

The Effects of Temperature on Lithium-Ion Battery Cells and Packs

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Anosh Mevawalla

Abstract

In the United States, transportation accounts for 28% of total greenhouse gas emissions. Electric vehicles are a significant step toward lowering emissions. Lithium-ion batteries are critical to the commercialization of electric vehicles; nevertheless, batteries are temperature sensitive, and sub-optimal temperatures can cause degradation, loss of power, loss of voltage, and thermal runaway. A lightweight, safe, and effective heat management system improves the vehicle's mileage, speed, safety, and longevity. The necessity for research into the effects of temperature on lithium-ion batteries and battery packs is obvious and important in order to develop electric vehicles that are widely adopted by the public. Models that quickly and accurately forecast the temperature and voltage depending on operational parameters can avoid thermal runaway, increase charging speed, prevent lithium plating, and increase cycle life.

The work consists of a thorough investigation of the temperature effect at both the cell and pack level on various battery parameters such as state of health, internal resistance, capacity and performance. Battery models based on both equivalent circuits and physiochemical models are produced and various battery pack designs are investigated. The effect of temperature on overpotential, current density, capacity and cycle life are also modeled. The writing is divided into four parts:

Part 1:

This section presents mathematical models for quick calculation that can be used in battery management systems (BMS) and battery thermal management systems (BTMS). This paper introduces two distinct models: an internal resistance (R_{int}) model and a physiological-chemical diffusion/Butler-Volmer-based partial differential 1-D model. The R_{int} model incorporates a relationship between internal resistance, state of charge (SOC), and C-rate. The investigations use thermocouples on both the battery's surface and tabs. At 4C, the battery temperature rose from 22.00°C to 47.40°C, while the tab temperature went from 22°C to 52.94°C. Simulation results are compared to experimental data at various C-rates (1, 2, 3, and 4C) at 22°C. Simulation findings indicate accurate temperature prediction using a simple R_{int} model. The reduced physio-chemical model with only three partial differential equations (PDEs) achieves comparable accuracy to the

Rint model. The Rint model accurately predicts battery internal resistance using a Pearson curve and hyperbolic sine function, based on current and state of charge.

Part 2:

This section shows three electrothermal equivalent circuit models with multiple input parameters (SOH, SOC, current, and temperature). The model allows us to estimate parameters like internal impedance using practical inputs, unlike traditional physiochemical models that rely on experimentally unavailable quantities like porosity and tortuosity. The study simulates the internal impedance resistance of a LiFePO_4 battery at various ambient temperatures (5, 15, 25, 35, 45 °C), discharge rates (1, 2, 3C), and SOHs (90%, 83%, 65%). The internal impedance surface fit experimental observations with a Pearson coefficient of 0.945. Three thermal models incorporated the internal resistance surface model. The first two thermal models were 0D and did not account for the battery's thermal conductivity. The first model assumed simple heating from internal resistance and convective energy loss, while the second incorporated the Bernardi Equation Reversible heat term. The third model was a 2D model that retained the earlier heat source terms while adding a tab junction heating source term. The 2D model was solved with a basic Euler approach and finite center difference method. The 0D thermal models had R^2 values of 0.9964 for simple internal resistance and 0.9962 for reversible heating. The R^2 for the 2D thermal model was 0.996.

Part 3:

This paper reported experimental data and model results for a LiFePO_4 cell at C-rates of 1C, 2C, 3C, and 4C and at an ambient temperature of approximately 23°C. During the experiment, thermocouples were installed on the battery's surface. Experiments were carried out at continuous current discharge. Temperature increased with C-rates on both the surface and tabs. At 4C, the battery temperature climbed from 22 °C to 47.40 °C, while the tab temperature increased from 22 °C to 52.94°C. Simulation results indicate that the cathode generates more heat than the anode, with electrolyte resistance being the dominant source of heat. Battery temperature was highest near tabs and within the battery's internal space. The simulation of lithium concentration in the battery revealed that the anode had a more uniform concentration than the cathode. These findings can aid in the precise design and control of Li-ion batteries.

Part 4:

The experimental setup consisted of 7 Panasonic NCA cells connected in parallel, with each cell rated at 3.2Ah capacity. Individual cell capacities were measured and averaged, and the experimentally determined value was 3.11Ah. The arrangement has no BMS, and the batteries were allowed to equilibrate to a steady voltage at the end of discharge. The limiting current of the cells was low, posing less safety issues. The cooling method tested was ambient air cooling, with all trials taking place at an ambient temperature of around 25°C. The battery's thermal behavior was measured at six different discharge rates (constant current): 0.5C, 0.75C, 1C, 1.25C, 1.5C, and 1.75C.

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Nomenclature

A	: surface area of battery [m^2]
C_{DL}	: capacitance of the double layer [F]
c_p	: specific heat capacity [$\text{J/kg}^\circ\text{C}$]
C_l	: electrolyte salt concentration [mol/m^3]
$C_{s,e}$	: concentration of lithium in solid phase [mol/m^3]
$C_{e,ref}$	: electrolyte reference concentration [mol/m^3]
$C_{s,p,max}$	: maximum solid Li^+ concentration for positive electrode [mol/m^3]
$C_{s,n,max}$	: maximum solid Li^+ concentration for negative electrode [mol/m^3]
D	: effective diffusion coefficient of the material domain [m^2/s]
E	: Youngs Modulus [Pa]
E_{eq}	: equilibrium potential/ open circuit voltage [V]
OCV	: electrode potential of the reaction or thermodynamic open circuit potential[V]
F	: Faraday`s constant [96485 coulomb/mol]
H	: convective heat transfer coefficient [$\text{W/m}^2\text{K}$]
I_0	: exchange current density [A/m^2]
i_0	: exchange current density [A/m^2]
I	: current [A]
J	: the flux of lithium-ions [$\text{mol/ m}^2\text{s}$]
L	: length of domain [m]
n_m	: number of electrons
$\dot{q}$	: heat generation rate [W/m^3]
$\dot{q}_{ECH}$	: reversible heat generation rate [W/m^3]
R_{int}	: internal resistance [Ω]
R	: universal gas constant [8.3143 kJ/kg mole. K]
R_p	: radius of solid active material particle [m]
$R_{s,p}$	: particle radius for positive electrode [m]
$R_{s,n}$	: particle radius for negative electrode [m]

SOC	:	state of charge
T	:	temperature [°C or K]
T_{amb}	:	ambient room temperature [°C or K]
t_+^0	:	transfer number of lithium-ion
T	:	time [s]
V	:	cell voltage or cell potential [V]
$V_{battery}$	:	volume of battery [m ³]

Greek Symbols

ρ	:	density [kg/m ³]
∇	:	gradient operator
ϕ_s	:	solid phase potential [V]
ϕ_l	:	electrolyte phase potential [V]
σ_l	:	electrolyte conductivity [S/m]
$\sigma_{l,eff}$	:	effective electrolyte conductivity in the porous electrode [S/m]
σ_+	:	effective electrical conductivity for positive tab [S/m]
σ_-	:	effective electrical conductivity for negative tab [S/m]
E	:	volume fraction of solid particle (active material) in electrode
η	:	overpotential [V]
μ	:	Chemical Potential [J/mole]
η_{ohmic}	:	overpotential due to ohmic resistance [V]
$\eta_{activation}$	:	overpotential due to activation losses [V]
$\eta_{concentration}$	:	overpotential due to mass transport losses [V]
$\eta_{AnodeInterface}$	:	overpotential at the anode electrolyte interface [V]
$\eta_{CathodeInterface}$	:	overpotential at the cathode electrolyte interface [V]
κ	:	Transmission Coefficient
α_a	:	transfer coefficient of anode
α_c	:	transfer coefficient of the cathode
α_{pol}	:	Polarizability
α_{th}	:	Coefficient of Thermal Expansion

Acronyms

BMS	Battery management system
BTMS	Battery thermal management system
C	Capacity
CC	Constant current
CD	Charge depleting
CV	Constant voltage
CAD	Computer aided design
CFD	Computational fluid dynamics
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DES	Detached eddy simulation
DRU	Data recording unit
EC	Ethylene carbonate
ECT	Electrochemical thermal
ECM	Equivalent circuit-based modeling
IR	Infra-red
Li-ion	Lithium-ion
LiCoO ₂	Lithium cobalt oxide
LiMn ₂ O ₄	Lithium manganese oxide
LiNiMnCoO ₂	Lithium manganese cobalt oxide
LiFePO ₄	Lithium iron phosphate
LFP	Lithium phosphate
LPM	Lumped parameter model
MSE	Mean Square Error
NMC	Lithium manganese cobalt oxide
NYCC	New York city cycle
NiMH	Nickel metal hydride
NiCad	Nickel cadmium
OCV/OCF	Open circuit voltage/Open circuit potential
PDEPE	Partial Differential Equation (Parabolic and Elliptic)

PE	Polyethylene
PP	Polypropylene
SEI	Solid electrolyte interface
SPI	Solid permeable interphase
SOC	State of charge
SOD	Start of discharge
SOH	State of health
TMS	Thermal management system
1D	One-dimensional

Chapter 1 Introduction

The overall goal of this research is to generate laboratory data to examine the effects of temperature on lithium-ion cells and battery packs, followed by the creation of mathematical models from this data that may be utilized for design, control techniques, and fault detection. The research issues we hope to solve include developing electrochemical and thermal models of cells and packs that can be utilized to reduce thermal management system energy consumption, boost charging speed, extend cycle life, power density, and total pack capacity.

1.1. Problem Definition

Though large databases are publicly available for Lithium-ion batteries the majority of them do not contain the effects of temperature on the performance of cells in detail. Temperature is critical in Cell degradation, performance and safety. The literature regularly reports on heightened degradation and capacity loss at temperatures deviating from 25 °C but lab data shows that for a multitude of cell chemistries including NMC and LiFePO₄ the capacity during the first cycle does in fact increase. This is true even if cooled to lower temperatures before starting the first run. Some cell chemistries, such as MnO₂, show this to not be the case.

Temperature is related to a variety of critical cell characteristics such as state of health, internal resistance, and current density. This thesis conducts comprehensive research on the issue.

1.2. Objectives and Subobjectives

The temperature of Lithium-ion Batteries at both the pack and cell level dramatically affects performance, capacity and cycle life. The objectives of this investigation are:

- Effect of Temperature on single cell
 - Investigate and model the effect of temperature on LiFePO₄ cells from the range of 5°C-45°C at 1-4C
 - Create thermal electrochemical models at these temperatures
 - Create response surfaces of the internal resistance under these conditions
- Battery pack investigation

- Design methods including Equivalent circuits and Finite Element Analysis for cell and tab placement which can be used for the design of cold plate flow rate, angle, channels and battery spacing
- Thermal model of battery pack discharging with applied temperature non uniformity in pack.
- To identify and quantify the locations of highest heat generation using IR imaging techniques

Chapter 2 Background and Literature Review

2.1. Fundamental Background and Theory

Lithium ion batteries play an essential role in the adoption of the electric vehicle into society. The battery is sensitive to temperature and sub-optimum temperatures can lead to degradation and thermal runaway. A light, safe, efficient thermal management system helps increase mileage, speed, safety and longevity of the vehicle.

The effect of temperature on the open circuit voltage can be predicted theoretically by the Nernst Equation, which is the foundation of electrochemistry.

$$\Delta G = -nFE = -RT \ln \left(\frac{K}{Q} \right) = \sum \mu dN + VdP + SdT = \Delta H - T\Delta S \quad (1)$$

Spontaneous reactions occur for negative Gibbs free energies and positive cell potential values. The equilibrium constant is a function of Temperature while the reaction coefficient and chemical potential are functions of temperature, concentration and pressure to name a few, other factors such as the electric and magnetic field also affect the chemical potential, this is commonly seen in the process of electrolysis. We note that the differentials dP , dN and dT are dependent on one another and that mathematically integrating these terms typically requires the use of cross factors (without any other means to cancel/decouple terms). We of course also know the chemical potential is also related to the activity/effective concentration as:

$$\mu_i = \mu_0 + RT \ln(a_i) \quad (2)$$

This explains why the natural logarithm of concentration is often found to be proportional to energy equations such as volta, Nernst and collision theory. The Nernst Equation is typically reproduced in various forms as Latimer, Pourbaix and Frost Diagrams which make various assumptions on the equation see Figure 7.

One of the most commonly discussed external factors that affect the Gibbs Free Energy is the solvent effect. This effect can be modeled simply using the atomic radius and the materials dielectric constant using Born Equation which takes into account electrostatic effects.

$$\Delta G = \frac{N_A(ze)^2}{8\pi\epsilon_0 r_0} \left(1 - \frac{1}{\epsilon_r}\right) \quad (3)$$

This plays an especially important role in electrochemistry as electrolysis involves the formation of ions which are only soluble in polar solvents (polar solvents have a high dielectric constant). Figure 1 shows the Coordination number and atomic radii.

In addition to the solvent polarity/dielectric constant one must also consider the initial state of the solute which is determined by bond strength and coordination number which is related to relative radii sizes below:

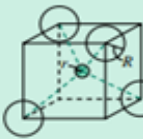
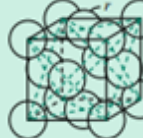
Coordination Number	Critical $\left(\frac{r}{R}\right)$ Value	$\left(\frac{r}{R}\right)$ Stability range	Geometry
2	0	$0 < \left(\frac{r}{R}\right) < 0.155$	Linear
3	0.155	$0.155 < \left(\frac{r}{R}\right) < 0.225$	
4	0.225	$0.225 < \left(\frac{r}{R}\right) < 0.414$	
6	0.414	$0.414 < \left(\frac{r}{R}\right) < 0.732$	
8	0.732	$0.732 < \left(\frac{r}{R}\right) < 1$	
12	1	$\left(\frac{r}{R}\right) = 1$	

Figure 1: Coordination number and atomic radii following Pauling's Rules [9]

We note the 3 bond types being Metallic, covalent and ionic based on the electronegativities and the difference in electronegativities of the atoms involved. Metallic bonds being between electropositive atoms with at least 3 valence (outer) electrons, covalent bonds being between electronegative atoms with at least 4 valence (outer) electrons and ionic bonds being between atoms where ΔEN is high.

Furthermore, the Born equation takes into account electrostatic interactions (permanent dipole dipole) neglecting transient interactions such as those through Van Der Waals and London dispersion. The dielectric constant can be related to both the macroscopic refractive index and the polarizability of a molecule through the Clausius–Mossotti relation and the Lorentz-Lorenz equation:

$$\frac{n_{ref}^2 - 1}{n_{ref}^2 + 2} = \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha_{pol}}{3\epsilon_0} \quad (4)$$

Where the refractive index squared (n_{ref}^2) is the constant of relative permittivity. The polarizability (α_{pol}) can further be related to the transient induced dipole and the local electric field

$$P = \alpha_{pol} E \quad (5)$$

The polarizability often affects precipitation with the atomic radii and ionic charge being the prime considerations of precipitate formation. Figure 2 below illustrates induced dipole interaction:

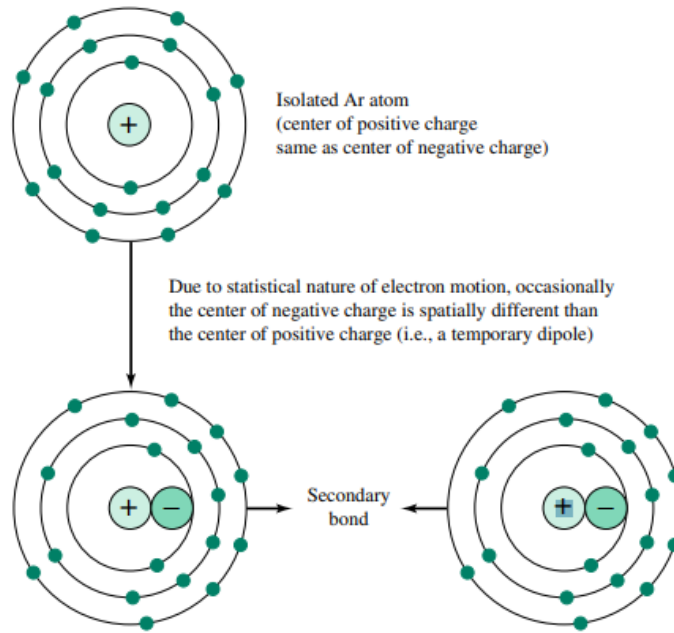


Figure 2: Polarization and induced dipoles illustrating the positive and negative centers effect on polarity and polarizability [10,11]

These intermolecular interactions (known as secondary bonds) can influence properties such as the melting point and Young's modulus when and if the primary bonds don't form a 3D network

(for coordination numbers less than or equal to 4). They are also important in chemical reactions as these intermolecular attractive forces lead to bond formation between the atoms of opposite charge. Mechanistically, electron rich atoms donate to electron poor atoms and form a transition complex, next the neighboring electropositive atom donates to the electronegative atom in the transition complex and breaks the old bond. A schematic for mechanisms is presented in the Figure 3 below:

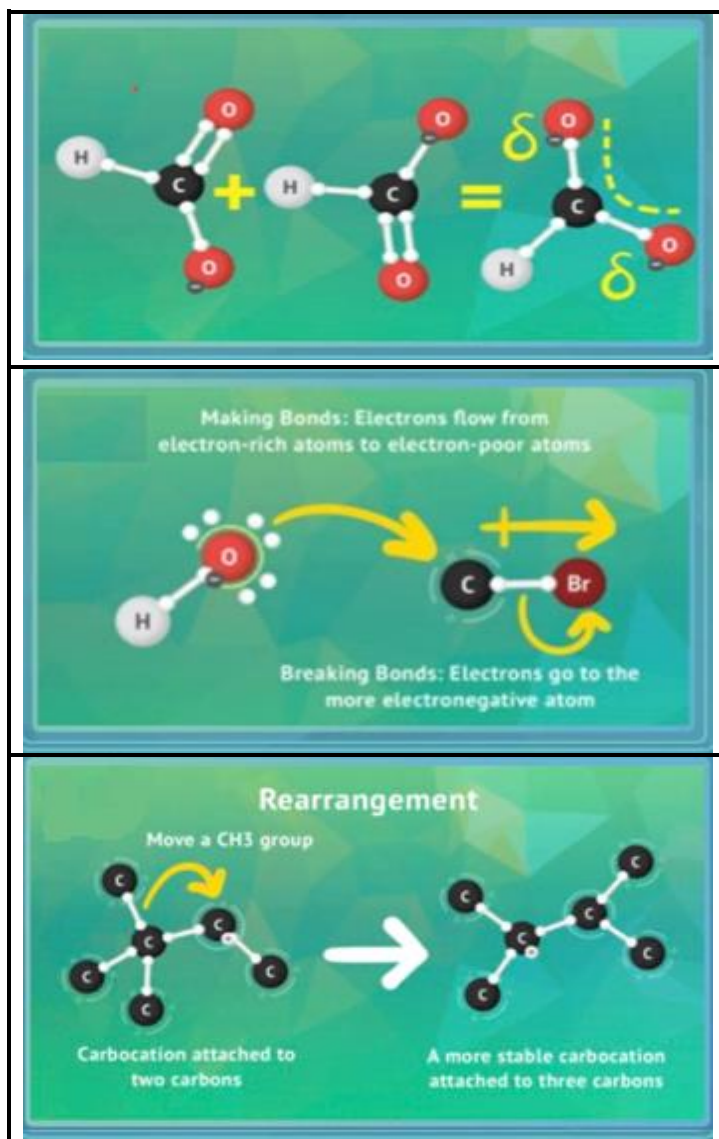


Figure 3: Chemical mechanism basic method based simply on lewis diagrams, oxidation states, electronegativity and resonance structure stabilization

We note the particularly important step of electron rich atoms donating to electron poor atoms. Bonds are formed along dipole-dipole interactions and induced dipoles. Electron rich atoms can

be identified by hand using oxidation states (and formal charges). Frost Diagrams can be used to determine stable oxidation states (stable oxidation states have half filled and fully filled orbitals with even number of valence electrons).

The entropy is proportional to the number of microstates of the system and is commonly appropriated to the change of moles when there is no change of state, if a gas is produced then the entropy is assumed to be positive. From the definition of Gibbs and the multivariable chain rule the entropy is seen to be:

$$S = -nF \frac{\delta E_{OCV}}{\delta T} \quad (6)$$

With the entropy of reaction typically expressed as a function of temperature as so:

$$S = R \left(a - \frac{C}{T^2} \right) \quad (7)$$

For gases the enthalpy is the difference in energy between bonds broken and bonds formed. Bond strength is proportional to bond length and number of bonds which increases as difference in electronegativities between bonded atoms increases. The enthalpy of reaction is commonly expressed as:

$$\Delta H_{Rxn} = \int C_p dT + \int V(1 - \alpha_{th}T) dP = -R \left(b + \frac{2c}{T} \right) \quad (8)$$

The multivariable chain rule can be used to deduce further relations with partial derivatives.

We note α is the coefficient of thermal expansion

$$\alpha_{th} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (9)$$

We note that the coefficient of thermal expansion can also be related to the bond energy. The Morse potential is one of the simplest equations used to determine the bond strength between two atoms, calculate bond length, vibrational energy of the bond and frequency of the bonds vibration (to rudimentally approximate IR Spectra) as shown in Figure 4.

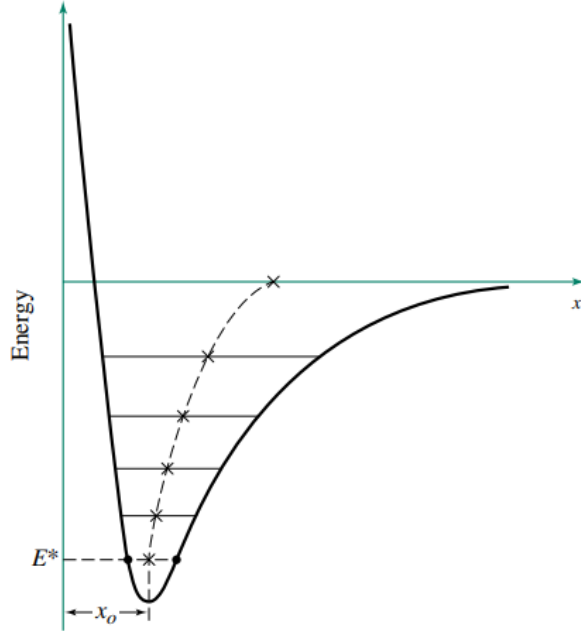


Figure 4: Bond Energy Curve and average bond length [12]

The bond length can then be related to the coefficient of thermal expansion in the equation below:

$$\frac{x_e - x_0}{x_0} = \alpha_{th}(T - T_0) \quad (10)$$

We also note a second macroscopic property to the bond energy. The curvature of the bond energy curve at the equilibrium length x_0 is proportional to the Young's modulus through a Geometric shape factor:

$$\frac{\partial^2 U}{\partial x^2} = aE \quad (11)$$

This equation holds strong for materials with coordination numbers >4 where primary bonds determine the 3D network as opposed to secondary intermolecular interactions.

The energy input into the system including pressure, temperature, electric field lead to increases in molecular energy levels seen in the bond energy curve. The 4 energies input is partitioned into are the translational, rotational, vibrational and electronic energy bands. Each has its own partition function and it is typically assumed (equipartition theorem) that the energy is shared equally between them (but this is frequently invalid). We note that the vibrational partition function contains a term for the electromagnetic frequency.

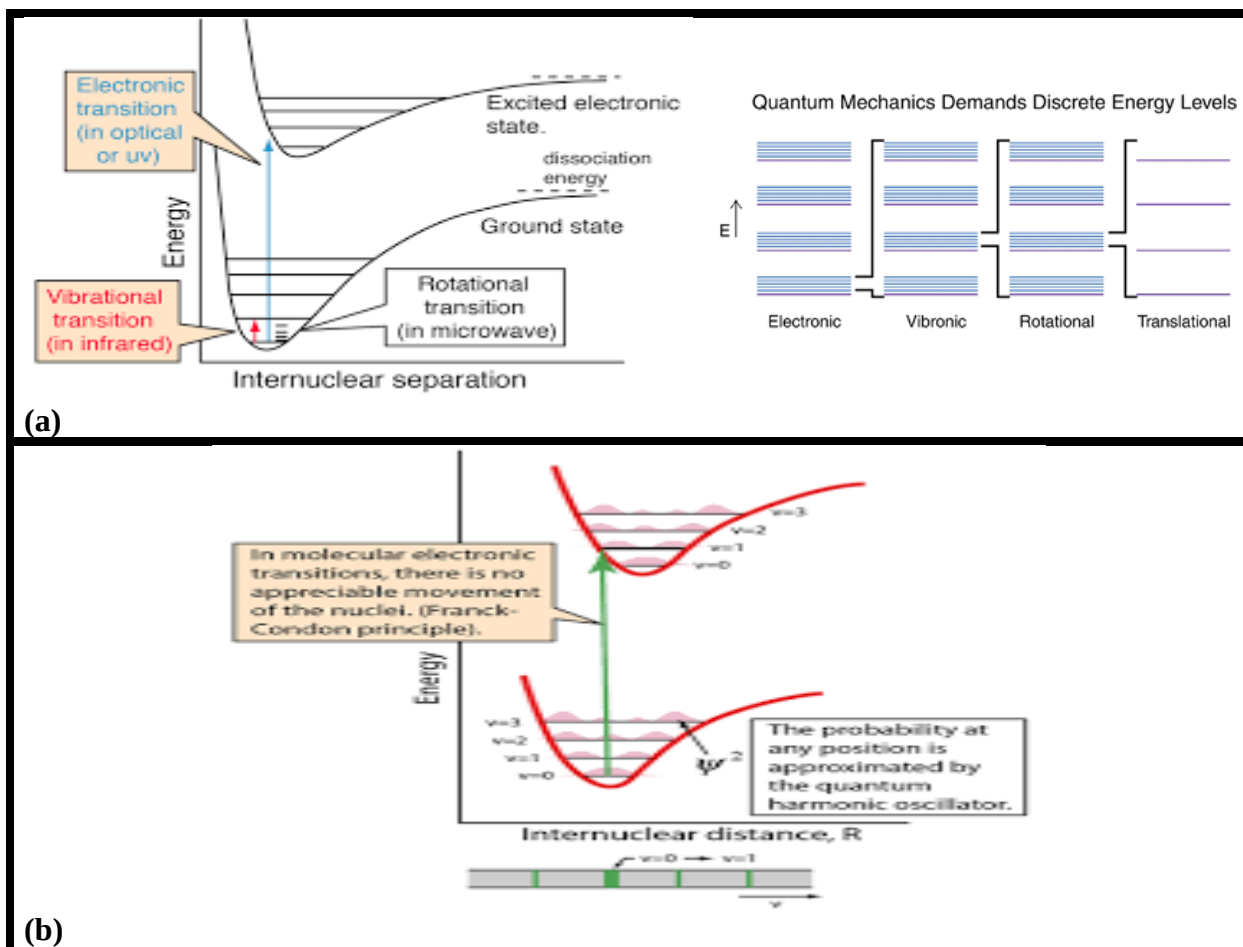


Figure 5: (a) Discrete Energy jump quantification for Electronic, Vibrational, Rotational and Translational energy levels in order (b) Franck Condon Principle illustrating nuclei are too heavy to move during electronic transition and can result in unequal energy level photon emission vs absorption when jumping back down (Anti-Stokes) [13]

Figure 5 shows that the translational energy level jumps are the smallest and can be taken as a continuous function of $3/2RT$ or discretized using Einstein Coefficients if necessary. For reactions that involve no phase change, the entropy can be estimated as the change in the number of moles between products and reactants where the predominant number of microsystem energy states is from the translational energy.

The Equilibrium constant is related to the enthalpy and entropy through a modified Gibbs equation:

$$\ln(K_{eq}) = \frac{-\Delta H_{Rxn}^{\ominus}}{RT} + \frac{-\Delta S_{Rxn}^{\ominus}}{R} = a + \frac{b}{T} + \frac{c}{T^2} \quad (12)$$

Or similarly the Vant Hoff Equation:

$$\frac{d}{dT} \ln(K_{eq}) = \frac{-\Delta H_{Rxn}^{\ominus}}{RT^2} \quad (13)$$

Electrochemical kinetics have to account for the effect of applied voltage, electrode surface area and diffusion coefficients along with temperature and concentration like regular chemical reactions. Typical chemical reaction rates are modeled as shown below:

$$v = \frac{dc}{dt} = k \prod_i c_i^m \quad (14)$$

Where the reaction rate constant is typically modeled using the Arrhenius, Modified Arrhenius or Eyring equation as:

$$k = Ae^{\frac{-E_a}{RT}} = AT^n e^{\frac{-E_a}{RT}} = \frac{\kappa k_b T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}} \quad (15)$$

Where the activation energy is the energy of the transition state and related to the strength of the bonds that need to be broken for the particular reaction seen in Figure 6.

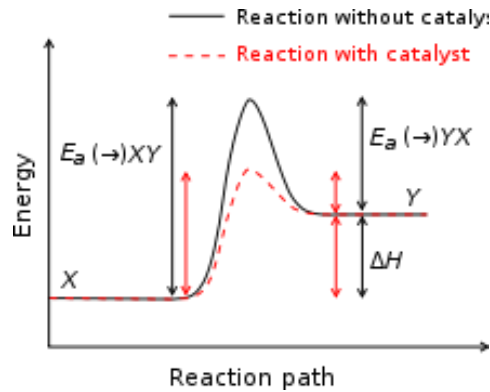


Figure 6: Effect of catalyst on Activation Energy and Transition State [14]

We see the reaction rate is dependent on the concentration, temperature, absorption of light, chemical composition, physical state, area of solid, presence of catalyst with pressure having an effect on gas phase reactions and very high pressures on condensed phase reactions(as they are not compressible and have less affect on the activity/effective concentration).

The effect of reactions occurring in a battery setup is catalytic in nature and is kinetically commonly expressed using Butler-Volmer or Modified Butler Volmer Kinetics:

$$j = j_0 \left\{ e^{\left[\frac{\alpha_a z F}{RT} (E - E_{OCV}) \right]} - e^{\left[\frac{-\alpha_c z F}{RT} (E - E_{OCV}) \right]} \right\} \quad (16)$$

With j_0 the exchange current density commonly expressed as a function of concentration. Figure 7 shows an example of a Pourbaix diagram.

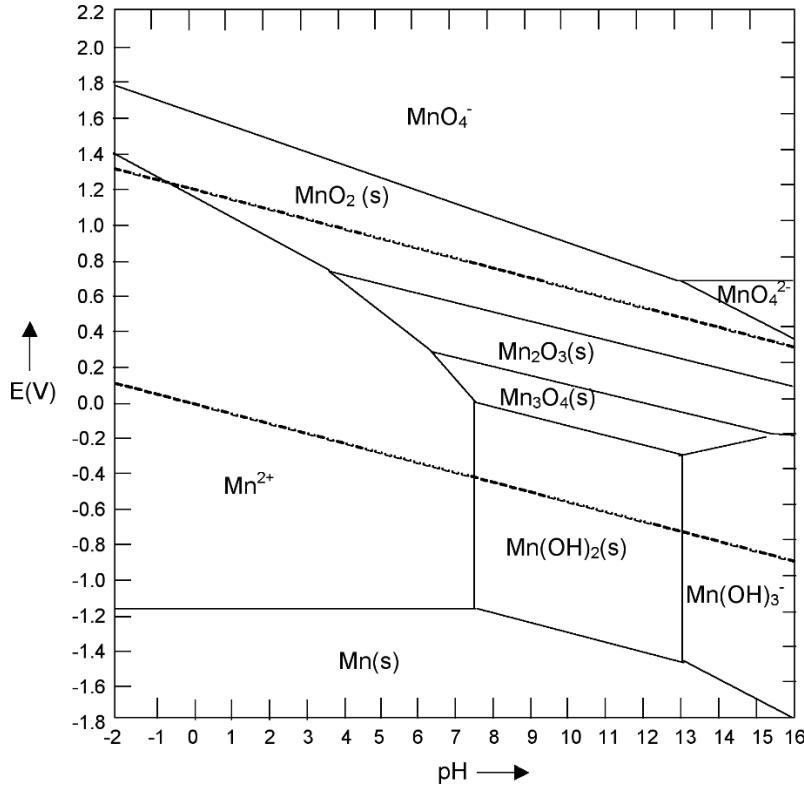


Figure 7: Pourbaix Diagram of Manganese Compounds [15]

Pourbaix diagrams are typically used for aqueous systems and assume room temperature, atmospheric pressure and molar concentrations of 10^{-6} M or 1 M to fully define the Nernst equation as a function of the pH. As such one can expect horizontal lines to mean that H^+ is neither a reactant or product in the reaction. Vertical lines occur when no electrons are exchanged between the neighboring compounds and the equilibrium is not influenced by cell potential. We note that oxidizing species are at the top of the diagram and reducing species are at the bottom, the cell potential at the specified conditions of the reduction reaction of the compound on top to the compound beneath the boundary at a given pH can be read off the y axis. Intermediate compounds whose areas are not found at the required pH disproportionate into the elements at the boundary of the intermediate. For example, at pHs below 12.5 MnO_4^{2-} disproportionates into MnO_4^- and MnO_2

with of course the charges of the reaction being balanced. If the bottom edge of a compound on the top and the top edge of a compound on the bottom are present we can calculate the cell potential of the spontaneous reaction to create compounds in the middle of both and the decomposition potential if the opposite reaction occurs. The diagrams also typically contain a dashed electrochemical window of the solvent (water). One can see that permanganate ion does in fact thermodynamically oxidize water even at these low concentrations and manganese metal reduces the solvent. A typical Frost Diagram is presented in Figure 8 below.

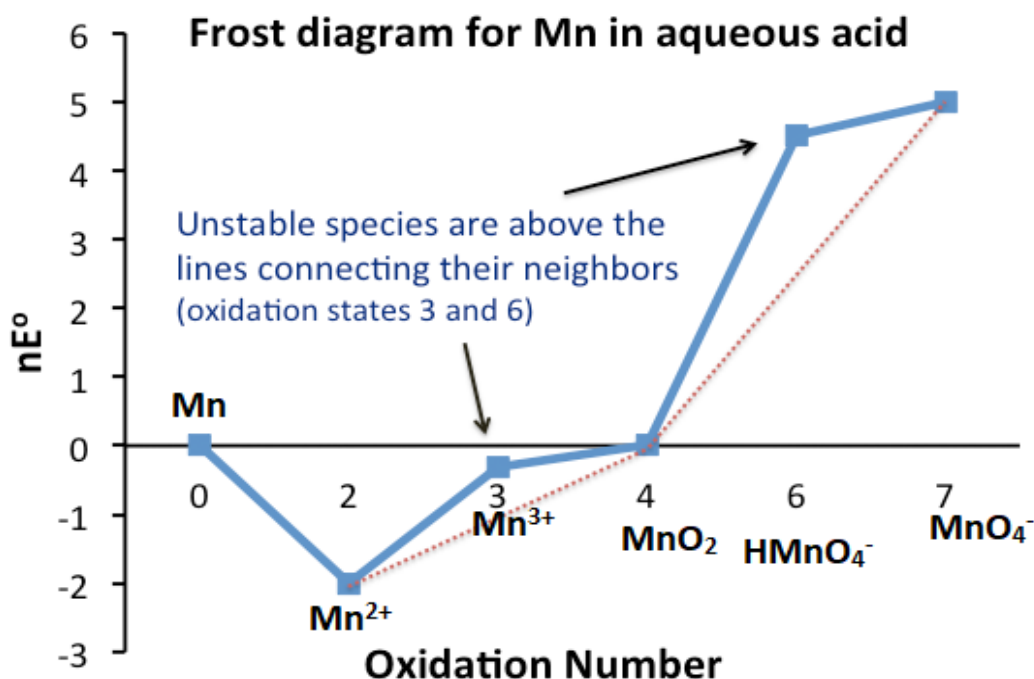


Figure 8: Frost Diagram of Manganese Compounds

The left axis is the standard Gibbs Free Energy divided by Faraday's constant, it is negative the standard cell potential multiplied by the number of electrons while the x axis is simply the oxidation state of the compound. Compounds low on the graph are more stable than those higher up. We note that for intermediate compounds, compounds in valleys are stable (such as Mn^{2+}) while compounds on hills or compounds that are above tie lines joining two points are unstable (such as Mn^{3+} , $HMnO_4^-$ disproportionate). The slope of the line connecting the oxidation states is simply the standard cell potential of reaction. Fermi Energy equation can be used to calculate the energy of the electron at various oxidation states along with Slater Rules (which considers the effect of shielding from shells and hybridization).

The 5 major thermal management systems in electric vehicles are air cooling, liquid cooling, phase change materials, heat pipes and thermoelectric devices. Air cooling and liquid cooling are commercially available methods of cooling while phase change materials and heat pipes are rising areas of research that show great potential. Thermoelectric devices are an advanced technology but have a high energy requirement. Thermoelectric devices are an advanced technology but have a high energy requirement. Passive cooling systems such as Phase change materials (PCM) and heat pipes allow for decreased energy usage increasing vehicle range and as such need to be investigated as thermal management solutions in electric vehicles. PCMs can be classified as eutectic, organic (paraffin and non-paraffin) and inorganic (salt hydrates and metallics). They typically have low conductivity thus a major field of research in PCM's is thermal conductivity enhancement. Thermal conductivity enhancement can be achieved through adding high conductivity elements such as metal fins, metal foams, porous media and using a combination of different PCM's. Hybrid PCM liquid cooling and PCM heat pipe systems show promise and are an area of investigation for this project.

Currently there are only 2 battery management systems widely available: air cooling and liquid cooling. Studies have shown the inadequacy of air cooling for EV's and series HEV's, they also find that air is not the best heat transfer fluid to maintain temperature uniformity for lithium-ion battery packs which have an intrinsic safety risk and is more common for NiMH batteries. Liquid cooling is observed to be a better solution as it is smaller, lighter and has a higher heat capacity and thermal conductivity.

PCMs, heat pipes and thermoelectric devices are all developing areas of research in BTMS. Both heat pipes and PCMs are passive methods that do not require power from the battery. The direct cooling of heat pipes is also an area of research investigation currently in the field.

Lithium-ion batteries are sensitive to temperature, and sub-optimum temperatures can lead to degradation and thermal runaway. At temperatures above 80°C, the solid electrolyte interface (SEI) layer begins to break down [16]. With the protective SEI layer broken, the lithiated carbon can now react and reduce the electrolyte; this is an exothermic reaction that occurs at temperatures around 100°C with the reaction peaking at 200°C [16,17]. At temperatures above 110°C, the electrolyte begins to breakdown, and at temperatures above 135°C, the separator melts [18]. The electrolyte evaporates at 140°C and the vapors of the typical organic electrolyte readily combust

in the presence of oxygen [17]. Since oxygen is released from the decomposition of the cathode at high temperatures (200-230°C), it is unsafe and the temperatures of the lithium-ion batteries must be controlled [16]. Thus, we can see that the maximum temperature of the battery pack must be controlled. Thermal runaway is a major concern for lithium-ion batteries. Elevated temperatures in batteries can trigger exothermic reactions which lead to a further increase in temperature and more deleterious reactions. Studies show the onset of thermal runaway varies with the state of charge (SOC). For LiCo₂ batteries, we see the onset of thermal runaway at 144°C for 2.8 V, at 109°C for 3.0 V, and at 104°C for 4.06 V [17].

During charging, low temperatures can lead to lithium plating which also typically occurs when charging at C-rates higher than 2C depending on the SOC and temperature [19]. When the anode potential is negative versus lithium (Li), lithium plating can occur as it is not the thermodynamically favored reaction. In Waldman et al. [20], the ageing behavior of NMC/MnO₂ blend cathode with graphite anode was tested in the range of -20°C to 70°C. It was found that the ageing rate is at a minimum at 25°C and that above 25°C, the predominant ageing mechanism was cathode degeneration including Mn dissolution and SEI layer growth at the anode. While at temperatures below 25°C, the major cause of ageing is lithium plating and the anode also suffers from low anode potential. It was found that both graphite and amorphous carbon anodes are negatively polarized with respect to Li/Li⁺ at temperatures from 20°C to -10°C, which leads to lithium plating. The ageing mechanisms for high and low temperature ranges were found not only through an Arrhenius plot but also through Post-Mortem analysis.

Temperature gradients within the cell and the pack must be minimized. In the case of a cell, a temperature gradient leads to uneven activity in the cell, which can lead to a non-uniform current density leading some sections to work harder than others causing degradation. Parasitic side reactions are also observed to increase at high temperatures leading to lower Faradic efficiency and shortening cycle life. A light, safe, efficient thermal management system helps increase mileage, speed, safety, and longevity of the vehicle. The battery is monitored both electrically and thermally using a battery management system (BMS) which ensures high performance and safe operation [21]. Through the accurate prediction of voltage, SOC, and temperature from mathematical models, the BMS and BTMS can work to prevent cell degradation, thermal runaway, and increase charging speeds.

A major component of the heat produced in batteries comes from the energy losses within the battery, with the three major energy losses being: 1) Ohmic losses; 2) activation loss due to sluggish electrochemical reactions; and 3) concentration/mass transport loss [16]. Other energy losses include parasitic side reactions which may produce a small amount of heat from the reaction (this is typically considered only at very high C-rates) and internal short circuit. The actual electrochemical cell reaction also produces a small amount of heat not accounted for by the energy losses and is known as the reversible heat or heat of reaction in battery thermal modeling. The energy losses mentioned are directly responsible for the overpotential which is the major contributor to the heat. Thus, the heat can be accurately predicted from good estimates of the open circuit voltage (OCV) and the cell voltage, or simply the overpotential. In Figure 9 we can see how each of the overpotential losses are related to the current.

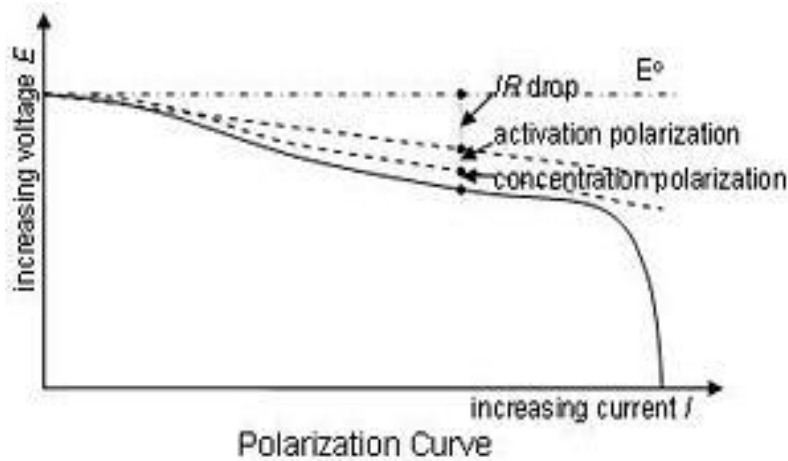


Figure 9: Overpotential as a function of current [22]

Ohmic losses are predicted by Ohms Law while the activation loss can be modeled by Butler Volmer equation. Mass transport losses are predicted through the Nernst Planck equation shown in Derivation 4. The limiting current density can be estimated as:

$$j_{limiting} = \frac{zFD_{eff}c^*}{\delta} \quad (17)$$

c^* is the concentration of the active species in the bulk electrolyte and δ is the diffusion layer thickness. The limiting current is seen to decrease with diffusion layer thickness and increase with effective diffusion coefficient and bulk concentration. We must not forget the surface area of the electrode plays an important role in the total current as seen in the Randles-Sevcik and Cottrell equations.

From our models the overpotential due to the mass transfer loss decreases with temperature while the overpotential due to the activation losses increase with temperature. This is due to the diffusion coefficient increasing in magnitude with respect to temperature in our models along with inverting the Butler-Volmer equation. The overall effect being a decrease in internal resistance with temperature.

Simplified thermal models typically include a joule heating/Ohmic heating term and an entropic effect/reversible heat term [16]. More sophisticated models include a reversible heat term that compensates for the heat from reaction and an irreversible heat term that includes Ohmic terms for both the solid and the electrolyte as well as mass transport losses and activation losses. Some models may even include the heat of mixing. At low discharge rates, the reversible heat term is the primary contributor to the total heat, but at high C-rates, the Ohmic heat terms dominate the total heat produced [16,23]. In Heubner et al. [23], heat generation in Lithium Cobalt Oxide (LCO) cathodes was investigated. Irreversible heat generation due to Ohmic resistance, charge transfer, and mass transfer losses were investigated along with the reversible heat. Irreversible heat generation due to ohmic resistance, charge transfer and mass transfer losses are investigated along with the reversible heat. These heat generation terms are determined from electrochemical measurements and are modeled as functions of the C-rate, temperature and lithium concentration in the active material. The C-rate is varied from -1C to 1C, the temperature is controlled between 10-30°C. It is found that the reversible heat is negative (endothermic) during charging and positive (exothermic) during discharging, though the total heat is typically always positive. The reversible heat contribution to the total heat was most significant at high temperatures and low C-rates. Among the irreversible heat terms, the mass transport loss term is the greatest contributor to the total heat. Total heat is observed to increase at low temperatures and high C-rates and is larger for discharging than it is for charging. The C-rate dependence and temperature dependence are shown in Table 1.

Table 1: Heat generation as a function of current and Temperature showing heat generation terms dependence on current (I) and temperature (T). The reversible heat ($\dot{q}_{rev}$), charge transfer resistance heat ($\dot{q}_{ct}$), mass transport loss heat ($\dot{q}_D$) and ohmic heat ($\dot{q}_\Omega$) are shown. E_A is the activation energy of the dominating diffusion process, R is the Universal gas constant. [23]

Approximate C-rate and temperature dependence of the individual contributions to the total

heat generation rate			
Heat Generation	f(I)	f(T)	f(T)/%K
q_{rev}	$\sim I$	$\sim T$	+0.35
q_{ct}	$\sim I^{1.2}$	$\sim \exp(E_A/RT)$	-6.4
q_D	$\sim I^{1.3}$	$\sim \exp(E_A/RT)$	-4.3
q_Ω	$\sim I^2$	$\sim T \exp(E_A/RT)$	-3.1

We observe that the reversible heat is a linear function of the temperature as predicted from thermodynamics and the Bernardi heat equation [24]:

$$Q_{rev} = IT \frac{\partial E_{OCV}}{\partial T} \quad (18)$$

This is derived from the Nernst equation and the multivariable chain rule seen in Derivation 1. We note other than the reversible heat all the other energy loss terms are inversely related to the temperature in the table. The Butler Volmer relation shows a decrease in reaction rate with an increase in temperature which is the reverse compared to the Arrhenius equation. Parasitic side reactions within the battery increase in rate with increases in temperature while still being dependent on the overpotential even though it is in fact present during charging. The Randles-Sevcik and Cottrell equation are typically used to model full redox events such as electrolyte oxidation and reduction and have the peak current being linearly dependent on the concentration of the analyte, the surface area and the square root of the diffusion coefficient over the temperature. We see in Table 1 that the ohmic heat is proportional to the square of current and $T \exp(E_A/RT)$. We know for a typical the ohmic resistance power is the square of current multiplied by the internal resistance. The ohmic heat is seen to decrease with temperature; for metals we typically observe a linearly proportional increase of resistance with temperature while for semiconductors this is the reverse as thermal energy allows for electrons to transfer into the conduction band. The mass transport heat loss is a function of the current and temperature dictated by Nernst Planck's law of diffusion. The result is that the energy loss goes down with temperature as the diffusion coefficient increases with an increase in temperature. The charge transfer heat loss is seen to also decrease with an increase in temperature. This is expected as the efficiency of reaction predicted by the Butler-Volmer equation increases with temperature and thus the heat produced should decrease. Battery degradation can be divided into four different stages as seen in the Figure 10:

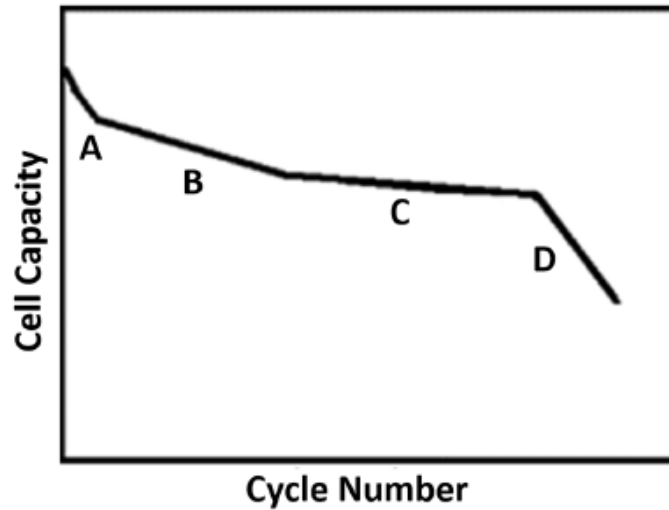


Figure 10: Battery Degradation split into its 4 principal stages [25]

Stage A

Stage A leads to a sharp decline in capacity but occurs for a short time period. During this phase a thin film known as the solid electrolyte interphase (SEI) forms on the anode during the first few charge cycles. This thin film formation leads to the loss of active lithium material. Unlike what is typical found for battery degradation in this stage it is observed that capacity loss is higher at low C rates than at high C rates due to the availability of lithium-ions [1].

Stage B

In this stage the anode is still the limiting electrode as the SEI layer leads to a loss of active material. Volume expansion during intercalation and deintercalation (Intercalation alludes a reversible chemical process of binding a molecule between other molecules. Deintercalation is the opposite process, causing the cathode to become more positive) leads to stresses in the electrode that cause cracks to develop in the SEI layer. These cracks expose the anode to fresh electrolyte which leads to the development of new SEI layer, leading to the growth of a less porous SEI film. This thickening SEI layer increases cell resistance and decreases lithium/electrolyte conductivity.

Stage C

In stage C the rate of degradation of active cathode material is higher than the loss of lithium. Like the previous stage the capacity loss is gradual and over a long period of time. We note that the lithium loss still plays the dominant role of capacity loss but the rate of degradation of the cathode

is higher. It is in this stage that a solid permeable interphase (SPI) layer forms on the cathode also leading to increased cell resistance and lowered lithium/electrolyte conductivity.

Stage D

During this stage the active cathode material is the limiting electrode. This means that the amount of active lithium is larger than what the cathode material can support and not all the lithium intercalated in the anode can be intercalated into the cathode during discharge. The state of charge of the cathode is continuously brought to its maximum leading to even faster degradation as characterized by the sharp capacity loss in this phase [1].

Different cell chemistries have different rates of degradation during these 4 stages. NCA, LFP and LTO show the largest cycle lives. The degradation of lithium iron phosphate is mainly due to SEI formation and loss of active anode material, the formation of the SPI layer is slow leading to a much larger cycle life.

Lithium-ion batteries capacity and cycle life are strongly affected by temperature. At low temperatures the predominant degradation mechanism is lithium plating while at high temperatures cathode dissolution and SEI growth is observed. It is noted that in the range of 30-40°C every degree rise in temperature leads to a 2-month reduction in cell life. The acceptable temperature gradient in a pack is estimated to be 5°C. There is enough evidence to suggest that to minimize ageing effect the lithium-ion battery should be kept between 25-30°C while standard operating temperatures range from 25-40°C. Consequently, the use of an effective thermal management system is necessary to ensure safety and minimize battery degradation. Growth of the SEI film also promotes lithium plating as lithium-ions can no longer intercalate quickly and the cell potential of the graphite vs. Lithium is negative.

The electrolyte must be chosen so that it is within the stability window shown in Figure 11. We can see the LUMO (Lowest Unoccupied Molecular Orbital) is related to the reduction potential while the HOMO (Highest Occupied Molecular Orbital) is related to the oxidation potential. When the SOC of the battery increases the cell potential widens and the anode potential becomes more negative while the cathode potential becomes more positive with the difference between the 2 being the cell potential. This increases the chance of the electrolyte being oxidized or reduced at either electrode.

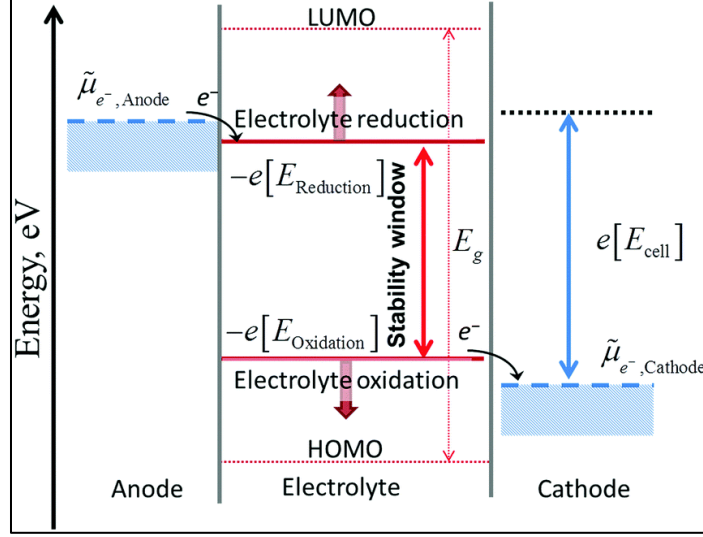


Figure 11: Electrolyte Decomposition [26]

We see that the HOMO and LUMO are related to the electrolyte reduction and oxidation stability window. The stability window is affected by intermolecular forces through the solvent and concentration and can cause the window to change.

Additional degradation mechanisms occur when the cell is operated outside its normal operating conditions. The primary constraints being both a lower and upper limits for both temperature and voltage and an upper limit for current. When operated within defined operating conditions we expect calendar degradation rates measured in years but if the temperature and voltage are both high this is no longer the case. The calendar degradation rate is observed to be a linear with the square root of time [27], models show that the mean square displacement for a diffusive process is equal to the diffusion coefficient multiplied by time. Parasitic side reactions that produce gassing are observed at high temperatures and at voltages beyond the set limits. At low SOCs gassing is observed and is produced from the decomposition of the SEI and SPI products on the electrodes along with dissolution of the current collectors.

Battery models typically fall into the following categories: 1) Neural networks 2) Equivalent circuit models (ECMs) 3) Physio-chemical methods or lumped parameter model (LPM). The circuit diagram for the 2 most common equivalent circuits used to model batteries are presented in Figure 12. The derivation for the 1RC model equation used is presented in Derivation 3.

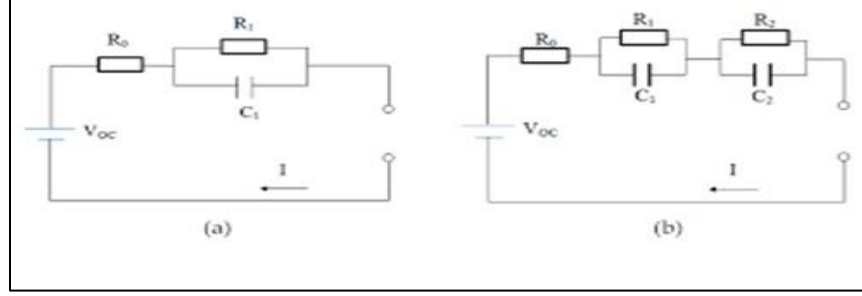


Figure 12: 1RC and 2RC Battery Equivalent Circuit Models [1]

The typical governing equations and boundary conditions for physiochemical models are presented in Table 2. They include conservation of mass and charge balances in the electrolyte and electrodes along with a modified Butler Volmer equation in which the exchange current density is a function of the lithium-ion concentration.

Table 2: Governing Equations for Physiochemical Models

	Equations	Boundary Conditions
Mass Balance, Solid	$\frac{\partial C_s}{\partial t} - \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_s}{\partial r} \right) = 0$	$D_s \left(\frac{\partial C_s}{\partial r} \right)_{r=0} = 0 \quad \text{and} \quad -D_s \left(\frac{\partial C_s}{\partial r} \right)_{r=r_p} = \frac{J_l}{a_v F}$
Mass Balance, Electrolyte	$\frac{\partial (\epsilon_e c_e) C_s}{\partial t} = \frac{\partial}{\partial x} \left(D_e^{eff} \frac{\partial C_e}{\partial x} \right) + \frac{1-t_+^0}{F} J_l$	$\left(\frac{\partial C_e}{\partial x} \right)_{x=0} = 0 \quad \text{and} \quad \left(\frac{\partial C_e}{\partial x} \right)_{x=L} = 0$
Charge, Solid	$\frac{\partial}{\partial x} \left(\sigma^{eff} \frac{\partial \phi_s}{\partial x} \right) = J_l$	$\begin{aligned} -\sigma_-^{eff} \left(\frac{\partial \phi_s}{\partial x} \right)_{x=0} &= \frac{I}{A} \\ +\sigma_+^{eff} \left(\frac{\partial \phi_s}{\partial x} \right)_{x=L} &= \frac{I}{A} \end{aligned}$
Charge, Electrolyte	$\frac{\partial}{\partial x} \left(k^{eff} \frac{\partial \phi_e}{\partial x} \right) + \frac{\partial}{\partial x} \left(k_D^{eff} \frac{\partial \ln c_e}{\partial x} \right) = -J_l$	$\left(\frac{\partial \phi_s}{\partial x} \right)_{x=l_n} = \left(\frac{\partial \phi_s}{\partial x} \right)_{x=l_n+l_s} = 0$ $\left(\frac{\partial \phi_e}{\partial x} \right)_{x=0} = \left(\frac{\partial \phi_e}{\partial x} \right)_{x=L} = 0$
Expressions	$j^{Li} = a_v i_0 \left\{ \exp \left[\frac{\alpha_a F}{R T} \eta \right] - \exp \left[\frac{\alpha_c F}{R T} \eta \right] \right\}$ $\eta = \phi_s - \phi_e - U$ $i_0 = k_m (C_e)^{\alpha_a} (C_{s,max} - C_{s,e})^{\alpha_a} (C_{s,e})^{\alpha_c}$ $\sigma_{l,eff} = \sigma_l \epsilon_e^\beta$ $a_v = 3 \frac{\epsilon_s}{r_p}$	

We note that temperature increases as C-rate increases; this is particularly important for electric vehicles undergoing fast charging. As vehicles fast charge at high C-rates, the temperature of the battery pack increases significantly. At these heightened temperatures, parasitic side reactions occur, which increases the degradation of the battery. An effective BTMS would allow for faster and safer charging.

Battery modeling provides information on battery discharging/charging and transient behavior as well as SOH status of the battery (battery degradation) as a function of different parameters (such as temperature and discharge rate). EV designers use battery models for sizing the required battery and to predict the battery performance. Battery models are also used for on-line self-learning performance and SOC estimation in BMS [28–30]. There are two basic types of modeling. 1) Electrochemical modeling and 2) equivalent circuit modeling.

2.2. Electrochemical Modeling

The partial differential equations used in electrochemical modeling are presented in Table 2. They consist of mass and charge balances in the electrolyte and electrodes with a source term determined by a modified Butler Volmer relation. The modified Butler Volmer relation relates the exchange current density to a function of the active species (Lithium) concentration in spherical particles, the electrolyte salt concentration, the charge transfer coefficients and the maximum intercalation concentration of the electrode material.

2.3. Equivalent Circuit Modeling (ECM)

Equivalent circuit models consist of modeling a battery as a circuit consisting of resistors and capacitors and sometimes other elements. The voltage source term in the model is typically a function of both temperature and SOC. Typical ECMs include the Rint model, 1RC Thevenin Model, 2 RC Model and 3RC model. The dynamic effects of battery charge and discharge can accurately be modeled using this technique, as typical for capacitors the current is seen to lead the voltage during the applied pulses with the size of the lag determined by the associated time constant for the resistance and capacitor in parallel. The impedance and energy storage within the double layer can be accounted for in RC modeling. In the 2 RC model the ohmic resistance is accurately modeled by the first resistor in series with the first RC pair which typically models activation losses. The first RC pair has a time constant in the range of seconds while the second RC pair

models concentration losses with a time constant in minutes. This allows us to account for both amplitude and duration of charge and discharge pulses. Equivalent circuit models are computationally efficient and can be used for real time applications such as BMS design.

Simpler models such as the R_{int} model and 1RC model group the ohmic, activation and concentration loss effects and this confounding does not allow for decomposition. R_{int} models, in fact, do not model energy storage dynamic behavior and are simply an immediate potential drop based upon current. In the following section, common ECMs used in PHEV applications are presented.

2.3.1 R_{int} model

The R_{int} model shown in Figure 13 is one of the simplest models. The model consists of an OCV (V_{oc}) power supply and a resistor (R_0). To account for different resistance values under discharging and charging to separate resistances may be used with diodes. The resistances result in an instantaneous voltage drop and overpotential as shown in Equation (19).

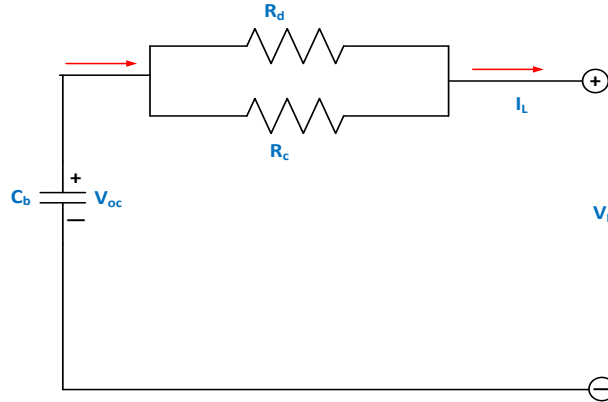


Figure 13: Circuit diagram of R_{int} model

$$V_L = V_{oc} - I_L R_0 \quad (19)$$

These two parameters model all forms of internal resistance, including internal ohmic and polarization resistances. As stated previously the OCV is a function of the temperature and the state of charge as shown in the Nernst Equation (1) while the internal resistances can be a function of SOC, Temperature, SOH and C Rate among other factors. I_L is the load current with a positive sign at discharging and a negative sign at charging. The battery terminal voltage (V_L) is represented

in Equation (19) as the OCV plus the voltage rise or drop across the resistor. As expected we see a voltage drop during discharge and a voltage increase during charge. The R_{int} model can be parameterized directly from the experimental data and is very efficient as there is no need to evaluate the differential equations. However, the model is unable to provide a simulation of transient or time-variant behaviour [31].

2.3.2 Thevenin model / 1RC model:

The Thevenin model connects a parallel RC pair in series to a R_{int} model, this allows us to capture the dynamic characteristics of the battery [31,32]. Figure 14 presents the circuit diagram for the 1RC model, it consists of three parts; an open-circuit voltage V_{oc} , internal resistances and equivalent capacitances. The internal resistances incorporate the ohmic resistance R_o and the polarization resistance R_{Th} . The equivalent capacitance C_{Th} is used to describe the transient response during both discharging and charging. V_{Th} represents the voltages across C_{Th} and R_{Th} the resistor in parallel. I_{Th} is the outflow current of C_{Th} . For pulses of large duration the capacitor reaches full charge and the resistances add in series. One of the simplest methods to predict the SOH of the battery is by measuring the capacitance of the Thevenin model. The derivation of the time series form for this model is presented in Derivation 3.

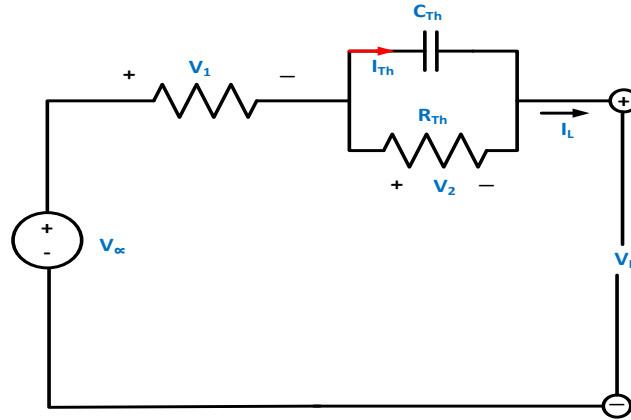


Figure 14: Circuit diagram of Thevenin model

(20)

$$V_{Th} = -\frac{V_{Th}}{R_{Th}C_{Th}} + \frac{I_L}{C_{Th}}$$

(21)

$$V_L = V_{oc} - V_{Th} - I_L R_o$$

2.3.3 2 RC Model:

Based on the test analysis of the characteristics of a lithium-ion power battery, an obvious polarization can be observed. The polarization characteristic could be simulated by the Thevenin model to some degree. However, the difference between the concentration polarization and electrochemical polarization leads to an inaccurate simulation for pulses of different time intervals and rest periods. The circuit diagram for this model is shown in Figure 15. The DP model is made out of three parts: (1) Open-circuit voltage V_{oc} ; (2) Internal resistances, such as the ohmic resistance R_o and the polarization resistances, which join R_{pa} to represent the effective resistance characterizing electrochemical polarization and R_{pc} to represent the effective resistance characterizing concentration polarization; and (3) The effective capacitances such as C_{pa} and C_{pc} , which are used to characterize the transient response during transfer of power to/from the battery and to depict the electrochemical polarization and the concentration polarization independently. V_{pa} and V_{pc} are the voltages across C_{pa} and C_{pc} respectively. I_{pa} and I_{pc} are the outflow currents of C_{pa} and C_{pc} respectively. The electrical behavior of the circuit can be represented by:

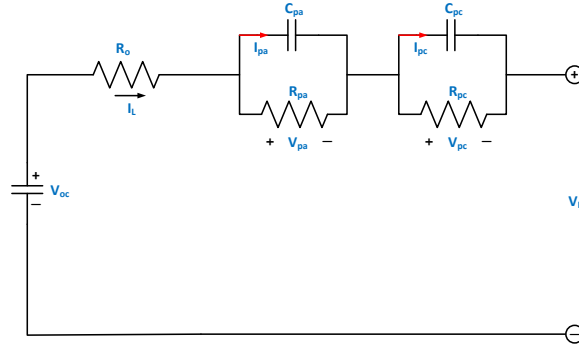


Figure 15: Circuit Diagram of DP model (modified from [1])

$$V_{pa} = -\frac{V_{pa}}{R_{pa}C_{pa}} + \frac{I_L}{C_{pa}} \quad (22)$$

$$V_{pc} = -\frac{V_{pc}}{R_{pc}C_{pc}} + \frac{I_L}{C_{pc}} \quad (23)$$

$$V_L = V_{oc} - V_{pa} - V_{pc} - I_L R_o \quad (24)$$

2.4. Battery Pack Theory

When linked in series, multi-batteries battery packs offer high voltage; while linked in parallel large capacity. Larger batteries carry greater current and when voltage is near to cut-off, current changes significantly [33]. Battery modeling is used to simulate and design battery packs of any capacity, quantity, and connections.

The BMS protects batteries against undervoltage/overvoltage, short-circuit and thermal runaway [34]. It monitors cell voltage, module current, temperature, SOC, and battery health (SOH). SOC operating limits are commonly set at 20-80% [35,36], and may be lower in certain demanding applications [37]. Lithium-based packs with BMS need different modelling methods.

SOH measurement is a commonly encountered issue in battery modeling. Measuring impedance is one experimental method that allows for immediate analyses Li-ion battery degeneration. The ideal frequency for EIS deterioration testing is 1 kHz since impedance at this frequency is connected to degrading battery capacity [38]. In addition to the BMS a thermal management system is often included to monitor the battery packs temperature. With regards to heat generation it is found that the Contact resistance affects thermal performance most [39]. The typical BTMS cold plate is aluminum with a liquid cooling to transfer cell heat to the liquid. Similar to pouch cell heat pipe cooling. Conduction elements separate cells from cooling liquid.

The busbar is another important element to battery packs. Bimetallic busbar joints and other Li-ion battery components must tolerate high voltages during charge and discharge. Busbars transfer high power to the vehicle's electric system. Due of its excellent electrical conductivity, Copper is commonly chosen for the busbar [40]. Aluminum alloys are becoming more popular since they're cheaper, lighter, and have superior electrical conductivity. We note in crash testing the busbar is commonly simulated. An accident may compromise busbar insulation, causing battery short circuits. The busbar is joined to the battery cells using several joining technologies. Ultrasonic welding, wire bonding, force fitting/mechanical assembly, soldering and brazing, laser and resistance spot welding are widespread commercial utilized joining technologies. Electrical and mechanical qualities, as well as manufacturing and operating requirements, must be considered when choosing a joining method. During electric vehicle operation, electrical and mechanical systems can face hazards that need to be considered and modeled.

2.4.1. Sizing

Multi-batteries battery packs provide high voltage when connected in series and high capacity when connected in parallel. Voltage, discharging capacity, and residual capacity of the pack and individual battery at each time unit can be calculated using simulation at a given discharge current. When one of the batteries in a series connection has a significantly lower capacity than the others, this battery discharges faster than the others [33]. The simulated current distribution of a battery pack consisting of two different-capacity batteries discharged in parallel demonstrates that, while the pack is discharged at constant current, current through each battery is neither constant nor proportional to its capacity. A larger capacity battery can carry more current. Near the end of the discharge process, when voltage is close to the cut-off value, a significant change in current is observed [33]. This simulation method can be extended to a battery pack of multiple batteries of any capacity, number, and connections.

Fouchard and Taylor [41] investigated the discharge characteristics of MOLICEL batteries in series and parallel. They believed that by connecting batteries in series, they could achieve better performance and a lower price despite the volumetric limitations of a battery pack. If a high discharge current density or a longer discharge duration is required, batteries should be connected in parallel. Batteries with similar parameters (type, resistance, and capacity) are typically used in parallel battery packs [33].

In a series connection, all currents flow through each battery at the same rate; meaning the current is almost certainly a known parameter. Also note the total system voltage for parallel packs is the same as the voltage of each parallel branch. When one of the batteries in series has a significantly lower capacity than the other, it is very likely that it will overdischarge and supply no power during the discharge process; however, this assumption cannot be derived solely from the overall system's voltage changes.

The simulated current distribution of a pack with parallel batteries demonstrates that, while the system is discharged at a constant current, current through each battery is neither constant nor proportional to their capacities; the currents change with respect to time and voltage changes. Individual current shared by batteries remains stable during the most stabilized plateau period of a discharge. However; near the end of the discharge, when the voltage approaches the cut-off value,

a significant change in current is observed. This has large consequences when considering CC-CV charging especially at high SOC's.

2.4.2. Modeling

In Tran et al. [42] a Battery pack is modeled through multiple cycles where not only voltage and SOC are simulated but the SOH of the cells is also modeled. They modeled cell replacement events to increase the total number of cycles for the battery packs, effectively extending the packs' lifespan. It has also been determined that this approach may be more cost effective than the current method of simple pack replacement. Individual cell monitoring and easy access to cells at the failure stage are two major design criteria that must be met for the cell replacement concept to be practical. Cell replacement is typically frowned upon and is handled by the OEM.

Batteries are protected from undervoltage/overvoltage, short-circuit (maximum current limit), and thermal runaway by the BMS [34]. It also measures cell voltage, module current, temperature, and estimate the state-of-charge (SOC) and state-of-health of the battery (SOH). In order to use the battery efficiently, the SOC operating limits are typically set to 20-80% [35,36], and may be even lower in some demanding applications [37].

The presence and operation of the BMS, packs based on lithium technologies require a different modelling approach than other technologies. Because no BMS is present, battery models for previous technologies that are still in use, such as nickel or lead, are solely based on the cell [43]. This practice has been extended to lithium technologies as well [44,45], ignoring the impact of BMS on battery operation. Some authors [46] have created simple electrical circuit models that include an ideal voltage source in series with a constant internal resistance. Because it does not provide information on the dynamic behavior of the battery, such a model can only be used at an early stage of battery sizing [46,47].

Some improved models have been proposed in order to account for other variables such as the state-of-charge (SOC) and electrochemical processes within the battery. However, all of these models are focused on the short-term dynamics of the battery and do not account for the operational limitations caused by BMS operation, as they assume that the battery behavior is the same from 0% to 100% SOC and do not account for the battery control restrictions present in practical applications. The short term dynamics will include transient diffusion and charge transfer

processes, whereas the long term will represent the internal voltage's long term dependence on the SOC.

Because of minor errors and deviations in their manufacturing processes, such as electrode fabrication, assembly, formation, and detection, cells have inherent inconsistency [48]. Even within the same batch of battery cells, variations in capacity, State of Charge (SOC), internal resistance, and self-discharge are unavoidable. The assembly process also causes variations in contact internal resistance. 2) In use, there is inconsistency in battery parameters. Variations in the initial parameters can result in differences in the current and temperature of each cell [49]. Temperatures in cells can vary due to their different positions and ventilation potentials [50,51]. Furthermore, the mechanisms of propagation are correlated and cross-dependent. For a long time, cells work in a complicated charge and discharge condition, so the un-uniform current, temperature, and Depth of Discharge (DOD) will exacerbate inconsistency in the initial parameters, accelerating ageing behavior. Capacity and internal resistance are two critical parameters in cell ageing. Due to cell production variability [49] the initial capacities of a batch of cells frequently fit a normal distribution [50], even after cells are matched and combined into a battery pack. In addition to the initial variation, their ageing rates vary with time and cycling, resulting in variations in inter-cell capacity. Internal resistance is divided into two components: ohmic resistance and polarisation resistance. The resistance of the positive and negative battery electrode materials, diaphragm materials, electrolytes, and other battery components determines ohmic resistance [52]. Errors in the uniformity of the positive and negative materials, electrolytes, and mixing during the manufacturing process can cause variations in ohmic resistance [53]. Polarization reactions within a battery pack cause polarisation resistance. SOC and Temperature may cause polarisation resistance variations because polarisation resistance is highly dependent on battery temperature and SOC [54]. The Self Discharge (SD) rate of a graphite sample is affected by particle size and specific surface area [55]. As a result, minor electrode errors may cause SD-rate variations. Uneven parallel current can cause OCV, which can result in overcharging, overdischarging, and other safety issues while cycling. Parallel connections can increase capacity while serial connections can increase voltage.

Under equal cumulative energy output, Liu Z. [56] simulated 1000 cycles of battery packs and discovered that the capacity fading rate of parallel-series was 20% higher than that of series-parallel (seen in Figure 16).

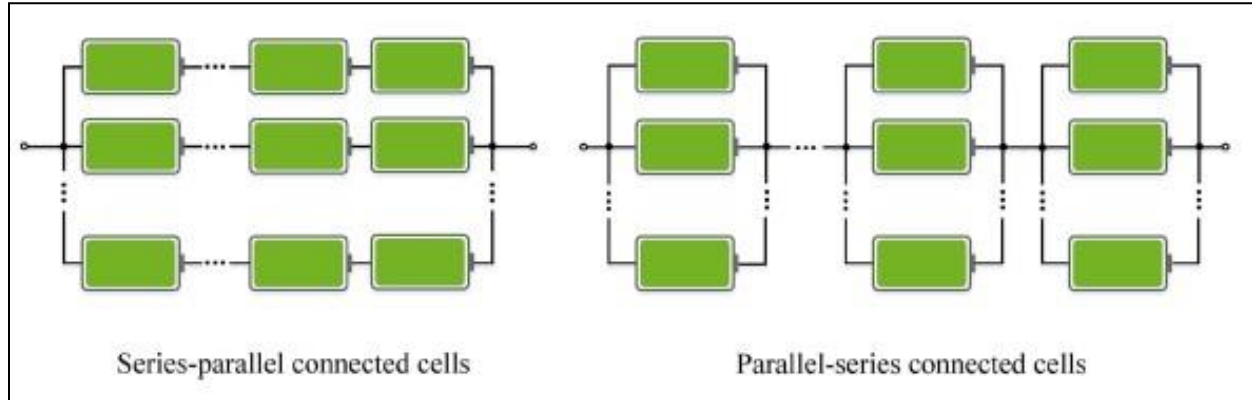


Figure 16: Series-Parallel and Parallel-Series Configurations

Parallel connection in series designs improve battery pack connection reliability. According to Liu [56], series-connection in parallel is appropriate for battery packs with a large number of cells because it improves SOC consistency at the end of discharging. Meanwhile, parallel-connection in series is appropriate for small battery packs because it provides more discharge energy. Uneven currents between parallel-connected cells are easily visible. Gong et al. [57] induced inconsistency mechanisms in parallel-connected cells with varying degradation levels: two cells with a maximum 20% degradation difference may operate at a current 40% higher than normal. used. Controlling temperature differences requires an effective thermal management system. A pack's consistency is acceptable if the temperature difference is kept between 3°C and 5°C. When the temperature difference exceeds 8 °C, the pack consistency deteriorates, resulting in an accelerated ageing rate. The battery shape, in addition to the battery cooling system, can influence the pack temperature distribution. Previous literature [58,59] primarily involves cylindrical, prismatic, elliptic, and pouch cells, with the cylindrical shape being commercially popular for the available small size batteries [59]. Each shape's thermal models and temperature distribution are quite different. Inui et al. created two- and three-dimensional simulation codes for cylindrical and prismatic Li-ion batteries. The outcome of battery thermal management may differ when different shapes are combined into a battery module and pack. Yang et al. [60] investigated the effects of longitudinal and transverse intervals on pack temperature uniformity by comparing the thermal performances of aligned and staggered cylindrical cell arrangements. Uneven temperatures can cause Self

Discharge rate, which in turn can cause capacity loss. Temperature is a major factor influencing internal resistance, and there is a strong negative relationship between temperature and the standard deviation of internal resistance. Polarization resistance decreases with increasing temperature, causing current variations in parallel or voltage variations in series. SOC and temperature have a greater impact on polarisation resistance than discharge rate. The more series-connected the cells are under the same cycling conditions, the shorter their cycling life and the worse their parameter inconsistency [44]. The greater the number of parallel-connected cells, the lower the current inconsistency, which is good for extending the cycling life of a battery [57]. The impact of internal resistance variation on the SOC decreases as the number of parallel cells increases [61]. Many studies [62] have found a self-balancing mechanism in parallel-connected cells that leads to parameter inconsistency convergence during cycling. At low temperatures (around 5 °C), the self-balancing mechanism is clearly visible [63], but it may be absent at high working temperatures.

2.4.3. Degradation Testing through Electroimpedance Spectroscopy

Capacity and impedance have a strong relationship [38]. This is applicable even when the pack includes not only a Li-ion battery but also a Positive Temperature Coefficient (PTC) device and a protection circuit connected in series, and the correlation is largely unaffected by the degree of charge. The results of measuring impedance revealed the possibility of assessing degradation in Li-ion battery packs quickly. Figure 17 shows a Cole–Cole plot of a fresh, fully charged Li-ion battery pack. Complex impedance data in the Cole–Cole plot was measured in a range from 100 mHz to 10 kHz. This kind of shape can be attained from the circuit diagram presented below:

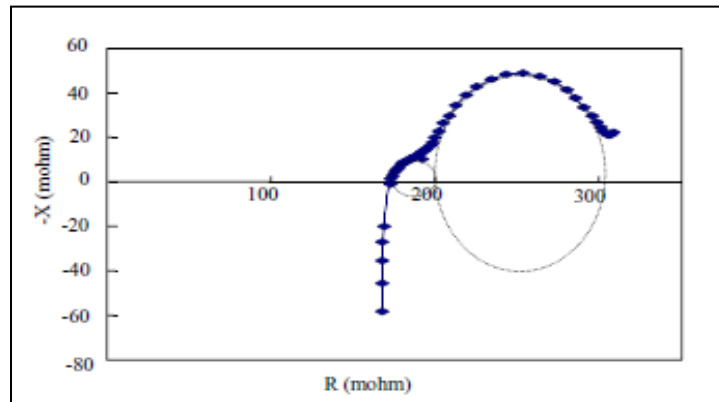


Figure 17: Cole-Cole Plot [38]

Figure 18 shows the simplified overall circuit diagram for a parallel Battery Pack where R_s denotes internal resistance, which is based on a liquid electrolyte, and $C1$, R_{p1} and $C2$, R_{p2} denote the respective reaction resistance and capacitance components on both electrode-electrolyte interfaces and the collector portion [38]. $R1$ is the sum of the on-resistance in two-serial FETs and the resistance of a PTC, and $L1$ is the inductance based on the battery pack wiring. $R1$ and $L1$ can also be placed on the adjacent side of the parallel battery box.

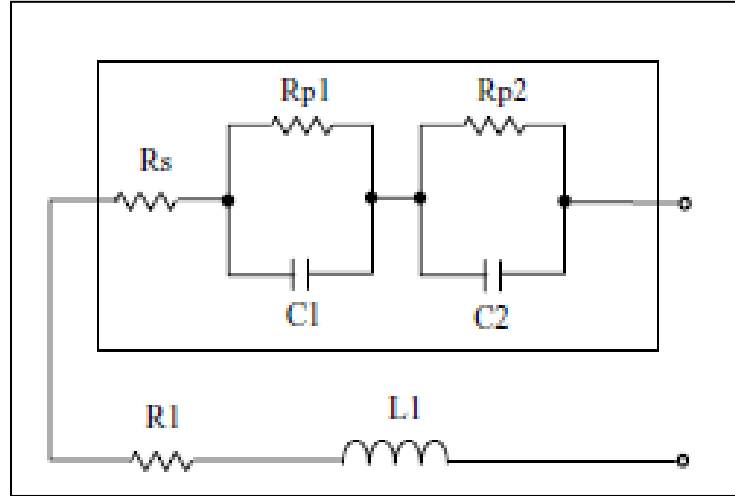
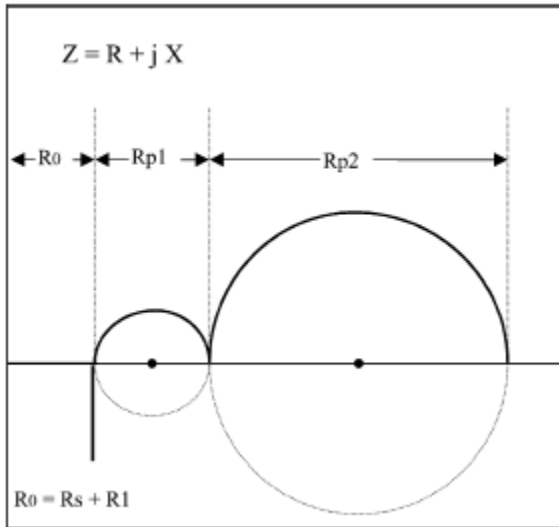
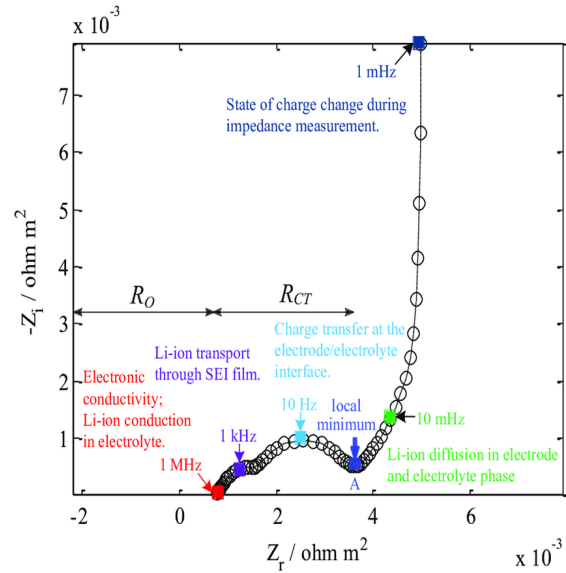


Figure 18: Battery Parallel Pack Circuit Diagram [38]



Parallel Pack Cole-Cole Plot



Single Cell EIS Plot

Figure 19: Comparison of Parallel Pack and Single cell Impedance Spectra [38]

In Figure 19 the horizontal axis in the parallel pack plot represents the real part of impedance (expressed as R), and the vertical axis represents the imaginary part of impedance (expressed as X). For a Li-ion battery, there are two half-cycles that reflect the reaction velocities at both electrode-electrolyte interfaces. R_0 in the figure represents the sum of R_S and R_1 , while R_{p1} and R_{p2} represent the reaction resistances of the negative and positive electrodes, respectively. Furthermore, the bold vertical line below the line is based on the wiring's inductance [38].

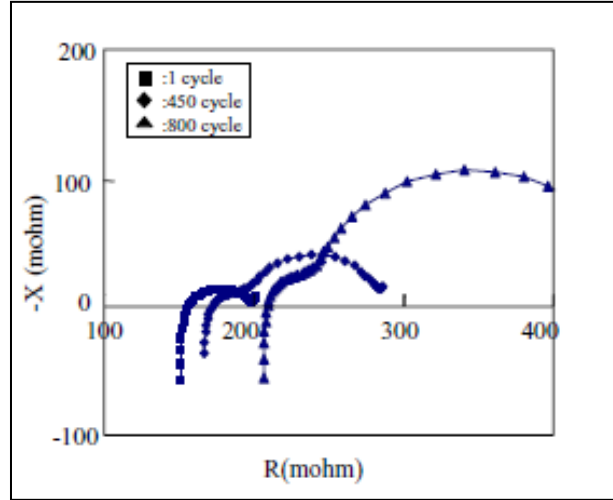


Figure 20: Degradation analysis from EIS [38]

Figure 20 clearly shows that there are two changes in the curves that are caused by battery deterioration. The first is the change in impedance (R_0), which has a zero imaginary part. Impedance (R_0) increases incrementally as the number of cycles increases. The second is the change in the two half-cycles in the Cole-Cole plots at several hundred hertz. In relation to the increase in the number of cycles, the diameter of the two half-cycles has increased and the centre of the two half-cycles has moved obliquely to the upper right. We believe that this phenomenon is caused by the incrementing of R_{p1} and R_{p2} , but determining these values precisely is difficult because the two half-cycles are not completely isolated. As the resistance increases with degradation the SEI layer thickens and the double layer capacity decreases. The cause of the change in impedance R_0 is thought to be a decrease in the effective surface area of the positive and negative electrodes, or a loose contact between active materials and current collector as the number of cycles increases. The decrease in liquid electrolyte in both electrodes is also thought to cause a decrease in electrolyte electric conduction and an increase in R_0 . The best test frequency in the experiment was around 1 kHz because impedance at this frequency is related to deteriorating

battery capacity and is not greatly influenced by the degree of charge [38]. Significant degradation in energy density, cycle life, and safety occurs with battery usage, thanks to discrepancies among cell parameters, such as resistance, capacity, and State of Charge [64].

2.4.4. Battery Thermal Management

A novel liquid coolant-based thermal management system for an 18650 battery pack must be compact and cost-effective without sacrificing safety. Contact resistance was discovered to have the greatest influence on the thermal performance of the pack [39]. The heat from the cells is carried to the liquid by aluminium conduction elements in a liquid cooling TMS. This method is similar to the heat pipe cooling that is currently used in pouch cells. The conduction elements also serve as a separator between the cells and the coolant liquid, reducing the possibility of coolant coming into contact with electrical connections even in the event of a leak, avoiding the production of harmful and combustible gases, and preventing short circuits through conductive dielectric liquids entering electronics. The contact resistance at solid-solid interfaces is a significant impediment to heat transfer. Such resistance occurs in the current thermal management system at the battery can-conduction element and conduction element-channel interfaces. The application of thermal interface material at solid-solid interfaces can reduce contact resistance. When the contact resistance is cut in half, the maximum temperature drops by about 0.74 K (20%). As contact resistance decreases, temperature uniformity between cells improves.

2.4.5. Busbar

The electrical components of lithium-ion (Li-ion) batteries, such as bimetallic busbar joints, should be able to withstand high voltages during charge and discharge processes. The busbar is a critical component that transmits high power to the vehicle's electrification system. The electrical conductivity at the weld interface influences the change in process parameters of Friction Stir Welded (FSW) samples. The formation of various intermetallics and changes in the grain size of the Al and Cu joints cause the variation in electrical conductivity with different busbars. The busbar with Cu-rich intermetallic, on the other hand, has a lower electrical resistivity. Cu was originally used for the busbar due to its high electrical conductivity, i.e., 5.87×10^7 S/m [40]. However, because of their lower cost, lighter weight, and higher electrical conductivity values, Al alloys are becoming more popular. The thermal expansion coefficient of Al is greater than that of Cu. The electrical connections are further deteriorated by the high thermal expansion rate and

oxidation of the Al. Furthermore, because of their different material combinations, connecting Al busbars to anode current collectors is complicated. Grain size reduction indicates an increase in Grain Boundary (GB). The Grain boundaries disrupt the crystal structure because they are disordered and amorphous. Defect-ridden Grain Boundaries will block carrier transitions, increasing electrical resistivity. More disordered atoms are found in materials with thicker grain boundaries. As a result of the reduced grain sizes and significant increase in GB, Al-Cu busbars have a higher resistivity. Grain growth may occur during fast cooling as the welding speed increases, increasing the TB fraction. Due to an increase in grain boundary defects, the busbar with higher hardness, i.e., small grain size at the weld interface, has lower electrical conductivity. As a result, the sample S3 had a microhardness of 238 HV and a grain size of 7.85 μm , yielding a lower electrical resistivity of $2.87 \times 10^{-5} \text{ cm}$. (3) The Al-rich (Al_2Cu) IMC busbar has poor electrical properties, with an electrical resistivity of $4.29 \times 10^{-5} \text{ cm}$, which is 33.1% higher than the Cu-rich (Al_4Cu_9) IMC.

Automotive high-voltage busbars are critical electrical components in electric vehicle battery systems because they connect individual battery modules and form the vehicle's powertrain connection. As a result, a vehicle crash can endanger safety by compromising busbar insulation, resulting in electrical short circuits inside the battery. These, in turn, can cause thermal chain reactions in the battery pack's cell modules. This study investigated the mechanical behavior of busbars and their insulation in order to ensure a safe design in future busbar applications. According to our findings, crashlike compressive and bending loads cause complex stress states that result in busbar insulation failure. Finally, we outline some potential approaches for increasing the safety of high-voltage busbars in electric vehicles based on the experimental and numerical results, such as selecting the insulating layer material based on the range of expected mechanical loads. Mechanical loads on the busbars and damage to their insulation can result from module displacement or battery housing intrusion. However, current crash safety battery research focuses on the analysis of battery cells and their components subjected to mechanical abuse [65–67], despite the fact that these undergo mechanical deformation after the surrounding electrical components. Few studies have been conducted to date on the safety of electrical battery components under mechanical loads. It was recently demonstrated that compressive loads using various impactor shapes on high-voltage busbars can cause electrical short circuits [68]. Such short circuits are especially dangerous when busbars are used to connect individual battery

modules; at worst, they can cause a cell short circuit, resulting in TR that propagates throughout the entire battery pack. Bending and compressive loads caused by intruding objects such as sheet metal edges or screw heads have a significant impact on busbars and must be considered in experiments. The thermal load during operation is another important factor influencing the mechanical behavior of the busbars. Busbars can reach temperatures of up to 80 degrees Celsius in operation due to short-term high currents within the battery system during charging and discharging, as well as during strong acceleration processes. This has a particular impact on the mechanical behavior of insulating materials, the glass transition temperature of which is lower than the operating temperature. HV busbars used for electrical module connection typically have a conducting copper core surrounded by thermoplastic insulation. Due to the possibility of high electrical currents, the copper cross-sectional area typically ranges between 70mm² and 90mm², according to manufacturers. Semi-crystalline polyamide PA12 and glass fiber-reinforced polyamide PA6GF30 are two of the most commonly used thermoplastic insulating materials. The temperature-dependent tests were carried out at 60 degrees Celsius and at the maximum busbar operating temperature of 80 degrees Celsius. In our investigations, we discovered that the copper material strongly dominates the component behavior under compression and bending until the insulation fails. The mechanical failure of the busbar insulation is determined by the load case, the insulation material used, and the impactor geometry. Large deformations were achieved during three-point bending tests using the PA12 busbar with no sign of material failure. The PA6GF30 busbar demonstrated higher mechanical strength but also brittle behavior, which resulted in material failure. When placed inside a battery, this could cause electrical short circuits, posing a safety risk during a vehicle crash. Both insulation materials failed under compression load with a sharp impactor geometry, though the PA6GF30 insulated busbar achieved higher critical forces and an electrical short circuit at larger displacements than the PA12. Busbars should be designed with vehicle safety and possible battery pack deformations in mind [69].

- Possible mechanical loads should be analyzed in the early development, using a material model that allows for tension–compression anisotropy
- The insulation material and its thickness should be chosen in accordance with possible mechanical loads and electrical properties
- A ductile unreinforced insulation material is recommended for possible bending loads

- A fiber reinforced insulation material should be used if compressive loads or penetrating objects can occur

In Werling et al. [70] Two types of high-voltage busbars were tested: one with a polyamide 12 insulation layer and one with a glass-fiber-reinforced (30%) polyamide 6 insulation layer. The test setup also included a 1000V electrical short circuit measurement to connect the electrical and mechanical failures. It was discovered that the safety of polyamide 12 insulated busbars in terms of insulation failure increases at high loading speeds when compared to quasi-static measurements. The fiber-reinforced polyamide 6 insulated busbar, on the other hand, demonstrated highly brittle material behavior, resulting in reduced bearable loads and intrusions. Electric potentials of up to 870 V [71] and currents of up to 400A are applied to the HVBs. These, combined with increasing battery capacities [70] pose a challenge for crash safety researchers and developers.

2.4.6. Busbar Joining Technologies

Automotive battery packs for electromobility applications are made up of a large number of interconnected individual battery cells. The interconnection of battery cells creates an electrical and mechanical connection that can be realized using various joining technologies. The adaptation of various joining technologies has a significant impact on the primary characteristics of the battery pack in terms of battery performance, capacity, and lifetime. As a result, selecting a suitable joining technology entails several considerations regarding electrical and mechanical properties, as well as an assessment of production and operational conditions. Specifically, challenges and mutual dependencies of the electrical and mechanical systems emerge during the operation of an electric vehicle. Ultrasonic welding, wire bonding, force fitting, soldering, laser beam welding, and resistance welding are the most common joining techniques. Friction stir welding, tungsten inert gas welding, joining by forming, and adhesive bonding are currently being developed [72].

When it comes to battery module operation and safety requirements, mechanical phenomena play a significant role. Battery modules are subjected to dynamic loading and random vibrations during operation, which can result in short circuits and fires [73]. Because of their periodic structure, random vibrations have a particularly strong influence on modules with a large number of single cells. The structural dynamics of the module may be harmed as a high modal density in many frequency ranges is promoted. Furthermore, the battery interconnection joints will be pre-stressed to some extent as a result of the interconnecting by joining, which may significantly affect the

dynamic response of the entire battery back. The dimensional changes of the cells during operation may enhance the above-mentioned effects when using thin prismatic or soft polymer cells. If different thermal expansion materials are joined and heat is generated at the contact interface, inhomogeneous thermal expansion may introduce shear loading and, in severe cases, plastic deformation or fracture in the contact region, which may negatively influence contact behavior and thus connection resistance.

When connecting batteries, regardless of joining technology and electric circuit type, i.e. parallel or series connection, an electrical resistance joint is unavoidable. This resistance will occur at the point of connection between the battery and the interconnect. This is referred to as connection resistance in this context. The presence of a connection resistance during charging and discharging of a cell, module, or pack has two direct effects, namely loss of electrical energy across the interface and heat generation in the contact region, both of which are dependent on the resistance. Saw et al. [74] discovered that the presence of a 10 m connection resistance caused detectable temperature gradients of up to 10 °C across cylindrical 18650 cells, which was just within the allowable temperature range and may impair cell capacity. Fatigue is a well-known and concerning phenomenon in structural applications, but it also promotes an increase in electrical resistance.

The most serious mechanism of degradation in mechanically joined electrical connections is oxidation of metal to metal contacts. Surface degradation at a metal-to-metal contact interface caused by oscillatory movements of the two surfaces with slip amplitudes less than 125 µm is referred to as fretting or fretting corrosion. When aluminium is a joining partner, the oxidation layer of aluminium grows quickly and is relatively thin in comparison to the size of conducting asperities (-spots), making it a less severe degradation mechanism. Copper oxidation, on the other hand, is more complicated; the oxidation layer grows at a slower rate, and it has been reported to have insulating and conducting properties [72].

Electrical and thermal requirements

- Resulting joints should have low electrical resistance with a narrow scattering range
- Thermal input during manufacturing should be as small possible
- High thermal fatigue resistance of created joints

Material and metallurgical requirements

- Low corrosion risk
- Joining of dissimilar materials
- Adaptability to a variety of surface conditions and materials

Mechanical requirements

- Strong interconnections
- Good fatigue and creep resistance
- Low pre-stress level
- Avoid mechanical or vibrational damage during joining

Economic requirements

- Suitability for mass production
- Low acquisition costs
- Good possibility to be stabilized and standardized

The interconnector will be directly joined onto the cell housing in the case of cylindrical cells, whereas pouch and prismatic cells have externally located connector tabs that are joined to the interconnector.

For Ultrasound Welding the resistance increased as the joint area decreased and was deemed acceptable and comparable to resistance welding. There is no scientific literature on wire bonding in relation to battery module manufacturing, but it is frequently mentioned as a process in the automotive industry. This is most likely due to the fact that Tesla Inc. has filed several patents for wire bonding for battery modules and is using the joining process in its Model S. The applied force/contact pressure as well as the material properties are critical to electrical contact resistance. Surface roughness was discovered to be insignificant, whereas oxidation layers or other films have a strong, increasing influence on contact resistance, particularly for aluminium and its oxidation layer. Taheri et al. [75] investigated pouch cells that were bolted to copper bars. They confirm the dependence of electrical contact resistance on applied pressure, but for the specific case of bolt joints, they recommend surface polishing to reduce connection resistance. Furthermore, they conclude that in the case of low-pressure joints, interfacial electrically conductive materials may be used to reduce electrical conduct resistance, whereas high-pressure joints do not require this. For bolted connections, including nut and bolt, flow drilling screw, and thread-forming screw

connections, connection resistance tends to increase over time. The resistivity of the joining partners, contact geometries of the joining elements, coatings of both joining partners and joining elements, and process parameter variation all have an impact on connection resistance for bolted and screw connections [72].

Figure 21 presents an overall comparison of electrical Contact Resistances for various joining technologies.

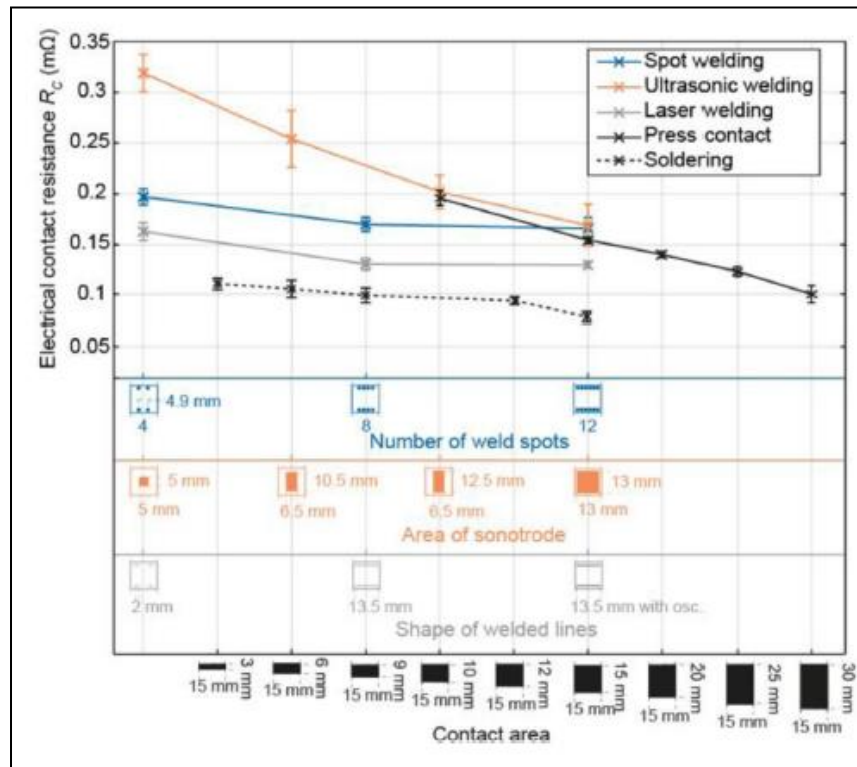


Figure 21: Electrical resistances of soldered battery cell connections [76]

When comparing battery welding joining technologies, it is clear that the applicability of a technology is dependent not only on the connection resistance and its scatter, but also on the specific joining task, i.e. the battery cell type. Ultrasonic welding appears to be particularly suitable for joining pouch cells. Wire bonding is appropriate for connecting prismatic or pouch cells, but not for large modules containing small cylindrical cells. Laser welding can be used to join cylindrical cells, but it may be less effective when joining large cells with geometrically large interconnectors. Resistance spot welding and its process variants are a flexible technology that can be deployed for all battery cell types because the welding occurs locally at the contacting surfaces,

as opposed to laser welding, which requires an entire melting of the connector regardless of its size.

2.5. Battery Thermal Management Systems (BTMS)

There are 5 major battery thermal management systems considered in the paper. The 2 commercially available options for EVs are air cooling and water cooling. Passive cooling methods such as heat pipes and PCMs are also an area of research for EVs. One of the major drawbacks of PCMs is the added weight to the battery pack that reduces EV mileage. Technological solutions such as Thermoelectric/Peltier devices are also presented but currently are inefficient and draw too much power to be implemented commercially. A comparison of the various battery thermal management system is presented in Table 3.

Table 3: BTMS Comparison Chart

Parameter	Forced Air	Heat Pipe	PCM	Thermoelectric	Cold Plate
Life	≥ 20 years	≥ 20 years	≥ 20 years	1–3 years	≥ 20 years
Ease of use	Easy	Moderate	Easy	Moderate	Moderate
Integration	Easy	Moderate	Easy	Moderate	Moderate
Maintenance	Easy	Moderate	Easy	Difficult	Moderate
Temperature Distribution	Uneven	Moderate	Even	Moderate	Moderate
Efficiency	Low	High	High	Low	Medium
Temperature Drop in cell	Small	Large	Large	Medium	Medium
Annual Cost	Low	Moderate	Low	High	Moderate
Capital Cost	Low	High	Moderate	High	High

2.5.1. Air Cooling

Air cooling methods excel for small packs and under normal conditions. At low SOC, high ambient temperatures, high C Rates and constant currents air cooling will not suffice and severely shortens cycle life while failing to maintain the temperature within safety limits. Air cooling is seen to be preferred at zero sub zero temperature conditions where heat is required and not needed to be removed from the battery pack. The Nissan Leaf is a famous example of air cooling BTMS

failure as reports show constant early failure and voided warranties. Battery Pack design is of particular importance if this BTMS is chosen. Both the temperature uniformity and maximum temperature of the pack are poor for this BTMS method. Both passive and active air cooling are found to be insufficient at high and low SOC's and when applying high currents.

2.5.2. Water Cooling/ Cold plate

Water Cooling is the predominant method of cooling commercially available. Several geometric designs are available and are presented in Figure 22. The channels can be straight, waved or in different shapes.

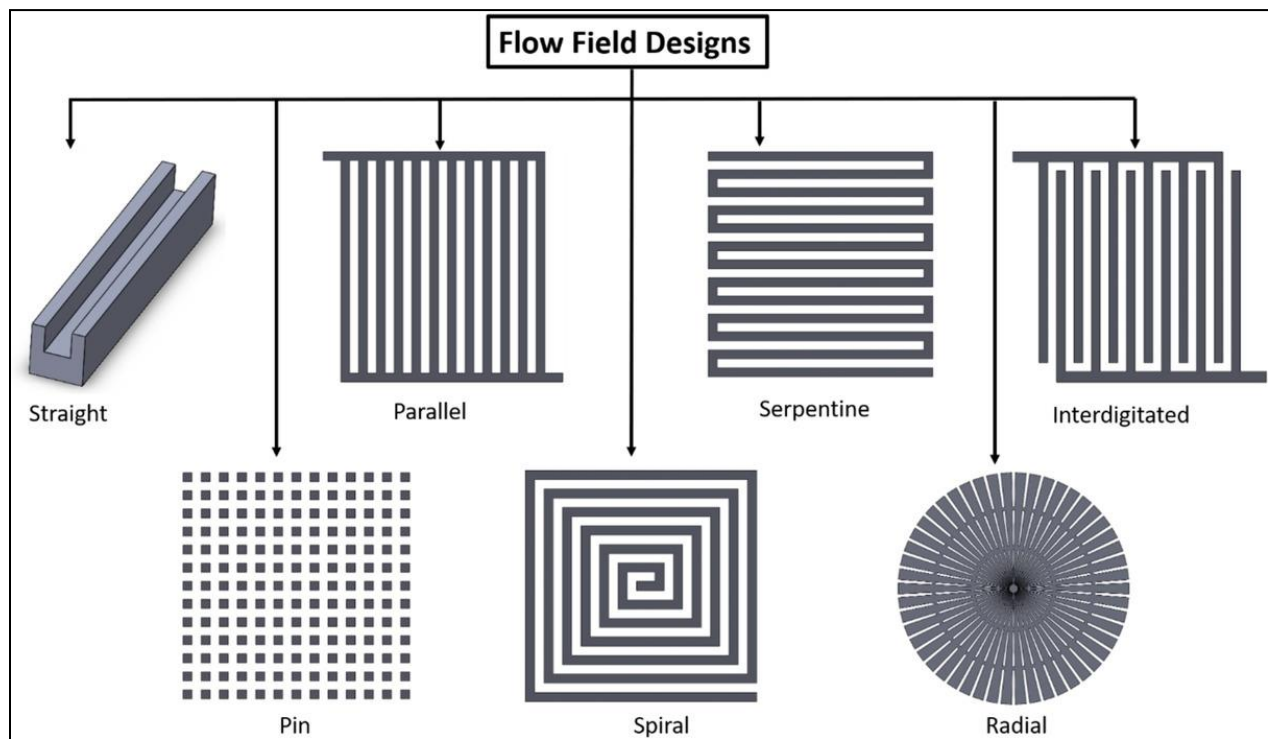


Figure 22: Cold plate Geometric Designs [77]

Typically, multiple channels are run in parallel or counter-parallel with the design being determined by inlet and outlet positions as shown in Figure 23. The pressure drop in Parallel Flow Fields is lower than in serpentine flow fields. Z type is seen to have a much larger pressure drop than U type with mixed Z and U types showing better flow distribution than conventional parallel flow fields. Novel flow field designs include zig zag flows.

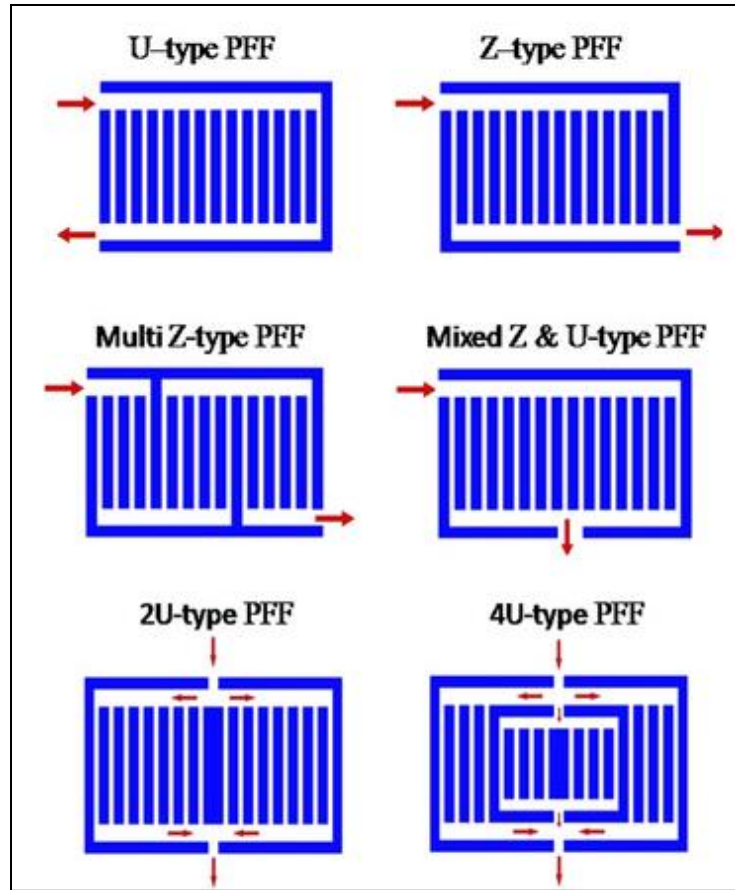


Figure 23: Cold plate Inlet Outlet Designs [77]

2.5.3. Heat pipe

A heat pipe combines both thermal conductivity and phase transition with natural convection to effectively transfer heat between two solid interfaces. At the hot interface of a heat pipe, a liquid in contact with a thermally conductive solid surface turns into a vapor by absorbing heat from that surface acting much like a phase change material. The vapor then travels along the heat pipe to the cold interface and condenses back into a liquid, releasing the latent heat. The liquid then returns to the hot interface through either capillary action, centrifugal force, or gravity and the cycle repeats. Due to the very high heat transfer coefficients for boiling and condensation, heat pipes are highly effective thermal conductors. The effective thermal conductivity varies with heat pipe length and can approach $100 \text{ kW}/(\text{m}\cdot\text{K})$ for long heat pipes, in comparison with approximately $0.4 \text{ kW}/(\text{m}\cdot\text{K})$ for copper. Heat pipes allow for direct liquid cooling through immersion into liquid cooling system as well as PCM.

2.5.4. Thermoelectric Peltier Devices

Thermoelectric devices are based on the Seebeck effect that is also seen in devices such as thermocouples. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, heat is transferred from one side to the other, creating a temperature difference. PN type devices often have this phenomenon of reversibility as shown in LEDs as well. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. For semiconductors heat allows electrons and charge carriers to jump the band gap into the conductive band and decreases resistance while for metals this is not the case as electrons are always in the conductive band. For gases it is known the temperature is the average kinetic energy of the particles present while in solids heat is transferred by phonons where the average vibrational speed of the molecules is proportional to the temperature thus moving charges in an electric current can lead to creating an increasing temperature differential. As emission is due to electrons this is postulated to be the case for blackbody radiation and the phenomenon of heat transfer. For metals the free moving electrons carry a substantial amount of the heat and thus the electrical conductivity is proportional to the heat conductivity. This means that when we apply current to the module a temperature difference occurs across the two sides of the device and this difference depends on how much voltage and current input. During operation of the Peltier device one side gets colder and the other side gets hotter. The maximum temperature differential is determined by the power of the unit and to maintain a minimum temperature on the cold side we should also maintain the temperature on the hot side as the temperature difference is the key factor. A major drawback of Peltier Devices is cost and performance efficiency.

2.5.5. Phase Change Materials (PCM)

When compared to liquid cooling through cold plate phase change materials show superior temperature distribution and efficiency. Phase change materials are also easier to integrate and use with less maintenance in comparison. The cost is cheaper and the effective temperature drop is larger. One of the most important selection criteria for phase change materials is the melting temperature. The melting temperature should be in the desired operating temperature range. Selection criteria include:

- Melting point in the desired operating range

- High latent heat of fusion per unit volume
- High specific heat, density and thermal conductivity
- Small volume changes during phase transformation and low vapour pressure
- High nucleation rate to avoid super cooling
- Complete reversible freeze/melt cycle
- Low degradation after cycling
- Non-corrosive, non-toxic, non-flammable and non-explosive
- Low Cost

Phase change materials allow for isothermal conditions as the temperature is constant during phase transition and create an even temperature distribution in the pack. They are a passive cooling system and do not drain energy from the battery.

Phase change material Types:

Thermal energy storage systems are typically divided into thermal and thermo-chemical. The thermal subtype can further be divided into sensible and latent heat systems. As the latent heat of fusion is typically larger than the specific energy latent heat systems have higher energy densities (5-14 times) and allow for isothermal conditions as the phase change happens at a fixed temperature.

Latent heat storage is achieved through changes in the state of matter those being solid to liquid transition, solid to gas and liquid to gas. Practically for PCMs only the solid to liquid and liquid to solid phase changes can be utilized. Although liquid to gas phase changes have a higher heat of transition than solid-liquid and liquid-gas they are impractical due to large volume and high pressure requirements. Solid-solid latent heat systems have low specific heat but do have small volumetric variation. PCMs can be divided into 3 main groups: Organic, inorganic and eutectic.

Organics are typically paraffin or non-paraffin compounds such as fatty acids. Organics typically have a latent heat of 128-200 kJ/kg and are promising for applications under 100°C along with inorganic salt hydrates. Inorganic PCMs can be divided into salt hydrates and metallics. Salt hydrates are of the chemical formula of a salt (AB) and water (H₂O) being AB(H₂O). During hydration the salt hydrate solidifies while during dehydration the salt hydrate melts. The process

is non-congruent as separation and sedimentation of the liquid water from the salt occurs during dehydration which leads to incomplete solidification during the charging phase. Eutectic mixtures have application for temperatures under 250°C. PCM containers can be divided into compact and encapsulated. Compact PCM systems are shell and tube systems where the PCM is within the shell and the heat transfer fluid is within the tubes. Compact systems have high energy density but slower heat transfer properties. Encapsulated PCM systems gave a high heat transfer area leading to higher power ratings.

Lithium ion batteries have a high energy density, which raises a number of safety concerns. Overall, large format lithium ion batteries are known to be thermally unstable, with prismatic and cylindrical cells prone to container rupture and explosion and pouch cells prone to swelling and catching fire. Thermal runaway is frequently caused by abusive conditions such as thermal abuse, overcurrent, excessive pressure, overvoltage, overcharge, and undercharge. These abusive conditions (whether caused by separator shrinkage, gassing/swelling, or jelly roll collapse) usually result in an internal short circuit (ISC), which is followed by thermal runaway. Depending on the battery format, the manufacturing process, application, and safety concerns differ (cylindrical, prismatic, pouch, coin). Cylindrical cells are well-known for their ability to withstand high internal pressures without deforming, and they have been used in applications requiring high charging C-rates.

Most batteries are safe to use in a temperature range of 0 to 60 °C. Low charge transfer occurs at low temperatures (10 °C) due to high electrolyte viscosity and an increased risk of Lithium plating. The main risk at temperatures between 60 and 120 °C is a breakdown of the SEI layer. BMS/current shut off can help to mitigate these risks. The separator begins to degrade and melt at high temperatures of around 120 °C. This causes internal short circuits and electrolyte gas emissions. The risk can still be contained and mitigated by using cell vents to release pressure and turn off the current. Even higher temperatures, above 180 °C, cause permanent damage to cell components such as the cathode, anode, or electrolyte, resulting in thermal runaway.

Positive temperature coefficient thermistors (PTC), positive temperature coefficient electrodes, current interrupt devices (CIDs), safety vents, protection circuitry, shutdown separators, electrolyte additives, and safe electrolytes at the cell level are all common safety strategies. Passive protection designs, such as thermal absorption materials and mechanical protection in battery

packages, are also implemented at the pack level, as are battery management systems. These safeguards prevent thermal propagation from cell to cell across the pack. However, keep in mind that propagation is primarily determined by electrical connectivity.

2.6. Safety Cell Level Technologies

Safety precautions will be extended to new cell forms in order to reduce resistance, weight, area, and cost. Improved electrode materials, stronger separators, nonflammable electrolytes, structured current collectors, and cell pack design improvements are all in the works.

Many safety technologies' primary goal is to prevent thermal runaway. During thermal runaway, the layered metal oxide cathodes LiCoO_2 (LCO), $\text{LiNi}_x\text{Mn}_y\text{Co}_z$ (NMC), and $\text{LiNi}_x\text{Co}_y\text{Al}_z$ (NCA) breakdown and release oxygen. When we investigate cathode materials other than layered metal oxides, we find comparable behavior, even though the processes differ and the temperatures of various events can vary dramatically. Cathode materials such as LiFePO_4 (LFP) and LiMn_2O_4 (LMO) frequently exhibit electrolyte breakdown, SEI, and anode decomposition but not energetic cathode breakdown.

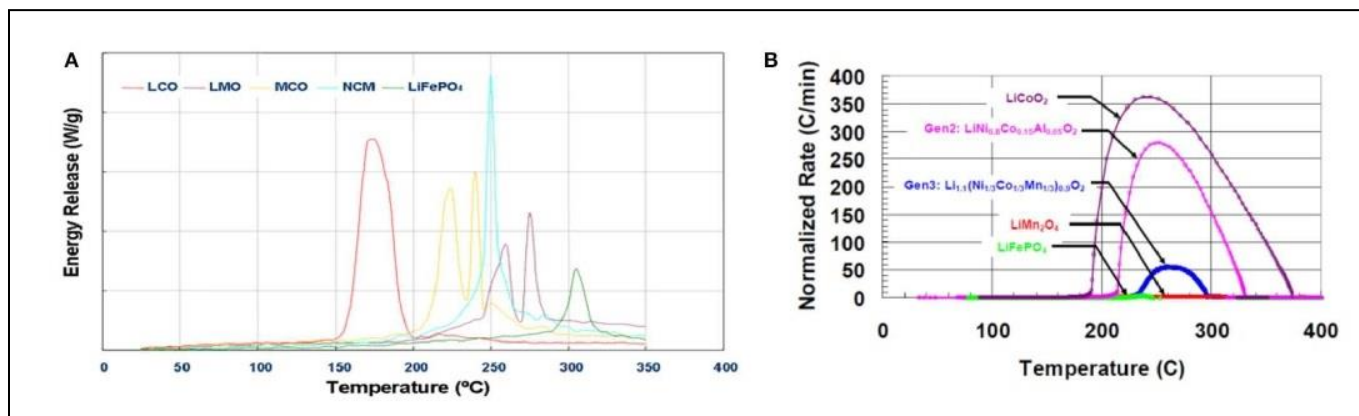


Figure 24: Cathode Chemistry's Influence on Total Energy Released from Combustion and Heat Generation Rate

Although LiFePO_4 cathode material is safe up to 400°C, LiCoO_2 decomposes at 250°C. All of the oxygen ions form strong covalent bonds with P^{5+} to form PO_4^{3-} tetrahedral polyanions, which support the entire three-dimensional framework and provide greater stability than other cathode materials [78]. Because Ni^{2+} has a comparable ionic size to Li^+ , the crystal structure of LiNiO_2 is unstable. At around 200°C, delithiated Li_xNiO_2 tends to convert to spinel-type LiNi_2O_4 (spinel)

and rocksalt-type NiO, with oxygen released into the liquid electrolyte, resulting in electrolyte combustion. By using atom doping and surface protective coatings, significant efforts have been made to improve the thermal stability of these cathode materials. Atom doping improves the thermal stability of multilayer oxide materials due to stable crystal structures. The thermal stability of LiNiO_2 or $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ is improved by replacing Ni or Mn with Co, Mn, Mg, or Al. Doping and alloying LiCoO_2 with Ni and Mn may raise the temperature at which decomposition begins [78].

The thermal runaway onset temperatures shown in Figure 24 are $\text{LCO} < \text{NCA} < \text{LFP} < \text{NMC} < \text{LMO}$, with LCO posing the greatest risk due to its lower onset temperature. Though the onset temperature for the first two cell chemistries (LCO/NCA) is the same as the temperature of no return, we find a trend deviation for the following three: NMC, LMO, LFP because LMO and LFP are not stacked cathodes and the heat release is slower than predicted by the onset temperature. While total energy released indicates $\text{NMC} > \text{LCO} > \text{NCA} > \text{LMO} > \text{LFP}$, NMC is the most dangerous and has the narrowest temperature band, whereas NCA and LMO have multiple peaks. Increasing the thermal stability of the cathode reduces capacity.

2.6.7. Positive Temperature Coefficient Devices

When positive temperature coefficient devices reach a certain temperature or current, their resistance abruptly increases. PTC thermistors are uncommon in commercial prismatic or pouch batteries, but are common in commercial cylindrical cell designs [79]. In certain prismatic batteries, the PTC thermistor is mounted externally to the cell cover [80]. External PTC devices function similarly to PTC thermistors in cylindrical batteries, providing current-limiting functionality.

Under normal operating conditions, the PTC of the cylindrical cells acts as a conductive component with a low resistance. When the current or temperature reaches the phase change point of the PTC, the resistance increases dramatically and the cell is disconnected. Not all cylindrical batteries contain a PTC thermistor. For example, the Samsung INR18650-25R is designed for high discharge rates (up to 20 A) but lacks a PTC. Although PTC thermistors have been shown to be useful at the cell level, they are rendered useless in large multi-cell battery systems when subjected to high-voltage short situations.

The polymer component of the PTC undergoes an abrupt phase shift and becomes amorphous above the glass-transition temperature (above 100 °C). Because the polymer returns to its crystalline state when cooled below the glass-transition temperature, the effect is reversible. The PTC maintains a low current until the temperature drops to a safe level, around 40 °C, at which point the bimetal disc is reset to reconnect the two plates. PTCs must be carefully chosen by matching the PTC to the current and voltage of a single battery.

2.6.8. PTC Electrodes

PTC thermistors can cause increased cell resistance as well as thermal losses. Most commercial cylindrical batteries have PTC thermistors built into the cap. Internal shorts are not covered using external PTCs. Thermal runaway, on the other hand, is typically initiated within the cell, such as at the SEI layer and electrodes. Because of the distance between the PTC thermistor and the internal hot spots of the battery, the PTC's response to high temperatures is delayed [81]. As a result, PTC electrodes with PTC components propose to significantly increase electrode resistance when batteries are overheated and can handle internal short circuiting [82]. Thermal runaway and ignition are common issues in current collectors, and the use of PTC electrode technology aims to address this problem at its source.

2.6.9. Current Interrupt Device Technology

A current interrupt device (CID) is a safety mechanism that is installed in cells to prevent overheating or excessive internal pressure. They destroy the electrical connection when the cell pressure (approximately 145 psi) or temperature is too high. CIDs are used in a wide range of commercial cell configurations (unlike PTCs). CIDs are classified into two types: pressure-responsive CIDs and temperature-responsive CIDs.

Pressure-responsive CIDs have frail connections that cut when internal pressure exceeds a certain level. Temperature-responsive CIDs break the circuit by melting the fuse at high temperatures determined by the fuse material's melting points. When CIDs are used, battery resistance increases while energy density decreases. To address this, many 18650 batteries' top disc serves as both a CID and a safety vent, saving weight and space.

2.6.9.1. Pressure CIDs

Assume the battery's internal pressure exceeds the limit, which is approximately 145 psi [83]. In this case, the CID will bend, pushing the top disc outwards and driving the centre point upwards, separating the metallic foil and top disc. According to this method, CIDs in cylindrical cells are a one-time protective system that, once activated, irreversibly destroy the battery (unlike PTCs). Because the voltage of a single cell is less than 5 V, a CID can interrupt the electrical current to protect the battery from thermal runaway in overload situations. Diao et al. [84] overcharged four different types of 18650 batteries to various voltage levels (5.27 V–5.42 V). In the paper, the CIDs of all batteries were activated prior to venting or thermal runaway. CIDs in high-voltage battery packages, on the other hand, have the potential to produce an electric arc. Augéard et al. [85] discovered that CID arcing could result in ignition and a persistent flame when the voltage was 20V or higher. Similar NASA testing revealed CID arcing at 55 V for the Moli ICR-18650J and 110 V for the Sony 18650HC.

2.6.9.2. Temperature Responsive CIDs

The starting temperature of SEI disintegration, according to Feng et al. [86], is 80 °C, with an internal short circuit around 130 °C. Cathode materials breakdown if the temperature rises above 150 °C for a LiCoO_2 battery and 160 °C for a $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ battery [87]. Thermal fuses, shape memory alloys, and other temperature-responsive CIDs are all intended to stop current flow at high temperatures (around 95 °C). Thermal fuses are built into batteries to stop current flow before it reaches dangerous levels.

2.6.10. Shape Memory Alloy Technology

Thermal fuses destroy the battery irreversibly by melting and interrupting the electrical circuit. Shape memory alloy is a reversible CID technology that deforms at one stage and then returns to its pre-deformed shape or size as a result of temperature or magnetic field [88].

2.6.11. Safety Vent Technology

When a battery is used at high temperatures, gas collection can occur, resulting in pressure buildup that can lead to the battery casing bursting if the pressure is not released quickly enough. A "vent" is a strategically placed weak spot on the battery casing that allows for the safe leakage of gas. Vents remove excess internal pressure from a cell or battery to prevent rupture and explosion.

Scorings are built in a variety of cell configurations to ensure that safety vents remain open at the proper pressure levels. If the primary safety vent becomes clogged and the internal pressure cannot be released in time, the battery casing may crack and even explode.

While single-safety vent designs are commonly used in commercial cells to relieve excess internal pressure and prevent blasts, the increasing energy density of modern cells necessitates the use of multiple vents. To respond to the threats posed by increased energy density, multiple security vents are expected to become the new normal. Sony and LG introduced a bottom vent in some cylindrical cells. When the internal pressure of the battery reaches a certain level, safety vents open to prevent case rupture, 113-128 psi (0.78-0.88 Mpa) for prismatic cells [89] and 406 psi (2.8 Mpa) for 18650 cylindrical batteries [89,90]. In cylindrical cells, the trigger pressure (406 psi [90]) is typically higher than in pressure-responsive CIDs (145 psi [83]). Thompson and Martucci [91] advocated for vent relocation. They designated areas of the prismatic battery for safe gas release. Park et al. [92] proposed a venting system that would direct venting through terminal tabs.

2.6.12. Protection Circuitry Technology

Protection circuitry protects against overcharge, over-discharge, electrostatic discharge, overcurrent, and overtemperature. Also in the event of an internal short circuit the technology has the potential to spread heat and current from the trigger zones. Protective circuitry is classified into three types based on the trigger cause: voltage protection, current protection, and temperature protection [93].

Wires soldered to the battery's bottom and running from the protection circuit board to the battery's cap connect the protective circuitry to the battery terminals. A controller chip for monitoring battery voltage/current and a switch for connecting/disconnecting the battery are two critical components on the protective circuit board. For safety reasons, the protective circuit board is normally installed on the cap plate of prismatic cells and welded to the terminal tabs of pouch cells. Prismatic cell and pouch cell protection circuit boards are typically low resistance, compact in size, lightweight, and flexible to reduce the impact on energy density.

2.6.13. Separator Technology

An incomplete/shrunk separator is a major source of concern because it can cause an internal short circuit. An internal short-circuit may form if the separator collapses due to shrinkage or cell

enlargement. The stored electric energy inside the battery will be released instantly as heat and gas generation increases [86] setting off a chain reaction that leads to thermal runaway. As a result, some criteria apply to the separator in Li-ion batteries. The separator is electrochemically and mechanically stable against electrodes and the electrolyte, its thickness is between 15 and 20 μm , its mechanical strength is greater than 98.06 MPa, its porosity is between 40% and 60%, its pore size is less than 1 μm , and shrinkage after 60 minutes at 90 $^{\circ}\text{C}$ is less than 5%. [94].

Polyethylene (PE) and polypropylene (PP) separators have a collapse temperature of around 135 $^{\circ}\text{C}$. As separator materials, most commercial Li-ion batteries use PE, PP, or their combination PE-PP bilayer separators or PP-PE-PP trilayers [95]. PE-PP blend [96], isotactic poly (4-methyl-1-pentene) [97], polyoxymethylene [96], polystyrene (PS)-PP blend, and poly (ethylene terephthalate) (PET)-PP blend polymers are also used in separator fabrication. Separator shutdown is the ability to stop electrochemical processes between two electrodes at temperatures slightly lower than the thermal runaway trigger temperature while maintaining the physical barrier between the two electrodes [98]. It forms the basis for separator shutdown technology. At high temperatures, polymeric material separators can be shutdown separators. The shutdown temperature of PE-PP bilayer separators, for example, is 130 $^{\circ}\text{C}$. [99]. As the temperature rises and the separator components begin to melt, the pores on the separator close and the ionic flow ceases [100]. The inner lower-melting-point PE layer closes holes to inhibit ionic conduction at around 135 $^{\circ}\text{C}$. The outer higher-melting-point PP layers, on the other hand, continue to provide physical barriers for electrodes up to about 165 $^{\circ}\text{C}$. As a result, the shutdown operation has no effect on the mechanical separation function because higher-melting-point components provide mechanical strength.

To avoid acid generation, lithium dendrites and plating the separator can be coated. In terms of cell material innovation, the inclusion of a heat resistant ceramic powder with a large surface area, a hydrophilic polymer binder, and the ceramic coated separator demonstrated good thermal stability and cycling performance. Lithium fluoride [101], lithium nitride [102], polymers [103], and carbon-based coatings regulate and suppress dendritic and SEI development [104].

2.6.13.1. Electroactive Separator

An electroactive separator can switch from an electronically isolating to a conductive state, resulting in a resistive internal short circuit that keeps the cell's voltage constant and prevents

overcharge. Polytriphenylamine (PTPAn) was synthesized and used in rechargeable lithium batteries as a separator material to provide self-activating overcharge protection [105]. The LiFePO₄ cells showed that when overcharged, the electroactive separator could transform from an electronically isolating state to a conductive state, resulting in a resistive internal short circuit that kept the cell's voltage at 3.75V. Furthermore, the electroactive PTPAn separator is reversible and has no negative effects on LiFePO₄ cell charge discharge behavior. Because this polymer can be oxidized to a conductive state at a relatively high potential of +3.75V (compared to Li⁺/Li) and is lithium stable, it is suitable for use as a single electroactive material in a commercial membrane separator or as a substrate material for the fabrication of a single layer membrane. Note that constant charging for hours at overcharge potentials, as with most overcharge technologies, can cause the reaction to become irreversible and consume all polymer available, allowing for the danger of eventual overcharge.

2.6.14. Current Collector Technology

Corrosion caused by electrolyte reaction is the primary safety risk of current collectors. It is critical to select current collectors that are inexpensive, lightweight, self-supporting, mechanically strong, and electrochemically inert within the voltage range of the battery. Furthermore, when the temperature of the battery rises, thermally switchable current collectors may stop electrochemical processes. Thermoresponsive polymer switching is built into the current collector (TRPS). TRPS thin films are composed of graphene-coated nanostructured nickel (GrNi) particles and a PE matrix with a high thermal expansion coefficient. At room temperature, as-fabricated polymer composite films have high conductivity; however, as the temperature approaches the switching temperature, the conductivity drops by seven to eight orders of magnitude in one second due to polymer volume expansion, which separates conductive particles and breaks conductive pathways. This mechanism is highly reversible and may function even after numerous overheating events. The current collectors are thin and thin film metal are prone to catching on fire while also exacerbating the inadequacy of flame retardants around molten metal salt solvents.

2.6.15. Electrolyte Additive Technology

Several electrolyte additions, such as overcharge prevention and flame-retardant (FR) additives, have been researched to improve the safety of Li-ion batteries. Additives are chemicals that are

added to electrolytes in small amounts ranging from 0.5 to 10% by weight to change their properties. They should, ideally, have no effect on the cycling performance of the battery [106].

Novel additive technologies, such as electrospinning and microcapsules, are being developed to alleviate physical property constraints in flame retardants and improve electrochemical performance [107]. The use of redox shuttles as electrolyte additives prevents overcharge. The operation of redox shuttles is based on a reversible redox process that "locks" a battery's voltage when it is charged [106]. If the battery is allowed to overcharge, the redox shuttle is reduced and oxidised to keep the voltage from rising to unfavourable levels. Diarylamine compounds were developed by Ergun et al. [108] as potential redox shuttles to modulate oxidation potential.

Shutdown additives provide a long-term solution for preventing battery overcharging [106]. There are two types of shutdown additives: those that emit gases and those that polymerize. Overvoltage can cause additives like biphenyl, cyclohexylbenzene, and pyrocarbonates to emit gases [109]. The rising pressure could cause the CID to turn off the battery. Polymerizable additives (e.g., biphenyl and other substituted aromatic compounds) impede ion transport in the electrolyte when the battery is overvoltage, causing the battery to shut down [106]. A combination of a redox shuttle and a shutdown additive can be used to protect Li-ion batteries from catastrophic failure due to overcharging. To improve the thermal stability of Li-ion batteries, FR additives are added to electrolytes to reduce their flammability [99]. Examples of flame retardant properties include reducing agents (such as halogenated chemicals) and compounds that produce radicals with high electronegativities (e.g. Phosphates).

The FR mechanism of these phosphorus-containing compounds is thought to be a chemical radical-scavenging reaction. During combustion, phosphorus-containing molecules can disintegrate into phosphorus-containing free radical species, which can then terminate the radicals responsible for ongoing combustion (for example, H and OH radicals). The additives reported thus must possess good solubility and have high diffusion coefficients in the organic electrolyte to operate effectively at required charging rates[110]. Future possibilities for improved electrochemical performance include multifunctional additives that protect against both overcharge and thermal runaway. Concurrently, multifunctional additives with polymerizable functionality, as well as fluorine, phosphorus, sulphur, and boron functional groups, are being developed.

2.6.15.1. Overcharge Additives

The charge-cutoff potential of most commercial lithium ion batteries is 4.2V, and oxidative decomposition of the electrolyte occurs at 5V. Overcharging protection additives should be polymerized above 4.2V and below 5V to avoid electrolyte decomposition. If the kinetic effect is taken into account, the electro-oxidative polymerization of the additives should occur at a high enough rate to provide an effective barrier. The additives, on the other hand, must have little negative impact on normal charge-discharge performance. Most of these additives are aromatic compounds like biphenyl, xylene, and cyclohexyl benzene.

2.6.15.2. Redox Shuttle Additives

Many studies have concentrated on redox shuttles with higher potentials than cathodic materials (referred to as "p-type shuttles" here). The redox shuttle's role is thus to impose an upper limit on the cell's potential, thereby avoiding potential damage to the electrolyte and electrode materials. Metallocenes, metal complexes, aromatic molecules, phenothiazine derivatives, 2,2,6,6-tetramethyl-1 piperidinyloxy (TEMPO)-like molecules, conducting polymer, and perfluoroborane cluster salts were all investigated. However, only 2,5-di-tert butyl-1,4-dimethoxybenzene shows promise in long-term cycling in LiFePO₄-based lithium ion batteries [110]. No redox shuttle for the protection of 4 V class cathodic materials has been identified due to the difficulty in reconciling high redox potential and stability. For the first time, this study shows that overcharge protection can be achieved by using a redox shuttle with potentials lower than those of the anodic materials, referred to as an n-type shuttle here. The onset reduction potential of the redox shuttle molecule should be slightly lower than that of the anodic material to prevent self discharge during storage and to allow for some overpotential during charging. Other requirements for such additives are similar to those for p-types: first, the redox shuttle molecule must be unreactive toward all cell components in both its oxidised and reduced forms; second, it must be present in sufficient concentration and have a high enough diffusion coefficient to provide a shunt current that matches the charging current of the cell. Importantly, the molecule must be sufficiently stable or reversible to support long-term cycling.

The disadvantage of this method is that the anodic materials can only be chosen if their potential is greater than that of the redox shuttle mediator. Because its potential is too close to that of lithium deposition, graphite cannot be used as an anodic material. The development of novel anode

materials with higher lithium insertion potentials, such as intermetallic alloys, 3D-nanostructured metal oxides (nitrides, sulphides, phosphides, fluorides), TiO_2 , and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, however, opens up a plethora of new possibilities for future battery applications.

2.6.15.3. Electrolyte Flame Retardant Additives

Based on the flame retardant mechanism and element types, the investigated flame retardant additives can be divided into four groups: phosphorus retardant additives, fluoride retardant additives, ionic liquid additives, and composite flame retardant additives. These various forms of flame retardant additives produce different flame retardancy and electrochemical effects due to differences in retardant free radicals and chemical structure. Microcapsules, electrospinning, and other cutting-edge technologies are now being used to further reduce the negative impact by reducing direct contact between additives and electrolytes.

2.6.15.4. Phosphorus Flame Retardant

Organic phosphorus retardant additives were initially studied extensively due to their wide range of applications, low toxicity, appropriate physical properties, high compatibility, and low cost. The commonly used alkyl carbonate organic solvent, when heated, produces hydrogen radicals (H). The formed H will then combine with oxygen, forming oxygen free radicals (O) and causing the formation of more free radicals [111]. The propagation of the radical reaction must be stopped to prevent the combustion of the electrolyte solvent. Organophosphorus flame retardants are effective radical scavengers, degrading at high temperatures to form H_3PO_4 , and H_3PO_4 will degrade further to form HPO_2 , PO, and PO_2 . The main disadvantage of using phosphate flame retardants as electrolyte additives is that they reduce and cointercalate on the anode. HPO_2 will accelerate carbonate carbonation, while PO and PO_2 will capture H and O [107]. During combustion, phosphorus-containing molecules can degrade to phosphorus-containing free radical species, which can terminate radicals (such as H and OH radicals) formed during chain reaction propagation, resulting in continuous combustion. As previously stated, the addition of phosphorus-based flame retardants reduces electrochemical performance.

2.6.15.5. Fluoride Based Flame Retardant

The most common halogen-containing flame retardants used in lithium ion batteries are organic fluorides. Unlike organic phosphorus additives, organic fluoride additions have low viscosity and excellent performance at low temperatures [78]. Because the C-F bond (105.4 kcal/mol) is

significantly stronger than the C-H bond (98.8 kcal/mol), breaking the C-F bond requires more energy, increasing thermal stability [107]. H radicals can also be reduced or eliminated by substituting fluorine atoms for hydrogen atoms, rendering the electrolyte nonflammable. As a result, organic fluorides are regarded as one of the best materials for producing nonflammable solvents. As a result, fluoride retardant additives outperform phosphate flame retardants in terms of retaining electrochemical performance. This is because the lowest unoccupied molecular orbital (LUMO) of these organic fluoride additives is lower than the LUMO of the electrolyte solvents (they have high electronegativity) [107].

2.6.15.6. Composite Flame Retardants

A few additions in a small amount can greatly improve flame retardant efficiency while also ensuring electrochemical performance [78]. A single flame retardant frequently requires a significant amount of addition, and the additive's solubility and electrolyte compatibility are severely limited. To create more appropriate additives for lithium ion batteries, a composite method that combines the benefits and drawbacks of various types of retardants is required. The most commonly studied composite retardant electrolyte additives are phosphorus-nitrogen and phosphorus-fluorine compounds. In terms of safety and electrochemical performance, fluorinated phosphates, phosphazenes, and their derivatives have received the most attention; they have good thermal stability and high retardant efficiency, and the products of their thermal decomposition are environmentally friendly and have low toxicity [78]. Fluorinated phosphates are the most common F-P compound additions. Fluorination of alkyl phosphates is one of the most common processes. Effective methods for lowering viscosity and fluorination degree, as well as the location and type of fluorinated groups, all have a significant impact on retardant and electrochemical properties [107].

2.6.15.7. Electrolyte Salt Stability

Lithium salts used in lithium ion batteries must typically have strong chemical stability, sufficient solubility, high conductivity, and low toxicity in terms of electrochemical performance. LiPF₆'s thermal instability is critical to the safety of standard commercial electrolytes. Instead of LiPF₆, one of the most effective methods will be to look for an appropriate lithium salt. LiPF₆, lithium perchlorate (LiClO₄), lithium triflate (LiOTf), lithium bis(trifluoromethanesulphonyl)imide (LiTFSI), tetraethylammonium tetrafluoroborate (TEABF₄), and lithium tetrafluoroborate (LiBF₄)

were studied by Lu et al. [34]. [107]. Although lithium bis(oxalate)borate (LiBOB) has good thermal stability, its solubility in carbonates solvents is limited. γ -butyrolactone (GBL) can be used as a LiBOB solvent, but it is easily hydrolyzed and has poor electrode compatibility. The combination of lithium hexafluoroarsenate (LiAsF₆) and tetrahydrofuran (THF) has high electrochemical and thermal stability, but LiAsF₆ toxicity limits its practical use.

To avoid aluminium ion dissolution, the lithium salts must also passivate the aluminium current collector. Continuous corrosion of the aluminium current collector, on the other hand, can cause the electrode material to lose contact with the current collector, introducing extra Al³⁺ into the electrolyte and resulting in performance failure. Decomposition of LiPF₆ can result in the formation of HF, which can then be used to form AlF₃, which can provide a protective passivation film on the aluminium current collector. Despite having extremely high thermal stability and suitable ionic conductivity, new lithium salts such as LiTFSI, lithium bis(fluorosulfonyl) imide (LiFSI), and LiOTf are sometimes stranded because they cannot passivate the aluminium current collector. Thus, using more stable lithium salts has the potential to reduce electrolyte decomposition and electrode corrosion by avoiding the formation of HF. Corrosion of aluminium current collectors must be addressed, which can be improved by adding appropriate additives or high concentrations of lithium salts. This is dependent on the advancement and cost-cutting techniques for these novel lithium salts.

2.6.15.7.1. Lewis Base Stabilizer for Salt

Another excellent method for increasing LiPF₆ thermal stability is to use a Lewis base stabiliser. Breakdown of LiPF₆ produces powerful Lewis acids PF₅ and HF, which induce electrolyte solvent and electrode corrosion side reactions, as described in the investigation of the thermal stability of typical organic electrolytes. LiPF₆ is sensitive to moisture and heat, which causes battery deterioration and safety concerns. A common nitrogen-containing addition, dimethyl acetamide (DMAC), is thought to improve the thermal stability of LiPF₆-based electrolytes. To reduce Lewis acid reactivity, DMAC may form an acid-base complex with LiPF₆ [107].

2.6.16. Non-Flammable Electrolytes

Li-ion batteries now use flammable liquid electrolytes, which pose inherent safety concerns. The decomposition reactivity of the electrolyte (decomposition start temperature and gas volume) is as follows: EMC > EC > DEC > DMC

The vapours remain on fire when Volatile Organic Compounds burn. Though electrolyte additions help prevent thermal runaway, they only play a minor role in increasing battery safety by changing the properties of standard electrolytes. The ultimate solution to the electrolyte's safety issues would be to develop naturally nonflammable electrolytes. Current research focuses on nonflammable liquid electrolytes, liquid-solid electrolytes, and all solid-state electrolytes. Current flammable electrolytes may be replaced with innovative electrolytes such as ionic liquids, polymer electrolytes, and inorganic solid-state electrolytes to obtain safe electrolytes.

Ionic liquids, particularly room temperature ionic liquids, have been extensively researched as nonflammable electrolytes due to their nonvolatility (no observable vapour pressure below 200°C) and nonflammability while having a broad temperature window. Ionic liquids have an excellent electrochemical stability window with cell voltages (up to 7 V), making them suitable for high-voltage electrolytes.

Inorganic solid-state electrolytes may be the most effective electrolyte enhancement strategy when compared to other electrolyte enhancement strategies. However, a number of potential issues, such as low ionic conductivity at room temperature, poor solid-solid contact between electrolyte and electrode, significant ionic transfer resistance, poor rapid charging performance, and high manufacturing costs, have made practical applications difficult.

2.6.17. Non-Flammable Electrodes

A battery's liquid electrolyte is not the only flammable component. Combustible lithiated anode materials (such as lithiated graphite) pose a serious safety risk when LIBs are strongly charged. Flame retardants are in high demand because they effectively prevent fires in solid-state materials. Flame retardants combine with graphite anode material in polymer binders or conductive frameworks. Binders can also be hydrophilic, which helps to avoid the formation of thermally decomposable products.

2.6.18. Pack Safety Technology

Even if cells were created at the exact same time and date with high-quality control, they are unlikely to remain homogeneous after many cycles of operation. Different temperatures across the battery pack, cell voltages, parallel branch currents, climatic conditions, and variable mechanical and electrical stress are a few of the causes.

The more cells in a pack that are connected in series, the greater the diversity between cells, causing cells to drift further apart. Cycling the pack with cells at different SOC's causes rapid deterioration. Pack-level safety measures are advantageous in large electrical applications for practical reasons. Battery-package designs and thermal runaway barriers can withstand high-impact forces, vibration, thermal propagation, and gas release. The battery management system, on the other hand, is concerned with heat management, estimating battery status, and troubleshooting (BMS). The collaboration of passive protection designs for battery packs and BMS can compensate for the shortcomings of cell-level safety measures.

Current solutions for incorporating passive propagation resistance into the pack include a combination of cell selection, cell spacing, pack design, and interstitial material such as mica sleeves. Cylindrical cells, such as those patented by Tesla and used in NASA space applications batteries, are frequently used in propagation-resistant designs. Because the geometric inefficiency of cylindrical cells wastes a lot of space, the volumetric energy density is also limited.

Pouch format cells are frequently wrapped in a lighter aluminized polymer, they have a significantly higher energy density (Wh/L) and a higher specific energy (Wh/kg). The brittle design of pouch cell terminal tabs makes maintaining space between them more difficult, and the pouch cells break apart at pressures as low as 50 psi, spilling flammable liquid electrolytes and vapours and resulting in larger fires. As a result, they are significantly more difficult to design in a system that considers propagation resistance.

2.6.12.1. Passive Protection

Passive protection solutions, such as package structural designs and thermal runaway barriers, play an important role in increasing battery package safety. Eberhard et al. proposed a battery packaging design with ventilation apertures and channels [112]. The proposed design aligns ventilation apertures in the conductor plate with the safety vents and configures ventilation channels to transport gas from the ventilation openings to the cover's edge. The top frame and O-rings create a pre-load to limit motion during vibration, and the O-ring can prevent hot gases from entering adjacent cells. As a result of the aperture and channel, gases from one battery's safety vent can be sent to the outside of the battery packaging, preventing other batteries in the battery packaging from heating up. To prevent side-wall ruptures in battery packaging, manufacturers include a bottom vent for cylindrical cells, such as the Sony US18650VC7. Anderson et al. [113] discovered

that a bottom rupture in a battery package caused a significantly lower temperature rise than a side wall rupture. Arora and Kapoor [114] proposed two battery packaging concepts for electric vehicles (EVs) that were intended to protect the batteries from high-impact forces, vibration, and thermal runaway. They advocate for a large number of pressure release valves, particularly for thermal runaways, to strategically release gases. The pressure release valve works similarly to the safety vent in a Li-ion battery. Furthermore, the spreading heat of thermal runaway may melt packing brackets. Thermal blocking, such as air gaps in the package, a stiff spacer, or a mica sleeve, aids in mitigating this problem.

2.6.18.2. BMS and BTMS Technology

In addition to sensing cell voltages, cell temperatures, and total current flowing through the battery pack, a BMS must provide a charge equalization solution. This ensures that the discharge and charge rates of each cell in the battery pack are comparable. Any application field that requires a battery pack system requires suitable isolation devices or a contactor controller that is managed and overseen by the BMS, in addition to the battery cells and BMS.

BMSs are sophisticated hardware and software integrated systems that not only monitor each cell's voltage, current, and temperature, but also: (1) calculates the leftover charge, (2) calculates the remaining cycle life, (3) manages data acquisition, (4) performs battery uniformity and equalization processes, (5) dynamically controls the charging and discharging rate, and (6) transmits and receives signals from other electronic components. A BMS is built on the accuracy of every external battery cell parameter in the battery pack system. The design criteria for monitoring and detecting circuits are quite demanding due to the reliance on measurement reliability, and assessment is required to ensure the required predicted values. The main current sensor, cell voltage sensor, and temperature sensors are the system's three primary inputs. Typical battery pack current accuracies for an electric vehicle are 0.5%-1.0% up to 450 A, 1-2 mV for cell voltages, and 0.1% for battery pack voltage up to 600 V. [115]. The lithium-ion phosphate (LFP) type battery chemistry requires high precision for measuring cell voltages due to the highly flat characteristic (voltage-capacity) curves.

The priority assessment determines the rate of data acquisition, or the sample durations for each data stream, with shorter sampling times, in the range of 10^{-3} s, required for critical measurements such as cell voltages and current to allow accurate state estimation. The BMS generates outputs

based on the data or information received, such as activating the safety contactors to isolate the battery pack if any parameters are out of range. Generic analogue or digital outputs include indicators that control fan speed for heat management, switching contacts, and communications. Other measures can withstand lower frequencies in order to reduce power consumption and the architecture complexity of the firmware system.

Another important consideration for measurement circuits is the electromagnetic compatibility of the layout design, particularly for automobile traction applications where all power electronic components are close to the BMS in most cases. A good anti-electromagnetic interference design for the BMS will ensure the reliability and quality of the data gathered while also improving the processing stage. Battery capacity in vehicle applications can degrade by up to 20%, while internal resistance can rise by up to 160% above its initial value [116]. In automotive applications, the BMS typically uses the Controller Area Network (CAN) bus for communication and networking, whereas in other applications, the USB, Integrated Circuit (I2C), and RS232 and EIA485 (formerly RS485) connections are equally well adapted [117].

Battery packs are made up of cells connected in series that degrade at different rates, resulting in differences in measured values over time, and battery equalization is a strategy used in BMS design to address this issue. A battery management system (BMS) is a type of electrical system that monitors and controls the status of one or more batteries. Performance management (e.g., cell monitoring and balancing), protection (e.g., thermal management), state estimation (e.g., estimation of state of health (SOH) and state of charge (SOC), fault diagnosis (e.g., fault diagnosis and prognosis), and communication (e.g., data storage and transmission) are all functions performed by a BMS [118]. Battery thermal management is required to keep the battery or battery pack temperature within acceptable limits [119]. Thermal management technologies such as air cooling [120], liquid cooling [121], and heat pipe cooling [122] have been developed to disperse produced heat and avoid temperature rise.

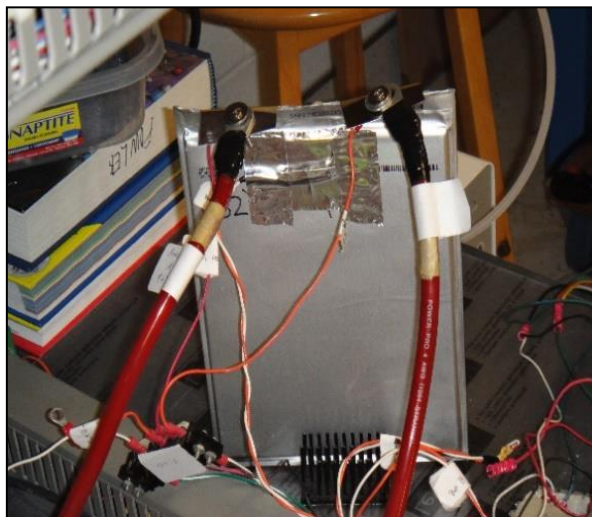
Chapter 3 Experimental Set-up

3.1. Cell Level Experiments

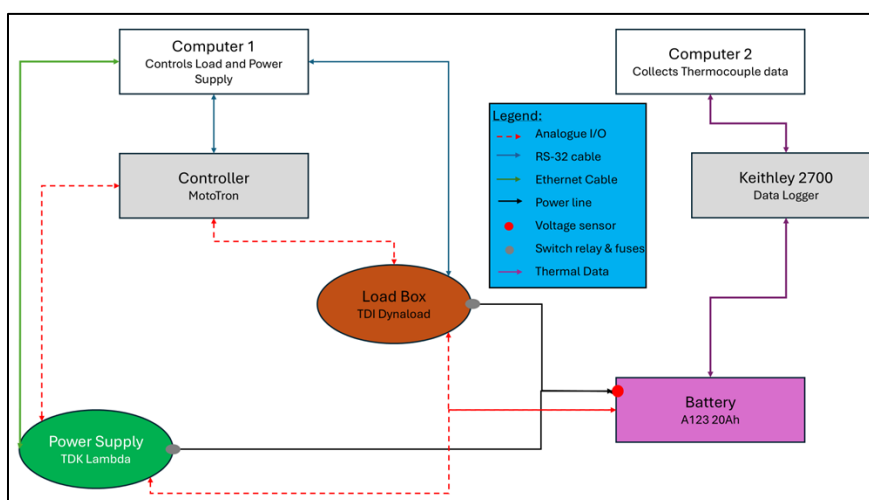
The experimental setup is shown in Figure 25. A 20-Ah prismatic LiFePO_4 A123 lithium-ion battery cell was used. The cell specifications are presented in Table 4. The cooling method was natural convection through air cooling, with the battery being placed vertically in a stand and the temperature in the laboratory being approximately 22°C . The test bench consisted of five components: 1) a charging unit; 2) a load box; 3) a LabVIEW National Instrument (NI) temperature measurement device; 4) computer 1; and 5) computer 2.



a) Experimental set-up



b) Picture of battery cell



c) Schematic of Experimental Setup

Figure 25: Experimental set-up and battery cell

The thermal behavior of the battery was recorded at four different constant current discharge rates: 1C, 2C, 3C, and 4C. The charge rate (constant current-constant voltage) was 1C. The XBL 50-150-800 Dynaload load box which has a maximum limit of 800 W was used to discharge the battery. A TDK-Lambda power supply with maximum limits of 20 V and 40 A was used to charge the cell. The load box was connected to the cell using heavy-duty copper cables with a 100 A fuse placed in between. The temperature was measured using T-type thermocouples. These thermocouples were connected to an NI temperature measurement device which was then connected to the computer. LabVIEW 8.2 software was used to control the NI temperature measurement device. The locations of the Thermocouples are shown in Figure 26.

The second paper's test bench consisted of four components: 1) Maccor battery tester; 2) thermal chamber; 3) 8 channel USB thermal couple; 4) computer. The experimental setup consisted of three 20-Ah prismatic LiFePO₄ A123 lithium-ion batteries at various SOH's whose cell specifications are listed in Table 4.

Table 4: Prismatic 20-Ah Lithium-ion (LiFePO₄) cell specifications

Specification	Value	Unit
Material for electrolyte	Carbonate based	-
Material for anode	Graphite	-
Material for cathode	LiFePO ₄	-
Voltage (nominal)	3.3	V
Dimensions	7.25 (t) x 160 (w) x 227 (h)	mm
Capacity of the cell (nominal)	72000	C
Discharge power	1200	W
Energy (nominal)	234000	J
Specific energy	471600	J/kg
Energy density	889.2	J/m ³
Operating temperature	- 30 to 55	°C
Storage Temperature	- 40 to 60	°C
Mass of the cell	0.496	kg

Specific power	2400	W/kg
Internal resistance	5e-4	Ω
Volume	2.63e-4	m ³
Storage temperature	- 40 to 60	°C
Number of cycles	Min. 300, approx. 2000	Cycles
Max Discharge Current	300	A
Max Charge Current	300	A

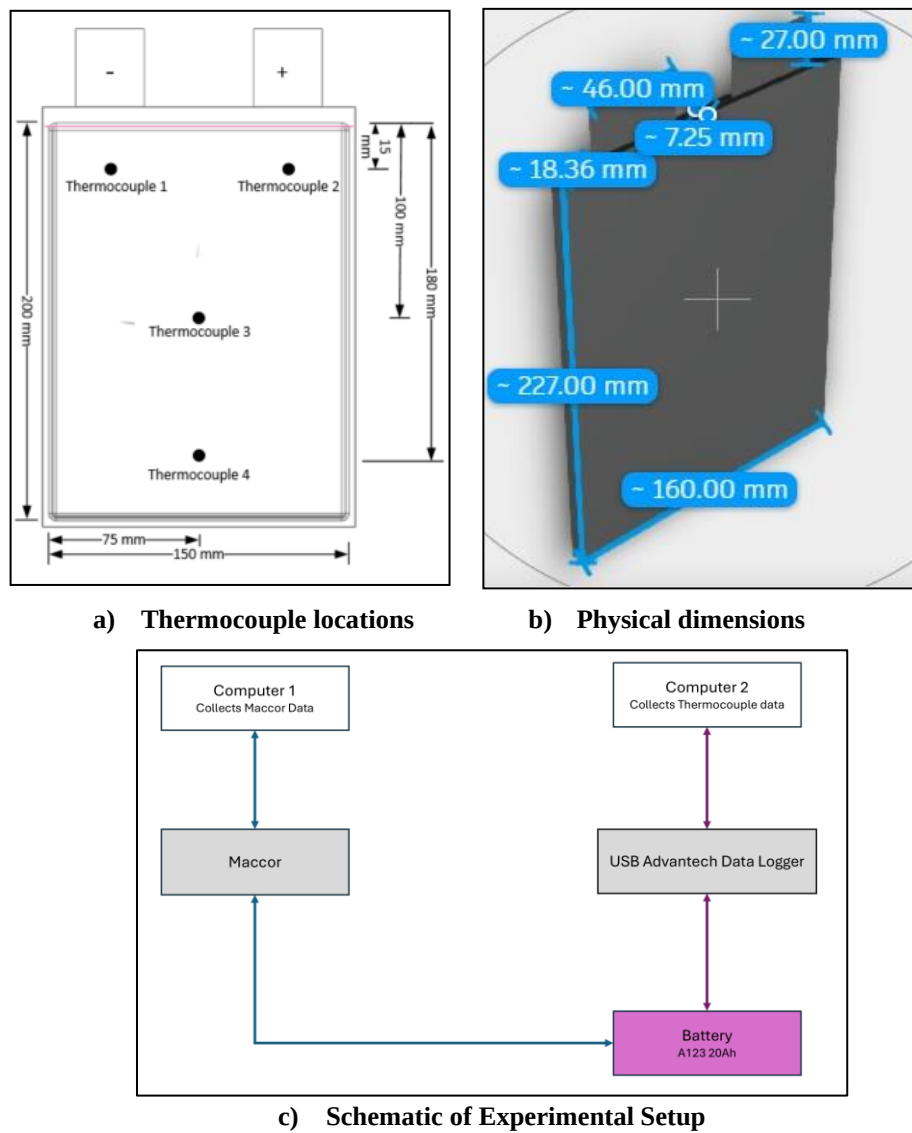


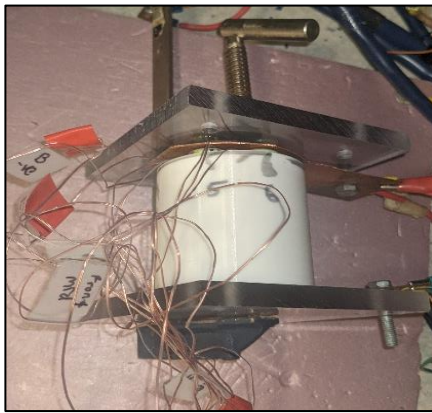
Figure 26: Thermocouple locations, physical dimensions and schematic of Experimental Setup

The cooling method was natural convection by air cooling, with the battery mounted vertically in a stand within the thermal chamber. The batteries were charged at constant current-constant voltage (CCCV) at 1C and left to rest for 2 hours to acclimate to the ambient temperature of the thermal chamber. The thermal couples then recorded the battery's performance at three different constant current discharge rates: 1C, 2C and 3C. The 5 ambient temperatures examined were at 5°C, 15°C, 25°C, 35°C, 45°C. Three batteries at 90.575%, 83.435%, 65.025% SOH were tested under the conditions described. The internal resistance was then modeled under these operating conditions.

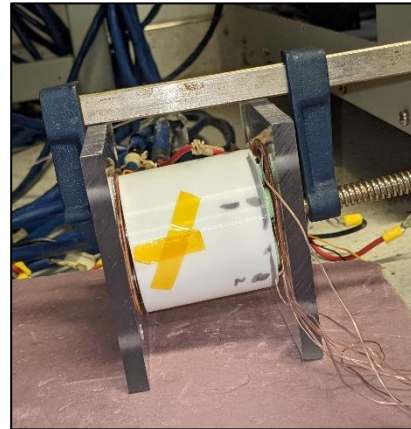
3.2. Experimental Setup and Procedure for Parallel Battery Pack

The Experimental Setup and procedure for our 7 parallel battery pack setup is shown in Figure 27. In the setup we see 7 Panasonic NCA cells connected in parallel each rated at 3.2Ah capacity. The individual cell capacities were measured and averaged and found to be 3.11Ah experimentally. The setup contains no BMS and batteries will discharge and charge to equilibrate voltage at end of discharge. The limiting current is low and thus this poses less safety hazards. Ambient air cooling was the method of cooling investigated with the ambient environmental temperature being approximately 22°C for all experiments.

The test bench consisted of five components: 1) a MACCOR Model 4200; 2) a USB 4718 Advantech thermocouple with 8 T-type thermocouples; 3) computer 1 for electrical data collection; and 4) computer 2 for thermal data collection. The thermal behavior of the battery was recorded at six different discharge rates (constant current): 0.5C, 0.75C, 1C, 1.25C, 1.5C, 1.75C. The charge rate (constant current-constant voltage) was 1C. The temperature was measured using T-type thermocouples. These thermocouples were connected to a USB 4718 Advantech datalogger which was then connected to the computer-2. The numbering convention of the cells is shown in Figure 28.



a) Pack with thermocouple locations



b) Clamping of battery cell

Figure 27: Parallel Battery Pack Setup

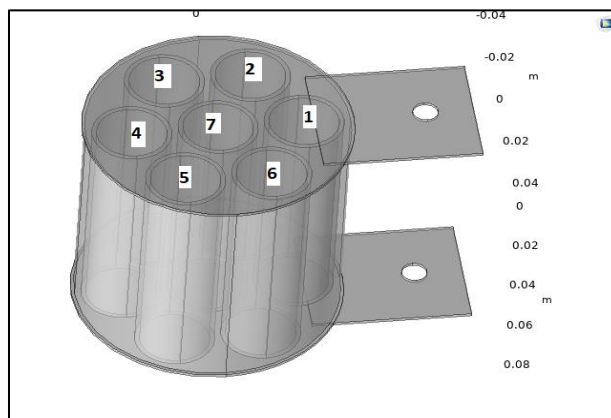


Figure 28: Cylindrical 7p pack cell numbering convention

Chapter 4 Model Development

4.1. Matlab PDEPE Model

4.1.1. R_{int} Model

The R_{int} model is developed with the Internal resistance as functions of SOC and C rate. These results are developed using the governing equations presented below.

4.1.1.1 R_{int} Model Governing Equation

The derivation for the final form is presented in Derivation 2. The R_{int} models are shown below

$$R_{int} = \left(A_1 + A_2 \frac{\ln \left(\frac{I}{A_3} + \sqrt{\frac{I^2}{A_3} + 1} \right)}{I} \right) e^{A_4 SOC} \quad (25)$$

$$R_{int} = \left(A_1 + A_2 \frac{\ln \left(\frac{I}{A_3} + \sqrt{\frac{I^2}{A_3} + 1} \right)}{I} \right) \left(A_4 \left(1 + \frac{SOC}{A_5} \right)^{A_6} \left(1 - \frac{SOC}{A_7} \right)^{A_8} \right) \quad (26)$$

The values for the coefficients are presented in Table 5.

Table 5: Parameters for Equations (25) and (26)

Coefficient	Equation (25)	Equation (26)
A_1	0.0009630	0.1892
A_2	0.1845	-39.2282
A_3	6.8271	-5.9383
A_4	-0.9523	0.3689
A_5	-	-63127901
A_6	-	-102858633
A_7	-	-0.0011964237
A_8	-	-0.9827

Both equations are used and presented in the results and discussion section with the results shown in Figure 39.

4.1.1.2 R_{int} Energy Equation

The energy balance equation for the R_{int} model is simply given by:

$$-hA(T - T_{amb}) + I\eta = \rho c_p \frac{\partial T}{\partial t} \quad (27)$$

h is the convective heat transfer coefficient, A is the surface area of the battery, ρ is the density, c_p is the specific heat, T_{amb} is the ambient temperature, T is the average temperature of the battery. This model assumes a uniform heat distribution; the source term, accumulation term and convective boundary condition have no spatial information.

4.1.2. Physiochemical Model

The Matlab physio-chemical model comes from a 1-D electrochemical model where the cathode length, anode length, and separator length are inputs. The governing equations, boundary conditions, material properties, and parameters used are presented in Table 2. We note that the effect of the distance between the electrodes ie the size of the separator is an important effect that is typically neglected in the Randles-Sevcik and Cottrell equation for example. We also note that the largest component of the heat and energy loss is from the potential drop across the separator which is approximately linear with length. In the electrodes the current is primarily carried through the solid electrode material with high conductivities with minimal electrolyte current while in the separator the electrolyte current is approximately the entire cell current and the electrolyte potential gradient is non negligible. The electrochemical model used can accurately predict the concentrations of the intercalated lithium and lithium-ions as well as the salt electrolyte concentration and the overpotential. These types of models allow us to understand the battery phenomenon precisely; even at the particle-level where we can, for example, solve for the particle surface concentration and its relationship to various electrochemical-thermal outcomes. Finally, the model results are compared against the experimental data of the surface temperature of the 20-Ah prismatic cell at 1C, 2C, 3C, and 4C discharge rates.

4.1.2.1 Energy Equation

The energy balance equation for the matlab model is given by [2]:

$$-hA(T - T_{amb}) + \dot{q} = \rho c_p \frac{\partial T}{\partial t} \quad (28)$$

and,

$$\nabla (\sigma_+ \nabla \phi_+) = -j = \frac{-I}{V_{battery}} \quad (29)$$

$$\nabla (\sigma_- \nabla \phi_-) = +j = \frac{I}{V_{battery}} \quad (30)$$

$$\dot{q} = \nabla (\sigma_+ \nabla \phi_+) \phi_+ + \nabla (\sigma_- \nabla \phi_-) \phi_- + \dot{q}_{ECH} \quad (31)$$

where $\dot{q}_{ECH}$ is the electrochemical heat and is given by [2]:

$$\dot{q}_{ECH} = \nabla (\sigma_- \nabla \phi_-) \left(T \frac{\partial E_{eq}}{\partial T} \right) \quad (32)$$

where $\dot{q}$ is the heat generation rate and includes joule heating expressed in an alternative form of voltage squared over resistance, activation loss/Ohmic loss/concentration loss expressed in an alternate form of the current multiplied by the overpotential, and the entropic heat (reversible heat) alternatively expressed as the temperature multiplied by the entropy and $V_{battery}$ is the battery volume. As this is a 1D model the heat produced has to be assumed to be uniform throughout the battery and this results in a model that cannot incorporate phenomenon such as thermal gradients due to tab temperatures. Table 6 contains the parameter values for the simulation.

Table 6: Parameters used for model development [2–8]

Parameter	Notation	Value	Unit
Thickness of positive (+ve) electrode	l_p	183e-6	m
Thickness of separator	l_s	52e-6	m
Thickness of negative (–ve) electrode	l_n	100e-6	m
Particle radius for +ve electrode	$R_{s,p}$	13e-06	M
Particle radius for –ve electrode	$R_{s,n}$	12.5e-06	M
Maximum solid Li^+ concentration for +ve electrode	$C_{s,p,max}$	21190	mol/m ³
Maximum solid Li^+ concentration for –ve electrode	$C_{s,n,max}$	31507	mol/m ³
Initial solid Li^+ concentration for +ve electrode	$C_{s,p,0}$	1900	mol/m ³

Initial solid Li ⁺ concentration for –ve electrode	$C_{s,n,0}$	30500	mol/m ³
Initial electrolyte salt concentration	C_o	3600	mol/m ³
Initial temperature	$T_{Initial}$	22.4	°C
Electrode phase volume fraction, +ve electrode	$\epsilon_{s,p}$	0.39	-
Electrode solid phase vol-fraction -ve electrode	$\epsilon_{s,n}$	0.379	-
Volume fraction for separator	ϵ_s	1	-
Diffusion coefficient for +ve electrode	$D_{s,p}$	3.2e-13	m ² /s
Diffusion coefficient for -ve electrode	$D_{s,n}$	1.45e-14	m ² /s
Diffusion coefficient for electrolyte	D_l	7.5e-11	m ² /s
Double layer capacity	Cdl	0.01	
Electrolyte conductivity	k	2	S/m
Conductivity for +ve electrode	σ_p	190	S/m
Conductivity for –ve electrode	σ_n	190	S/m
Equilibrium potential	U	SOC-OCV curve	V
Exchange current density	i_0	1.5e-2	A/m ²
Anodic transfer coefficient	α_a	1	-
Cathodic transfer coefficient	α_c	1	-
Electrolyte reference concentration	$C_{e,ref}$	1000	mol/m ³
Electrolyte diffusivity	D_e	7.5e-11	m ² /s
Transport number for electrolyte	t_+	0.5	-
Reference temperature	T_{ref}	298	K
Heat transfer coefficient	H	15	W/m ² K
Universal gas constant	R	8.3144	kJ/kg mole K
Faraday’s constant	F	96487	coulomb/mole
Density for battery material	ρ_a	2055.2	kg/m ³
Specific heat for active zone	C_p	1399.1	J/kg-K
Thermal conductivity for active zone	K_a	0.89724	W/m-K

This table contains all the values necessary to perform the simulation in MATLAB. $\frac{\partial E_{eq}}{\partial T}$ values for various states of charge are presented in Table 7 and Table 8.

Table 7: Open circuit partial derivative with respect to temperature for the iron phosphate cathode

SOC	dEq/DT	SOC	dEq/DT	SOC	dEq/DT
1	8.62E-06	0.69	-1.97E-05	0.38	-7.13E-05
0.99	8.62E-06	0.68	-2.15E-05	0.37	-7.29E-05
0.98	2.88E-05	0.67	-2.34E-05	0.36	-7.47E-05
0.97	4.27E-05	0.66	-2.54E-05	0.35	-7.66E-05
0.96	5.15E-05	0.65	-2.74E-05	0.34	-7.87E-05
0.95	5.64E-05	0.64	-2.94E-05	0.33	-8.10E-05
0.94	5.81E-05	0.63	-3.15E-05	0.32	-8.33E-05
0.93	5.75E-05	0.62	-3.37E-05	0.31	-0.00014
0.92	5.51E-05	0.61	-3.58E-05	0.3	-0.00014
0.91	5.15E-05	0.6	-3.79E-05	0.29	-0.00015
0.9	4.70E-05	0.59	-4.00E-05	0.28	-0.00015
0.89	4.21E-05	0.58	-4.21E-05	0.27	-0.00015
0.88	3.69E-05	0.57	-4.41E-05	0.26	-0.00016
0.87	3.18E-05	0.56	-4.61E-05	0.25	-0.00016
0.86	2.67E-05	0.55	-4.80E-05	0.24	-0.00017
0.85	2.19E-05	0.54	-4.98E-05	0.23	-0.00017
0.84	1.74E-05	0.53	-5.15E-05	0.22	-0.00017
0.83	1.32E-05	0.52	-5.32E-05	0.21	-0.00021
0.82	9.43E-06	0.51	-5.47E-05	0.2	-0.00017
0.81	5.98E-06	0.5	-5.62E-05	0.19	-0.00017
0.8	2.86E-06	0.49	-5.75E-05	0.18	-0.00017
0.79	5.61E-08	0.48	-5.88E-05	0.17	-0.00017
0.78	-2.48E-06	0.47	-6.00E-05	0.16	-0.00017
0.77	-4.79E-06	0.46	-6.12E-05	0.15	-0.00017
0.76	-6.91E-06	0.45	-6.24E-05	0.14	-0.00017
0.75	-8.88E-06	0.44	-6.35E-05	0.13	-0.00017
0.74	-1.08E-05	0.43	-6.47E-05	0.12	-0.00016
0.73	-1.26E-05	0.42	-6.58E-05	0.11	-0.00016
0.72	-1.43E-05	0.41	-6.71E-05	0.1	-0.00016
0.71	-1.61E-05	0.4	-6.84E-05	0	-0.00031
0.7	-1.78E-05	0.39	-6.98E-05		

Table 8: Open circuit partial derivative with respect to temperature for the graphite anode

SOC	dEq/DT
0	0.0003
0.17	0
0.24	-6.0e-05
0.28	-0.00016
0.5	-0.00016
0.54	-9.0e-05
0.71	-9.0e-05
0.85	-0.0001

Since the major component of the energy loss and the heat produced within the battery comes from the overpotential caused by the potential drop across the electrolyte layer or more simply the resistance of the electrolyte, we then relate the electrolyte potential drop to the overpotential at the electrolyte/electrode interface. This is true as the electrolyte current within the electrode is negligible compared to the electrolyte current within the separator. The equation is then:

$$\dot{q} = \nabla (\sigma_+ \nabla \phi_+) \eta_{AnodeInterface} - \nabla (\sigma_+ \nabla \phi_+) \eta_{CathodeInterface} + \dot{q}_{ECH} \quad (33)$$

where $\eta_{AnodeInterface}$ is the overpotential at the anode/electrolyte interface and $\eta_{CathodeInterface}$ is the overpotential at the cathode/electrolyte interface.

4.2. Matlab Practical Rint Thermal Model

The internal impedance surface fit experimental measurements with a Pearson coefficient of 0.945. 3 thermal models were then created that implemented the internal resistance model. The first two thermal models were 0D models that did not include the influence of the thermal conductivity of the battery. The first model assumed simple heating through internal resistance and convection energy loss while the second also included the Bernardi Reversible heat term. The final third model was a 2D model that included all A mathematical model is used to calculate the internal impedance resistance of a LiFePO4 battery at five various ambient temperatures (5, 15, 25, 35, 45 °C), three different discharge rates (1C, 2C, 3C), and three different SOH values (90%, 83%, 65%). Equivalent circuit models are well-known for their ease of construction, simple structure, and integration with Kalman filter estimates [123]. They do, however, require massive data tables that

model parameters as functions of temperature and SOC. They are particularly weak as SOH varies [124,125], and this research attempts to remedy the problem by estimating resistance whilst lowering the size of the data table. Overall, similar circuit models need minimal computational effort to fit parameters while maintaining physical meaning. Typical physiochemical models include variables like porosity and tortuosity that are hard to directly measure; instead, this method allows model parameters such as internal resistance to be easily calculated with more practical measurements.

The internal impedance surface fit the experiments and had a Pearson's coefficient of 0.945. Three thermal models were subsequently developed to implement the internal resistance concept. The first two thermal models were 0D models, which failed to account for the battery's thermal conductivity. The first model assumed simple heating via internal resistance and convection energy loss, while the second included the Bernardi Reversible heat term. The third model was a two-dimensional model that included all previous heat source terms as well as tab heating.

4.2.1. Rint Model

Internal resistance is one of the most important battery parameters when modeling lithium ion batteries. The time constants for RC pairings might vary from a few seconds to hundreds of seconds [124]. Because the time constants for a 1RC model are minimal and our experiments are conducted at constant current, the simulation employs a single Rint model.

Characteristic energy losses in the battery include the mass concentration loss, the activation loss and the ohmic loss. Along with the reaction's reversible heat, all these energy losses cause the battery to produce heat. The reversible heat of reaction is not included in the internal resistance term; however, because it does not contribute to an overpotential. The following model is then derived to model the internal resistance as a function of the SOH, SOC, T and C-rate.

$$\begin{aligned}
 R_{int} = & A_1 + (A_2 + 1)SOH * A_3 + (A_2 + 1)SOH * T * SOH * A_4 * \frac{\operatorname{asinh}\left(\frac{I * SOC}{A_5}\right)}{I * SOC} \\
 & + \frac{\left(A_6 * \ln((A_2 + 1)SOH * I * SOC) + A_7 + \frac{A_8}{T}\right)}{\frac{I * SOC}{(A_2 + 1)SOH * \ln\left(\frac{1}{SOC}\right) * \exp\left(\frac{A_{10}}{T}\right)}} + A_9
 \end{aligned} \tag{34}$$

The proposed model is a 10 parameter nonlinear equation that has been fit using matlabs nlinfit function. The parameter values are presented in Table 9.

Table 9: Parameter values of Rint model for 20-Ah Lithium-ion (LiFePO₄) cell

Parameters	Value
A_1	0.00464525014640678
A_2 (soh $\leq$ 0.75)	2195.59542219420
A_2 (soh $>$ 0.75)	0
A_3	-1.46270584472594e-05
A_4	3.59581952923939
A_5	65135338.3641966
A_6	0.00423167528877116
A_7	-0.308670691280175
A_8	97.6415477501266
A_9 (soh $\leq$ 0.35)	52690.0765564303
A_9 (soh $>$ 0.35)	0
A_{10}	-7642.78883082046

4.2.2. Thermal Models

4.2.2.1. 0D Models

The first thermal model is a simple thermal model that applies the values in Table 9 and Equation (34) to solve the differential Equation (27). The second thermal model includes an additional heat source term, the heat of reaction, and is the 0-D form of the Bernardi heat equation:

$$I^2 R_{int} + IT \frac{dV_{ocv}}{dT} - hA(T - T_{amb}) = \rho c_p \frac{dT}{dt} \quad (35)$$

Table 7 and Table 8 show the values of the open circuit voltage derivative with respect to temperature as a function of SOC for the anode and cathode, respectively. The open circuit voltage derivative with respect to temperature is represented as a function of SOC, and it is worth noting that the reversible heat of reaction is an exact differential that is not path dependent; like latent heat which is a simple phase change heat. Furthermore, the change in sign of the differential suggests a change in entropy, implying that the number of moles of products versus reactants in the proposed reaction is not constant.

The model parameters are shown in Table 10. Along with the cell specifications in Table 4, these parameters are sufficient to solve the simulation equations.

Table 10: 0D Model Parameters

Parameters	Value
h	30 W/m ² -K
C _p	1399.1 J/Kg-K

4.2.2.2. 2D Thermal Model

The 2D model solves the finite center difference in 2 dimensions as

$$T_n(i, j) = T_{n-1}(i, j) + dt * Dx * (T_{n-1}(i + 1, j) - 2T_{n-1}(i, j) + T_{n-1}(i - 1, j)) + dt * Dy * (T_{n-1}(i, j + 1) - 2T_{n-1}(i, j) + T_{n-1}(i, j - 1)) + dt * (\dot{Q}) \quad (36)$$

Where $T_n(i, j)$ is the current temperature at the current particular point in the mesh, $T_{n-1}(i, j)$ is the temperature at the current point in the mesh at the previous time step, $T_n(i + 1, j)$ is the temperature at the current time one step forward in the x direction and $T_n(i, j + 1)$ is the temperature at the current time one step forward in the y direction.

$\dot{Q}$ is the sum of the drains and sources of heat generation namely the heat of reaction, the heat due to internal resistance and the convection loss

$$\dot{Q} = dt * \left(\frac{hA_s * (T_n(i, j) - T_{amb}) + I^2 R_{int} + IT \frac{dV_{ocv}}{dT}}{mc_p} \right) \quad (37)$$

Where Dx and Dy are related to the thermal diffusivity D as:

$$D = \frac{K}{\rho c_p} \quad (38)$$

$$Dx = \frac{D}{dx^2} \quad (39)$$

$$Dy = \frac{D}{dy^2} \quad (40)$$

These equations are integrated over time using Euler's method, while ensuring the time step is below the Lyapunov Stability requirement (which ignores the heat source term's effect on integration instability). The condition is shown as follows:

$$dt \leq \frac{1}{2D \left(\frac{1}{dx^2} + \frac{1}{dy^2} \right)} \quad (41)$$

The mesh is made by dividing the rectangular battery in 32 sections lengthwise and widthwise.

The Boundary and initial conditions are shown below:

$$T_0(i, j) = T_{amb} \quad (42)$$

$$T_{OuterEdges} = T_{amb} + dt * \left(\frac{hA_s * (T_n(i, j) - T_{amb})}{mc_p} \right) \quad (43)$$

$$T_{Tab} = T_{amb} + dt * \left(\frac{I^2 R_{tab} + hA_s * (T_n(i, j) - T_{amb})}{mc_p} \right) \quad (44)$$

The parameter values for the simulation of the 3 different batteries at the experiments 3 different SOH's are provided in Table 11.

Table 11: 2D Thermal Model Parameter Values for Battery at 3 Experimental SOH's

Parameters	Value
K_1	0.0377757588962245 W/m-K
K_2	0.0178121519590705 W/m-K
K_3	0.0624207807204560 W/m-K
C_{p1}	3986.00308951209 J/Kg-K
C_{p2}	2986.66515688565 J/Kg-K
C_{p3}	2021.05662188790 J/Kg-K
ρ_1	5301.72113058348 Kg/m ³
ρ_2	5287.68681411875 Kg/m ³
ρ_3	5001.48714291314 Kg/m ³
h_1	32.4700692138125 W/ m ² -K
h_2	32.2759597374317 W/m ² -K
h_3	43.3441981300425 W/ m ² -K
$R_{TabCathode1}$	0.177245139786570 ohms

$R_{\text{TabCathode2}}$	0.164424608688326 ohms
$R_{\text{TabCathode3}}$	0.185427892281434 ohms
$R_{\text{TabAnode1}}$	0.175497948667648 ohms
$R_{\text{TabAnode2}}$	0.175348069630722 ohms
$R_{\text{TabAnode3}}$	0.155335133882801 ohms

4.3. COMSOL Model

The COMSOL model are produced using the same prismatic Li-ion cell with the same dimensions and chemistry (LiFePO_4) as the Matlab model data. The electrolyte modeled was LiPF_6 in ethylene carbonate plus solvent mixture with electrolyte parameters given in Table 12.

Table 12: Parameters used for model development [3,6]

Parameter	Notation	Value	Unit
Thickness of +ve electrode	l_p	183	μm
Thickness of separator	l_s	52	μm
Thickness of -ve electrode	l_n	100	μm
Particle radius for +ve electrode	$R_{s,p}$	8×10^{-6}	m
Particle radius for -ve electrode	$R_{s,n}$	5.5×10^{-6}	m
Maximum solid Li^+ Concentration for +ve electrode	$C_{s,p,\text{max}}$	21,190	mol/m^3
Maximum solid Li^+ Concentration for -ve electrode	$C_{s,n,\text{max}}$	31,507	mol/m^3
Initial solid Li^+ concentration for +ve electrode	$C_{s,p,0}$	1900	mol/m^3
Initial solid Li^+ concentration for -ve electrode	$C_{s,n,0}$	30,500	mol/m^3
Initial electrolyte Salt Concentration 1C	C_o	3600	mol/m^3
Initial electrolyte Salt Concentration 2C	C_o	2700	mol/m^3
Initial electrolyte Salt Concentration 3C	C_o	2700	mol/m^3
Initial electrolyte Salt Concentration 4C	C_o	2100	mol/m^3
Initial Temperature 1C	T_{Initial}	22.40049894	$^{\circ}\text{C}$
Initial Temperature 2C	T_{Initial}	22.93849524	$^{\circ}\text{C}$

Initial Temperature 3C	$T_{Initial}$	23.15404348	°C
Initial Temperature 4C	$T_{Initial}$	22.88495268	°C
Electrolyte phase volume fraction, +ve electrode	$\epsilon_{l,p}$	0.54	-
Electrode phase volume fraction, +ve electrode	$\epsilon_{s,p}$	0.39	-
Electrolyte phase volume fraction, -ve electrode	$\epsilon_{l,n}$	0.6	-
Electrode Solid phase vol-fraction -ve electrode	$\epsilon_{s,n}$	0.379	-
Volume fraction for separator	ϵ_s	1	-
Filler fraction for +ve electrode	$\epsilon_{f,p}$	0.07	-
Filler fraction for -ve electrode	$\epsilon_{f,n}$	0.021	-
Diffusion Coefficient for +ve electrode	$D_{s,p}$	3.2×10^{-13}	m ² /s
Electrolyte Conductivity	K	$\sigma_1 \left(\frac{C}{C_{e,ref}} \right)$	S/m
Burggeman porosity exponent	B	1	-
Conductivity for +ve electrode	σ_p	91	S/m
Conductivity for -ve electrode	σ_n	100	S/m
Equilibrium Potential	U	$E_{eq}(SOC) \frac{dE_{eq}}{dT}(SOC) \times (T - 298)$	V
Temperature derivative of equilibrium potential	$\frac{dE_{eq}}{dT}$	$\frac{dE_{eq}}{dT}(SOC)$	V/K
Maximum -ve electrode state of charge		0.98	-
Minimum -ve electrode state of charge		0	-
Maximum +ve electrode state of charge		0.9	-
Minimum +ve electrode state of charge		0.01	-
Reference exchange current density for +ve electrode	$i_{0ref,pos}$	20	A/m ²
Reference exchange current density for -ve electrode	$i_{0ref,neg}$	25	A/m ²
Anodic Transfer Coefficient	α_a	0.5	-

Cathodic Transfer Coefficient	α_c	0.5	-
Electrolyte Reference Concentration	$C_{e,ref}$	1000	mol/m ³
Electrolyte diffusivity	D_e	7.5×10^{-11}	m ² /s
Transport number for electrolyte	t_+	0.363	-
Activity Dependence of the electrolyte	$\frac{\partial \ln f_{\pm}}{\partial \ln C_e}$	0	-
Film Resistance on -ve electrode 1C	R_{film}	0.05	Ωm^2
Film Resistance on -ve electrode 2C	R_{film}	0.05	Ωm^2
Film Resistance on -ve electrode 3C	R_{film}	0.04	Ωm^2
Film Resistance on -ve electrode 4C	R_{film}	0.02	Ωm^2
Nominal capacity of cell	C	20	Ah
Minimum stop voltage	V_{min}	2.0	V
Maximum stop voltage	V_{max}	4.1	V
Reference temperature	T_{ref}	298	K
Universal gas constant	R	8.3143	kJ/kg mole K
Faraday's constant	F	96485	coulomb/mol e

A 1-D electrochemical model is created where the cathode length, anode length, and separator length are input with an added extra dimension for particle radius along with the relevant parameters to calculate the heat generated from the battery. The average heat from the 1-D electrochemical model is then used as a heat source in addition to the Ohmic heat source in the tabs to calculate the temperature distribution in the 3D model.

The governing equations, boundary conditions, material properties, and parameters used are presented in the next section. The electrochemical model used can accurately predict the behavior of the anode and cathode by considering the material phase-change inside the active electrode particles. These types of models allow us to understand the battery phenomenon precisely; even at the particle-level where we can for example solve for particle surface concentration and its relationship to various electrochemical-thermal outcomes. Finally, the model results are compared against the experimental data of the surface temperature of the 20 Ah prismatic cell at 1C, 2C, 3C, and 4C discharge rates.

Figure 29 includes the functions used to calculate the thermal properties of aluminum tabs for the model.

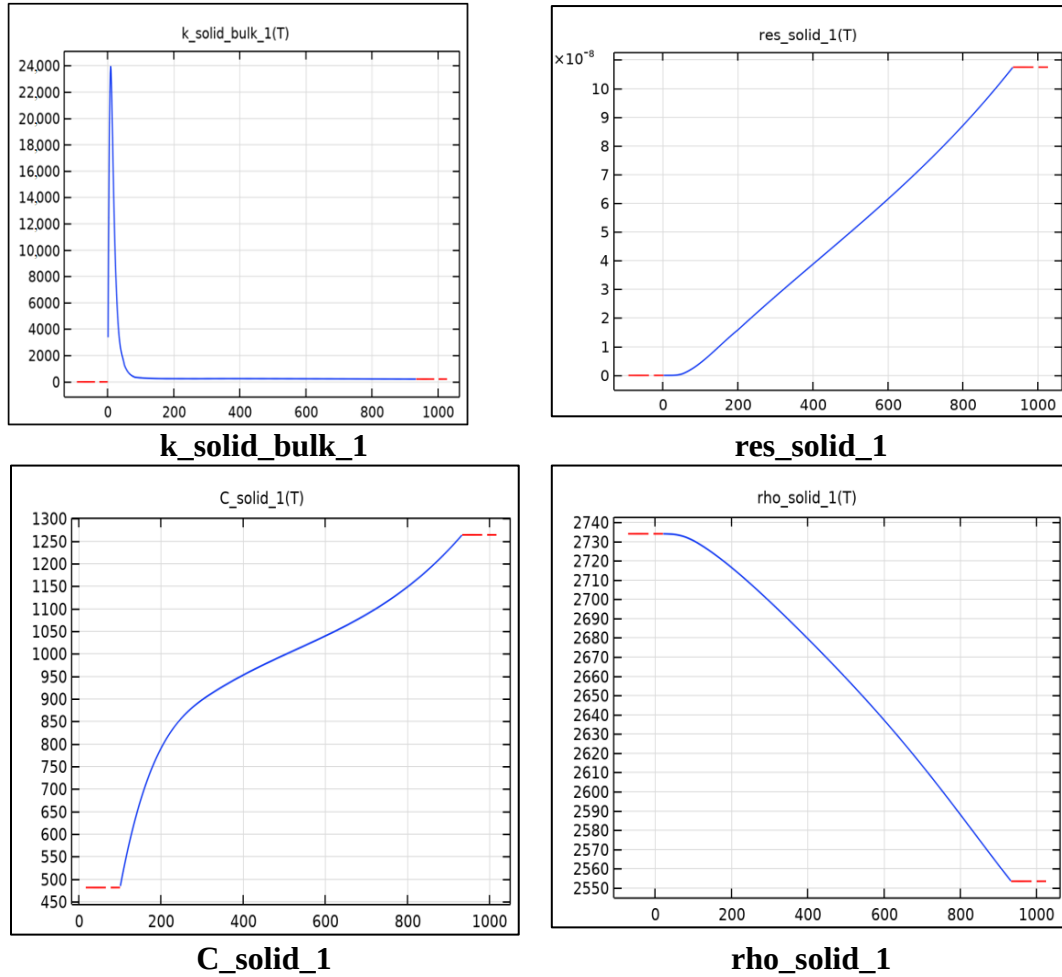


Figure 29: Material parameters as a function of temperature for the thermal conductivity, resistivity, specific heat capacity and density respectively

The thermal conductivity, resistivity, specific heat capacity, and density are all calculated using these functions. The functions shown are functions of temperature and can be read from Figure 29. The resistivity is used to calculate the Ohmic heat source term for the tabs, this is calculated as the current squared multiplied the resistivity into a third constant term Table 13. The major heat source in the tabs is the junction resistance. When two surfaces are in contact, there is a large resistance and voltage drop across the surfaces due to inadequate contact and typically an oxide layer. The resistance can be minimized by increasing the contact pressure and by running current through the junction, a phenomenon known as creeping resistance. In our model, the junction resistance is

modeled as a gain factor multiplied by the resistivity. The density, specific heat capacity, and thermal conductivity are used in the heat equation to calculate the temperature. We see the effect of tab cooling in Figure 30 below for various sizes of pouch cell.

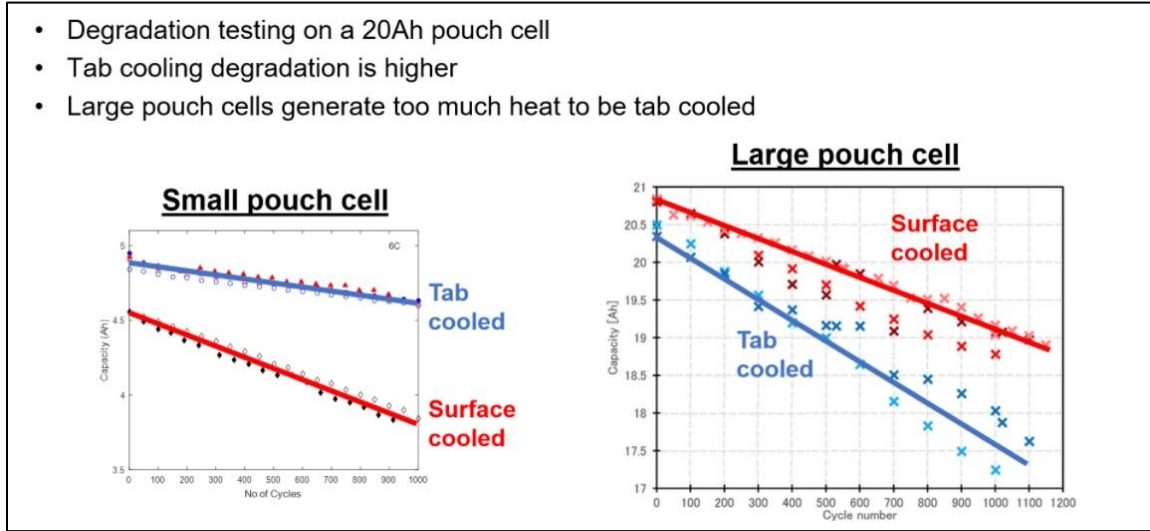


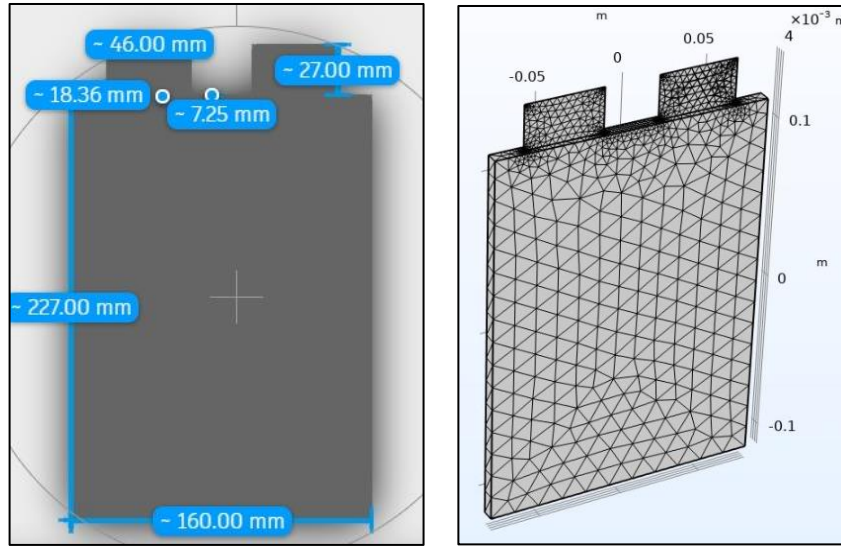
Figure 30: Tab cooled cycle life versus surface cooled cycle life experimental results [127,128]

The effect of non-uniform temperature at the cell level has a profound effect on cycle life. Temperature non-uniformities lead to unequal current densities in the electrodes and non uniform lithium deposition and SOC's across the surface of the electrode which accelerates degradation appreciably as seen in Figure 30.

4.3.1. Geometry and Meshing

The 20 Ah-LiFePO₄ battery used for simulation is identical to the experimental battery and its geometry is shown in Figure 25 with its mesh shown in Figure 31. The tab dimensions along with other cell dimensions such as cell thickness are also shown in Figure 31.

The mesh for the 3D thermal simulation is made up of 1394 tetrahedron elements and 976 triangular elements. It has a minimum element quality of 0.1807 and an average element quality of 0.5398. The maximum element size is 0.0227 and the minimum element size is 0.00409. The curvature factor is 0.6 with the resolution of narrow regions being 0.5 and the maximum element growth rate being 1.5.



(a) Cell dimensions

(b) Meshing

Figure 31: Battery Mesh and Dimensions

4.3.2. Governing Equations and Boundary Conditions

The general governing equations that are used to simulate Li-ion batteries are presented in Table 2 [2–4]. These are the mass and charge balances on both the electrodes and the electrolyte, and an insertion particle concentration variant of the Butler-Volmer equation. The particular governing equations used in COMSOL are presented in the section below in detail. This section covers the governing equations of charge and lithium conservation in both the solid and electrolyte phases as well as the electrochemical kinetics and the heat equation for the 3D battery domain along with their boundary conditions. Table 12 contains the parameter values for the simulation while the material properties are within Table 13. These tables contain all the values necessary to perform the simulation within COMSOL.

Table 13: Material properties used for model development [20]

Property	Symbol	Value	Unit
Density for battery material	ρ_a	2055.2	kg/m ³
Specific heat for active zone	$C_{p,a}$	1399.1	J/kg-K
Thermal conductivity for active zone	K_a	0.8972	W/m-K
Tab heat source constant 1C	$K_{\frac{L}{A}}$	15,000	1/m

Tab heat source constant 2C	$\frac{K_L}{A}$	11,000	1/m
Tab heat source constant 3C	$\frac{K_L}{A}$	15,000	1/m
Tab heat source constant 4C	$\frac{K_L}{A}$	4500	1/m

4.4. Parallel Pack Model

Figure 32 depicts a circuit diagram demonstrating the effect of busbar resistances on both the anode and cathode busbars, as well as a charge conservation condition across the battery (ie I_0 into battery equals I_0 out of battery).

The thermal circuit for the connectivity between the cells through the busbar is shown in Figure 33. The circuit consists of dividing the pack into 7 major sections with busbar conductivities connecting the sections and heat generated through the battery internal resistance, cathode and anode resistances. Figure 34 shows the thermal circuit for the pack casing with the casing divided into 7 sections connected to the busbar and with casing conductivity connecting the pieces. Table 14 includes the values used in the Simulink model.

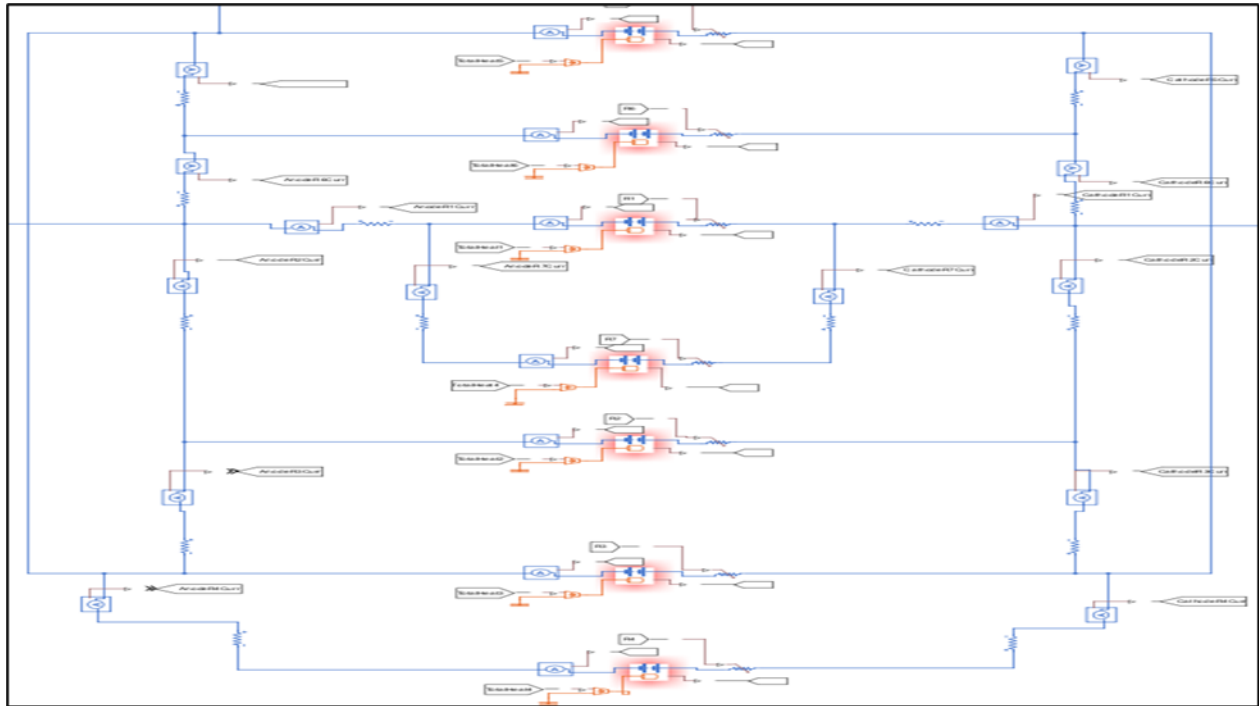


Figure 32: Electrical Circuit for Parallel Pack Geometry

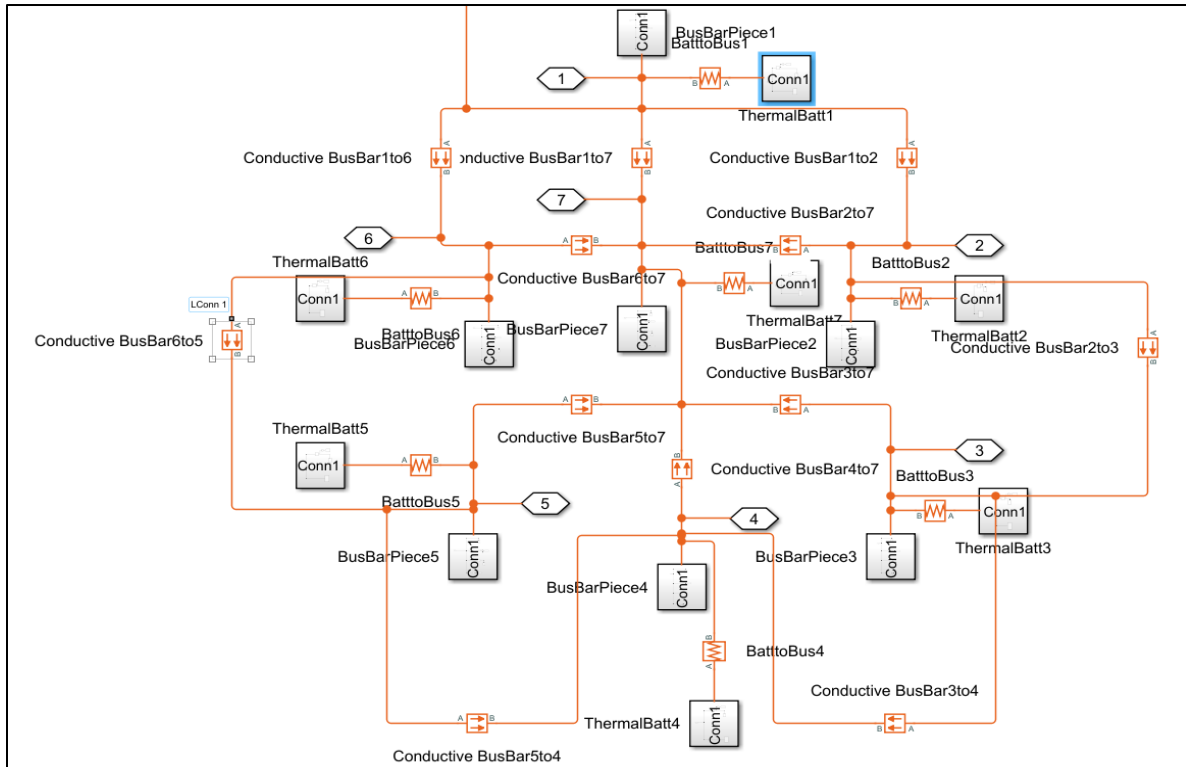


Figure 33: Thermal Circuit for Busbar and Batteries

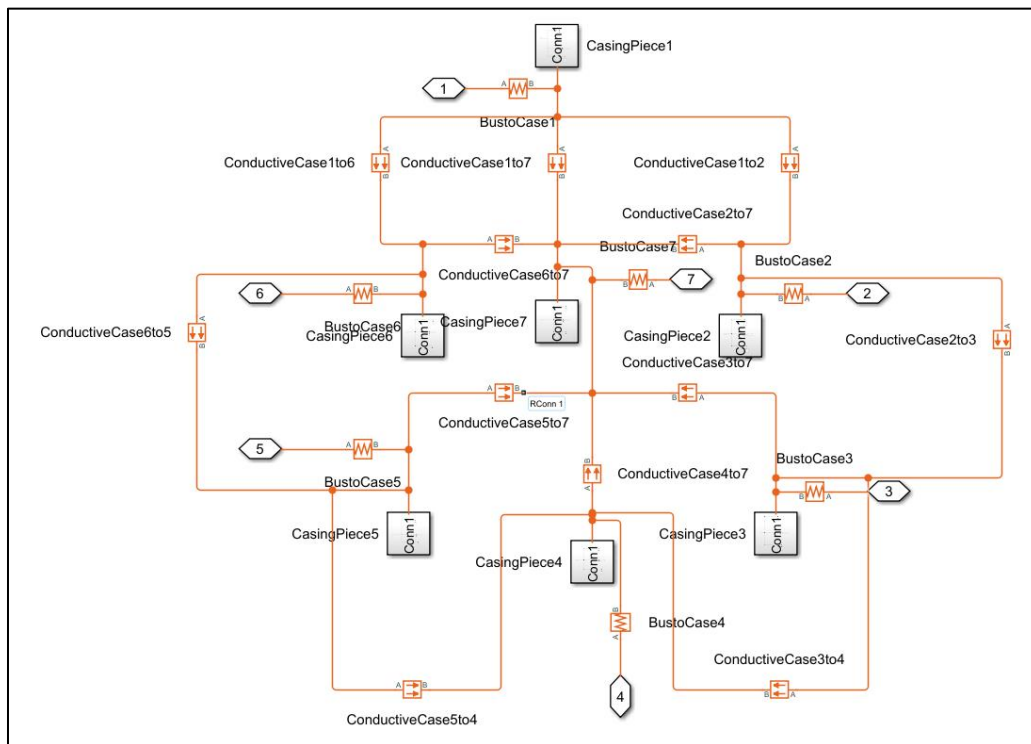


Figure 34: Thermal Circuit for Pack Casing

Table 14: Material properties used for Simulink model

Property	Value	Unit
Cathode Resistances Cells 1-3, 5-6	0.0046	Ω
Cathode Resistances Cell 4	0.092	Ω
Cathode Resistances Cells 7	0.003067	Ω
Anode Resistances Cells 1-3, 5-6	0.0046	Ω
Anode Resistances Cell 4	0.092	Ω
Anode Resistances Cells 7	0.003067	Ω
Busbar Conductivity	302	W/m-K
Busbar Mass	0.4	Kg
Busbar Specific Heat Capacity	376	J/kg-K
Casing Conductivity	0.25	W/m-K
Casing Mass	0.2	Kg
Casing Specific Heat Capacity	900	J/kg-K
Battery Mass	0.04	Kg
Battery Specific Heat	1020	J/kg-K
Convective Heat Transfer Coefficient -External	7	W/m ² -K
Convective Heat Transfer Coefficient- Internal Battery Spacing	0.15	W/m ² -K

Chapter 5 Results and Discussion

The results and discussion section consists of 2 main parts a section on single cell LiFePO₄ batteries aircooled and a section on a 7p Parallel pack analysis. The first section is further split into 2 parts, one for each published paper.

5.1. Matlab PDEPE Results

As mentioned previously, the values of the internal resistance from the experimental data are given in Table 15. The data is presented in graphical form in Figure 35.

Table 15: Internal resistance at different states of charge (SOCs)

SOC	C-Rate			
	1C	2C	3C	4C
100%	0.007633	0.006333	0.005930	0.004695
90%	0.008217	0.006711	0.006244	0.005169
80%	0.008461	0.006696	0.006083	0.004952
70%	0.008029	0.006330	0.005631	0.004657
60%	0.00847	0.006541	0.005646	0.004676
50%	0.009059	0.006875	0.005797	0.004755
40%	0.009283	0.006875	0.005862	0.004809
30%	0.009499	0.007026	0.005873	0.00484
20%	0.012206	0.008467	0.006789	0.005395
10%	0.023704	0.013245	0.010059	0.007005

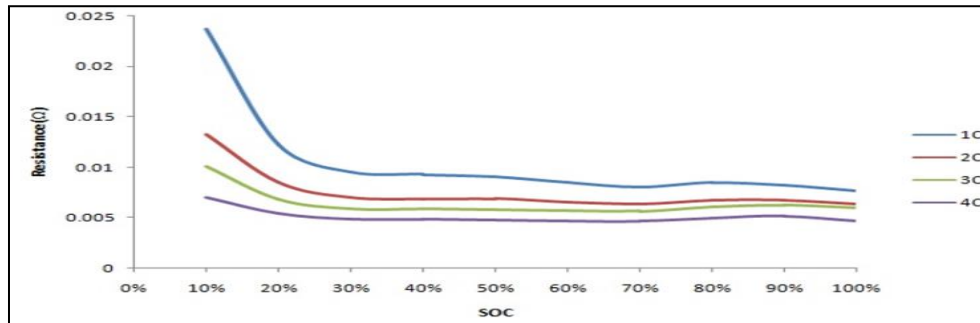


Figure 35: Experimentally calculated R_{int} resistances compared at 1-4 C-rates for different states of charge (SOCs)

We can see that the internal resistance increases with the depth of discharge and decreases with C-rate. It should be noted that this does not mean the overpotential and total energy loss decrease with C-rate, as those are given by the product of the current and the internal resistance. The overpotential does, however, increase with depth of discharge (DOD). The greatest increases occur towards the end of discharge at low SOC. It is here that the largest discrepancies in the effect of C-rate were observed. In Figure 36, the cell potential from the R_{int} model is estimated and found to be a good fit when the resistance is fitted in 10 % discharge intervals. In Figure 36, the temperature is predicted using the R_{int} model and is also found to be a good fit to the experimental data at all C-rates.

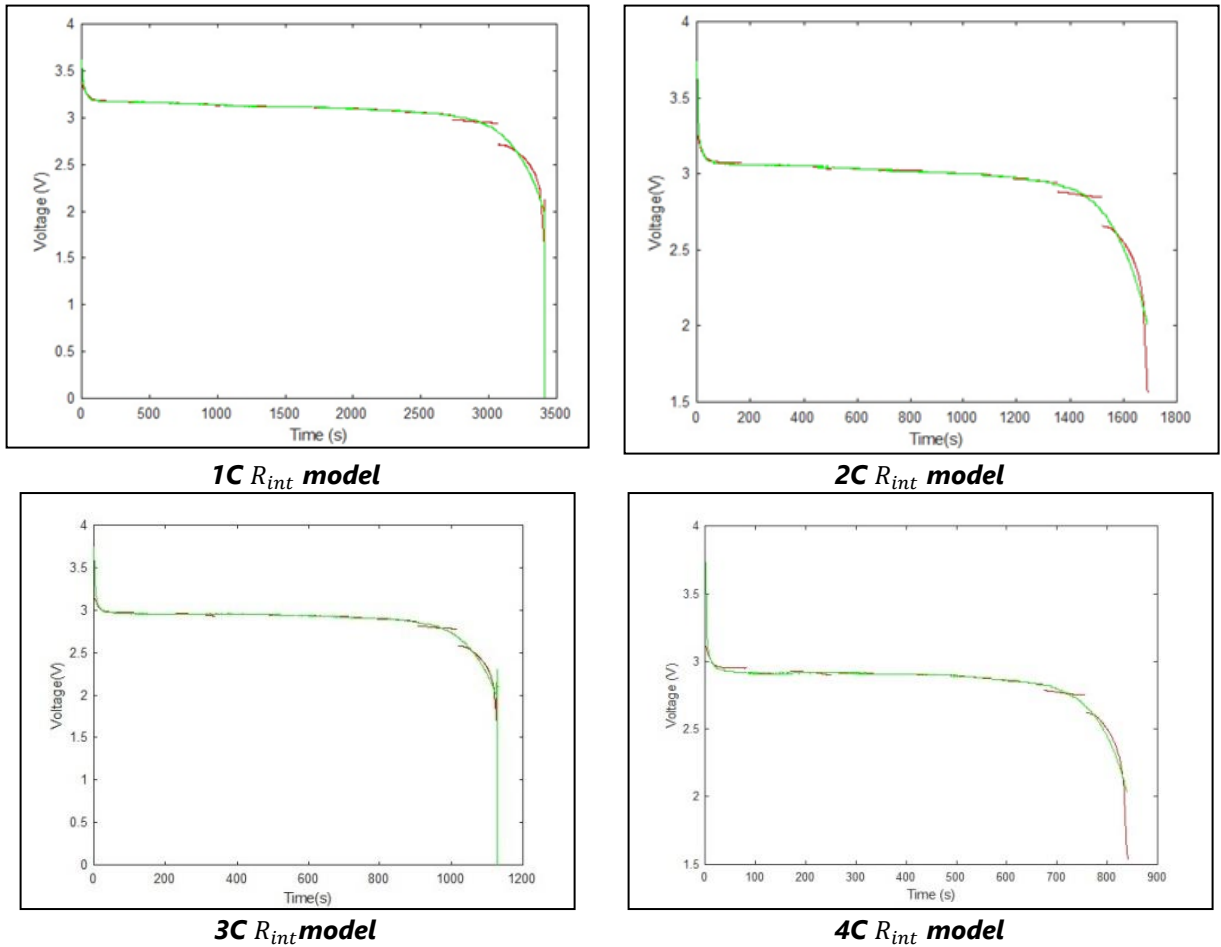


Figure 36: R_{int} model voltage predictions (in red) compared to experimental data (in green) at selected C-rates

The model predictions are found to be higher than the experimental temperatures for all C-rates, but this changes towards the end of discharge. As the heat transfer coefficient increases with an

increase in temperature difference between the environmental temperature and the battery, and the overpotential is predicted accurately, the additional heat required for this temperature increase must be from the reversible heat term. We note that even though the internal resistance increases exponentially at low states of charge, the voltage and heat produced from this overpotential are accurately gauged. At low SOC, we find that the $\frac{dE_{eq}}{dT}$ term is a heating term while discharging for both the anode and the cathode while at higher SOC, it is exothermic while discharging at the iron phosphate cathode and not at the graphite anode.

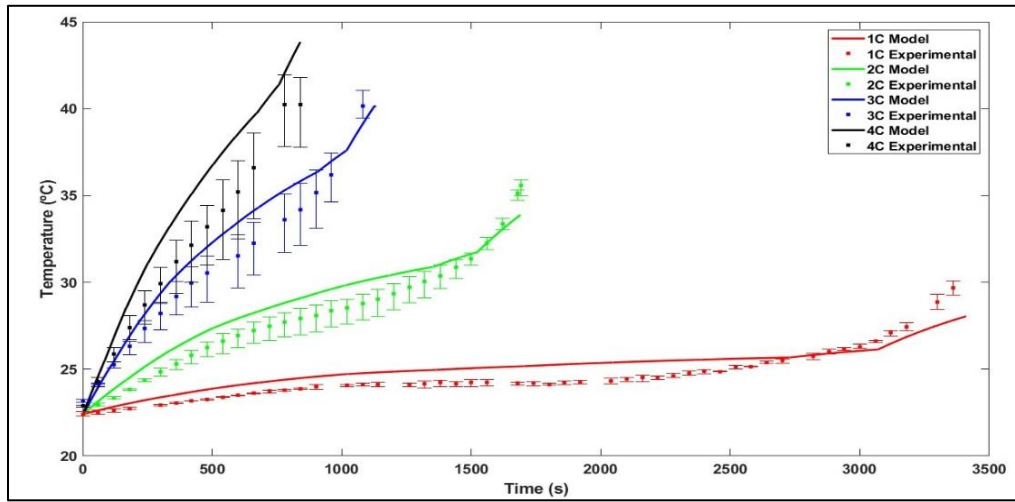


Figure 37: R_{int} model temperature predictions compared to experimental data at selected C-rates

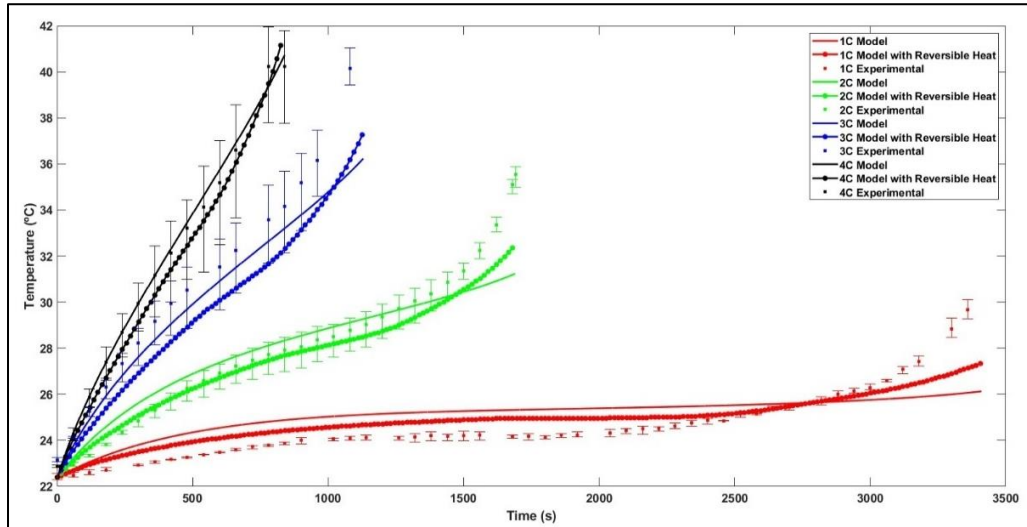


Figure 38: Physio-chemical model predicted temperatures versus experimental data for selected C-rates

Thus, the simplified Bernardi Equation used in our model may not yield as accurate results at low SOC. This additional increase in temperature at low SOC is in fact found to be the case in our physio-chemical model with reversible heat as shown in Figure 38. We also find that there is a decrease in temperature as required at high SOC due to the endothermic effect at the anode when we include the reversible heat term. We note that both Figure 37 and Figure 38 show that the maximum temperature ranges occur at the middle of discharge with smaller error bars at the beginning and end of the discharge cycles. We also see that the temperature nonuniformity increases with C-Rate with the maximum temperature being at the tabs at all times measured.

The model presented in Equation (25) requires 4 parameters and assumes an exponential decay with SOC while the model presented in Equation (26) requires 8 parameters and relates the internal resistance to SOC with a Pearson curve. The predicted internal resistances from the models are then compared to the experimental data in Figure 39.

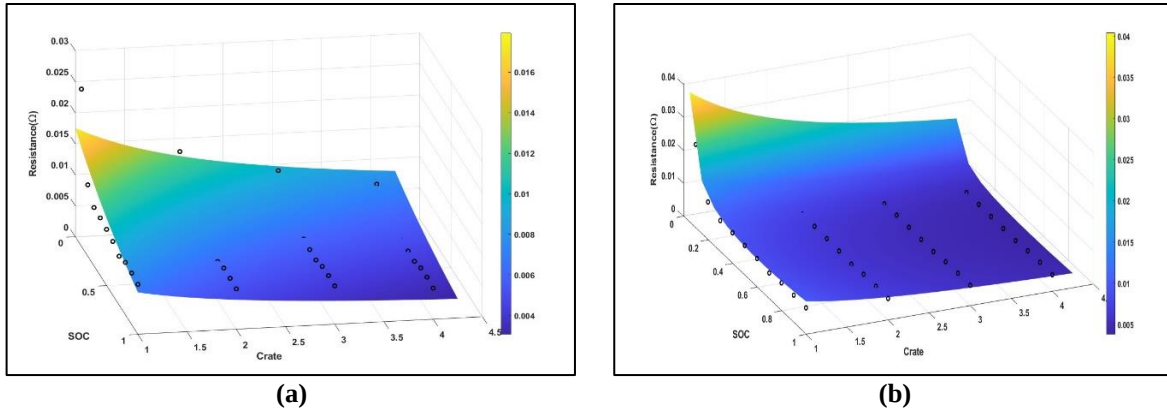


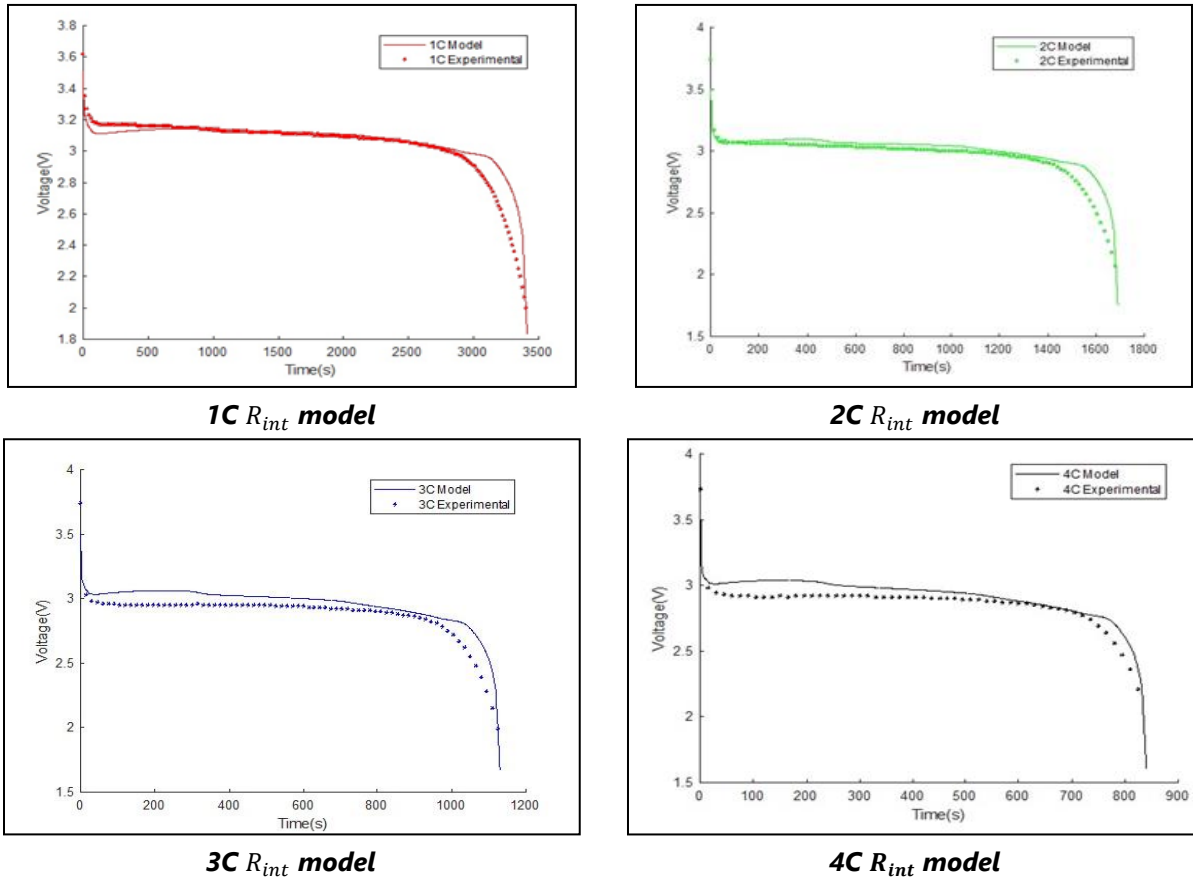
Figure 39: R_{int} model resistances predicted from (a) Equation(25) and (b) Equation(26) (experimental data shown in circles)

We see the Pearson curve is a better fit to the data than the exponential decay especially at low SOC and low C-rates. The mean square error (MSE) Resistance value for the exponential curve is $4.80e-06$ while the MSE for the Pearson Resistance curve is $2.64e-06$. As mentioned previously the Pearson curve has a lower MSE and is a better fit to the experimental data. The MSE values predicted by the R_{int} model from Equation(26) for the voltage are presented in Table 16.

Table 16: Mean squared error (MSE) values of battery surface temperature for R_{int} model

C-Rate	MSE of Temperature	MSE of Voltage
1	0.5445	0.005069
2	0.8899	0.001777
3	1.512	0.01408
4	6.123	0.003637

No observable trend with the C rate is observed with predicted values being quite close to the experimental data. The MSE values for the predicted temperatures from the R_{int} model are presented in Table 16. The error is observed to increase with C rate even though the voltages predicted and thus the heat source term did not show this trend. One explanation for this is that the convective heat transfer coefficient is not simply a constant as the temperature increases and is instead a function of the temperature difference as with increased at temperature differentials we experience increase convection currents.

**Figure 40: Physio-chemical model predicted voltages versus experimental data for selected C-rates of (a) 1C, (b) 2C, (c) 3C, and (d) 4C**

Both the physiochemical and R_{int} models assume a uniform heat distribution and tab temperature is neglected. These assumptions are a drawback of both models as degradation prediction, non-uniform current densities and other predictions of electrochemical phenomenon influenced by thermal gradients are not possible. Figure 38 and Figure 40 (a-d) show the predicted voltages and temperatures from the physio-chemical model. In Figure 40 (a-d), the voltage fits the experimental voltage at high SOC's and low C-rates, while at high C-rates the voltage is more accurately predicted at low SOC's. Table 17 shows the MSE values for the voltage of the physiochemical model at different C rates, no observable trend in errors is observed.

Table 17: Mean squared error (MSE) values of battery voltage for the physio-chemical models

C-Rate	MSE of Voltage
1	0.01097
2	0.008092
3	0.01958
4	0.008794

The highest error is observed at 3C. Next the modeled temperature at low C-rates is found to be higher than the experimental temperature for high SOC's. The experimental temperature surpasses the predicted temperature at low SOC's. At high C-rates, the predicted temperature is found to be lower than the experimental value at all SOC's, with an even larger discrepancy at low SOC's. Once the reversible heat term is added into the model, we find that the curve of the model more closely resembles the experimental data, with the rate of increase in temperature increasing at the end of discharge and being lower at the start just as required. As mentioned previously, at low SOC's, both the anode and cathode reversible heats are exothermic while at high SOC's, the reversible heat is endothermic. The MSE values for both models are presented in Table 18 and show a maximum deviation at 3C for both physio-chemical models. The MSE of the reversible heat model is found to be lower than that of the physio-chemical model with no reversible heat at low C-rates (1C and 2C).

Table 18: Mean squared error (MSE) values of battery surface temperature for the physio-chemical models

C-Rate	No reversible Heat	With Reversible Heat
1	1.2341	0.4876
2	1.0877	0.5971
3	2.1030	3.3076
4	0.1307	0.6003

It should be noted that although the ECM model is a better fit, the physio-chemical model is more robust and does not require experimental data. The physio-chemical model can predict the temperatures and voltages at various temperatures and C-rates. The elapsed time to solve the system of PDE's for the physical model was approximately 4.9 seconds. The physiochemical model is modeled in only 1 dimension while reducing the number of PDE's to only 3 with a mesh size of 50 line intervals for each electrode, this allows for the reduced computation times compared to typical finite element analysis simulations. Farmaga et al. [126] state the computation time is a function of the number of nodes, elements and the bandwidth of the banded stiffness matrix all of which are kept to a minimum in our physiochemical model.

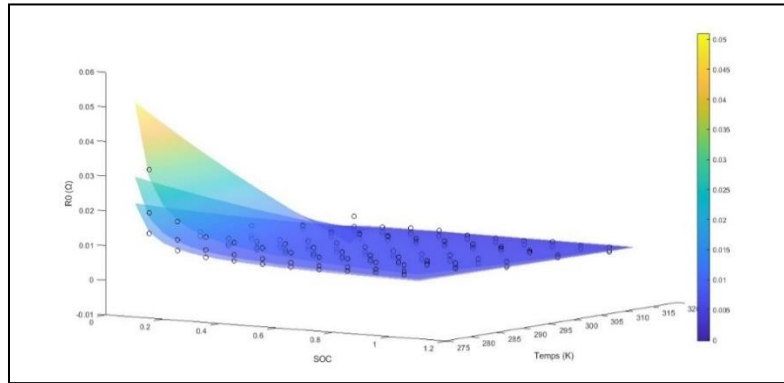
5.2. Matlab Practical Rint Thermal Results

The proposed model is a 10 parameter nonlinear equation that has been fit using matlabs nlinfit function. The Pearson Coefficient for the 45 experiments (3 C-rates x 3 SOHS x 5 Temperatures) was 0.945. Figure 41 depicts the model in the form of numerous surface plots. The figures show internal resistance surfaces at the 3 different experimental C rates, with each figure itself being for the specified SOH.

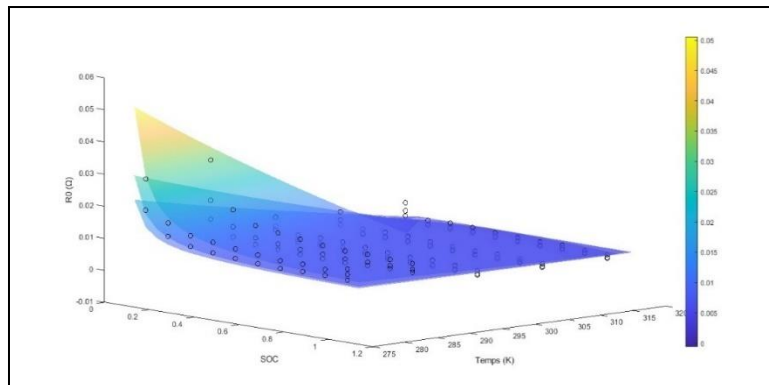
We can see that as the C rate increases, the internal resistance decreases. The overall energy loss, however, increases as the C-rate rises. The increased impedance at low temperatures is mostly due to the electrolyte's reduced diffusion coefficient. The experimental data is shown up to 5°C. At low SOC, mass transfer losses become more significant, and impedance increases exponentially.

Figure 41 shows the residuals for the internal impedance. The residuals exhibit a trend with both SOC and temperature and are not scattered randomly along the vertical axis. They are, however, spread reasonably uniformly along the zero error line, which is illustrated in red.

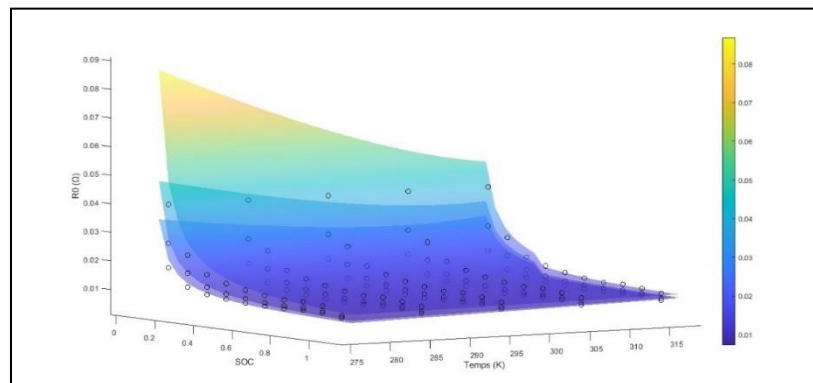
We can see that as the C rate increases, the internal resistance decreases. The overall energy loss, however, increases as the C-rate rises. The increased impedance at low temperatures is mostly due to the electrolyte's reduced diffusion coefficient. The experimental data is shown up to 5°C. At low SOC, mass transfer losses become more significant, and impedance increases exponentially.



(a) 90.575% SOH



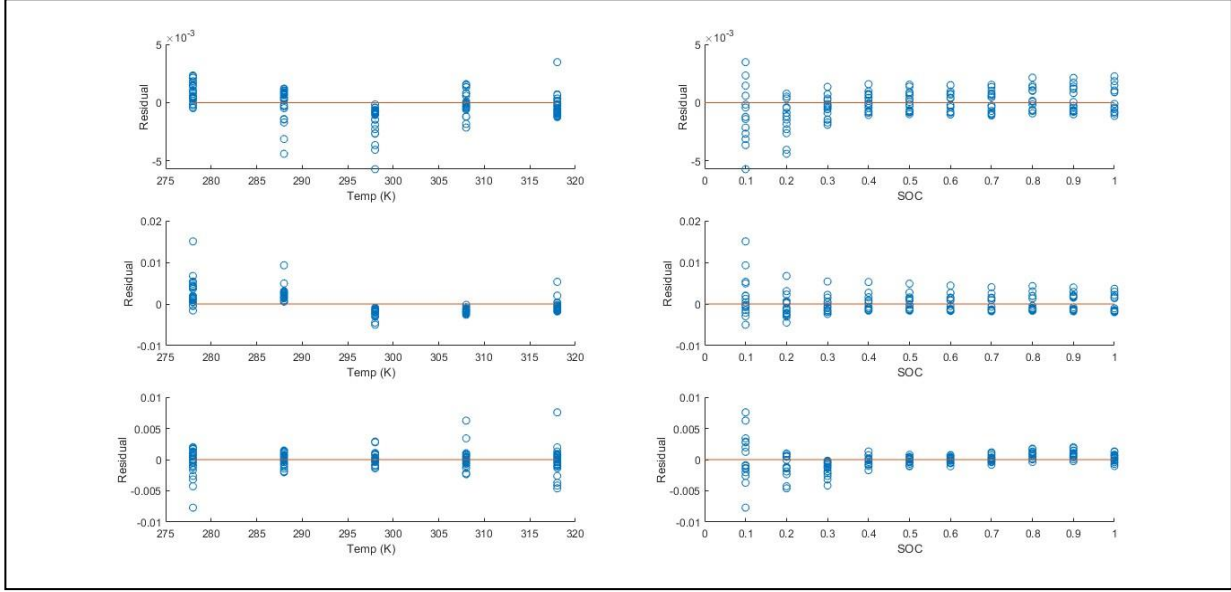
(b) 83.435% SOH



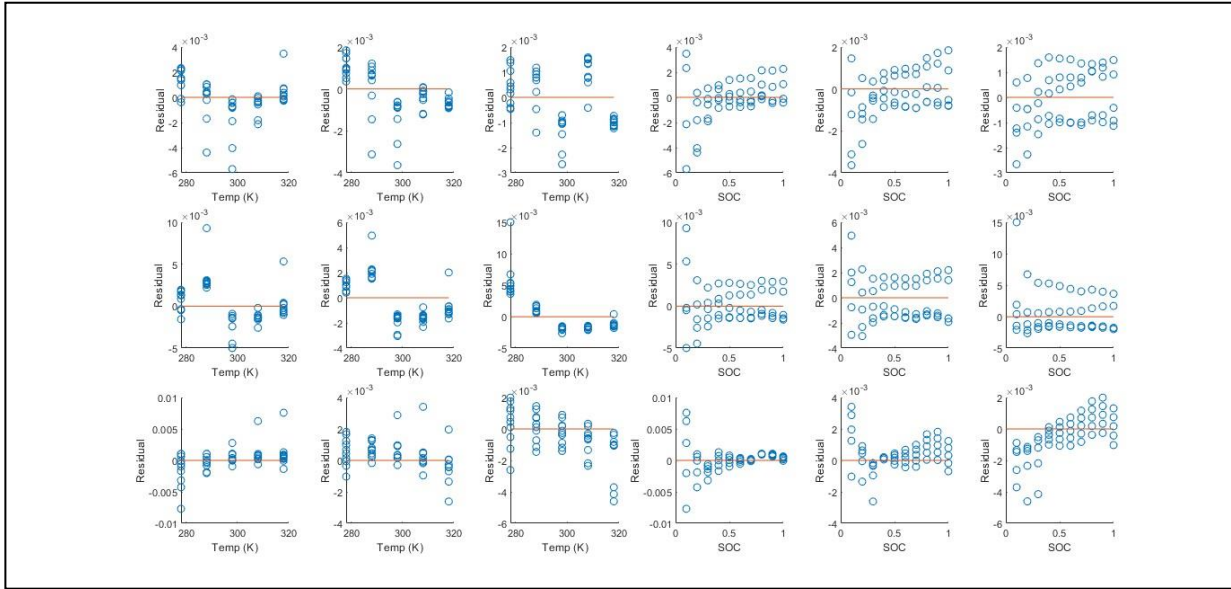
(c) 65.025% SOH

Figure 41 (a-c): Surface plots of Internal Impedance modeled from equation(26) with each surface being at the shown C-rate and each figure for the stated SOH

Figure 42 shows the residuals for the internal impedance. The residuals show a trend with both SOC and temperature and are not scattered randomly along the vertical axis. They are, however, spread reasonably uniformly along the zero error line, which is illustrated in red.



a)

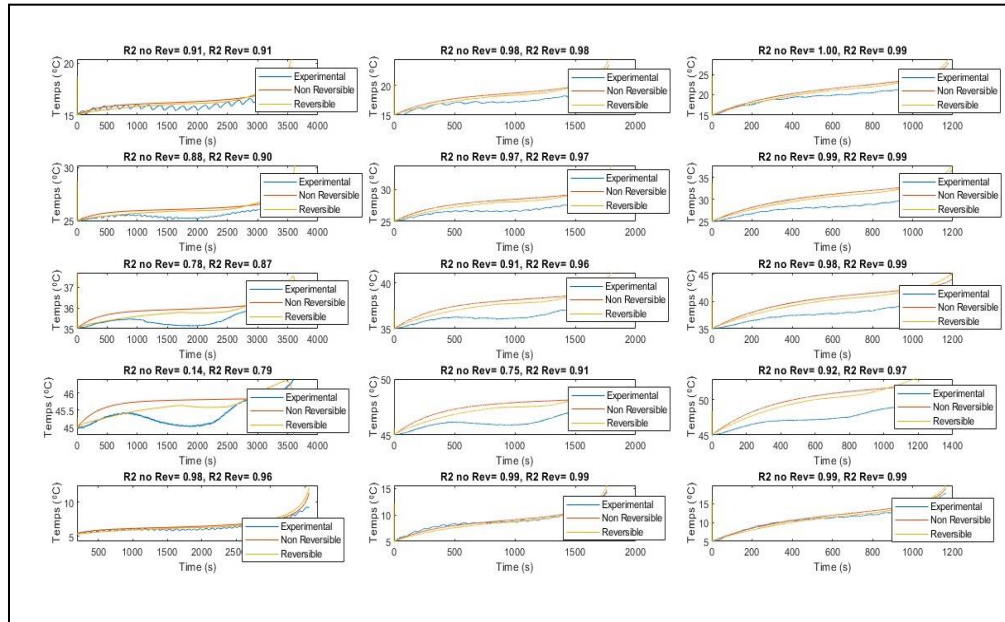


b)

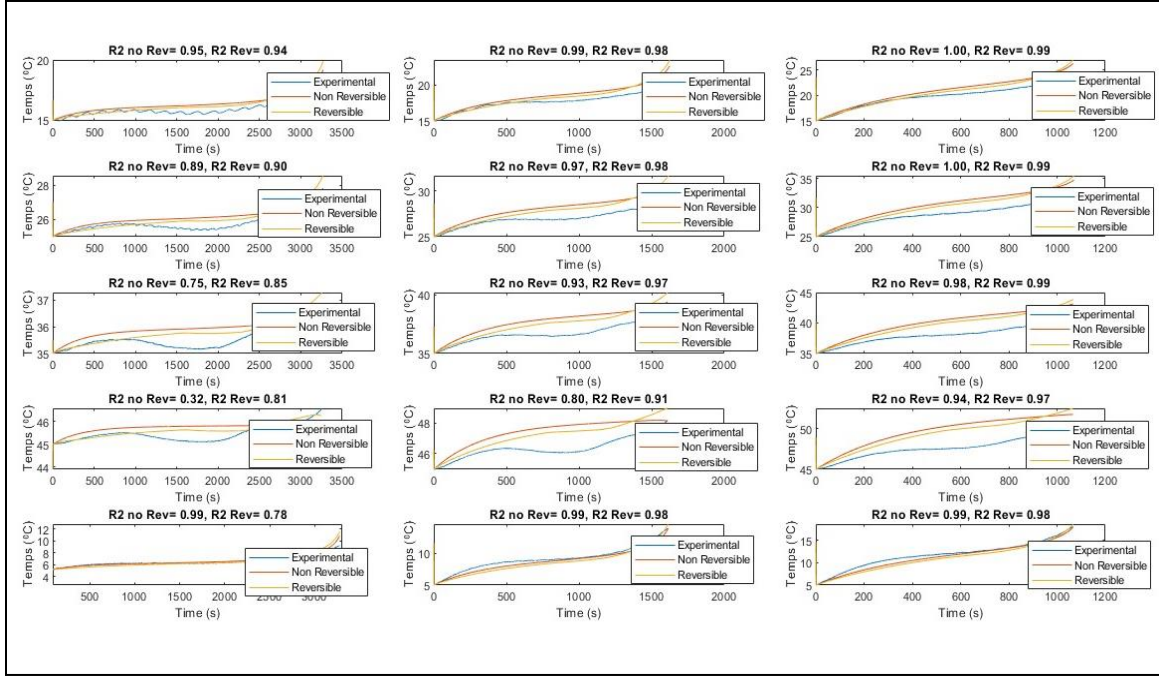
Figure 42: (a) Residual plot of Internal Impedance modeled from equation(26) with residuals plotted against Temperature and SOC (b) Residual plot of Internal Impedance modeled from equation(26) with residuals plotted against Temperature and SOC with each C-rate on a separate plot

The figures reveal a trend indicating that the internal resistance is a nonlinear function of SOC and Temperature (or a variable that covaries with both) that is not captured by the model. We see the trend at 83% SOH and 3C to conclude that the SOC term in the model is best described conditionally with an interaction between SOH and current. We find that while comparing the residuals, the current plays an important influence. Once again, at 83% SOH and 3C, we have a nonlinear temperature trend that the model does not reflect. The residuals also show heteroscedasticity, which normally suggests the absence of an interaction term between the input variable and the independent variable. The interaction term at the lowest SOH 65% and 1C exhibits heteroscedasticity that converges with SOC, whereas for higher C rates, the residual variance drops before increasing again. At 3C and 65% SOH, the residuals vary linearly with SOC, revealing a missing interaction component that is linear at high C and depends on both SOH and C rate.

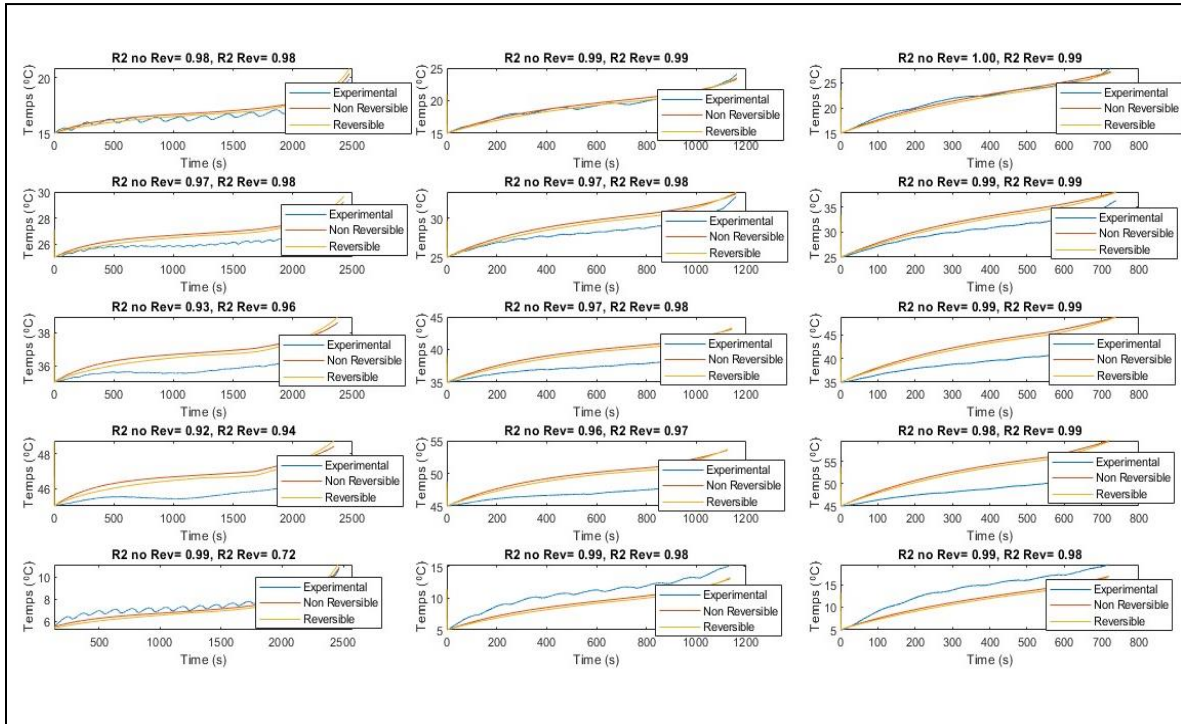
Figure 43 depicts simulated temperatures. The models are in good accord with experimental results. The reversible model has lower Pearson coefficients than the simpler model without a reversible heat term at temperatures of 5°C and 15°C for experimental SOHs of 83% and 90%, respectively. For temperatures above 25°C, the reversible heat model is more accurate, with SOH values between 83% and 90%. For SOH of 65%, the non-reversible model is more accurate with a lower 5°C margin.



(a) Simulated temperatures at ambient temperatures shown and with C rates of 1C,2C,3C from left to right with an SOH of 90%.



(b) Simulated temperatures at ambient temperatures shown and with C rates of 1C,2C,3C from left to right with an SOH of 83%



(c) Simulated temperatures at ambient temperatures shown and with C rates of 1C,2C,3C from left to right with an SOH of 65%

Figure 43: (a-c) Reversible and simple Rint heat models for battery at stated SOH at 5 different ambient temperatures and 3 stated C rates

Figure 43 demonstrates that the Rint model can accurately model the temperature under all 45 experimental conditions. The model is shown to be robust while remaining relatively accurate in simulating the average battery temperature from all 8 thermocouples. The effect of the reversible heat is seen to be cooling at high SOC's with a steep heating effect at lower SOC's. This shows that the entropy is negative at low SOC's and is positive and high SOC's. This is a thermodynamic oddity. Table 19 shows the Pearson coefficients for all 0D models.

Table 19: Pearson Values for 0-D thermal models with and without Reversible Heat Term

SOH	Temp (K)	Current (Amps)	R No Reversible Heat	R Reversible Heat
0.65025	288	18	0.979177865393035	0.982514356376451
0.65025	288	36	0.986924647103290	0.987855320410401
0.65025	288	54	0.995780549147039	0.989028611296972
0.65025	T=288K ALL		0.992063373758613	0.985619847458627
0.65025	298	18	0.968077217706392	0.981939024308647
0.65025	298	36	0.973213896790838	0.981904009562313
0.65025	298	54	0.991580222471278	0.989727854750511
0.65025	T=298K ALL		0.992259245545052	0.992104025940737
0.65025	308	18	0.934321827445685	0.960898427135247
0.65025	308	36	0.968916988342210	0.979900899011933
0.65025	308	54	0.988382732791897	0.988777798379419
0.65025	T=308K ALL		0.988631798983792	0.992057047246447
0.65025	318	18	0.915016591705728	0.944984815865819
0.65025	318	36	0.962595643244635	0.974063503933853
0.65025	318	54	0.984437423205924	0.985303113605181
0.65025	T=318K ALL		0.982616087199752	0.987427694781736
0.65025	278	18	0.989621996130223	0.715313522537181
0.65025	278	36	0.992395478193975	0.981126009838796
0.65025	278	54	0.988285192474701	0.977967645763114
0.65025	T=278K ALL		0.983934784742391	0.916461070965243

0.65025	ALL T		0.997383755119004	0.997068761006412
0.83435	288	18	0.951218044847353	0.944554344306450
0.83435	288	36	0.990829466787542	0.976203083926803
0.83435	288	54	0.996597900204779	0.986161245986556
0.83435	T=288K ALL		0.993833431575029	0.978473425558501
0.83435	298	18	0.889435812453325	0.898566327613884
0.83435	298	36	0.974963316238162	0.977564083110444
0.83435	298	54	0.995574016877892	0.991026761541425
0.83435	T=298K ALL		0.993021225445422	0.986487689408858
0.83435	308	18	0.750679433046954	0.850150115945573
0.83435	308	36	0.926700749244452	0.966337673000224
0.83435	308	54	0.977163141470752	0.988542877463185
0.83435	T=308K ALL		0.976754656792624	0.987602428431748
0.83435	318	18	0.315532806102462	0.810779356376338
0.83435	318	36	0.797575222436363	0.912164386756628
0.83435	318	54	0.940506677346341	0.973860357055070
0.83435	T=318K ALL		0.936524062709090	0.971504066363726
0.83435	278	18	0.987027169907371	0.776773386874513
0.83435	278	36	0.992367785301845	0.984982095080588
0.83435	278	54	0.993390258857196	0.983703560545529
0.83435	T=278K ALL		0.991588545173945	0.948265522129714
0.83435	ALL T		0.998937791174159	0.998695072886527
0.90575	288	18	0.913081259656133	0.911240181287283
0.90575	288	36	0.984099717017561	0.982086989255883
0.90575	288	54	0.995779231738598	0.990512827091736
0.90575	T=288K ALL		0.989947128118859	0.978955605332610
0.90575	298	18	0.878719818203357	0.895148890748533
0.90575	298	36	0.970692729102040	0.972240359818755
0.90575	298	54	0.992768291206532	0.990159981450564
0.90575	T=298K ALL		0.990333131982975	0.983968910771086
0.90575	308	18	0.780913370402260	0.872010698912291
0.90575	308	36	0.909595331992183	0.957238789520150
0.90575	308	54	0.976507949912191	0.991050190080139
0.90575	T=308K ALL		0.971006443376185	0.986690684699857

0.90575	318	18	0.135634402185078	0.791111521751327
0.90575	318	36	0.745231797886920	0.910111981122814
0.90575	318	54	0.920932184216096	0.973007254777626
0.90575	T=318K ALL		0.912638523184148	0.963662621212581
0.90575	278	18	0.980056336511131	0.960834723375769
0.90575	278	36	0.987928269345204	0.991088530206457
0.90575	278	54	0.993225104484002	0.991558685738187
0.90575	T=278K ALL		0.991990214478245	0.982983870511176
0.90575	ALL T		0.998319304991072	0.998243677855997
	T=288K		0.983261838220007	0.971166792457424
	T=298K		0.983001597912984	0.975404292376781
	T=308K		0.972305532403450	0.985707858386788
	T=318K		0.922222947299276	0.964625763603077
	T=278K		0.981544408498384	0.965696206988520

With regards to SOH both reversible and non-reversible models have the highest correlation coefficients at 83% followed by 91% and finally 65% SOH displaying the least accuracy in large part due to rapid degradation and changes in the SOH itself. Overall, we notice that the accuracy of the non reversible heat model increases from 278K to 288K and then decreases with temperature; whereas the Pearson Coefficient for the reversible heat model increases from 278K to 308K and then drops from 308K to 318K.

Figure 44 shows the simulated output from the finite difference simulation. We see that the boundary conditions with the tab heat source are included in the simulation. The surface mesh is divided into 32 sections both lengthwise and widthwise. Each battery at each individual SOH has its own simulation parameters.

Figure 45, Figure 46 and Figure 47 show the beginning of discharge, middle of discharge and end of discharge time steps for all 45 experimental runs with each figure being at the specified SOH. The 3 C rates are presented in each row while the time of the discharge is shown in the columns. The models agree well with experimental results and are numerically stable under all conditions, indicating that the model is robust. The timestep is adequately small and satisfies the stability conditions of all experimental runs, despite the steep temperature gradient between the tabs and the battery surface.

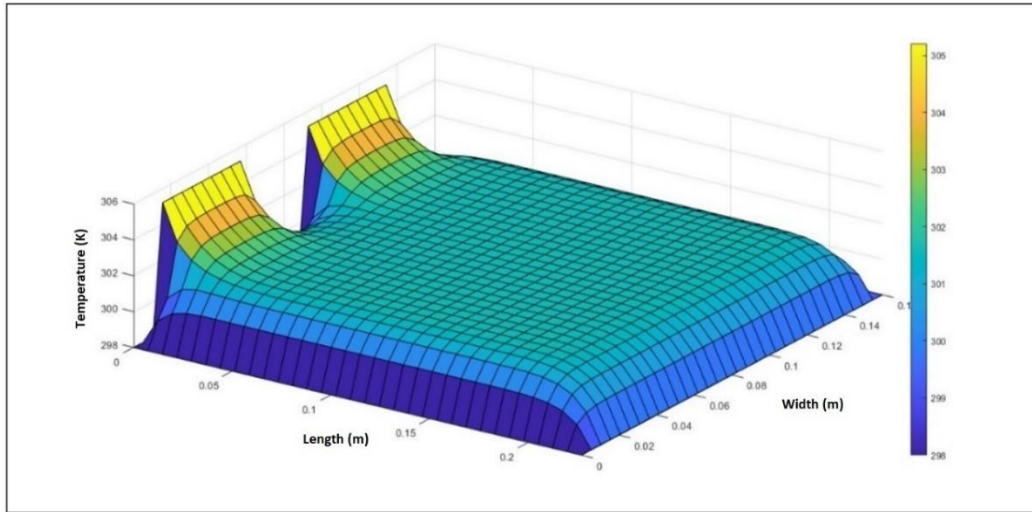
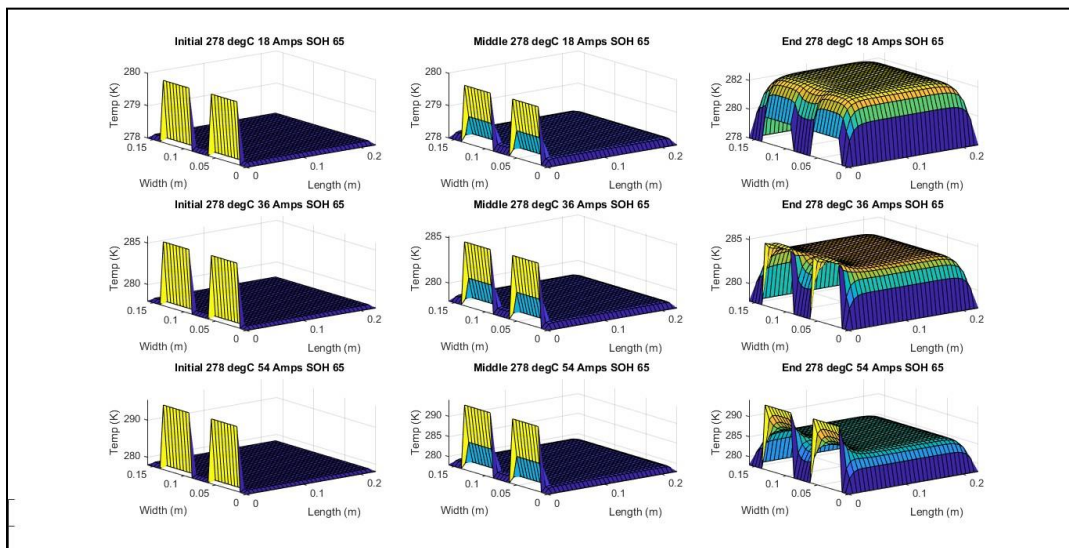
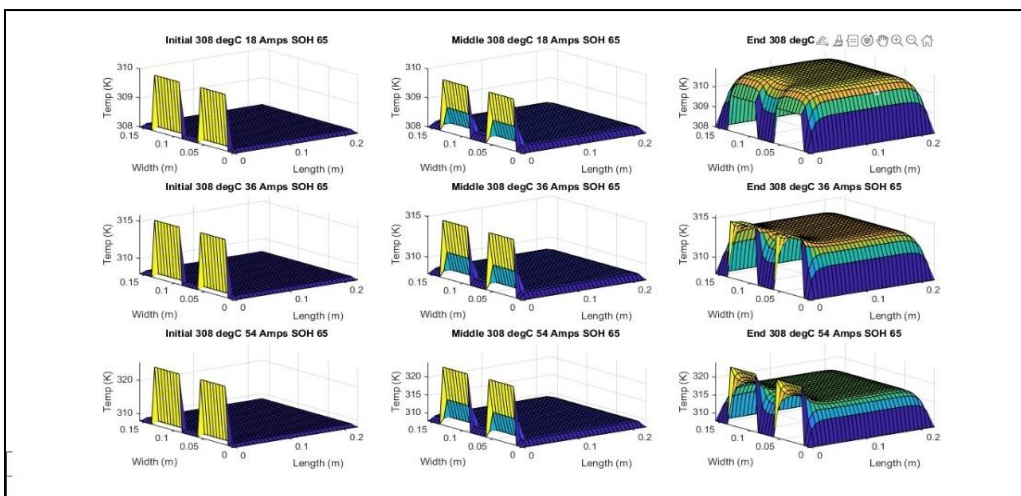
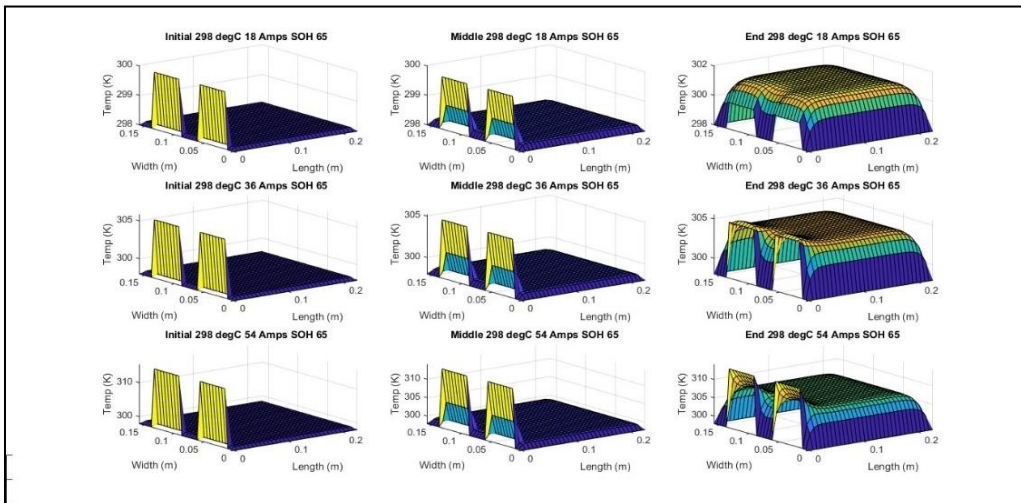
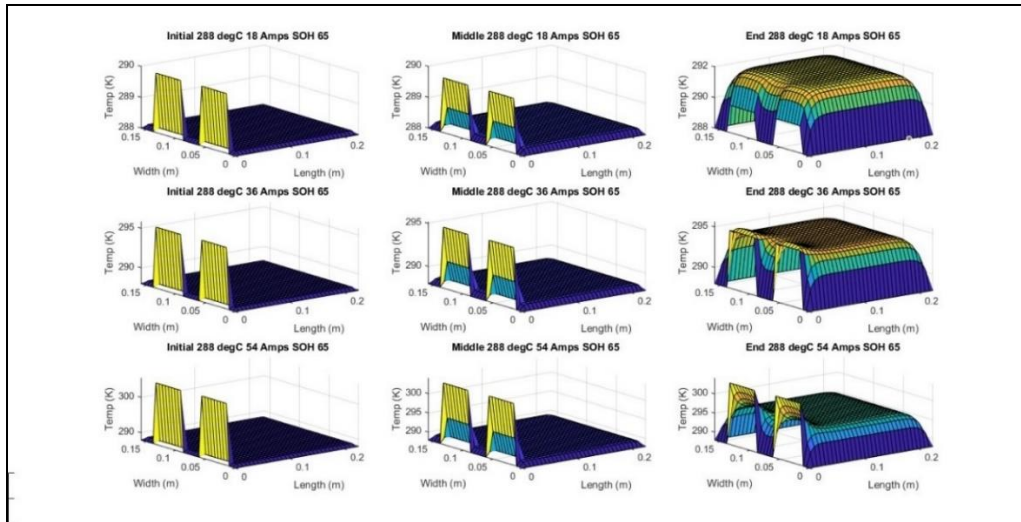


Figure 44: Sample of Surface Temperature (K) Produced by 2D Model





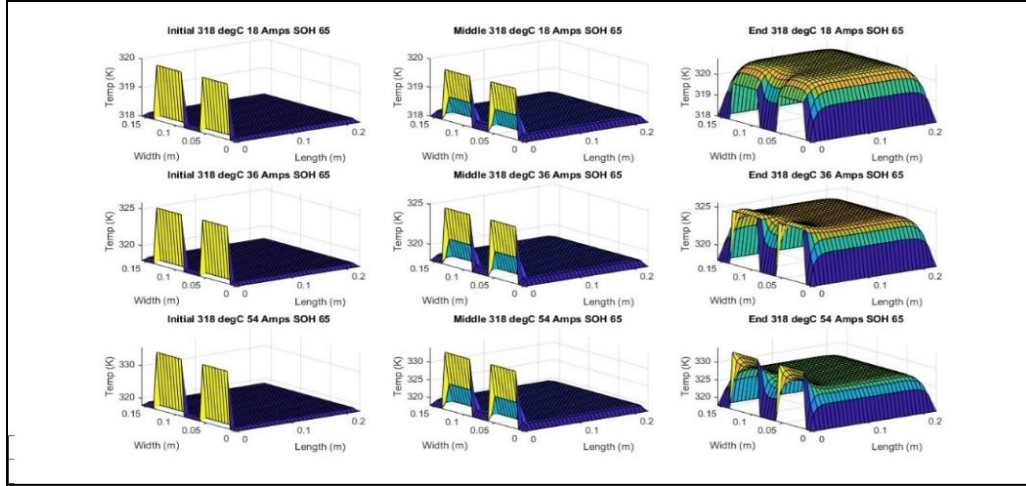
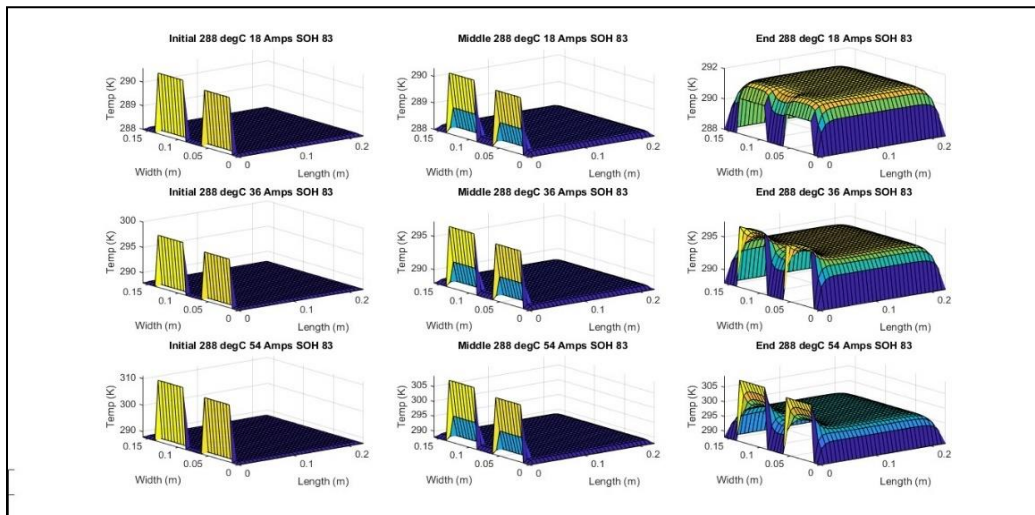
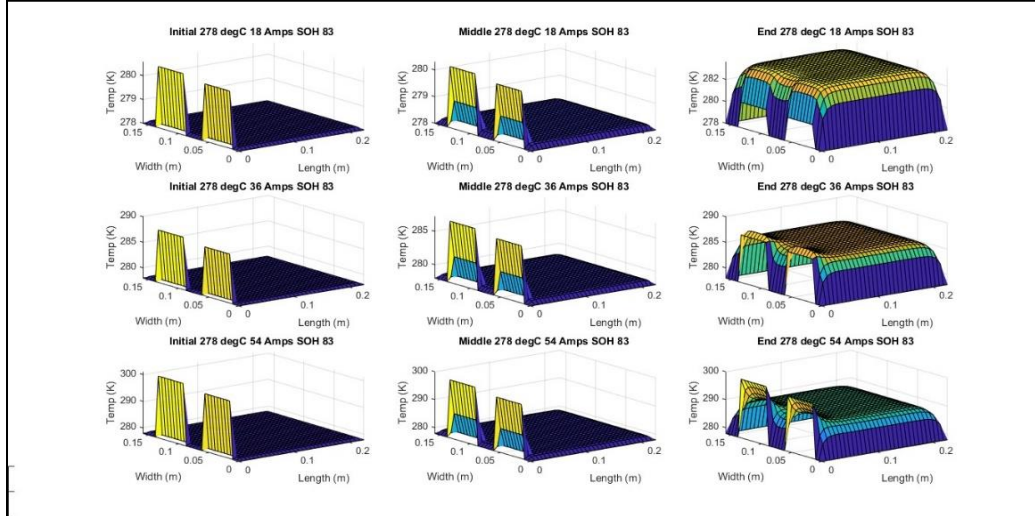


Figure 45: Initial, middle and end Surface Temperatures for SOH 65% at 278K, 288K, 298K, 308K, 318K and for 1C, 2C, 3C C-rates



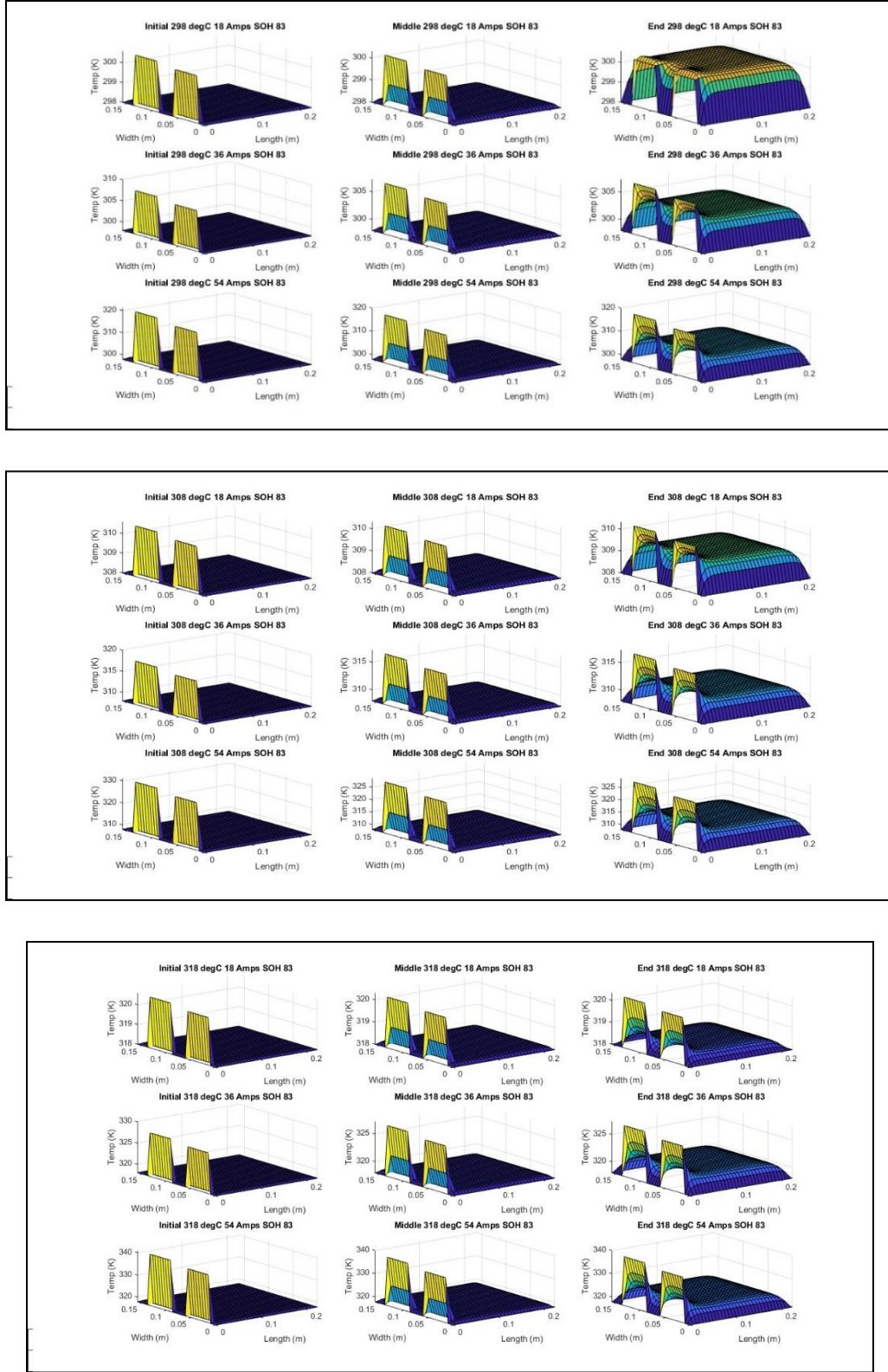
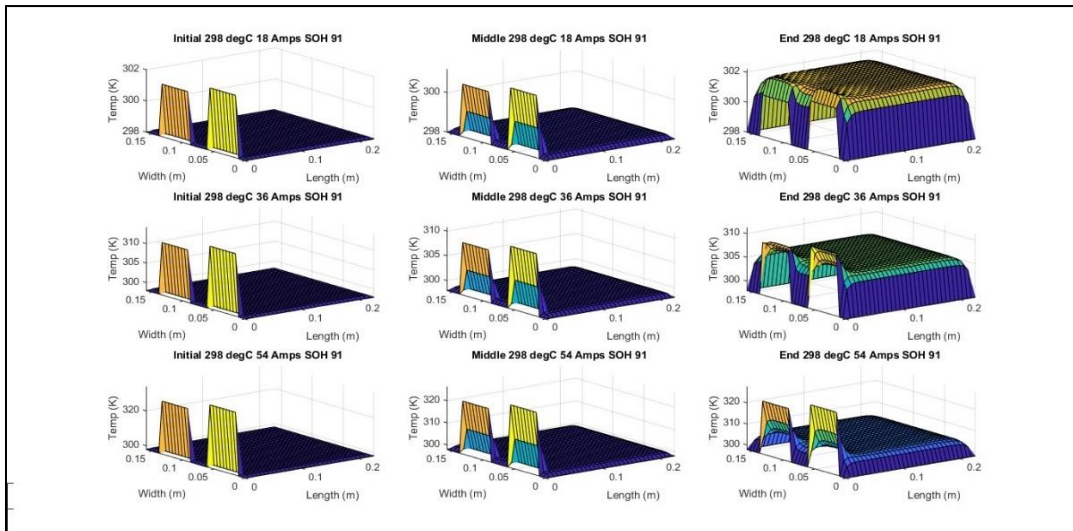
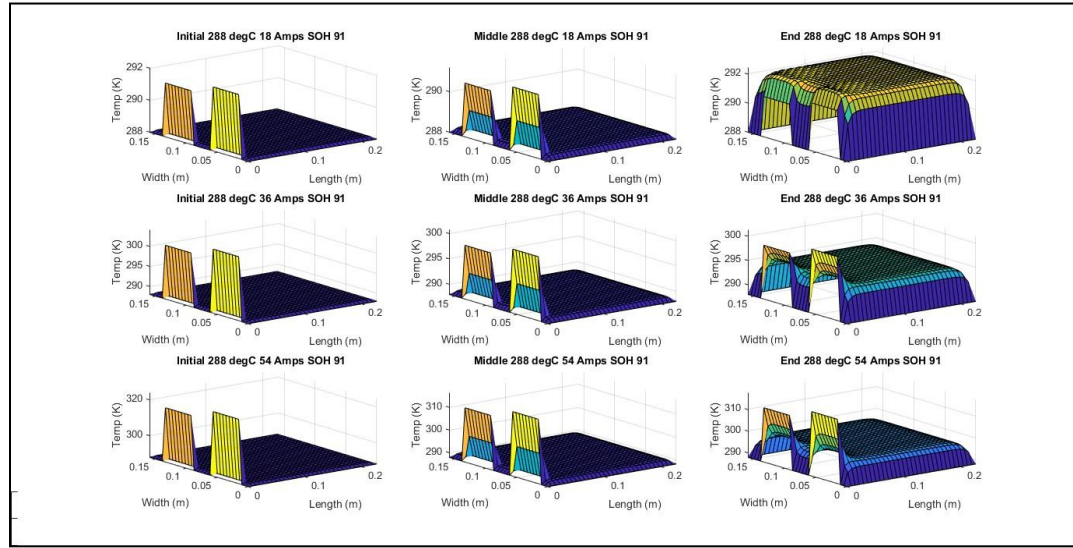
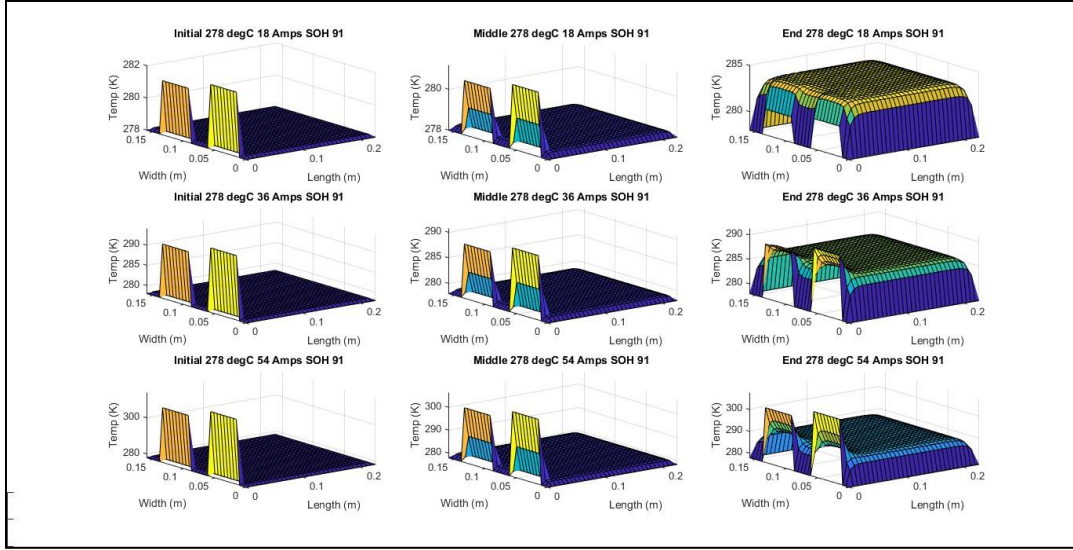


Figure 46: Initial, middle and end Surface Temperatures for SOH 83% at 278K, 288K, 298K, 308K, 318K and for 1C, 2C, 3C C-rates



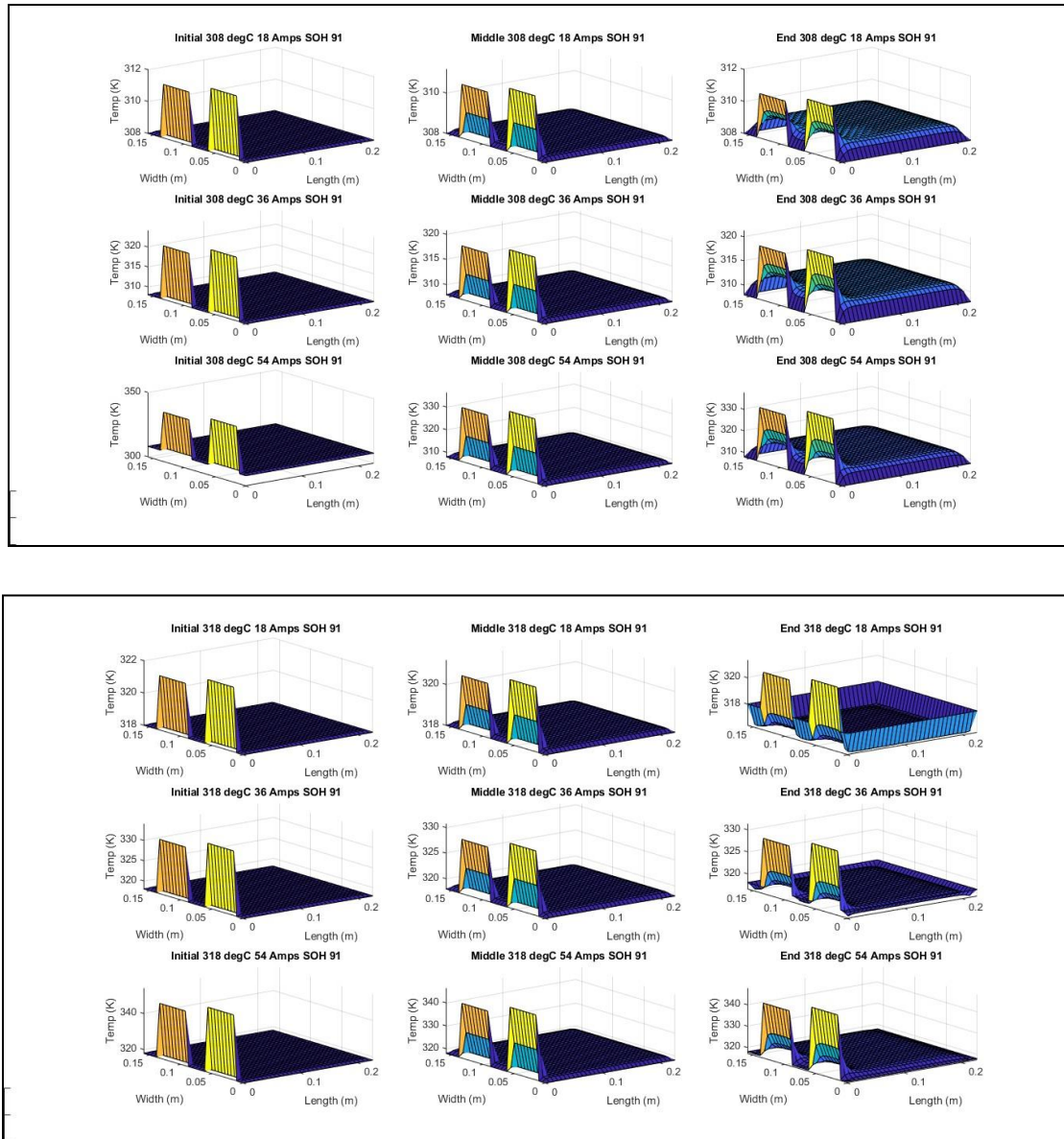


Figure 47: Initial, middle and end Surface Temperatures for SOH 91% at 278K, 288K, 298K, 308K, 318K and for 1C, 2C, 3C C-rates

The Pearson coefficients for the 2D model are shown in Table 20. They are found to be in good agreement with experimental results using only the thermal parameters listed in Table 20.

Table 20: Pearson Coefficients for 2D Model at given SOHS, Ambient Temperatures and Currents

SOH	T _{amb}	Current	R	SOH	T _{amb}	Current	R
0.65025	288	18	0.880814	0.83435	318	36	0.788402
0.65025	288	36	0.91583	0.83435	318	54	0.866131
0.65025	288	54	0.952475	0.83435	T=318 Total		0.891423
0.65025	T=288 Total		0.961966	0.83435	278	18	0.951127
0.65025	298	18	0.843163	0.83435	278	36	0.971996
0.65025	298	36	0.889039	0.83435	278	54	0.973421
0.65025	298	54	0.929056	0.83435	T=278 Total		0.983957
0.65025	T=298 Total		0.956204	0.83435	ALL T		0.998991
0.65025	308	18	0.797272	0.90575	288	18	0.867422
0.65025	308	36	0.870725	0.90575	288	36	0.94532
0.65025	308	54	0.910825	0.90575	288	54	0.935921
0.65025	T=308 Total		0.943982	0.90575	T=288 Total		0.968205
0.65025	318	18	0.773908	0.90575	298	18	0.8204
0.65025	318	36	0.854982	0.90575	298	36	0.844612
0.65025	318	54	0.880574	0.90575	298	54	0.880708
0.65025	T=318 Total		0.925566	0.90575	T=298 Total		0.939296
0.65025	278	18	0.91765	0.90575	308	18	0.777065
0.65025	278	36	0.946588	0.90575	308	36	0.809052
0.65025	278	54	0.956122	0.90575	308	54	0.763914
0.65025	T=278 Total		0.961957	0.90575	T=308 Total		0.886583
0.65025	All T		0.996437	0.90575	318	18	-0.29694
0.83435	288	18	0.911915	0.90575	318	36	0.298538
0.83435	288	36	0.954568	0.90575	318	54	0.562378
0.83435	288	54	0.952472	0.90575	T=318 Total		0.772904
0.83435	T=288 Total		0.979624	0.90575	278	18	0.960738
0.83435	298	18	0.830404	0.90575	278	36	0.977633
0.83435	298	36	0.921984	0.90575	278	54	0.97567
0.83435	298	54	0.918414	0.90575	T=278 Total		0.98212
0.83435	T=298 Total		0.960366	0.90575	All T		0.998729
0.83435	308	18	0.740577		T=288K		0.95696
0.83435	308	36	0.855363		T=298K		0.934427
0.83435	308	54	0.899749		T=308K		0.897884
0.83435	T=308 Total		0.932978		T=318K		0.804559
0.83435	318	18	0.394938		T=278K		0.9654

The table shows the model is more accurate at low temperatures than at high temperatures. The model is most accurate at 83%SOH and least accurate at 65%SOH, with 91%SOH falling in between.

5.3. COMSOL Results

In Figure 48 we see how well the COMSOL 3D Mesh simulation fit the experimental data at 1C, 2C, 3C and 4C discharge rates.

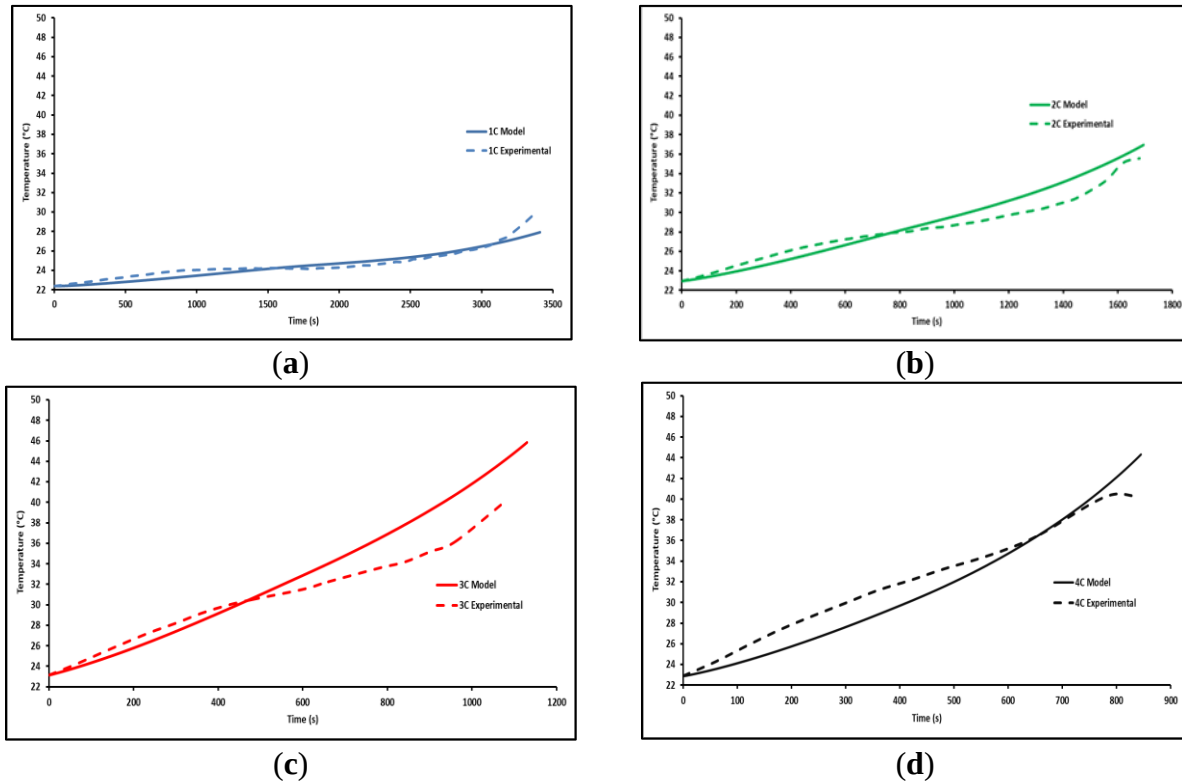


Figure 48: Comparison of experimental and model discharge temperature profiles at 22°C boundary condition (BC) for (a) 1C, (b) 2C, (c) 3C, and (d) 4C

The average battery surface temperature recorded by the four thermocouples, based upon their area, is plotted as a function of time. The temperature of the model is simply the average surface temperature of both sides of the battery. The experimental data shows that the thermocouples at TC-1 and TC-2 have the fastest rate of increase; these are the thermocouples nearest to the tabs of the battery. The high temperatures at these locations suggest the highest heat accumulation in these areas indicating an increased current draw and Ohmic heating at the tabs. Though the conductivities of the tabs are high there is still a large voltage drop at the tabs due to the junction

resistance. The figure shows that temperature increases with C-rate with 4C being the highest and 1C being the lowest. The data shows this to be true for all thermocouple locations. The highest temperatures were recorded at the end of discharge and the values were 28.68°C for 1C, 38.02°C for 2C, 47.87°C for 3C, and 47.49 for 4C.

Overall, the experimental data and model results were in good agreement. The model's temperature depends on the heat generated by losses in the battery cell (primarily Ohmic, activation, and mass transfer/concentration losses), the thermal mass of the battery cell, and the heat transfer to the environment. At high C-rates (3C and 4C) the model accuracy decreases with time, one major reason for this decrease is a non-constant convective heat transfer coefficient which increases with increasing temperature differential.

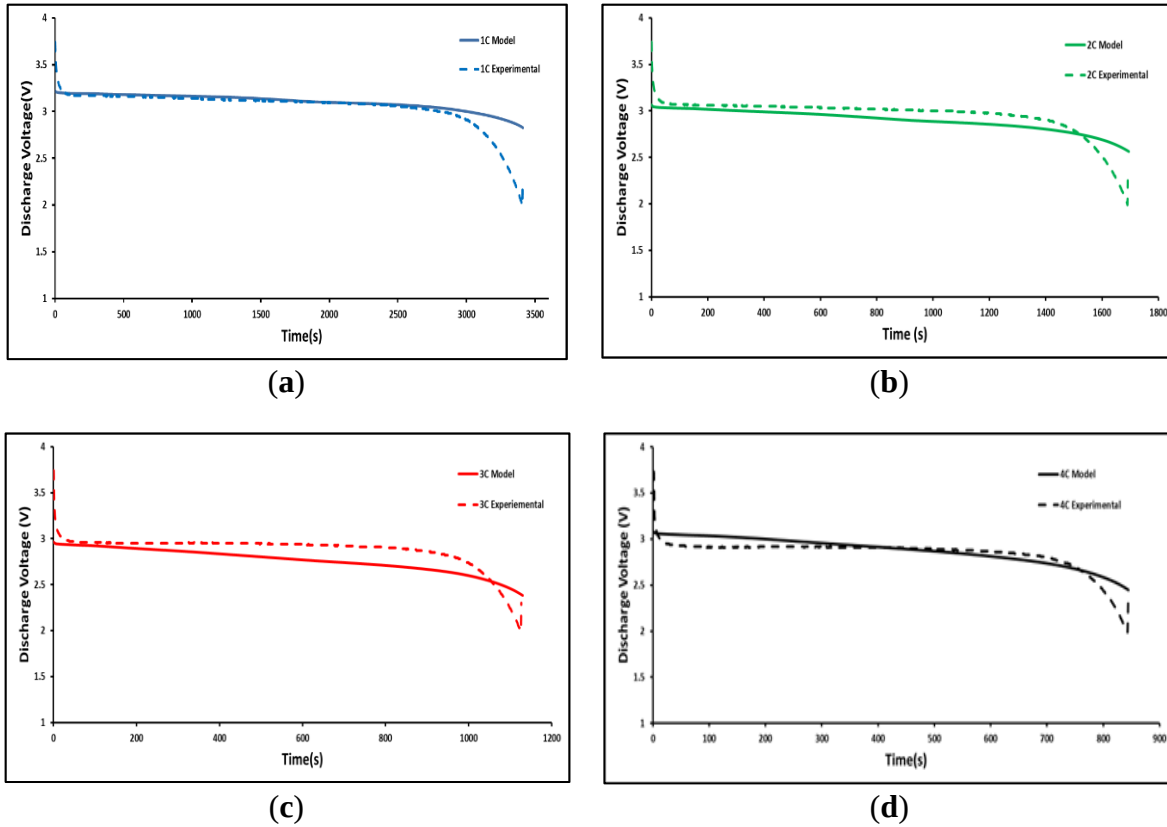


Figure 49: Comparison of experimental and model discharge voltage profiles at 1C, 2C, 3C, 4C at 22°C ambient

Figure 49 shows the experimental and model voltage profiles at 1C, 2C, 3C, and 4C discharge rates held at an ambient temperature of 22°C. The model is a great fit to the experimental data and

demonstrates the robustness and accuracy of the model as both the average surface temperature and the voltage profiles are accurate.

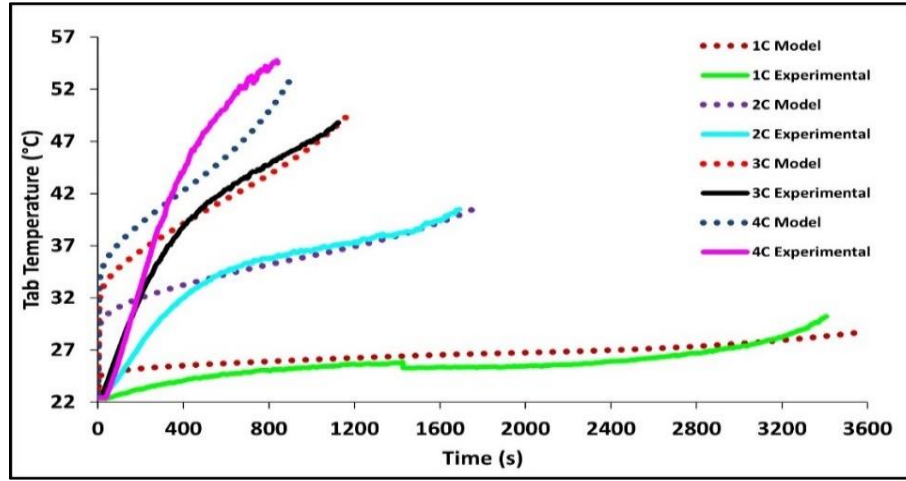


Figure 50: Comparison of experimental and simulated tab temperature profiles at 1C, 2C, 3C, 4C at 22°C ambient

Figure 51 and Figure 52 show the temperature of the battery at the half-way and the end of the discharge cycle.

Figure 50 compares the experimental and model tab temperatures at 1C, 2C, 3C, and 4C discharge rates. The figure shows tab temperatures are always higher than the surface temperature. The tabs, just as the battery, experienced their highest temperature profiles at 4C and their lowest at 2C following the expected trend. It is observed that increased discharge rates result in increased tab temperatures. The highest temperatures were recorded at the end of discharge with the values of 28.718°C for 1C, 40.52°C for 2C, 49.85°C for 3C, and 52.92°C for 4C. It is seen that the model closely follows the tab temperatures for the later time periods, while during the initial stage, the error is large, this is the case as a uniform heat source is assume in the volume of the tab instead of Ohmic heating between the areas of which current is flowing. We note that the initial temperature does match but due to the initial rapid increase in temperature the figure looks incorrect. The effect of non-uniform temperature at the cell level has a profound effect on cycle life. Temperature non-uniformities lead to unequal current densities in the electrodes and non uniform lithium deposition and SOCs across the surface of the electrode which accelerates degradation appreciably as seen in Figure 30.

A convective boundary condition is assumed at all boundaries of the battery with a convective coefficient of 5 W/m²K and an ambient temperature of approximately 23°C. There are 2 heat sources in this thermal model, the first is the heat generated from the electrochemical 1-D model of the battery while the second is the Ohmic resistance within the tabs. The 1-D battery heat is calculated as the irreversible heat, which is calculated as the local current source multiplied by the overpotential, in addition to the reversible heat and an electrolyte conductivity loss term. The reversible heat is calculated as the local current source multiplied by the temperature multiplied by the derivative of the equilibrium potential with respect to temperature.

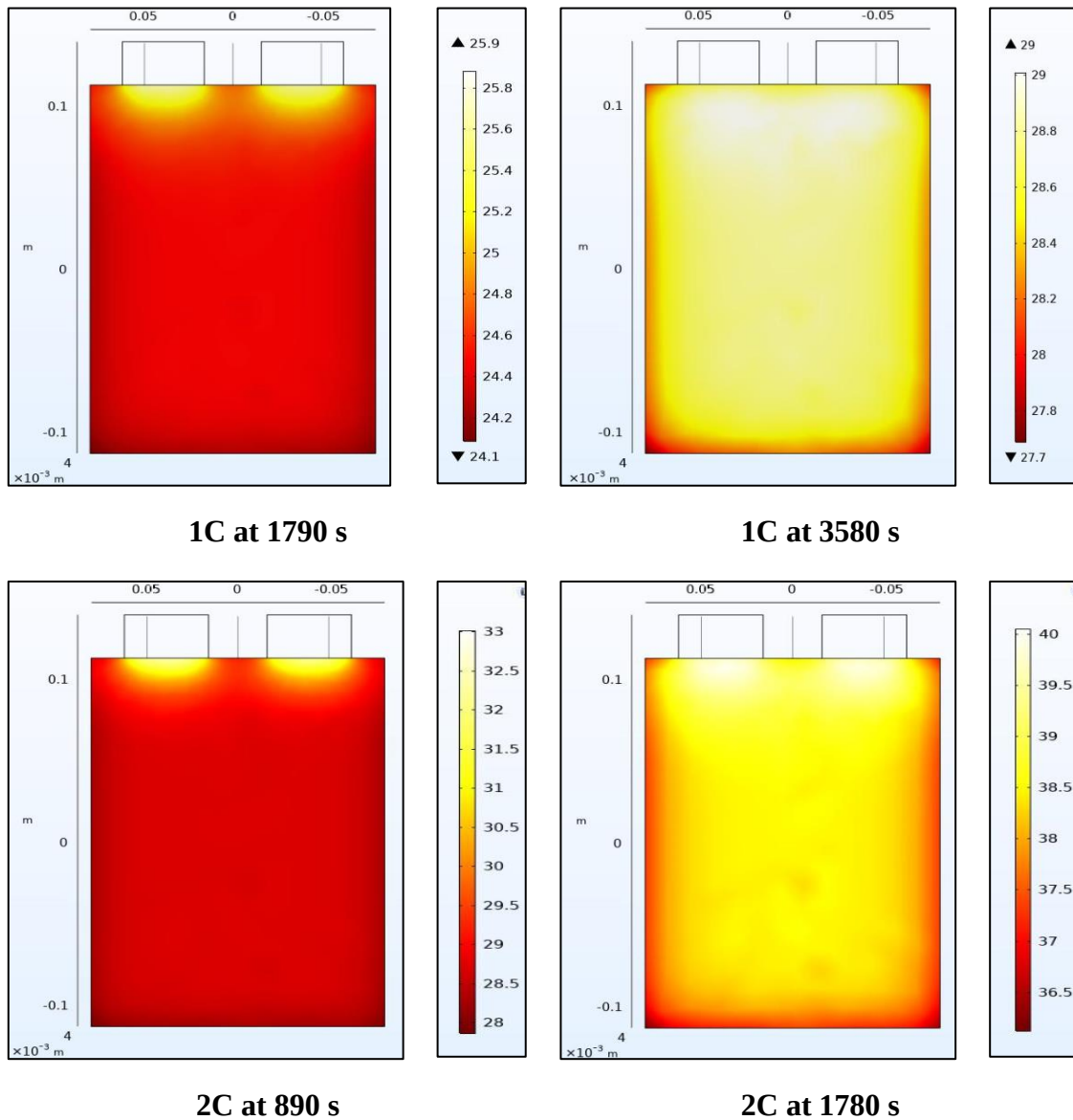


Figure 51: Temperature contours at 1C and 2C at the middle and end of discharge

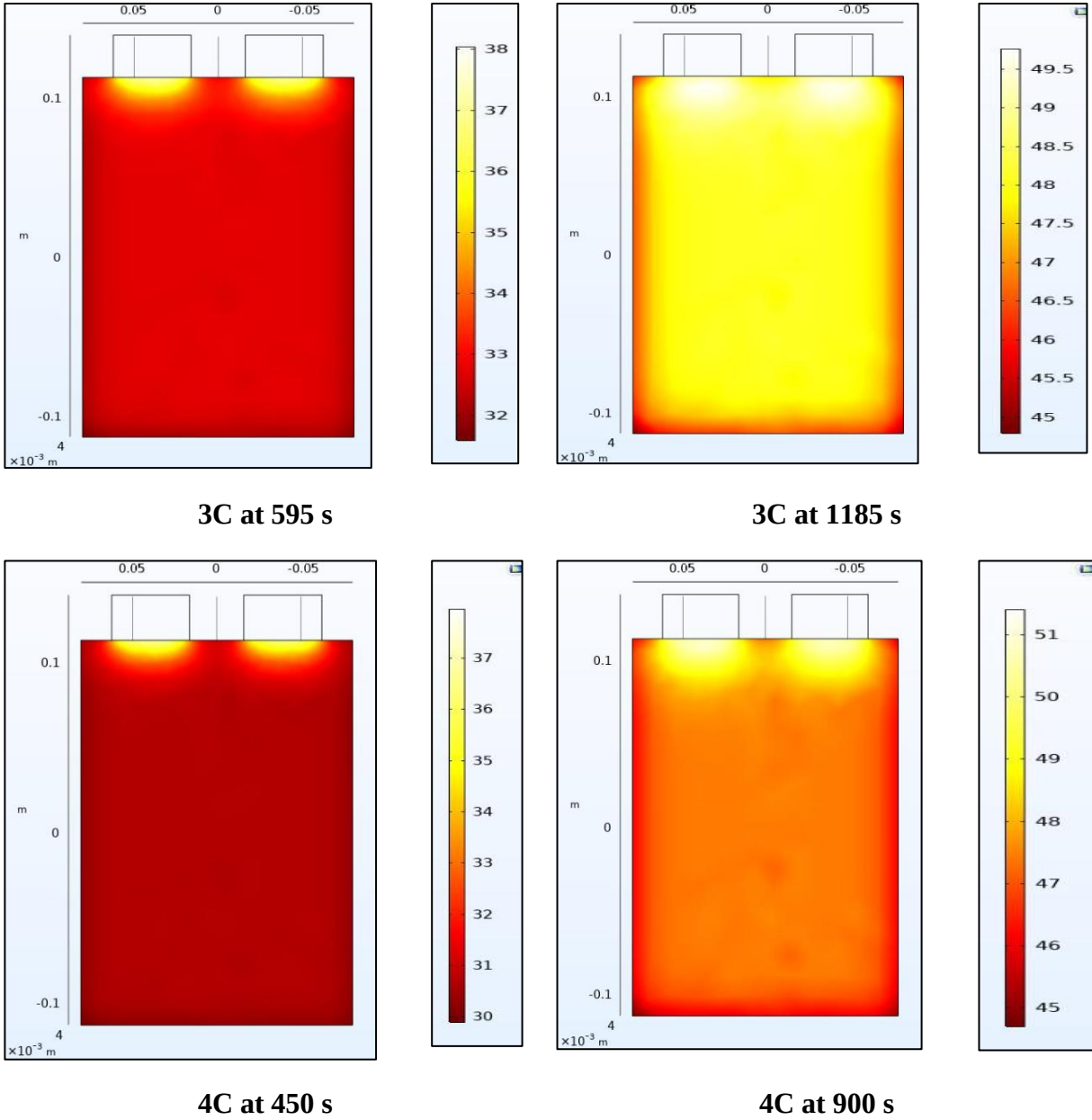


Figure 52: Temperature contours at 3C and 4C at the middle and end of discharge

The electrolyte conductivity loss term is made up of two terms: (1) the first is being the electrolyte current density multiplied by the derivative of the electrolyte potential, and (2) the second being the electrode current density multiplying the derivative of the electrode potential in the x-direction. Both the reversible and irreversible heat are included in the model, but the heat of mixing is neglected. We observe that heating at the tabs due to Ohmic heating leads to increased temperatures at the top of the battery compared to the bottom. The temperature range within the

battery is larger at half discharge than at full discharge with higher C-rates having larger temperature ranges. Non-uniform temperatures within the battery lead to different parts of the battery delivering different current outputs and ultimately lead to degradation. This is why tab cooling has been a leading field of research. Temperature uniformity at the pack and cell level is a necessity to prolong battery life.

Figure 53 shows that the total energy lost as heat is the sum of the heat in the separator, electrolyte loss, irreversible loss, and reversible loss. We can see that the total heat increases with C-rate along with its constituent components with the only exception being the reversible heat which becomes increasingly negative. It is observed that the largest contributors to the heat are the electrolyte resistance terms in both the electrodes and the separator. ie the electrolyte heat and the separator heat. Figure 54 shows that for discharge the reversible heat in the cathode is positive while that in the anode is negative with the total reversible heat being negative at these C-rates and with the given parameters. This means that the anode produces heat during charge and absorbs heat during discharge, the reverse is true for the cathode. We also note the electrolyte loss is larger in the cathode than in the anode.

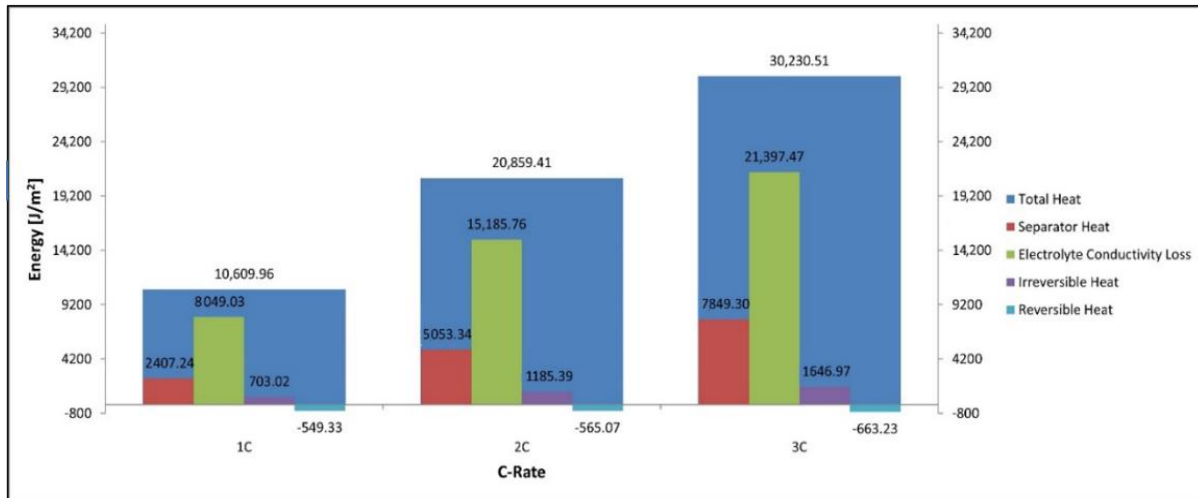


Figure 53: Total power, separator heat, electrolyte, irreversible, and reversible heat

We see from Figure 54 that the total heat produced in the cathode is higher than that of the anode, this is true for all heat components including the electrolyte, irreversible, reversible components. The cathode's larger electrolyte loss means that the contribution of the electrolyte current to the total current in the electrode is larger in the cathode than in the anode. The electrolyte current

experiences a much larger spatial voltage gradient ($\frac{\partial \phi_l}{\partial x}$) and subsequent voltage drop than the spatial voltage gradient for the solid electrode ($\frac{\partial \phi_s}{\partial x}$) thus we have a larger energy loss in the electrolyte heat term in the cathode as this is where we have a larger electrolyte current. The reversible heat for the anode during discharge is in fact negative and has a cooling effect, while this is the opposite for the cathode as stated in Heubner et al. [23]. Finally, we see the irreversible heat term is also larger in the cathode than the anode thus the sum of all heat terms for the cathode is larger than the anode.

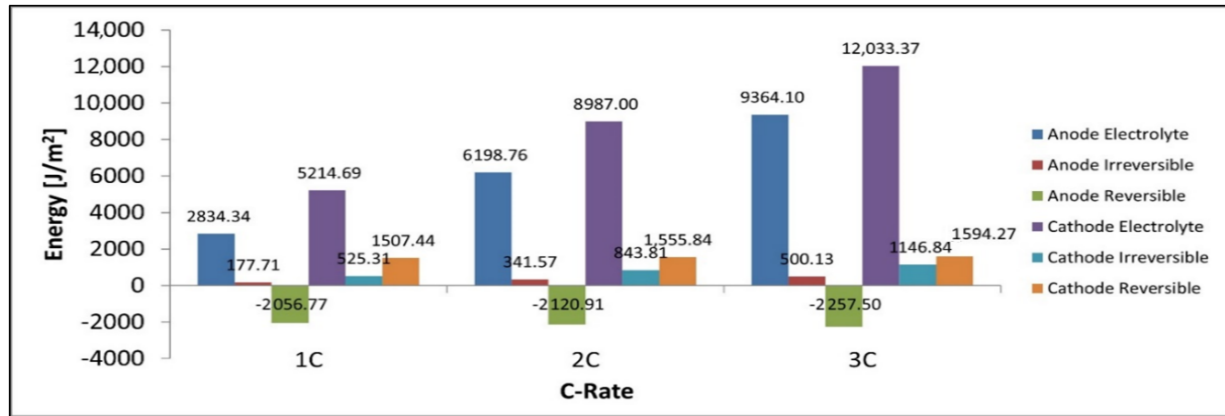


Figure 54: Anode electrolyte, anode irreversible heat, anode reversible heat, cathode electrolyte, cathode irreversible heat, cathode reversible heat

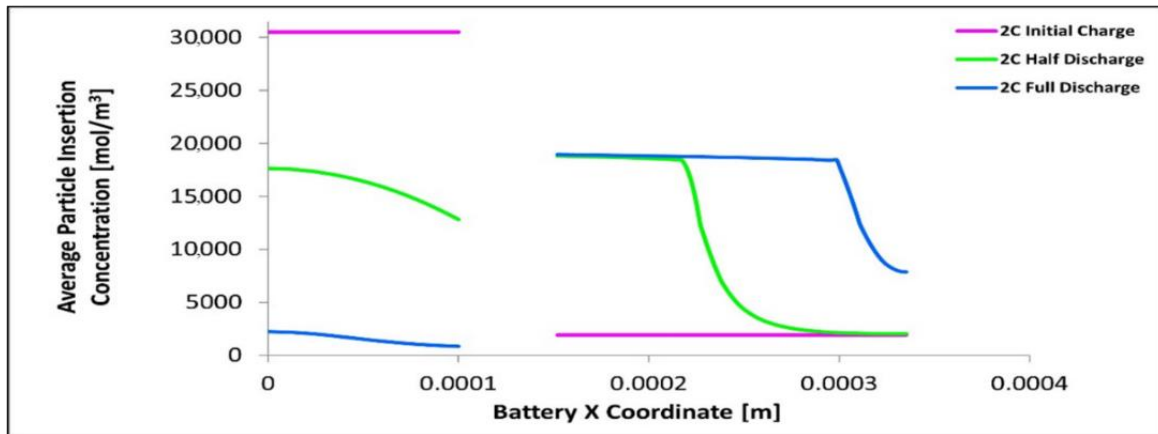


Figure 55: Average insertion particle concentration as a function of x-position shown at 0s, 890s, and 1780s

Figure 55 shows the lithium concentration in the electrodes as a function of position and time. We have noted that the results for 1C, 2C, and 3C C-rates are similar in shape and pattern and have been neglected for clarity, instead just the data for 2C is chosen and presented in the figure. As expected the average lithium concentration in the particles decreases with time in the anode and increases with time in the cathode. We noted that the average lithium particle concentration for the cathode is higher near the electrolyte-electrode interface and lower the deeper the position in the cathode porous electrode, this situation is reversed for the anode. We noted that for the cathode the average lithium concentration near the electrolyte surface is relatively constant from the halfway discharge to full discharge while the deeper layers do change in concentration. For the anode, we observed that even at the electrode-electrolyte interface there is still a change in concentration with time at the specified times. We note the plateau for the cathode at approximately $19,000 \text{ mol/m}^3$ this is close to the maximum Lithium concentration in the positive electrode of $21,190 \text{ mol/m}^3$. We also found that the presence of excess cathode material as the concentration within the cathode in the deeper layers is lower than the maximum at the end of discharge. This excess cathode material is one of the factors that contribute to the non-uniform concentration in the cathode. We also note that the cathode achieves close to full saturation (maximum intercalation concentrations) before intercalating into deeper layers and this is yet another contributor to the increased uniformity in the anode than the cathode. The excess cathode material explains the shape of the degradation graph in Figure 10. We note that the surface concentration is given by the PDE Equation (5) and that the diffusion coefficient in this temperature range is about 100 times larger for the anode than the cathode with the porosity of the anode also being larger, thus as expected the anode has a more uniform surface concentration due to the ease of intercalation into the electrode particles.

5.4. Parallel Pack Results

The dynamics of unequal voltages in parallel are complex and have a large effect on pack cycle life, energy efficiency, capacity and power density. We see in Table 22 the effect of geometry and C rate on end of charge and discharge voltages. This nonuniformity leads to enhanced cell degradation as the SOC is a key determining factor to cycle life. The pack geometry and internal resistances are the key components to determining the current delivered from each cell with the cells closest to the tabs delivering the highest currents if all internal resistances are the same and

both anode and cathode tabs are in the same direction. Figure 56 and Figure 57 show that the pack capacity is highly correlated to compound variable of Average Resistance and distance to output terminal.

We see the effect is more pronounced for the end of charge resistance than the average resistance during full discharge. This implies that the voltages are about equal throughout the process when the busbar resistances are small though the current is severely affected by even minute differences.

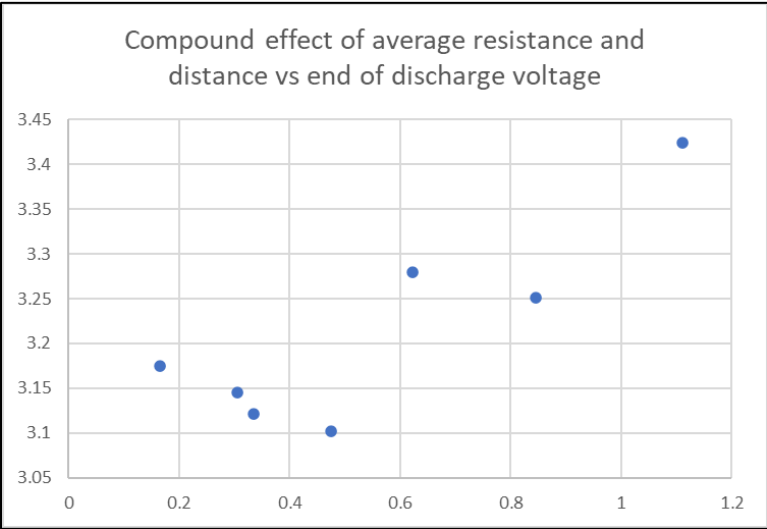


Figure 56: End of discharge voltages versus compound effect of distance to tab and average internal resistance

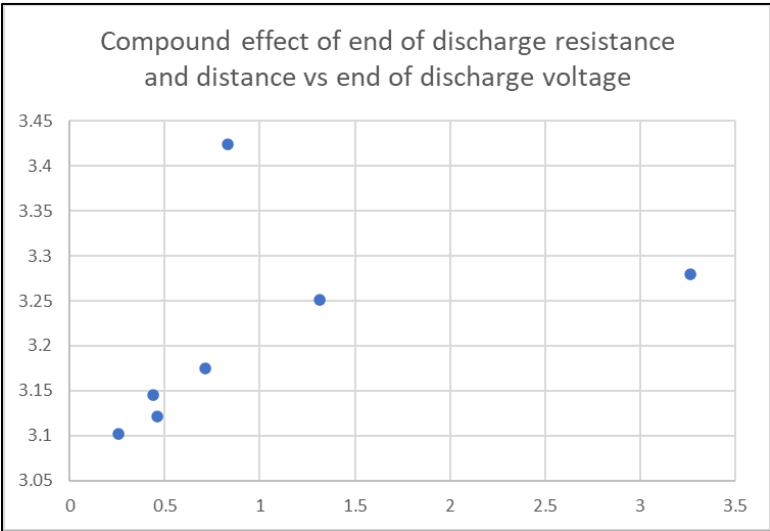


Figure 57: End of discharge voltages versus compound effect of distance to tab and 90% DOD internal resistance

In order to create a more uniform cell discharge current throughout the pack the tabs can be moved. We know from both physiochemical models and from circuit models the current through each cell must be conserved at either terminal. We see the effects of tab manipulation in Figure 58.

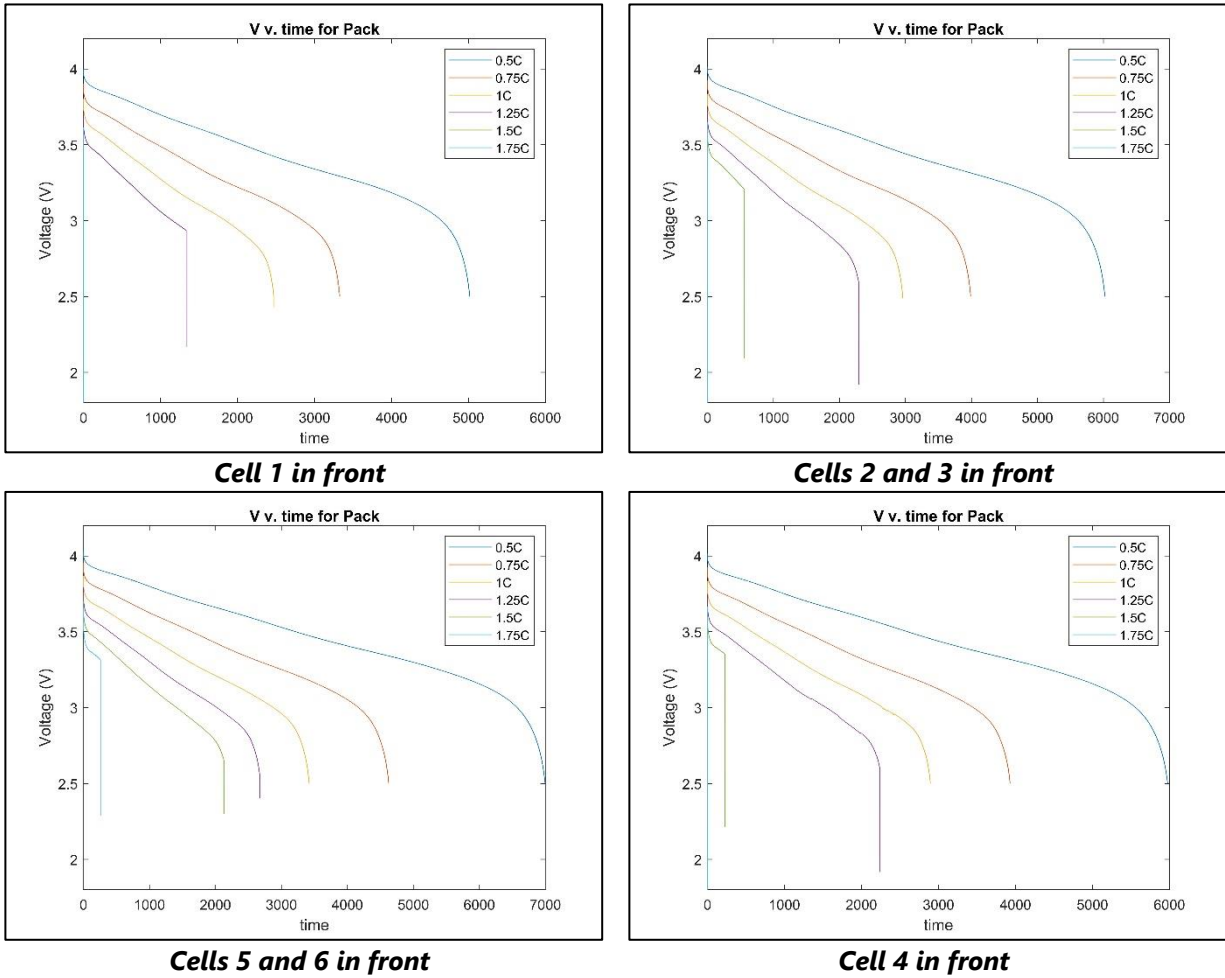
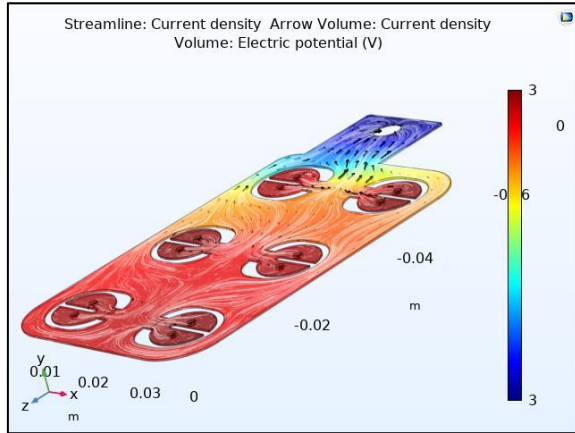


Figure 58: Voltage versus time plots showing the effect of rotating pack at 90 degree turns

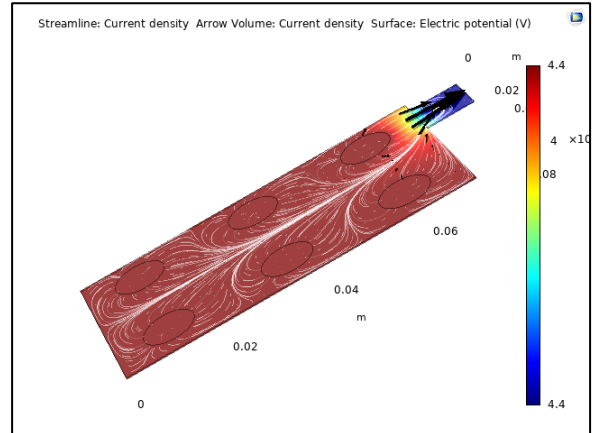
The Figure shows that the pack's capacity is drastically affected by the positioning of the cells and the geometry of the pack. We note that this is especially true as the C rate increases. We note that at 1.75C the capacity suddenly drops. This is the limiting current density and is due to mass transfer losses at the cell level. The concentration of the active species cannot meet the demand at such high current densities.

Variables such as temperature and capacity are highly correlated to cell current densities and can also be used to statistically model the pack. The heat produced is predominantly from the cell

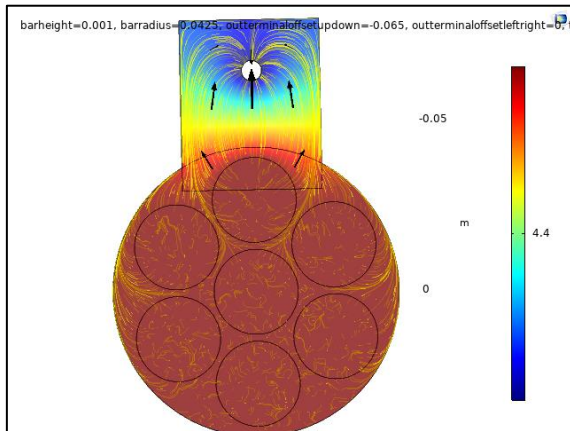
internal resistance, thus the current can be predicted by solving the heat equation. A typical current density profile is presented in Figure 59, we see that tab placement can drastically effect the packs capabilities.



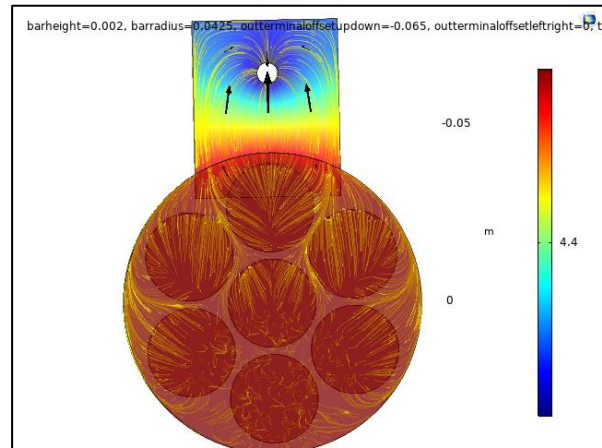
(a) 6 Cell Busbar



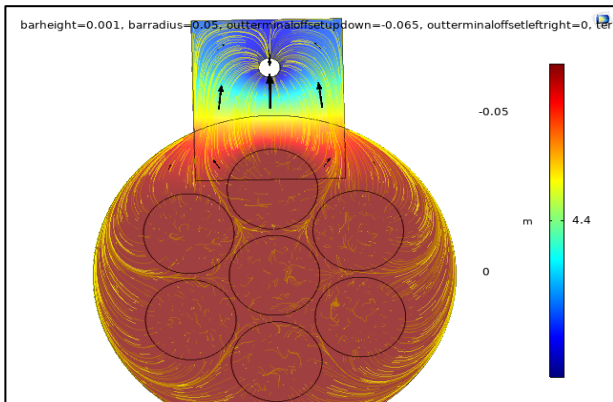
(b) 6 Cell Busbar no hole



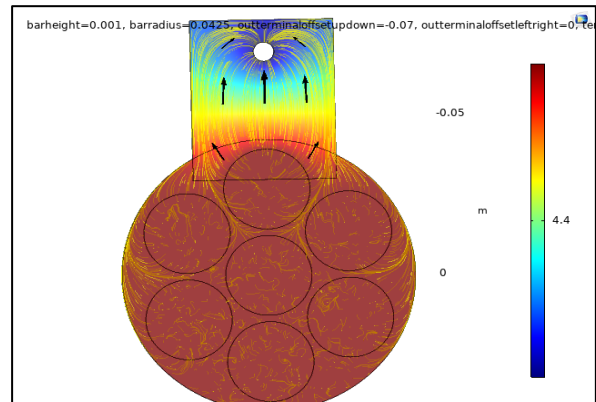
(c) Lab Bubar Simulation



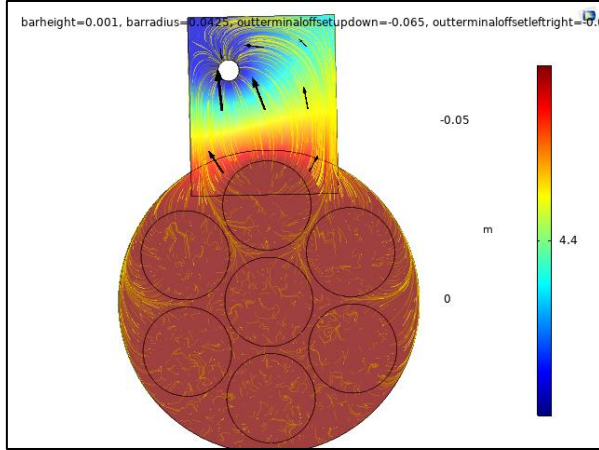
(d) Increased Thickness



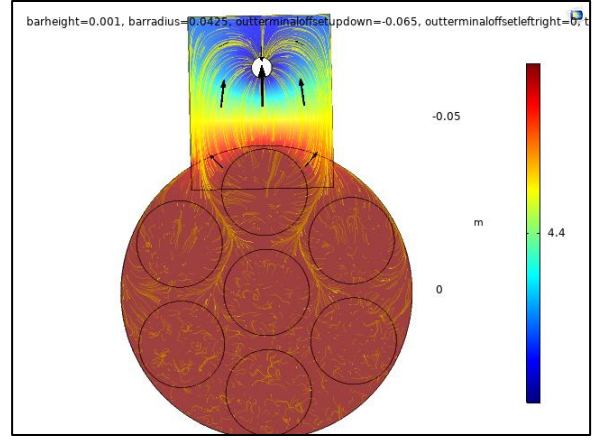
(e) Increased Radius



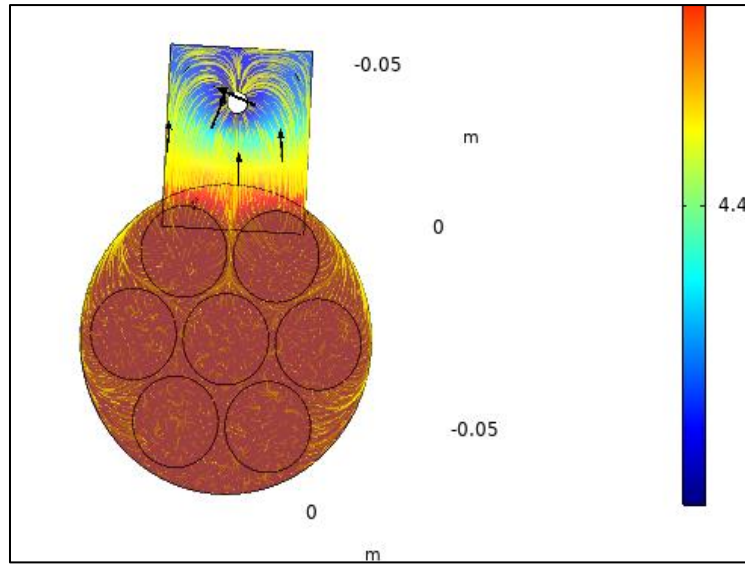
(f) Output Terminal Shifted Up



(g) Output Terminal Shifted Left



(h) Increased Distance between Battery Terminals



(i) Battery Pack Rotated 30°

Figure 59: Current Densities, Streamlines and Voltage Potentials in various busbar configurations with equal voltage from cell terminals

The placement of high internal resistance cells further from the tabs can result in much larger maximum current and power delivery as large voltage drops are seen at high C-rates when these cells are placed near the terminal. Placing tabs on opposite ends of the pack also can lead to more uniform current densities and temperatures throughout the pack. The currents and standard deviations from the various terminals in Figure 59 a-i are presented in Table 21.

Table 21: Simulated Current Profiles of Battery Terminals presented in Figure 59 a-i

Case	A	B	C	D	E	F	G	H	I
Terminal 1	10.9209	17.87	19.998	19.9945	19.9993	19.99	19.99	19.99	9.818
Current (A)	5226	931	865	57	8797	883	883	879	749
Terminal 2	5.66871	1.971	5.39E-	0.00261	2.89E-	5.57E-	7.05E-	5.77E	10.17
Current (A)	5454	04	04	72	04	04	04	-04	811
Terminal 3	1.61102	0.076	9.68E-	1.31E-	2.98E-	1.00E-	1.27E-	3.12E	0.001
Current (A)	1374	741	09	07	06	08	08	-11	862
Terminal 4	1.20626	0.070	2.15E-	-4.00E-	2.96E-	-	-	2.40E	1.32E
Current (A)	8946	39	11	11	08	9.31E- 13	4.01E- 11	-11	-08
Terminal 5	0.31512	0.001	9.25E-	1.29E-	3.02E-	9.57E-	7.26E-	3.66E	8.91E
Current (A)	2666	246	09	07	06	09	09	-11	-09
Terminal 6	0.27791	0.001	5.95E-	0.00282	3.17E-	6.15E-	4.69E-	6.35E	0.001
Current (A)	927	269	04	5366	04	04	04	-04	276
Terminal 7									
Current (A)	NA	NA	-1.41E- 10	2.89E- 08	-1.58E- 10	- 1.72E- 10	- 1.07E- 10	3.08E -09	2.35E -06
Standard	4.21810	7.167	7.5587	7.55688	7.55901	7.558	7.558	7.558	4.879
Deviation	1061	971	8928	9457	9582	772	772	755	531

The table shows that the C rate at the cell level can be split in half by simply placing the outlet at an angle between the cells. This is shown to match our experimental data shown in Figure 58. We also note that the presence of a simple gap around the terminal allows for a drastic increase in current uniformity within the pack as shown in columns (a) and (b). The existence of obtrusions

along the current channel impacts the pack's uniformity, with voltages between the battery terminal and the exit terminal significantly raising busbar resistance and voltages behind them decreasing busbar resistance. The current flow can also be guided through well-designed perforations, as shown in Column B. We see in Table 22 that during charging a CCCV charge actually results in a higher standard deviation in the pack voltages.

Table 22: End of Discharge/Charge voltages for battery pack with Geometrical Considerations

Title	30A 1 facing tab After pack test	4.2 V cutoff charge	CCCV 4.2 V 0.2A	4 Facing Tab 30A discharge end of test	4 Facing Tab 25A discharge end of test
Cell#					
1	3.175	3.735	4.197	4.176	2.767
2	3.121	3.822	4.198	4.179	2.628
3	3.28	3.829	4.198	4.019	3.037
4	3.251	3.824	3.803	4.013	3.038
5	3.424	3.816	3.795	4.007	3.035
6	3.145	3.333	4.186	4.032	3.036
7	3.102	3.817	4.198	4.017	3.033
Deviation	0.105085	0.168640664	0.179132376	0.072578459	0.15728539

Table 23 shows the average internal resistance of each cell and is one of the most important considerations for both modeling the current density and the temperature in the pack.

Table 23: Average Internal Resistance and Cell Number

Cell Number	Average Internal Resistance
1	0.165948
2	0.334147
3	0.6216
4	0.845226
5	1.110953
6	0.305474
7	0.474126

We also observe that the cell placement also drastically affects the maximum capacity deliverable at a fixed C-rate. In Figure 58 and Figure 60 we see the effect geometry has on capacity and maximum current.

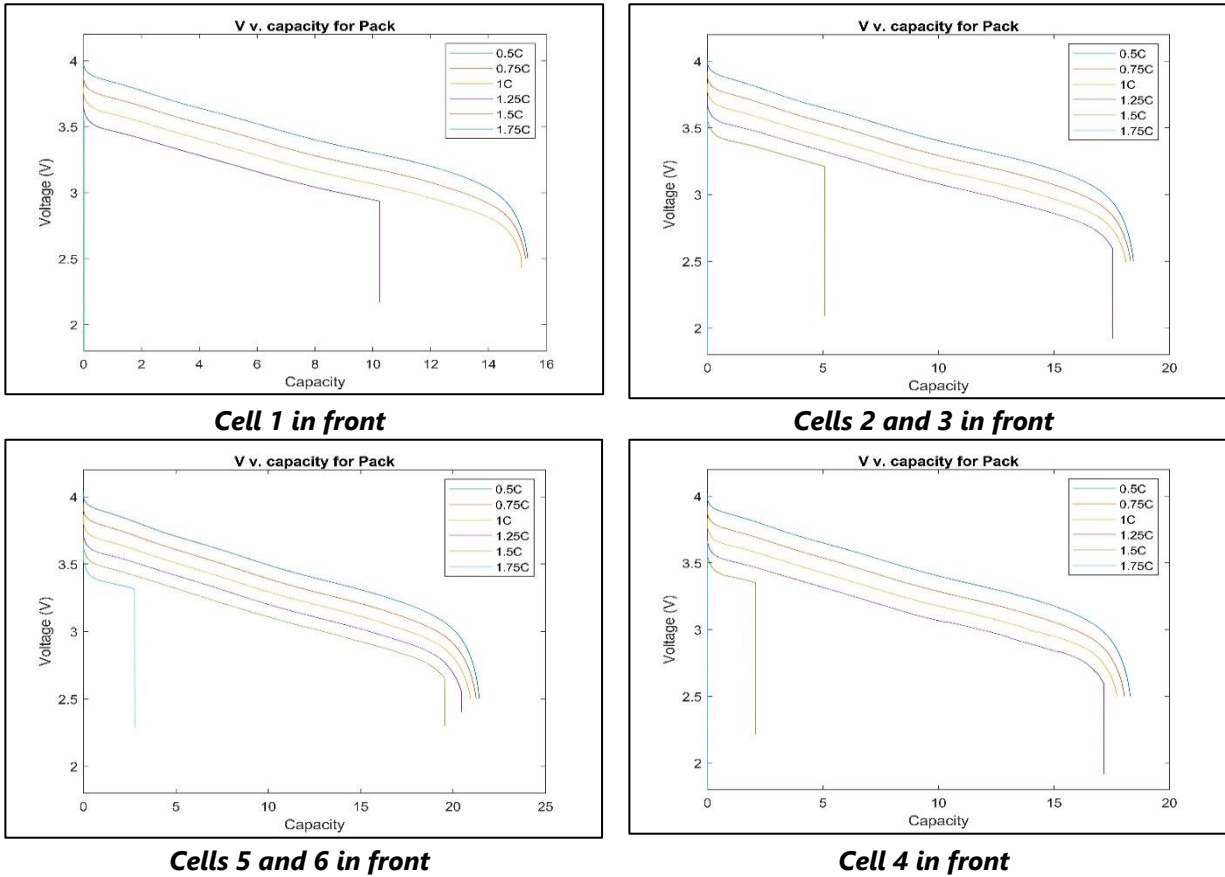


Figure 60: Voltage versus capacity plots showing the effect of rotating pack at 90 degree turns

In general we see that having 2 cells face the tab provides more capacity than a single cell arrangement. The potential across the highly conductive busbar is approximately uniform with no measurable voltage drop yet it is still one of the major influencing factors in determining the uniformity of the pack as even these small differences determine the current. Figure 61 shows surface plots for the internal resistance of the 7 cells in the pack. The surface is fit to equation (26). These are then used in the Simulink model as the battery internal resistance. As before we see an exponential rise in resistance values at low SOC's with the resistance also being larger at low C-rates.

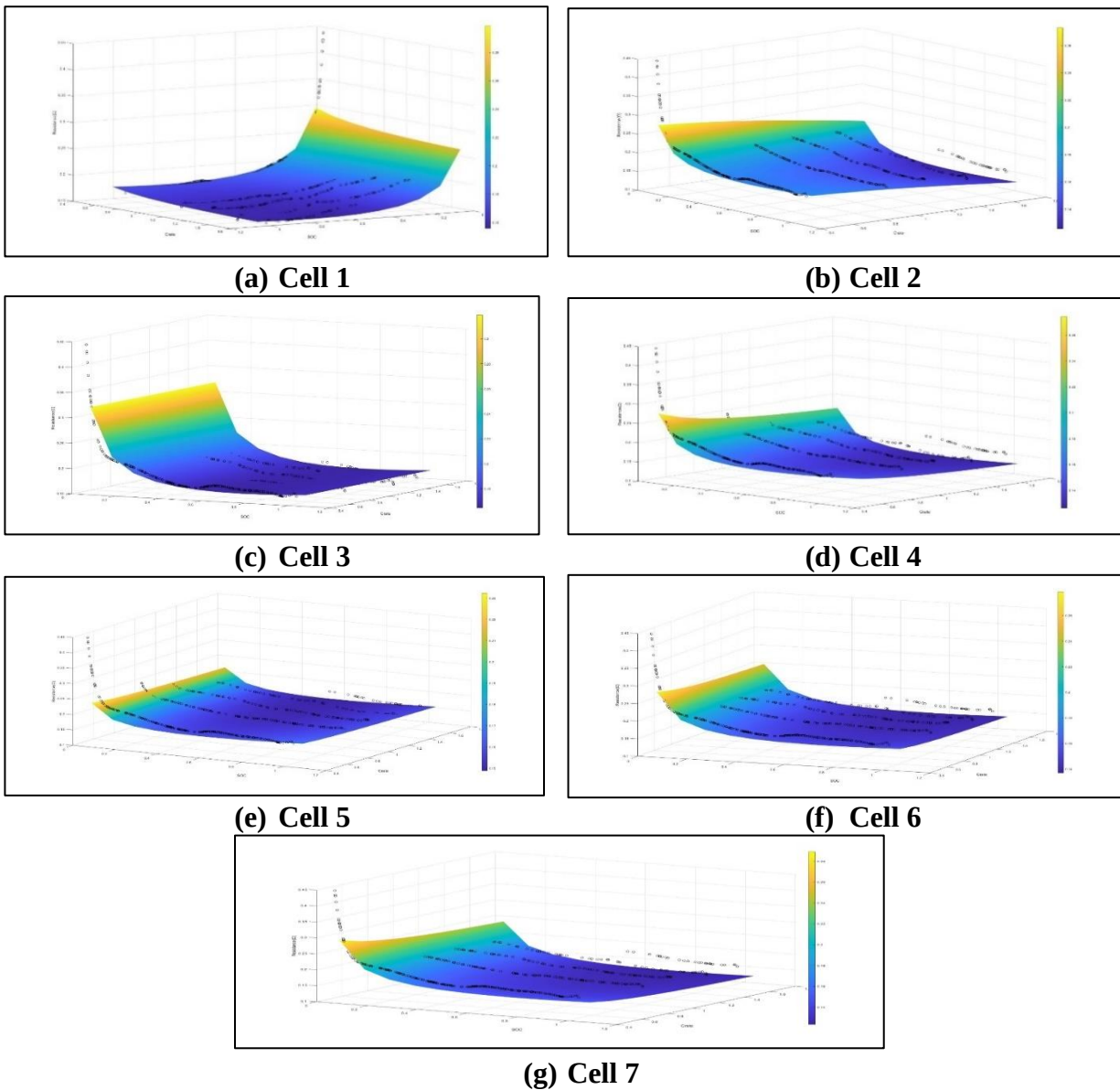
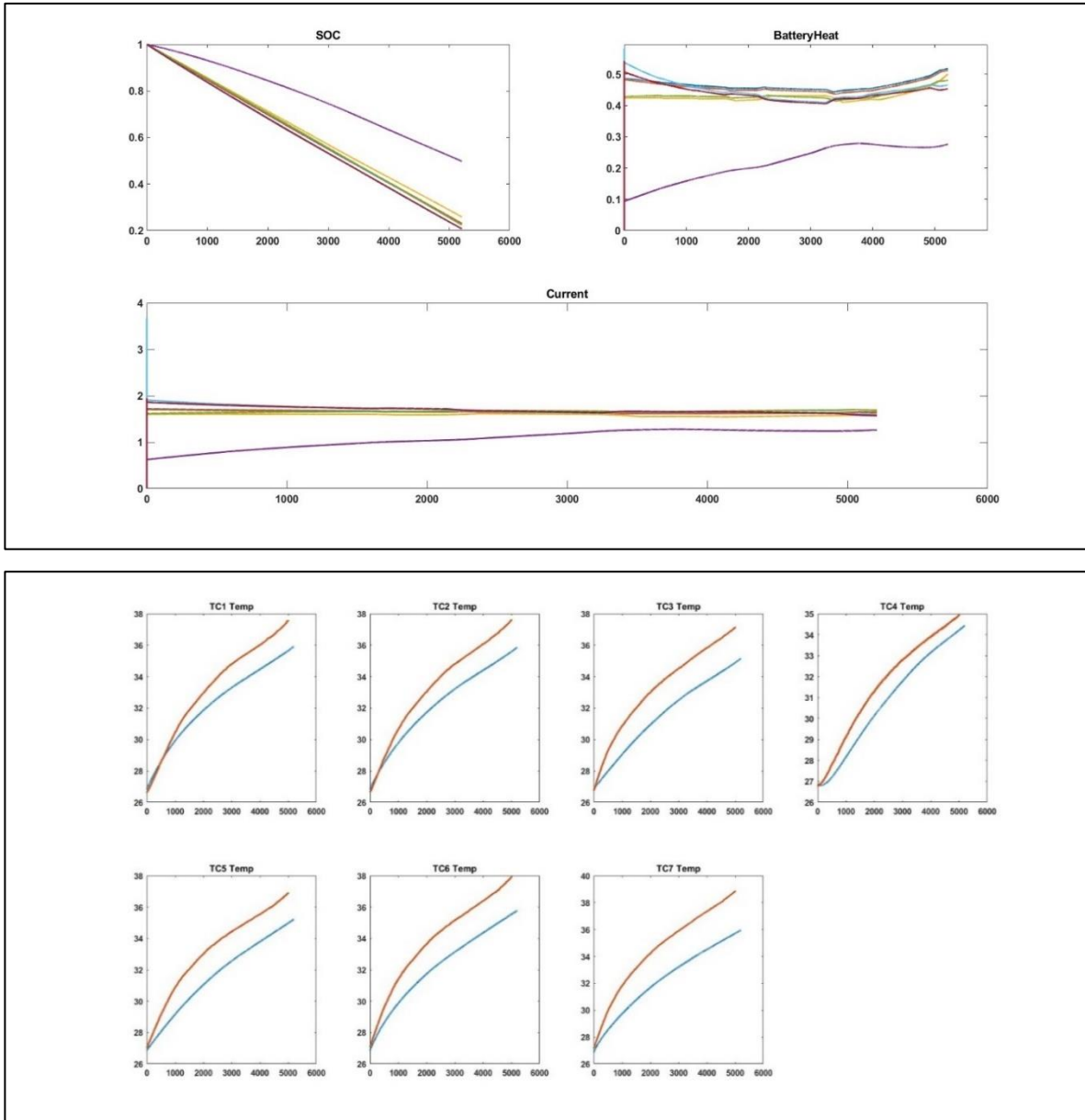
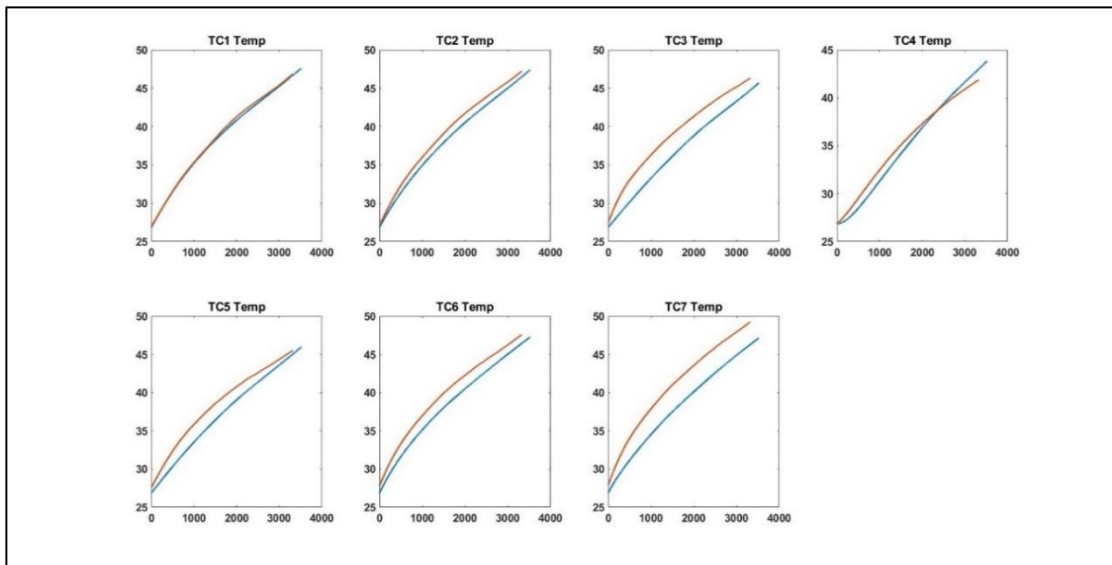
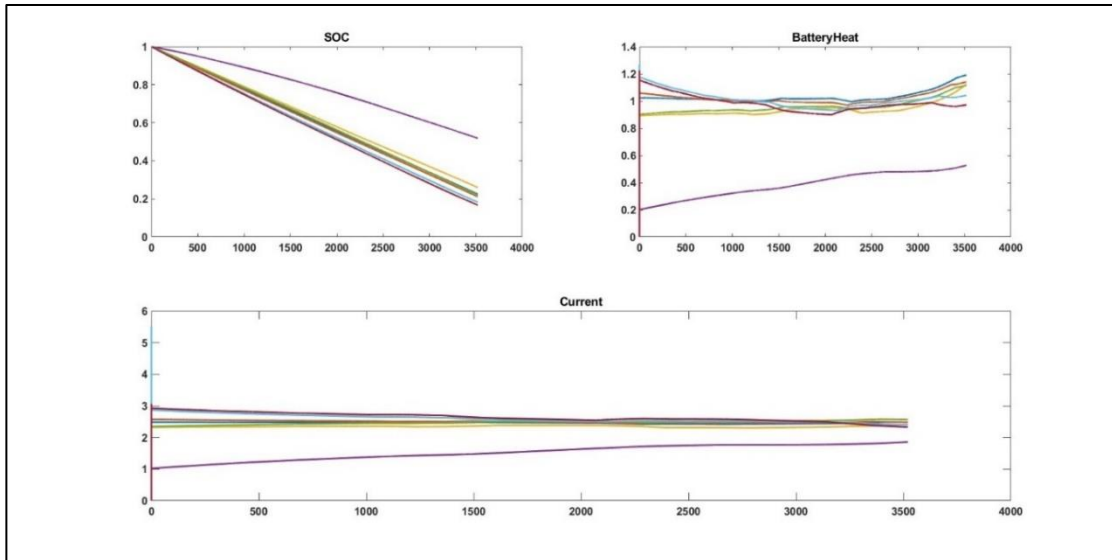


Figure 61: Internal Resistance Surface plots for the 7 Cells using Equation (26)

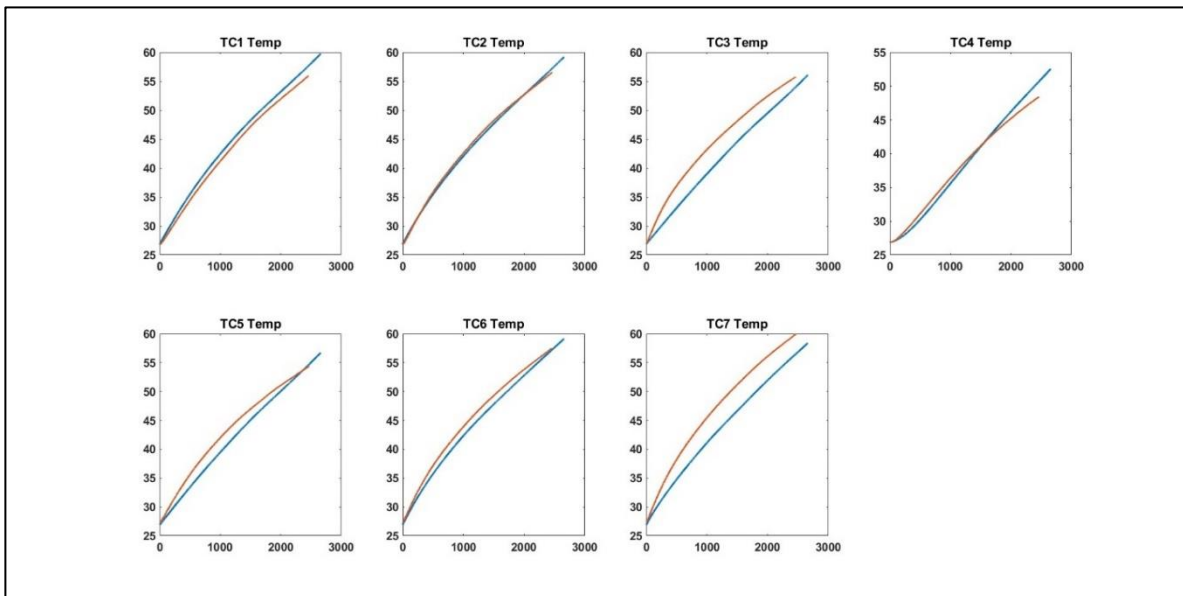
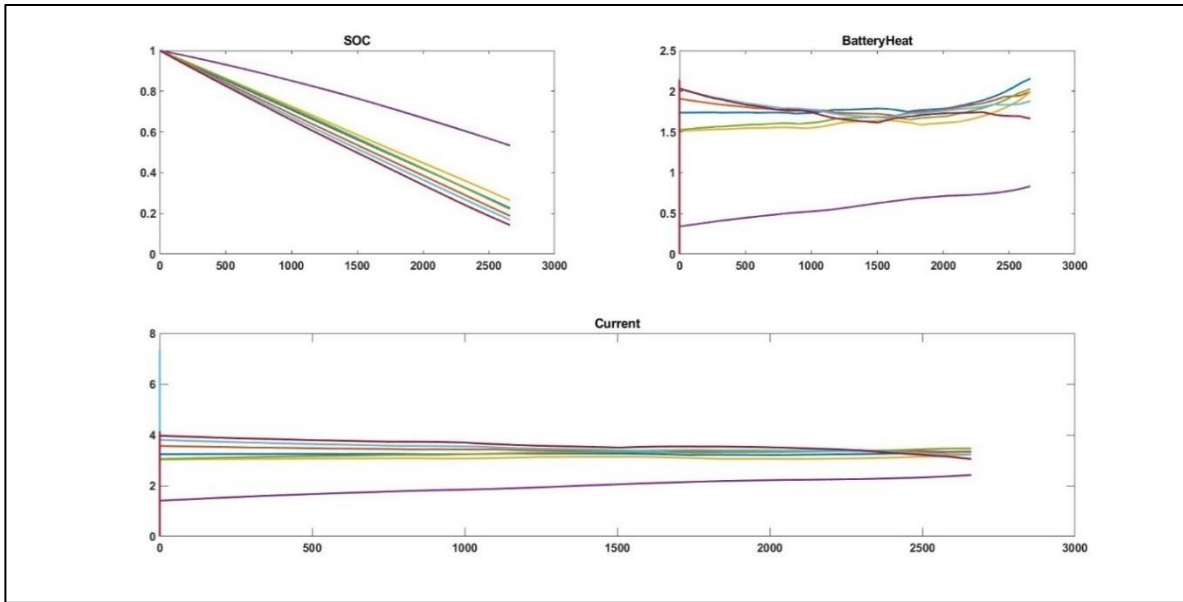
Figure 62 shows the output from the Simulink model with cell 1 in front. We see that the anode and cathode resistances for cell 4 need to be compensated for as the other voltages are in the path to the terminal and is not just a function of length. This resistance is seen to be 20 times more than the average with a corresponding drop in current and heat generated. We note that this cell retains a significantly higher SOC than the others. Cell 7 Cathode and Anode Resistances are seen to have a resistances 1.5 times less than average.



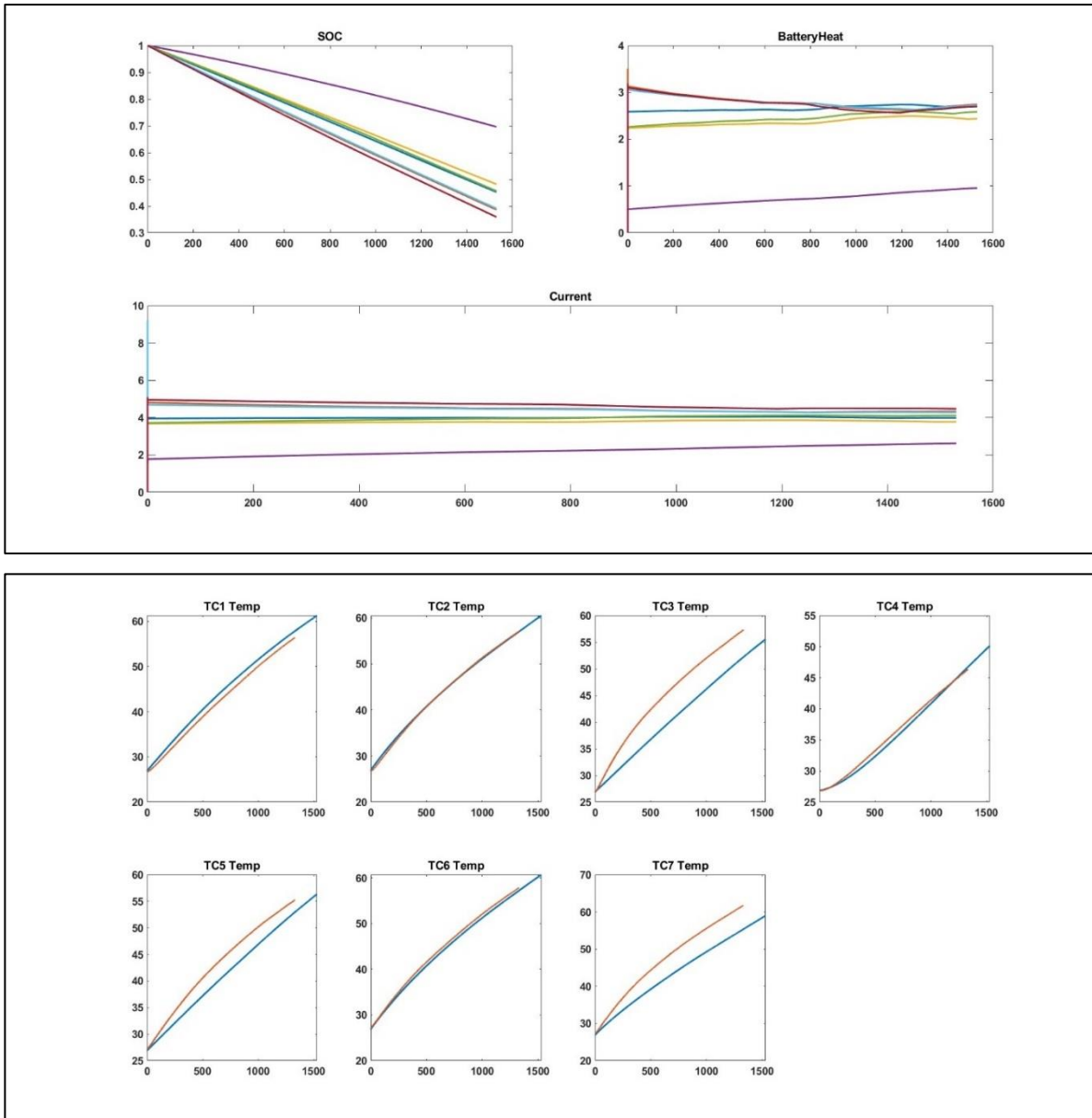
(a) 0.5 C-Rate



(b) 0.75 C-Rate



(c) 1 C-Rate



(d) 1.25 C-Rate

Figure 62: SOC, Current, Battery Heat and Temperature of 7P Simulation Cell 1 Infront. Blue Simulation Values are compared against Red Thermocouple Experimental Values

At high C-rates we see the greatest variance in SOC between the cells, this dramatically affects the overall deliverable pack capacity. High C-rates result in increased battery heat and higher temperatures. We note the particularly large difference for Cell4 in the Cell 1 infront setup. Cell 4 is seen to have the highest capacity and lowest heat generation.

Chapter 6 Conclusions and Recommendations

6.1. Conclusions

In this thesis, an experimental thermal characterization of a lithium-ion battery cell and a 7p NCA pack was done in accordance with the study's objectives, and the following conclusions are taken from the findings:

- Tab temperatures are always higher than surface temperatures.
- The battery's surface temperature rises with C-rate.
- The anode has a more homogeneous lithium insertion concentration than the cathode.
- The electrolyte resistance is the principal source of heat in the battery. The cathode generates approximately 7 times more heat than the anode at 1C, and 2 times more at 2C and 3C.
- Internal resistance rises with depth of discharge and decreases with C-rate.
- According to the physio-chemical model, lithium flux depends on particle surface concentration, electrolyte salt concentration, and overpotential.
- Busbar and cell location have a significant impact on the pack's current limit and SOC uniformity.
- Busbar resistances and current flow paths past other cells have a substantial impact on cell heat generation.

6.2. Contributions

The main contributions and novelty of the thesis are listed below:

- Developed R_{int} surface models that are functions of SOC, SOH, C-Rate and Temperature
- Decompose Heat Generation into components in anode and cathode separately
- Reversible Heat simulated as a function of SOC for both anode and cathode (time)
- Created 1D PDE Electrochemical model incorporating double layer capacity affect
- Created fast solving FDTD 2D R_{int} thermal model
- Developed parallel pack model where each cell has its own current and SOC
- Parallel pack heat loss includes convective heat loss based on battery spacing

6.3. Recommendations

Several recommendations can be made for future research as listed below:

- Implementation of R_{int} model in process control charging techniques at the pack and module level to prevent significant overpotentials resulting in plating and overheating
- Model the influence of SOC, C rate, SOH, and temperature on cell capacitance.
- BTMS/Cold Plate flow rate, angle, channels, and spacing designed utilizing cycle GANs and Neural Networks.
- Thermal control system in Simulink and COMSOL using NN CFD for minimize energy flow rate while minimizing the temperature difference and minimizing the maximum temperature in the pack. Modeling to check heat transfer coefficient of different materials glycol etc. different flow regimes of cooling plate parallel series etc.
- Busbar design in COMSOL using Optimization Module
- Develop EIS Pack Level models to estimate SOH
- Modeling of intercalative and thermal expansion stresses effects on cell degradation
- The developed two dimensional electrochemical-thermal model with current collector heating effects

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Appendix A: Derivations

Derivation 1:

Derivation of the Reversible heat term from the Bernardi Equation [1]. Reversible heat is the heat from reaction.

$$\Delta G = -nFE_{\text{cell}} = \sum \mu dN + VdP + SdT \quad (1)$$

Typical assumptions are to hold temperature and pressure constant and neglect the last 2 terms to give:

$$\Delta G = -nFE_{\text{cell}} = \sum \mu dN \quad (2)$$

The multivariable chain rule then follows as such:

$$\frac{df(x, y, z, t)}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x} \frac{dx}{dt} + \frac{\partial f}{\partial y} \frac{dy}{dt} + \frac{\partial f}{\partial z} \frac{dz}{dt} \Rightarrow \quad (3)$$

Thus the term with no differential term is the partial of the function with respect to the derived variable. In this case we see:

$$S = \frac{\partial G}{\partial T} = -nF \frac{\partial E_{\text{cell}}}{\partial T} \quad (4)$$

$$Q_{\text{rev}} = TS = IT \frac{dE_{\text{cell}}}{dT} \quad (5)$$

Derivation 2:

Derivation of R_{int} as a function of the current and the SOC is shown below. It relies on Figure 9 where we observe that the ohmic overpotential due to current is linear. We also make this assumption for the concentration overpotential though it is best solved for through simplifications Fick's law with a source term.

$$\eta = \eta_{\text{Activation}} + \eta_{\text{Concentration}} + \eta_{\text{Ohmic}} \quad (6)$$

$$I = I_0 \cdot \left\{ \exp \left[\frac{\alpha_a z F}{RT} (\eta_{\text{Activation}}) \right] - \exp \left[-\frac{\alpha_c z F}{RT} (\eta_{\text{Activation}}) \right] \right\} \quad (7)$$

$$\eta = IR_{\text{int}} \quad (8)$$

$$\eta_{\text{Activation}} = \frac{RT}{\alpha z F} \ln \left(\frac{I}{2I_0} + \sqrt{\frac{I^2}{4I_0^2} + 1} \right) \quad (9)$$

$$R_{\text{int}} = \frac{\eta_{\text{Activation}}}{I} + \frac{\eta_{\text{Concentration}}}{I} + \frac{\eta_{\text{Ohmic}}}{I} \quad (10)$$

$$R_{\text{int}} = A_1 + \frac{A_2 \ln \left(\frac{I}{2I_0} + \sqrt{\frac{I^2}{4I_0^2} + 1} \right)}{I} \quad (11)$$

$$R_{\text{int}} = A_1 + \frac{A_2 \sinh \left(\frac{I}{A_3} \right)}{I} \quad (12)$$

We note that R_{int} is a function of the SOC meaning that A_1 and A_2 are a function of SOC and the following modification is

$$R_{\text{int}} = \left(A_1 + \frac{A_2 \sinh \left(\frac{I}{A_2} \right)}{I} \right) e^{A_4 \text{SOC}} \quad (13)$$

Derivation 3:

We derive the solution to the 1RC battery model shown in **Figure 12**. First we will solve for the differential form as:

$$I = I_C + I_{R1} \quad (14)$$

$$U = I_{R1}R_1 \Rightarrow I_{R1} = \frac{U}{R_1} \quad (15)$$

$$Q = CV \Rightarrow I_C = C \frac{dU}{dt} \quad (16)$$

$$\frac{dU}{dt} = \frac{I_C}{C} = \frac{I - I_{R1}}{C} = \frac{I}{C} - \frac{U}{R_1C} \quad (17)$$

This is a first order linear non homogenous equation if we assume the current to be non-dependent on time:

$$U = A \exp \frac{-t}{RC} + IR_1 \quad (18)$$

This solution however is inadequate and is instead solved using time series analysis as so:

$$\dot{x}(t) = ax(t) + bu(t) \Rightarrow x[k+1] = e^{a\Delta t}x[k] + \frac{1}{a}(e^{a\Delta t} - 1)bu[k] \quad (19)$$

$$a = -\frac{1}{R_1C} \quad (20)$$

$$bu(t) = \frac{I}{C} \quad (21)$$

$$\dot{x} = \frac{dU}{dt} \quad (22)$$

$$U_{i+1} = e^{-\frac{\Delta t}{R_1 C}} U_i - I R_1 \left(e^{-\frac{\Delta t}{R_1 C}} - 1 \right) \quad (23)$$

$$U_{i+1} = U_i \exp \frac{-\Delta t}{R_1 C} + I R_1 * \left(1 - \exp \frac{-\Delta t}{R_1 C} \right) \quad (24)$$

Derivation 4:

The Nernst Planck equation is used to predict the flow of species in a convective, migrative and diffusive field. It follows from the continuity equation for conserved quantities and is shown below:

$$\frac{\partial c}{\partial t} = -\nabla \cdot J \mid J = - \left[D \nabla c - uc + \frac{Dze}{k_B T} c \left(\nabla \phi + \frac{\partial \mathbf{A}}{\partial t} \right) \right] \quad (25)$$

$$\Leftrightarrow \frac{\partial c}{\partial t} = \nabla \cdot \left[D \nabla c - uc + \frac{Dze}{k_B T} c \left(\nabla \phi + \frac{\partial \mathbf{A}}{\partial t} \right) \right] \quad (26)$$

The divergence of the total flux is shown as the divergence of each flux component individually. The first term is the diffusive flux where the flux is determined by Ficks First Law. The second term is the convective flux due to fluid flow and the term is due to migration seen here in both electric and magnetic fields. Einstein's Relation states:

$$D = \mu k_B T \quad (27)$$

Thus the third convective term can be derived as:

$$\mu = \frac{v_d}{F} = \frac{v_d}{EQ + QV \times B} = \frac{v_d}{\left(\frac{\partial \phi}{\partial x} + \frac{\partial A}{\partial t} \right) ze} \quad (28)$$

For static electromagnetic conditions we can ignore the Magnetic vector potential term.

$$\mu = \frac{v_d}{F} = \frac{v_d}{EQ} = \frac{v_d}{\frac{\partial \phi}{\partial x} ze} \quad (29)$$

$$D = \mu k_B T \quad (30)$$

$$J = v_d C = \frac{Dze}{k_B T} \frac{\partial \phi}{\partial x} \quad (31)$$

The modified Nernst Planck equation is derived as follows:

$$J_i = -D \frac{\partial C}{\partial x} \Rightarrow d(\ln(C)) = \frac{dC}{C} \Rightarrow J_i = -\frac{D c_i}{RT} \frac{\partial \mu_i}{\partial x} = -\frac{D c_i}{RT} \frac{RT}{\partial x} \frac{\partial \ln(C)}{\partial x} \quad (32)$$

$$D \left(1 + \frac{d \ln f}{d \ln C} \right) = \frac{2RT\kappa}{F} (t_+ - 1) \left(1 + \frac{d \ln f}{d \ln C} \right) = \kappa_{eff} \quad (33)$$

$$\text{Current Density} = \nabla(\kappa_{eff} \ln(C)) \quad (34)$$

Derivation 5:

Derivation of the voltage from unequal parallel voltage sources as shown in Figure 63.

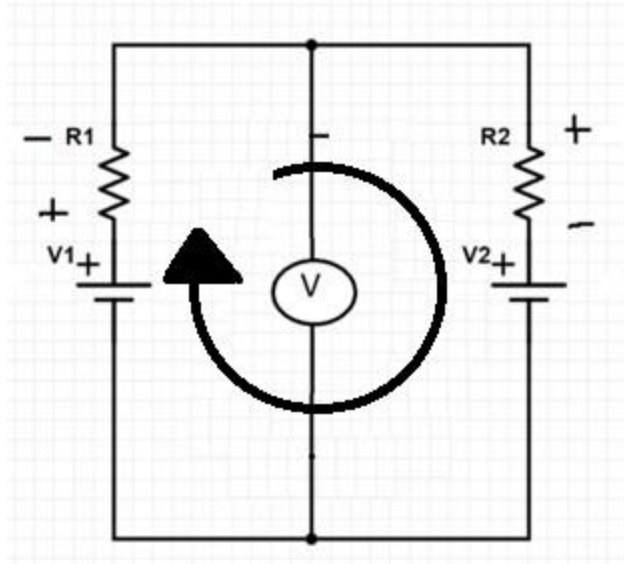


Figure 63: Unequal voltages in parallel

This scenario is found in situations such as battery charging and in battery packs where cells are in parallel. Here we consider a simple 2 battery scenario and utilize Kirchoff's Laws to derive the voltage of the pack.

$$I_1 = \frac{E_1(R + r_2) - E_2R}{R(r_1 + r_2) + r_1r_2} \approx \frac{E_1 - E_2}{r_1 + r_2} \quad (35)$$

$$I_2 = \frac{E_2(R + r_1) - E_1R}{R(r_1 + r_2) + r_1r_2} \approx \frac{E_2 - E_1}{r_1 + r_2} \quad (36)$$

$$V = \frac{R(E_1r_2 + E_2r_1)}{R(r_1 + r_2) + r_1r_2} \approx \frac{E_1r_2 + E_2r_1}{r_1 + r_2} \quad (37)$$

Appendix B Battery Definitions

Battery Cycle	Consists of 1 complete charging process and 1 complete discharging process.
Charge Rate	Charge rate is a measurement of the current applied to recharge the battery. Applied current [A] divided by capacity of battery [Ah] gives the charge rate [h^{-1}]. For a fully discharged 100 Ah battery, a 1C charge rate would apply 100 A for 1 hour to reach 100% SOC.
Discharge Rate	Discharge rate is a measurement of the current applied to discharge the battery. Current drawn divided by capacity of battery [Ah] gives the discharge rate [h^{-1}]. For a fully discharged 100 Ah battery, a 1C charge rate would apply 100 A for 1 hour to reach 100% SOC.
Battery Capacity	The coulometric capacity, the total amp-hours available when battery is discharged at a certain discharge current (specified as a C-rate) from 100% SOC to the cut-off voltage. Capacity is calculated by multiplying the discharge current (in Amp) by the discharge time (in hours) and decreases with increasing C-rate.
Nominal Energy	The “energy capacity” of the battery, the total watt-hours available when battery is discharged at a certain discharge current (specified as a C-rate) from 100% SOC to the cut-off voltage. Energy is calculated by multiplying the discharge power (in watts) by the discharge time (in hours). Like capacity, energy decreases with increasing C-rate.
Intercalation	The reversible inclusion of a chemical species (ion, molecule, etc.) between two other chemical species.
Battery Cell	A cell is the smallest, packaged form a battery can take and is generally on the order of one to six volts
Battery Module	A module consists of several cells generally connected in either series or parallel.

Battery Pack	A battery pack is then assembled by connecting modules together, again either in series or parallel.
State of Charge (SOC)	The state of charge (SOC) is a percentage measure of charge remaining in a battery relative to its predefined “full” and “empty” states. Manufacturers typically provide voltages that represent when the battery is empty (0% SOC) and full (100% SOC). SOC is generally calculated using current integration to determine the change in battery capacity over time.
Depth of Discharge (DOD)	The depth of discharge (DOD) is a percentage measure of the amount of energy extracted during a discharge process, compared to a fully charged state. Depth of discharge is the complement of state of charge (SOC). A battery at 60% SOC is also at 40% DOD.
Cycle life	Cycle life refers to the number of times a battery must be charged and discharged before its nominal capacity falls below 80% (or some other predetermined threshold) of its rated value. Cycle life is given for a particular DOD and determined at specific charge and discharge conditions.
Open Circuit Voltage (OCV)	The open circuit voltage (OCV) is the voltage when no current is flowing in or out of the battery, and, hence no reactions occur inside the battery. OCV is a function of state-of-charge and is expected to remain the same during the life-time of the battery. However, other battery characteristics change with time, e.g. capacity is gradually decreasing as a function of the number of charge-discharge cycles.
Terminal Voltage (V)	The voltage between the battery terminals with load applied. Terminal voltage varies with SOC and discharge/charge current.
Nominal Voltage (V)	The reported or reference voltage of the battery, also sometimes thought of as the “normal” voltage of the battery.
Cut-off Voltage (V)	The minimum allowable voltage. It is this voltage that generally defines the “empty” state of the battery

Charge Voltage (V)	The voltage that the battery is charged to when charged to full capacity. Charging schemes generally consist of a constant current charging until the battery voltage reaches the charge voltage, then constant voltage charging, allowing the charge current to taper until it is very small.
Specific Energy (Wh/kg)	The “energy capacity” of the battery, the total watt-hours available when a battery is discharged at a certain discharge current (specified as a C-rate) from 100% SOC to the cut-off voltage. Energy is calculated by multiplying the discharge power (in watts) by the discharge time (in hours). Like capacity, energy decreases with increasing C-rate.
Energy Density (Wh/L)	The energy density of a battery is expressed as a nominal energy per unit volume, such as Wh/L. It is highly dependent on the battery chemistry and packaging.
Power Density (W/L)	The power density of a battery is expressed as a nominal power per unit volume, such as W/L or kW/L. It is highly dependent on the battery chemistry and packaging.
PHEV	Plug-in hybrid electric vehicle.
SOD	Start of discharge
EOD	End of discharge