell with activated carbon as electrodes. The cell specifications are listed in Table 3.2.

The cell contains non-aqueous electrolyte allowing the maximum rated voltage of 2.7 V.
Six of these cells are connected in series to build the SC module with a nominal voltage of 16.2 V. Similar to the battery a first order model with a single $RC$ branch is chosen and parameterized. The $OCV$, capacity, series resistance, resistance and capacitance of the $RC$ pairs are the parameters to be identified based on the method used in [147]. The actual capacity and the $OCV$ are obtained by charging the SC from zero to its maximum nominal voltage under a low current of 0.225 A. The SC is then discharged to zero with a similar current rate, to obtain the capacity and $OCV$ for discharging. The difference between charging and discharging $OCV$ is small due to low current and small internal resistance. Despite the linear behavior in an ideal capacitor the $OCV$ profile as a function of $SOC$ is slightly nonlinear for the chosen SC and could be approximated by the following $4^{th}$ order polynomial:

$$V_{ocv} = -0.18(SOC)^4 + 0.59(SOC)^3 - 1.2(SOC)^2$$

$$+ 3.5(SOC) - 1.9 \times 10^{-4}$$

(3.8)

Specific pulse-relation experiments as proposed in [147], are used to identify $R_s$, $R_1$, and $C_1$. The following set of experiments at room temperature is designed for the identification of the SC model:

- Charge the empty cell by applying a 135 A of constant current for 3 seconds which is equivalent to a 5% increase in $SOC$ according to (3.4).
- Relax the cell for 20 seconds then repeat the pulse relaxation till 100% $SOC$.
- Repeat a similar procedure for the discharging cycle.

The identification is performed similar to the battery by minimizing the square error be-

<table>
<thead>
<tr>
<th>Table 3.2: Supercapacitor specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (V)</td>
</tr>
<tr>
<td>Nominal Capacity (F)</td>
</tr>
<tr>
<td>Specific Power (Wkg$^{-1}$)</td>
</tr>
<tr>
<td>Specific Energy (Whkg$^{-1}$)</td>
</tr>
</tbody>
</table>
Figure 3.7: Parameterization results for the SC cell.
between the measured and simulated terminal voltages at each time instant. Fig. 3.7 shows the parameterization results for the SC cell for the mentioned set of pulse relaxation experiment. The RMS error for the voltage is 17.5 mV which indicates the model and experiment are in agreement. Table 3.3 summarizes the estimations for $R_s$, $R_1$, and $C_1$. The variation of the parameters with $SOC$ for the SC is negligible. In case of large temperature variations and in order to consider the effect of temperature on model parameters, refer to the complete model developed in [147].

Table 3.3: Estimated parameters for the SC cell

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (mΩ)</td>
<td>0.46</td>
</tr>
<tr>
<td>$R_1$ (mΩ)</td>
<td>8.3</td>
</tr>
<tr>
<td>$C_1$ (F)</td>
<td>104417</td>
</tr>
</tbody>
</table>

3.3 Hybrid Battery-Supercapacitor Energy Storage

In this section the HES topology is described first. Next, the digital converter design and control is presented. Finally, the power management governing the power flow between the battery and SC, and its advantages are explained.

3.3.1 HES Topology

Fig. 3.8 shows a schematic of the hybrid configuration. This architecture is inspired by the series hybrid electric powertrain. In the series hybrid the engine is decoupled from the wheels. It only charges the batteries while operating in its most efficient region and the battery supplies all the load demand. In the HES topology proposed in this study, the battery, identical to the engine in the series hybrid electric vehicle, is decoupled from the load and the SC satisfies all the load demand. The battery in this topology functions as an on-board charger for the SC module. In order to apply this idea the topology in Fig. 3.1(b) is chosen. The DC/DC converter is located between the battery module and the SC.
3.3.2 Digital Converter Design and Control

In this study the single unidirectional DC/DC converter is located between the 12 V battery module and the 16.2 V bank of SCs. The phase-shift modulated (PSM) full-bridge converter can achieve high efficiency and power density in many applications [148]. Unlike the traditional pulse width modulated (PWM) bridge converter, this topology uses a fixed duty cycle close to 50%. Furthermore a phase between the bridge columns is introduced to cause an overlap in conduction time between the top and bottom switches. These characteristics along with the delay in PWM of each column, result in an oscillation of the metal oxide semiconductor field-effect transistor (MOSFET) voltage due to resonance of the MOSFET’s capacitances and the leakage inductance of the transformer. Hence the voltage goes to zero before the next turn-on period. In this way zero voltage switching (ZVS) is achieved resulting in almost no turn-on switching loss and hence a significant improvement in efficiency. Higher frequency operation also enables the use of smaller magnetic components. A 32-bit micro-controller (μC) is used to control the power electronics. Two single input single output (SISO) control loops are implemented. The fast inner control loop manages the switch currents for each PWM cycle. The second control loop regulates the battery input current with respect to a desired set-point. The μC also manages the balancing between the SC cells as well as the over-current and over-voltage circuit protection. The μC communicates with the host personal computer (PC) through universal serial bus (USB), where new set-point commands
are received. Also via the same connection the measured data is transferred, to be logged by the PC for future analysis. The overall function of the converter is to regulate and supply a predefined amount of constant current from the battery to the SC.

### 3.3.3 Power Management Strategy

The control strategy that is integrated inside the μC is responsible for the power management. In this control strategy the battery is commanded to continuously supply a preset amount of constant current. Constant current charging is shown to be the optimal charging strategy for SCs [71]. The amount of the constant charging current is chosen such that: (i) the voltage variation on the SC side is minimized which waives the need for an extra hardware for SC voltage regulation, (ii) minimize the DC/DC converter’s output voltage ripple which increases the converter’s efficiency. This bang-bang control strategy charges the SC with a constant current regulated by the DC/DC converter at all times subject to the following constraints:

- The charging current is cut off when the SC module reaches its upper voltage limit of 16.2 V.
- A hysteresis band on SC voltage is applied in order to decide when to restart the charging of the SC. The hysteresis band in this study is 100 mV. In other words, the SC terminal voltage should drop by at least 100 mV from the upper voltage limit until the charging command is resent.
- The charging will stop if SOC of the lead-acid battery reaches 65% or the lower voltage limit of the SC is reached.

The combination of the architecture and control strategy allows to minimize the stress on the battery by decoupling it from the load and letting the low impedance SC to provide all the positive (traction) and negative (braking) power demands. In case of the battery driven vehicle due to the low charging rate capability of lead-acid and also life cycle considerations, the acceptable regeneration rate is almost zero. One important advantage of this structure is the ability to efficiently regenerate the braking energy with the SC being connected to the load which otherwise would be
wasted in friction braking. In this strategy the power requirement from the battery is much lower, which allows the usage of cheaper battery chemistries with lower power densities. Operating the battery at a low discharge rate, extends the battery life and also helps overcome the shortcomings of the battery operation at low temperatures. This computationally efficient and effective control strategy also allows to minimize the number of converters and their power rating. Also since the SC has a much lower internal resistance compared to different battery chemistries the efficiency of charging and discharging is improved on the load side.

3.4 Simulation and Experimental Results

3.4.1 Load Simulation

In order to obtain a real world duty cycle to be used in simulations and experiments, a power cycle is extracted considering the following:

- A 48 V electric scooter with the characteristics listed in Table 3.4.
- The velocity profile of the New York City driving cycle which consists of frequent stop and start sequences as shown in Fig. 3.9(a). This cycle is 1.9 km (1.18 miles) with a maximum speed of 44.6 kph (27.7 mph). This data is gathered by the United States environmental protection agency (EPA).

However, the developed HES model is scalable, and any other vehicle platform could be integrated and studied. The velocity of New York City driving cycle at each time step is used as the input to the vehicle dynamics to calculate the power requirement of the cycle. The longitudinal vehicle dynamics at time step $t$ assuming zero road incline is governed by:

$$F(t) = Ma(t) \pm C_r mg \pm \frac{1}{2} \rho AC_d V^2(t)$$

(3.9)

where the positive and negative signs are during traction ($V(t+1) \geq V(t)$) and braking ($V(t+1) < V(t)$) modes, respectively. The first term in (3.9) is due to the longitudinal and rotational inertias.
The mass is \( m \) and the equivalent rotational mass is chosen to be 5% of \( m \). The total mass is then \( M \).

The acceleration (deceleration) at each time step \( a(t) \), is calculated with the knowledge of velocity of the vehicle at each time step and assuming a constant acceleration (deceleration) at each time interval. The second term in (3.9) is due to the rolling resistance where \( C_{rr} \) is the corresponding coefficient. The last term in the equation is the contribution of drag resistance, where \( \rho \), \( A \), and \( C_d \) are the air density, vehicle frontal area, and drag coefficient respectively.

\[
\begin{align*}
\Delta x &= x(t+1) - x(t) = v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 \\
E(t) &= F(t)\Delta x \implies P(t) = \frac{E(t)}{\Delta t}
\end{align*}
\]

**Figure 3.9:** New York City driving cycle and the extracted power profile using the scooter platform.

The distance traveled at each time step with the assumption of constant acceleration (deceleration) is:

\[
\Delta x = x(t+1) - x(t) = v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2
\]

Knowing the force required and the distance traveled at each time step the amount of required energy and consequently the power is derived as:

\[
E(t) = F(t)\Delta x \implies P(t) = \frac{E(t)}{\Delta t}
\]
The final power profile (duty cycle) obtained using the 48 V scooter platform and the New York City driving cycle is shown in Fig. 3.9(b). This single duty cycle is stacked back to back to construct the load profile used in this study. The power profile calculated from the scooter is associated with a 48 V system, however, the HIL setup is based on a 12 V system. Consequently, the developed power profile is scaled down by a factor of four to match the power rating of the experimental setup.

### 3.4.2 Hardware In the Loop (HIL) Setup

All the experiments related to parametrization and validation of the electrical models for the battery, SC, and also HIL experiments on the hybrid setup are conducted using Bitrode FTV1-200/50/2-60 cycler which is capable of supplying currents up to 200 A, which is suitable for running the pulse-relaxation and also the driving cycle validation tests. Fig. 3.10 shows the real setup with the components used in the experiments.

![Hybrid battery-SC experimental setup.](image)

**Figure 3.10:** Hybrid battery-SC experimental setup.
Figure 3.11: Current and terminal voltage of the stand-alone battery from the HIL experiment.
### Table 3.4: Scooter specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vehicle + Passenger Mass ((m))</td>
<td>108+70 (kg)</td>
</tr>
<tr>
<td>Drag Coefficient ((C_d))</td>
<td>0.75</td>
</tr>
<tr>
<td>Frontal Area ((A))</td>
<td>0.6 (m²)</td>
</tr>
<tr>
<td>Rolling Resistance ((C_r))</td>
<td>0.0007</td>
</tr>
<tr>
<td>Air Density ((\rho))</td>
<td>1.125 (kgm⁻³)</td>
</tr>
<tr>
<td>Wheel Radius ((R))</td>
<td>0.21 (m)</td>
</tr>
</tbody>
</table>

#### 3.4.3 Range Results for the Stand-Alone Battery

The first step in simulation and experiments is to run the HIL test for the stand-alone battery to evaluate the range of the battery driven vehicle. In this case, the amount of regeneration during braking is considered to be zero. This is due to high internal resistance of lead-acid batteries which leads to thermal and physical stresses resulting in a lower life span for the battery, under high charging currents. The maximum allowable charging current for the module used in this study is 6.6 A which is much smaller than the peak regeneration currents of 75 A. Fig. 3.11 depicts the current applied to the battery and the terminal voltage dynamics of the module both for simulation and experiments. The results show that the modeled battery terminal voltage is in good agreement with experimental measurements. The range and the RMS error results are shown in Table 3.5. The simulation is stopped and the range is calculated at the point where the \(SOC\) of the battery reaches 65%. This is because of the 35% DOD, recommended by the manufacturer.

#### 3.4.4 Range Results for the HES

In the HES configuration the SC is responsible of providing the total amount of the requested load. In this case regenerating the braking energy is feasible as the SC is capable of being charged at high rates due to its low internal resistance. At the beginning of every test on the HIL setup, the battery and the SC are fully charged. Depending on the load demand the SC is discharged during traction and charged during regenerative braking. However the constraints are set to avoid over-charge or over-discharge of the module. The only role of the battery is to charge the SC with
a constant current. In case the SC voltage reaches the upper voltage limit the charging current from the battery is cut off. Simulation results are compared to three experimental measurements at 0%, 10%, and 20% regeneration rates. The results for the 0% regeneration case is shown in Fig. 3.12. This result shows that the SC satisfies the total requested load while the measured terminal voltage dynamics of the SC is followed by the model. According to the power management strategy the battery provides a constant current of 5.5 A (also shown in Fig. 3.12) at all times unless the \( SOC \) of the SC is equal to one with an active hysteresis band of 100 mV on the SC terminal voltage. The amount of the constant charging current is chosen to be the lowest current possible based on the hardware limitations. Lower currents than 5.5 A resulted in unacceptable ripple on the converter’s output voltage and consequently lower converter efficiency. The \( SOC \) of the SC bank varies between 100% and 94%. This narrow voltage window close to the higher end of \( SOC \) is where the SC operates more efficiently [71]. Furthermore this small voltage window on the SC side resolves the drawback of such a topology where usually there is a large operating voltage window not favorable for the inverter efficiency between the SC and the electric motor. The modeled terminal voltage behavior of the battery is also in agreement with measurements with a RMS error of 41 mV. Similar to the stand-alone case the experiment and simulation is stopped when the \( SOC \) of the battery hits the preset lower limit of 65%.

The range of the hybrid battery-SC in the case of 0% regeneration is 11.5% less than the stand-alone battery case. The DC/DC converter efficiency is governed by:

\[
\eta_{\text{converter}} = \frac{P_{\text{out}}}{P_{\text{in}}} \tag{3.12}
\]

where \( P_{\text{in}} \) is the input power from the battery and \( P_{\text{out}} \) is the output power of the converter. The efficiency of the converter during 0% regeneration operation is around 86%. The hybrid structure used in this study reduces the total impedance on the load side, by directly connecting the low impedance SC to the load. However even this configuration could not compensate for the losses of the converter. This confirms that the converter efficiency is the bottleneck of active hybrid topologies. In order to compensate for the losses of the converter we make advantage of the configuration of the
Table 3.5: Range results for the stand-alone battery and HES system

<table>
<thead>
<tr>
<th>Stand-Alone Battery Range (Miles)</th>
<th>HES Range (Miles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% 10% 20%</td>
<td>0% 10% 20%</td>
</tr>
<tr>
<td>11.19 NA NA</td>
<td>9.9 10.7 12.4</td>
</tr>
</tbody>
</table>

hybrid setup and run experiments at 10% and 20% regeneration. Table 3.5 summarizes the range results for 0%, 10%, and 20% regeneration tests. The results show that a regeneration rate of 20% improves the total range by 10%. Higher amounts of regeneration will result in even better range. The available amount of regeneration in heavier vehicle platforms is higher and such a design will result in even better range extension in such applications.

Figure 3.12: Current and terminal voltage of the battery and SC in the HES system with 0% regeneration rate from the HIL experiment.
3.5 Conclusions

This study investigated the circumstances under which, the hybridization of a lead-acid powered vehicle using SCs, will result in extended range. In the first step, the lead-acid battery model is developed and integrated with a validated SC model to form the HES model. The combination of the topology and proposed power management strategy allowed a simple implementation, relaxed battery operation, small SC voltage variation, and regenerative braking capability. The results show that the efficiency of the converter is the bottleneck of the HES system. Capturing 20% or higher amounts of the regenerative braking energy by connecting the SC to the load improves the range of the hybrid system compared to the stand-alone battery. The improvement in range could be even higher in heavier vehicles with a larger amount of available rate of regeneration.
Chapter 4

Heuristic versus Optimal Charging of Supercapacitors, Lithium-Ion, and Lead-Acid Batteries: An Efficiency Point of View

4.1 Literature Review

Batteries have become an indispensable part of our daily life. They can be found almost everywhere from powering our electronic gadgets, computers, and phones to electrifying our vehicles and also form a critical part of the modern centralized and distributed power grids. Supercapacitors on the other hand are the premier energy storage devices in terms of power density, long cycle life, and the ability to operate at extreme temperatures. Much research and development is spurred towards studying important factors influencing the efficiency and cycle life of batteries and SCs, such as monitoring and control of the cell charging method, current rate, number of charging/discharging cycles, and temperature [8, 10, 12, 21, 149–153].

Studies that investigate the optimization of efficiency over the entire driving cycle, mask
the fundamental bottlenecks of efficiency in the electrical energy storage systems. In stand-alone operation and during discharge, the cycle is often imposed by the required load and therefore there is little that can be done in reducing resistive losses. During charging however, there is the opportunity to choose the charging time and profile such that resistive losses are reduced. Battery manufacturers often have a recommended charging profile which may be sub-optimal.

There are numerous studies focusing on different charging methods to achieve objectives such as decreasing the charging time, life span and efficiency maximization, or cost minimization. Optimal charging of Li-ion batteries is studied in [154], where minimizing the charging time while satisfying specific physical and thermal constraints is considered. In [71], an optimal charging problem is solved for a SC during regenerative braking with the objective of minimizing ohmic losses. Suthar et al. in [155], use a single-particle model and aim to find the optimal current profile, with the objective of maximizing the charge stored in the cell in a given time and with the constraint of minimal damage to the electrode particles during intercalation. Bashash et al. in [156], focus on optimizing the timing and charging rate of a plug-in hybrid electric vehicle from the power grid where the goal is to simultaneously minimize the total cost of fuel and electricity and the total battery health degradation. Optimizing the battery charging power in photovoltaic battery systems is studied in [157] where different objectives such as charging time, battery life time, and cost of charging are considered. Inoa et al. in [158] suggest optimal charging profiles in order to minimize charging losses and reach a preset temperature at the end of the charging time for Li-ion batteries. More recently, [159] and [160] have solved the optimal charging problem for Li-ion batteries considering the trade-off between charging time and energy loss in the objective function; however neither of these papers consider the transient effect of temperature on electrical model parameters of the Li-ion battery. One important output of the mentioned studies is the charging/discharging current profile that satisfies the specific objective functions. For example there are studies with the objective of reducing the charging time which result in different types of constant current (CC) charging methods such as multistage charging [161–165], impedance compensation [166–168] and pulse charging [169]. Constant voltage (CV) charging has been used to improve charging speed by combining the battery pack and charger models and the results are compared to the CC method [170]. Constant
power (CP) charging and discharging is also of interest to researchers as it corresponds to real world operating conditions such as in hybrid and electric vehicles. Modeling the thermal behavior of Li-ion batteries under CP charging and discharging cycles is investigated in [171]. Under constant power, the relationship between the available energy in a battery and charging power has been investigated in [172]. The aging of SCs under CP charging condition is studied in [19].

In this research we shed light on achievable charging efficiencies for the supercapacitors, lead-acid, and Li-ion batteries. The common aspects of the problem formulation and analysis are:

- In all optimal charging formulations the objective function is to maximize the charging efficiency by minimizing the resistive losses in a given charging time and for a specified range of state of charge (SOC).

- All problems are formulated using Pontryagin’s minimum principle with the intention to solve them analytically. In cases where analytical solution is not feasible, the problem is solved using numerical methods.

- The constant power and optimal charging current profiles and efficiencies are obtained and compared for all modules.

- Both slow and fast charging times are investigated.

We begin with lumped models for each module with the upper and lower bounds on SOC being the only constraint considered in the optimal control problem formulations. This provides a basic understanding on the effect of charging time of the charging current and efficiencies under different charging strategies. Later on, we solve the optimal charging problem for the Li-ion battery by coupling a reduced order, two state thermal model to the electrical model. In the electrical models used in this study, $R_s$ indicates the ionic and electronic resistance of electrolyte and also the electronic resistance of the electrode. The other two parameters are the charge-transfer resistance $R_1$ which is in parallel with the double layer capacitance $C_1$ formed at the interface between the electrode and electrolyte [173]. At steady state, the sum of $R_s$ and $R_1$ is called the total internal resistance ($R$) in this chapter.
In case of the SC, the electrical dynamics is modeled using a constant total internal resistance \((R)\). The open circuit voltage \((OCV)\) is assumed to have a linear relationship with \(SOC\). Another assumption is constant ambient temperature of 25 °C during charging. Due to high power density of SCs the fast and slow charging times are chosen to be 30 seconds and 6 minutes, respectively. The optimal charging current and efficiency for the SC have analytical solutions and are compared to the CC and CV strategies. For the lead-acid battery, similar to the SC, the module is modeled using a total constant internal resistance \((R)\) at a constant ambient temperature of 25 °C. The difference in the problem formulation for the lead-acid battery is the strong dependence of \(R\) on \(SOC\) which is integrated into the electrical model. Both \(OCV\) and \(R\) are approximated by 2nd order polynomials as a function of \(SOC\). The fast and slow charging times are chosen to be 6 minutes and 1 hour, respectively. Considering these conditions for the lead-acid battery, the optimal charging formulation results in a two point boundary value problem, which is solved numerically. The obtained optimal charging current and efficiency are compared to CP and CC methods. For the Li-ion battery in the first step only the electronic resistance \((R_s)\) with a constant value at a constant charging temperature of 25 °C is considered. In the second step, the effect of charge transfer resistance \((R_1)\) and double layer capacitance \((C_1)\) are added to the model. The dependence of \(R_s\) on \(SOC\) is negligible at room temperature and the variation of \(R_1\) and \(C_1\) on \(SOC\) has not been considered. Similar to the lead acid battery the charging times studied are 6 minutes and 1 hour for rapid and slow charging strategies, respectively. Finally, in order to investigate the effect of temperature on the electrical model parameters, a validated 3 state electro-thermal model is utilized and the optimal charging problem is solved using the numerical method of dynamic programming. The optimal solution in this case is obtained subject to \(SOC\), voltage, and temperature constraints. The unconstrained optimal charging scenarios were partially reported in [71] and [103]. The direct contribution of this study is considering the effect of temperature dependent model parameters on the optimal charging current along with the CP charging derivation and efficiency analysis for different charging methods.

The remainder of this chapter is organized in the succeeding order. In Section 4.2 the charging of the SC, including the model used, CV, CP, and optimal charging strategies are presented.
Section 4.3 covers the efficiency analysis of the SC. Sections 4.4 and 4.5 explain the charging and efficiency analysis of the lead-acid battery. Sections 4.6 and 4.7 describe the charging and efficiency analysis of the Li-ion battery. Section 4.8 presents the electro-thermal model and the optimal charging current profile considering the temperature effect as well as the voltage and temperature constraints for the Li-ion battery. Section 4.9 presents the conclusions.

### 4.2 Charging of the Supercapacitor

#### 4.2.1 Supercapacitor Model and Specifications

The SC utilized in this research is a Maxwell BCAP3000 cylindrical double layer cell. The specifications of the cell are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1: Supercapacitor cell specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Voltage (V)</td>
</tr>
<tr>
<td>Nominal Capacitance (F)</td>
</tr>
<tr>
<td>Mass (kg)</td>
</tr>
<tr>
<td>Specific Power (W/kg)</td>
</tr>
<tr>
<td>Specific Energy (Wh/kg)</td>
</tr>
</tbody>
</table>

The nominal energy capacity of the SC according to Table 4.1 is 3 Wh. The equivalent electric circuit model for this cell is identified using pulse-relaxation experiments for a wide range of temperatures from -40 to 60°C in [147, 174]. The model indicates that the dependence of the model parameters such as $R$ in Fig. 4.1 on $SOC$ and also the current magnitude is negligible. Also as mentioned in the introduction, we do not include the thermal constraints in the charging problem formulation and efficiency analysis for the SC. The value of constant electronic resistance ($R$) is 2.97 mΩ for this cell at 25°C. A linear relationship between the $OCV$ and the $SOC$ is considered.
4.2.2 Constant Voltage Charging of the Supercapacitor

It is well known that charging a capacitor and similarly a SC, from zero charge to full charge, with a constant voltage source results in 50% energy loss irrespective of the internal and line resistances. This can be easily shown by writing the differential equation governing the SC’s stored charge $q(t)$, for the circuit shown in Fig. 4.1:

$$R \frac{dq}{dt} + \frac{q}{C} = V_{dc} \tag{4.1}$$

where $C$ is the nominal capacitance, $R$ is the total internal resistance, and $V_{dc}$ is the charging voltage. If $V_{dc}$ remains constant over time, the solution to the above differential equation from a zero initial charge condition can be obtained to be:

$$q(t) = CV_{dc} \left[ 1 - e^{-t/RC} \right] \tag{4.2}$$

and the constant voltage charging current $I_{chg} = I_{cv}$ is then:

$$I_{cv}(t) = \frac{V_{dc}}{R} e^{-t/RC} \tag{4.3}$$

The resistive energy loss is obtained by integrating the resistive power loss $RI_{cv}^2$ over the entire
charging interval \([0, +\infty)\) as:

\[
E_{\text{loss, cv}} = \frac{V_{dc}^2}{R} \int_{0}^{\infty} e^{-2t/RC} dt = \frac{1}{2} CV_{dc}^2
\]

(4.4)

This amount is equal to the total energy stored in the SC. In other words, the efficiency of charging an empty SC with a constant voltage source is 50\%, independent of resistance \(R\). Note that the charging efficiency depends on both the initial and final state of charge. For example charging a SC from half to full charge with constant voltage has an efficiency of 75\%. Using the definition of efficiency, charging a SC from an initial state of charge \((SOC_i)\) to a final state of charge \((SOC_f)\) with a constant voltage source is:

\[
\rho_{cv} = \frac{1}{1 + \frac{(1 - SOC_i)^2}{SOC_f - SOC_i}}
\]

(4.5)

### 4.2.3 Constant Power Charging of the Supercapacitor

Consider charging the SC with the model in Fig. 4.1 by replacing the constant voltage source with a constant power source of \(P_0\). Applying Kirchhoff’s voltage law to the circuit the stored charge dynamics is:

\[
R \dot{q} + \frac{q}{C} = P_0 \rightarrow \dot{q} = I_{cp} = \frac{-q}{\dot{q} + \sqrt{\left(\frac{\dot{q}}{\dot{q}}\right)^2 + 4RP_0}}
\]

(4.6)

where \(I_{cp}\) is the constant power charging current. Equation (4.6), which is a nonlinear differential equation, can be solved numerically to find the charge and current. Consider charging the cell from zero to full charge. Figs. 4.2 and 4.3 show the charge stored in the SC and the constant power charging current for charging in 6 minutes and 30 seconds, respectively. The maximum charge storable in the SC is \(3000 \times 2.7 = 8100\) Coulombs. The constant power for charging the cell in 6 minutes and 30 seconds is 32 W and 595 W, respectively. The maximum current that the cell undergoes in the slow charging (6 minutes) and fast charging (30 seconds) is 104.5 A and 447.6 A, respectively. The efficiency analysis for the constant power charging will be presented in Section
Figure 4.2: Charging the SC with constant power from zero to full charge in 6 minutes.

Figure 4.3: Charging the SC with constant power from zero to full charge in 30 seconds.

4.2.4 Optimal Charging of the Supercapacitor

The next natural question to ask is what charging current profile maximizes the charging efficiency. That is the current that would charge the SC to a desired level of charge with minimum resistive losses. Let’s choose the optimization variable to be the charging current, \( u(t) = I_{\text{chg}}(t) \). The SC state of charge \( \text{SOC} = \frac{q(t)}{q_{\text{max}}} \) quantifies the amount of charge stored in the SC bank normalized by the maximum charge it can accept \( q_{\text{max}} \). The dynamics of \( \text{SOC} \) as the single state \( x_1 \)
of the problem is derived by coulomb counting using the current \( u(t) \), fed into the SC as follows:

\[
\frac{d}{dt}x_1(t) = \frac{u(t)}{q_{max}} = \frac{u(t)}{CV_{max}} \tag{4.7}
\]

where \( V_{max} \) is the voltage across the SC at maximum charge. Let’s assume the SC is initially free of charge \( x_1(0) = SOC_i = 0 \) and in \( t_f \) units of time is charged to its final desired state of charge \( SOC_f \); therefore \( x_1(t_f) = SOC_f \). The optimal input \( u(t) \) is one that minimizes the resistive losses in the time period \([0, t_f]\) characterized by the subsequent cost function:

\[
J = \int_0^{t_f} Ru^2(t)dt \tag{4.8}
\]

This is an optimal control problem and can be solved using Pontryagin’s minimum principle [175]. First form the Hamiltonian:

\[
H(x_1, u, t) = Ru^2(t) + \lambda_1(t)\frac{u(t)}{CV_{max}} \tag{4.9}
\]

where \( \lambda_1 \) is a co-state. The optimal co-state should satisfy the subsequent dynamic equation:

\[
\frac{d}{dt}\lambda_1(t) = -\frac{\partial H}{\partial x_1} = 0 \tag{4.10}
\]

implying that in this specific problem the optimal \( \lambda_1 \) must be a constant. The unconstrained optimal solution will also need to satisfy the condition:

\[
\frac{\partial H}{\partial u} = 0 \rightarrow u(t) = -\frac{1}{2} \frac{1}{RCV_{max}}\lambda_1(t) \tag{4.11}
\]

showing that the optimal input (charging current) must be a constant. At this point, we can integrate (4.7) and use the boundary conditions \( x_1(0) = SOC_i \) and \( x_1(t_f) = SOC_f \) to find the value of this optimal and constant input:

\[
u_{opt}(t) = I_{opt, SC} = \frac{CV_{max}(SOC_f - SOC_i)}{t_f} \tag{4.12}
\]
where the subscript “opt” denotes the optimal solution. This is in fact the minimizing solution since \( \frac{\partial^2 H}{\partial u^2} > 0 \). Given a specific charging time, the most efficient way to charge the SC will be applying a constant current equal to (4.12). The optimal charging current is a constant current of 30.8 A and 270 A for charging the SC from zero charge to full charge in 6 minutes and 30 seconds, respectively.

4.3 Efficiency Analysis for the Supercapacitor

In order to obtain the charging efficiency of the SC, the total storable energy is required. By the integration of power over the entire charging time and using the definition of SOC, the total energy stored in the SC is obtained as:

\[
E_{sc} = \frac{1}{2} C V_{\max}^2 \left[ \text{SOC}_f^2 - \text{SOC}_i^2 \right] \quad (4.13)
\]

The energy loss in the SC during optimal charging is already known and is equal to \( \int_0^{t_f} R u_{\text{opt}}^2(t) dt \). Then the optimal charging efficiency is:

\[
\rho_{\text{opt}} = \frac{\frac{1}{2} C V_{\max}^2 (\text{SOC}_f^2 - \text{SOC}_i^2)}{\int_0^{t_f} R u_{\text{opt}}^2(t) dt + \frac{1}{2} C V_{\max}^2 (\text{SOC}_f^2 - \text{SOC}_i^2)},
\]

Substituting for \( u_{\text{opt}} \) from (4.12) yields:

\[
\rho_{\text{opt,SC}} = \frac{1}{1 + \left( \frac{2RC}{t_f} \right) \left( \frac{\text{SOC}_f - \text{SOC}_i}{\text{SOC}_f + \text{SOC}_i} \right)} \quad (4.14)
\]

Fig. 4.4 shows the SC charging efficiency as a function of initial state of charge and \( t_f \). This figure implies the expected result that longer charging times and/or smaller RC values improve the charging efficiency. When \( t_f \) approaches infinity the charging efficiency approaches 1, which is a 100% improvement over the case with CV charging. Another observation is that beginning the charging from a higher initial SOC and also charging within a narrower range of SOC results in improved efficiency. Furthermore (4.14) and the first two profiles that are on top of each other in Fig. 4.4, show that when starting from zero initial SOC, the charging efficiency is independent of
the final $SOC$ and it is only a function of charging time. The optimal charging current from zero to full charge for slow (6 minutes) and fast (30 seconds) charging methods are 22.5 A and 270 A, respectively. The maximum peak current of the Maxwell SC cell used in this study is 2165 A and the maximum continuous current is 147 A. Although with these upper limits the fast charging scenario is not practical, it is insightful to compare the corresponding charging currents and efficiencies with the slow charging example. Table 4.2 shows the dependence of SC charging efficiency for three $SOC$ levels, two charging times, and for CV, CP, and optimal charging strategies. Optimal charging the SC from zero to full charge in 6 minutes is 1.53% and 45.28% more efficient than CP and CV charging, respectively. The efficiency of charging in the range of 50 to 100% $SOC$ (which consists of 75% of the total energy of the SC) is almost equal for CP and CC charging methods. Constant current is the favorable charging strategy as it is not only more efficient but also easier to supply than the nonlinear CP charging current.

![Figure 4.4: The effect of charging time, initial $SOC$, and range of $SOC$ on SC charging efficiency.](image)
Table 4.2: Efficiency comparison for the supercapacitor

<table>
<thead>
<tr>
<th>SOC</th>
<th>Slow Charging (6 Minutes)</th>
<th>CP</th>
<th>Optimal</th>
<th>Fast Charging (30 Seconds)</th>
<th>CP</th>
<th>Optimal</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-100</td>
<td>93.4</td>
<td>95.28</td>
<td>61.2</td>
<td>62.73</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-50</td>
<td>93.4</td>
<td>95.28</td>
<td>61.2</td>
<td>62.73</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50-100</td>
<td>98.32</td>
<td>98.37</td>
<td>83.27</td>
<td>83.47</td>
<td>75</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.4 Charging of the Lead-Acid Battery

4.4.1 Lead-Acid Battery Model and Specifications

The lead-acid battery used in this study is a AP-12220EV-NB module. The module specifications are listed in Table 4.3.

Table 4.3: Lead acid module specification

<table>
<thead>
<tr>
<th>Nominal Voltage (V)</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Capacity (Ah)</td>
<td>22</td>
</tr>
<tr>
<td>Mass (kg)</td>
<td>6.4</td>
</tr>
<tr>
<td>Specific Energy (Wh/kg)</td>
<td>42</td>
</tr>
</tbody>
</table>

The real capacity of the module is obtained by discharging the fully charged module with a low current of 0.55 A from upper voltage limit to the lower voltage limit. This measured capacity is 19.7 Ah. Specifically designed pulse-relaxation tests such as the method used in [176], is utilized to estimate the total internal resistance $R$ of the cell as a function of $SOC$. Fig. 4.5 shows that the internal resistance of lead-acid battery strongly depends on $SOC$.

The open circuit voltage of the lead-acid battery is obtained by applying a small current of 0.05 A to charge the battery from zero to full charge. The recorded $OCV$ for this battery as a function of $SOC$ is shown in Fig. 4.6.
Figure 4.5: $R$ versus $SOC$ for the lead-acid battery.

Figure 4.6: Measured $OCV$ versus $SOC$ for the lead-acid battery.
4.4.2 Constant Power Charging of the Lead-Acid Battery

The relationship between the total internal resistance and \( SOC \) of the lead-acid battery is approximated by fitting a second order polynomial to the profile in Fig. 4.5 as follows:

\[
R = a_1(SOC)^2 + a_2(SOC) + a_3
\]  
(4.15)

A second order polynomial is fitted to the \( OCV \) as a function of \( SOC \) profile in Fig. 4.6 as follows:

\[
OCV = b_1(SOC)^2 + b_2(SOC) + b_3
\]  
(4.16)

The polynomial coefficients are listed in Table 4.4.

<table>
<thead>
<tr>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( b_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.098</td>
<td>-0.12</td>
<td>0.061</td>
<td>-0.56</td>
<td>2.2</td>
<td>11</td>
</tr>
</tbody>
</table>

As the lead-acid battery is modeled with a total internal resistance of \( R \), applying Kirchoff’s voltage law to the circuit that is charging the lead-acid battery with a constant power source \( (P_0) \) results in:

\[
I_{cp} = \frac{-(OCV) + \sqrt{(OCV)^2 + 4RP_0}}{2R}
\]  
(4.17)

Substituting (4.15) and (4.16) in (4.17) and solving the nonlinear differential equation, the charge and constant power charging current is obtained. Consider charging the empty lead-acid battery to full charge in an hour where \( P_0 = 248 \) W. The maximum charge storable in this lead-acid battery is 19.7 Ah\( \times 3600 = 70920 \) Coulombs. Fig. 4.7 shows the charge and constant power charging current profiles for charging in one hour.

For the fast charging case consider charging the same lead-acid module with a constant
power of 3660 W which is equivalent to charging the module in 6 minutes. Fig. 4.8 shows that for the lead-acid battery both the magnitude and shape of the constant power charging current vary for the slow and fast charging cases.

4.4.3 Optimal Charging of the Lead-Acid Battery

The lead-acid battery is modeled by a single internal resistance and the only state is the \( SOC \) of the battery governed by (4.7). The objective is to minimize the losses associated with the
The total internal resistance as in 4.8. Therefore the Hamiltonian is:

$$H(x, u, t) = R(x_1)u^2(t) + \lambda_2(t) \frac{u(t)}{q_{\text{max}}}$$  \hspace{1cm} (4.18)

where $R$ is the total internal resistance and $\lambda_2(t)$ is the co-state. $R(x_1)$ also shown in Fig. 4.5 is approximated by the second order polynomial in (4.15). The necessary conditions to be satisfied are:

$$-\frac{\partial H}{\partial x_1} = -\frac{dR(x_1)}{dx_1}u^2(t) = \frac{d}{dt}\lambda_2(t)$$  \hspace{1cm} (4.19)

$$\frac{\partial H}{\partial u} = 2R(x_1)u(t) + \frac{\lambda_2(t)}{q_{\text{max}}} = 0$$  \hspace{1cm} (4.20)

Solving for $u(t)$ in (4.20), the optimal charging current is obtained as follows:

$$u_{\text{opt}}(t) = -\frac{1}{2q_{\text{max}}} \frac{1}{R(x_1)} \lambda_2(t)$$  \hspace{1cm} (4.21)

Substituting $u_{\text{opt}}(t)$ from (4.21) in (4.7) and (4.19), the consecutive set of two coupled nonlinear ordinary differential equations (ODE) are obtained:

$$\frac{dx_1(t)}{dt} = -\frac{1}{2q_{\text{max}}} \frac{1}{R(x_1)} \lambda_2(t)$$  \hspace{1cm} (4.22)

$$\frac{d\lambda_2(t)}{dt} = -\frac{1}{4q_{\text{max}}} \frac{dR(x_1)}{dx_1} \frac{1}{R^2(x_1)} \lambda_2^2(t)$$  \hspace{1cm} (4.23)

Charging the lead-acid battery in $t_f$ units of time from zero to full charge requires the initial and final conditions to be satisfied:

$$x_1(0) = \text{SOC}_i, \quad x_1(t_f) = \text{SOC}_f$$  \hspace{1cm} (4.24)

The system of two nonlinear ODEs with one initial and another final condition forms a two point boundary value problem which could only be solved using numerical methods. One way to
solve this system of ODEs is to specify the initial condition for the $SOC$ and iteratively guess the initial condition for $\lambda_2$ until $SOC$ reaches the final specified value. Consider the case of charging the lead-acid battery module from zero to full charge in 1 hour. Fig. 4.9 shows the variation of optimal charging current, $SOC$, and $\lambda_2$ with time.

Figure 4.9: Optimal charging current, $SOC$, and $\lambda_2$ profiles for charging the lead-acid battery from zero to full charge in 1 hour.

As shown in the numerical results, the optimal charging current for lead-acid battery, unlike the SC, is not constant. In order to compare the constant current charging with the optimal charging strategy, the energy losses in both methods are calculated. For the case of charging the lead-acid battery from zero to full charge in an hour, the resistive losses in the optimal charging strategy is 46.18 kJ compared to 48.9 kJ for constant current charging. This is a 5.5% of less energy converted to heat which could be significant in thermal management of battery packs.
Table 4.5: Efficiency comparison for the lead acid battery

<table>
<thead>
<tr>
<th>Slow Charging (1 hour)</th>
<th>Fast Charging (6 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>CP</td>
</tr>
<tr>
<td>95.19</td>
<td>95.34</td>
</tr>
</tbody>
</table>

4.5 Efficiency Analysis for the Lead-Acid Battery

The efficiency for three charging strategies including CP, CC, and optimal charging is calculated based on the definition of efficiency:

\[
\rho = \frac{E_{\text{battery}}}{E_{\text{battery}} + E_{\text{loss}}} \tag{4.25}
\]

According to the lead-acid battery specification listed in Table 4.3, \( E_{\text{battery}} \) is 268.8 Wh for this module. The energy loss \( E_{\text{loss}} \) is obtained by numerically integrating the power loss \( (RI^2) \) during the charging time. Table 4.5 compares the efficiency values for charging the lead-acid battery from zero to full charge for three strategies and two charging times. The efficiency of optimal charging is slightly higher than the other two strategies as expected. If factors such as cost of supplying a non-constant current is considered, one may prefer to charge the lead-acid battery with constant current and neglect the effect of the slightly lower charging efficiency. The efficiency of constant power charging is higher than constant current charging for the lead-acid battery.

4.6 Charging of the Li-ion Battery

4.6.1 Li-ion Battery Model and Specifications

The Li-ion battery used in this research is a A123-26650 cell with LiFePO\(_4\) chemistry. The cell specifications are listed in Table 4.6. The cell model is developed using pulse-relaxation experiments to identify equivalent electric circuit model parameters. The estimation is performed
by minimizing the least square error between the experimental and modeled terminal voltage [100].

Table 4.6: Li-ion cell specification

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Voltage (V)</td>
<td>3.3</td>
</tr>
<tr>
<td>Nominal Capacity (Ah)</td>
<td>2.5</td>
</tr>
<tr>
<td>Mass (kg)</td>
<td>0.076</td>
</tr>
<tr>
<td>Specific Power (W/kg)</td>
<td>2600</td>
</tr>
</tbody>
</table>

For the lithium ion battery two models are studied. First only electronic resistance ($R_s$) is considered and in the next step the effect of polarization resistance ($R_1$) is also included by adding a single R-C branch to the model as shown in Fig. 4.10. The dependence of model parameters $R_s$, $R_1$, and $C_1$ on $SOC$ can be neglected at room temperature [100]. The values for $R_s$, $R_1$, and $C_1$ are $0.01 \, \Omega$, $0.016 \, \Omega$, and $2200 \, \text{F}$, respectively.

![Figure 4.10: Schematic of the single R-C model for the Li-ion battery.](image)

The $OCV$ of the Li-ion battery as a function of $SOC$ is depicted in Fig. 4.11. As shown in the figure, the $OCV$ can be approximated by a linear function using the $OCV$ data in the range of 10% to 95% $SOC$. This linear fit makes the analytical efficiency analysis possible. The linear approximation is governed by:

$$OCV(t) = aSOC(t) + b \quad (4.26)$$

The relationship between $OCV(t)$ and the charge stored $q(t)$, in the battery is obtained by substi-
tuting the definition of $SOC$ in (4.26) as follows:

$$OCV(t) = \frac{a}{q_{\max}}q(t) + b$$

(4.27)

where $a$ and $b$ for this specific battery are 0.156 and 3.226, respectively.

![Figure 4.11: Actual and approximated $OCV$ versus $SOC$ for the Li-ion battery.](image)

4.6.2 Constant Power Charging of the Li-ion Battery

Consider charging the Li-ion battery modeled with only the electronic resistance represented with constant $R_s$ in Fig. 4.10 with a constant power source of $P_0$ and the linear $OCV$ assumption of Fig. 4.11. Applying Kirchhoff’s voltage law to the circuit, the stored charge dynamics is:

$$R_s \dot{q} + \left[ \frac{a}{q_{\max}}q(t) + b \right] = \frac{P_0}{q}$$

(4.28)

Solving for the constant power charging current:

$$\dot{q} = I_{cp} = \frac{-\left[ \frac{a}{q_{\max}}q(t) + b \right] + \sqrt{\left[ \frac{a}{q_{\max}}q(t) + b \right]^2 + 4R_sP_0}}{2R_s}$$

(4.29)
The nonlinear differential equation in (4.29) is solved numerically. For the cell used in this study the maximum storable charge is \(2.5 \text{Ah} \times 3600 = 9000\) Coulombs. Fig. 4.12 shows charge and constant power charging current profiles for charging the battery from zero to full charge in 6 minutes. The constant power charging current is linear with small variation during the charging time and a peak amount of 25.4 A. The manufacturer recommends a fast charging of 12 minutes with a C-rate of 4 (10 A) for this cell. However, in the literature there are reported Li-ion batteries with nano-particles of \(\text{LiFePO}_4\) (LFP) and \(\text{Li}_4\text{Ti}_5\text{O}_{12}\) (LTO) for the positive and negative electrodes that can undergo charging from zero to full charge with C-rates equal to 10C (6 minutes) and 15C (4 minutes) safely [177]. The efficiency analysis for the constant power charging will be presented in section (4.7).

![Figure 4.12: Charging the Li-ion battery with constant power from zero to full charge in 6 minutes.](image)

**4.6.3 Optimal Charging of the Li-ion Battery**

Two scenarios are considered in the optimal charging of the Li-ion battery.

1) First scenario: In this step only \(R_s\) as depicted in Fig. 4.10 is considered. The value of \(R_s\) is constant and equal to 0.01 \(\Omega\). The single state is the \(SOC\) of the battery \(x_1\), governed by (4.7). The objective is minimizing the ohmic losses associated with \(R_s\) during the given charging time \(t_f\) as
follows:

\[ J_1 = \int_0^{t_f} R_s u^2(t) dt \]  \hspace{1cm} (4.30)

The optimal charging problem is formulated using Pontryagin’s minimum principle. The result of the optimal charging strategy in this case is also constant current. Similar to the SC case, the value of this optimal charging current for the Li-ion battery is:

\[ u_{opt}(t) = I_{opt} = \frac{q_{max}(SOC_f - SOC_i)}{t_f} \] \hspace{1cm} (4.31)

Similar to the constant power case, consider charging the Li-ion battery from zero charge to full charge in 6 minutes. According to (4.31) the optimal charging current is constant and equal to 25 A. In this scenario the constant power and optimal charging current profiles are almost identical.  

2) Second scenario: In this scenario, the R-C branch is added to the model to include the effect of the polarization resistance \( R_1 \). The value of \( R_1 \) is assumed to be constant and not a function of temperature or \( SOC \). The value for \( R_1 \) is 0.016 \( \Omega \) which is an average value over the \( SOC \) range [100].

Assume \( I_1 \) and \( I_2 \) are the currents passing through \( R_1 \) and \( C_1 \), respectively (see Fig. 4.10). Applying the Kirchoff’s current and voltage laws to the R-C branch, the second state equation governing the dynamics of \( I_1 \) is obtained. The problem in this case is to solve for the optimal charging current for a second order system governed by the state equations:

\[ \frac{d}{dt} x_1(t) = \frac{u(t)}{q_{max}}, \quad \frac{d}{dt} x_2(t) = \frac{1}{R_1 C_1} \left[ u(t) - x_2(t) \right] \]  \hspace{1cm} (4.32)

where the two states \( x_1 \) and \( x_2 \) are the \( SOC \) of the battery and the current \( (I_1) \) passing through the polarization resistance \( (R_1) \). The objective, similar to the first scenario, is to maximize the charging efficiency. The difference is that the contribution of the polarization resistance to the total ohmic
losses should also be considered. Therefore, the cost function to be minimized is:

\[ J_2 = \int_0^{t_f} \left[ R_s u^2(t) + R_1 x_2^2(t) \right] dt \] (4.33)

The Hamiltonian in this case is given by the subsequent equation:

\[ H(x, u, t) = R_s u(t) + R_1 x_2^2(t) + \lambda_3(t) \frac{u(t)}{q_{\text{max}}} + \frac{\lambda_4(t)}{R_1 C_1} \left[ u(t) - x_2(t) \right] \] (4.34)

where \( \lambda_3 \) and \( \lambda_4 \) are the co-states. The necessary conditions for optimality are:

\[ -\frac{\partial H}{\partial x_1} = \frac{d}{dt} \lambda_3(t), \quad -\frac{\partial H}{\partial x_2} = \frac{d}{dt} \lambda_4(t), \quad \frac{\partial H}{\partial u} = 0 \] (4.35)

From the first two conditions in (4.35) the dynamics of the co-states are derived and the solution to the third condition is the optimal input as follows:

\[ u_{\text{opt}}(t) = \left[ -\frac{1}{2R_s q_{\text{max}}} \right] \lambda_3(t) + \left[ -\frac{1}{2} R_s R_1 C_1 \right] \lambda_4(t) \] (4.36)

Substituting the optimal input into the state equations of (4.32), the optimal state dynamics are derived. The result is a set of four linear first order ODEs:

\[ \begin{align*}
\frac{d}{dt} x_1(t) &= a_1 \lambda_3(t) + a_2 \lambda_4(t) \\
\frac{d}{dt} x_2(t) &= b_1 x_2(t) + b_2 \lambda_3(t) + b_3 \lambda_4(t) \\
\frac{d}{dt} \lambda_3(t) &= 0 \\
\frac{d}{dt} \lambda_4(t) &= c_1 x_2(t) + c_2 \lambda_4(t)
\end{align*} \] (4.37)
where \( a_1, a_2, b_1, b_2, b_3, c_1, \) and \( c_2 \) are constant parameters equal to:

\[
\begin{align*}
    a_1 &= -\frac{1}{2R_s q_{\text{max}}} , \\
    a_2 &= -\frac{1}{2R_s R_1 C_1 q_{\text{max}}} , \\
    b_1 &= -\frac{1}{R_1 C_1} , \\
    b_2 &= -\frac{1}{2R_s R_1 C_1 q_{\text{max}}} , \\
    b_3 &= -\frac{1}{2R_s R_1^2 C_1^2} , \\
    c_1 &= -2R_1 , \\
    c_2 &= \frac{1}{R_1 C_1}.
\end{align*}
\] (4.38)

Solving this system of coupled linear ODEs simultaneously, results in four algebraic equations with four unknowns. The unknown constants are obtained by applying the boundary conditions specific to this problem which consist of two initial and two final conditions. The initial and final condition for \( x_1 = SOC \) are similar to (4.24). On the other hand, in this specific problem the charging time is specified and fixed while the values of the second state at the initial and final time are free. This results in the succeeding equations for the remaining two boundary conditions [175]:

\[
\begin{align*}
    \frac{\partial h}{\partial x_2}(x_2(t_0)) &= \lambda_4(t_0) = 0 \rightarrow \text{Initial condition for } x_2 \\
    \frac{\partial h}{\partial x_2}(x_2(t_f)) &= \lambda_4(t_f) = 0 \rightarrow \text{Final condition for } x_2
\end{align*}
\] (4.39)

In general \( h(x(t), t) \) is the term involving the final states and final time in the cost function which in this study is zero. Given all boundary conditions, one can solve for the states and co-states and thus the optimal input is obtained. Consider charging a battery cell from zero charge \( SOC_i = x_1(0) = 0 \) to full charge \( SOC_f = x_1(t_f) = 1 \) in one hour. The result for this example is depicted in Fig. 4.13.

The optimal charging current for this scenario is slightly different from the result of the first scenario. The optimal input in this case is almost a constant current equal to 2.5 A, in the majority of times. It may be insightful to also show the result for a fast charging case. Fig. 4.14 shows the optimal charging current and the two states of the system when the cell is charged from zero to full charge in 6 minutes.

This charging strategy may not be practical due to thermal and physical constraints plus safety and lifetime issues. However it may be interesting to observe that by reducing the charging
Figure 4.13: Optimal charging current, $I_1$, and $SOC$ for charging the Li-ion battery from zero charge to full charge in 1 hour.
Figure 4.14: Optimal charging current, $I_1$, and $SOC$ for charging the Li-ion battery form zero charge to full charge in 6 minutes.
4.7 Efficiency Analysis for the Li-ion Battery

In order to find the optimal charging efficiency, the total energy stored in the battery and energy loss is required. Assuming a constant total internal resistance \((R = R_s + R_1 = 0.026 \Omega)\) makes the analytical efficiency analysis possible. The energy loss in the battery during optimal charging is already known and is equal to \(\int_0^{t_f} R u_{\text{opt}}^2(t)dt\). The total energy stored in the battery is:

\[
E_{\text{battery}} = \int_0^{t_f} V I dt = \int_0^{t_f} V \frac{dq(t)}{dt} dt = \int_0^{q_f} V dq
\]

(4.40)

where \(I, V, \) and \(q\) are the battery current, \(OCV\), and the charge in Ah, respectively. Using the linear relationship between \(OCV\) and the charge stored in the battery from (4.27) and the definition of \(SOC\), the maximum energy stored in the battery is obtained as follows:

\[
E_{\text{battery}} = q_{\text{max}}(SOC_f - SOC_i) \left[ \frac{a}{2}(SOC_f + SOC_i) + b \right]
\]

(4.41)

where the unit for energy is Watt-hours (Wh). The real maximum amount of energy which the battery can store is obtained by integrating the original \(OCV\)-\(q\) profile which results in 8.2 Wh for the cell used in this study. Using (4.41) and charging the battery from 0 to 100\% the maximum battery energy calculated is 8.26 Wh. This illustrates that the linear approximation of \(OCV\) for Li-ion battery is an effective approach to perform analytical efficiency analysis. Substituting the expressions for \(E_{\text{loss}}\) and \(E_{\text{battery}}\) in (4.25), the optimal charging efficiency for Li-ion battery is obtained as follows:

\[
\rho_{\text{opt}} = \frac{1}{1 + \frac{R_{\text{max}}(SOC_f - SOC_i)}{t_f \left( \frac{a}{2}(SOC_f + SOC_i) + b \right)}}
\]

(4.42)

where \(t_f\) is the charging time in hours and \(R\) is the total internal resistance in ohms. Similar to the SC, starting the charging from a higher initial \(SOC\) results in better efficiency. Also faster charging
will result in higher currents and lower efficiency. For the Li-ion battery, the constant power and the two optimal charging scenarios are almost identical in terms of the charging current profiles and also the efficiency values.

4.8 Effect of Temperature On Optimal Charging of the Li-ion Battery

In this section, unlike the unconstrained cases solved in the previous sections, the optimal problem is solved subject to voltage and temperature constraints. This approach represents a more realistic solution of the optimal charging of the Li-ion battery.

4.8.1 Electro-Thermal Model of the Li-ion Battery

In order to investigate the effect of temperature on the optimal charging current a thermal model needs to be coupled with the electrical model and integrated in the optimal charging formulation. The electrical model considered for this section is a single resistance model which represents the total internal resistance as the sum of the electronic and polarization resistances \( R = R_s + R_1 \). The dynamics of the electrical model is governed by the single state equation (4.7) with current being the input. On the other hand, the thermal model is a reduced order model represented by two states. For further details on reducing the governing PDE to two linear ODEs, please refer to [108]. The thermal model is identified and validated for the A123-26650 cell with specifications listed in Table 4.6. The state space representation of the thermal model is:

\[
\dot{x} = Ax + Bu, \quad y = Cx + Du
\]

(4.43)

where \( x = [\bar{T} \quad \bar{\gamma}]^T \), \( u = [Q \quad T_\infty]^T \), and \( y = [T_c \quad T_s]^T \) are state, input, and output vectors respectively. The states of the thermal model are the volume-averaged temperature \( \bar{T} \) in Kelvin (K) and the volume-averaged temperature gradient \( \bar{\gamma} \) in (K/m). The inputs are the ambient temperature \( T_\infty \) in Kelvin and the total heat generation rate \( Q \). The outputs of the model are the battery’s surface temperature \( T_s \) and core temperature \( T_c \) both in Kelvin. The linear system matrices \( A, B, C, \) and \( D \) are:
\[
A = \begin{bmatrix}
\frac{-48\beta h}{r(24k_t + rh)} & \frac{-15\beta h}{24k_t + rh} \\
\frac{-320\beta h}{r^2(24k_t + rh)} & \frac{-120\beta (4k_t + rh)}{r^2(24k_t + rh)} \\
\end{bmatrix}
\]

\[
B = \begin{bmatrix}
\frac{\beta}{k_t V_{cell}} & \frac{48\beta h}{r(24k_t + rh)} \\
0 & \frac{320\beta h}{r^2(24k_t + rh)} \\
\end{bmatrix}
\]

\[
C = \begin{bmatrix}
\frac{24k_t - 3rh}{24k_t + rh} & \frac{-120r_k + 15r^2 h}{8(24k_t + rh)} \\
\frac{24k_t}{24k_t + rh} & \frac{15r_k}{48k_t + 2rh} \\
\end{bmatrix}
\]

\[
D = \begin{bmatrix}
0 & \frac{4rh}{24k_t + rh} \\
0 & \frac{rh}{24k_t + rh} \\
\end{bmatrix}
\]

where \( r, V_{cell}, \rho, c_p, k_t, \) and \( h \) are radius, volume of the cell, volume-averaged density, specific heat, conduction coefficient, and convective heat transfer coefficients respectively. The parameter \( \beta = \frac{k_t}{\rho c_p} \) is the thermal diffusivity. The values for these measured and estimated parameters for the cell used in this research are summarized in Table 4.7.

The total heat generation rate obtained from the electrical model is equal to \( RI^2 \) and is fed into the thermal model. To complete the coupling and form the electro-thermal model, core temperature as an output of the thermal model is fed into the electrical model to tune \( R \). The variation of \( R \) with core temperature is estimated by pulse-relaxation experiments at different temperatures range-
Table 4.7: Li-ion physical and thermal parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius</td>
<td>( r )</td>
<td>12.93e-3</td>
<td>m</td>
</tr>
<tr>
<td>Volume</td>
<td>( V_{\text{cell}} )</td>
<td>3.4219e-5</td>
<td>m(^3)</td>
</tr>
<tr>
<td>Density</td>
<td>( \rho )</td>
<td>2047</td>
<td>kg/m(^3)</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>( c_p )</td>
<td>1109.2</td>
<td>J/kgK</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>( k_t )</td>
<td>0.61</td>
<td>W/mK</td>
</tr>
<tr>
<td>Convection Coefficient</td>
<td>( h )</td>
<td>58.6</td>
<td>W/mK</td>
</tr>
</tbody>
</table>

The described electro-thermal model consists of three states. Formulating the efficiency maximization problem using Pontryagin’s minimum principle will result in three state equations and three co-state dynamic equations with three unknown initial conditions that need to be guessed. This makes the problem tedious to solve using normal nonlinear ODE solvers. Dynamic programming (DP) is used instead, to solve this optimal control problem relying on Bellman’s principal of

\[ R(T_c) = c_1 Z^6 + c_2 Z^5 + c_3 Z^4 + c_4 Z^3 + c_5 Z^2 + c_6 Z + c_7 \]

where \( Z = (T_c + d_1)/d_2 \)

\[ (4.44) \]

The coefficients of the polynomial are listed in Table 4.8.

Table 4.8: Polynomial coefficients for \( R \) as a function of \( T_c \)

| \( c_1 \) | 0.0063599 | \( c_4 \) | 0.0071517 | \( c_7 \) | 0.035803 |
| \( c_2 \) | -0.011979 | \( c_5 \) | 0.0094349 | \( d_1 \) | -284.77 |
| \( c_3 \) | -0.0017172 | \( c_6 \) | -0.023463 | \( d_2 \) | 22.165 |

4.8.2 Optimal Fast Charging Considering The Temperature Effect for the Li-ion Battery

The described electro-thermal model consists of three states. Formulating the efficiency maximization problem using Pontryagin’s minimum principle will result in three state equations and three co-state dynamic equations with three unknown initial conditions that need to be guessed. This makes the problem tedious to solve using normal nonlinear ODE solvers. Dynamic programming (DP) is used instead, to solve this optimal control problem relying on Bellman’s principal of
optimality. We are interested in investigating fast charging scenarios to be able to trigger the voltage and temperature limits, in order to study their effect on efficiency and the optimal charging current profile. For this reason charging in 10 minutes is chosen where the initial charging temperature is $T_{\infty}=25^\circ C$. The resolution for the time in the DP code is 20 seconds. At each time instant $t_i$, all three states of the electro-thermal model are quantized and represented by $(SOC_i, T_i, \gamma_i)$. Fig. 4.16 demonstrates the implementation of DP. As shown in this figure, each grid represents the three states $(SOC_i, T_i, \gamma_i)$ moving from time $t_{i-1}$ to $t_i$ with multiple possible transitions. However, only the transitions that satisfy the state equations are acceptable which are named the admissible transitions in this study. The first phase of the DP algorithm is solved backwards in time. During the backward phase and for every admissible transition, the minimum cost-to-go is obtained for each time instant to the final time along with all the corresponding optimal control inputs.

During the forward phase of DP with the knowledge of the initial conditions for the states, the optimal control input which in this study is the optimal charging current is obtained.

At first similar to the other sections in the chapter, the constraints are relaxed and the efficiencies obtained from DP and CC charging from zero to full charge in 10 minutes are compared. This result is summarized in Table 4.9 where the optimal charging efficiency is slightly higher than CC charging.
A real world implementation would require constraints on the terminal voltage and core temperature. In the second step, the similar optimal charging problem is solved subject to a voltage constraint of $2 \, V \leq V_T \leq 3.6 \, V$ for both DP and CC charging. In the final step, keeping the terminal voltage constraint, the optimal trajectory and efficiency is obtained by adding the core temperature constraint of $T_c \leq 39 \, ^\circ C$ to both the DP and CC charging methods. Neither CC nor DP directly apply a limit on the maximum charging current as the voltage and temperature constraints indirectly result in limited charging current when they become active. The amounts for the voltage and temperature limits in the constraints are chosen from the manufacturers recommended operating conditions. In all these cases the battery is charged from 0% to 90% since charging the battery fully is not possible due to the aforementioned constraints as well as the short charging time of 10 minutes. The odd columns of Table 4.10 and Fig. 4.17 present the results for the CC charging. For comparison reasons, the unconstrained CC and DP charging scenarios are re-simulated for charging from 0% to 90%. Constant current constant voltage (CCCV) charging is the CC charging with the voltage constraint imposed. Also CCCV* is the notation for CC charging with both voltage and temperature constraints active. During CCCV charging as the inset in the first subplot in Fig. 4.17 shows, the current drops at the end of charging as the terminal voltage hits the limit of 3.6 V. During the CCCV* charging the amount of initial current (20 A) is chosen such that the battery could be
charged to 90% \textit{SOC}. According to Fig. 4.17 at about 30 and 200 seconds into the CCCV* charging, the voltage and temperature limits are reached respectively, which results in a stepwise decrease in current. Comparing the efficiencies listed in Table 4.10 for CC, CCCV, and CCCV* shows that imposing constraints on the CC charging results in smaller values for efficiency.

The even columns of Table 4.10 and Fig. 4.18 show the results for the optimal charging using DP. The unconstrained DP, voltage constrained, and the double voltage/ temperature constrained problems are indicated as DP\textsubscript{1}, DP\textsubscript{2}, and DP\textsubscript{3}, respectively. The results obtained using DP as the optimal charging currents have a slightly higher efficiency compared to their equivalent CC charging scenarios. The general trajectory of all the three DP cases shows a warm up period at the beginning of charging followed by a constant current charging section. The physical reason behind this behavior is that the higher current at the beginning of charging results in a rapid increase in core temperature which consequently decreases the total internal resistance. The lower total internal resistance is in favor of minimizing the charging losses according to the objective function in (4.8). The larger current at the beginning of charging results in terminal voltage reaching the upper limit which results in a decrease in current for DP\textsubscript{2} and DP\textsubscript{3} scenarios. For DP\textsubscript{3} as also shown via the inset in the second subplot in Fig. 4.18, the temperature limit is activated towards the end of charging, which results in an instant decrease in current to avoid overheating. The DP results are based on a 20 second resolution on time which maybe the reason for the ripples in current specifically obvious in the DP\textsubscript{2} case.

These optimal solutions are computed using Clemson University’s Palmetto cluster because of the high memory requirements of the DP implementation. In this particular problem, the three state variable of \textit{SOC}, \textit{T}, and \textit{γ} are quantized to \(n_{\text{SOC}} = 200\), \(n_{\text{T}} = 25\), and \(n_{\text{γ}} = 25\), respectively. This requires each grid of Fig. 4.16 to accommodate \(n_{\text{SOC}} \times n_{\text{T}} \times n_{\text{γ}} = 125000\) cells. Moreover each grid is stored by 125000\times125000 cells in the implementation as each cell at time instant \(t_{i-1}\) has also 125000 possible transitions to the next cell at time instant \((t_i)\). In the implemented DP code, 10 variables are involved in DP backward computation with mixed single/double precision (6 bytes on average). This would mean that the minimum required memory allocation is \(10\times125000\times125000\times6\) bytes or \(\approx 870\) GB. The involved variables are the two inputs to the objective function \((R\text{ and }I)\),
Table 4.9: Unconstrained CC and optimal charging in 10 minutes

<table>
<thead>
<tr>
<th></th>
<th>Unconstrained</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC</td>
<td>DP</td>
</tr>
<tr>
<td>Charging Current (A)</td>
<td>15</td>
<td>20 max.</td>
</tr>
<tr>
<td>Core Temperature (°C)</td>
<td>43 max.</td>
<td>42 max.</td>
</tr>
<tr>
<td>Terminal Voltage (V)</td>
<td>3.8 max.</td>
<td>3.7 max.</td>
</tr>
<tr>
<td>State-of-Charge @ t_f</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Energy Loss (J)</td>
<td>2682</td>
<td>2638</td>
</tr>
<tr>
<td>Efficiency</td>
<td>91.72%</td>
<td>91.84%</td>
</tr>
</tbody>
</table>

CC: Constant Current  
DP: Dynamic Programming

Table 4.10: CC and optimal charging in 10 minutes considering voltage and temperature constraints

<table>
<thead>
<tr>
<th></th>
<th>Unconstrained</th>
<th>Voltage-constrained</th>
<th>Temperature-constrained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CC</td>
<td>CCV</td>
<td>CCCV</td>
</tr>
<tr>
<td>Charging Current (A)</td>
<td>13.5</td>
<td>13.6 max.</td>
<td>19 max.</td>
</tr>
<tr>
<td>Core Temperature (°C)</td>
<td>41 max.</td>
<td>41 max.</td>
<td>39 max.</td>
</tr>
<tr>
<td>Terminal Voltage (V)</td>
<td>3.6 max.</td>
<td>3.6 max.</td>
<td>3.6 max.</td>
</tr>
<tr>
<td>State-of-Charge @ t_f</td>
<td>90%</td>
<td>90%</td>
<td>90%</td>
</tr>
<tr>
<td>Energy Loss (J)</td>
<td>2254</td>
<td>2280</td>
<td>2325</td>
</tr>
<tr>
<td>Efficiency</td>
<td>92.95%</td>
<td>92.87%</td>
<td>92.74%</td>
</tr>
</tbody>
</table>

CC: Constant Current  
CP: Dynamic Programming  
CCCV: Constant Current Constant Voltage  
Voltage-constrained: 2V ≤ V_T ≤ 3.6V  
Temperature-constrained: T_c ≤ 39 °C

98
Figure 4.17: CC charging results for charging from 0% to 90% in 10 minutes considering the temperature and voltage constraints.
Figure 4.18: Optimal charging results via DP for charging from 0% to 90% in 10 minutes considering the temperature and voltage constraints.
three state variables \((SOC, T, \eta)\), one combined constraint, and four cost functions (cost-to-go functions between \(t_i, t_{i-1},\) and \(t_f\)).

### 4.9 Conclusions

This study solved the optimal charging problem for different energy storage systems considering different levels of model complexity and also compared the optimal charging current with constant power, constant current, and constant voltage charging strategies. Efficiency analysis was also performed to compare different charging strategies. For the supercapacitor and the first scenario of the Li-ion battery, the optimal charging strategy is constant current. In the supercapacitor case, the constant power charging current has peaks that may make it less favorable to apply as it is also less efficient. In the Li-ion case, there is not much difference in applying constant power or constant current considering the efficiency and shape of the current profile. For the lead-Acid battery, the optimal strategy has a better efficiency than constant power charging, while constant current charging has the least efficiency. Finally, the effect of temperature dependent model parameters as well as the voltage and temperature limits on the optimal fast charging of the Li-ion battery was investigated. This constrained optimization problem was solved using dynamic programming and was compared to constant current charging. The results show that the charging efficiency of the optimal scenario is slightly higher than constant current charging.
Chapter 5

Fast Charging Challenges in Lithium-Ion Batteries

5.1 Literature Review

The ever-growing world energy demand as well as dwindling fossil fuel resources motivates exploring alternative solutions to the global energy problem. The transportation sector powered by combustion engines, the industrial plants and residential buildings running on electricity produced by non-renewable sources, are all gradually stepping towards a sustainable and low carbon model with a zero carbon footprint within the horizon. Higher degrees of renewable penetration in the grid alongside the electrification of ground vehicles will set the stage for a sustainable development in both transportation and power generation sectors. Within this area of research, energy storage has a pivotal role in electric vehicles. It is also a key component in grid applications helping improve efficiency and system performance by allowing better supply and demand management particularly for grids with higher renewable shares. The need to reduce the time required to charge a module resonates with the needs of the end-users and the acceptability of the technology in many applications. for example, in public transportation sector there is a tendency to explore electric driven buses. The predefined and available information regarding the route and the stops during passenger boarding are the driving force to explore the possibilities of fast charging. Justino et al., have designed ultra
fast charging stations for ultracapacitor driven electric buses in order to charge in a time interval of 10-30 seconds with a required power rating of 400 kW [178]. The reason for such a high rate capability is the high power capacity of supercapacitors [174]. In another study, Mapelli et al., study the fast charging of an urban electric bus powered by a hybrid battery/supercapacitor energy storage system [179]. In both of these examples the supercapacitor module is charged during stops and not the batteries. The reason that batteries can not be used in such fast charging scenarios (under 20 minutes) is that, the electrochemical, mechanical, and thermal constraints limit the rate of charging of the cell. The efforts to improve the charging time of lithium ion batteries can be categorized in the following directions:

- Modeling the cell using lumped or detailed electrochemical models to deeply understand the electrical and thermal dynamics of the battery. This approach allows to push the charging rate to the feasible limits of the cell without violating critical constraints.

- Exercising different control strategies to charge the battery in a shorter amount of time compared to the standard charging protocols currently in use.

- Seeking for novel materials for the cell components such as electrodes and the electrolyte with higher power capacity which allow charging at higher rates.

Understanding the electrochemical, thermal, and mechanical dynamics as well as limitations of lithium ion batteries, provides a powerful tool to analyze the operation bottlenecks and therefore push the limits in order to achieve performance goals such as faster charging times. Within this context, an accurate model will serve the purpose in the case of fast charging. The knowledge of different ionic and electronic resistances such as charge transfer, diffusion, and electrolyte resistances beside the electronic resistance of the current collector will facilitate the development of cells where the current flows in and out in higher rates which in return results in faster charging times. This study will review the models capable of capturing the dynamics of the cell during fast charging.

The standard charging protocol for lithium ion batteries is the constant current-constant voltage (CC-CV) scheme [180–182]. It consists of two phases. At the beginning the battery is
charged by a constant current till it reaches a predefined upper voltage limit. The next step is maintaining a constant terminal voltage which results in a tapered decreasing current. The charging is terminated when the current drops below a certain threshold. This charging mechanism is believed to be conservative while satisfying the safety standard during charging. Constant current charging without the constant voltage phase in another option. However, the drawback is the limited capacity utilization unless applying a very low charging current which substantially prolongs the charging time. There are other numerous charging algorithms applied to lithium ion batteries with different objectives that are not necessarily aiming to reduce the time of charging. Strategies that replace the CV stage of a CC-CV charging with pulse of multi-step CC charging are reported [163, 183, 184]. Some studies use pulse currents for the whole duration of charging [185–187]. The term C-rate is used in the battery literature to define a relationship between the capacity of the battery in ampere hours (Ah) and the charging (discharging) current as well as time. Consider “C” to stand for capacity of the cell and “n” to be a real number. In this context, a C-rate equal to “nC” is defined as the amount of current with a magnitude of “n.C”, that is able to charge the cell in $\frac{1}{n}$ hour. With this definition it is clear that applying a higher current will result in a shorter charging time. Having this in mind, boost charging which features higher CC charging intervals compared to the charging rate of a CC-CV protocol, results in a shorter charging time [188, 189]. More recently, Keil and Jossen have experimentally investigated the effect of different charging protocols on the cycle life of three lithium ion chemistries where they conclude that the influence of the charging rate on the deterioration of the cell is higher than the effect of the discharging current [190]. In the later sections, the control strategies applied to the problem of charging with the objective of reducing the charging time will be discussed.

The materials used to fabricate a lithium ion cell is another area where the power capacity and rate performance can be improved. A battery cell consists of two circuits. The internal circuit is the pathway for the ionic transmission, the external circuit is a passage for the electronic charge. These two circuits guarantee the charge conservation. The internal circuit in case of the lithium ion battery is the corridor for the transmission of lithium ions where they move from one electrode to another through the electrolyte and the separator. The function of separator is to insulate and prevent
electronic short circuit between the electrodes. The most commonly use material for the commercialized lithium ion battery anode is graphite. Among the wide spectrum of material for cathode, LiMO₂ (M: Co, Mn) are the favorites with LiCoO₂ being the most prevailing [191, 192]. During discharging, the lithium atom that was stored in the bulk of the anode material during charging, is extracted in the form of a lithium ion by losing a single electron (oxidation reaction) and migrating through the electrolyte toward the cathode. The lithium ion is then intercalated into the bulk of the cathode material by gaining an electron through a reduction reaction. Research to increase the rate of discharge in lithium ion battery by the means of new materials often focus on the cathode composition [193–201]. On the other hand, the charging process which is the interest of this study, consists of the redox reactions in the opposite direction of discharging. The review of the anode materials that are capable of undergoing high current for fast charging purposes will be discussed in the coming sections.

On the charger hardware and the infrastructure side, there are three charging levels [202]. The level 1 charging is slow and the charger is an on-board single phase charger with a power rating of 1.4-1.9 kW used to charge an electric vehicle (16-50 kWh) over night (11-36 h). The semifast, level 2 charger is also on-board, often single phase, with a power of 4-19.2 kW which is capable of charging the electric vehicle (3-50 kWh) in 2-3 hours. The third level which is the fast charging case, is a 3-phase, off-board charger and suitable to charge an electric vehicle in 10-30 minutes [203]. According to studies such as the one conducted by Botsford et al., the expectation of the stop time for charging is even less than what the level 3 charger can provide. The aim is to compete with the 3 minute stop time of a regular gasoline driven vehicle [204]. To achieve such a goal all the subsystems involved, from the battery to the charging infrastructure need to dramatically improve. In this research, we will focus on the battery as the system of interest and review the literature to report the current research and development efforts on the modeling, control, and material selection that focus on improving the charging time of the lithium ion batteries.

The remainder of this chapter is organized in the following order. In Section 5.2, the unwanted side effects of high rate charging are reviewed. In Section 5.3, the models facilitating the study of fast charging are described. Section 5.4, covers the control strategies with the objective
to minimize the charging time. Sections 5.5 and 5.6, discuss the anode materials suitable for fast charging and conclusion remarks, respectively.

5.2 Side Effects of Fast Charging

5.2.1 Lithium Plating

This phenomena is referred to the deposition of reduced lithium cations on the surface of the carbonaceous anode material during charging events. This process is opposed to the lithium intercalation that is suppose to normally occur in the negative electrode of a lithium ion battery. The major macroscopic factors that cause lithium plating are high current rates as in fast charging as well as low temperature conditions. Lithium metal deposition on the graphite is accountable for severe battery performance, health, and safety degradation. This is the motivation for a vast body of literature to detect the occurrence of lithium plating by the means of experiments as well as modeling approaches [205]. Using a wide spectrum of models, researchers have elucidated that the concentration saturation of lithium ions in the vicinity of the anode is an important factor that triggers the lithium deposition [206]. On the other hand, it has been proven that the overpotential of the lithium deposition reaction vs. Li/Li$^{+}$ being less than zero is another indicator of the onset of lithium plating [207, 208]. Perkins et al., have developed a reduced order model that captures the overcharge lithium depositions by tracking the resulting capacity loss and resistance rise [209]. While these studies at large focus on the intercalation kinetics in the anode, the electrolyte composition is also of significant importance in order to determine lithium plating [210]. On the qualitative side and by the means of scanning electron microscope (SEM) and optical in-situ microscopy, the reactions on the anode have been studied under high charging currents. In one of the earlier studies, Orsini et al., correlated the morphology of the lithium deposit with the current density for three types of anode (Li, Cu, and graphite) and a LiMn$_2$O$_4$ cathode. The SEM micrographs showed lithium dendrites formed on the Li and Cu electrodes under high currents, and mossy shape lithium under low currents. No special morphology was observed for the deposited lithium on the surface of the graphite electrode [211]. More recently, Uhlmann et al., induced plating on the anode in graphite half cell by
applying pulse-relaxation currents up to 10C. Terminal voltage and changes in anode morphology were analyzed during pulses and the subsequent relaxations. The pulse-relaxation measurements indicated a specific bending in the voltage transient during charging followed by a potential plateau in the relaxation period in case of a plating event. Furthermore, the lithium plating was confirmed by both SEM and In-situ optical observations [212].

Efforts have been made to detect lithium plating by monitoring the variation of coulombic efficiency [213], change in thermal heat flow via electrochemical microcalorimetry [214], and increase in cell thickness [215,216]. The other operation condition that makes the anode susceptible to lithium plating is low temperature [217,218]. Zinth et al., utilize in situ neutron diffraction method to study lithium deposition on the anode in a NMC/graphite cell, in a temperature of -20 °C and under charging currents of C/5 and C/30. Results show that the rate of plating is higher under the higher current of C/5. Also the percentage of the deposited lithium in a 20 hour relaxation period is 17% while this rate is 19% for a discharging event right after a C/5 charging rate. The authors also conclude that the length of the plateau observed in the discharging voltage profile is a measure of the amount of plated lithium. Also unlike other methods they conclude that the neutron diffraction method shows that a huge fraction of the lithium plating is reversible [219]. In another study, Schindler et al., look at the relaxation period right after charging the cell to a certain capacity at sub-zero temperatures and combine voltage differential and electrochemical impedance spectroscopy methods to identify the lithium deposition by tracking any changes in the cell impedance [220].

5.2.2 Mechanical Failure

The insertion/ extraction of lithium ion into the volume of the anode and cathode induces mechanical stress in the host material. The stress occurs when the battery is charged at a rate higher than the rate that lithium can homogenize in the active material by diffusion [221]. This lithiation-induced stress appears in the form of fracture or structural deformation in the majority of active materials such as graphite, silicon, LiFePO4, LiMn2O4, and LiCoO2 [222–230]. One approach has been to use mathematical modeling and fracture mechanics, to simulate the failure mechanisms in the battery [231–237]. Christensen et al., developed a mathematical model to calculate the volume
expansion/contraction and the associated stress in a spherical particle of the electrode material. The model is based on the fact that by lithium insertion a strain differential is induced between the inner and outer regions of the sphere. This strain differential causes a stress that increases with the rate of intercalation and will result in particle fracture, if surpasses the yield stress of the material. The particle size, diffusion coefficient, and the charging rate have been considered in the model. The model predicts that the carbon based materials will fracture at high power applications [238]. Applying a similar concept, the same authors modeled the fracture in LiMn$_2$O$_4$ electrodes, considering solid-state diffusion in a one-phase material and moving-boundary insertion in a two-phase material. The results show that in a discharging event it is important to avoid over-discharge as it results in immediate fracture [239]. In another study, Zhang et al., numerically simulate 1D spherical as well as 3D ellipsoidal particles for a LiMn$_2$O$_4$ cathode. The results suggest to synthesize the electrode particles to have smaller size and larger aspect ratio, in order to reduce the intercalation stress. Furthermore, to decrease the resistive heat generation rate and the intercalation-induced stress, the authors show that ellipsoidal particles with larger aspect ratios are preferred over spherical particles [240, 241]. The conclusion that smaller particle size will result in less lithiation-induced stress is also true for electrodes with different silicon material geometries such as nanowires, spheres, and cylinders [242–246]. More recently Chen et al., combine the fracture formation and impedance model to investigate the effect of mechanical degradation mainly caused by cracks, on the impedance behavior of the cell. Results indicate that the microcracks have a larger influence on the impedance response during delithiation compared to the lithiation process. Furthermore, porous electrode impedance response suggests that the diffusion induced damage at low temperature and high discharge/charge currents, has a larger influence on the resistance. The higher concentration gradient explains the reason for this behavior [247]. Laresgoiti et al., propose a model based on spherical graphite particle with solid electrolyte interphase (SEI) layer. The paper focuses on the stress in the graphite and the SEI layer, induced by diffusion and the graphite expansion, respectively. The paper further assumes that the SEI layer is more susceptible to fracture than graphite and concludes that unlike the active material, stress in the SEI is not influenced by the current rate, diffusion coefficient, and the particle size [248]. Barai et al., utilize a stochastic approach based on
the lattice spring model to come up with a fracture phase map to identify the safe/unsafe operating conditions in terms of charging rate and particle size [249]. Researchers have also elucidated the damage under high currents, experimentally. Choe et al., used acoustic emission (AE) technique to study the damage taking place in a coin-type battery with lithium cobalt oxide/carbon electrodes under accelerated cycle tests. The short duration and high amplitude of the AE signals indicated cracking of the lithium cobalt oxide while the long duration and low amplitude signals explained the bubbling due to the SEI layer formation on the anode [250]. In another study Kostecki et al., use different experimental techniques such as atomic force microscopy, scanning electron microscopy, gas chromatography, Raman spectroscopy, and synchrotron IR microscopy with the goal of identifying detrimental indicators under high current operation and storage at elevated temperatures. The results suggest that the SEI deterioration on the anode, morphology change, and increase of impedance in the cathode contribute to the loss of power in the cell [251].

5.3 Suitable Models for Fast Charging

The terminal voltage, current, and temperature are the only measurable parameters in a battery cell. In order to obtain a comprehensive understanding of the electrochemical and thermal dynamics of a cell, having a reliable and accurate model is inevitable. In general, there are two categories of models: first principle full-order models and the reduced order models. The deciding factor in the level of model complexity, is the application and operating conditions of the battery. Depending on the purpose of the application, the importance of model accuracy versus computational efficiency is weighted. In the full-order models, all the underlying physics in a battery cell is taken into account. This macroscopic approach is formulated by considering the porous electrode and concentrated solutions theory. Such models include partial differential equations governing the lithium ion concentration in the solid and electrolyte phases, solid and electrolyte potentials, electrolyte ionic current, and the intercalation kinetics [252–255]. The large computational memory and power required to numerically solve the coupled system of PDEs is a burden in real time applications. This has motivated a large community of scientists to seek techniques of reducing
the complexity of the full order models [209, 256–261]. One direction pursued in the literature, is using numerical methods such as volume averaging and parabolic approximation of the solid-phase concentration [111, 262–264], residue grouping [265], Pade approximation [266], and proper orthogonal decomposition method [267]. These group of models will be referred as numerically reduced order models (NROM) within this paper. Another direction in model reduction that has led to a lower fidelity but widely used model, is the single particle model (SPM) [268–271]. It acquires its name due to modeling each electrode with a single sphere particle with a surface area equivalent to the active material area of the porous electrode. The simplification in this model results by assuming that the lithium concentration in the electrolyte is constant in both space and time. Another popular set of reduced order models are the equivalent electric circuit models [100, 103, 272, 273]. This group of models are computationally efficient but are unable to fully capture electrochemical states and parameters of interest. The model suitable for fast charging scenarios, should be accurate enough to facilitate studying the effect of high currents on the electrochemical and thermal dynamics of the cell. Among the models discussed the full order or NROM electrochemical models are the most promising in simulating the galvanostatic charging behavior in fast charging events. These group of models are capable of capturing the ionic transfer in both solid (electrode) and liquid (electrolyte) phases. The SPM model lacks the complete dynamics of the lithium ion concentration. As this factor is important at high C-rates [271], therefore the SPM model is not suitable for fast charging studies. Lumped equivalent electric circuit models lack the level of accuracy required to mimic the electrochemical processes that limit the performance of lithium ion batteries at high currents. On the other hand, the thermal dynamics of the battery cell will also be of significant importance due to large temperature variation caused by high currents. The coupling of full order or NROM electrochemical models with a thermal model through the total heat generation and the temperature dependent parameters [274–276], will facilitate studies that focus on high charging rates. Hasan et al., utilized a coupled 1D electrochemical-thermal model reported in [277], and the software AutoLion-1D, to study the performance of lithium ion batteries under different charging protocols, electrode designs, and the basic mechanisms of fast charging at -20 °C (low), 25 °C (moderate), and 45 °C (high) temperatures. The results elaborate that the electrolyte resistance dominates the fast
charging process at moderate and high temperatures, while the charge transfer resistance is the dominant factor at subzero temperatures. It is shown that at subzero temperatures, adiabatic conditions compared to isothermal conditions, result in a lower charging time and higher coulombic efficiency. The reason is the elevated temperature of the cell under adiabatic conditions due to the trapped heat, generated inside the cell, which suppresses the charge transfer limitations and the electrolyte resistance [278]. In another study, Ye et al., investigate the effect of thermal contact resistances during fast charging in prismatic battery packs by taking a close look at temperature, temperature gradient, and the spatial non-uniformity of current and state of charge (SOC) in the cross plane direction. The model utilized in this study was a two dimensional electrochemical thermal model [279, 280]. The results show that during fast charging neither constant current nor pulse charging are effective charging methods from a thermal point of view, as even intensifying the external cooling in not adequate to avoid thermal runaways. Authors propose optimized battery design by reducing the cell thickness as a solution to this thermal management problem [281]. Smith et al., study the charging of lithium ion battery with a capacity of 6 Ah and nominal voltage of 2.7 V with a upper voltage limit of 3.9 V, during charging. The authors conclude that the lithium deposition does not occur when charging the battery from different initial SOCs to the upper voltage limit of 3.9 V, with currents rated at approximately 15C. They suggest that setting the difference in solid and electrolyte potential rather than the upper voltage limit as an indicator of the lithium plating occurrence increased the allowable charging rates by 50%. The model used in this study is also a 1D electrochemical-lumped thermal model which has allowed such detailed analysis [282]. Zou et al., discretized a 1D electrochemical coupled with a thermal model and tune the level of discretization and order of polynomial approximations as a function of the charging rate to achieve higher model accuracy. The results show that in order to achieve a normalized root-mean-square of 1% in the terminal voltage, compared to the full order model, the single particle model will no longer be accurate for charging rates above 1C [283].
5.4 Controls in Fast Charging

Unlike the discharging event that depends on the requested load, the charging process is controllable. Certain parameters and constraints are taken into account during charging to ensure safety, reliability, and the feasibility of the process. Considering safety from a macroscopic point of view, the terminal voltage and temperature of the cell should be bounded in a certain range to avoid over-potential and thermal runaways. Having cost in mind, in the long run it is favorable to extend the battery cycle life and maintain its state of health. On the other hand, the efficiency of charging has an important role in determining the charging strategy as it is directly linked to the cost, aging, and safety of the cell. Last but not the least, is the charging time that is a game changer in terms of enhancing the feasibility and acceptability of the lithium ion technology. Within this domain, control engineering facilitates the implementation and realization of the various objectives. The controls literature consists of studies that shed light on the charging of lithium ion batteries with the battery cycle life in mind [165,190,284–290]. Many researchers have also investigated the charging problem with the objective to minimize losses and improve the charging efficiency [103, 160, 291]. The main focus of this section will be on reviewing papers that emphasize on the minimum time problem by using different control strategies [188, 189, 292]. Torchio et al., apply a quadratic dynamic matrix control (QDMC) approach to a pseudo two-dimensional (P2D) model of a lithium ion battery with the objective of minimizing the charging time. To overcome the computational burden in solving this optimal control problem, the authors have developed an approximation for the P2D model using the least square approach. This framework which satisfies the constraints on output voltage, input current, and battery temperature results in charging times as low as 1200 seconds [293]. In [294], Klein et al., also use a macro-homogeneous 1-D electrochemical model of the lithium cell with the aim to challenge the conservative constraints on current and voltage usually used in CC-CV charging scheme. The constrained optimal control problem with the objective of achieving the fastest charging time is formulated using nonlinear model predictive control (NMPC). The results show a 50% decrease in the charging time compared to the CC-CV method. In another study Moura et al., use the electrochemical states with the assumption of full state measurements.
along with a reference governor (RG) algorithm to impose constraints such as side reaction over-potential, rather than the conventional upper voltage limit. The charging time of the RG method is 24 min vs 38 min for CC-CV [295]. Liu et al., in [163], introduced a multi-stage constant current charging profile by the means of Taguchi-based algorithm and orthogonal arrays that resulted in charging the lithium ion battery to 95% in 130 minutes which was 11.2% less than the CC-CV charging time.

5.5 Anode Materials for Fast Charging

There is an exuberant stream of literature delving into the different materials to be used in lithium ion batteries as electrodes and electrolyte [296]. In this section the focus is on the materials used for the negative electrode of lithium ion batteries due to its importance during the charging process. Beside graphite that is the most widely used anode material many other materials have also been studied. Goriparti et al., categorize the anode materials based on the chemical reaction mechanisms [297]. First is the carbonaceous materials, where the intercalation/de-intercalation is the dominant reaction. Porous carbon [298], carbon nanotubes [299,300], graphene [301–303], and carbon nanofibers [304,305] are in this category. The second group, includes materials with the alloy/de-alloy mechanism such as silicon [306,307], silicon oxides [308–310], germanium [311–314], and tin [315]. The last category are the conversion materials such as metal oxide, nitride, phosphide, and sulfides [316–325]. To be able to summarize the efforts on the material side, in this study we focus on studies of anode materials with a nano-scale particle size for the active material, which report a charging rate of 3C (20 minutes) or faster. Yang et al., examine a set of three hard carbons with different nano-sized porous structures. With a high C-rate of 5C the cell demonstrates a capacity of 332.8 mAhg$^{-1}$. The reason that the cell can undergo higher charging rates, is lower resistance and shorter pathways as a result of the nano-sized porous texture which also contributes to the larger surface area for additional intercalation sites for the lithium ion [326]. Lee and Park in [327], utilize a specific process to synthesize 3D porous SiO (silicon monoxide) similar to approaches in [328–330], without altering the chemical and physical properties of SiO. The final
carbon-coated silicon monoxide demonstrated a high capacity of 1490 mAh\textsuperscript{−1} after 50 cycles and a high rate capability of 74% at 3C compared to 0.1C rate. Seng \textit{et al.}, compare the capacity of GeO\textsubscript{2}/Ge/C, GeO\textsubscript{2}/C, nanosized GeO\textsubscript{2}, and bulk GeO\textsubscript{2} as anode materials. The GeO\textsubscript{2}/Ge/C sample showed the highest rate capability compared to others where the capacity was 1750 mAh\textsuperscript{−1} and 1680 mAh\textsuperscript{−1} at the 5C and 10C rates, respectively. The capacity for the 10C rate was only 10% less than the recorded capacity of 1850 mAh\textsuperscript{−1} at a rate of 0.1C [331]. In another study, Wang \textit{et al.}, directly deposit Ge on the surface of pre-synthesized Cu nanowire arrays via an rf-sputtering method and use it as the electrode material. The Cu-Ge nanowire arrays display a capacity of 734 mAh\textsuperscript{−1} after 80 cycles and under 60C current rate [332]. In another example of a germanium based anode, Yuan \textit{et al.}, utilized specifically synthesized germanium nanowires that can undergo currents as high as 11C with 555 mAh\textsuperscript{−1} reported capacity [333]. Titanium oxide (TiO\textsubscript{2}) based anodes also exhibit high rate characteristics. Liu \textit{et al.}, have synthesized microspheres of TiO\textsubscript{2}-B with a pore size on 12nm. This material has showed promising results in terms of being a high power anode material where it has a capacity of 120 mAh\textsuperscript{−1} at a charging rate of 60C [334]. Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} (LTO) is another anode material in lithium ion batteries. Prakash \textit{et al.}, reported using LTO as high power anode materials with capacities of 140 mAh\textsuperscript{−1} and 70 mAh\textsuperscript{−1} at 10C and 100C current rates, respectively. The nano and highly porous morphology of the electrode contributes to the high rate capability by shortening diffusion paths [335]. Spindle-like porous $\alpha$-Fe\textsubscript{2}O\textsubscript{3} has been the main focus of Xu and his colleagues in [336], as an anode material. The simple synthesize process beside the smaller size of $\alpha$-Fe\textsubscript{2}O\textsubscript{3} nanoparticles cause shorter distance for transportation of Li ions, which is critical to the rate capability. The reported capacity for such an anode was 911 mAh\textsuperscript{−1} after 50 cycles with a rate of 0.2C. Cycling under a rate of 10C, the achieved capacity was 424 mAh\textsuperscript{−1}. Cobalt oxides are another material used as anodes in lithium ion batteries. For example, Guan \textit{et al.}, fabricated CoO octahedral nanocages, where it was tested as anode material and exhibited good rate capability. Under a current rate of 5C, the anode could deliver a reversible capacity of 474 mAh\textsuperscript{−1} [337]. Lu \textit{et al.}, have successfully practiced fabricating a composite Ni\textsubscript{5}P\textsubscript{4}/C material for use as anode material in lithium ion batteries. The carbon shell enhances the conductivity and limits the aggregation of active particles which in return results in structural stability and reversibility during
cycling. This composite material can retain a capacity of 644.1 and 357.1 mAh g\(^{-1}\) under currents rates of 0.1C and 3C, respectively [338].

5.6 Conclusions

The potential to recharge an electric vehicle in an equivalent time to refuel a gasoline vehicle as well as charging electronic devices in a fraction of the time that takes to charge them nowadays, is the motivation for many researchers to address the problem of fast charging. A large decrease in charging time is often associated with high currents. High current induces different types of stress on the battery. Thermal runaway, lithium plating, mechanical failure are a few of the unwanted circumstances of high current. A search through a wide spectrum of models for lithium ion batteries, reveals that due to the sensitivity of the electrochemical and thermal processes to high currents, the development and utilization of detailed first principle models provides the edge to implement more effective fast charging strategies. On the other hand, it is identified that there is a need for advanced control strategies that rely on the electrochemical-thermal modeling of lithium ion batteries, as well as taking different electrical and thermal constraints into account while aiming to reduce the charging time. Within the material science and engineering community there is a vibrant search for feasible cost effective and high rate materials to address the charging time problem. Having the charging process in mind, different anode materials such as carbonaceous, alloy/de-alloy, and conversion materials with nanostructure morphologies show promise in high rate applications.
Chapter 6

Dissertation Summary

6.1 Contributions

The major contribution of this dissertation is the proposition and validation of models and control strategies that overcome imperative problems such as limited driving range of electric vehicles and long charging times in batteries. The summary of each study is presented in this chapter.

In chapter 2, an electro-thermal model for a supercapacitor is derived and experimentally validated. The contributions are:

1. The dependence of the electrical model parameters on temperature (range: -40 °C to 60 °C), state of charge (SOC) (range: 0-100), current direction (charge/discharge), and also for the first time, current magnitude (range: 20-200 A) is embodied in the model.

2. The experimentally validated results show that the terminal voltage dynamics is captured with high accuracy (20-87 mV), suitable for all kind of power system applications.

3. The computationally efficient thermal model captures temperature dynamics with high accuracy (0.17-0.21 °C) suitable for real-time thermal management systems.

4. The coupled electro-thermal model is validated using a practical driving cycle rather than simple constant current cycles often used in the literature.
Chapter 3, describes the benefit analysis on driving range extension, for a lead-acid driven vehicle hybridized via supercapacitors. The contributions are:

1. The control strategy is simply implementable using inexpensive commercial micro controllers and the converter is specifically built for this study, which enables monitoring the real world efficiency bottlenecks of the hybrid energy storage (HES).

2. The developed HES model is fully scalable. For validation purposes, a 12 V hardware in the loop (HIL) setup is used to implement the control strategy and extract the driving range results.

In chapter 4, specifically focuses on improving the charging efficiency and duration of supercapacitor, lead-acid, and Li-ion batteries by the means of analytical and numerical methods in optimal control. The contributions are:

1. The comparison of different charging strategies (constant voltage, constant current, and constant power) and the associated efficiencies with their optimal charging counterpart. In case of the lithium ion battery, the effect of temperature dependent model parameters on the optimal charging current is investigated, by the means of using a validate electro-thermal model and dynamic programming as the numerical technique.

2. The intention to solve this optimal control problem analytically and the gradual increase in the model complexity, gives the study a tutorial touch which can be used as a basis for research focusing on charging and in a larger scale, studies choosing to analytically solve optimal control problems.

In chapter 5, the focus is on bottlenecks of fast charging in lithium ion batteries. The contribution is through providing guidelines from the modeling, control, and material science and engineering fields, that contribute to decreasing the time required to charge lithium ion batteries.
6.2 Discussions and Future Work

Beside the implementable results reported in this dissertation there is a huge potential to expand beyond the presented studies. In the transportation sector, the electric vehicle technology is in its infancy. Despite the noticeable progress in the past couple of decades in increasing the energy density of batteries, the limited range of these vehicles are still an ongoing challenge. One direction in addressing this problem is to seek for new materials that improve the energy density while at least maintain the current performance requirements as well as competing with the decreasing cost of the current technology. Another venue to investigate is the implementation of alternative energy storage technologies in either stand-alone scenarios or in combination with batteries. In this regard, supercapacitor with its high power density was studied as the alternative storage technology in this dissertation. With the decreasing cost of supercapacitors in the coming years, their utilization in different applications will grow. The driving range extension study in the third chapter, is only one example of integrating supercapacitors in a vehicle level. Another interesting area that is also covered in this dissertation is the issue of charging time. Due to the high currents applied in order to reduce the charging time, the batteries undergo extreme electrochemical and mechanical stresses. Reduced order electrochemical modeling and control is a area of research with a high potential to facilitate the realization of fast charging. Such models can accurately capture the dynamics of the cell and help impose realistic constraints on different parameters of the battery while ensuring safety, acceptable cycle life, and feasibility to operate in real world applications.

As reported by the Energy Information Administration (EIA), the worldwide total installed capacity of the renewable electricity generation by the year 2014, accounted for 24% (1700 GW) of all electricity generated. This number for the U.S. is only 15.5% of the total electricity generated in the country (180 GW). The main challenges in exploiting these energy sources, are cost and availability. Wind and solar energies are not always available where and when needed which results in intermittent generation. Storage technologies are a viable solution to such problems. Within the wide variety of energy storage systems, the retired electric vehicle batteries, and also the redox flow batteries show a lot of potential. The architecture of flow batteries makes it possible to independently
design the storage capacity and the power output. This allows optimal sizing of the energy storage, unlike other battery technologies that are usually oversized due to the coupled energy and power densities. This feature, beside utilization of cheaper organic electrolytes facilitates a lower cost per kWh. On the other hand, batteries retired from operation in electric and hybrid electric vehicles have a decent amount of capacity left to be used in a secondary application such as in power generation.

6.3 Dissemination of the Dissertation

6.3.1 Journal Publications


6.3.2 Peer Reviewed Conferences


6.3.3 Patent

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