

Comparison of the effect of internal thermal gradients on the
performance of Lithium Ion batteries caused by external air
convection versus surface conduction and the consequences on
electrochemical model parameters fitting

MOHD IBTHISHAM ARDANI

Electrochemical Science and Engineering Group
Department of Mechanical Engineering
Imperial College London

A thesis submitted for the degree of
Doctor of Philosophy of the Imperial College London

September 2017

Abstract

Electrochemical models are essential to solving many problems involving lithium ion batteries. However, they require many parameters, some of which cannot be directly measured and must be inferred by fitting to cell testing data. Battery performance is strongly affected by temperature which is well documented in the literature and can be mathematically represented by the Arrhenius equation. When fitting data to a cell model, the temperature must be constant, known, and uniform, to be mathematically consistent. However, it is impossible to test a cell without causing its surface temperature to vary. This will eventually induce thermal gradients which could affect the cell performance. Despite this, there is a significant amount of literature on fitting test data to isothermal models. It is difficult to quantify the non-uniformity inside the cell, therefore a battery model which accounts for internal and surface region has been adopted. By using this model, the deviation of current between surface and internal region can be up to 4% at the constant surface temperature of 5 degree Celsius.

To explore the thermal variation issues, the effect of applying different thermal boundary conditions, using forced air convection and surface cooling plates, was investigated experimentally. This was not to evaluate cooling effectiveness, but rather to show the effect of using data generated with different thermal boundary conditions on parameter estimation when fitting to an isothermal model. When fitting the model to the data, the estimated diffusion coefficient of the positive electrode was four times larger using the data gathered using forced air convection compared to surface cooling at low operating temperature. This was achieved by using a four-point surface cooling rig, which was designed to maintain tabs/surfaces of a pouch cell at the constant temperature, to be as close as experimentally possible to isothermal conditions without interfering with the cell.

Buat ayah dan ibu...

I declare this thesis to be my own work and the appropriate citations are included to acknowledge the work of others.

Mohd Ibthisham Ardani

Copyright Declaration

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build on it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Acknowledgement

I wish to take this opportunity to express my gratitude to my supervisors, Professor Ricardo Martinez-Botas and Dr Gregory J. Offer for their continuous support and constant guidance throughout my PhD journey. Overall, it has been a wonderful journey, full of unexpected challenges yet so satisfying. It is almost impossible to find any decent words beyond the ‘thank you’ to describe how I’m very indebted to both of my supervisors. I would also like to thank Dr Yatish Patel in assisting me particularly with experimental and test rig setup. The experimental work would have become more difficult without his support. My gratitude also extended to Universiti Teknologi Malaysia for funding my studies here at Imperial College London. These four years have been great with tremendous support from turbocharger and battery group. Special thanks to Turbocharger Group, especially Izzal, Uswah, Peter Newton, Kun Cao, Torsten Palenschat, Wan Saiful-Islam, Jonathan Hey, Srithar Rajoo, Aaron Coastal, Alessandro Romagnoli, Harminder Flora, Mingyang Yang, Marie-Therese von Srbik, Maria Esperanza Barrera, Miles Robertson, Hasbullah, Karim Gharaibeh, Karl Hohenberg, Balamurugan, Jose Francisco Cortell Fores, Bijie Yang. Not to forget special thanks to Electrochemical Science and Engineering group, especially Ian Hunt, Yan Zhao, Billy Wu, Alexander Holland, Edmund Noon, Yu Merla, Ian Campbell, Monica Marinescu, Krishnakumar, Teng Zhang and Khairul Amilin, thank you very much for the friendship, critical ideas and constructive comments. I would also like to thank my best buddies Zulhafiz, Badrin Hanizam, Erwan, Hazmil, Aizat, Khairil, Sudin, Rafik and all of the HLMB and Ducaners members. Special dedication to my beloved wife, Maziah Abdul Rahman for her continuous love, support and patience and also to my children Irfan Muslim and Insyirah Marissa which have cherished my life and given me the strength to complete my PhD journey. To my parents Saadiah Laiman and Ardani Siren, thank you for the continuous support and prayers and also thank you for creating millions of opportunities for me and let me explore the journey since i was born. Not to forget special thank to my sister Julianee for the continuous moral support and love.

Contents

1	Introduction	1
1.1	Thermal impact on batteries	6
1.2	Research motivation	8
1.3	Objectives and research questions	10
1.4	Thesis outline	10
2	Literature research	12
2.1	Battery testing from thermal perspective	12
2.1.1	Surface boundary condition	12
2.1.2	Battery tabs contact resistance	16
2.1.3	Determination of the effective thermal conductivity in-plane and through-plane direction	18
2.1.4	Surface and Internal temperature measurement	23
2.2	Current and temperature non-uniformity on battery performance . .	33
2.2.1	For single battery	33
2.2.2	For a series connected battery	36
2.2.3	For a parallel connected battery	37

2.3	Integration thermal with electrochemical aspects from numerical point of view	44
2.4	Parallel battery model	52
2.5	Conclusion	54
3	Creating isothermal boundary conditions	55
3.1	Introduction : Constant temperature operation	55
3.2	Utilizing high thermal conductivity region	56
3.2.1	Controlling cell tabs temperature	56
3.2.2	Contact resistance	59
3.2.3	Cell performance evaluations (Battery tabs temperature control)	61
3.2.3.1	Temperature non-uniformity across battery surface and thermal equilibrium	62
3.2.3.2	Un-equal thermal resistance of battery tabs	64
3.3	Creating isothermal condition : Experimental method and procedures	70
3.3.1	Four points temperature control (Conduction thermal control)	71
3.3.1.1	Temperature deviation during pulse test near isothermal condition	73
3.3.2	Convection thermal control	76
3.4	Conclusion	78
4	Battery performance at different thermal conditions	79
4.1	Introduction	79
4.2	Comparison : Conduction and Convection thermal control	80
4.2.1	Cell performance comparison	80

4.2.1.1	Performance during convection tests	81
4.2.1.2	Performance during conduction tests	83
4.3	Battery model	84
4.3.1	Governing Equations and Discretization	86
4.3.1.1	Lithium in Solid Phase	86
4.3.1.2	Lithium in Electrolyte Phase	88
4.3.1.3	Charge Conservation in Electrolyte Phase	89
4.3.1.4	Charge Conservation in Solid Phase	91
4.3.1.5	Reaction Current	93
4.3.1.6	Iterative solution	95
4.3.1.7	Grid independent analysis	96
4.3.2	Thermal aspect	97
4.3.2.1	Thermal parameter calculation	97
4.3.2.2	Indication of temperature uniformity	99
4.3.3	Lumped capacitance thermal model and Arrhenius linked parameters	102
4.3.4	Dual uni-directional current battery model	104
4.3.5	Open circuit voltage extraction	107
4.4	Results analysis : Modelling and experimental comparison	112
4.4.1	Pulse discharge comparison for conduction and convection	112
4.4.2	Battery parameterisation by using inverse modelling	115
4.4.3	Physiochemical parameter comparison	124
4.4.3.1	Parameter sensitivity analysis	124

4.4.3.2	Diffusion and Charge transfer coefficient of positive cathode	126
4.4.3.3	Effect given by diffusion and charge transfer coefficient on battery performance	129
4.4.3.4	Parameter fitting by temperature adjustment	134
4.4.4	Full discharge comparison	135
4.4.5	Temperature prediction	137
4.4.5.1	Calculation of heat transfer coefficient	137
4.4.5.2	Surface temperature prediction using lumped capacitance thermal model	139
4.4.5.3	Surface and internal prediction using dual uni-directional current battery model	141
4.4.6	Current deviation under thermal gradient	145
4.5	Conclusion	149
5	Effect of conductive surface cooling/heating on batteries connected in parallel	151
5.1	Introduction : Internal temperature of a parallel connected battery	151
5.2	Assumptions and experimental technique	152
5.2.1	Set-up	154
5.2.2	Calibration of the internal temperature measurement	155
5.3	Experimental results	158
5.4	Modelling approach	159
5.5	Results analysis : Modelling and experimental comparison	160
5.5.1	Pulse discharge comparison : Voltage, local current and internal temperature	160

5.5.2	Full discharge comparison : Voltage, local current and internal temperature	166
5.6	Conclusion	170
6	Conclusion and future work	172
6.1	Summary	172
6.2	Conclusion	173
6.2.1	Objective 1	173
6.2.2	Objective 2	174
6.2.3	Objective 3	175
6.3	Research Impact	177
6.4	Proposed Future Work	178
6.4.1	Entropy measurement	178
6.4.2	Investigation for battery with different chemistry and form factor	178
	Bibliography	179
	Appendices	190

List of Figures

1.1	Comparison of several energy storage system (Reproduce from Sandia National Laboratories)	2
1.2	Energy density evolution of batteries extracted from Zu and Li (2011) : (a) Development of battery energy density for various types of battery, (b) Comparison of energy density of several lithium ion battery chemistry	3
1.3	Battery performance at different temperature given from the specification sheet for : (a) 0.83 Ah Panasonic battery, extracted from Panasonic (2002), (b) 31 Ah Kokam battery, extracted from Kokam (2009)	4
2.1	Calorimeter to provide adiabatic condition from Eddahech et al. (2013)	14
2.2	Controlling battery surface temperature by conduction extracted from Troxler et al. (2014)	14
2.3	Resistance due to contact between battery tabs and load cable connector given from various method extracted from Veth et al. (2014) .	16
2.4	Temperature variation due to interconnect resistance extracted from Wu et al. (2013)	17
2.5	Common battery geometries extracted from Wang et al. (2016)	19
2.6	(a) Steady state thermal gradient by Maleki et al. (1999), (b) Steady state thermal gradient with guarded heat flow meter by Song et al. (1997)	20

2.7	(a) Thermal conductivity in plane and through plane for cylindrical battery as function of SOC by Wenwei et al. (2014), (b) In-plane thermal conductivity for pouch battery as function of SOC reproduced from Bazinski et al. (2016)	21
2.8	Position of temperature sensor for measuring battery internal temperature by Mutyala et al. (2014)	23
2.9	(a) Internal temperature measurement by using thermocouple from Li et al. (2013), (b) Internal temperature measurement by using polymer embedded thin film thermocouples from Mutyala et al. (2014)	24
2.10	Experimental set-up and thermocouple location for measuring cell individual temperature extracted from Heubner et al. (2013)	24
2.11	(a) Temperature evolution under charge/discharge at 0.5C Heubner et al. (2013), (b) Thermography image of cell stack and temperature increase during charge/discharge at 5C Heubner et al. (2014)	25
2.12	Summary of heat generation contribution of each component on cell level extracted from Heubner et al. (2015)	26
2.13	Relationship of 40Hz phase shift at 50%SOC at various ambient temperature extracted from Srinivasan (2012)	27
2.14	Comparison of internal temperature prediction by using phase shift at 40 Hz from EIS with measure surface temperature by Srinivasan (2012) : (a) Under ambient temperature of 23°C, (b) Under ambient temperature of 0°C	27
2.15	Variation of real part of resistance given from EIS measurement at 10.3kHz by Schmidt et al. (2013)	28
2.16	Impedance measurement under different thermal gradient by Troxler et al. (2014)	29
2.17	Experimental set-up for battery under thermal gradient : (a) Using thermoelectric module with fin under convection at low temperatures by Schmidt et al. (2013), (b) Using thermoelectric module with liquid cooling by Troxler et al. (2014)	30

2.18	Experimental set-up for a cylindrical battery for internal temperature prediction and validation Richardson et al. (2016)	30
2.19	Current distribution for thin electrode system at : (a) 45°C, (b) 21°C, (c) 0°C and (d) Experimental setup by Zhang et al. (2013)	33
2.20	Evolution of surface and internal battery temperature at different cooling direction, T_1 (internal), T_2 and T_3 (surface temperature) under drive cycle load : (a) Cooling in along plane direction, (b) Cooling in through plane direction extracted from Richardson et al. (2016) . . .	35
2.21	Individual battery voltage in series string with non-uniform battery condition extracted from Fouchard and Taylor (1987)	36
2.22	Current re-distribution during relaxation period extracted from Fouchard and Taylor (1987)	38
2.23	(a) Pack and individual battery voltage, (b) Current distribution of battery with different capacity connected in parallel extracted from Miyatake et al. (2013)	38
2.24	Current deviation given from different battery operating temperature : (a) Cell 1 (5°C) - Cell 2 (10°C), (b) Cell 1 (5°C) - Cell 2 (15°C) extracted from Yang et al. (2016)	39
2.25	Discharge performance at different temperature and thermal gradient extracted from Yang et al. (2016)	40
2.26	Different degradation rate given from two sets of battery connected in parallel extracted from Shi et al. (2016)	41
2.27	Current spike due to thermal gradient at end of charging and end of discharging extracted from Shi et al. (2016)	42
2.28	Rate of degradation due to : (a) Current discharge rate, (b) Ambient temperature extracted from Gu et al. (2014)	42
2.29	Progression of battery thermal model with electrochemical interaction. Image extracted from Wu et al. (2002); Inui et al. (2007); Xiao and Choe (2012); Guo and White (2013); Zhang et al. (2016)	47

2.30	Current deviation and point of current crossover due to difference in temperature extracted from Yang et al. (2016)	53
3.1	Structure of battery layer	56
3.2	(a) Thermal test platform, (b) Base plate battery holder, (c) Cell holder assembly which obtained from Troxler et al. (2014)	57
3.3	(a) Battery holder for tabs temperature control, (b) Cooling pipe circuit	58
3.4	Location of measured temperature	58
3.5	Exploded view of battery holder (Tabs temperature control)	59
3.6	Schematic of current paths due to uneven interface Taheri et al. (2011)	60
3.7	(a) Impedance at approximately 20% SOC at 15°C, (b) Resistance and heat generated difference between treated and un-treated brass block at different applied bolt torque (This work is carried out by Ali Siddiq, Imperial College London, Mech. Eng. Undergraduate)	61
3.8	Treated (left) and Un-treated brass block (right)	61
3.9	Steady state temperature by controlling both tabs temperature at, (a) 45°C, (b) 25°C and (c) 5°C	62
3.10	Pathway of heat for battery tab temperature control	63
3.11	Kokam battery positive and negative tab	64
3.12	(a) Thermal gradient for 25°C at positive tab and 5°C at negative tab, (b) Thermal gradient for 5°C at positive tab and 25°C at negative tab	64
3.13	Comparison of tabs construction. (a) Positive tab , (b) Negative tab .	65
3.14	Switching tabs temperature. (a) 25°C positive tab & 5°C negative tab, (b) 5°C positive tab & 25°C negative tab, (c) Voltage curve comparison	66
3.15	Switching tabs temperature. (a) 45°C positive tab & 5°C negative tab, (b) 5°C positive tab & 45°C negative tab, (c) Voltage curve comparison	67

3.16	Comparison of power consumed by Peltier element at different tab location and temperature point. (a) 45°C positive tab & negative tab, (b) 5°C negative tab & positive tab	68
3.17	Temperature gradient diagram for case 45°C positive tab & 5°C negative tab with its respective 1-D thermal resistance network	69
3.18	Battery holder for both tabs and surfaces temperature control	71
3.19	(a) Surface temperature control system with edge temperature measurement , (b) Temperature comparison under 45°C convection inside thermal chamber	72
3.20	(a) Exploded view of battery holder (Tabs and surfaces temperature control), (b) Actual test-rig setup	73
3.21	Comparison of temperature between both tabs and edge at : (a) 45°C, (b) 35°C, (c) 25°C, (d) 15°C and (e) 5°C	74
3.22	Liquid pathway for peltier element cooling in four points temperature control rig	74
3.23	Series and charge transfer resistance comparison for fresh battery and after cycling during performance tests	76
4.1	(a) 10A pulse discharge under conduction thermal control, (b) 10A pulse discharge under convection thermal control	80
4.2	Comparison of voltage curve and edge temperature during pulse discharge	82
4.3	Schematic of pseudo 2-D electrochemical battery model with 1-D radial spherical and 1-D unit cell representation	85
4.4	(a) Comparison of the guess reaction current density to the Butler-Volmer solution, (b) Condition of the current conservation iteration	96
4.5	Convergence analysis for a 300 seconds discharge under 10A at 45°C : (a) Spatial nodes in x-direction, (b) Spatial nodes in r-direction	97
4.6	Electrochemical-thermal coupling diagram	103

4.7	Simplification for dual uni-directional current battery model	104
4.8	Top view of the battery arrangement under forced air convection . . .	105
4.9	Evolution of surface and internal battery temperature at different cooling direction, T_1 (internal), T_2 and T_3 (surface temperature) under drive cycle load : (a) Cooling in along plane direction (along the battery tab), (b) Cooling in through plane direction (through the battery surface) extracted from Richardson et al. (2016)	106
4.10	Battery modelling algorithm for dual uni-directional current	108
4.11	(a) Continuous pulse discharge at C/10 for 12 minutes followed by 30 minutes rest, (b) Extracted open circuit voltage	109
4.12	Anode and cathode potential given from Gaussian function fitting . .	111
4.13	Comparison between simulated data and test data obtained from conduction thermal control	113
4.14	Comparison between simulated data and test data obtained from convection thermal control	114
4.15	Effect of parameters on battery performance extracted from Bae et al. (2014) : (a) Effect given by changing particle radius, (b) Effect on changing solid diffusion coefficient	117
4.16	Battery parameter fitting algorithm	118
4.17	Fitting and linearisation of : (a) Diffusion coefficient at cathode, (b) Diffusion coefficient at anode	122
4.18	Fitting and linearisation of electrolyte phase conductivity coefficient .	122
4.19	Fitting and linearisation of : (a) Charge transfer coefficient at cathode, (b) Charge transfer coefficient at anode	123
4.20	Fitting and linearisation of electrolyte diffusion coefficient	123
4.21	Simulated physiochemical parameters analysis	125

4.22	Physiochemical parameter obtained from simulation data for conduction and convection thermal control : (a) Diffusion coefficient, (b) Charge transfer coefficient	126
4.23	Physiochemical parameter comparison between the isothermal data and ratio of conduction to convection for : (a) Diffusion coefficient, (b) Charge transfer coefficient	129
4.24	Comparison of stoichiometric generation due to temperature for : (a) Anode at 5°C and 45°C, (b) Cathode at 5°C and 45°C	131
4.25	Comparison of : (a) Overpotential at 45°C and 5°C, (b) Exchange current density at 45°C and 5°C	133
4.26	Comparison of : (a) Solid phase concentration at 45°C and 5°C, (b) Electrolyte phase concentration at 45°C and 5°C	134
4.27	Comparison of diffusion and charge transfer coefficient by temperature adjustment	135
4.28	Full discharge comparison under isothermal condition : (a) 1-C rate, (b) 2-C rate	136
4.29	The regions for heat transfer coefficient calculation	137
4.30	Linearisation of temperature evolution after current interruption based on : (a) Interruption after first pulse, (b) Interruption after second pulse	138
4.31	Comparison of simulated voltage curve along with temperature prediction with voltage obtained from convection thermal control at : (a) 45°C, (b) 35°C, (c) 25°C, (d) 15°C and (e) 5°C	140
4.32	Prediction of voltage,surface and internal temperature by using dual uni-directional current battery model	143
4.33	Histogram showing the comparison between internal and surface temperature at different isothermal temperature	144
4.34	(a) Current deviation at different region, (b) Current deviation point at different temperature	146

4.35	Temperature difference between surface and internal region	146
4.36	Non-dimensional capacity comparison between internal and surface region	147
5.1	Experimental set-up for : a) Prismatic LiFePO ₄ -Graphite battery in parallel by Zhang et al. (2016), b) Two 5Ah Kokam battery connected in parallel with conductive surface temperature control	152
5.2	Physical comparison of a single battery with the parallel connected battery for internal temperature prediction/measurement	154
5.3	Arrangement of thermocouple : a) Two thin thermocouple to measure internal temperature, b) Top view of the connected batteries, c) Front view of the connected batteries	155
5.4	Temperature evolution at several location in the transverse direction at temperature gradient of 45°C/5°C	156
5.5	(a) Thermocouple location along the transverse direction (View from top), (b) Temperature gradient under steady-state condition at the average temperature of 25 °C and 15 °C (The circle represent the internal temperature)	157
5.6	(a) Voltage curve under 20A pulse discharge for two 5Ah Kokam battery connected in parallel under a constant surface temperature, (b) Internal temperature increase	158
5.7	Schematic for battery modelling for two batteries connected in par- allel with constant surface temperature	160
5.8	Comparison of voltage and internal temperature under pulse dis- charge between simulated data and experimental data obtained from surface conductive thermal control at : (a) 45°C, (b) 35°C, (c) 25°C, (d) 15°C and (e) 5°C	161
5.9	Current deviation at different region for constant surface temperature of 45°C to 5°C	162
5.10	Non-dimensional capacity comparison between internal and surface region	163

5.11 Non-dimensional capacity comparison for parallel connected battery- (10Ah) with single battery-(5Ah)	164
5.12 Histogram showing the difference between the internal and surface temperature for 10Ah and 5Ah battery	165
5.13 Comparison of voltage and internal temperature under full discharge between simulated data and experimental data obtained from surface conductive thermal control at : (a) 45°C, (b) 25°C and (c) 5°C	166
5.14 Comparison of local current distribution between the internal and surface region at constant surface temperature of 45°C, 25°C and 5°C	167
5.15 Current crossover points at different SOC for full discharge at : (a) 45°C, (b) 25°C and (c) 5°C	168

List of Tables

2.1	Summary of published work on measuring battery effective thermal conductivity	22
2.2	Summary of published work on measuring/predicting battery internal temperature	32
2.3	Summary of published work on battery thermal model in relation with electrochemical model	48
3.1	Battery dimensional parameter for tabs analysis	69
3.2	Calculated thermal parameter	69
4.1	Battery dimensional parameter for the 5Ah Kokam battery	98
4.2	Cell level parameter obtain from Taheri et al. (2013)	99
4.3	Calculated bulk thermal parameter for battery	99
4.4	Calculated Biot number for different thermal model	100
4.5	Calculated bulk thermal parameter for battery	101
4.6	Arrhenius based parameter	103
4.7	Limit for residual on each loop	107
4.8	Parameter for anode potential	111
4.9	Parameter for cathode potential	111
4.10	Type of fitted parameter	115

4.11 Comparison of model fitted parameter to reported values	116
4.12 Battery model parameters	119
4.13 Fitted activation energy for physiochemical properties	121
4.14 Reference value for several physiochemical properties at 25°C	121
4.15 Parameter change and calculated error for sensitivity analysis	125
4.16 Fitted activation energy for physiochemical properties	127
4.17 Fitted reference physiochemical properties for cathode from different thermal conditions	128
4.18 Battery model temperature input for conduction and convection by allowing all physiochemical parameters to be changed	135
4.19 Error comparison for 1C and 2C full discharge at different temperature	136
4.20 Comparison of RMSE and maximum deviation between lumped ther- mal capacitance model and dual uni-directional current model	142

Nomenclature

Acronyms

BEV	battery electric vehicle
BMS	battery management system
COP	coefficient of performance
ECM	equivalent circuit model
EIS	electrochemical impedance spectroscopy
GITT	galvanostatic intermittent titration technique
HEV	hybrid electric vehicle
OCV	open circuit voltage
SOC	state of charge
SOH	state of health

Greek Symbols

δ	electrode thickness [cm]
ϕ_e	electrolyte phase potential [V]
ϕ_s	solid phase potential [V]
Ψ	physiochemical parameter
ρ	bruggeman coefficient
Θ	non-dimensional capacity
ε_e	electrolyte volume fraction

ε_s	solid active material volume fraction
ρC_p	volumetric heat capacity [$\text{J cm}^{-3} \text{ K}^{-1}$]

Roman Symbols

A	effectives electrodes area [cm^2]
A_s	battery surface area [cm^2]
a_s	specific interfacial surface area [$\text{cm}^2 \text{ cm}^{-3}$]
C_e	volume averaged concentration of lithium in electrolyte [mol cm^{-3}]
C_s	volume averaged concentration of lithium in solid [mol cm^{-3}]
D_e^{eff}	electrolyte phase diffusion coefficient [$\text{cm}^2 \text{ s}^{-1}$]
D_e	electrolyte phase diffusion coefficient [$\text{cm}^2 \text{ s}^{-1}$]
D_s	solid phase diffusion coefficient [$\text{cm}^2 \text{ s}^{-1}$]
E_{act}	activation energy for various physiochemcial properties [J mol^{-1}]
F	Faraday's constant [C mol^{-1}]
h	convective heat transfer coefficient [$\text{W cm}^{-2} \text{ K}^{-1}$]
I	applied current [A]
j_{Li}	reaction current density [A cm^{-3}]
k_y	effective thermal conductivity in through plane direction [$\text{W cm}^{-1} \text{ K}^{-1}$]
k_{ct}	charge transfer coefficient [$\text{cm}^{2.5} \text{ mol}^{-0.5} \text{ s}^{-1}$]
L_n	length of negative electrode [cm]
L_p	length of positive electrode [cm]
l_{cell}	distance between cell unit [cm]
q_c	heat from internal contact resistance [W]
q_j	ionic ohmic heat [W]
q_r	heat from reaction current density [W]
R	gas constant [$\text{J mol}^{-1} \text{ K}^{-1}$]

R_f	current collector contact resistance [$\Omega \text{ cm}^2$]
R_s	radius of active material particle [cm]
t	time
t^{0+}	transference number
T_1	cell surface temperature [K]
T_2	internal cell temperature [K]
T_∞	controlled ambient temperature [K]
U^+	cathode potential [V]
U^-	anode potential [V]
V	cell terminal voltage [V]
v^{vol}	cell volume [cm^{-3}]
x_{stoi}	anode stoichiometric
y_{stoi}	cathode stoichiometric
RMSE	root mean square error

Subscripts

∞	ambient condition
1	surface region
2	internal region
act	activation
conduc	conduction
convect	convection
ct	charge transfer
e	electrolyte
neg	negative
pos	positive

ref	reference
s	solid
stoi	stoichiometric

Chapter 1

Introduction

The transition from reliance on fossil-based energy to renewable energy create a huge challenge. According to Hoag (2011), a lack of sensible energy storage systems is one of the key challenges which could hinder renewable energy being widely used. There are several types of energy storage devices, which include, pumped hydroelectric, supercapacitor, flywheel and battery. All of these devices have distinct attributes whereby a single kind of energy storage cannot be used to provide power for a broad range of application. For instance, the supercapacitor is not a sensible choice to be used as a secondary energy supply for household applications. Although the capacitor has high power density, its energy density is relatively low. Fig. 1.1 gives an overview and comparison of several energy storage systems. It can be seen that the pumped hydroelectric has the highest energy storage capability. However, despite its ability to operate at a relatively longer duration, its implementation is rather limited due to the geographical factor.

The development of the battery as a reliable energy storage device is still ongoing. Bourzac (2015) points out that the energy density of the battery needs to increase substantially before the battery can be used as a primary source of energy for a broad range of vehicles. Recent research, has therefore focused on increasing the battery capacity as illustrated in Fig. 1.2 (a). Moreover, a thermodynamic analysis of the energy densities of various lithium ion based chemistries conducted by Zu and Li (2011), found that several other chemistries could be used to enhance the battery energy density as illustrated in Fig. 1.2 (b). This growing trend implies that the battery industry is trying to adapt to the pace of the energy demand. According to Zu and Li (2011), the average energy density given by the current lithium-ion battery is approximately 210 Wh kg^{-1} , which is still far from the desired energy

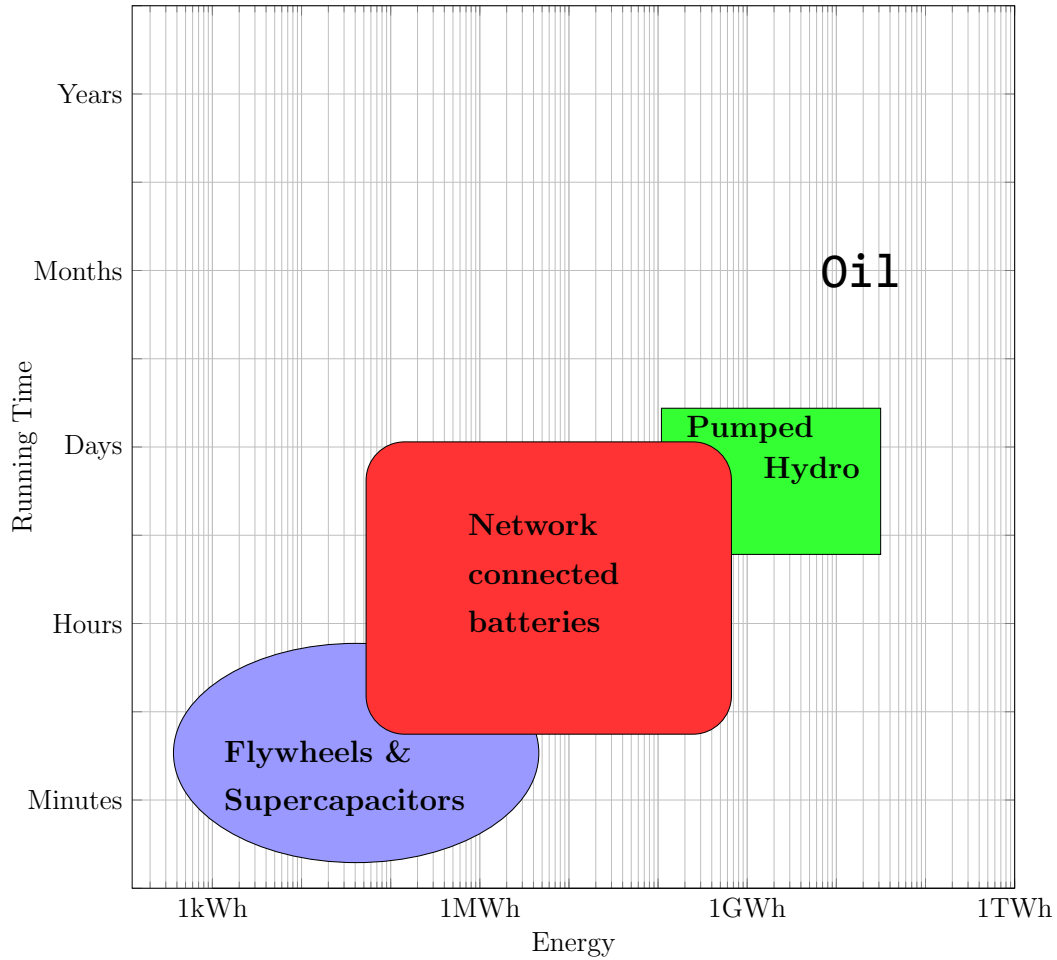
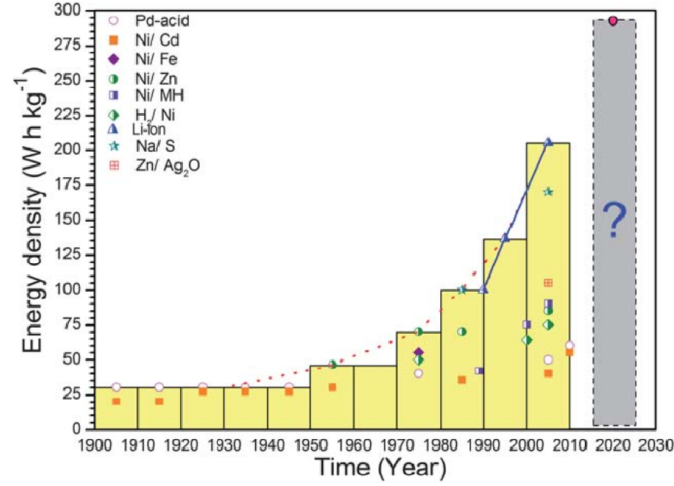


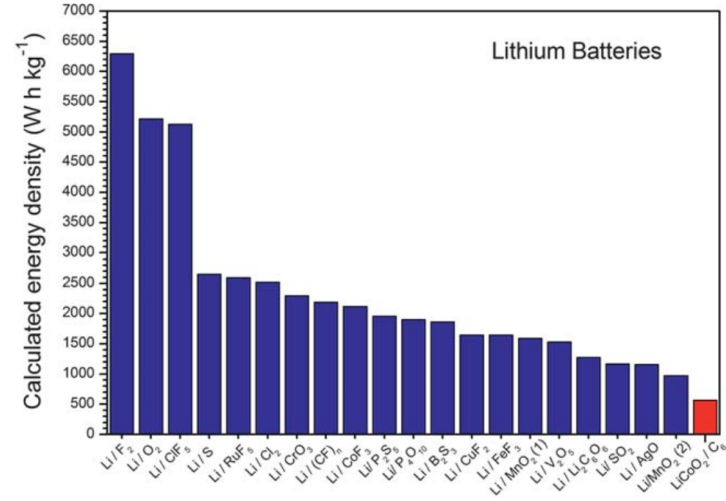
Figure 1.1: Comparison of several energy storage system (Reproduce from Sandia National Laboratories)

density for electrical vehicle application which is around 500 Wh kg^{-1} . A battery pack requires a significant amount of cells connected in series and parallel to meet the energy requirement. Consequently, the battery pack will be heavy, and due to lots of cells involved, the battery monitoring will be difficult. The difficulty is mainly due to more cells that need to be monitored therefore increases the loading on the hardware of the Battery Management System (BMS).

The shift to a greener energy source is deemed necessary due to climate change which necessitate the reduction of CO_2 emission. For instance, the UK Carbon Plan HMG (2009) sets a blueprint to essentially shift away from the dependency on fossil fuel for generating electricity. This plan causes a dramatic change in management of energy through electrification, particularly on the network of public transportation. Additionally, this program also encourages the use of hybrid and full electric vehicle by giving incentives and developing charging infrastructure to



(a)

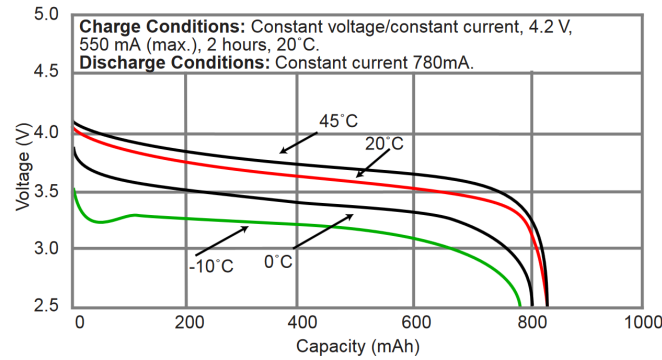


(b)

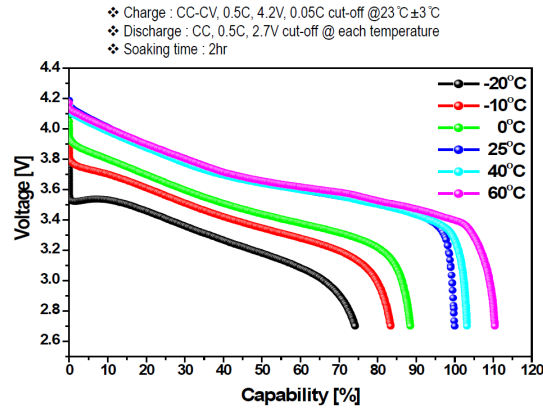
Figure 1.2: Energy density evolution of batteries extracted from Zu and Li (2011) : (a) Development of battery energy density for various types of battery, (b) Comparison of energy density of several lithium ion battery chemistry

facilitate the utilisation of the fully electric vehicles. The deployment of electric powertrain is perceived as a significant shift for the automotive industry as the use of internal combustion engine is still dominant particularly in road vehicles. Efforts to improve the efficiency of the internal combustion engines through research and development are still ongoing. However, the improvement is not significant because the engine works on an irreversible cycle. This cycle generates a significant amount of energy losses. According to Holmberg et al. (2012), the total energy loss from an engine is approximately 70%. This condition shows that the level of energy losses is greater than the actual energy used to move the vehicle. In some cases, a tur-

bocharger is used as an energy recovery device. Nevertheless, this device, which is fitted on the engine exhaust tailpipe is not able to fully capture the total energy losses from the engine. Hence, by switching to an electric powertrain, the energy losses from the power plant are significantly reduced because the energy conversion efficiency of a battery to vehicle can be close to 90-95%, which is the efficiency of the current output of the battery pack based on the input charging energy. Therefore, the electrochemical energy stored in the battery can be converted into electrical energy with minimal losses.



(a)



(b)

Figure 1.3: Battery performance at different temperature given from the specification sheet for : (a) 0.83 Ah Panasonic battery, extracted from Panasonic (2002), (b) 31 Ah Kokam battery, extracted from Kokam (2009)

Typically, the energy from a battery pack is controlled by the battery management system. This system is responsible for controlling charge/discharge and at the same time regulating the internal thermal conditions of the battery pack. The rate of cooling/heating in a battery pack is decided based on the measured battery temperature. However, since the battery pack is composed of many cells, monitoring of each cell would be very demanding. According to Lu et al. (2013), battery unifor-

mity or cell to cell variations is one of the key concerns of the BMS. Although the battery pack or module is comprised of the same type of cell, the cell State of Charge (SOC), State of Health (SOH) and internal resistance can vary due to manufacturing process and temperature. Therefore, it is likely that each of the cells generates heat at a different rate causing temperature variation across the battery pack. Nevertheless, these variations can be reduced by employing active cooling/heating which is efficient in suppressing temperature increase and reliable in keeping the temperature difference between cells to a minimum. Phase change material with conductive matrix is one of the best candidates for reducing the temperature non-uniformity according to Zhao et al. (2015). Therefore, this thermal management only requires a single temperature measurement. This condition greatly lessens the effort of the BMS in measuring temperature. Although the measurement points are reduced, it is still inherently difficult to obtain the battery SOC, SOH and internal resistance. The reason is that the parameters cannot be directly measured. Typically, the parameters are estimated and predicted based on the measurement of current, voltage and surface temperature in comparison to a model.

Lithium-ion batteries come with different chemistries, capacity and size, with the electrochemical performance such as its nominal voltage and rated capacity, defined by the manufacturer. The latter changes significantly based on temperature. The battery performs better at high temperature due to the reduction of resistance and improved kinetics. Usually, a battery specification sheet gives information about the battery performance at different temperatures as illustrated in Fig. 1.3 (a) and (b) for various battery types. However, the temperature information is too generic, which does not acknowledge the specific thermal condition imposed on the battery. Therefore, it's hard to reproduce the same voltage curve due to the unknown thermal condition. Moreover, the specification sheet typically indicates the ambient temperature where the battery test is carried out but assumes the battery behaves according to the isothermal condition. This assumption causes error particularly for the prediction of the SOC, SOH and battery internal resistance. The error is generated because the thermal condition for the battery parameter fitting is not the same as the thermal condition when the prediction is made. Hence, in order to improve the accuracy of predicting some of the battery parameters, a thermal baseline condition is, therefore, necessary. This thermal state must be based on the actual battery temperature rather than the temperature of the battery thermal boundary condition.

1.1 Thermal impact on batteries

There are several types of thermal conditions which can be imposed on a battery external surface namely convection (Eqn. 1.1), adiabatic (Eqn. 1.2) and isothermal (Eqn. 1.3). Each of the thermal conditions has their specific target in evaluating the battery performance. For instance, the adiabatic condition is imposed to assess the amount of heat which is generated at certain C-rate of charge/discharge and different ambient temperature. This condition causes the heat generation from the battery to be utilised solely to increase the battery temperature. The adiabatic thermal condition is relatively easy to be implemented with insulation.

$$q = hA(T - T_{\infty}) \quad (1.1)$$

$$q = kA \frac{dT}{dx} = 0 \quad (1.2)$$

$$q_{in} = q_{out}, T_{in} = T_{out} \quad (1.3)$$

The convection thermal condition is frequently chosen to evaluate cooling effectiveness. This condition can be carried out using two media, liquid or air. The cooling medium will be forced by a fan or a pump to flow at the vicinity of the battery surface to absorb heat. The convective air condition is relatively straightforward to be carried out by using a thermal chamber with a fan to force the air flow. Conversely, the isothermal condition is challenging to achieve particularly at low ambient temperature. This condition requires the battery temperature to be constant during charge/discharge. Technically, to obtain an isothermal condition, the device which controls the temperature of the battery, must be able to cope with the highly non-linear heat generated by the battery. Mathematically speaking, to obtain close to the isothermal condition, the external cooling/heating rate must be equal to the rate of the heat generation. This condition is necessary, to ensure the thermal imbalance to be at a low level. However, this condition is surprisingly difficult to achieve and can only be done by heat transfer through conduction mechanism. This is because the heat transfer via conduction gives a better response as compared to the heat transfer via convection and radiation. With the almost constant temperature operation, the battery performance can be mapped for fitting

the battery. Hence, the battery performance can be predicted based on the battery temperature rather than its external boundary temperature.

1.2 Research motivation

The understanding of how a battery behaves under different thermal conditions are crucial. This is due to its strong dependence on temperature at a given current or C-rate of charge/discharge. The external thermal condition causes the battery temperature to change, depending on whether the environment acts as a thermal heat sink or a source. Therefore without a particular thermal environment, it is inherently difficult to differentiate the differences in the battery performance.

1.2.1 Impact of different thermodynamics process and thermal condition towards battery performance

Previously, it was assumed that the heat generation at a given C-rate could be ignored at a very broad temperature range as stated by Ye et al. (2012). Recent study by Grandjean et al. (2017) on the dependency of the battery capacity on temperature have demonstrated that this assumption is inaccurate in that it is only valid at a high ambient temperature. The work showed that the capacity of the cell is relatively unchanged at various discharge rate at high ambient temperature. This provides the impetus for a thorough investigation to be conducted particularly in creating a better experimental design which resembles the correct definition of the thermodynamic processes and thermal condition.

1.2.2 Interplay between thermal discretisation with electrochemical behaviour for coupled electrochemical-thermal battery model

Technological advancements in computer simulation and programming tools have enabled a complex mathematical solution to be solved in a reasonable time. Therefore, a higher order dimension of a battery thermal model can be made and integrated into a physics based electrochemical model. This model closely represents the actual physical condition of the battery. Typically, the thermal-electrochemical interaction is often simplified. Although the thermal model is constructed in a higher dimensionality, the electrochemical model still uses the average temperature calculated from the thermal model which conducted by Bahiraei et al. (2017) and Ghalkhani et al. (2017). As a consequence, the resulting thermal non-uniformity either across or along the battery surface is primarily caused by the heat transfer. Therefore, the impact of electrochemical heat generation on temperature variation could be very minimal. This is due to the fact that the heat generation at a different location of the battery is considered uniform. Hence, this study aims to find the synergy

between the direction of thermal discretization with battery performance which is caused by the local current distribution.

1.2.3 Battery internal temperature and effect of external thermal gradient

Thermal conditions in a battery pack are complex due to the occurrence of non-uniform current distribution which occurs mainly due to different cell to cell non-uniformities. These conditions will eventually drive variability of heat generation given by each of the individual cells. Therefore, an external thermal gradient in a smaller scale such as at a module level has become increasingly important to be comprehended. This behaviour could not be ignored or treated as a lumped temperature since the interaction of current and temperature particularly for a parallel connected cell is important. Additionally, most of the research evaluate the current distribution based on temperature difference between the batteries without considering the surface temperature evolution of the independent battery which was conducted by Yang et al. (2016). This assumption or simplification might affect the predicted internal current deviation. Therefore, the relationship of local temperature and resistance needs to be considered because Kirchoff law dictates the conservation of current in a parallel connected cell. This drives as another motivation for conducting a test by replicating condition at a module level and furthermore understanding the effects it gives through an electrochemical-thermal battery model.

1.3 Objectives and research questions

The area of investigations of this thesis are built upon the internal and external thermal aspects of a battery with the objectives listed below :

- To develop an experimental technique which can represent particular thermal boundary conditions for a broad temperature range relevant to automotive application.
- To explore techniques to address several thermal issues from a numerical perspective.
- To investigate the variation of the battery internal non-uniformities at different thermal boundary condition.

The objectives of the thesis, as stated above aims to provide answers to the following research questions:

- What are the range of operating temperature and C-rate for an isothermal assumption to be valid under convection thermal control?
- How does thermal gradient influence battery performance?

1.4 Thesis outline

The following are the outline of this thesis which is divided into six chapters :

Chapter 2 : Literature research

Numerous publications with regards to the present work are reviewed and discussed. It also analyses the current state-of-art of the lithium ion batteries that are pertinent to this research with the aim to find the gaps in the academic literature.

Chapter 3 : Creating isothermal boundary conditions

This chapter describes the challenges faced when controlling battery temperature through battery tabs. It also describes the procedure and experimental methodology for controlling the external thermal boundary condition along with techniques

to reduce thermal resistance at battery tabs.

Chapter 4 : Battery performance at different thermal conditions

This chapter highlights the error of fitting physiochemical parameters given from two types of thermal conditions. The chapter further goes into detail of the mathematical architecture for the development of a physics-based electrochemical model with a thermal coupling which can predict the internal battery temperature.

Chapter 5 : Effect of thermal gradient towards performance for a parallel connected battery

This chapter discusses the influence of constant surface temperature towards battery behaviour. It also highlights that surface conduction is unable to provide isothermal condition even when the battery is subjected to a moderate C-rate of discharge. Furthermore, by using a physics-based battery model, the impact of thermal gradient on battery performance is revealed.

Chapter 6 : Conclusion and future work

This chapter outlines the findings based on the previous chapter and responds to the research questions. It also recommends some future work resulting from the present work.

Chapter 2

Literature research

This chapter provides the contemporary battery research with regards to its performance on thermal and electrochemical perspective, certain experimental technique, integration of thermal and electrochemical. All of these aspects were chosen in-line with the aim of unfolding the effect of non-uniformity towards battery performance.

2.1 Battery testing from thermal perspective

2.1.1 Surface boundary condition

Testing of battery consists of charge/discharge at certain current rate and temperature. On one hand it looks straight forward, however without appropriate control from both electrical and thermal aspects, the result can be sometimes questionable. Typically, electrical control such as charge/discharge and impedance measurement are well established and embedded in a battery cyclers or electrochemical control device. Therefore it leaves only thermal aspects, to be controlled independently based on certain test objectives. In general, there are three modes of heat transfer which are conduction, convection and radiation. These three modes reflect how the battery thermal boundary conditions are being managed. Nonetheless, only two modes are plausible to be used, which are conduction and convection. The latter has been utilised extensively for investigating battery performance from both electrochemical and thermal point of view, rate of battery degradation and cooling/heating effectiveness.

Convection thermal control is perceived as a straightforward technique which can be implemented with the aid of thermal or climate chamber. With the ease of use of the thermal chamber, some thermal aspects have been overlooked by assuming the behaviour of the battery during testing to follow a certain thermodynamic process. For instance, isothermal conditions are the term which describes a constant temperature operation and if this condition is taken into consideration, the battery temperature must be at a constant level in accordance with the testing temperature. In order to achieve this, a thermal balance must be satisfied all the time in which, the rate of heat generation from battery must be equal to the heat dissipation rate. Ye et al. (2012) conducted a test to evaluate battery performance at different temperature and fitted some physiochemical parameters which cannot be measured directly based on testing which was carried out in a thermal chamber. However, the model has been assumed to be isothermal or to follow the thermal chamber setting temperature and hence any deviation from this assumption in the test data will cause errors in the parameter fitting and validation of the battery model. Pals and Newman (1995) and Ji et al. (2013) came out with a battery model to predict voltage curve at different temperatures by assuming constant temperature operation. The battery model might be useful to determine the range of operation, but not to be used as a reference to predict the real battery operation condition.

On the other hand, an adiabatic process is another thermodynamic process which is commonly associated with the battery testing. This process assumes no heat loss or no heat travel away from the battery during testing. There are several reasons why adiabatic condition are needed such as, to evaluate the evolution of temperature as a function of C-rate and ambient temperature and for measuring entropy at several SOC. Eddahech et al. (2013) conducted an experiment to determine entropy and its effect towards battery heat generation by using a potentiometer and calorimetric tests as shown in Fig. 2.1. The later was carried out under adiabatic conditions to mitigate the effect of cooling. This work highlights that reversible heat gives a significant proportion of heat generation due to entropy particularly at high ambient temperature and low C-rate. The entropy measurements were carried out by measuring the battery open circuit voltage (OCV) at a different temperature under equilibrium, and this particular work was done under convection environment. In general, this test requires a long period of testing duration to allow the battery to reach thermal equilibrium. However, work by Troxler et al. (2014) shows that by controlling battery surface temperature via conduction, the time for entropy determination can be remarkably reduced. It can be seen that the complexity of the test equipment increases if the battery testing is based on isothermal assumption as

illustrated in Fig. 2.2. More emphasise particularly on battery surfaces are required to improve temperature uniformity.

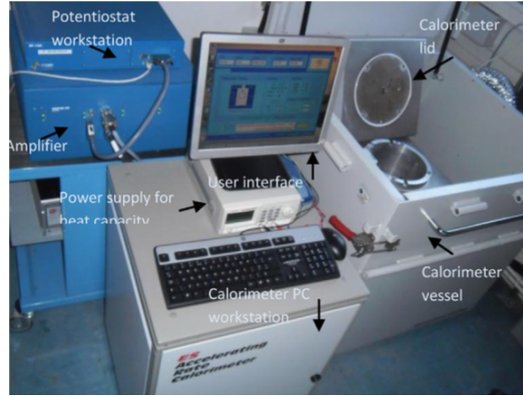


Figure 2.1: Calorimeter to provide adiabatic condition from Eddahech et al. (2013)

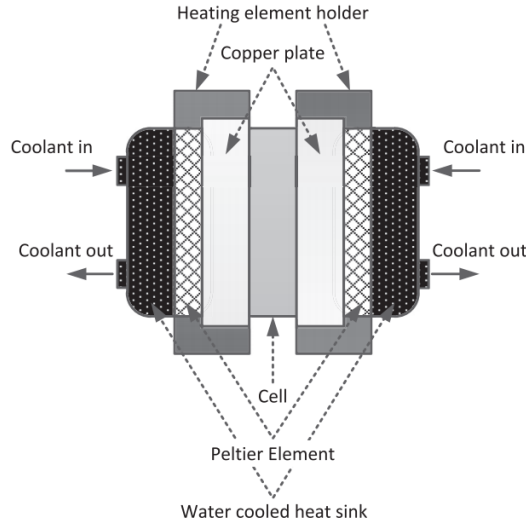


Figure 2.2: Controlling battery surface temperature by conduction extracted from Troxler et al. (2014)

In order to achieve adiabatic conditions, the battery must be properly insulated to minimise heat transfers to ambient. Therefore the heat generated by the battery can be used entirely for increasing the battery temperature. From a modelling perspective, both adiabatic and isothermal condition are easy to be implemented. They are analogous regarding its electrochemical, but the calculated heat generation is treated differently. For a battery model which adopts adiabatic assumption, the calculated heat generation will be feed back to energy balance equation for calculating temperature increase. On the other hand, no thermal model is required for the isothermal case, therefore, reduces the complexity of the overall electrochemical-thermal integration. This signifies that isothermal battery model is

relatively easy to be constructed however the data to match the model assumption requires an experimental rig which can adapt to the dynamic change of heat generation during charge/discharge. Hence, by assuming isothermal condition when in reality the battery surface temperature is not constant, will introduce error particularly in fitting the physiochemical properties.

The isothermal assumption can be valid under adiabatic and convection thermal condition under certain circumstances such as during EIS. This measurement is taken with low currents at different open circuit potentials. Therefore, it is highly unlikely for a cell to generate a significant amount of heat. However, during charging and discharging at C-rate approaching one or more, the isothermal behaviour is surprisingly difficult to achieve. At high currents operation, heat generated will be significant and the battery will be at a different temperature from the target temperature. Errors which come from this assumption are rarely discussed or taken into consideration and instead models are fitted to the data based on the assumption that the cell is at the same temperature of the thermal chamber which was conducted by Ye et al. (2012).

Clearly, the assumption that the cell is at the temperature of the thermal chamber is invalid to a certain degree since it is based on the thermal chamber temperature rather than the cell temperature itself. The errors resulting from this must be quantified to understand if work based upon this assumption is valid or not. The thermal boundary conditions must be far more carefully controlled experimentally and then, those same boundary conditions applied to a model that correctly allows for the resulting thermal gradients to form in order to fit models to the experimental data to extract parameters that cannot be measured directly. This is necessary because of the inverse exponential relationship between temperature and impedance of various processes within the cell which gives rise to significant non-uniform current densities within a cell according to Veth et al. (2014). This will be particularly exacerbated at low temperatures and low SOC where the cell impedance is high. The thermal chamber is a particularly poor choice of device to maintain constant thermal boundary conditions as they cannot easily adapt to the changing rate of heat generation within a cell to maintain constant cell surface temperature. A better method to maintain cell surface temperature is to use conduction rather than forced air convection, as it is more reliable and better in transferring heat.

2.1.2 Battery tabs contact resistance

Battery tab is normally connected to load cable by several electrical conductive connectors such as crocodile clip, copper block and welded tabs. All of these connectors will be acting as an external heat source if the contact resistance between the connector and tab is appreciable. Veth et al. (2014) conducted an experiment with the aim to investigate thermal aspects particularly thermal gradient such as a hot spot on a battery surface at high current discharge. Since the discharge current in the experiment reached up to 300A, any significant contact resistance will give rise to additional heat generation. This will eventually cause an inward flow of heat towards battery surface from its tabs to cell centre. Fig. 2.3 compares effect on contact resistance given from various method. The conventional connection method by using a bolt causes an increase of contact resistance over time due to the continuous growth of oxide layer as conducted by Veth et al. (2014). A stable connection by using conductive epoxy containing silver was used as connection medium from load cable to battery tab, which seems to be successful to reduce the contact resistance.

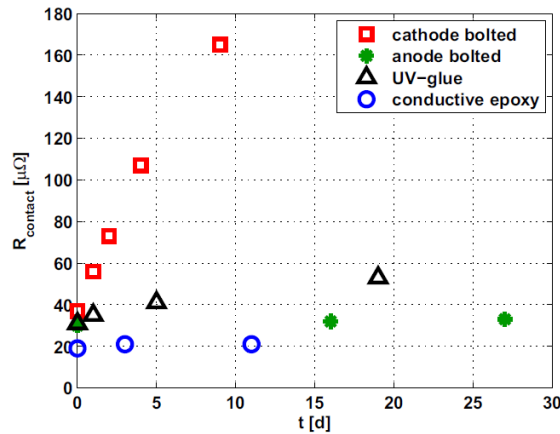


Figure 2.3: Resistance due to contact between battery tabs and load cable connector given from various method extracted from Veth et al. (2014)

On a bigger scale particularly for parallel connected batteries, the contact resistance of an individual battery will eventually cause interconnect resistance. This effect was investigated by Wu et al. (2013) which showed that interconnect resistance will cause a certain battery to be hotter and un-even interconnect resistance will exacerbate the temperature difference, therefore, creating non-uniform thermal behaviour across the parallel connected battery as shown in Fig. 2.4. It can be seen that the effect given from contact resistance causes the battery to receive additional heat generation where the amount of heat generated at some point can

be comparable to the actual heat generated due to electrochemical effect (during charging/discharging).

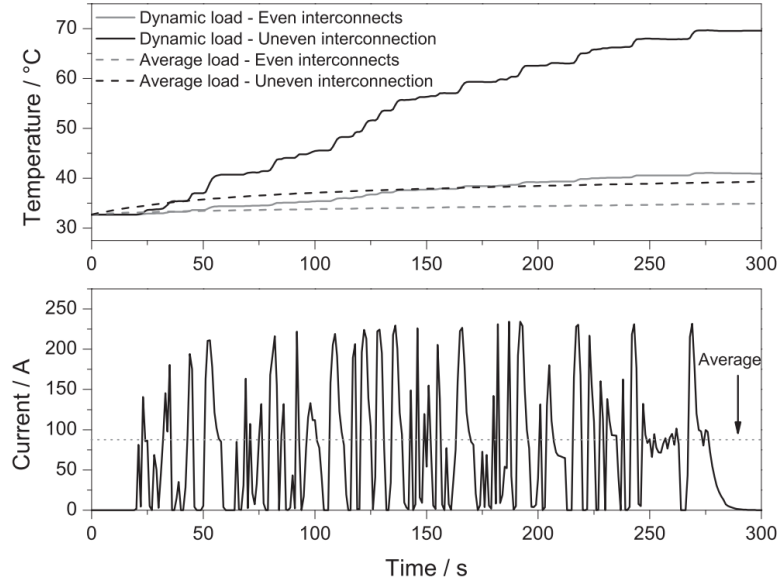


Figure 2.4: Temperature variation due to interconnect resistance extracted from Wu et al. (2013)

2.1.3 Determination of the effective thermal conductivity in-plane and through-plane direction

A lithium ion battery is made from alternating layers of a positive electrode, separator, negative electrode and current collectors with each of them having appreciable differences in thermal conductivities and non-trivial thermal contact resistances between them. The layered structure of a battery causes effective thermal conductivity in through-plane direction to be exceptionally low as compared to its value in along the plane direction with differences up to two orders of magnitude.

Batteries are made from different size and form factor. Fig. 2.5 summarises the common battery geometries which are used in a vehicle. Although cylindrical, prismatic or pouch type battery is different in terms of geometrical aspect, they share a common thermal property which is anisotropic thermal conductivity. An appreciable difference of the thermal conductivity in along the plane and through the battery layer causes the thermal transport inside the battery to be distinct. This will eventually create thermal non-uniformity if the external heat source/sink from different battery axis remains at the same rate.

Table 2.1 summarises work with the aim of measuring battery thermal conductivity from single component to a lumped effective value from different direction. Song et al. (1997) and Song and Evans (1999) measured thermal conductivity of several battery components which are separator and cathode. They systematically created a steady state condition by applying and at the same time controlling heat to ensure it travels in one direction. By establishing steady state thermal gradient, temperature difference at top and bottom sample were used to calculate the thermal conductivity. They also indicated that thermal conductivity of cathode varies linearly with temperature, particularly in through-plane direction. However, the variation can be considered insignificant considering the applied temperature was significantly large. In the test, the highest temperature was 150°C which is technically beyond the typical maximum allowable operating temperature of lithium battery as described by Wang et al. (2012). The battery operating temperature needs to be under 80°C, to prevent exothermic reaction or occurrence of thermal runaway. Since the normal operating temperature will not affect the value of thermal conductivity because it is far from maximum temperature studied by Song et al. (1997) and Song and Evans (1999), therefore it is acceptable to assume constant thermal conductivity in both through-plane and in-plane direction.

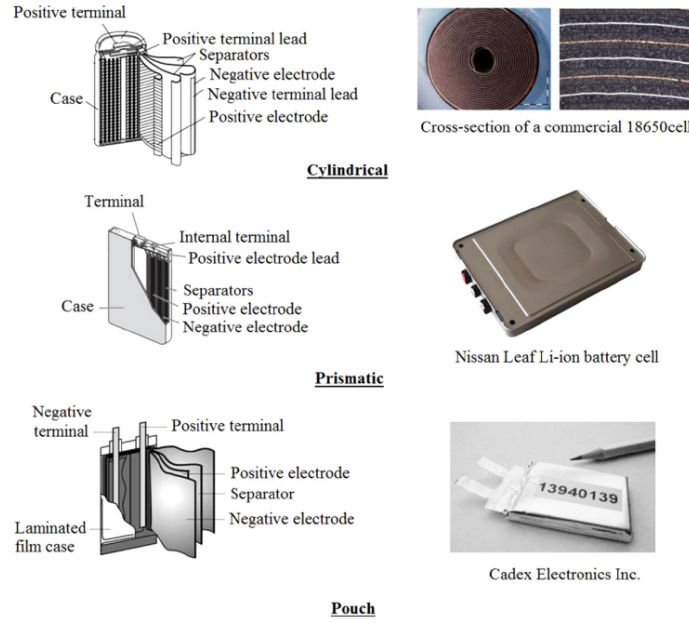


Figure 2.5: Common battery geometries extracted from Wang et al. (2016)

Maleki et al. (1999) studied the relationship of the thermal conductivity with SOC by using steady and unsteady approach. The steady method was used by creating an artificial thermal gradient across a set of anode/separator/cathode. However, the results were not comparable with the value from reported literature due to heat losses to the surrounding. In this work, polystyrene foam was used to insulated the test specimen. However, this was unable to minimise the heat loss. On the other hand, Song et al. (1997) used a heat guarded flow meter to minimise heat loss to surrounding hence creating a uni-axial flow of heat from the hotter region to colder region. The comparison of different techniques in determining thermal conductivity based on steady state technique are shown in Fig. 2.6 (a) and (b). The unsteady approach was used to measure thermal diffusivity by using xenon light. Despite this technique requires more experimental apparatus, different thermal diffusivity as result of different heat flow path direction can be recorded. This was achieved by placing the test specimen at a different angle. Maleki et al. (1999) pointed out that the thermal conductivity in-plane can be higher up to ten times than in through-plane direction.

Variation of the effective thermal conductivity with SOC is not significant in through battery plane direction, however, in the plane direction it changed due to structural adjustment after lithiation or de-lithiation according to Maleki et al. (1999). This will eventually add complexity particularly for controlling battery temperature due to continuously changing the rate of heat transport during

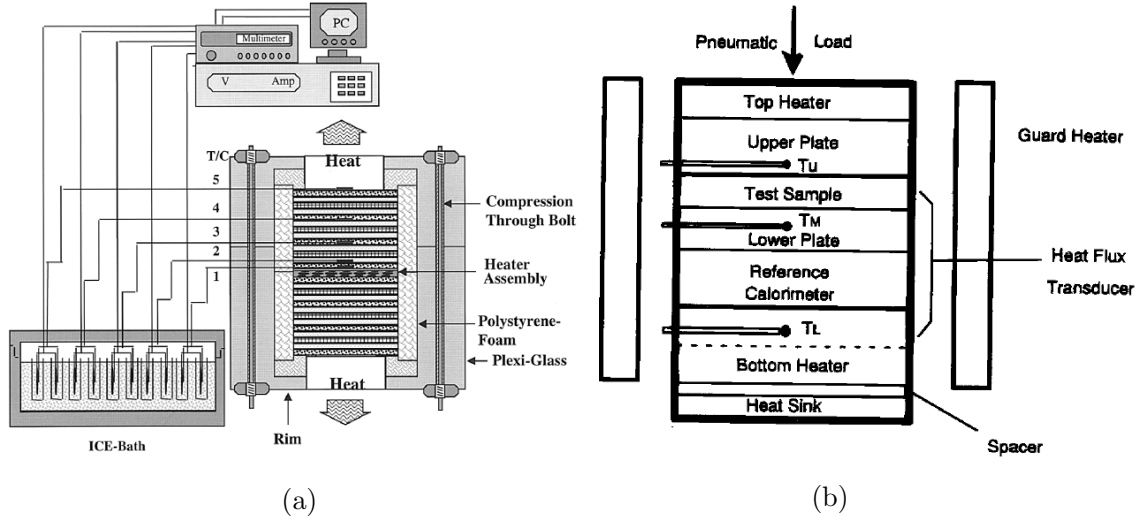


Figure 2.6: (a) Steady state thermal gradient by Maleki et al. (1999), (b) Steady state thermal gradient with guarded heat flow meter by Song et al. (1997)

charge/discharge. Considering the amount of heat generation is significant at high C-rate operation, in which the charge/discharge proceeds at a short period, it is still reasonable to assume constant thermal conductivity in the plane direction.

The determination of anisotropic thermal conductivities from component level (anode/seperator/cathode) or cell level reveals some insight about how heat is transported. As development continues, batteries are made with different geometry and thickness with the aim of offering better usable capacity. Therefore, the thermal conductivity at a cell level cannot be perceived as a representation of a battery effective thermal conductivity. However, works at the cell level can be replicated to certain extent in order to determine the value of thermal conductivity on a larger scale. Murashko et al. (2014) conducted an experiment to determine the thermal conductivity of a pouch cell in through-plane direction by using external heat by means of an incandescent bulb. The method is analogous with Maleki et al. (1999); however, it relies on the establishment of a linear temperature gradient across the battery surface in order to calculate the effective thermal conductivity in the through-plane direction. This technique was coupled with simple steady thermal model and showed that the thermal conductivity in through-plane direction is significantly low and does not show appreciable variation with SOC. These findings are corroborated by the study conducted by Maleki et al. (1999) and Wenwei et al. (2014). This highlights that during charge/discharge if the external cooling or heating can be kept at a constant rate, the internal thermal transport, particularly in through-plane direction, can also be kept at a constant rate unlike along the in-plane direction

where the thermal conductivity changes at different SOC.

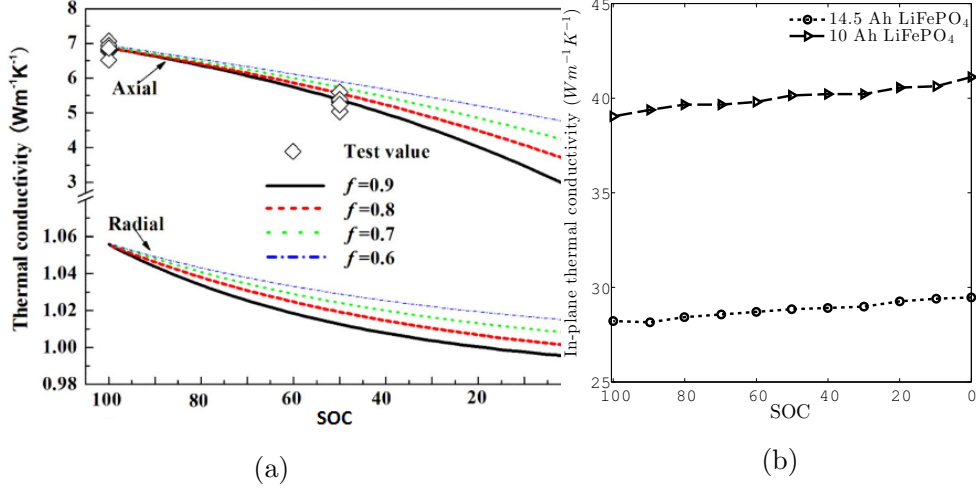


Figure 2.7: (a) Thermal conductivity in plane and through plane for cylindrical battery as function of SOC by Wenwei et al. (2014), (b) In-plane thermal conductivity for pouch battery as function of SOC reproduced from Bazinski et al. (2016)

There are similarities between the variability of in-plane thermal conductivity with SOC which was conducted by Wenwei et al. (2014) with those described by Maleki et al. (1999). However the behaviour of in-plane thermal conductivity with SOC which was conducted by Bazinski et al. (2016) behave differently. From the study, it shows a weak positive correlation as discharge proceeds or from high to low SOC. Fig. 2.7 compares the behaviour of in-plane thermal conductivity. Different battery geometry and different battery chemistry might contribute to the differences in thermal conductivity behaviour at different SOC.

Table 2.1: Summary of published work on measuring battery effective thermal conductivity

Author	Type of cell	Measurement technique	Measured value ($\frac{W}{cmK}$)	Advantages/Highlights
Song et al. (1997)	Thermal conductivity of separator	Using heater to create steady state thermal conditions	0.0012 to 0.0022	Thermal conductivity for separator vary according to temperature
Song and Evans (1999)	Thermal conductivity of composite cathode	Using heater to create steady state thermal conditions	0.002 to 0.005 from 25 to 150°C	Investigate thermal conductivity variations with temperature
Maleki et al. (1999)	Cylindrical 18650 cell	Heater and xenon light	0.034 (radial) 0.285 (axial)	Different behaviour of thermal properties at different SOC due to phase change
Murashko et al. (2014)	Pouch cell	Gradient heat flux sensor	0.00657 (through plane)	Fast technique and coupled with simple heat transfer equation to calculate the thermal conductivity
Wenwei et al. (2014)	Cylindrical cell	Heater, heated in axial direction	0.01 (radial) 0.068 (axial)	Change of thermal conductivity in axial and radial at different SOC
Zhang et al. (2014b)	25Ah pouch cell	Heater placed between two cell	0.0048 (in through plane) 0.21 (in plane)	Using 2D thermal model to fit value of thermal conductivity
Drake et al. (2014)	Cylindrical cell	Flexible heater at different location (axial and radial)	0.0015 (radial) 0.32 (axial)	Heat is transported differently due to huge differences between thermal conductivity from axial and radial

2.1.4 Surface and Internal temperature measurement

Numerous attempts have been performed to determine and predict the battery internal temperature by using a non-intrusive and intrusive method. This is important due to the behaviour of a battery is dictated by its hottest region as shown by Troxler et al. (2014). Surface temperature can be measured easily, however, the internal temperature requires a tremendous amount of effort such as changing the battery structure. Li et al. (2013) inserted several thermocouples into a pouch cell and also measured its surface temperature as shown in Fig. 2.8 (a). They recorded temperature difference of 1.1°C between the surface and internal under adiabatic and 1.5-C discharge. This technique also showed significant temperature variation where the both surface and internal temperature near the positive tabs possessed high temperature as compared to the other measured locations. Although this technique showed the capability of measuring the temperature at several locations both external and internal, the presented temperature difference is not pronounced partly due to the low C-rate operation, hence questioning the credibility of placing thermocouple inside a battery. Mutyala et al. (2014) approached this problem differently by using an internal temperature sensor made from flexible thin thermocouple which was attached directly to a current copper collector, allowing temperature measurement at high C-rate. Nevertheless, the embedded sensor was placed at the top of electrode stack which is in the vicinity of the battery casing and might not be a good representation of a battery internal temperature as shown in Fig. 2.8.

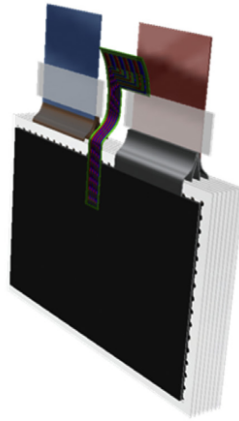


Figure 2.8: Position of temperature sensor for measuring battery internal temperature by Mutyala et al. (2014)

Fig. 2.9 compares the intrusive techniques in measuring battery internal temperature by using a thermocouple and flexible thin sensor. It can be seen that

the internal temperature sensor is not visible from the battery surface which makes it more presentable. This technique also demonstrated that the installation of the internal temperature sensor would just add some additional effort from the conventional battery assembly, proving that internal temperature sensor can be equipped in an economically way. Although these intrusive techniques in measuring internal temperature are accurate and at some point maybe proved to be cost-effective, it seems impractical to be implemented in vehicle platform level. This is due to inserting sensor in a battery might affect the electrochemical process when the battery is subjected to aggressive charge/discharge and fluctuation of ambient temperature.

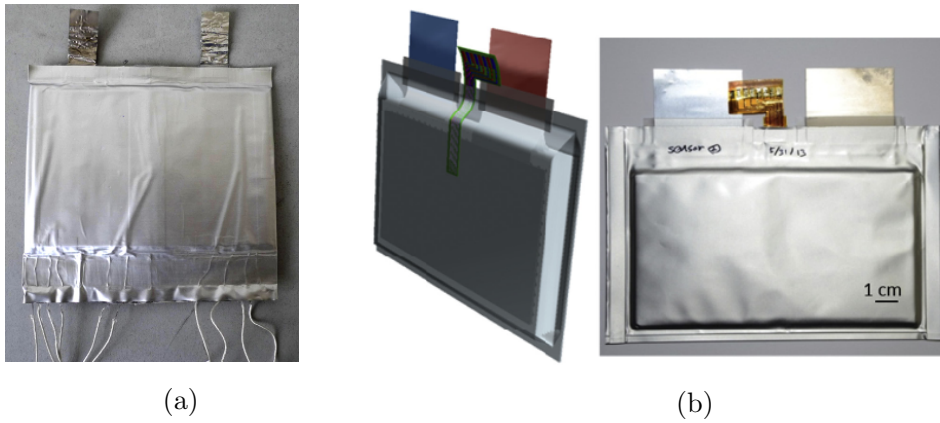


Figure 2.9: (a) Internal temperature measurement by using thermocouple from Li et al. (2013), (b) Internal temperature measurement by using polymer embedded thin film thermocouples from Mutyala et al. (2014)

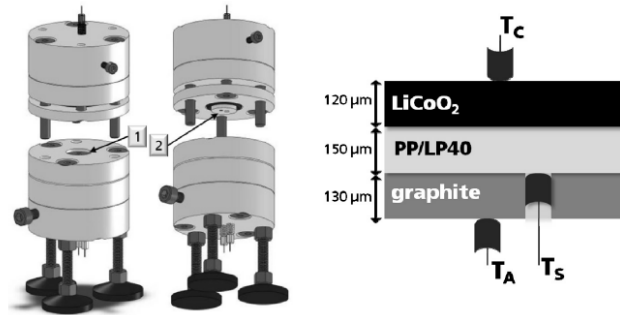


Figure 2.10: Experimental set-up and thermocouple location for measuring cell individual temperature extracted from Heubner et al. (2013)

Although the idea to embed a sensor inside a battery can be risky which will eventually cause an internal short circuit, this method can be used to explore the non-uniform heat generation on components level. This is important to investigate the thermal transport rate of heat generation on a micro cell level. Heubner et al. (2013) conducted an experiment to measure the individual contribution of heat

generation based on a unit cell basis as shown in Fig. 2.10. The cell unit consists of two electrode configuration of anode/separator/cathode with each of them having its own thermocouple. Cathode dominated the overall heat generation, particularly during discharge. However, the differences were not noticeable due to low C-rate charge/discharge. Further improvement was made again by Heubner et al. (2014) by modifying the cell unit into three electrode type which resulted in more significant temperature difference given from all of the three components. This technique was coupled with temporal temperature evolution or in-situ thermograph. At high C-rate operation, the highest amount of heat generated was given by cathode during charge and discharge. Fig. 2.11 (a) and (b) illustrate the temperature evolution of individual components in unit cell which is based on different electrode configuration. It can be seen that high C-rate operation gives significant rise of heat generation given by the cathode. This is translated by higher temperature difference during charge and discharge.

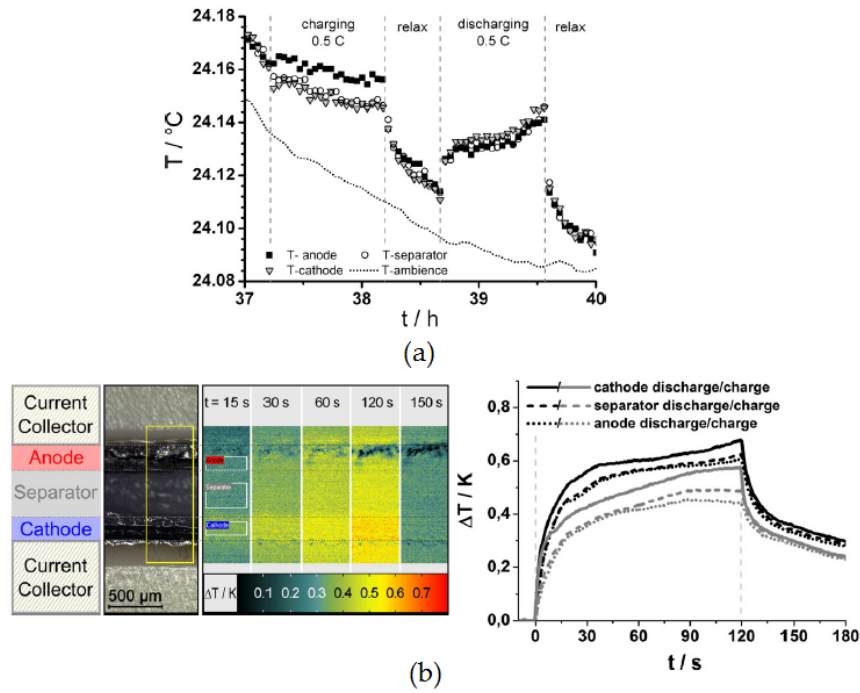


Figure 2.11: (a) Temperature evolution under charge/discharge at 0.5C Heubner et al. (2013), (b) Thermography image of cell stack and temperature increase during charge/discharge at 5C Heubner et al. (2014)

Heubner et al. (2015) investigated the dependency on heat generated at various charge/discharge. The effect of reversible heat generation is important, particularly at low C-rate operation. The work revealed that the difference in temperature trends during the same C-rate of charge and discharge are due to asymmetric

heat generation. Fig. 2.12 shows the amount of heat generated by individual components at various C-rate for charge and discharge. Clearly, high C-rate operation causes the cathode to release relatively high heat generation compared to the other components. Nonetheless, the dominant cathode effect on high C-rate is only valid for discharging. The entropy effect, as well as difference in kinetic limitation during charging, induces different behaviour for the cathode which can be seen in Fig. 2.12.

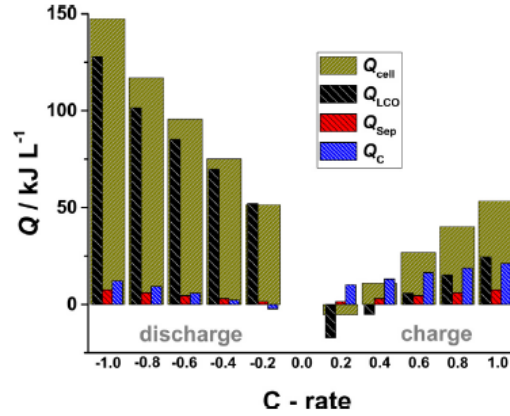


Figure 2.12: Summary of heat generation contribution of each component on cell level extracted from Heubner et al. (2015)

A non-intrusive technique such as EIS and in-situ x-ray diffraction were conducted to predict the battery internal temperature. The later was conducted by Lin et al. (2013) which measured cathode and anode temperature by measuring its respective current collector during overcharge. Both anode and cathode temperature were uniform at low voltage level, however, when the battery voltage started to go beyond the typical maximum allowable voltage which is 4.2V, noticeable temperature differences between anode and cathode were manifested. The temperature difference was approximately about 10°C. This highlights the capability of the technique to probe the temperature of anode and cathode independently and shows that even at small scale level, the temperature of electrode pair can be significantly different. Nonetheless, this technique is not feasible to be coupled with BMS for on-board monitoring due to its complexity.

Another type of non-intrusive technique which requires less intricate experimental device is by using EIS. This was carried out by Srinivasan et al. (2011) by taking an EIS measurement from low to high temperature and at different SOC. However, this technique requires a long period of waiting time for both voltage and temperature to reach equilibrium to obtain a good EIS data. Correlation of resistance with temperature based on the EIS data was presented, however, there was

no internal temperature prediction during charge/discharge. Further improvement was made by integrating battery surface temperature with EIS measurement which was conducted again by Srinivasan (2012). The internal temperature was inferred by using the phase shift from EIS data at 40Hz at various ambient temperature, this information is presented in Fig. 2.13.

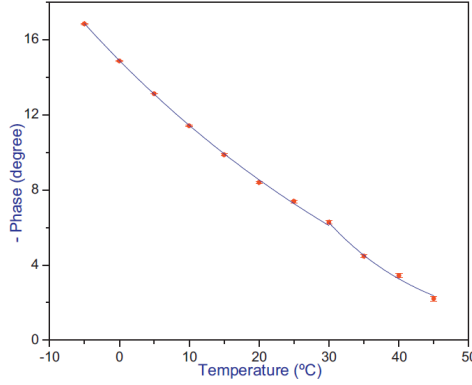


Figure 2.13: Relationship of 40Hz phase shift at 50%SOC at various ambient temperature extracted from Srinivasan (2012)

Fig. 2.14 (a) and (b) show temperature difference between predicted internal and measured surface temperature at different ambient temperature. Interestingly, this technique can display the effect of different heat generation rate at a different temperature. It can be seen that the internal temperature deviates far from the measured surface temperature at the ambient temperature of 0°C. On the other hand, the deviation of the predicted internal temperature under 23°C of ambient temperature is not as apparent as shown under low ambient temperature. This behaviour is expected due to the negative exponential relationship of EIS with temperature.

A major concern with the impedance based temperature measurement is that the dependency of SOC on the impedance itself is limited to approximately around 5 and 95% SOC. Technically, an EIS can be performed at 100% to 0% SOC, however, to prevent the battery from being used outside of its stable thermodynamic potential, limits on SOC need to be applied. This is primarily to prevent the battery from overcharge and over-discharge at high and low SOC respectively. During EIS measurement, sinusoidal current will be applied, and if the voltage level is at 100% SOC, the battery will be overcharge and voltage will go beyond the maximum allowable level. This behaviour can also occur at low SOC but in a reverse manner. Another issue with regards to using EIS for predicting internal temperature is that this technique requires a full range of EIS measurement from high to low SOC. Ad-

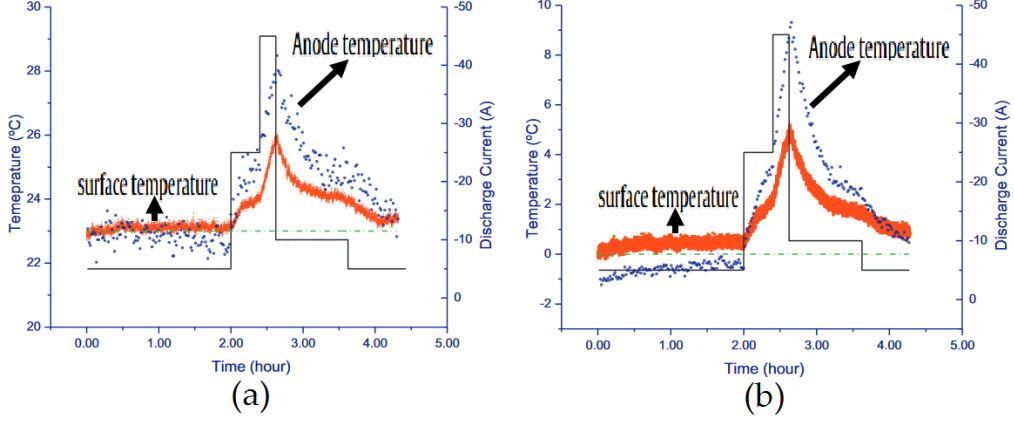


Figure 2.14: Comparison of internal temperature prediction by using phase shift at 40 Hz from EIS with measure surface temperature by Srinivasan (2012) : (a) Under ambient temperature of 23°C, (b) Under ambient temperature of 0°C

ditionally, frequency in which the phase shift is considered to predict the internal temperature must not have a dependency on SOC. This frequency can vary depending on the battery chemistry and capacity. For instance, Srinivasan et al. (2011) and Srinivasan (2012) used phase shift from EIS measurement at 40Hz for prismatic battery with graphite anode- $LiCoO_2$ cathode battery, Spinner et al. (2015) used phase shift at the frequency of 300Hz for cylindrical battery with graphite anode- $LiCoO_2$ cathode battery and Schmidt et al. (2013) used phase shift at frequency of 10.3kHz for graphite anode- $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode. Clearly, although this technique looks quite straightforward, it lies some variability which requires numerous attempts of EIS measurement to find the suitable frequency which is independent on SOC.

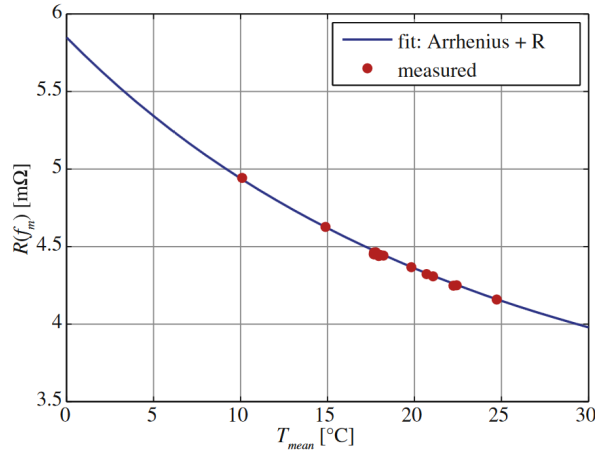


Figure 2.15: Variation of real part of resistance given from EIS measurement at 10.3kHz by Schmidt et al. (2013)

Schmidt et al. (2013) conducted series of EIS measurement under several thermal variations such as convection and conduction thermal control. At first, the battery was subjected to convection thermal condition at several temperatures until it reached equilibrium before the EIS can be measured. This is to evaluate the reliance of the real part of resistance at 10.3kHz on temperature by assuming the battery temperature is identical with the thermal chamber setting temperature. Subsequently, the battery was subjected to artificial thermal gradient by using conductive thermal control. This was achieved by controlling the battery top and bottom surface temperature independently by using the thermoelectric module. The resistance at 10.3kHz for thermal gradient was then fitted and compared with the resistance obtained from convection thermal control. The comparison was made by taking the average temperature based on the value of the applied gradient which shown in Fig. 2.15. This was used as a basis for the internal temperature prediction in which the average value based on the applied thermal gradient was substituted to represent mean cell temperature; however, Troxler et al. (2014) showed that a battery under thermal gradient cannot be represented by taking an average temperature between two surfaces. This is primarily due to the difference in EIS measurement as illustrated in Fig. 2.16.

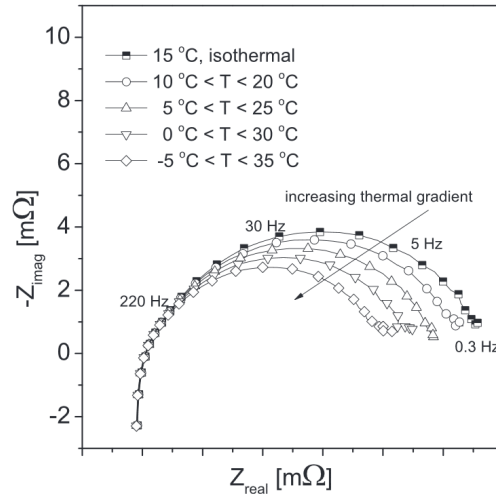


Figure 2.16: Impedance measurement under different thermal gradient by Troxler et al. (2014)

The idea of using the average temperature given from thermal gradient to predict the internal temperature which was conducted by Schmidt et al. (2013) could be imprecise which is based on the presented evidence by Troxler et al. (2014). However, the experimental technique particularity for controlling temperature by the nature of heat conduction paves the way in reducing temperature non-uniformity on

battery surface. At some point, the technique is analogous to Troxler et al. (2014) as shown in Fig. 2.17 (b). The main difference lies in the cooling mechanism for the thermoelectric module, where Schmidt et al. (2013) opted for natural convection at 0°C with fins attached to the thermoelectric module to improve heat transfer, while Troxler et al. (2014) used circulating water to remove heat.

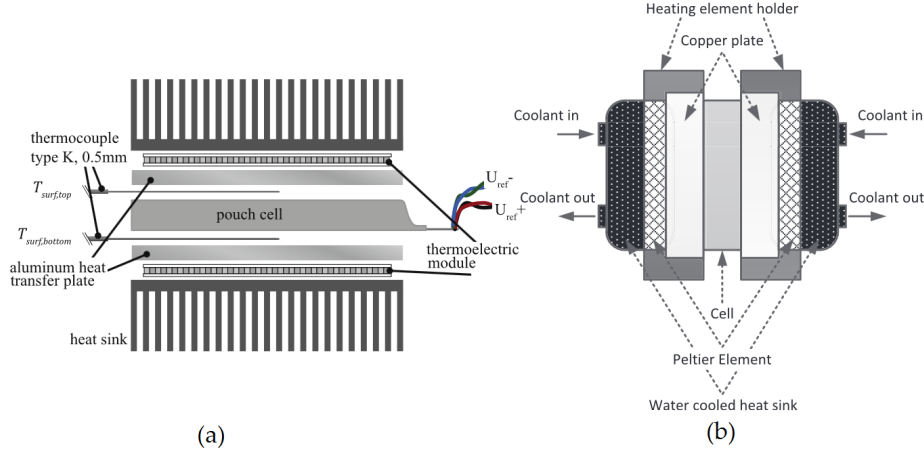


Figure 2.17: Experimental set-up for battery under thermal gradient : (a) Using thermoelectric module with fin under convection at low temperatures by Schmidt et al. (2013), (b) Using thermoelectric module with liquid cooling by Troxler et al. (2014)

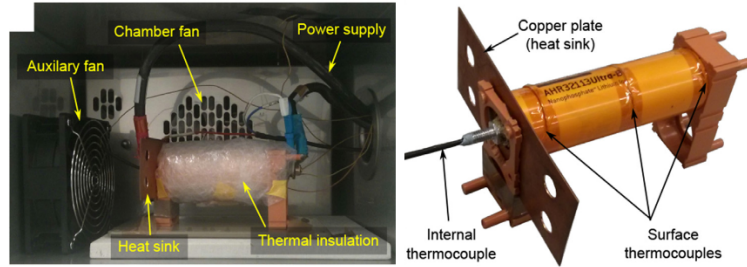


Figure 2.18: Experimental set-up for a cylindrical battery for internal temperature prediction and validation Richardson et al. (2016)

Table 2.2 summarises several published works with the focus to determine or predict the internal state of the battery particularly on thermal aspect. Research in early period started with non-intrusive technique, however, to further probe and validate the result, a direct internal temperature measurement seems to be a more sensible approach. Although the latter provides a more accurate result, the test was limited to low C-rate operation. Nevertheless, Richardson et al. (2016) used the idea of combining the EIS measurement and surface temperature to predict the internal temperature. The predicted internal temperature was then validated by data given

by thermocouple which was embedded in the core of a cylindrical battery as shown in Fig. 2.18. This technique allows for an on-board internal temperature prediction. The imaginary part of impedance at 215 Hz and measured surface temperature were used simultaneously to predict the internal temperature based upon vehicle drive cycle. This frequency was chosen because the impedance is independent of the battery SOC. The imaginary part of EIS measured at 215 Hz was required for parametrisation of the cell impedance which was based on second order polynomial. This makes the technique suitable to be embedded in a BMS due to its simple approach and proved to be accurate. In this research, the selected frequency is 215 Hz. The reason for this is that, it is well known that the selection of the frequency must be independent on battery SOC. This is to ensure the change in impedance is due to the temperature change rather than the change of SOC in order to ensure the change in impedance is due to the temperature change rather than the change of SOC.

Table 2.2: Summary of published work on measuring/predicting battery internal temperature

Author	Boundary	Measuring/Predicting technique	Measured/Predicted temperature difference	Basis of comparison
Srinivasan et al. (2011)	Convective	EIS based on 40Hz	No comparison	None
Srinivasan (2012)	Convective	EIS based on 40Hz	No comparison	Surface temperature
Schmidt et al. (2013)	Conductive	EIS based on 10.3kHz	Temp. higher up to 20% from surface temp at 0°C ambient	Surface temperature
Li et al. (2013)	Conductive	Thermocouple inside battery	1.1°C at 1.5C discharge	Internal temperature
Lin et al. (2013)	Convective	In-situ XRD	8°C at cathode during overcharge	Internal temperature
Mutyalu et al. (2014)	Convective	Flexible thin thermocouple	30°C internal temperature at 0°C ambient at 7C discharge	Internal temperature
Zhang et al. (2014a)	Convective	Thermocouple surface/internal	5°C difference from surface temperature at 22°C ambient and 4.8A full discharge	Surface and internal temperature
Richardson et al. (2014)	Convective	Thermocouple surface/internal EIS at 215Hz	10°C difference from surface temperature at 0°C ambient and 20A pulse discharge	Surface and internal temperature
Spinner et al. (2015)	Convective	EIS at 300Hz	No comparison	Surface temperature
Zhang et al. (2016)	Convective	Thermocouple between cell	10°C difference from surface temperature at 5°C ambient at 30A pulse discharge	Surface and internal temperature
Richardson et al. (2016)	Convective	Thermocouple surface/internal EIS at 215Hz	9°C difference from surface temperature at 8°C ambient and 50A pulse discharge	Surface and internal temperature

2.2 Current and temperature non-uniformity on battery performance

2.2.1 For single battery

On a small scale level, due to the intrinsic configuration of a battery which is made in a layered structure, the current entering each pair of electrodes are different albeit the temperature of each layer is not significantly distinct. Zhang et al. (2013) made an experimental cell which consists of one negative electrode which is made from copper (along with active material coated on both sides), two layers of separators, and ten positive electrode segments which are made from aluminium (along with active material coated on both sides). It can be seen from Fig. 2.19 (a)-(c), although the cell can be considered very thin and therefore the temperature of each layer can be assumed to be identical, local current distribution can be seen clearly regardless of the applied ambient temperature.

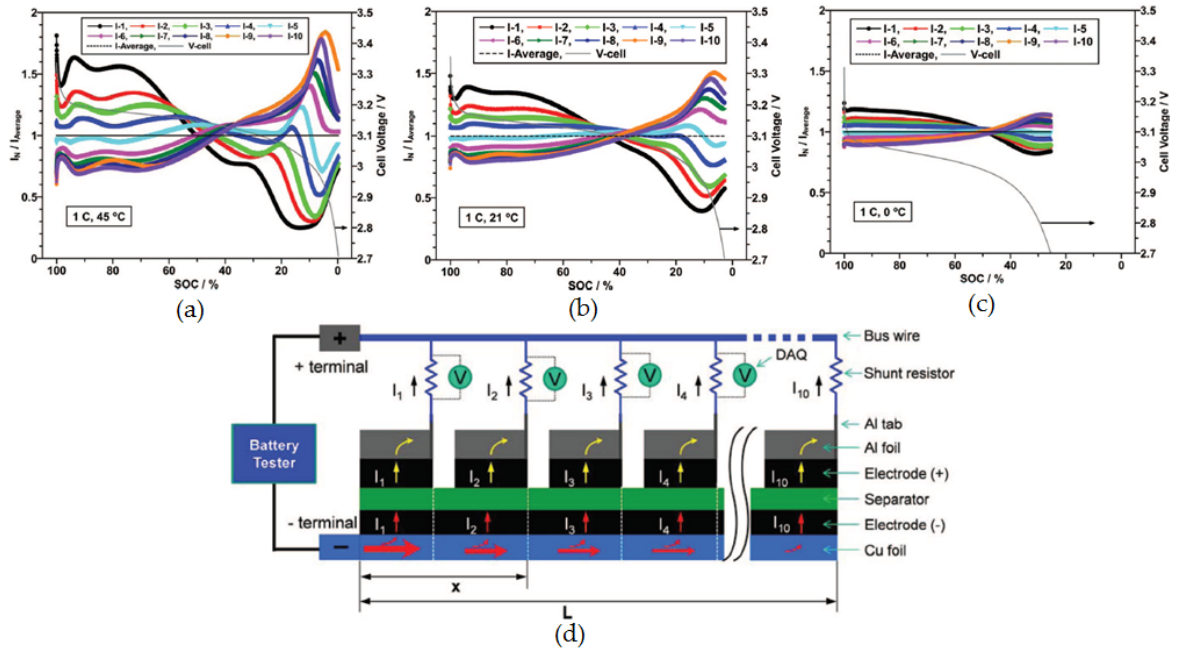


Figure 2.19: Current distribution for thin electrode system at : (a) 45°C, (b) 21°C, (c) 0°C and (d) Experimental setup by Zhang et al. (2013)

Fig. 2.19 (d) shows the experiment setup, the region which is located farthest from the negative terminal experiencing high voltage drop as compared to the region near to the negative terminal. This is due to the resistance given by the copper foil. When current flows from the negative terminal during discharge,

voltage drop due to the resistance causes local overpotential to change. Higher voltage drop will cause lower overpotential and consequently lower current will be generated. Hence the region which is located far from negative terminal experienced lower current and this behaviour is consistent regardless of the ambient temperature as can be seen in Fig. 2.19 (a)-(c). The behaviour follows the current-overpotential relationship which is described by Butler-Volmer equation.

Reduced battery performance at low temperature is expected due to increase in battery internal resistance. The increased in resistance gives an impact to the current distribution where the currents distribute in a more uniform manner. On the other hand, higher temperature resulted in monotonous variation of the current distribution which can be seen in Fig. 2.19 (a). This is a reflection of various plateaus given from the OCV. At this condition, local SOC non-uniformity governs the local current distribution. Conversely, the battery resistance superseded the resistance of the copper foil at low temperature. Therefore, the current distributions are predominantly determined by its inherent resistance. Since the cell is thin, the temperature of each parallel tab can be considered to have small variations over the period of discharged but remain unchanged over its dimension. This work highlighted even at a cell level, the non-uniformity behaviour is apparent.

However, the cell which was used in this experiment is not comparable with the commercial battery regarding its thickness. Hence the thermal transport experienced in the commercial battery regardless of its form factor would be significantly distinct. In which thermal gradient is likely to occur which depends on the operating temperature and the applied current, therefore, the resulting temperature difference will eventually alter the current distribution which is described by Fleckenstein et al. (2011). In this work, three identical batteries were used and each of the battery was insulated differently to represent the innermost, middle and outer region of a single battery in a through-plane direction. This work reaffirmed that the local current of each battery behaves differently in which the local current at the innermost region experienced the highest value of absolute current regardless of charging or discharging while the outer region experienced the lowest current. This finding is in agreement with Ye et al. (2014) which highlighted that larger thermal gradient particularly in the through-plane direction as a result of increasing the cooling intensity will cause differences of local current to be larger. It will eventually induced higher depth of discharge at the region which is hotter, therefore generating non-uniform SOC.

The monotonous current behaviour is manifested at all conditions whether the non-uniformity is caused by the temperature gradient, different battery capacity and battery with different SOH which are connected in parallel as described by An et al. (2016) and Brand et al. (2016). This highlights that if a temperature gradient exists although the gradient occurs at low temperature, the current distributions still show the reflection of its respective OCV. These behaviour are rather contradictory with the findings of Zhang et al. (2013). Nevertheless, this comparison is not based on the battery which is dimensionally on the same length scale. Therefore it could be the uniform current distribution at low temperature is only valid for an electrode pair system.

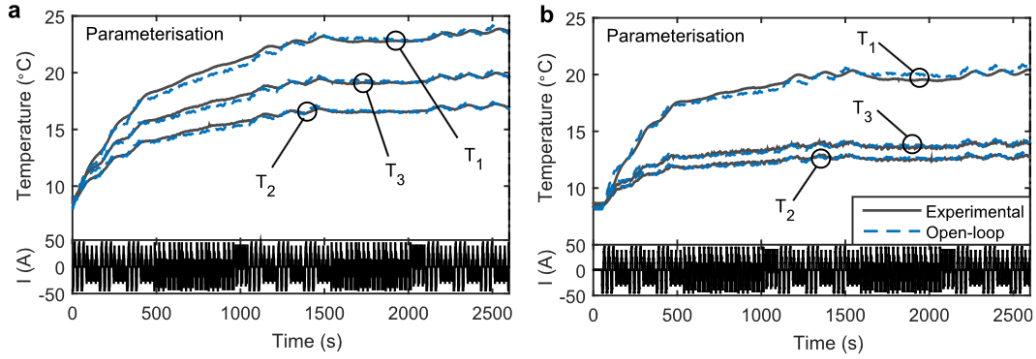


Figure 2.20: Evolution of surface and internal battery temperature at different cooling direction, T_1 (internal), T_2 and T_3 (surface temperature) under drive cycle load : (a) Cooling in along plane direction, (b) Cooling in through plane direction extracted from Richardson et al. (2016)

Owing to the inherent anisotropic thermal conductivity of a battery, different heat transfer path will cause the deviation between the surface and internal temperature to be distinct. Forgez et al. (2010) experimentally determined the difference between surface and internal temperature by applying periodic current at the rate of ± 10 , ± 15 and ± 20 at the frequency of 2Hz. The Larger deviation was manifested at higher currents. The battery was placed in an ambient condition in a thermal chamber. Therefore, it could be that the thermal transport was predominantly governed by the surface convection.

The high rate of heat generation at high currents surpassed the rate of heat removal given from the surface convection hence caused larger temperature deviation between the surface and internal. It is a consensus that high C-rate operation causes the internal heat generation of a battery to increase and consequently resulting larger temperature deviation. However, Richardson et al. (2016) showed that if the

cooling direction is switched to a high thermal conductivity region which in this case is along the battery plane region, the difference between the internal and surface temperature can be reduced compared to surface cooling as illustrated in Fig. 2.20 (a) and (b). The Larger cooling area provided by surface cooling seems to be more effective to suppress temperature increase both external and internal. However, it creates greater temperature deviation. The cooling which is based on high thermal conductivity region can be enhanced by increasing the fans speed or switch to a conductive cooling mechanism. Nevertheless, the presented investigations highlight the different behaviour by changing heat transfer path, therefore has shed some light particularly in reducing thermal non-uniformities in a battery.

2.2.2 For a series connected battery

Fouchard and Taylor (1987) conducted the earliest experimental investigation on the behaviour of a battery connected in parallel and series. In a series array, the pack voltage is determined by the sum of the individual voltage and the value of the local current is equivalent to the pack current. If the individual battery is identical regarding impedance, SOH and thermal condition, the batteries will be cycled in an ideal manner. A battery with lower capacity or different impedance will cause imbalance. This is supported by Spurrett et al. (2002) which stated that battery imbalance which could be caused by the difference in resistance or SOH would lead to overcharge or over discharge. This will eventually lead to a certain battery to be charged/discharged beyond its thermodynamically stable voltage window and can reach 0V which subsequently cause permanent damage as illustrated in Fig. 2.21.

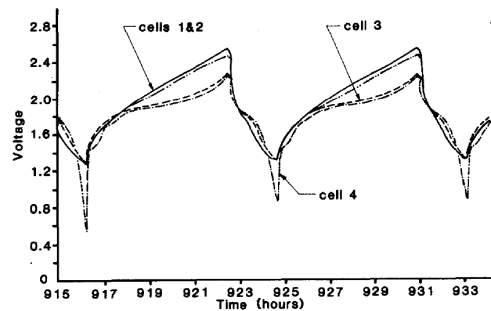


Figure 2.21: Individual battery voltage in series string with non-uniform battery condition extracted from Fouchard and Taylor (1987)

As a consequence, the pack capacity in a series string is determined by the battery which has the lowest capacity. This is an important aspect to be tracked

particularly for BMS to prevent any individual battery to be operated outside its limit. According to Wu et al. (2006), battery with low capacity will be discharged relatively faster, therefore, can reach 0% SOC while the other batteries in the string still have a more remaining capacity. As investigated by Miyatake et al. (2013), since the current for battery in a series string is common, battery with high resistance will cause a larger voltage drop, therefore, will reach the cut off earlier.

This will be the main concern if the charging/discharging is conducted without considering the individual battery condition. As stated by Andrea (2010), if the system that regulates the charge is based on total voltage to determine the limit of charging such as CC-CV (constant current-constant voltage) charging, the system will give an inaccurate sense of safety. Therefore to prevent from catastrophic event given from either over-charge/over-discharge, the pack capacity needs to be reduced based on the battery with has the lowest capacity, high impedance/resistance or low SOH.

2.2.3 For a parallel connected battery

A battery connected in a parallel string is deemed necessary to increase the energy density of a battery pack. This architecture is commonly adapted especially for the electric vehicle. It is commonly known that in a parallel string, the pack voltage is identical to the individual battery terminal voltage and the current of each battery is divided evenly based on numbers of battery involved in the string. The latter can be achieved if all of the batteries are identical regarding thermal operating conditions, SOH and resistance/impedance. If one of the battery has a different condition, the current distribution will be imbalanced. For instance, Fouchard and Taylor (1987) measured individual battery current in a parallel string and shown that due to the difference in impedance, it took a long time for the each of the battery OCV to settle at the same value during relaxation. This is reflected by the current redistribution as illustrated in Fig. 2.22. It can be seen that during the relaxation, some of the batteries were still charged and discharged although there was no current applied. This behaviour occurs due to all of the batteries having different SOC when relaxation starts, therefore, battery at high SOC was discharged and the ones at low SOC was charged. The charge re-balancing happened until all of the battery SOC reached an equilibrium level.

Temperature non-uniformity causes each battery to behave differently due

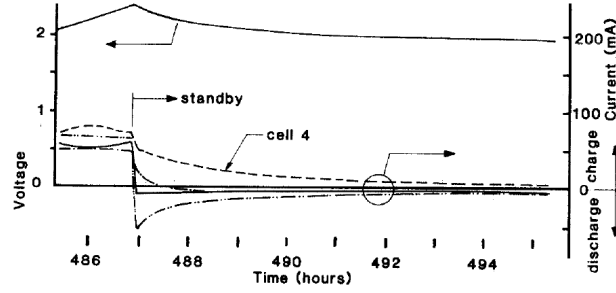


Figure 2.22: Current re-distribution during relaxation period extracted from Fouchard and Taylor (1987)

to change of resistance. This eventually creates a non-uniform current flowing into individual battery in a parallel string. Surprisingly, the resistance change as a result of temperature gradients of 10°C is higher than the resistance variation due to manufacturing uniformity as stated by Spurrett et al. (2002). In a battery pack, temperature variations are inevitable, however, if the variations can be kept at a minimum level, it will reduce the load to the BMS particularly in monitoring individual battery current in a parallel string. With fewer temperature variations, batteries connected in a parallel string can be considered as a single battery according to Wu et al. (2006). Apart from temperature, batteries with different capacity also experience local current deviation. This behaviour was experimentally measured by Wu et al. (2006) and Miyatake et al. (2013) which stated that battery with high capacity draws more current than the lower ones.

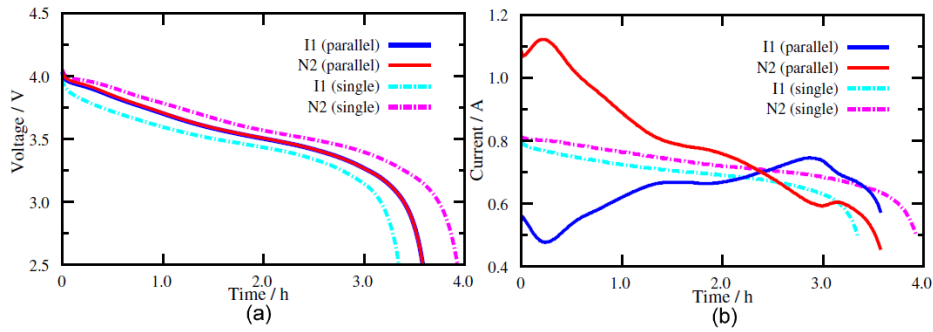


Figure 2.23: (a) Pack and individual battery voltage, (b) Current distribution of battery with different capacity connected in parallel extracted from Miyatake et al. (2013)

Different on capacity causes the battery impedance to be distinct; this is the main reason for the non-uniform current behaviour in which the currents are not equally distributed as shown in Fig. 2.23. It can be seen that the currents split at the early stage of the discharge process, in which the current for high capacity

battery goes significantly higher. This indicates that the resistance at approximately 100% SOC is considerably low for battery with high capacity and this behaviour is analogous to the batteries connected in a parallel string with both having the same capacity but operating at a relatively different temperature as shown in Fig. 2.24. The main factor that governs both phenomena is the difference of the inherent resistance at different condition either temperature or capacity. Battery with lower resistance will be discharged at a comparatively higher rate. Therefore, the pack capacity will be reduced due to the battery reaches the cut-off voltage sooner than the battery with high resistance.

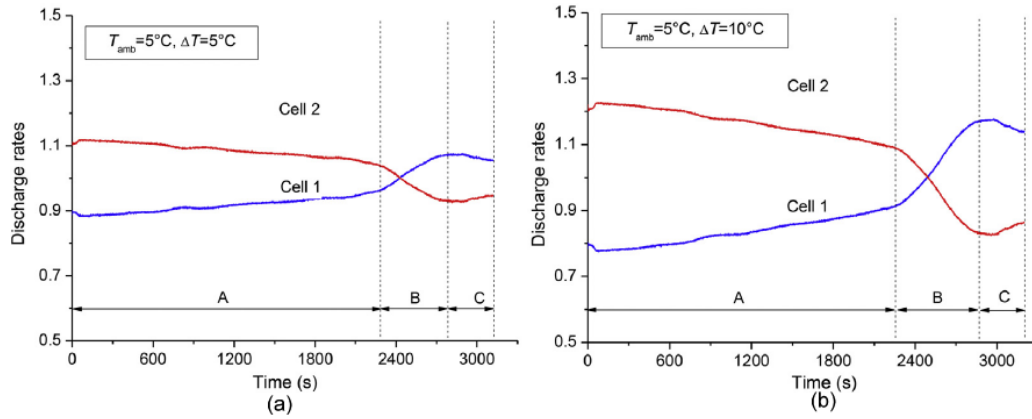


Figure 2.24: Current deviation given from different battery operating temperature : (a) Cell 1 (5°C) - Cell 2 (10°C), (b) Cell 1 (5°C) - Cell 2 (15°C) extracted from Yang et al. (2016)

Another important behaviour for batteries connected in a parallel string is the interdependency of local current and OCV during relaxation. This is often neglected due to inability to measure the OCV of the individual battery directly. However, An et al. (2016) and Brand et al. (2016) measured the current for individual battery during long relaxation period for a battery which possessed different capacity and resistance. Both showed an exponential decreased and increased of current depending on the SOC of the respective OCV before relaxation period started. An et al. (2016) showed that if the two batteries connected in the parallel string have the same conditions, the drawn current is divided equally which is shown by the measured individual battery current. Brand et al. (2016) came out with a model to predict the individual OCV by mapping the current distribution and demonstrated that the charge rebalancing happened due to inhomogeneity of battery resistance. However, the study was rather limited due to there were no synergies shown between the individual OCV and the terminal voltage during relaxation.

The impact of thermal gradient on the parallel connected battery towards the battery performance has been studied by Yang et al. (2016). This was conducted by placing two batteries at a different ambient temperature to create a non-uniform thermal condition. The voltage and discharge capacity slightly increased when the temperature difference increases at high ambient temperature which was at 25°C. On the other hand, the increase of voltage and discharge capacity are much more notable although the same temperature differences were applied at the low operating temperature which was at 5°C. Larger differences at low operating temperature albeit the same temperature difference was applied, is caused by the change of resistance at a different temperature. Another factor which could affect the result is the temperature increased during the discharging. Since both of the batteries were operated under convective environment, battery heating cannot be avoided, and the temperature increase is significant at low operating temperature. Moreover, the average temperature of two batteries connected in parallel with large temperature difference is higher than the ones at relatively low temperature difference, therefore, improves its performance. The average temperature in each case were calculated and shown in the dotted rectangular box along as illustrated in Fig. 2.25. As a consequence, the improved battery performance due to thermal gradient is not primarily due to the interplay of resistance at the different temperature. The different rate of heat generation at a different ambient temperatures also contributes to the improved in performance.

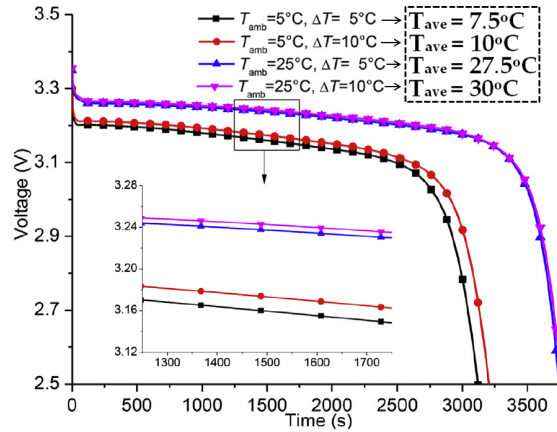


Figure 2.25: Discharge performance at different temperature and thermal gradient extracted from Yang et al. (2016)

As a result of the thermal gradient, non-uniform charge/discharge occurs with magnitude closely related to the degree of the thermal gradient and the operating temperature. This will eventually result in non-equal degradation if it happens continuously. Ganesan et al. (2016) performed the study of non-equal degradation

on a battery pack connected in series and parallel. The results showed that higher rate of degradation occur when the battery pack operates at high temperature and it gets worse with the occurrence of a thermal gradient. There are similarities regarding the degradation rate with the occurrence of thermal gradient which was performed by Yang et al. (2016). Nevertheless, neither of the works can experimentally prove that non-equal current truly causes the increased of degradation rate. The presented evidence are not conclusive in which there is a possibility that the increase in the degradation rate could have been caused by cycling at higher average temperature. This is because the applied thermal gradient is controlled mainly by convection which can cause the controlled temperature difference to be physically incorrect over the period of charge/discharge due to increase in battery temperature.

However, the approach which was taken by Shi et al. (2016) shows that higher degradation rate for two batteries connected in parallel with a configuration temperature of 25°C and 50°C is dictated by the battery operating at 25°C. On the other hand, degradation rate for the individual battery connected in parallel for both batteries operating at 25°C showed resemblance with the behaviour given from a reference battery cycled at the same temperature as illustrated in Fig. 2.26. Differences in behaviour for the individual battery happened because of the current imbalance especially at the end of charging and end of discharging as depicted in Fig. 2.27. It can be seen that battery which is operated at a lower temperature, continuously possessed high current magnitude especially at the end of charging and end of discharging. This causes the rate of degradation at this temperature to be greater than at high temperature.

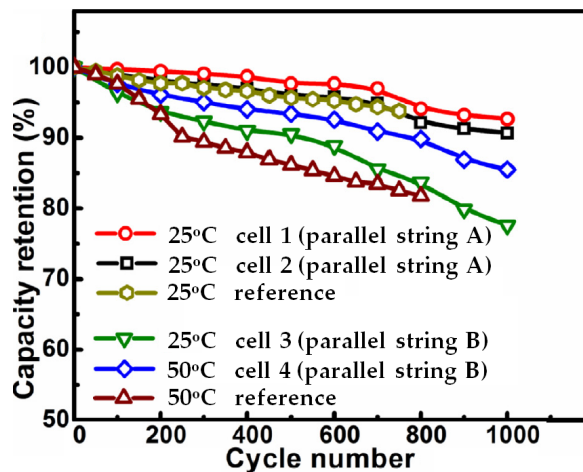


Figure 2.26: Different degradation rate given from two sets of battery connected in parallel extracted from Shi et al. (2016)

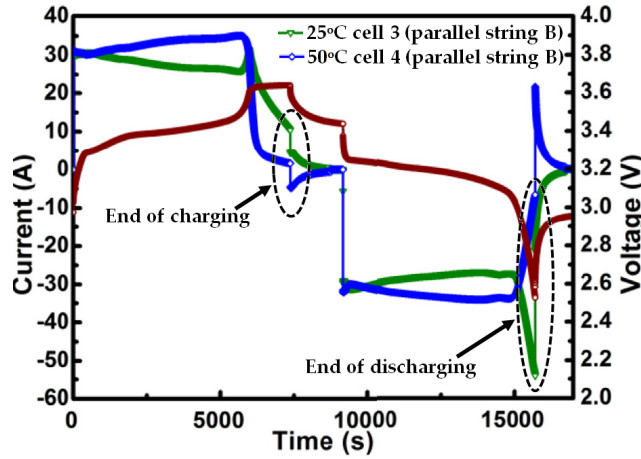


Figure 2.27: Current spike due to thermal gradient at end of charging and end of discharging extracted from Shi et al. (2016)

According to Shi et al. (2016), high rate of lithium intercalation at high SOC and de-intercalation low SOC contributes to lithium losses. This will eventually lead to lithium plating at high SOC and increase in SEI layer at low SOC. This finding could be relevant for full electric vehicle where the operating SOC is considerably wide as compared to HEV. It is generally accepted that higher temperature promotes higher degradation rate, however the study conducted by Shi et al. (2016) shows that the degradation rate for a parallel connected battery is dictated by the battery which possesses the lowest temperature. Perhaps, more analysis is required in order to quantify the main cause of the battery degradation and explain whether it is caused by operating the battery at higher temperature or discharging/charging at higher current.

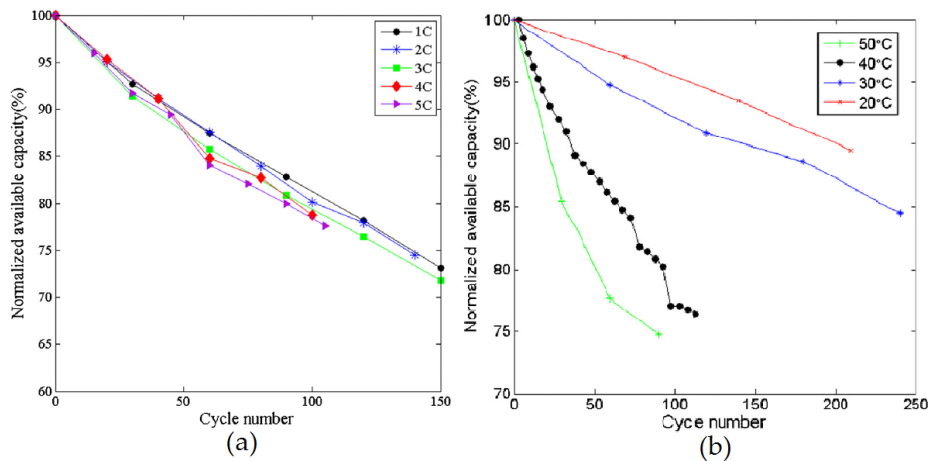


Figure 2.28: Rate of degradation due to : (a) Current discharge rate, (b) Ambient temperature extracted from Gu et al. (2014)

Gu et al. (2014) investigated the impact of temperature, current rate and depth of discharge on battery degradation. The study shows that the ambient temperature is the main factor which governs the rate of degradation rather than the current discharge rate as depicted in Fig. 2.28 (a) and (b) for the effect of C-rate and ambient temperature respectively. The comparison suggests that the battery operating temperature must be the priority and be kept at the optimum level to reduce the rate of degradation. This finding contradicts the finding of Shi et al. (2016), which stated that high C-rate particularly at end of discharge is the main factor that increases the rate of degradation. The rate of degradation is commonly related to the Arrhenius relationship in which the degradation behaves exponentially with the battery operating temperature as described by the study of Purewal et al. (2014). This study also shows that the operating temperature is the most important aspects followed by C-rate and depth of discharge which is analogous to the finding of Gu et al. (2014). High battery operating temperature improves the battery performance due to reduction in the battery internal resistance. On the other hand, imposing battery at high temperature will ultimately reduce the lifetime of the battery mainly due to accelerated side reaction and formation/growth of solid electrolyte interface which described by Purewal et al. (2014).

Issues of non-equal current that are closely related to the real driving conditions were investigated by Bruen and Marco (2016) and Pastor-Fernandez et al. (2016). The works encapsulate the cumulative effect for batteries having different properties such as the difference in capacity or impedance particularly for batteries connected in a parallel string. Such battery variability is common which could be manifested due to variations of the thermal condition in the battery pack. Bruen and Marco (2016) highlighted that the current convergence could occur at a short period which caused by a very dynamic load cycles. Furthermore, the magnitude of peak current due to current convergence is different between the hybrid electric vehicle and battery electric vehicle application. For instance, battery with the lowest resistance experiences the highest peak current in a hybrid electric vehicle application. On the other hand, the higher peak current is manifested for battery with the highest resistance for a battery electric vehicle application. These findings are consistent with those presented by Shi et al. (2016). As a result of higher peak current particularly at the end of charge and discharge, the individual SOH of batteries connected in parallel will converge at some point. This shows the effect it can give and the complexity encountered when batteries in parallel string possess variation either differences in impedance, capacity or thermal condition.

2.3 Integration thermal with electrochemical aspects from numerical point of view

The interaction of thermal with the electrochemical aspect is essential towards battery performance. However, the connection of thermal-electrochemical is often simplified, and instead, the thermal models have been assumed to be isothermal to reduce the complexity. This will eventually give different behaviour of voltage and capacity. The simplest thermal model is given in the form of zero-dimensional or lumped thermal model. It can be implemented by using bulk thermal parameter, for instance, effective volumetric heat capacity calculated from the actual battery dimension. This type of thermal model is often used to represent a temporal change of battery temperature and ignores the spatial temperature variation. This is acceptable to be used at a high operating temperature where the heat generated at this condition is low. Another aspect that needs to be taken into account before adopting this model is the value of Biot number. Essentially, the size of the battery and the direction of applied cooling/heating are the main parameters which determine the level of temperature uniformity. Fang et al. (2010) used lumped thermal model as a temperature input for the electrochemical model and showed a good agreement with the experimental data given from a three-electrode cell. The Biot number calculated from the cell parameters are low primarily due to its thin structure. Therefore, thermal variation, particularly in the through-plane direction can be ignored. On the other hand, Ji et al. (2013) adopted lumped thermal model for the thermal representation of a cylindrical battery with 2.2Ah capacity. There was some discrepancy given from the simulated voltage curve especially at low temperature. This is partly due to the inability of the thermal model to consider the effect of non-uniform current distribution given from the thermal gradient which is likely to occur particularly at the low temperature.

The impact of having a variation of battery surface temperature has transformed the thermal model into a different dimension in order to capture the effect it gives to the battery performance. To reduce this complexity, the assumption of spatially uniform surface temperature is typically applied. Nevertheless, this is only valid for a battery with a small surface area such as for coin cell. As the battery evolves, its form factor increases due to demand of high capacity battery. Many works have been reported in the literature over a different type of thermal model either two or three-dimensional thermal-electrochemical model and it can be

categorised from two different perspectives which are for single battery and module/-pack level. Kim et al. (2011) and Lee et al. (2013) presented the same comprehensive multi-scale multi-domain analysis. Both works are analogous in term of evaluating the interaction given from thermal-electrochemical at different length scale. However, the layer to layer non-uniformities was based upon the calculated value of potential distribution on a two-dimensional surface rather than due to thermal gradient as a result of low thermal conductivity in through-plane direction. The same similar approach was conducted by Xiao and Choe (2012) on a pouch battery geometry. In this work, more emphasis was placed on calculating potential at both current collector and the resulting surface temperature variations were determined from the distribution of the potentials. Yi et al. (2013) used a three-dimensional thermal model with an anisotropic value of thermal conductivity to represent a different rate of conduction in through and along the plane direction. Although the thermal model is technically closed to the physical representation of the actual battery, there was no electrochemical interaction in through-plane direction and the variations in surface temperature were caused dominantly by the surface potential distribution which is described by Poisson equation. Most studies concerning thermal-electrochemical coupling particularly in two and three dimensional have only been carried out with the focus to investigate potential and temperature non-uniformity in-plane direction. However, Ye et al. (2014) used a three-dimensional thermal model with anisotropic thermal conductivity and considered the interplay between thermal and electrochemical in the through-plane direction. Therefore this technique can be viewed as a couple of single cells connected electrically in parallel and thermally in series. Although it seems that this could be computationally intensive, the method indicates that by having discretisation across battery layers, a large temperature gradient is manifested particularly at high C-rate operation, therefore, causes local current to deviate depending on its local temperature. Furthermore, by using this approach, Ye et al. (2014) highlighted that increasing cooling intensity could suppress temperature increase, but it also promotes significant temperature gradient between the surface and internal of the battery.

On a bigger scale, modelling of a module or battery pack will be more challenging due to the interconnection between battery and effect of the cell to cell variation either in a parallel or series string. Zhang et al. (2011) conducted a three-dimensional thermal modelling of a module which consists of three cylindrical batteries connected in series. The batteries were modelled separately without the cell to cell interaction either from thermal or electrochemical aspect. Furthermore, the thermal conductivity was assumed to be isotropic with uniform heat generation

at the core of battery. This model is very generic and it does not portray the actual condition of a module. However, Guo and White (2011) used a lumped thermal model coupled with physics based electrochemical model independently for each of the 24 batteries in an architecture of 3 series and 8 parallel connection. The thermal connection on each battery was carried out by using thermal resistance network allowing the batteries to experience the effect of the cell to cell variation. The highest temperature in the middle of the three batteries is reasonably close to the measured temperature. Besides, current deviations are also shown due to the impact of thermal gradient hence, highlighting the importance to consider interdependency of thermal and electrochemical rather than to have a thermal model with higher dimensions. Most of the studies with the aim of modelling the thermal behaviour in pack level, assumed the individual battery to be spatially uniform, therefore lumped thermal model is applicable as conducted by Zhu et al. (2013); Karimi and Li (2013); Xun et al. (2013). Although these methods ignored the internal thermal behaviour or thermal gradient that could experience by the individual battery in the pack, it appears to be a viable method which allows the effect of the cell to cell variation to be included which is more physically representative.

In essence, the way that the thermal-electrochemical coupling is carried out depends on the nature of the electrochemical model. If a physics based model such as porous electrode theory model is employed, the interaction between thermal and electrochemical is given from the calculated heat generation due to electrochemical processes such as electronic ohmic heat from contact resistance, heat given from overpotential and ionic ohmic heat from motion of lithium in the solid and electrolyte phase as stated by Wu et al. (2013). Subsequently, the sum of the calculated heat generation will cause the temperature to vary therefore changes the value of physiochemical parameters. Arrhenius relationship describes the behaviour of these parameters in which the parameters behave exponentially with the increase of temperature. This thermal-electrochemical coupling will cause change, especially in voltage and capacity if temperature changes occur. On the other hand, the thermal coupling for electrical circuit model (ECM) typically uses heat generation due to the overpotential which can be described by the difference between OCV with the voltage terminal times the applied current. This approach does not give any feedback to the electrochemical performance, and the thermal connection to the model is mainly isolated from the electrochemical system. Therefore it is much more suitable for temperature monitoring purpose which is described by Forgez et al. (2010). However, Jung and Kang (2014) developed a more comprehensive thermal model by placing an ECM on each node on the two-dimensional surface. This method

can capture the non-uniform behaviour of temperature caused by potential and current density distribution in two-dimensional level. Nevertheless, several resistances needed to be fitted against experimental data at wide SOC and temperature range. Summary of thermal-electrochemical interplay is presented in Table 2.3.

Based on the literature review, a trend has been discovered with regards to the development of thermal models, particularly for a single battery. Fig. 2.29 summarises the development which starts from a higher dimension and can be viewed as a standalone model as it does not have a feedback for electrochemical. A two-dimensional model is essentially focused on describing the non-uniform behaviour of potential which then causes temperature gradient on the two-dimensional surface. As the battery gets thicker, the importance of having discretization in the through-plane direction seems to be vital. This helps to discover the current deviation due to the thermal gradient which will ultimately cause layers in a battery to be charged/discharged at a different rate.

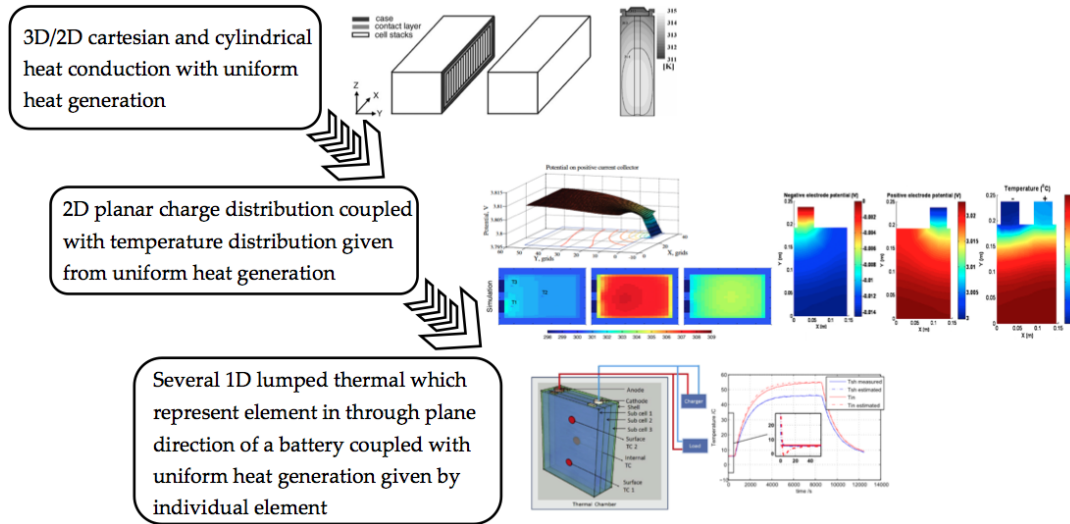


Figure 2.29: Progression of battery thermal model with electrochemical interaction. Image extracted from Wu et al. (2002); Inui et al. (2007); Xiao and Choe (2012); Guo and White (2013); Zhang et al. (2016)

Table 2.3: Summary of published work on battery thermal model in relation with electrochemical model

Author	Battery model/Electrochemical technique	Thermal model	Coupling	Advantages/Highlights
Wu et al. (2002)	Use electrochemical ohmic heat as input heat to battery model	2D cylindrical	Used ohmic heat from electrochemical to add to thermal model	Convective cooling adds to more temperature non-uniformity
Chen et al. (2005)	Use heat generation for look up table (ohmic heat)	3D rectangular	Heat generation from look up table to feed into thermal model	Stacks of cell with anisotropic thermal conductivity will have high temperature non-uniformity
Smith and Wang (2006)	Pseudo 2D	1D lumped capacitance	Arrhenius equation	Exploring pulse power capability from both electrochemical and thermal
Inui et al. (2007)	Measured internal resistance	2D/3D cylindrical	Measured internal resistance to add to thermal model	Effect of different cross section to suppress temperature increase
Kumaresan et al. (2008)	Pseudo 2D	Averaging of 1D unsteady heat conduction	Arrhenius equation	Effect of temperature dependant parameter towards cell performance
Forgez et al. (2010)	ECM	Lumped thermal resistance network	Fitting resistor to match external/internal temperature	Simple thermal model to be used in BMS to predict internal temperature

Zhang et al. (2011)	Heat generation from look up table	Averaging of 3D unsteady heat conduction	Heat generation from look up table to feed into thermal model	Temperature difference of the cells during cooling
Kim et al. (2011)	Averaging of pseudo 2D	Averaging of 3D unsteady heat conduction	Arrhenius equation	Evaluate distribution of charge, temperature for different cell tabs configuration
Fleckenstein et al. (2011)	ECM	3D heat conduction in cylindrical	Heat given from ECM model	Prediction on cell internal behaviour by connecting 3 cell with different imposed thermal boundary
Guo and White (2011)	Single particle model (from pseudo 2D)	Integration of lumped and thermal resistance network	Arrhenius equation	Thermal gradient effect in a module design
Xiao and Choe (2012)	2D for charge conservation using pseudo 2D model	2D unsteady heat conduction	Arrhenius equation	Show charge and temperature distribution in planar for pouch cell
Jiang et al. (2013)	3D charge and species conservation using porous electrode theory model	3D unsteady heat conduction	Arrhenius equation	Show contribution of heat from each battery region
Wu et al. (2013)	Pseudo 2D	1D lumped capacitance	Show effect of cell performance at different temperature and effect of contact resistance	

Lee et al. (2013)	Pseudo 2D	2D cylindrical coordinate	Arrhenius equation	Evaluate layer-to-layer differences in electrical potential along current collectors, and electric current in the winding direction due to having different tabs config.
Mahamud and Park (2013)	Ohmic heat obtained from lookup table average over SOC, only function of temp.	Modification of lumped thermal capacitance using Hermite function	Heat given from ECM model	Manifestation of both surface and internal temperature by modification of lumped capacitance thermal model
Guo and White (2013)	2D for charge conservation using pseudo 2D model with averaging	2D unsteady heat conduction with averaging	Arrhenius equation	Averaging of temperature and solid phase potential can reduce time of simulation while retaining the same accuracy as full discretise model
Yi et al. (2013)	Potential and current density are based on look-up table. Potential in 2D given by Laplace equation	3D unsteady heat conduction with anisotropic thermal conductivity	Heat given from the look-up table parameter	3D thermal model can predict the surface temperature better than 2D model
Ji et al. (2013)	Pseudo 2D	1D lumped capacitance	Arrhenius equation	Investigates battery performance at sub-zero temperature
Jung and Kang (2014)	Applying ECM model in Laplace equation	1D unsteady heat conduction	Current density for solid charge distribution has Arrhenius relationship	Planar non-uniformity of large form factor cell

Ye et al. (2014)	Pseudo 2D	3D rectangular and 3D cylindrical unsteady heat conduction	Arrhenius equation	Impact on thermal contact resistance on internal temperature and cell geometry optimization
Yang et al. (2016)	Pseudo 2D	2D unsteady cylindrical heat conduction	Arrhenius equation	Effect of having thermal gradient on cell performance and degradation in parallel connected cell
Zhang et al. (2016)	ECM model	2 lumped thermal capacitance model to describe surface and internal temperature	Heat given from fitted internal resistance	Simple thermoelectric model to predict thermal gradient

2.4 Parallel battery model

Development of a battery modelling which able to portray the behaviour of two batteries connected in a parallel string can be made either based on a physical model or ECM. Although the latter is relatively straightforward to be made, the synergy between local temperature, local current and SOC are often overlooked. Current experienced by the individual battery for a series string connection is common. Therefore, each of the battery will have the same amount of charge throughput. On the other hand, non-uniform current is likely to occur in a parallel string. According to Al-Hallaj and Selman (2002), this can happen due to non-uniform impedance and difference in thermal condition. One of the earliest attempt yet comprehensive for a battery modelling in the parallel string was conducted by Spurrett et al. (2002). The work includes behaviour when two batteries in parallel are in a balanced state, under non-uniform temperature and different capacity. However, the main weakness of the work is oversimplification particularly for analysis of batteries with different temperature. Behaviour in this condition was modelled by adjusting the resistance on one of the battery by 30% difference relative to another battery. This is primarily to represent the difference in temperature. Therefore, no actual temperature are implemented, and the offset of resistance is kept constant implying that both batteries operate under different isothermal condition.

Dubarry et al. (2016) used an ECM to describe spontaneous transient balancing current for batteries having significantly wide SOC difference connected in parallel. It is acceptable that in this work, thermal aspect is not taken into consideration because no external charging/discharge is applied and the battery resistance can be assumed to be relatively constant during the transient period. However, if charging/discharging is taken into account, local temperature variation needs to be included considering that the temperature has a direct influence towards the internal battery resistance. This will eventually alter the magnitude of the current distribution. It has been commonly found that many works either by using a physics based model or ECM ignore the local temperature variation and yet the temperature have been assumed to be isothermal throughout the charge/discharge period as conducted by An et al. (2016) and Brand et al. (2016) by using ECM. Nevertheless, the predicted current distributions have a good agreement with the experimental data. This is expected because the model used in this work is considered to be data driven type of model. Guo and White (2011) included temperature variation by using lumped thermal model for three batteries connected in parallel. However, the resulting cur-

rent distribution due to non-uniform temperature cannot be validated because the local current was not measured. On the other hand, Yang et al. (2016) measured the distribution of local current for two batteries operated at the different ambient condition and used a physic based model for predicting the degradation rate under thermal gradient condition. Local temperature variation is not presented indicating that the batteries are operated at the same temperature as the ambient temperature or under isothermal condition. As a result, the model over-predict the point of current crossover. During discharging, battery at higher temperature reaches fully discharge state sooner than the battery at relatively lower temperature. However, at some point, the current experienced by the battery at higher temperature drops while the current for battery at lower temperature increases. This behaviour occurs due to the balancing of SOC. If temperature variation is included in the model, the current crossover could be predicted better because of the battery temperature will be higher than the ambient temperature due to heat generation. Therefore causes the battery internal resistance to be lower and consequently promotes higher local current. This could be the reason of the offset point of current crossover given from the model as illustrated in Fig. 2.30.

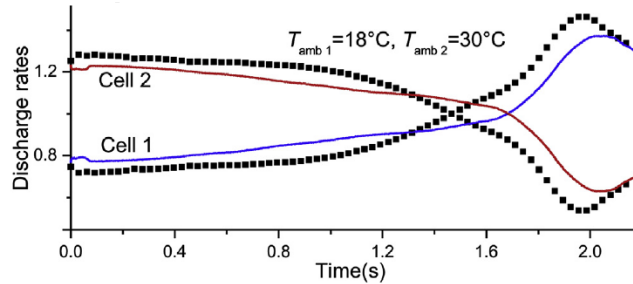


Figure 2.30: Current deviation and point of current crossover due to difference in temperature extracted from Yang et al. (2016)

The key aspect of modelling batteries in a parallel string is defined through the interaction between its local current and the common voltage. The difficulty of doing this is much greater if the initial battery resistance between two batteries is not identical. Therefore, the local current cannot be directly calculated. This requires an iterative solution by setting the difference between the individual voltage to be as low as 1 μ V as stated by Wu et al. (2006). Several studies have described the methodology of modelling two batteries in a parallel string based on physics approach as described by Wu et al. (2006) and Yang et al. (2016) however, the studies are rather limited for only two batteries without thermal consideration.

2.5 Conclusion

From the presented literature review, it is obvious that lots of experimental work have been focused on determining the inherent isotropic thermal conductivity given from either a cylindrical or pouch type battery. Determination of the thermal conductivities either from axial or radial (for the case of cylindrical battery) and in-plane or through-plane (for pouch cell) can be divided into two different strategies namely steady and unsteady. The steady technique does not require a thermal model to map the temperature profile, on the other hand, the unsteady method needs a transient thermal model with a fitting algorithm. From the experimental point of view, the unsteady thermal control is relatively easy to be implemented. Conversely, the steady thermal control is difficult to be built due to the heat transfer from one point to the other point needs to be contained properly to ensure minimum heat loss to surroundings.

Cooling of batteries is not essentially about suppressing the temperature increase. Keeping the surface and internal temperature to be relatively identical is also one of the criteria to ensure the battery longevity. However, this requires information about the internal thermal condition which can be obtained through direct temperature measurement or prediction using model. Without such information, it can be a stumbling block to design a better cooling system which can ensure batteries are operated at safe temperature region and able to minimised degradation rate particularly due to the cell to cell variation.

Chapter 3

Creating isothermal boundary conditions

3.1 Introduction : Constant temperature operation

As an electrochemical device, the battery is significantly affected by its operating temperature. In general, they will perform better at higher temperatures. This is due to the increased in the solid and electrolyte diffusion, and reduced charge transfer resistance. These physiochemical properties, which govern the performance of the battery, follow Arrhenius relationships and so change exponentially with temperature. In order to correctly evaluate the impact of temperature on the performance of the battery, it is necessary to implement truly isothermal conditions.

By holding the battery temperature nearly constant, all of the parameters mentioned above can be fitted based on a particular test temperature, thus making it both physically and mathematically more relevant with regards to the test temperatures. On the other hand, the isothermal condition reduces the complexity of the thermal boundary condition for a battery thermal-electrochemical model. The external thermal boundary condition for a thermal model which adopts the isothermal assumption is only based on its isothermal temperature. Conversely, heat transfer coefficient and cooling surface effective area need to be considered if the battery testing is conducted under convection environment.

3.2 Utilizing high thermal conductivity region

Typically, a lithium ion battery is made from alternating layers of a positive, negative electrode, separator and current collectors, as shown in Fig. 3.1 with each of them having an appreciable difference of thermal conductivities. As discussed in the literature, the thermal conductivity along the current collector in the longitudinal direction (k_x) is approximately one order of magnitude greater than the thermal conductivity across the current collector in the transverse direction (k_y). This is due to the arrangement of the battery layers as depicted in Fig. 3.1. Since the difference in thermal conductivity is large, it seems that by utilising high thermal conductivity region as a primary path to control heat transfer will give an advantage. This is supported by the calculated value of Biot number for along and through the plane region. The latter provides a very low value as compared to the Biot number given for along the plane direction. This implies that heat conduction is dominant as the heat transfer mechanism and it also reflects that the temperature will be uniform as such temperature gradients can be assumed negligible.

There are two possible directions for controlling the battery temperature which are in along the battery plane direction (from the battery tabs) and through battery plane direction (from the battery surface). Initially, the heat transfer was controlled via battery tabs. This is because the areas that need to be kept at constant temperature are relatively small compared to the surface area of the battery. In this work, both battery tabs were maintained at a constant temperature, and the battery surface was properly insulated with cotton wool in order to approximate an adiabatic boundary condition.

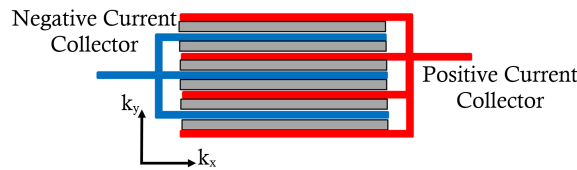


Figure 3.1: Structure of battery layer

3.2.1 Controlling cell tabs temperature

The isothermal condition tests by controlling tabs temperature were carried by using rig developed by Troxler et al. (2014). The rig is known as HAMSTER Cage (Heat And MasS Transfer Rig for Controlled And Gauged Experiments) which couples

the capability of cooling/heating with battery voltage measurement. The thermoelectric device which in this case is a Peltier element is responsible for controlling the battery temperature. The temperature control is carried out by placing the Peltier element on a copper plate. This plate acts as a heat distributor which is positioned on both sides of the battery surface. Two Peltiers are used in this rig, and it can be controlled independently, therefore, giving more flexibility regarding setting the battery thermal condition. Two PID controllers are used to control each of the Peltier elements. These controllers will keep the temperature set-point to be constant. Furthermore, it also regulates power required to the Peltier element if there is disturbance which typically comes from cell heating during charge/discharge. The advantage of this rig as compared to thermal/climate chamber is the transient thermal response is significantly improved.

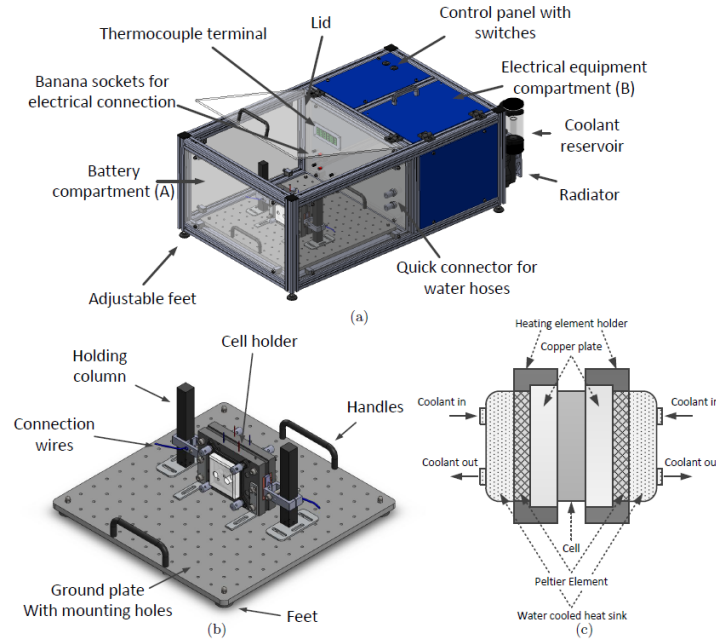


Figure 3.2: (a) Thermal test platform, (b) Base plate battery holder, (c) Cell holder assembly which obtained from Troxler et al. (2014)

The rig consists of two parts which are the thermal test platform and cell holder as depicted in Fig. 3.2 (a) to (c). However, this rig is made specifically to control the battery surface temperature. Hence, the cell holder was modified to allow the temperature of the cell tabs to be controlled independently. Fig. 3.3 (a) shows the modified cell holder in which two Peltier elements have been installed at negative and positive tab respectively. The battery was insulated by using cotton wool to ensure cooling/heating given by Peltier elements from both directions is contained. Fourteen thermocouples were used in which 12 of them were used for measuring

battery surface temperature (6 on each side), and the remaining two were taped at each battery tab as depicted in Fig. 3.4. The latter is essential because it acts as a PID input to regulate power to the Peltier element and furthermore maintains the desired temperature. The Peltier elements were placed at a brass block with internal water channel as illustrated in Fig. 3.5. A closed loop water circuit for cooling the Peltier element is connected to brass block as shown in Fig. 3.3 (b). This water circuit will help the Peltier element to operate efficiently by absorbing heat from the Peltier element. The heat will be subsequently blown away by a radiator to keep the cooling water at low temperature, therefore, promotes better heat absorption.

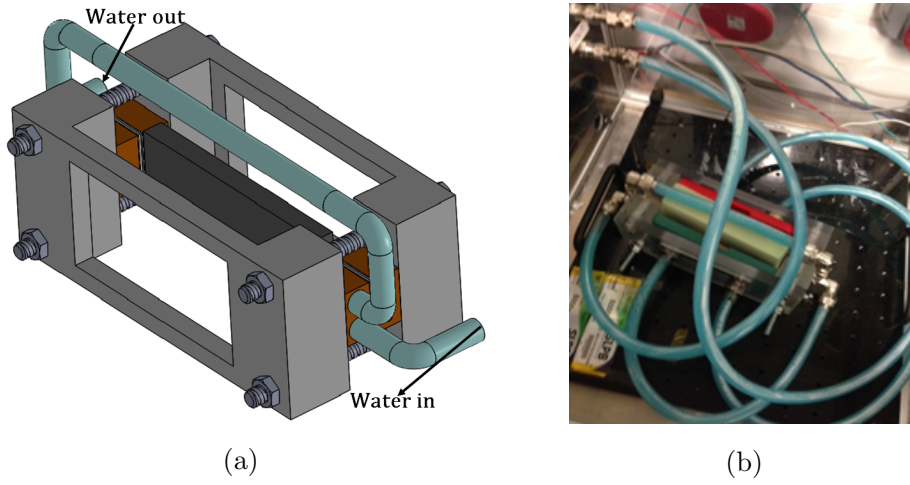


Figure 3.3: (a) Battery holder for tabs temperature control, (b) Cooling pipe circuit

Locations of thermocouples are numbered as illustrated in Fig. 3.4. Since the battery is insulated, the temperature variations on each surface are relatively similar. Therefore for this analysis, an average temperature for each battery surface has been used, and the surface for measuring temperature has been divided into three separate regions namely Region A (near to positive tab), Region B (centre of the battery) and Region C (near to negative tab). Further analysis of the tabs temperature control will be based on these five temperature measurement points.

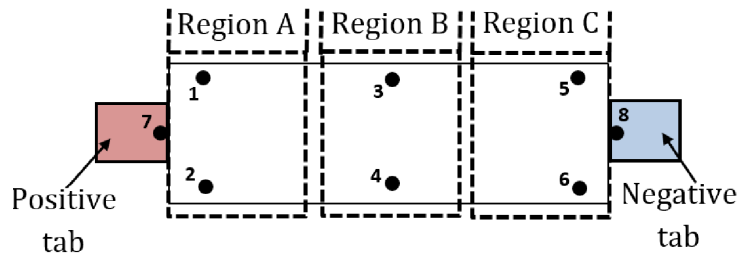


Figure 3.4: Location of measured temperature

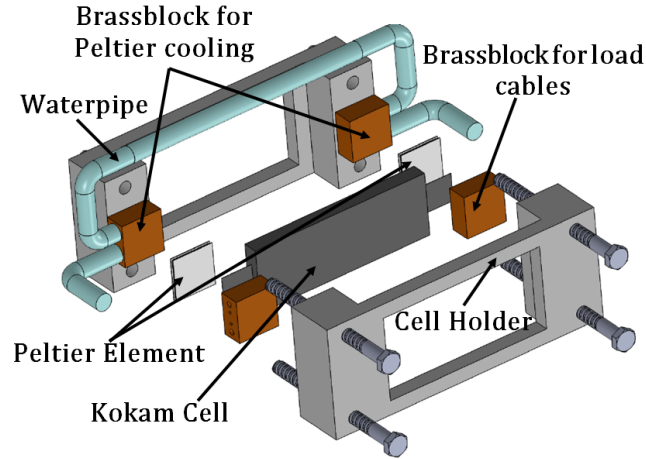


Figure 3.5: Exploded view of battery holder (Tabs temperature control)

3.2.2 Contact resistance

Two separate systems were used for controlling electrochemical and thermal. For electrochemical control, a Biologic HCP-1005 with 100A current booster was used while the HAMSTER Cage and thermal chamber were used for controlling the temperature. Two brass blocks were used at each terminal for connecting load cables from Biologic HCP-1005 as illustrated in Fig. 3.5. Load cables (positive and negative terminal) for controlling charge/discharge which comes from the Biologic were connected to each of the brass blocks. Since the goal of this experiment is to provide near to isothermal condition, any heating which is not related to electrochemical should be minimised. Significant heat will be generated due to appreciable contact resistance between the brass block and the cell tab at each terminal. The generated heat will disrupt the control of the Peltier element thus, by reducing the contact resistance, the Peltier element can be operated efficiently, therefore, reducing disturbance to the system.

Another technique which can be used for connecting battery tab to load cables is by using crocodile clips which were used by Bazinski and Wang (2014). However this method can initiate joule heating because of the area where the clip connects to the battery tab is rough, therefore causes the current lines to flow close together to travel along the micro-contact spots as shown in Fig. 3.6. High concentration of current in a micro-contact area generates heat due to the existence of electrical contact resistance as described by Taheri et al. (2011). Therefore by using brass block which provides a more uniform surface area, unwanted heat generation can be eliminated.

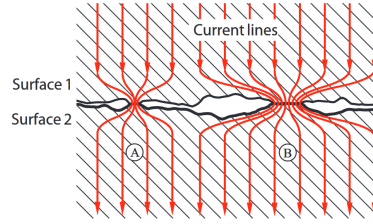


Figure 3.6: Schematic of current paths due to uneven interface Taheri et al. (2011)

In order to reduce the contact resistance between the brass blocks and cell tabs to a negligible value, the surfaces need to be smooth, clean and sufficient pressure applied. The applied pressure is in the form of a constant clamping torque applied on the bolts which hold both of the brass blocks. This work found that the contact resistance due to poor connection and surface roughness can be of the same order of magnitude of the cell impedance as shown in Fig. 3.7 (a) and (b). The battery impedance was measured at approximately 20% SOC at the ambient temperature of 15°C. The internal resistance of the battery is given by the intersection of the impedance curve at the x-axis. It can be seen that the value of the internal resistance is in the same order of magnitude of the resistance due to the contact resistance. The contact resistance was quantified by passing a known current through the contact while measuring the voltage drop across it. The importance of ensuring the smooth surface is not only down to removing additional heat, but it is also important when doing EIS measurement. This is because additional overpotential will be generated due to the presence of additional resistance as described by Wu (2014).

Treatment is carried out by polishing the brass to a mirror finish to reduce surface roughness and cleaning with citric acid to remove surface oxides followed by acetone to remove any grease and oils from handling, before clamping the brass block with the cell tabs as illustrated in Fig. 3.8. The cell tabs were not polished but were cleaned with isopropanol. After applying pressure to the untreated brass block, the contact resistance initially reduced but plateaued with a value of the same order of magnitude as the cell impedance as shown in Fig. 3.7 (b). In this experiment, the cell was charged/discharged mostly at a 2C rate (10A), therefore without proper treatment, heat generated due to contact resistance would have been comparable to the heat produced by the cell as illustrated in Fig. 3.6 (b) as described by Eddahech et al. (2013). In contrast, the contact resistance of the treated brass block and cell tab reduced to negligible values with minimal pressure applied, therefore any additional heat due to contact resistance can be minimised.

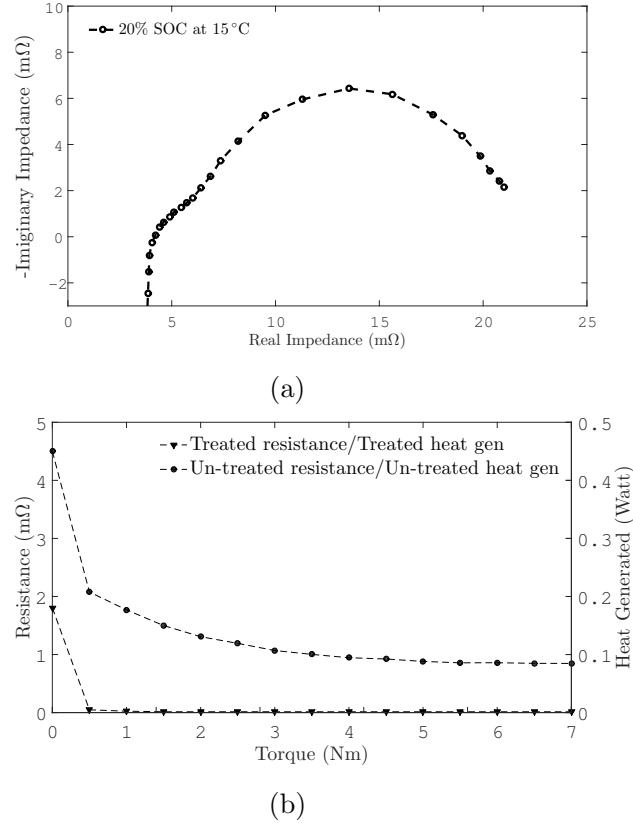


Figure 3.7: (a) Impedance at approximately 20% SOC at 15°C, (b) Resistance and heat generated difference between treated and un-treated brass block at different applied bolt torque (This work is carried out by Ali Siddiq, Imperial College London, Mech. Eng. Undergraduate)

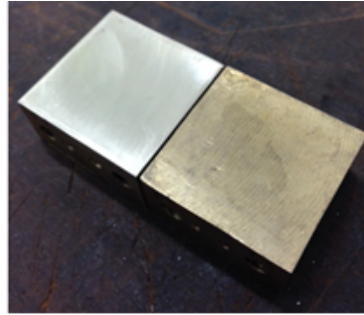


Figure 3.8: Treated (left) and Un-treated brass block (right)

3.2.3 Cell performance evaluations (Battery tabs temperature control)

The battery used in this study was a Kokam 5 Ah lithium-polymer battery. This battery is a pouch type format cell which uses carbon as an anode material and

Lithium Cobalt Manganese Oxide (NMC) as cathode material while for the electrolyte, lithium hexafluorophosphate (LiPF_6) in a mixture of EC and Ethyl-Methyl Carbonate (EMC) and organic solvents is used, as described by Wu (2014). Every parameterisation and experiments hereafter refer to this type of battery.

3.2.3.1 Temperature non-uniformity across battery surface and thermal equilibrium

Fig. 3.9 (a) and (c) indicate that the Peltier element at both battery tabs worked efficiently at all temperature range. It is also worth to noticing that the time required to reach thermal equilibrium is considerably better. Different type of battery might need longer waiting time to reach thermal equilibrium especially battery with high form factor which possesses high thermal capacity. As pointed out by Kowal et al. (2015), 26650 lithium ion battery with 2.5 Ah capacity and with a weight approximately 76 grammes, requires 1 to 1.5 hours of waiting time. That is the time needed to heat the battery by 25°C of the temperature difference in a forced convective environment. On the other hand, the Kokam battery in this study, with the weight of 1.5 times heavier than the 26650 battery gives a shorter period of waiting time. At the temperature set point of 5°C and 45°C , the time required to change the temperature by 20°C of temperature difference is approximately 15 minutes as shown in Fig. 3.9 (a) and (c).

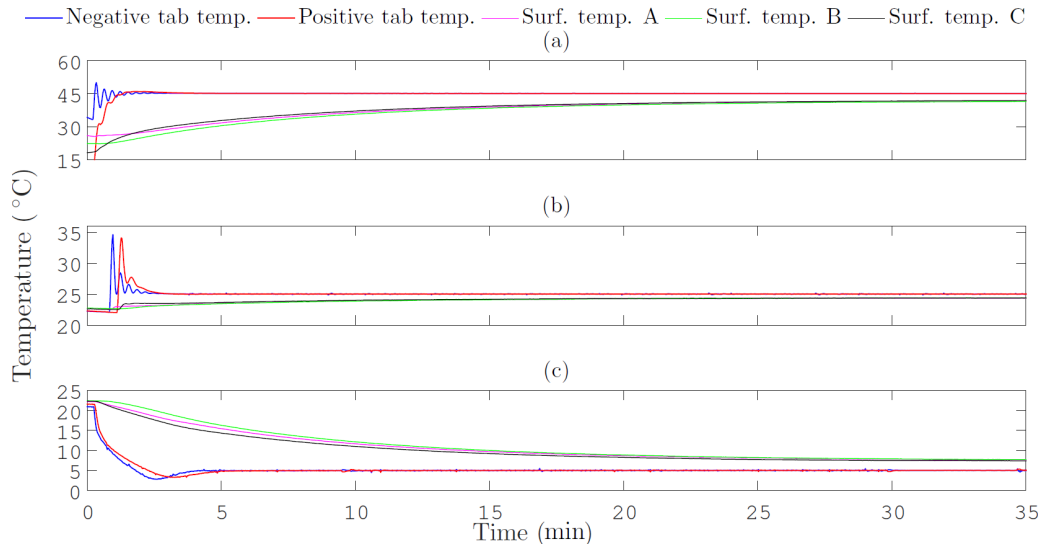


Figure 3.9: Steady state temperature by controlling both tabs temperature at, (a) 45°C , (b) 25°C and (c) 5°C

Isothermal conditions can be achieved in this experiment; however, it was

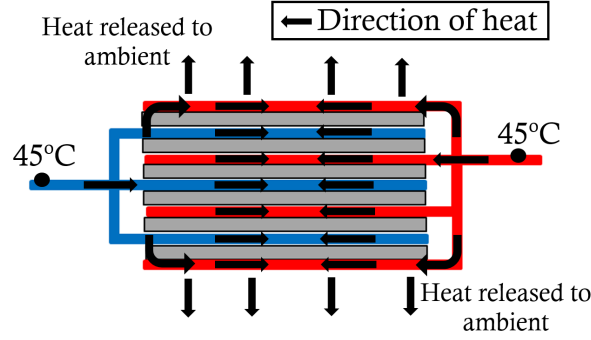


Figure 3.10: Pathway of heat for battery tab temperature control

limited only to the temperature close to ambient or lab temperature as shown in Fig. 3.9 (b). The measured lab temperature was in a range of 21-23°C. It can be seen that by holding both battery tabs at 25°C, the surface temperatures can be kept almost close to the tabs temperature. Since the difference between battery temperature with lab temperature was small, less heat is dissipated from the battery surface. On the other hand, if the set point temperature of the battery tabs is switched to 5°C and 45°C, the surface temperatures deviate from the set point temperature with a maximum deviation of 4°C. This deviation occurs because of the temperature difference between the battery surface temperature with the ambient temperature is greater at high and low set point temperature as compared to the set point temperature of 25°C therefore, increasing the thermal losses. Even though the battery was insulated by using cotton wool, this did not provide sufficient insulation of the battery to approximate an adiabatic boundary condition, as illustrated in Fig. 3.10. Ideally, adiabatic boundary condition must be in place which is considered to be vital to obtain isothermal condition by controlling battery tabs temperature.

The temperature at the battery tabs behaves in a sinusoidal manner in the early stage of the stabilisation period. This is the effect given by the PID control to regulating power for the Peltier element to heat or cool the battery tab until it meets the desired set point temperature. The gain in PID setting was manually tuned by increasing/decreasing its value to avoid a temperature spike which would take the battery beyond its allowable temperature. The Peltier element works efficiently in achieving and maintaining the set point temperature nevertheless due to heat transfer to surroundings; it is inherently difficult to obtain an isothermal condition by just controlling the tabs temperature. At high set point temperature, heat transfer occurs in the direction from battery surface to ambient whereas the at the low temperature set point, the direction of heat is reversed. This behaviour can be seen as depicted in Fig. 3.9 (a) and (c).

3.2.3.2 Un-equal thermal resistance of battery tabs

It has been shown that a better thermal response can be obtained by controlling the battery tab temperature. However, there are limitations particularly when the difference in the set point temperature with the ambient temperature is considerably large. Therefore, more detail experiment was carried out to further probe the occurrence of non-uniformity of temperature on the battery surface.



Figure 3.11: Kokam battery positive and negative tab

It has been found that if the same thermal gradient is applied to different battery tabs location (switching from positive to negative tab or vice versa), the surface temperatures are comparatively different as illustrated in Fig. 3.14 and Fig. 3.15. Physically, the Kokam 5Ah positive tab looks similar to its negative tab as illustrated in Fig. 3.11. Fig. 3.12 (a) and (b) show a one-dimensional diagram of the battery where the tabs temperature are set to be at high temperature on one end and low temperature on the other end. This is primarily to create an artificial thermal gradient. According to Fourier's Law, the thermal gradient along the battery surface or in longitudinal direction, should be of the same magnitude once steady state condition has been reached, albeit the location of set point temperature is reversed. Theoretically, the thermal gradients for both cases in Fig. 3.12 (a) and (b) should be of the same magnitude, only the sign of the gradient is different due to different heat transfer direction.

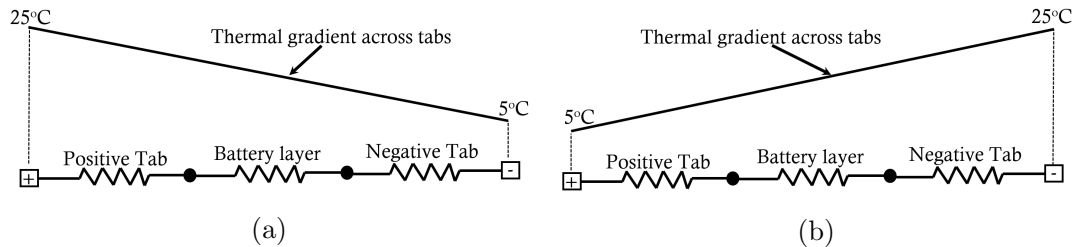


Figure 3.12: (a) Thermal gradient for 25°C at positive tab and 5°C at negative tab, (b) Thermal gradient for 5°C at positive tab and 25°C at negative tab

A thorough analysis of the battery structure was carried out by Hunt et al. (2016) for the same 5Ah Kokam battery. The investigation suggests that the structure of the positive and negative tab are different as shown in Fig. 3.13 (a) and (b) respectively. It can be seen that there are three materials involved in the positive tab region. On the other hand, the negative tab is made from only two materials. The thermal resistance of the positive tab is comparatively greater than the negative tab. For comparison, the current collector of the positive tab is made mainly from aluminium with the value of thermal conductivity relatively lower than the thermal conductivity of the current collector of the negative tab which is made from copper. The low value of thermal conductivity added with extra material as shown in Fig. 3.13 (a), causes the effective thermal resistance of the positive tabs to be higher. Therefore, causes heat transfer via conduction from positive tab to the battery surface to be comparatively harder than heat travelling from negative tab to the battery surface. Higher thermal resistance reflects that the region possesses low effective thermal conductivity in the longitudinal direction (x-direction).

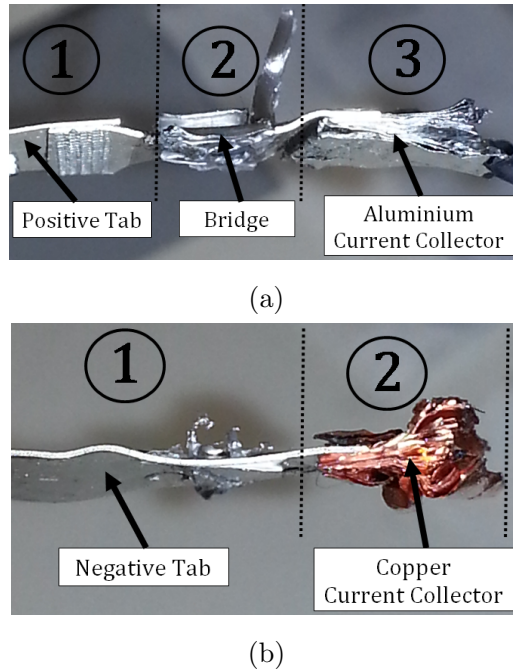


Figure 3.13: Comparison of tabs construction. (a) Positive tab , (b) Negative tab

The difference in the effective thermal conductivity causes steady state temperature to be different despite the fact that the same thermal gradient is applied to battery tabs. This behaviour can be clearly seen from Fig. 3.14 (a) and (b) for thermal gradient set point temperature of $25^{\circ}\text{C}/5^{\circ}\text{C}$. The total average temperature of Region A, B and C is slightly higher when the high temperature was imposed at the region of low thermal resistance which in this case is the negative tab. The

average steady temperature before discharging period starts is equal to 15.31°C , for set point temperature of 25°C positive tab/ 5°C negative as depicted in Fig. 3.14 (a). If the thermal gradient temperature set-point is reversed to 5°C positive tab/ 25°C negative, as illustrated in Fig. 3.14 (b), the average surface temperature is 17.33°C . Although the magnitude of the thermal gradient is similar, the average temperature surface temperature will be higher if the highest temperature from the thermal gradient is applied at the region which possesses low thermal resistance. The average temperature during 1-C discharge (5A), for 5°C positive tab/ 25°C negative tab is 19.12°C while for the reversed thermal gradient set-point temperature is 17.21°C . It is apparent that negative tab region dictates the average surface temperature, and this effect is translated into the difference in voltage curve for 1-C discharge which can be seen in Fig. 3.14 (c). The high temperature at negative tab gives better battery discharge performance as compared to the discharge performance of having the high temperature at the positive tab.

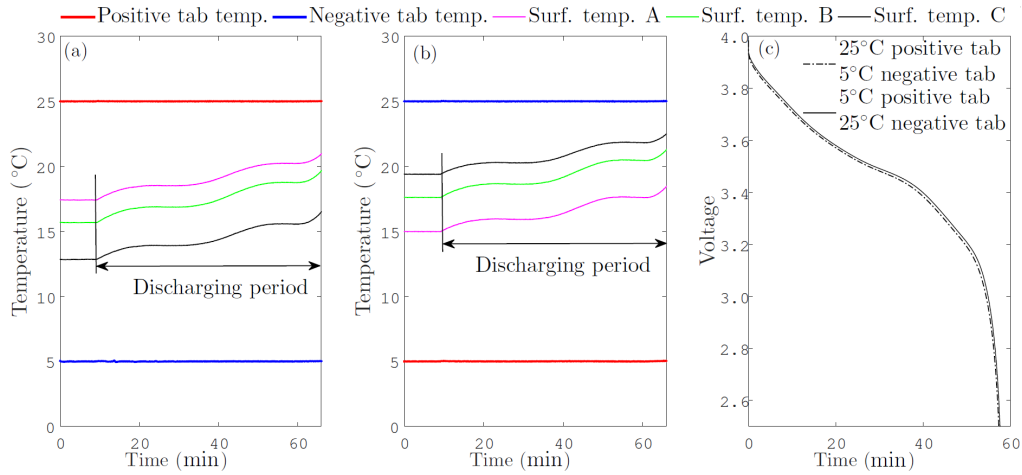


Figure 3.14: Switching tabs temperature. (a) 25°C positive tab & 5°C negative tab, (b) 5°C positive tab & 25°C negative tab, (c) Voltage curve comparison

The improved performance is not pronounced because the difference in the average surface temperature is not significant. However, by increasing the magnitude of the thermal gradient to 40°C which represented by the battery tabs temperature of $45^{\circ}\text{C}/5^{\circ}\text{C}$, a larger difference in the average temperature is observed. This causes the difference in battery performance to be noticeable as illustrated in Fig. 3.15 (c). By having the highest temperature set point at the negative tab causes the average battery surface temperature to be relatively higher approximately 4°C as compared to the mean temperature of having the highest temperature set point to be at the positive tab. The temperature difference is calculated from the surface temperature variation as shown in Fig. 3.15 (a) and (b) for temperature combination of 45°C

positive tab/5°C negative tab and 5°C positive tab/45°C negative tab respectively. From both sets of temperature gradients, it can be deduced that negative tab region possesses high thermal conductivity. Therefore, it gives a better path for heat to transfer through conduction. This is confirmed by the different power required at different battery tabs as depicted in Fig. 3.16 (a) and (b) during steady state and discharging period of 45°C and 5°C.

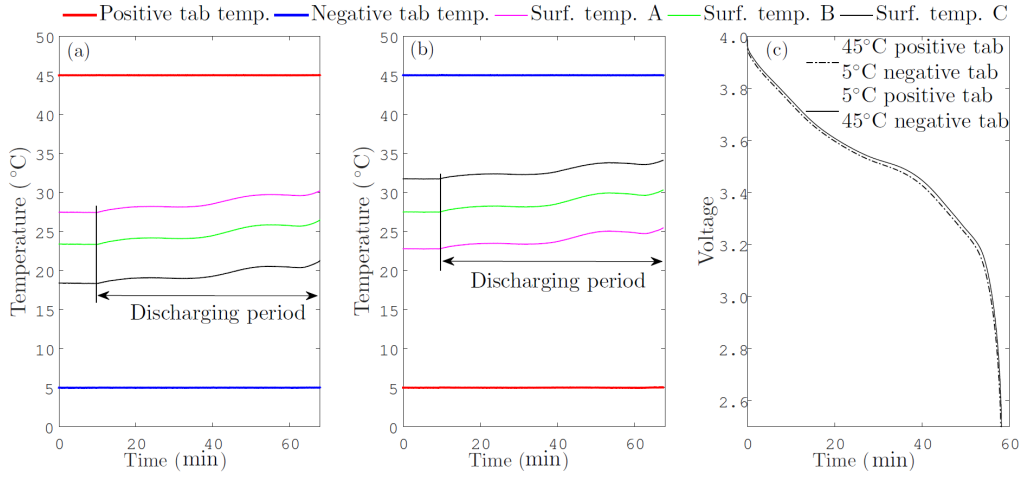


Figure 3.15: Switching tabs temperature. (a) 45°C positive tab & 5°C negative tab, (b) 5°C positive tab & 45°C negative tab, (c) Voltage curve comparison

Maintaining a constant temperature at positive tab region requires more power to be consumed by the Peltier element unlike at the negative tab region. However, the differences in power are not significant if the Peltier element is operated as a heater, which in this case is used for maintaining tabs temperature at 45°C as illustrated in Fig. 3.16 (a). Conversely, substantial power differences can be seen if the Peltier element is operated as a cooler or to maintaining the battery tabs at 5°C as shown in Fig. 3.16 (b). Operating the Peltier element as a cooler causes its COP to drop. This is because, when the Peltier element works as a thermoelectric cooler, it needs to remove two types of heat which are heat from the battery and its internal heat due to resistance. The accumulation of heat causes the temperature gradient across the Peltier element to be substantial. Hence, more power is required to reduce the temperature gradient. Occasionally, applying more power is not an effective way of reducing the temperature gradient because the heat due to its resistance will also increase following the relationship of I^2R . The dependency on the power input can be reduced if the liquid cooling which is used to cool the hotter side of the Peltier element is kept at low temperature. During discharge, power to maintain the low temperature at both negative and positive tab increase gradually over time while the power to maintain high temperature at both battery tabs decrease. This

is a reflection of heat being transferred from a high-temperature region to a low-temperature region across the battery surface.

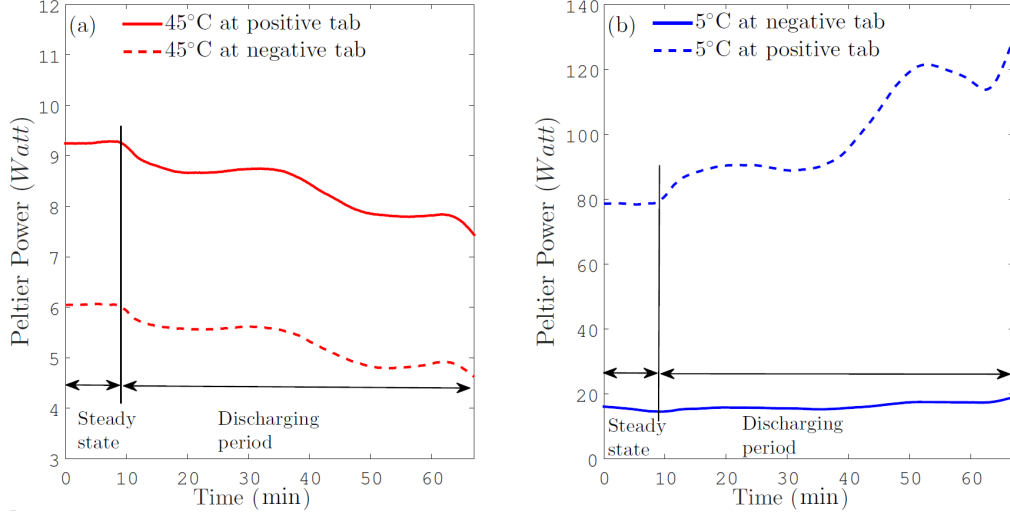


Figure 3.16: Comparison of power consumed by Peltier element at different tab location and temperature point. (a) 45°C positive tab & negative tab, (b) 5°C negative tab & positive tab

By analysing the temperature distribution on battery surface before the discharging period starts, the differences in thermal conductivity between the positive tab and negative tab region can be calculated. Fig. 3.17 summarises the value of steady state temperature from positive to negative tab which is based on data from Fig. 3.15 (a). Work by Hunt et al. (2016) highlights that the thermal resistance of the 5 Ah Kokam battery in through plane (y-direction) and along plane (x-direction) are 2.4 KW^{-1} and 3.7 KW^{-1} respectively. Using the data in the steady state region from Fig. 3.17 and thermal resistance in along place direction given by Hunt et al. (2016), the effective thermal conductivity of the battery in x-direction ($k_{x,batt}^{eff}$) can be calculated by using Eqn. 3.1 and this value can be further used to calculate steady-state heat by using Eqn. 3.2. Since this analysis is carried out in steady state region, this allows the calculated heat value to be used in calculating thermal conductivity by using equation Eqn. 3.3 and Eqn. 3.4 for positive and negative tab respectively.

$$R_{th} = \frac{L_{surface}}{(A_{yz})(k_{x,batt}^{eff})} \quad (3.1)$$

$$q_{x,steady} = (k_{x,batt}^{eff})(A_{yz})\frac{dT_{batt}}{L_{batt}} \quad (3.2)$$

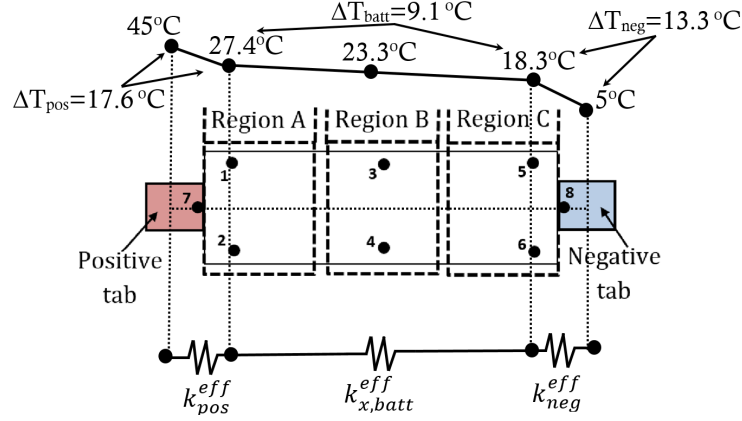


Figure 3.17: Temperature gradient diagram for case 45°C positive tab & 5°C negative tab with its respective 1-D thermal resistance network

$$k_{pos}^{eff} = \frac{(q_{x,steady})(L_{pos,tab})}{(A_{yz})(dT_{pos})} \quad (3.3)$$

$$k_{neg}^{eff} = \frac{(q_{x,steady})(L_{neg,tab})}{(A_{yz})(dT_{neg})} \quad (3.4)$$

Table 3.1: Battery dimensional parameter for tabs analysis

Parameter	Value
Surface length ($L_{surface}$)	11.7 cm
Length of positive tabs region ($L_{pos,tab}$)	1.25 cm
Length of negative tabs region ($L_{neg,tab}$)	1.25 cm
Battery cross sectional area (A_{yz})	4.88 cm ²

Table 3.2: Calculated thermal parameter

Parameter	Value
Effective thermal conductivity of battery ($k_{x,batt}^{eff}$)	64.69 Wm ⁻¹ K ⁻¹
Steady state heat ($q_{x,steady}$)	2.45 Watt
Effective thermal conductivity of positive tab region (k_{pos}^{eff})	3.56 Wm ⁻¹ K ⁻¹
Effective thermal conductivity of negative tab region (k_{neg}^{eff})	4.73 Wm ⁻¹ K ⁻¹

Table 3.1 and Table 3.2 show the value of battery dimensional parameter and thermal parameter calculated by using Eqn. 3.1 to 3.4. From the calculation, the effective thermal conductivity for the negative tab is 1.3 times higher than the positive tab. Although the difference is not considerably large, it could lead to

thermal non-uniformity if the temperature gradients between the battery tabs are significant. With the constant temperature at both tabs, thermal gradients in the vicinity of the battery tabs are unlikely to occur. However, heat is accumulated predominantly at the centre of the battery, therefore, creating a thermal gradient along its surface. The non-uniformity of temperature along battery surface was eliminated by adding surface temperature control device which will be explained below.

3.3 Creating isothermal condition : Experimental method and procedures

According to Bazinski and Wang (2014), the total heat generated during charge/discharge consists of an internal and external factor which is elucidated by Eqn. 3.5. Technically, to obtain an isothermal condition, both types of heat need to be absorbed or eliminated. However, the internal heating cannot be removed because it is a part of the electrochemical process. On the other hand, heat from the external factor is purely joule heating which occurs when there is an appreciable amount of resistance due to improper and rough surface contact between the battery tabs and load cable connector. The external heat will disrupt the quest in obtaining isothermal condition by causing a disturbance on the temperature controlling mechanism.

$$q_{total} = q_{anode\ tab} + q_{battery\ core} + q_{cathode\ tab} \quad (3.5)$$

Therefore the thermal test rig has been modified to overcome the problem by adding two additional Peltier elements on battery surface, allowing its surface temperature to be controlled along with battery tabs temperature. With this configuration, the surface temperature control will dampen heat generated from the internal factor while the tabs temperature control will take care of both internal and external factors by providing cooling at the rate of equivalent or close to the internal heating rate.

3.3.1 Four points temperature control (Conduction thermal control)

The adjustable cell holder has been modified to allow the temperature of the two pouch battery surfaces and both battery tabs to be controlled simultaneously. This modification causes the cooling system to expand with two additional cooling points as illustrated in Fig. 3.18. Two CPX200DP power supplies (rated at 180W) were used for providing power for the Peltier elements during the conduction tests. Two copper plates were used to provide thermal contact on both sides of the cell surface. The purpose of using the copper plate is to spread the heat which is given from the Peltier element. Three grooves for thermocouples were made on each of the copper plates for measuring and controlling the surface temperature. Two PicoLog TC-08 data loggers were used to record temperature by using type-K thermocouples for cell surfaces and tabs. One additional thermocouple was used to measure the temperature at the cell edge. The purpose of securing thermocouple at this location is to check whether the cell temperature reading is consistent with the surfaces temperature controlled by the Peltier element as there are no other independent surfaces available as shown in Fig. 3.19 (a).

To ensure the temperature reading at this location is consistent with the temperature measured on the battery surface, the temperature variation was compared during a 2-C discharge. This test was conducted inside a thermal chamber at the environment temperature of 45°C. Fig. 3.19 (b) shows the temperature variations of the battery surfaces (T_1 and T_2) and temperature at the edge of the battery (T_3). It can be seen that the temperature profile at different battery locations during the discharge are reasonably similar. Therefore, due to the space constraint of the conduction thermal control rig, the edge temperature was used as the point of the temperature comparison at different thermal conditions.

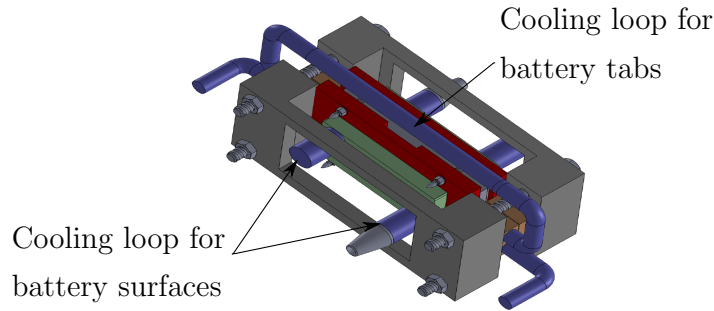
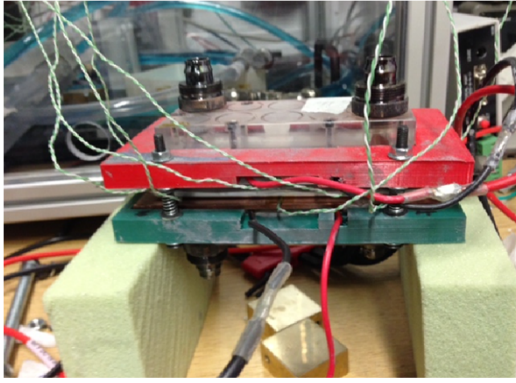
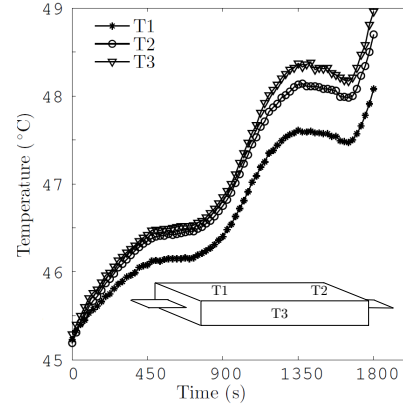


Figure 3.18: Battery holder for both tabs and surfaces temperature control



(a)



(b)

Figure 3.19: (a) Surface temperature control system with edge temperature measurement , (b) Temperature comparison under 45°C convection inside thermal chamber

Two computer ram coolers were attached to the Peltier element to absorb heat from the hotter side of the Peltier element. The additional components for controlling the battery surface temperature were held together by a 3-D printed battery holder as depicted in Fig. 3.20 (a). The holder was designed mainly because of there was no available components that can hold all the surface control temperature components firmly. Since the holder is made from plastic, therefore, it is flexible and able to isolate the cooling components from a direct electrical contact hence, making the system safer and reliable.

The surface temperature control system was assembled first before tabs temperature control can be connected. The actual four points temperature control rig is shown in Fig. 3.20 (b). As the temperature of cell increases, its impedance decreases, and the rate of heat generation for the same current decreases, therefore the higher the operating temperature, the closer to isothermal operating conditions can be achieved. In order to quantify this, the following experimental procedures were undertaken, which consists of a 2-C (10A) discharge for 12 minutes with 36 minutes relaxation in between the two discharge events. This will be discussed in the next chapter.

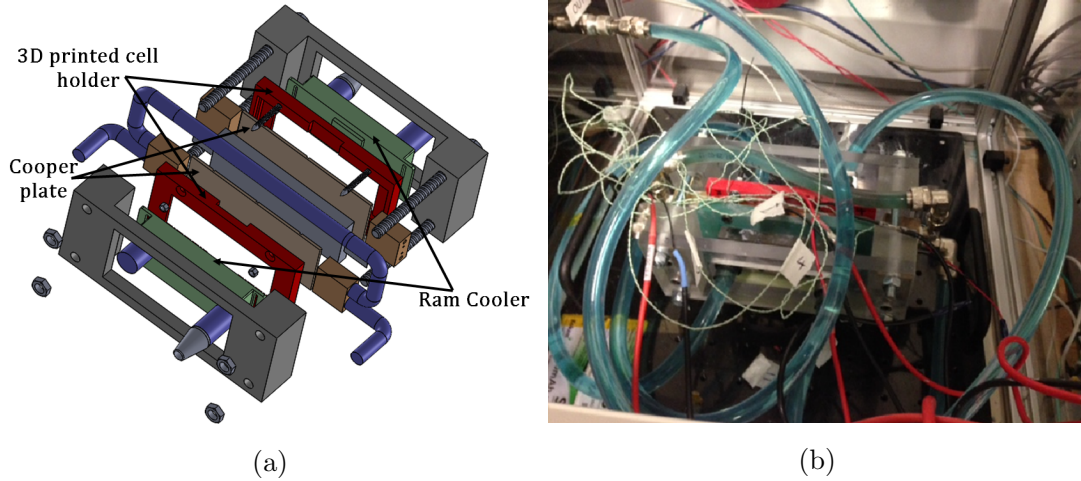


Figure 3.20: (a) Exploded view of battery holder (Tabs and surfaces temperature control), (b) Actual test-rig setup

3.3.1.1 Temperature deviation during pulse test near isothermal condition

Fig. 3.21 (a)-(e) illustrate the reaction of both tabs temperature and the edge temperature, in maintaining the set point temperature during pulse discharge procedure from 45°C to 5°C . As discussed earlier, it is inherently difficult to obtain close to an isothermal condition by just controlling the tabs temperature. The capability of maintaining the battery temperature has improved due to the modification. As a result, the four points temperature control rig has shown exceptional capability in keeping the battery temperature close to the desired temperature during the pulse discharge. The two battery surface temperatures which are directly controlled by the Peltier element are not shown in Fig. 3.21. This is because the controlled temperatures on both battery surfaces are nearly constant with very minimal disturbance as compared to the behaviour of tabs temperature.

Although a PID control regulates both temperature control point (for surfaces and tabs), it is still challenging to keep the tabs temperature to remain unchanged particularly during the period of the second discharge event as shown in Fig. 3.21. At the second discharge period, the battery resistance is high. Therefore, the amount of heat generated at this condition is relatively greater than the amount of heat generated during the first discharge period. As a consequence, the PID sends a signal to allow the Peltier elements at both battery tabs to draw more current. The immediate current increase causes temperature spike at both battery tabs which can be seen in Fig. 3.21 (e). It is worth noting that the temperature

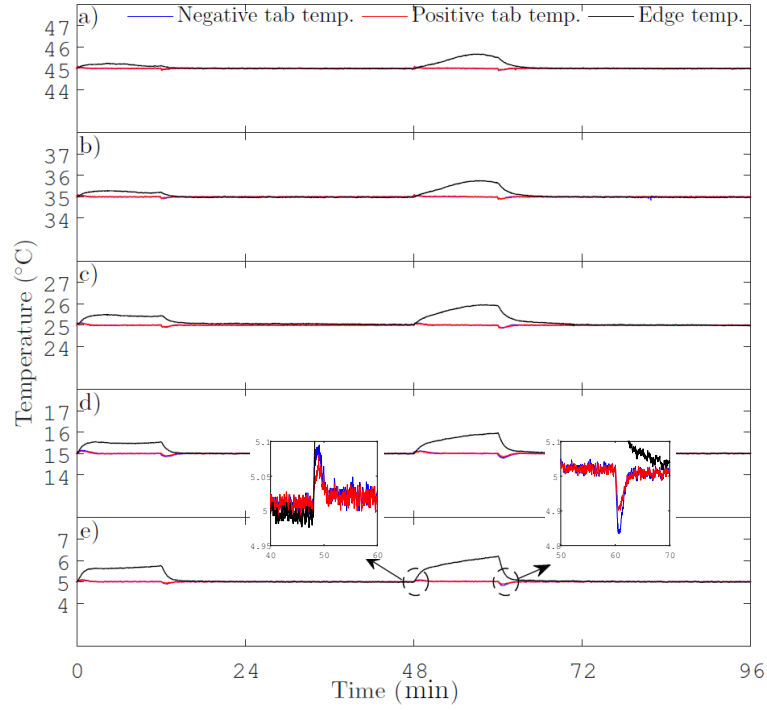


Figure 3.21: Comparison of temperature between both tabs and edge at : (a) 45°C, (b) 35°C, (c) 25°C, (d) 15°C and (e) 5°C

spike only occurs at the onset of discharging and at the end of discharging period and the magnitude of the temperature spike is higher at the second discharge event as compared to the first discharge event. Nevertheless, the effect of the temperature spike on battery performance can be assumed negligible because the temperature spike magnitude is considerably small which is around 0.1°C.

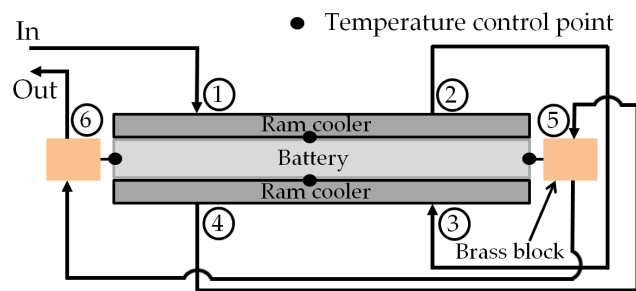


Figure 3.22: Liquid pathway for peltier element cooling in four points temperature control rig

The difficulty in controlling the tabs temperature is not only because of the variation of the battery resistance. It is also due to the arrangement of the inlet and outlet of the liquid cooling array for all of the four Peltier elements. Due to space constraint, the path taken by the liquid cooling is constructed as such the

cooling liquid needs to cool the Peltier elements which control the battery surface temperature first, before the liquid can flow to cool the Peltier elements which control the battery tabs temperature as illustrated in Fig. 3.22. The cooling water inlet which has a low temperature approximately equal to the ambient temperature enters the ram cooler from the section 1 and exit at section 4. When the liquid cooling flows out of section 4, the liquid temperature could be at high temperature after absorbing heat rejected by the Peltier elements which control the battery surface temperature. The increase in temperature reduces the ability of the liquid cooling to absorb heat rejected by the Peltier elements at the battery tabs. Therefore, causes larger thermal gradient across the Peltier element which subsequently forces the Peltier element to draw more currents. In general, the synergy between surface and tab cooling has proven its effectiveness by keeping all of the set point temperatures to be relatively close to the desired temperature. This is reflected by the variation of the edge temperature where its maximum temperature is relatively closed to the desired temperature for every case as illustrated in Fig. 3.21 (a)-(e) for 45°C to 5°C respectively.

3.3.2 Convection thermal control

Typically, the evaluation of the battery performance at several test temperatures is conducted by using a thermal/climate chamber. Hence, this test condition was replicated and compared with the test conducted in a thermal test rig which has been previously described. These comparisons can quantitatively gauge the battery performance differences as a result of having different thermal conditions. The same battery was used for both thermal conditions. The test temperatures range and the discharge rate were chosen to be within the battery specification primarily to minimise degradation. Characterisation of the battery was conducted before and after the complete set of experiments to ensure the effect of degradation is minimal. Fig. 3.23 compares the total resistance between the pristine battery with the battery which has undergone several charge-discharge cycles. It can be seen that the difference in resistance is not noticeable, hence any performance differences can be related to the different of thermal conditions. This resistance was obtained by a pulse discharge at a 2-C rate with 30 minutes of relaxation period. Each of the pulse discharge moves the SOC by 10%. The pulse discharge was conducted from 100% SOC until the lowest allowable voltage was reached which is 2.7V.

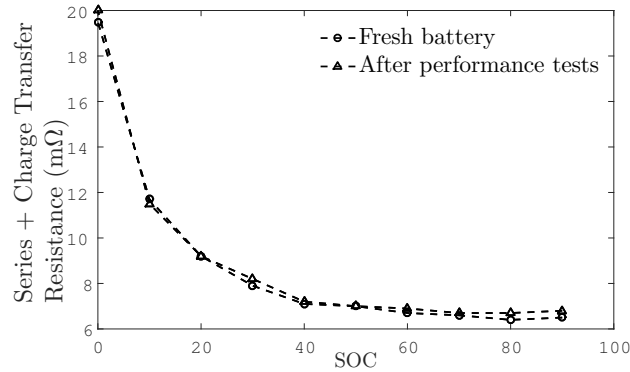


Figure 3.23: Series and charge transfer resistance comparison for fresh battery and after cycling during performance tests

For the convection tests, the battery was placed on a polycarbonate holder, and the cell tabs were clamped by using a brass block. Six thermocouples were used to measure cell surface temperature, where three thermocouples were attached to the top, and bottom surfaces. Besides, two additional thermocouples were secured at each of the cell edges by using the Kapton tape. Since convection controls the battery temperature, its surface temperature non-uniformity is expected as previously shown in Fig. 3.19 (b). However, the resulting temperature gradient is not apparent and can be neglected.

Convective thermal control was conducted in a Binder KB 23 with 20-liter capacity, a programmable controller, a temperature range of 0-100°C and temperature variation of $\pm 0.3^\circ\text{C}$. Five target temperatures of 5°C, 15°C, 25°C, 35°C and 45°C were selected in this experiment to investigate the impact on the performance of having different thermal boundary conditions. A charging protocol of constant current-constant voltage (CC-CV) at 25°C was used. This charging protocol ensures the battery to be at 100% SOC by allowing the battery voltage to reach the upper voltage limit which is 4.2V. The constant voltage charging is carried out right after the battery voltage reaches 4.2V by allowing the current to drop below 50mA. This charging protocol was repeated during the battery performance tests to ensure the battery has the same SOC before switching to different test temperatures as the voltage for a given SOC can change with temperature due to entropy effects.

3.4 Conclusion

This chapter evaluates the feasibility of obtaining close to an isothermal condition by initially considering the path which has high thermal conductivity. However, it turns out that the tabs region is merely useful in getting a better thermal transient response. Although the battery is insulated, heat transfer to ambient particularly when the difference between battery and the ambient temperature is significant will cause the battery surface temperature to be distinct from the target temperature applied at both tabs. Effect of ambient temperature and non-equal thermal resistance given from both tabs will hinder the surface temperature to be identical to its tabs temperature. Therefore, an isothermal condition cannot be assumed by using this method. Nevertheless, by integrating surface temperature with tabs temperature control, the battery temperature can be maintained closer to the desired temperature. Further analysis by comparing the edge temperature has shown that this technique is more appropriate if the isothermal condition is concerned.

This novel method shows the capability of holding the battery temperature at any external region of the battery surface to be relatively unchanged during discharge. Additionally, this technique also proves that the thermal chamber is not a good choice for battery external thermal control if the isothermal assumptions is required. Furthermore, the experiment procedure has documented a way to reduce additional thermal contact resistance which could affect the effectiveness of the temperature controlling devices. This experiment procedure could be useful in creating a baseline thermal conditions which is particularly useful for fitting battery model parameters.

Chapter 4

Battery performance at different thermal conditions

4.1 Introduction

Since most of the battery model validation are based on data gathered from the convective environment, a rigorous thermal control is therefore necessary in order to map the battery performance at its true temperature. The procedure and the underlying mechanism in keeping the battery temperature close to its target temperature have been described in the previous chapter.

This section aims to distinguish the battery performance given by imposing the external battery surface to a different type of thermal boundary conditions. The first part of this section explains the resulting differences from an experimental point of view. Subsequently, an electrochemical battery model is described. This is followed by the validation procedures by fitting physiochemical parameters based on the Arrhenius equation. The second part compares the effect of having a different thermal approach for the thermal coupling of the electrochemical model.

4.2 Comparison : Conduction and Convection thermal control

4.2.1 Cell performance comparison

Fig. 4.1 (a) and (b) show the voltage curve under different temperature for conduction and convection thermal control respectively. It can be seen that the trend of the voltage curve given from both thermal conditions is reasonably similar due to the same amount of applied current. However, the voltage polarisation is significantly higher for battery under the conduction thermal control as compared to convection thermal control, particularly at low operating temperature. The aim of this comparison is to assess the validity in assuming an isothermal boundary condition based on the commonly use convective thermal control.

In essence, the isothermal condition necessitates the battery temperature to be closed to the target temperature. Hence, any thermal conditions can be imposed which acts as a heat sink or source depending on the target temperature for the battery with the aim to keep its temperature relatively unchanged. The temperature deviation will be the figure of merit in order to gauge the effectiveness of the chosen thermal control. Therefore, without temperature data, the isothermal assumption cannot be justified.

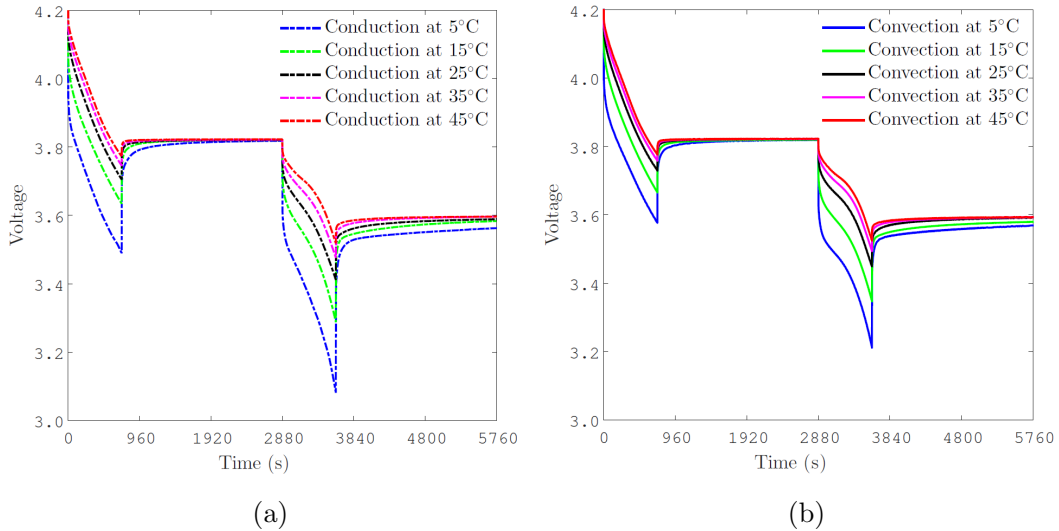


Figure 4.1: (a) 10A pulse discharge under conduction thermal control, (b) 10A pulse discharge under convection thermal control

4.2.1.1 Performance during convection tests

At high temperatures, the cell impedance decreases giving rise to lower voltage drops under load and higher usable capacities. The performance at a different temperature is measured in a typical way by setting the thermal chamber to specific test temperatures with maximum fan speed. Reproducing typical discharge curves for different temperatures is possible. However, further investigation shows that the battery temperature is not actually at the thermal chamber temperature as depicted in Fig. 4.2 (a)-(e). The deviation of the battery surface temperature is notable particularly at the low ambient temperature which is at 5°C. This is due to the increase in internal battery resistance which causes the battery to generate more heat. This behaviour highlights the inability of the thermal chamber to cope with high and dynamic heat generation during discharge. At this point, the rate of accumulation of heat is significantly larger than the rate of heat dissipated, therefore, causes the battery temperature to increase. Subsequently, when discharging stops after the first and second pulse, the temperature spike can be restored back to the desired set-point temperature.

The rate of heat dissipated during the relaxation period is larger, particularly at the low temperature. This can be seen by the steep gradient of temperature from both relaxation periods. However, the gradient decreases as the set point temperature increases, suggesting that the rate of heat transfer from battery surface to ambient condition changes according to the ambient temperature which represented by the internal condition of the thermal chamber. This can be explained by Eqn. 4.1 which reflects heat being transported due to forced convection. During convection tests, the thermal chamber fan was set to a constant speed. Therefore the convection coefficient (h) in the Eqn. 4.1 can be kept constant. The Large temperature difference between the battery surface and ambient condition especially at the low temperature causes the rate of heat transport through convection (q_{convec}) to increase. However, at high ambient temperature, the rate of heat transport reduces due to the reduction of the temperature difference between the battery surface and ambient temperature.

$$q_{convec} = (h)(A_{surface})(T_{batt} - T_{\infty}) \quad (4.1)$$

The sinusoidal behaviour of temperature at 25°C as shown in Fig. 4.2 (c), is due to the thermal chamber operating close to lab temperature and therefore the

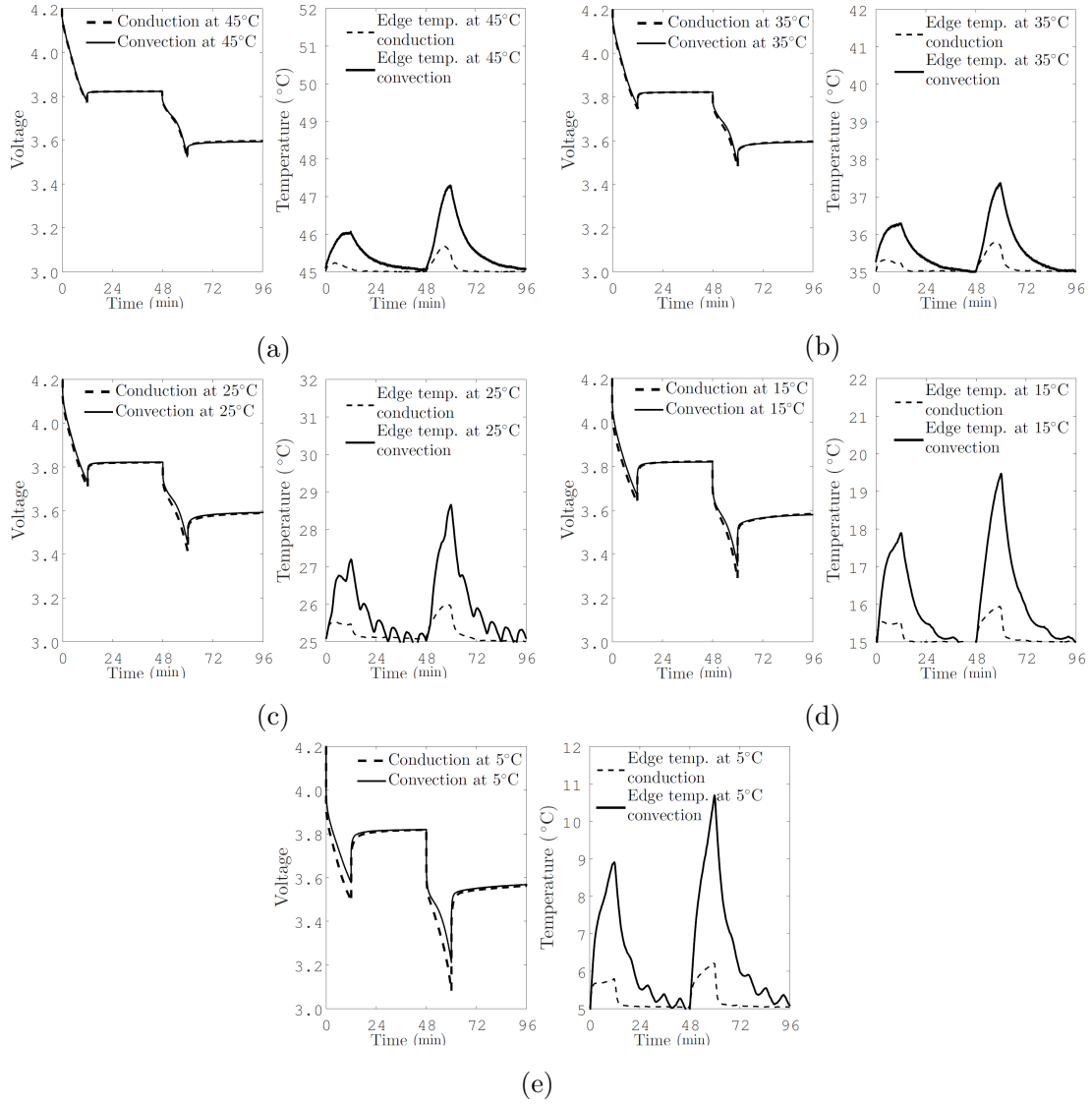


Figure 4.2: Comparison of voltage curve and edge temperature during pulse discharge

system is constantly switching between heating and cooling, trying to maintain a constant temperature. This is a common problem with thermal chambers set close to the temperature of the surroundings.

4.2.1.2 Performance during conduction tests

The edge temperature from the conduction tests are compared with edge temperature from convection tests. At all temperature set-point in this tests, the conduction method is capable of keeping the cell temperature much closer to the set-point temperature, with the largest deviation of 1.5°C when the set-point temperature is set to 5°C as illustrated in Fig. 4.2 (e). It is apparent that the isothermal condition can be achieved better at high set-point temperature. This is because less heat is generated at high temperature.

At low temperature, more heat is generated and consequently forces the conduction control system to provide an adequate cooling to keep the battery temperature relatively constant. The temperature spike at two discharge events is significantly lower, indicating the effectiveness of all the Peltier elements in maintaining the battery temperature to be closed to the desired temperature. The effectiveness is even more notable when the discharge stops whereby the temperature spike is rapidly brought down to the set-point temperature.

The deviation of temperature at the second discharge event is slightly greater for all of the temperature set-point due to the battery having higher resistance at low SOC. When the difference between the set-point temperature with the battery temperature is noticeable, deviation of performance can be seen as reflected by the voltage curve. This happens for testing at 25°C to 5°C as shown in Fig. 4.2 (c)-(e). Higher average operating temperature given from convection thermal control causes the battery voltage to be less polarised as compare to battery performance given by the conduction thermal control for the same temperature set-point.

Perhaps, more compelling observation of the battery performance is manifested at the temperature set-point of 5°C where the deviations between the temperature from both thermal control are significantly distinct. The battery temperature for convection thermal control reaches 11°C at the second discharge event, which is 2.2 times higher than its desired set-point temperature. This improves the overall performance of the battery, however, when the isothermal condition is concerned, the assumption of getting constant temperature by convection thermal control is incorrect. The deviation of voltage curve between the two thermal control is appreciable, particularly at the second discharge event. The deviation is more than 100mV as depicted in Fig. 4.2 (e). Therefore ignoring the heating effect and assum-

ing the battery is at the same temperature as the thermal chamber will lead to a significant overprediction in the battery performance. On the other hand, there is no significant performance difference between the two thermal control, especially at 45°C. At high temperature, heat generated by the battery is appreciably low therefore the difference in temperature between the two thermal control is not apparent. At this condition, the battery which operates under the convection thermal control has an average temperature of 1.5°C higher than its set-point temperature. Therefore voltage curve between the two thermal condition does not exhibit significant difference as illustrated in Fig. 4.2 (a).

The maximum temperature difference at 25°C between conduction and convection thermal control is 4°C. The same value of temperature difference is also recorded at the test temperature of 15°C. However, the voltage curve for the case of 15°C differs relatively more especially in the second pulse, as compared to 25°C case. It is thought that the internal thermal gradient could be one of the contributing factors which cause this behaviour. This will be discussed in a different section.

4.3 Battery model

The electrochemical battery model which is described below is based on the porous electrode theory which is originally developed by Newman and co-authors Newman and Tobias (1962) and Doyle (1993) . There are three electrochemical domains modelled in this work which are a negative electrode, positive electrode and a separator as illustrated in Fig. 4.3. In reality, the active species are not uniform in size and arrangement, however, to reduce the model complexity by just considering the macroscopic level, assumptions of uniformity have been made in both x and y-direction (for a unit cell) and radial direction (for active species in the negative and positive electrode). By using these assumptions, the model can be further reduced to 1-D (in the x-direction) for unit cell and 1-D (in the r-direction) for active species.

The resulted simplification can be called pseudo 2-D model. The model is divided into three regions namely negative electrode, separator and positive electrode. The electrolyte phase exists across all of the three regions while the solid phase only exists in the negative and positive electrode. A macroscopic analysis in porous electrode theory was used to describe insertion and de-insertion of lithium ion in both anode and cathode in the solid phase. The model uses macroscopic consideration. Therefore, the actual geometric structure of the pores is treated to be

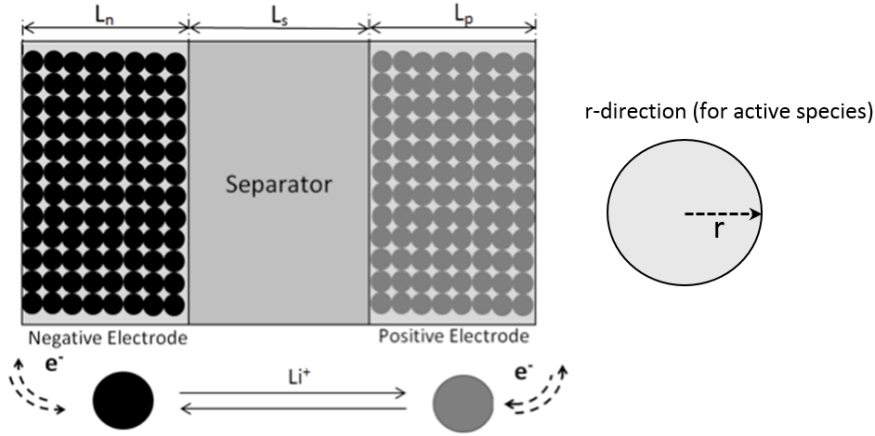


Figure 4.3: Schematic of pseudo 2-D electrochemical battery model with 1-D radial spherical and 1-D unit cell representation

continuous in space and time as described by Newman (2004). Furthermore, volume average quantities were used to eliminate the complexity of the actual structure and to capture the large scale phenomena which lie in the region of interest.

To integrate electrolyte with both electrodes, all of the media are considered as a superposition of two continua in which one part will be viewed as a solution and the other part will be represented as the matrix. Mass transfer in the electrolyte is described by material balance, current flow and electroneutrality. All of these aspects are combined which make up the concentrated solution theory. This theory is used to link the movement of lithium ions from anode to cathode or vice versa depending on the applied current. Another two physical representations which describe by mathematical expression in a steady state manner are the charge conservation in electrolyte and solid. The latter is dictated by the Ohm's law while in electrolyte phase, the charge is driven by the flux of current from solid phase as described by Rahn (2013). These two mathematical expressions serve as superficial part of the battery system equation and will be used for the determination of the battery terminal voltage. The battery model in this work has been modified which is based on the initial work of Wu (2014). The significant contribution is the replacement of the explicit numerical solution to one that employs an implicit scheme. Additionally, explicit solution necessitates setting of appropriate time step which can be avoided with an implicit solution. This difficulty is because the battery model has lots of parameters therefore, employing explicit method causes the parameters to have a direct influence on the temporal discretisation which results to the issue of numerical instability. The battery model in this work is based on the equation which can be found in Smith and Wang (2006).

4.3.1 Governing Equations and Discretization

4.3.1.1 Lithium in Solid Phase

It is assumed that the battery is made up from several active species which is systematically arranged in the x-direction as depicted in Fig. 4.3. The active species are spherical in shape which represents porous electrode material. Fick's law of diffusion governs the active spherical species diffusion process in the radial direction as shown in Eqn. 4.2. However, this equation cannot be used when the particle radius approaches zero. Based on this equation, particularly the second part on the right-hand side of the equation, it can be seen that if the radius of the spherical approaches zero, the solution will be asymptotic, therefore, the system of the equation at that particular point will be difficult to solve. By differentiating the numerator and denominator of the second term which follows the L'Hopital's rule, the asymptote solution can be eliminated as shown in Eqn. 4.3. The resulting modification of the equation when the spherical radius approaches 0 is written in Eqn. 4.4.

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial r^2} + \frac{2D_s}{r} \frac{\partial c_s}{\partial r} \quad (0 < r \leq R) \quad (4.2)$$

$$\lim_{r \rightarrow 0} \frac{2D_s \partial c_s}{r \partial r} = \lim_{r \rightarrow 0} \frac{2 \frac{\partial}{\partial r} (D_s) \partial c_s}{\frac{\partial}{\partial r} (r) \partial r} \quad (4.3)$$

$$\frac{\partial c_s}{\partial t} = 3D_s \frac{\partial^2 c_s}{\partial r^2} \quad (r=0) \quad (4.4)$$

During discharge, lithium ions deintercalated from the negative electrode at a rate which is based on reaction current density given by Butler-Volmer equation. The rate is given by surface flux boundary condition as shown in Eqn. 4.5. At the centre of the spherical, zero flux is applied while at the end of the spherical, species flux dictates the reaction of each solid phase particle. Macroscopic property of the specific interfacial surface area of each electrode is calculated by using Eqn. 4.6.

$$\left. \frac{\partial c_s}{\partial r} \right|_{r=0} = 0, -D_s \left. \frac{\partial c_s}{\partial r} \right|_{r=R} = \frac{j_{Li}(x, t)}{a_s F} \quad (4.5)$$

$$a_s = \frac{3\varepsilon_s}{R} \quad (4.6)$$

The resulting equations are discretized by using Finite Difference Method and solved by using Crank-Nicholson approach as shown in Eqn. 4.7 and Eqn. 4.8 for two different range of radius. These implicit form of equation are combined with its boundary condition to form a diagonal matrix and solved by using LU decomposition method.

$$c_s^{i,t+1} - c_s^{i,t} = \frac{D_s \Delta t}{2\Delta r^2} (c_s^{i+1,t+1} - 2c_s^{i,t+1} - c_s^{i-1,t+1} + c_s^{i+1,t} - 2c_s^{i,t} - c_s^{i-1,t}) + \frac{2D_s \Delta t}{2r\Delta r} (c_s^{i+1,t} - c_s^{i-1,t}) \quad (0 < r \leq R) \quad (4.7)$$

$$c_s^{i,t+1} - c_s^{i,t} = \frac{3D_s \Delta t}{2\Delta r^2} (c_s^{i+1,t+1} - 2c_s^{i,t+1} - c_s^{i-1,t+1} + c_s^{i+1,t} - 2c_s^{i,t} - c_s^{i-1,t}) \quad (r=0) \quad (4.8)$$

All of the parameter constants are grouped to form new three parameters as shown Eqn. 4.9 - 4.11 which will be used to form a diagonal matrix. In order to execute the Crank-Nicolson method to solve the partial differential equation which describes the solid concentration, the current known value of the concentration must be separated as described in Eqn. 4.12 and 4.13 for radius more than zero and equal to zero respectively. All of the unknown value are placed on the left-hand side whilst the known value are placed on the right-hand side of the equation. As the solution starts to marching in time, the unknown value on the left-hand side will be updated based on the known value. This can be viewed more clearly by arranging the equations in a matrix form as shown in Eqn. 4.14. Two identical matrices are created to represent solid phase concentration of anode and cathode.

$$\alpha = \frac{D_s \Delta t}{2\Delta r^2} \quad (4.9)$$

$$\beta = \frac{2D_s \Delta t}{2r\Delta r} \quad (4.10)$$

$$\gamma = \frac{3D_s \Delta t}{2\Delta r^2} \quad (4.11)$$

$$\begin{aligned}
 & (-\alpha + \beta)(c_s^{i-1,t+1}) + (1 + 2\alpha)(c_s^{i,t+1}) + (-\alpha - \beta)(c_s^{i+1,t+1}) \\
 & = (\alpha - \beta)(c_s^{i-1,t}) + (1 - 2\alpha)(c_s^{i,t}) + (\alpha + \beta)(c_s^{i+1,t}) \quad (0 < r \leq R)
 \end{aligned} \tag{4.12}$$

$$\begin{aligned}
 & (-\gamma)(c_s^{i-1,t+1}) + (1 + 2\gamma)(c_s^{i,t+1}) + (-\gamma)(c_s^{i+1,t+1}) \\
 & = (\gamma)(c_s^{i-1,t}) + (1 - 2\gamma)(c_s^{i,t}) + (\gamma)(c_s^{i+1,t}) \quad (r=0)
 \end{aligned} \tag{4.13}$$

$$\begin{bmatrix} 1+2\gamma & -2\gamma & & & \\ & \ddots & \ddots & \ddots & \\ & & -\alpha+\beta & 1+2\alpha & -\alpha-\beta \\ & & & \ddots & \ddots \\ & & & & 1+2\alpha & -2\alpha \end{bmatrix} \begin{bmatrix} c_s^{i,t+1} \\ \vdots \\ c_s^{i+1,t+1} \\ \vdots \\ c_s^{n,t+1} \end{bmatrix} = \begin{bmatrix} (2\gamma)(c_s^{i+1,t}) + (1-2\gamma)(c_s^{i,t}) \\ \vdots \\ (\alpha-\beta)(c_s^{i-1,t}) + (1-2\alpha)(c_s^{i,t}) + (\alpha+\beta)(c_s^{i+1,t}) \\ \vdots \\ (2\alpha)(c_s^{n-1,t}) + (1-2\alpha)(c_s^{n,t}) - \frac{(4\Delta r)(jLi)(\alpha+\beta)}{a_s D_s F} \end{bmatrix} \tag{4.14}$$

4.3.1.2 Lithium in Electrolyte Phase

The electrolyte serves as a medium to transport lithium-ion from negative electrode to positive electrode or vice-versa. During charge or discharge, lithium concentration gradient occurs due to changes in the concentration distribution of lithium in the electrolyte. The gradient is represented by Fick's law of diffusion with source term governed by the Butler-Volmer equation as shown in equation Eqn. 4.15. Zero flux boundary condition is applied at both ends of the anode and cathode indicating that no ions are allowed to pass beyond the region of the active material as shown in Eqn. 4.16.

$$\frac{\partial(\varepsilon c_e)}{\partial t} = \frac{\partial}{\partial x} (D_e^{eff} \frac{\partial}{\partial x} c_e) + \frac{1-t_+^0}{F} (j_{Li}(x, t)) \tag{4.15}$$

$$\left. \frac{\partial c_e}{\partial x} \right|_{x=0} = 0, \quad \left. \frac{\partial c_e}{\partial x} \right|_{x=L_p} = 0 \tag{4.16}$$

$$D^{eff} = D_e \varepsilon^p \tag{4.17}$$

To account for tortuosity effect, the Bruggeman relation is used for calculating the effective diffusion coefficient of lithium in the electrolyte as depicted

in Eqn. 4.17. Subsequently, the equation which described the motion of lithium in the electrolyte is discretized by using Finite Difference Method and solved by using Crank-Nicholson method as shown in Eqn. 4.18. Parameters involved in this equation are grouped together as a constant that only varies with temperature, and the discretized equation is re-arranged as shown in Eqn. 4.19 and 4.20 respectively. The resulting diagonal matrix from this system of equation is illustrated in Eqn. 4.21 which is solved by employing LU decomposition method.

$$c_e^{i,t+1} - c_e^{i,t} = \frac{D_e^{eff} \Delta t}{2\varepsilon \Delta x^2} (c_e^{i+1,t+1} - 2c_e^{i,t+1} + c_e^{i-1,t+1} + c_e^{i+1,t} - 2c_e^{i,t} + c_e^{i-1,t}) + \frac{1-t_+^0}{\varepsilon F} j_{Li}(x, t) \quad (4.18)$$

$$\Omega = \frac{D_e^{eff} \Delta t}{2\varepsilon \Delta x^2} \quad (4.19)$$

$$\begin{aligned} & -(\Omega)(c_e^{i-1,t+1}) + (1 + 2\Omega)(c_e^{i,t+1}) - (\Omega)(c_e^{i+1,t+1}) \\ & = (\Omega)(c_e^{i-1,t}) + (1 - 2\Omega)(c_e^{i,t}) + (\Omega)(c_e^{i+1,t}) \end{aligned} \quad (4.20)$$

$$\begin{bmatrix} 1+2\Omega & -2\Omega & & & \\ & \ddots & \ddots & \ddots & \\ & & -\Omega & 1+2\Omega & -\Omega \\ & & & \ddots & \ddots & \ddots \\ & & & & 1+2\Omega & -2\Omega \end{bmatrix} \begin{bmatrix} c_e^{i,t+1} \\ \vdots \\ c_e^{i+1,t+1} \\ \vdots \\ c_e^{n,t+1} \end{bmatrix} = \begin{bmatrix} (2\Omega)(c_e^{i+1,t}) + (1-2\Omega)(c_e^{i,t}) + \frac{1-t_+^0}{\varepsilon F} j_{Li} \\ \vdots \\ (\Omega)(c_e^{i-1,t}) + (1-2\Omega)(c_e^{i,t}) + (\Omega)(c_e^{i+1,t}) + \frac{1-t_+^0}{\varepsilon F} j_{Li} \\ \vdots \\ (2\Omega)(c_e^{n-1,t}) + (1-2\Omega)(c_e^{n,t}) + \frac{1-t_+^0}{\varepsilon F} j_{Li} \end{bmatrix} \quad (4.21)$$

4.3.1.3 Charge Conservation in Electrolyte Phase

In the electrolyte, ions are carried throughout the cell during charge/discharge, and the distribution of charge in this medium is conserved based on Eqn. 4.22. Since the charge conservation in the electrolyte is described by two phenomena namely electrostatic in conductive medium and diffusion of charged species associated with the concentration gradient, therefore two types of electrolyte conductivity are involved according to Rahn (2013). The electrolyte conductivity and diffusional conductivity in the electrolyte are given by Eqn. 4.23 and 4.24 respectively. These equations are linked by Bruggeman relation in order to account for tortuosity effect as shown in Eqn. 4.25.

$$\frac{\partial}{\partial x} \left(K^{eff} \frac{\partial}{\partial x} \phi_e \right) + \frac{\partial}{\partial x} \left(K_D^{eff} \frac{\partial}{\partial x} \ln c_e \right) + j_{Li}(x, t) = 0 \quad (4.22)$$

$$K = 15.8c_e \exp(-13472c_e^{1.4}) \quad (4.23)$$

$$K^{eff} = K \varepsilon_e^p \quad (4.24)$$

$$K_D^{eff} = \frac{2RTK^{eff}}{F} (t_+^0 - 1) \quad (4.25)$$

$$\left. \frac{\partial \phi_e}{\partial x} \right|_{x=0} = 0, \left. \frac{\partial \phi_e}{\partial x} \right|_{x=L_p} = 0 \quad (4.26)$$

Charge conservation in the electrolyte phase is a steady state problem. However, this cannot be solved directly due to having two Neumann type of boundary conditions as described in Eqn. 4.26 which imposed at the vicinity of the current collector region. This causes the matrix which is generated from the discretised equation to be zero determinant. The boundary conditions represent the physical distribution of charge where its movement is restricted not to be allowed to go beyond the current collector as given by zero-flux boundary condition. Nevertheless, the physical representation cannot be solved numerically. Consequently, a node is fixed as a reference value to allow for the system of equation to have a unique solution. This is achieved by imposing potential at positive electrode to zero which acts as a reference value according to Chaturvedi et al. (2010) while on the other end, the boundary condition remains the same which is zero flux as shown in Eqn. 4.27.

$$\left. \frac{\partial \phi_e}{\partial x} \right|_{x=0} = 0, \phi_e \Big|_{x=L_p} = 0 \quad (4.27)$$

The equation is discretized by using Finite Difference Method as shown in Eqn. 4.28 and subsequently arranged into diagonal matrix form as shown in Eqn. 4.31 by using the grouped parameters given from Eqn. 4.29 and 4.30.

$$K^{eff} \left(\frac{\phi_e^{i+1} - 2\phi_e^i + \phi_e^{i-1}}{\Delta x^2} \right) + K_D^{eff} \left(\frac{\ln c_e^{i+1} - 2\ln c_e^i + \ln c_e^{i-1}}{\Delta x^2} \right) + j_{Li}(x, t) = 0 \quad (4.28)$$

$$\Phi = \frac{K^{eff}}{\Delta x^2} \quad (4.29)$$

$$\nu = \frac{K_D^{eff}}{\Delta x^2} \quad (4.30)$$

$$\begin{bmatrix} 1 & & & & \\ & \ddots & & & \\ & & \ddots & & \\ & & & \Phi & -2\Phi & \Phi \\ & & & & \ddots & \ddots & \ddots \\ & & & & & 2\Phi & -2\Phi \end{bmatrix} \begin{bmatrix} \phi_e^i \\ \vdots \\ \phi_e^{i+1} \\ \vdots \\ \phi_e^n \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ -(\nu)(\ln c_e^{i-1,t}) + (2\nu)(\ln c_e^{i,t}) - (\nu)(\ln c_e^{i+1,t}) - j_{Li} \\ \vdots \\ -(2\nu)(\ln c_e^{i-1,t}) + (2\nu)(\ln c_e^{i,t}) - j_{Li} \end{bmatrix} \quad (4.31)$$

4.3.1.4 Charge Conservation in Solid Phase

Ohm's law governs potential in the solid phase in which it only exists and continuous at both anode and cathode domain as represented by Eqn. 4.32. To account for tortuosity effect, the solid phase conductivity is linked by the Bruggeman relationship as depicted in Eqn. 4.33. Since the active species are only tabulated in the negative and positive electrode, there is no interaction occur in the region of the separator. Therefore, zero flux boundary conditions are applied at both interphases of anode/separator and cathode/separator as shown in Eqn. 4.34. On the other hand, at the interphase of current collector/electrode, Neumann boundary conditions are applied which in the form of current flux shown in equation Eqn. 4.35.

$$\frac{\partial}{\partial x} \left(\sigma^{eff} \frac{\partial \phi_s}{\partial x} \right) = j_{Li}(x, t) \quad (4.32)$$

$$\sigma^{eff} = \sigma \varepsilon_s^p \quad (4.33)$$

$$-\sigma_-^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=L_n} = 0 \quad \sigma_+^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=L_s} = 0 \quad (4.34)$$

$$-\sigma_-^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=0} = \frac{I}{A_{electrode}} \quad \sigma_+^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=L_p} = \frac{I}{A_{electrode}} \quad (4.35)$$

This equation is in the form of steady state problem with two Neumann boundary conditions on each electrode. Therefore no unique solution can be found for this physical problem. Since Butler-Volmer reaction links the solid phase potential, re-arrangement of the reaction equation can be used to replace the zero-flux boundary condition at anode/separator and cathode/separator region as shown in Eqn. 4.36 and 4.37 respectively. However, both anode and cathode must have the same amount of charge which can be calculated given by Eqn. 4.38 and 4.39. This is primarily to ensure that conservation of charge is satisfied at both electrodes before the new boundary condition which in the form of Dirichlet boundary condition can be applied. The resulting boundary conditions in the form of reference potential are applied to the interphase of electrode/separator by using manipulation of the Butler-Volmer equation as described by Chaturvedi et al. (2010), and the current flux is applied at both current collector/electrode region as depicted in Eqn. 4.40 and 4.41.

$$\begin{aligned} \phi_s(L_n) = \phi_e(L_n) + U(L_n) + \frac{RT}{\alpha F} \sinh^{-1} \left(\frac{jLi(L_n)}{2a_s i_0(L_n)} \right) - \frac{RT}{F} \left(\ln \frac{c_s(L_n)}{c_s} \right) \\ - \frac{RT}{F} \left(\ln \frac{c_e(L_n)}{c_e} \right) \end{aligned} \quad (4.36)$$

$$\begin{aligned} \phi_s(L_s) = \phi_e(L_s) + U(L_s) + \frac{RT}{\alpha F} \sinh^{-1} \left(\frac{jLi(L_s)}{2a_s i_0(L_s)} \right) - \frac{RT}{F} \left(\ln \frac{c_s(L_s)}{c_s} \right) \\ - \frac{RT}{F} \left(\ln \frac{c_e(L_s)}{c_e} \right) \end{aligned} \quad (4.37)$$

$$A_{electrode} \int_a^{L_n} jLi(x) dx = I \quad (4.38)$$

$$A_{electrode} \int_{L_s}^{L_p} jLi(x) dx = I \quad (4.39)$$

$$-\sigma_-^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=0} = \frac{I}{A_{electrode}} \quad \phi_s \Big|_{x=L_n} = \phi_s(L_n) \quad (4.40)$$

$$\phi_s \Big|_{x=L_s} = \phi_s(L_s) \quad \sigma_+^{eff} \frac{\partial \phi_s}{\partial x} \Big|_{x=L_p} = \frac{I}{A_{electrode}} \quad (4.41)$$

The equations are discretised by using FDM as shown in Eqn. 4.42 along with its grouped parameter as depicted in Eqn. 4.43. The discretized equation is transformed into two different diagonal matrices to represent anode and cathode as shown in Eqn. 4.44 and 4.45 respectively. The potential distribution is calculated based on the value given from the reference potential as a result of the interaction between solid phase concentration and electrolyte concentration. The system of equations is then subsequently solved by using lower upper (LU) decomposition method to obtain the solid phase potential at each time step. In essence, two unsteady equations are solved first before another two steady equations can be calculated.

$$\sigma^{eff} \left(\frac{\phi_{i+1} - 2\phi_i + \phi_{i-1}}{\Delta x^2} \right) = j_{Li}(x, t) \quad (4.42)$$

$$\Upsilon = \frac{\sigma^{eff}}{\Delta x^2} \quad (4.43)$$

$$\begin{bmatrix} -2\Upsilon & 2\Upsilon & & & \\ & \ddots & \ddots & \ddots & \\ & & \Upsilon & -2\Upsilon & \Upsilon \\ & & & \ddots & \ddots & \ddots \\ & & & & 1 \end{bmatrix} \begin{bmatrix} \phi_s^i \\ \vdots \\ \phi_s^{i+1} \\ \vdots \\ \phi_s^n \end{bmatrix} = \begin{bmatrix} j_{Li} - \frac{2I(t)}{A\Delta x} \\ \vdots \\ j_{Li} \\ \vdots \\ \phi_s(L_n) \end{bmatrix} \quad (4.44)$$

$$\begin{bmatrix} 1 & & & & \\ & \ddots & \ddots & \ddots & \\ & & \Upsilon & -2\Upsilon & \Upsilon \\ & & & \ddots & \ddots & \ddots \\ & & & & 2\Upsilon & -2\Upsilon \end{bmatrix} \begin{bmatrix} \phi_s^i \\ \vdots \\ \phi_s^{i+1} \\ \vdots \\ \phi_s^n \end{bmatrix} = \begin{bmatrix} \phi_s(L_s) \\ \vdots \\ j_{Li} \\ \vdots \\ j_{Li} - \frac{2I(t)}{A\Delta x} \end{bmatrix} \quad (4.45)$$

4.3.1.5 Reaction Current

Surface overpotential describes the departure of the electrode potential from its equilibrium potential as shown in Eqn. 4.46. The surface overpotential is normally used to describe the relationship between current and overpotential which determine

the electrode reaction in the form of Butler-Volmer equation. However, this does not include the mass transport limitation particularity at high currents operation. Therefore, another two types of overpotential are added which will be described below. The reaction equation connects the two steady and un-steady equation which dictate the rate of intercalation/de-intercalation of lithium depending on the applied current as depicted in Eqn. 4.50.

$$\eta_{surface}(x, t) = \phi_s - \phi_e - U \quad (4.46)$$

During high current charge/discharge, the bulk species concentration at the electrode region diverges from its surface, where the reaction occurs. This causes localised concentration gradient and subsequently potential drop. This overpotential namely diffusion overpotential is described by Eqn. 4.47 which relates the different of concentration between bulk and surface.

$$\eta_{solid}(x, t) = \frac{RT}{F} \left(\ln \frac{c_s^{surface}(x, t)}{c_s^{bulk}(x, t)} \right) \quad (4.47)$$

Concentration gradients which occur in the electrolyte due to electrical and interaction forces between lithium ions and the host atoms also contribute to potential drop. This overpotential namely electrolyte overpotential as shown in Eqn. 4.48, gives the deviation of lithium ions moving in the electrolyte, relative to the electrolyte concentration as described by White et al. (1983) and Srbik et al. (2016). Therefore the total overpotential is used for reaction current equation which involves the contribution from kinetics (surface overpotential) and mass transport (diffusion and electrolyte overpotential) for the battery system as depicted in Eqn. 4.49 with the reaction current density as described in Eqn. 4.50.

$$\eta_{electrolyte}(x, t) = \frac{RT}{F} \left(\ln \frac{c_e(x, t)}{c_e^{ref}} \right) \quad (4.48)$$

$$\eta_{total}(x, t) = \eta_{electrolyte}(x, t) + \eta_{solid}(x, t) + \eta_{surface}(x, t) \quad (4.49)$$

$$j_{Li}(x, t) = a_s i_0 \left(\exp \left[\frac{\alpha_a F}{RT} \eta_{total}(x, t) \right] - \exp \left[\frac{\alpha_a F}{RT} \eta_{total}(x, t) \right] \right) \quad (4.50)$$

The solid phase and electrolyte concentration are present in the exchange current density equation as shown in Eqn. 4.51. This equation is derived from the forward and backward rate constant reaction as described by Bard et al. (2001) with the rate constant (k_{ct}) followed an Arrhenius dependence on temperature. The battery terminal voltage is calculated based on the difference between solid phase potential of cathode and anode with potential drop due to current collector contact resistance as described in Eqn. 4.52.

$$i_0(x, t) = Fk_{ct}c_e^\alpha(c_{s,max} - c_{s,surface})^\alpha c_{s,surface}^\alpha \quad (4.51)$$

$$V^{terminal} = \phi_s^+ - \phi_s^- - \frac{R_f I}{A_{electrode}} \quad (4.52)$$

4.3.1.6 Iterative solution

The described battery model requires two iterative solutions namely Butler-Volmer and charge conservation iteration. The reaction current density dictates the rate of intercalation/deintercalation which is based on the solid phase concentration, electrolyte concentration, potential in the electrolyte and potential in the solid phase. However, all of these parameters are initially unknown. Therefore the reaction current density needs to be guessed in order for the system of the equations to have an initial value to start the calculation. The Butler-Volmer iteration is required to ensure the guess value of reaction current density to be close or similar to the value given by Butler-Volmer equation. On the other hand, the charge conservation iteration is responsible for ensuring that both electrodes have the same amount of current. In general, the Butler-Volmer iteration is accountable for controlling the pattern of the guess value of the reaction current density while the charge conservation iteration acts a current magnitude controller.

The initial guess can be chosen from any arbitrary number. However, the sign of the current at anode and cathode must be different. The current sign can be either negative or positive depending on the convention of charging and discharging. In this model, discharging has been described by a positive current while charging has been described by a negative current. Therefore, for a discharging case, a positive guess current density must be set at the anode while negative current density is set at the cathode. This is to represent a lithium ion movement from anode to cathode

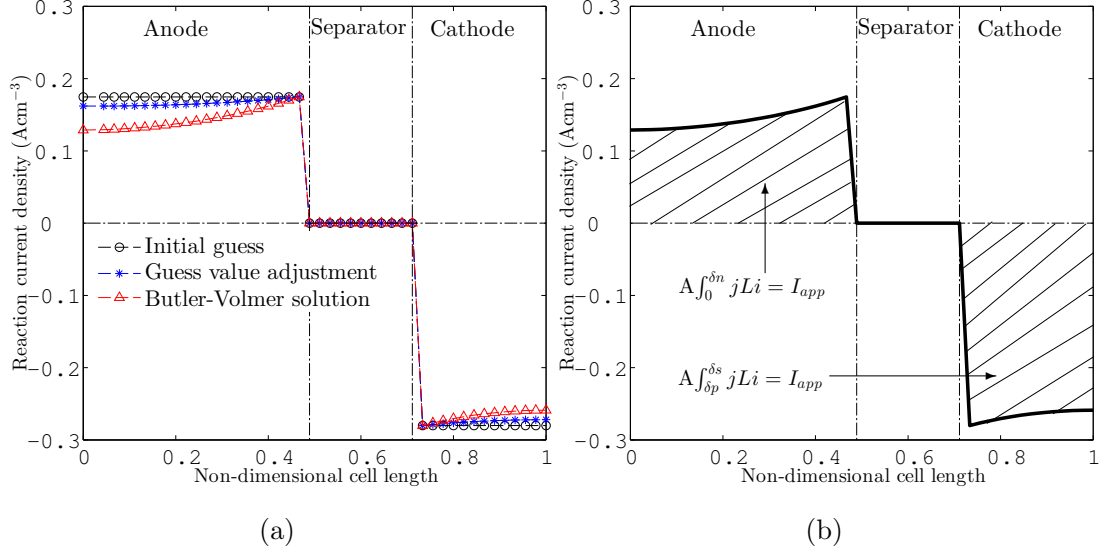


Figure 4.4: (a) Comparison of the guess reaction current density to the Butler-Volmer solution, (b) Condition of the current conservation iteration

which happens during discharging. The guess value is adjusted through an iterative algorithm to closely match the actual reaction value based on the Butler-Volmer equation. This can be seen from Fig. 4.4 (a). The guess value will keep on iterating until the residual given from the guess value with the reaction current density given by the Butler-Volmer solution is within a convergence limit.

After the condition for reaction current density based on Butler-Volmer solution is met, the iteration process is continued, to check the charge conservation on each electrode. Technically, the area under the curve of the reaction current density on each electrode should be equal to the applied current as shown in Fig. 4.4 (b). This can be calculated by integrating the reaction current density over its respective electrode length. Due to non-linearity of the reaction current density, trapezoidal rule is adopted as numerical tools to replace the definite integral. The total current given from the current integration on each electrode is subsequently compared to the applied current. This will determine whether any amount of current should be added or subtracted from each of the electrodes to closely match the integrated current density to the applied current with a preset convergence limit.

4.3.1.7 Grid independent analysis

Two discretisation or numerical grid are accounted which are along the electrode length (x-direction) and particle length (r-direction). Therefore, the grid resolutions

towards the battery voltage need to be considered. The numerical error can be reduced by ensuring the voltage to be independent of the grid resolutions either from the x-direction or r-direction. By analysing the resolution of the grid, the minimum grid number which is independent of the result can be obtained. This can help to reduce the computational effort.

The parameters used by Wu (2014) for Kokam battery with the capacity of 4.8Ah has been used for this grid independent analysis. Fig. 4.5 (a) and (b) show the variation of the voltage at a different number of nodes in x and r direction respectively. The test was conducted by applying a 10A discharge for 300 seconds at the constant temperature of 45°C. This procedure is chosen because the current used in the experiment is within the 10A limit with the maximum operating temperature of 45°C. It can be seen that the voltage converges at different number nodes in the x-direction with an error of 0.01 by using radial discretization of 17 nodes. From this analysis, 45 nodes were chosen for the discretization in the x-direction. Similarly, the voltage converges with the increase in the number of nodes in the radial direction as illustrated in Fig. 4.5 (b). However, the magnitude of the change in voltage is not significant. In this test, the number of nodes in x-direction was set to 45. From this grid independent analysis, 45 nodes are chosen for the grid in x-direction and 17 nodes for the grid in r-direction.

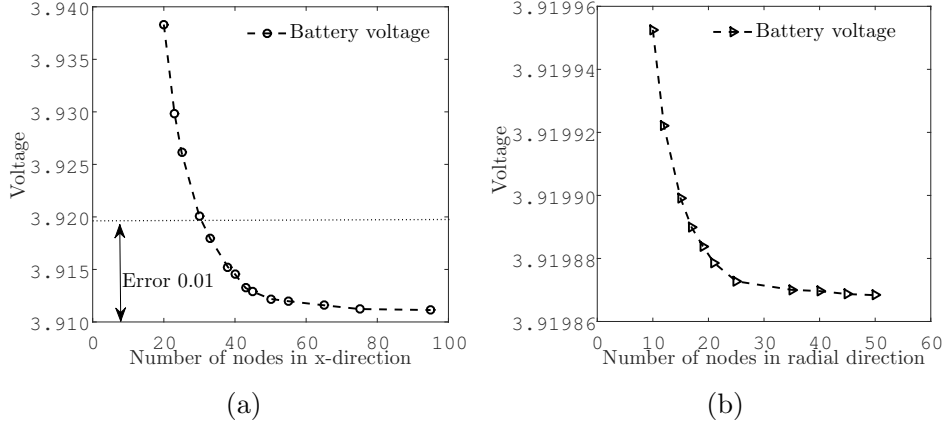


Figure 4.5: Convergence analysis for a 300 seconds discharge under 10A at 45°C :
(a) Spatial nodes in x-direction, (b) Spatial nodes in r-direction

4.3.2 Thermal aspect

4.3.2.1 Thermal parameter calculation

The battery which consists of a negative, a positive electrode and a separator as described earlier in Fig. 4.3, are used as the basis for the thermal parameter calculations which are used for the battery thermal modelling. Two types of lumped capacitance thermal models are used in this study with difference mainly on its electrochemical integration. Since the structures of the battery are layered between the individual materials, the effective thermal parameters such as bulk volumetric heat capacity, effective thermal conductivity in through and along plane direction have been calculated which is based on its actual dimension and its individual parameter value as depicted in Table 4.1 and 4.2 respectively.

Table 4.1: Battery dimensional parameter for the 5Ah Kokam battery

Parameter	Value
Battery length ($L_{x,batt}$)	14.2 cm
Battery width ($L_{y,batt}$)	4.25 cm
Battery depth ($L_{z,batt}$)	1.15 cm
Battery convection surface (A_{conv})	120.7 cm^2
Battery conduction surface in y-direction (A_{conduc})	60.35 cm^2
No. of layers for copper current collector	50 ^{Huntet al. (2016)}
No. of layers for anode	100 ^{Huntet al. (2016)}
No. of layers for separator	104 ^{Huntet al. (2016)}
No. of layers for cathode	100 ^{Huntet al. (2016)}
No. of layers for aluminium current collector	51 ^{Huntet al. (2016)}

The average and effective value of the thermal parameters are calculated according to Eqn. 4.53 to 4.55 by using parallel resistor analogy for calculating effective thermal conductivity in x-direction while for y-direction, series resistor analogy is used. It can be seen from Table 4.3 that the effective thermal conductivity in the y-direction (k_y^{eff}) is significantly low as compared to the value in the x-direction. This is expected as a result of the layered structure of the battery and the dominant materials of the battery which are the electrodes, having a low value of thermal conductivity. The thermal conductivity in this direction will be used for calculating the Biot number to gauge the level of temperature uniformity.

Table 4.2: Cell level parameter obtain from Taheri et al. (2013)

Parameter	Cu C.C	Anode	Separator	Cathode	Al. C.C
Thickness (δ, cm)	2.1×10^{-3}	4.1×10^{-3}	2.4×10^{-3}	2.55×10^{-3}	2.1×10^{-3}
Density ($\rho, \frac{\text{kg}}{\text{cm}^3}$)	8.93×10^{-3}	1.56×10^{-3}	1.02×10^{-3}	2.90×10^{-3}	2.70×10^{-3}
Heat capacity ($C_p, \frac{\text{J}}{\text{kgK}}$)	385	1437	1978	1270	903
Thermal conductivity ($k, \frac{\text{W}}{\text{cmK}}$)	3.98	0.0104	0.00034	0.0158	2.38

$$\rho C_p^{eff} = \frac{\sum_i \rho_i C_{pi} V_i}{V_{total}} \quad (4.53)$$

$$k_x^{eff} = \frac{\sum_i k_i V_i}{V_{total}} \quad (4.54)$$

$$k_y^{eff} = \frac{V_{total}}{\sum_i \frac{V_i}{k_i}} \quad (4.55)$$

Table 4.3: Calculated bulk thermal parameter for battery

Parameter	Value
Average volumetric heat capacity ($\rho C_p^{eff}, \frac{\text{J}}{\text{cm}^3 \text{K}}$)	2.65
Effective thermal conductivity along plane direction ($k_x^{eff}, \frac{\text{W}}{\text{cmK}}$)	0.62
Effective thermal conductivity through plane direction ($k_y^{eff}, \frac{\text{W}}{\text{cmK}}$)	0.00143

4.3.2.2 Indication of temperature uniformity

The Biot number is a justification on how far the assumption of the uniform temperature of a certain solid body can be made. Theoretically, the lower the Biot number, the closer to uniform temperature it can get because it manifests the ability of the solid body to conduct heat. Since the Biot number compares the relative transport of heat between external to internal or the ratio between surface convection to internal conduction, having lower Biot number indicates the solid body possesses high thermal conductivity. It is accepted that the lumped system analysis is applicable if Biot number is less or equal to 0.1 according to Cengel (1998). Three calculations of Biot number from a different perspective are made for assessing the feasibility

in assuming lumped thermal capacitance method. In the Biot number calculation, heat transfer coefficient has been assumed to be constant.

Since one of the battery performance tests were conducted in a thermal chamber in which the heat transfer is governed predominantly by forced convection, the heat transfer coefficient for calculating the Biot number has been assumed to be constant with the value of $2.5 \times 10^{-3} W cm^{-2} K^{-1}$. In this calculation, it is assumed that the forced convection in the thermal chamber provides relatively the same value of heat transfer coefficient as recorded by Cengel (1998). Although this assumption seems to be too generic, the main objective is just to investigate the effect of battery dimension on the Biot number and not to evaluate the Biot number at different rate of cooling/heating. Three different calculation of Biot number are listed in Table 4.4 which represent different battery dimension namely calculation for a whole battery that uses bulk average parameter, calculation for a single cell level which includes only an anode, a cathode and a separator and calculation for dual¹ current battery model which employs half of the dimension of the whole battery.

Table 4.4: Calculated Biot number for different thermal model

Parameter	Value
Whole battery	0.745
Single cell	0.00948
Dual	0.464

$$L_{battery}^{ch} = \frac{V_{battery}}{A_{battery}} \quad (4.56)$$

$$L_{cell}^{ch} = \frac{V_{cell}}{A_{cell}} \quad (4.57)$$

$$Bi_{battery} = \frac{(h)(L_{battery}^{ch})}{k_y^{eff}} \quad (4.58)$$

$$Bi_{cell} = \frac{(h)(L_{cell}^{ch})}{k_{y,cell}^{eff}} \quad (4.59)$$

¹A model that describes a battery having independent internal and external temperature which will be discussed in the next section

Table 4.5: Calculated bulk thermal parameter for battery

Parameter	Value
Battery volume ($V_{battery}, cm^3$)	69.40
Cell volume (V_{cell}, cm^3)	0.799
Total battery area ($A_{battery}, cm^2$)	163.13
Total cell area (A_{cell}, cm^2)	121.19
Effective thermal conductivity in through plane direction for battery ($k_y^{eff}, \frac{W}{cmK}$)	0.00143
Effective thermal conductivity in through plane direction for cell level ($k_{y,ce}^{eff}, \frac{W}{cmK}$)	0.00174

Table 4.4 shows the three calculated value of Biot number which are determined according to Eqn. 4.56 to 4.59. The calculation of individual Biot number is based on its calculated bulk value listed in Table 4.5. It can be seen that Biot number for a whole battery is larger by seven times from the suggested value by Cengel (1998). This suggests that thermal non-uniformity is very likely to occur and if the thermal capacitance method is built upon this bulk value, the occurrence of the thermal gradient will not be manifested. On the other hand, Biot number for a single cell is exceptionally low therefore passes the criteria for a lumped thermal capacitance method. However, relying on single cell dimension as a representation of a battery will be inappropriate. This is because, most of the batteries are typically made from several hundred layers of an anode, separator and cathode. Therefore a cell layer with up to two orders of magnitude difference in terms of thickness is not a good physical representation of a whole battery.

From this analysis, a model which has Biot number more than 0.1 has been selected to investigate the effect of thermal gradient on battery performance. The dual uni-directional current battery model which will be described later in the next section has an overall Biot number of 40% less than a whole battery as shown in Table 4.4. Although the value is not generally close to 0.1, the thermal capacitance method is still reasonably to be applied because the main priority is to determine the temperature difference between internal and external region. Therefore, high accuracy of surface temperature variation in space is not fundamentally important in the analysis. By dividing the battery into two regions (for dual uni-directional current battery model), the Biot number has been reduced as compared the whole battery.

This shows that high Biot number caused by the battery having low ther-

mal conductivity in through-plane direction can be reduced by adding more thermal discretisation. Adding more element can neutralise and furthermore reduce the Biot number. However, it will add complexity both thermally and electrochemically. For comparison, lumped thermal capacitance model and dual uni-directional current model are used to compare the ability of each model to predict the thermal and electrochemical performance of the 5Ah Kokam battery.

4.3.3 Lumped capacitance thermal model and Arrhenius linked parameters

The lumped capacitance thermal model is described by an energy balance equation which is shown in Eqn. 4.60. This is subsequently derived to a mathematical expression that uses the calculated bulk average volumetric heat capacity which represents the lumped thermal parameter as shown in Eqn. 4.61. The first term on the right-hand side of the equation represents the heat loss through forced convection. The heat loss is assumed to be constant over time, with its value calculated from the relaxation period which will be described below.

$$(Increase\ in\ the\ energy\ of\ the\ body) = (Heat\ transfer\ into\ the\ body) \quad (4.60)$$

$$\rho C_p^{eff} V_{total} \frac{dT}{dt} = -hA_s(T - T_\infty) + q_c + q_j + q_r \quad (4.61)$$

There are three types of heat generation involved in calculating the change in battery in battery temperature as shown by the three terms on the right-hand side of Eqn. 4.61. These heat generations are highly non-linear depending on the battery operating temperature and SOC. These are divided into three parts namely heat from internal contact resistance (q_c), ionic ohmic heat from the motion of lithium ions (i.e. diffusion and migration) (q_j) and heat from reaction current density (q_r) respectively as described by Smith and Wang (2006). All of the heat generation equations are lumped as a source term into the lumped thermal capacitance model for calculating the temperature variations.

$$q_c = I^2 \frac{R_f}{A} \quad (4.62)$$

$$q_j = A \int_0^{L_p} \sigma^{eff} \left(\frac{\partial \phi_s}{\partial x} \right)^2 + K^{eff} \left(\frac{\partial \phi_e}{\partial x} \right)^2 + K_D^{eff} \left(\frac{\partial \ln c_e}{\partial x} \right) \left(\frac{\partial \phi_e}{\partial x} \right) dx \quad (4.63)$$

$$q_r = A \int_0^{L_p} j_{Li} \left(\phi_s - \phi_e - U \right) dx \quad (4.64)$$

There are six physicochemical properties exist in the battery model, and these properties behave according to Arrhenius equation which is listed in Table 4.6 in accordance to Smith and Wang (2006) and Jiang et al. (2013). Each of the parameters has their value of activation energy which regulates temperature sensitivity. These parameters are integrated with the Arrhenius equation as shown in Eqn. 4.65. Therefore the effect of temperature change will affect the physicochemical properties. The calculated temperature from Eqn. 4.61 will be subsequently fed into the Arrhenius equation to form the thermal-electrochemical coupling. The coupling of electrochemical battery model with the lumped thermal capacitance model is described by closed loop feedback as shown in Fig. 4.6. The battery model gives an input to the thermal model in the form of heat generation, and the thermal model will subsequently calculate temperature changes and feed the calculated temperature back to the battery model, and this process continues over the charge/discharge period.

Table 4.6: Arrhenius based parameter

Parameter	Symbol
Diffusion coefficient for anode & cathode	D_s^+, D_s^-
Diffusion in electrolyte	D_e
Charge transfer coefficient for anode & cathode	k_{ct}^+, k_{ct}^-
Electrolyte phase conductivity coefficient	κ

$$\Psi = \Psi_{ref} \exp \left[\frac{E_{act}^\Psi}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (4.65)$$

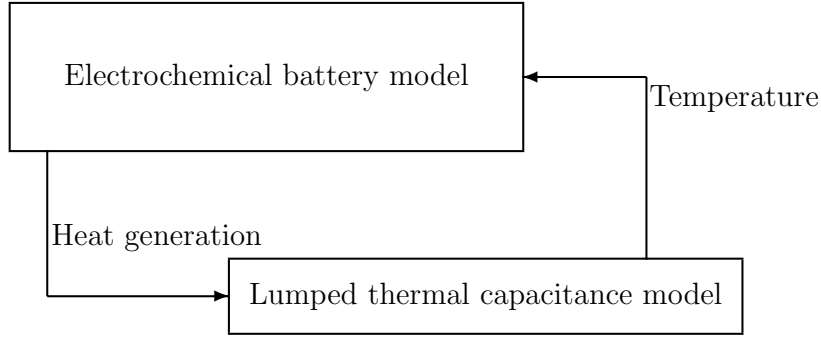


Figure 4.6: Electrochemical-thermal coupling diagram

4.3.4 Dual uni-directional current battery model

To probe the effect of thermal gradients, the battery is treated as multiple individual cells in parallel representing some layers. In the thermal chamber, the same boundary condition was achieved at the top and bottom cell surfaces, therefore, enables asymmetric thermal condition along the cell centre line to be assumed. In this work, the cell is modelled as two lumped regions which represent the layers at the surface and the layers at the middle. These two regions are electrically connected in parallel and thermally connected in series which illustrated in Fig. 4.7. It is possible to discretise the cell into more regions, which would increase the accuracy of the model, but at the expense of computational power.

This modelling technique seems to be a viable option owing to its ability being thermally dependent on each layer and electrically connected. The data from the single battery model and the dual uni-directional current battery model are comparable. This is because although the latter model has a reduced current input by the factor of 0.5 as compared to the single battery model, the reduction has been compensated by reducing the effective area by half. This modification causes the value of the reaction current density to be identical to the single battery model.

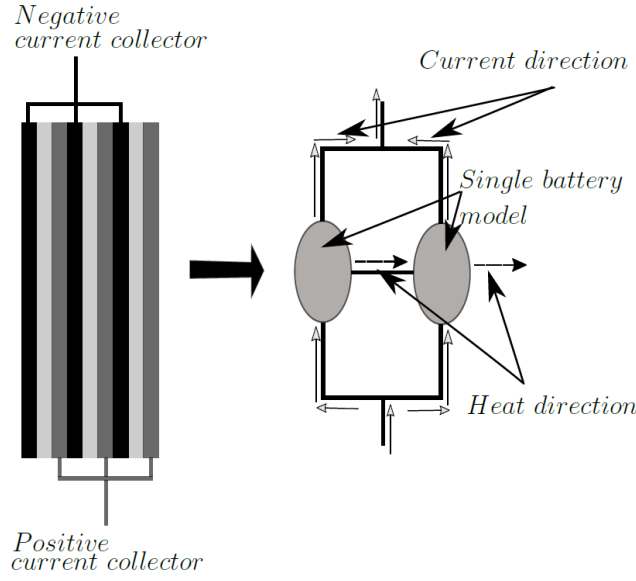


Figure 4.7: Simplification for dual uni-directional current battery model

Heat generated by the internal cell processes as described in the previous section are used at each of the lumped regions. A lumped thermal model is used for each region. Heat is connected in series by low conduction in the through-plane direction by using the calculated value of effective thermal conductivity in the through-plane direction (k_y^{eff}) between the two regions. The surface region is exposed to the convective condition therefore, the convective boundary condition is applied whereas the internal unit cell sees the line of symmetry. No heat transfer occurs except in the direction of through the surface region of the unit cell. The heat transfer through top and bottom of the battery surfaces are dominant when testing under forced convection. This is because the location of the fan inside the thermal chamber focuses on the battery surface as shown in Fig. 4.8. This assumption is applied according to the finding of Richardson et al. (2016). Richardson et al. (2016) showed that if the heating/cooling of a battery is controlled in the direction of high thermal conduction region, which in this case is from the battery tab, the difference between surface and internal temperature is not apparent. On the other hand, if the cooling/heating is controlled in the direction of low thermal conductivity, the difference between the surface and internal temperature will be apparent as illustrated in Fig. 4.9.

In order to reduce the complexity in the model, it assumed that the heat transfer only occurs in the through-plane direction due to heat transfer being dominant in this region. Therefore, initially, the internal layer will be at the same temperature with the surface. However, as discharge proceeds, the internal layer

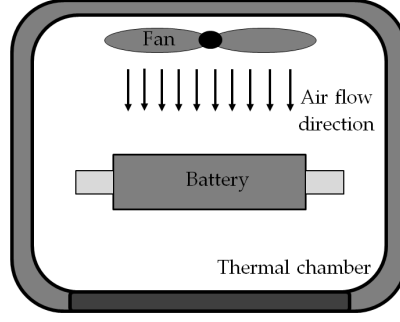


Figure 4.8: Top view of the battery arrangement under forced air convection

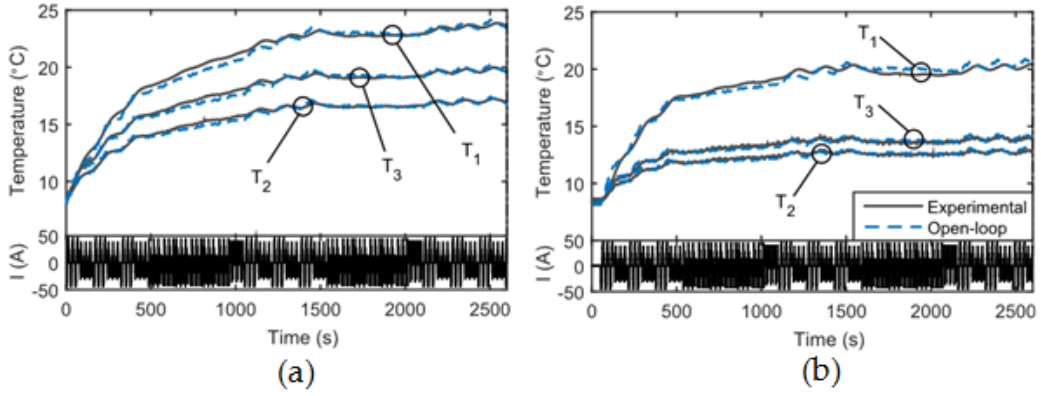


Figure 4.9: Evolution of surface and internal battery temperature at different cooling direction, T_1 (internal), T_2 and T_3 (surface temperature) under drive cycle load : (a) Cooling in along plane direction (along the battery tab), (b) Cooling in through plane direction (through the battery surface) extracted from Richardson et al. (2016)

will be hotter than the surface layer. Therefore the accumulation of heat generation is treated from internal to external according to Eqn. 4.66 and 4.67 for top surface (T_1) and the internal surface (T_2) respectively.

$$\rho C_p^{eff} V_{half} \frac{dT_1}{dt} = -h A_{convec} (T_1 - T_\infty) + q_c^1 + q_j^1 + q_r^1 + k_y A_{conduc} \frac{dT_1}{dl} \quad (4.66)$$

$$\rho C_p^{eff} V_{half} \frac{dT_2}{dt} = q_c^2 + q_j^2 + q_r^2 - k_y A_{conduc} \frac{dT_2}{dl} \quad (4.67)$$

Fig. 4.10 illustrates a flowchart that describes the numerical method involved to solve partial differential equations for the battery. The initial solving process until to the determination of battery terminal voltage requires continuous iterations. There are three loops of iteration process required in the battery model,

the first two loops are based on the work of Wu (2014) which are loop to compare reaction current density and loop to check charge balance on each electrode. The third loop is purposely made to address the issue of variation of voltage between cell unit in a parallel configuration. This loop ensures both cell regions to have the same voltage due to parallel connection. The first two loops are described previously. Table 4.7 summarises the convergence criteria for residual in each loop. The residual value at each loop must be sufficiently small or less than the criteria which have been set before it can proceed to the next time step according to the flowchart. Both of the modelled regions are solved simultaneously, however, due to parallel connection, the terminal voltage given by each region must be the same. Therefore, current on each region is regulated based on its operating temperature until the difference of voltage between the two regions become less or equal than the convergence criteria which is 1mV. These numerical techniques were programmed in MATLAB programming environment.

Table 4.7: Limit for residual on each loop

Loop type	Residual limit
Loop for current density (Loop 1)	$1\text{mA}^{Wu (2014)}$
Loop for charge balance (Loop 2)	1mA
Loop for Voltage for parallel connection (Loop 3)	1mV

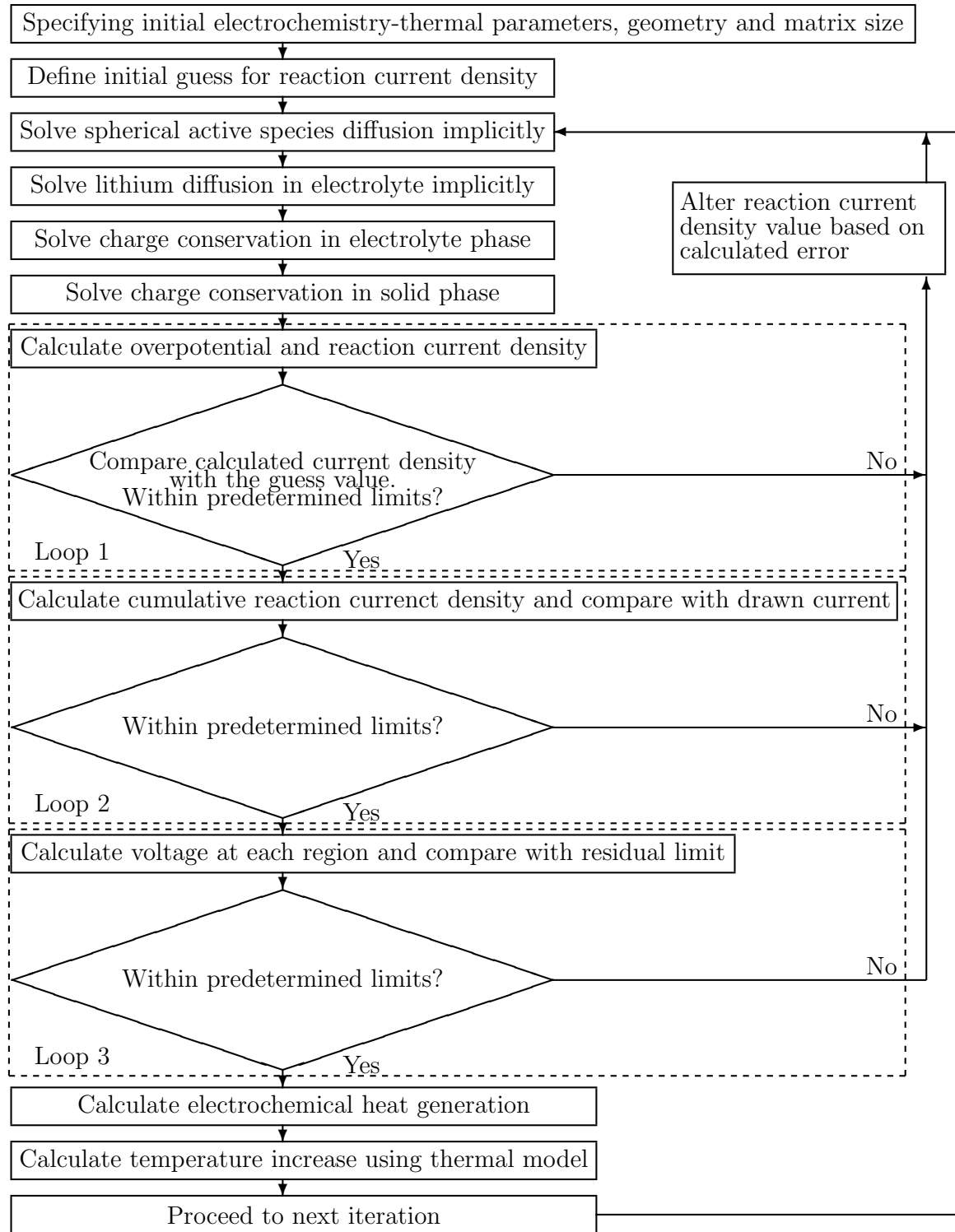


Figure 4.10: Battery modelling algorithm for dual uni-directional current

4.3.5 Open circuit voltage extraction

To obtain a good battery model with a capability of predicting voltage at different SOC, a reliable OCV is necessary. There are many available values for negative and positive electrode potential available in the literature which depends on its respective material or property. However, in this study, anode potential was obtained from the literature while the cathode potential was determined by using Galvanostatic Intermittent Titration Technique. This technique consists of continuous low current charge or discharge pulses with relatively long relaxation period from fully state or charge to fully discharge state or vice versa. It allows determination of OCV and diffusion coefficients of certain species which involve in a battery electrochemical system. In the interest of estimating diffusion coefficient of certain species, a half cell is required as evaluated by Dees et al. (2009) and Shen et al. (2013). However, in this study, no half cell was made to allow diffusion to be measured; therefore the diffusion for anode and cathode were taken from the literature. The OCV is obtained only by a pulse discharge. This will result in slightly different OCV profile than by a pulse charging. The difference in the OCV profile is due to hysteresis effect, this effect is ignored in this study since the analysis is only focused on discharge.

A low current of 0.5A or C/10 for 12 minutes discharge followed by 30 minutes of relaxation period was used for obtaining the battery OCV. Significantly low current with long relaxation time were chosen primarily to keep the battery close to its equilibrium state. During the slow discharge at the rate of C/10, the potential slightly drops, and then it slowly increases during relaxation period and reaches equilibrium as illustrated in Fig. 4.11 (a). The battery OCV was obtained at the end point of relaxation period when the $dV_{OCV}/dt \approx 0$ as shown in Fig. 4.11 (b) for a complete OCV from 100% to 0% SOC.

The thermodynamic potential of the battery was divided into its respective anode and cathode potential by using a relationship as described in Eqn. 4.68. As mentioned earlier, the anode potential was obtained from the literature. A half cell which was made by Birkel et al. (2015) by using the same battery chemistry, was chosen as an anode potential. The same stoichiometric value from Birkel et al. (2015) for anode and cathode were also used for this study.

$$V_{cathode} = V_{OCV} + V_{anode} \quad (4.68)$$

Both potentials need to be fitted and transformed into a mathematical expression before it can be combined with the battery pseudo 2-D model. During charge/discharge, the stoichiometric from both anode and cathode will change based on its respective solid phase concentration given from the battery model. Each stoichiometric will give a different value of potential, therefore error which comes from fitting the potential curve causes the battery model to deviate from its true attribute. Typically, polynomial fitting is used for transforming the potential curves into a mathematical expression. Owing to the nature of highly non-linear curve of both anode and cathode potential, the polynomial fitting will be very likely to be pushed up to the 9th order. At this stage, the coefficient from the resulted fitting will be numerically unstable and requires accuracy at a very high decimal points. Therefore, it's hard to re-produce the same anode or cathode potential curve although the fitting has a relatively small variance of errors.

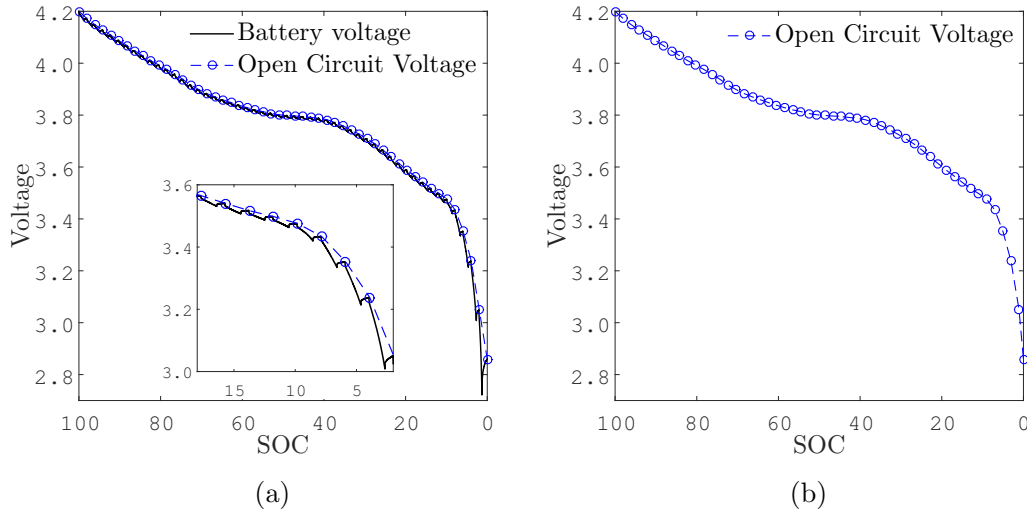


Figure 4.11: (a) Continuous pulse discharge at C/10 for 12 minutes followed by 30 minutes rest, (b) Extracted open circuit voltage

Therefore Gaussian function which is embedded in the MATLAB fitting tool was considered for the final fitting technique. This technique uses an exponential expression to map the anode and cathode potential. Despite its relatively longer process time, it can give a high accuracy of fitting without any decimal or numerical difficulties. Table 4.8 and Eqn. 4.69 summarise the mathematical expression for anode potential while the mathematical expression for cathode can be found in Table 4.9 and Eqn. 4.70. The resulting potential curve from the mathematical expressions for both anode and cathode are depicted in Fig. 4.12.

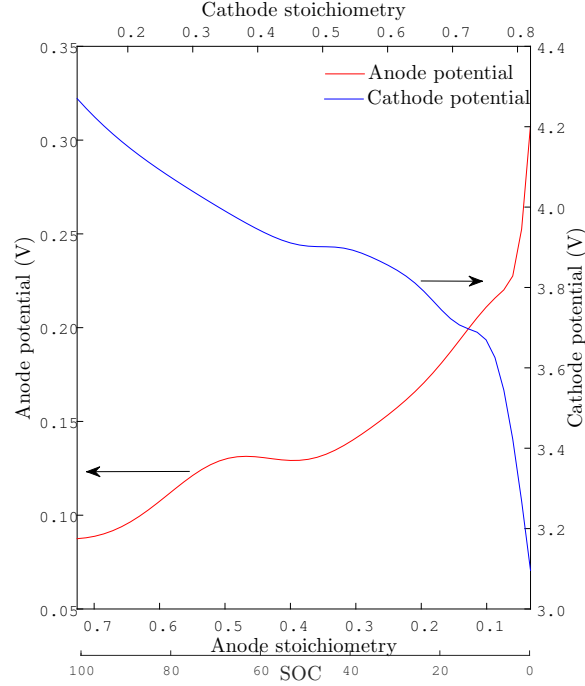


Figure 4.12: Anode and cathode potential given from Gaussian function fitting

Table 4.8: Parameter for anode potential

Constants	Term 1	Term 2	Term 3	Term 4	Term 5	Term 6	Term 7
a_i	0.06929	0.09137	0.1991	0.08659	58.78	-0.06336	0.1856
b_i	0.005336	0.02094	0.02	0.8768	-0.1442	0.3784	0.3752
c_i	0.009271	0.02244	0.1761	0.2858	0.06212	0.132	0.2402

$$U^- = \sum_{i=1}^7 a_i e^{-\left(\frac{x_{stoi}-b_i}{c_i}\right)^2} \quad (4.69)$$

Table 4.9: Parameter for cathode potential

Constants	Term 1	Term 2	Term 3	Term 4	Term 5
a_j	5.658	2.569	0.02509	0.2814	1.329
b_j	-0.4546	0.4839	0.5315	0.7765	0.7643
c_j	0.7131	0.4452	0.05809	0.05625	0.2348

$$U^+ = \sum_{j=1}^5 a_j e^{-\left(\frac{y_{stoi}-b_j}{c_j}\right)^2} \quad (4.70)$$

4.4 Results analysis : Modelling and experimental comparison

4.4.1 Pulse discharge comparison for conduction and convection

Figure 4.13 (a) to (e) show simulated pulse discharge for five different temperatures which are from 45°C to 5°C as well as their experimental data from the conduction thermal control. It can be seen that the simulation data can pick up the voltage curve reasonably well during discharge and relaxation period. The same observations are also found in Fig. 4.14 (a) to (e) for comparison of simulated pulse discharge with the convection thermal control data. The effect of temperature on battery performance under load and relaxation is clearly observed from both simulated data for conduction and convection thermal control. However, due to the different actual cell temperature, the voltage during relaxation period for convection simulated data, plateaus faster than for the conduction simulated data. These behaviours are mainly because of the temperature dependence parameters particularly the diffusion coefficient and reaction rate constant at the positive electrode according to Ye et al. (2012). However, at 5°C, simulated data from both thermal conditions show some deviations particularly at near the end of the first pulse discharge. Nevertheless, the magnitude of the deviations is not considerably large with root mean square error (RMSE) of 42mV or 3.9% deviation based on the total operating voltage at 5°C.

Since the conduction thermal control can keep the battery temperature relatively constant during discharge, from a modelling point of view, it allows an isothermal assumption to be applied to the thermal coupling for the battery model. Therefore, the simulated data which are shown in Fig. 4.13 (a) to (e) are obtained by just changing the battery model temperature. The same thermal method is also applied for predicting voltage curve given from the convection thermal control data as illustrated in Fig. 4.14 (a) to (e). The actual increase in battery temperature is ignored in this condition primarily to investigate the effect it gives on fitting the physiochemical parameters given from different thermal control. The change of temperature for both simulation cases will give significant impact on the six physiochemical properties hence the performance change at different temperature can be modelled accordingly.

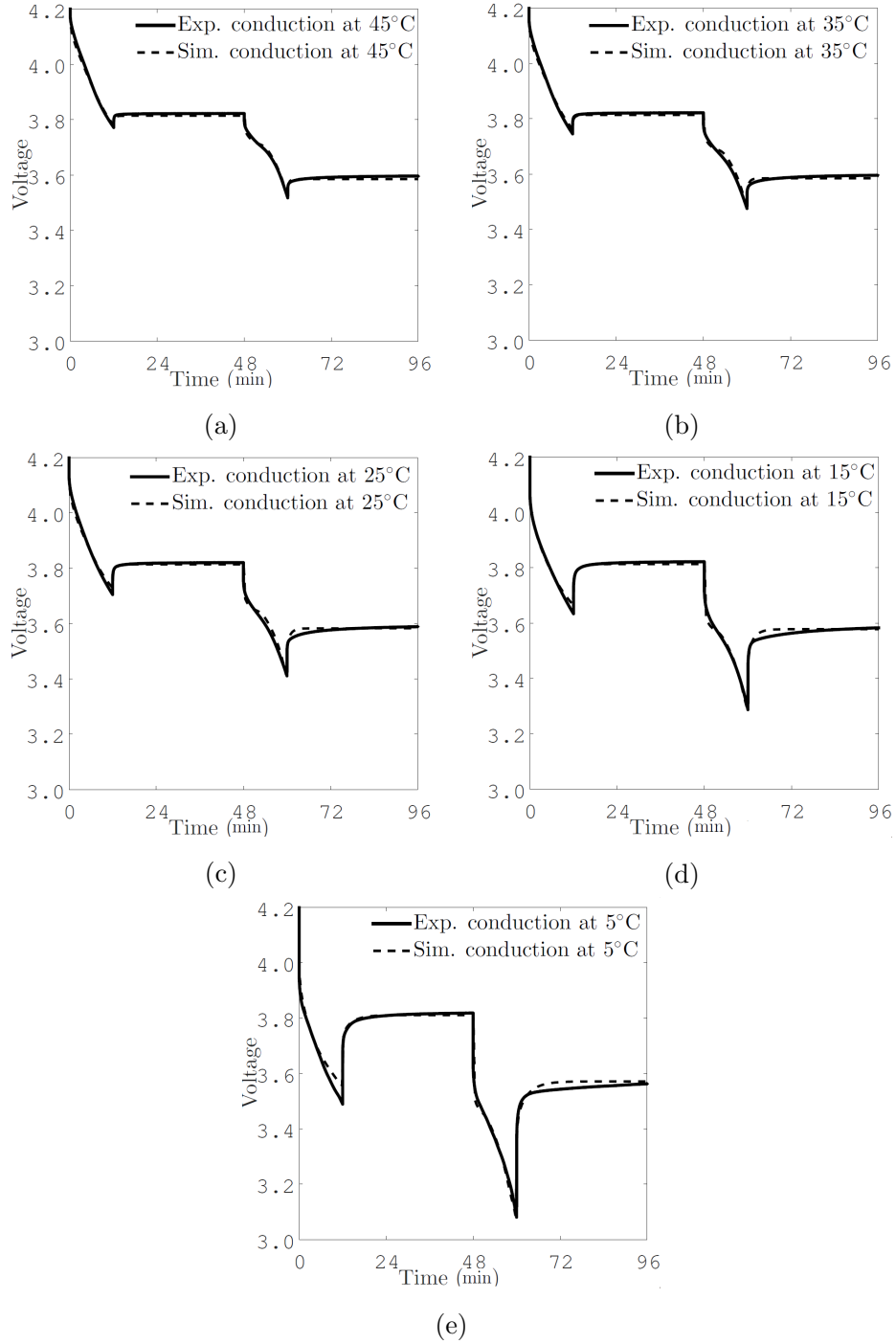


Figure 4.13: Comparison between simulated data and test data obtained from conduction thermal control

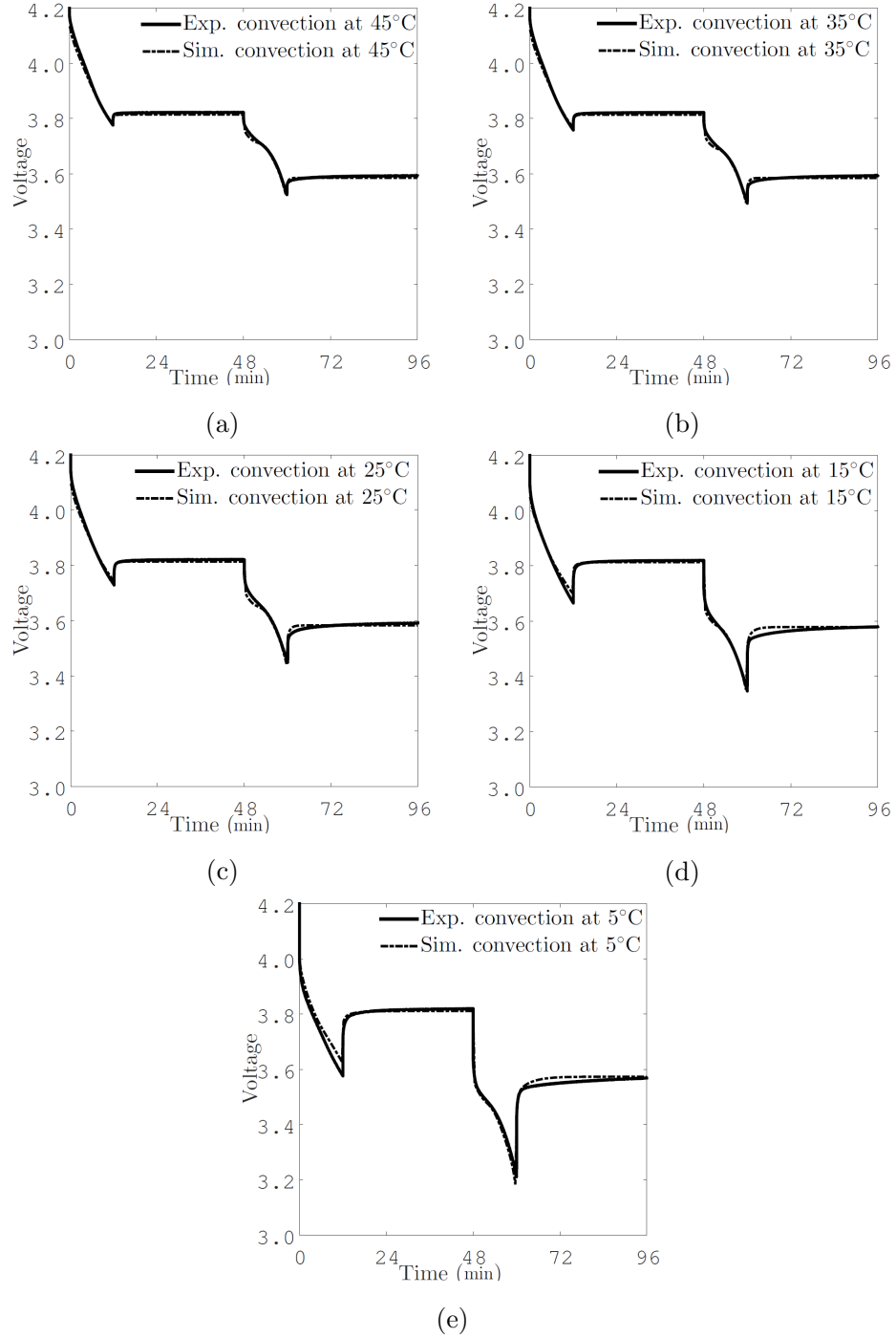


Figure 4.14: Comparison between simulated data and test data obtained from convection thermal control

As previously discussed, the convection thermal control or test conducted using thermal chamber causes battery temperature to increase at a different rate depending on the ambient temperature. Therefore the setting temperature of the thermal chamber is not a representation of the actual battery temperature. However, for comparison and to essentially gauge the limit of isothermal assumption in a convective condition, the simulation at various temperatures are assumed to be isothermal. Only diffusion and charge transfer coefficient of the cathode are altered to fit the experimental data. These two physiochemical parameters are chosen to be changed because of the strong relationship of the parameters during relaxation and dynamic response during charge/discharge according to Ye et al. (2012) and Bernardi and Go (2011). Justification on altering these parameters to fit the battery model will be discussed in the next section.

4.4.2 Battery parameterisation by using inverse modelling

It is commonly known that a physics based battery thermal-electrochemical model has lots of variables and parameters with some of the parameters are interrelated. Since the determination of the battery parameters for the actual 5Ah battery is not the main objective of this work, therefore lots of parameters used in the model are obtained from the literature. These parameters are approximated, fitted or evaluated which reflect the actual battery attribute to the best of the author's knowledge.

Table 4.10: Type of fitted parameter

Type of parameter	Fitting basis
Effective electrode area ($A_{electrode}$)	reference voltage
Particle radius (R_s^+, R_s^-)	reference voltage
Solid active material volume fraction ($\varepsilon_s^+, \varepsilon_s^-$)	reference voltage
Solid phase lithium diffusion coefficient (D_s^+, D_s^-)	linearisation of Arrhenius eqn.
Charge transfer coefficient (k_{ct}^+, k_{ct}^-)	linearisation of Arrhenius eqn.
Electrolyte phase diffusion coefficient (D_e^+)	linearisation of Arrhenius eqn.
Electrolyte phase conductivity coefficient (κ)	linearisation of Arrhenius eqn.

In order to conduct a parameter fitting process, a reference condition is required. Normally, a battery which performs at room temperature is chosen as a reference condition. Hence, the voltage curve under isothermal conditions at

25°C is used as a reference data for fitting some parameters which are listed in Table 4.10. The first three parameters are fitted based on the reference voltage by using a heuristic method. This method is based on the principle of learning by doing; therefore it cannot be perceived as an optimum solution. However, at some point, it yields an optimum result with minimum effort. Nevertheless, the fitting can be further improved by employing a more sophisticated algorithm, but this is beyond the scope the study.

Since the three types of parameters are not dependent on temperature, the adjustments are made within the reported value as shown in Table 4.11. By having test data obtained from close to an isothermal condition, the dependency of certain parameters on temperature change can be minimised. This reduces the effort in parameterising the battery model.

Table 4.11: Comparison of model fitted parameter to reported values

Parameter	Reference	Reported value	Fitted value
Particle radius (R_s^+, R_s^- , cm)	Ecker et al. (2015)	6.49×10^{-4} , 8.7×10^{-4}	
	Smith and Wang (2006)	1×10^{-4} , 1×10^{-4}	0.9×10^{-4} , 0.7×10^{-4}
	Forman et al. (2012)	0.16×10^{-4} , 3.6×10^{-4}	
Solid active material volume fraction ($\varepsilon_s^+, \varepsilon_s^-$)	Ecker et al. (2015)	0.296, 0.329	
	Smith and Wang (2006)	0.500, 0.580	0.555, 0.460
	Forman et al. (2012)	0.520, 0.618	

Fig. 4.16 systematically summarises the overall fitting technique for parameterising which can be divided into two section. Initially, this algorithm is constructed by changing the three main parameters which can be found in Table 4.11, one at a time. The changes on the parameter value's is primarily to investigate its impact on the voltage curve profile. This initial work requires a long duration of time since it was done manually. The aim of this initial work is to find the most important parameter which has a direct influence on the voltage curve without the intervention of temperature. The impact of temperature on the three main parameters needs to be isolated because the impact of temperature on voltage curve is only considered in the physiochemical parameters. This is the reason why an isothermal battery performance is required. Based on the algorithm presented in Fig. 4.16, the cell effective area is the most important parameters which dictates the voltage curve and battery capacity, followed by particle radius and solid active material volume fraction.

The parameters fitting at the first section (Loop 1) is based on the reference voltage given from an isothermal condition and the second section (Loop 2) is for fitting the physiochemical parameters. An isothermal battery model is used with preset parameter values to initially predict the voltage level at the first relaxation period as shown in the dotted rectangular box (Loop 1) as shown in Fig. 4.16. At this stage, the effective electrode area (A) in the battery model is regulated until it reaches the same value with the reference voltage. Subsequently, the particle radius and solid active volume fraction are adjusted until the difference between the predicted voltage curve with the reference voltage as highlighted in the dotted rectangular box in Fig. 4.14 is within the tolerance which has been set. The particle radius has a significant influence in dictating the shape of the voltage curve. According to Bae et al. (2014), increasing the particle radius enlarges the overall shape of the voltage curve as shown in Fig. 4.15 (a). Although it is stated that the diffusion coefficient can also influence the shape of the voltage curve as shown in Fig. 4.15 (b), this parameter is kept unchanged during the first two parameterisations in Loop 1. This is due to the fact that the reference voltage curve is obtained from a thermal condition which is closed to the isothermal condition, therefore, the influence of temperature change at that particular isothermal temperature on the diffusion coefficient can be ignored

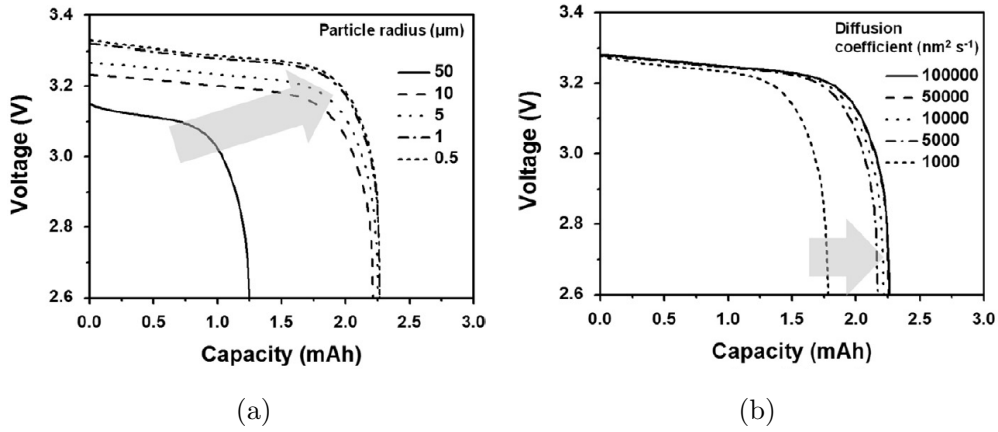


Figure 4.15: Effect of parameters on battery performance extracted from Bae et al. (2014) : (a) Effect given by changing particle radius, (b) Effect on changing solid diffusion coefficient

The final adjustments are made by changing the value of the physiochemical parameter along with the temperature in the battery model. At this condition, the changes are not necessarily required since the simulated voltage curve is closely matched to the experimental data. Nevertheless, slight changes in the parameters can be made without any constraint because the value of the physiochemical param-

eter at this reference condition will be linearized based on the Arrhenius equation. Once the reference parameters have been obtained, the experimental voltage curve which acts as a reference voltage at the isothermal temperature of 25°C is changed to a new reference voltage obtained at different isothermal temperature. At this stage, fitting of parameters are made only to the physiochemical parameters and the battery model temperature as shown by Loop 2 in Fig. 4.14. The latter changes the physiochemical parameters indirectly because each of the parameters is linked to the temperature by the Arrhenius equation. Table 4.12 shows the whole battery parameter as a result of this fitting, along with other parameters obtained from the literature.

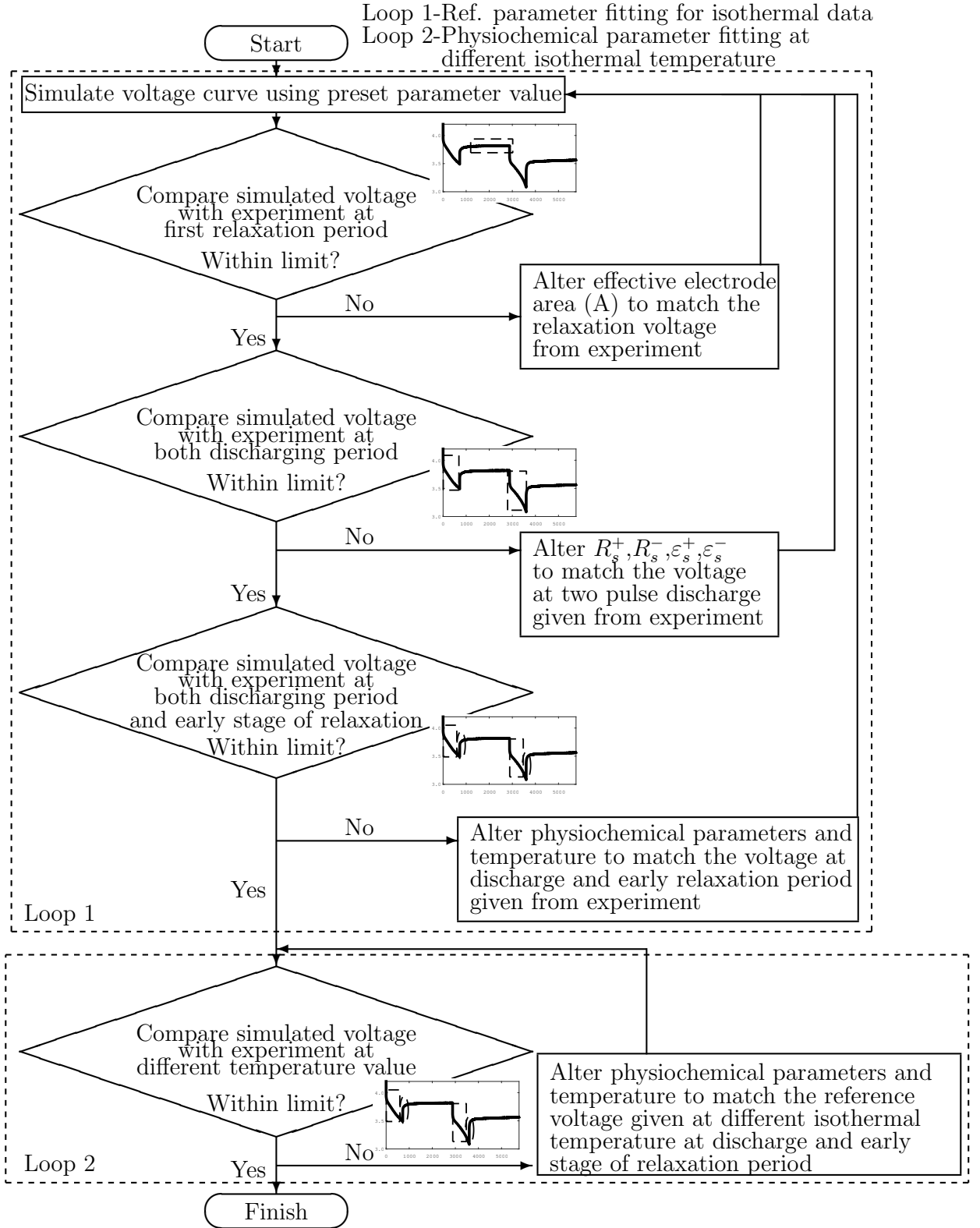


Figure 4.16: Battery parameter fitting algorithm

Table 4.12: Battery model parameters

Parameters	Negative electrode	Separator	Positive electrode
Thickness, δ (cm)	40.9×10^{-4a}	25.4×10^{-4a}	25.5×10^{-4a}
Particle radius, R_s (cm)	0.7×10^{-4e}	-	0.9×10^{-4e}
Solid active material volume fraction, ε_s	0.455 ^e	-	0.545 ^e
Electrolyte volume fraction, ϵ_e	0.330 ^a	0.500 ^a	0.340 ^a
Maximum solid phase concentration, $c_{s,max}$ (mol cm ⁻³)	16.1×10^{-3b}	-	23.9×10^{-3b}
Stoichiometry at 0% SOC	0.033 ^d	-	0.820 ^d
Stoichiometry at 100% SOC	0.726 ^d	-	0.122 ^d
Initial electrolyte concentration, c_e (mol cm ⁻³)	1.20×10^{-3b}	1.20×10^{-3b}	1.20×10^{-3b}
Anodic/Cathodic transfer coefficient, α_n α_p	0.5 ^b	-	0.5 ^b
Solid phase lithium diffusion coefficient, D_s (cm ² s ⁻¹)	4.572×10^{-12e}	-	6.013×10^{-12e}
Charge transfer coefficient, k_{ct} (cm ^{2.5} mol ^{-0.5} s ⁻¹)	8.829×10^{-7e}	-	8.776×10^{-7e}
Solid phase conductivity, σ_s (S cm ⁻¹)	1.0 ^b	-	0.1 ^b
Electrolyte phase diffusion coefficient D_e (cm ² s ⁻¹)	3.37×10^{-6e}	3.37×10^{-6e}	3.37×10^{-6e}
Bruggeman porosity exponent, p	1.99 ^c	1.87 ^c	2.01 ^c
Electrolyte phase conductivity, κ (S cm ⁻¹)	$\kappa = 47.35c_e \exp(-13,472c_e^{1.4})^{b,e}$ $\kappa = 47.35c_e \exp(-13,472c_e^{1.4})^{b,e}$		
Lithium-ion transference number ^e , t_+^0	0.363 ^b	0.363 ^b	0.363 ^b
Effective electrode Area, $A_{electrode}$ (cm ²)	8400 ^e		
Current collector contact resistance, R_f (Ω cm ²)	20 ^b		

^a Wu (2014)

^d Birkel et al. (2015)

^b Smith and Wang (2006)

^e fitted

^c Ecker et al. (2015)

The base value for the activation energy along with its reference parameter for each of the physiochemical parameters are obtained from Wu (2014). By using the base values, the physiochemical parameters and the battery model temperature are changed until the voltage curve gets closer to the experimental curve. Because the battery model temperature is changed randomly; therefore calibration of the activation energy along with its reference parameter are required. The calibration is carried out by the linearization of Arrhenius equation as shown in Eqn.4.71. The linearised equation is compared to the general equation of a straight line as shown in Eqn.4.72 where the calculated physiochemical parameters at each temperature are viewed as (Y) and the ratio between the activation energy of each parameter to the gas constant is perceived as a gradient of a straight line (m). Therefore, by having five isothermal data points, each of the physiochemical parameters can be linearised and subsequently form a straight line. The gradient from each of the straight line is used to calculate the new activation energy. The reference parameter value at the reference temperature of 25°C is determined by finding the value of intersection on Y-axis. Eqn.4.73 directly compares the relationship given by Arrhenius equation with the linear equation for calculating the new value of activation energy along with the reference value of various physiochemical parameters.

$$\ln(\Psi) = \frac{E_{act}^{\Psi}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) - \ln(\Psi_{ref}) \quad (4.71)$$

$$Y = mX + c \quad (4.72)$$

$$Y = \ln(\Psi), m = \frac{E_{act}^{\Psi}}{R}, X = \left(\frac{1}{T_{ref}} - \frac{1}{T} \right), c = -\ln(\Psi_{ref}) \quad (4.73)$$

Since this fitting are based on the tests conducted in conduction thermal conditions from 5°C to 45°C, the battery performance can be predicted within this range of temperature regardless of the applied thermal boundary conditions. Nevertheless, the performance prediction can also be extended to go beyond this temperature region by extrapolating the linearised equation; however additional physical phenomenon needs to be added to the model particularly for low temperature performance prediction. Fig. 4.17 to 4.20 illustrate the individual physiochemical parameter behaviour at different temperature along with its linearized form. As a result of fitting and linearization, a new set of activation energy and the reference value given from various physiochemical parameters are obtained based on the

reference temperature of 25°C as shown in Table 4.13 and 4.14 respectively.

Table 4.13: Fitted activation energy for physiochemical properties

Activation energy	Conduction data (J mol ⁻¹)
Solid phase diffusion, E_{act}^{Ds+} , E_{act}^{Ds-}	27737.3, 46495.2
Exchange current density, E_{act}^{io+} , E_{act}^{io-}	74407.2, 45602.3
Electrolyte phase diffusion, E_{act}^{De}	11760.6
Electrolyte phase conductivity, E_{act}^{κ}	45431

Table 4.14: Reference value for several physiochemical properties at 25°C

Type of coefficient	Reference value (Ψ_{ref})
Solid phase diffusion, (cm ² s ⁻¹)	$D_s^+=6.013 \times 10^{-12}$, $D_s^-=4.572 \times 10^{-12}$
Electrolyte phase conductivity, (S cm ⁻¹)	$\kappa=1$
Charge transfer, (cm ^{2.5} mol ^{-0.5} s ⁻¹)	$k_{ct}^+=8.776 \times 10^{-7}$, $k_{ct}^-=8.829 \times 10^{-7}$
Electrolyte phase diffusion, (cm ² s ⁻¹)	$D_e=3.37 \times 10^{-6}$

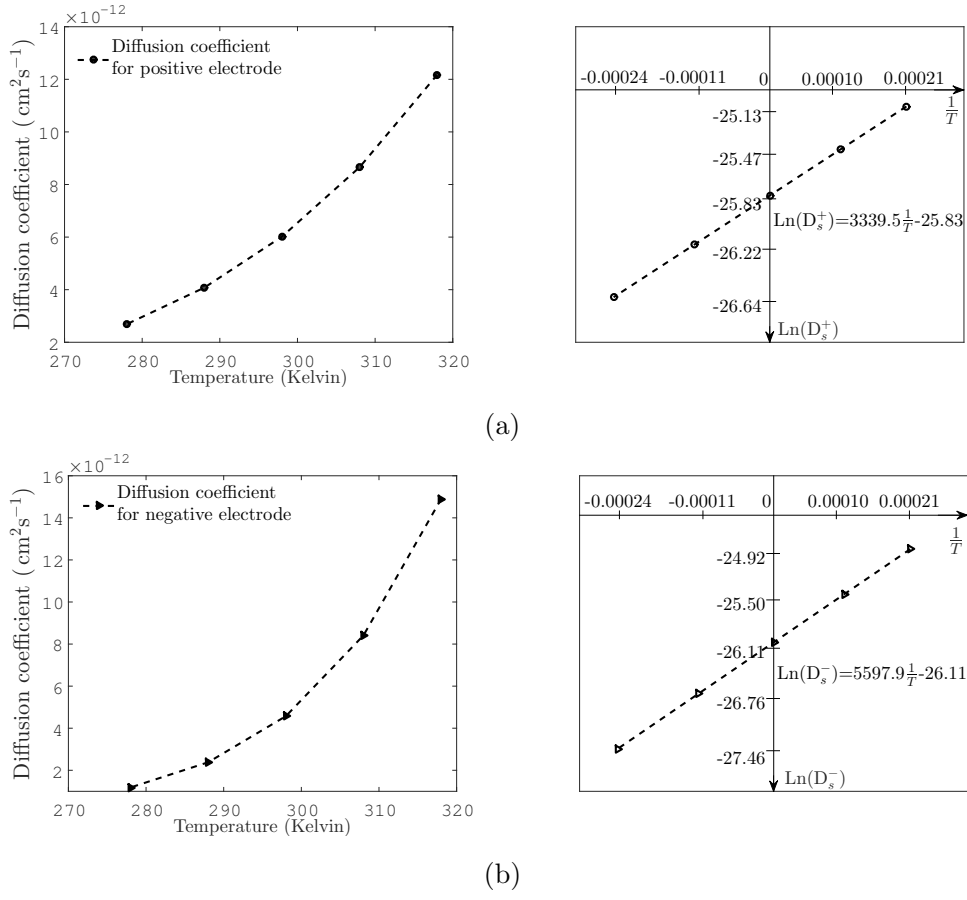


Figure 4.17: Fitting and linearisation of : (a) Diffusion coefficient at cathode, (b) Diffusion coefficient at anode

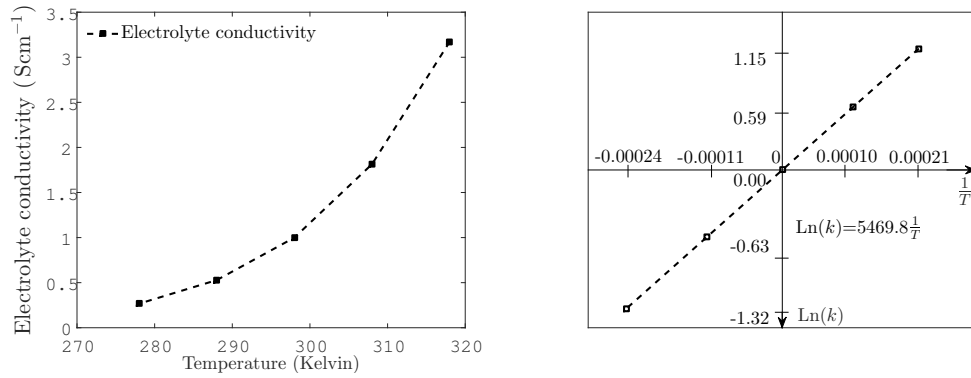


Figure 4.18: Fitting and linearisation of electrolyte phase conductivity coefficient

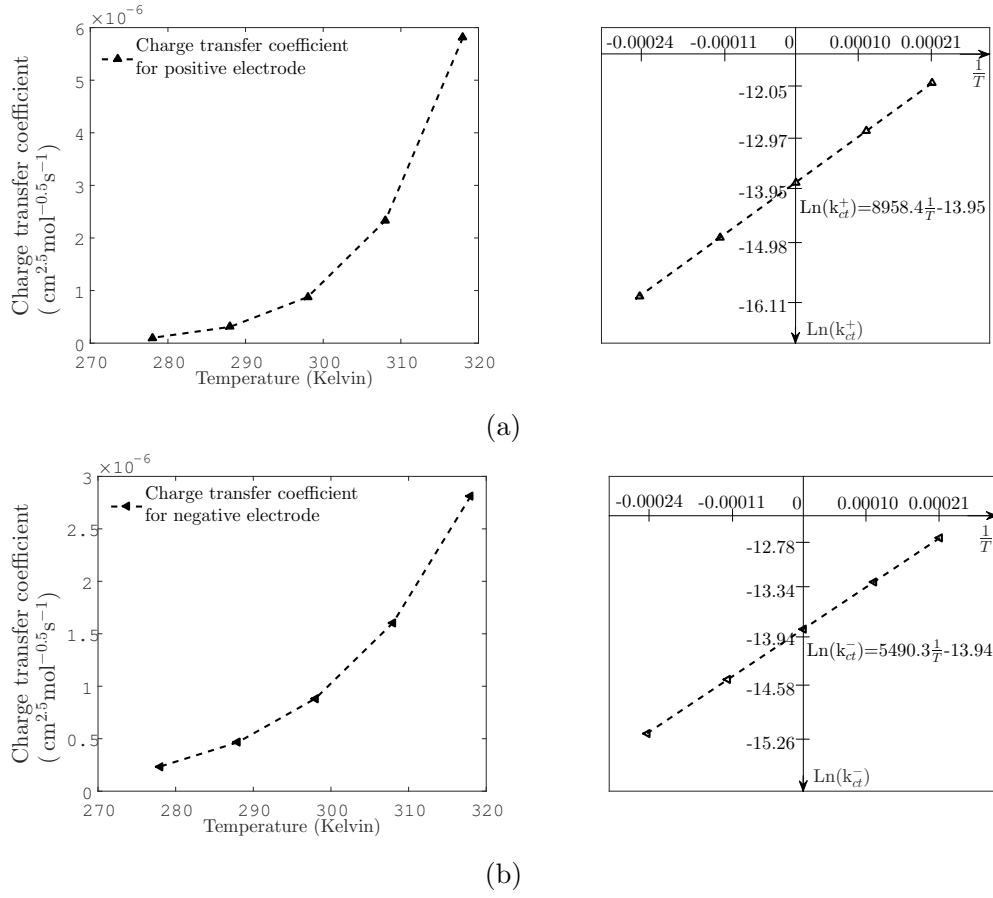


Figure 4.19: Fitting and linearisation of : (a) Charge transfer coefficient at cathode, (b) Charge transfer coefficient at anode

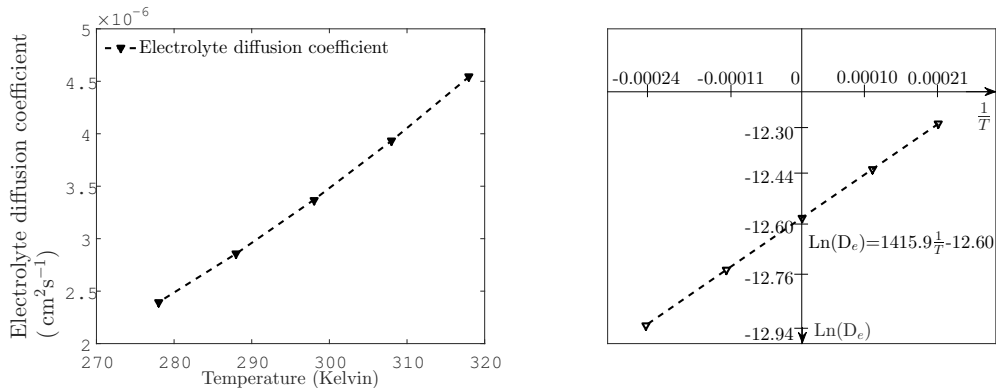


Figure 4.20: Fitting and linearisation of electrolyte diffusion coefficient

4.4.3 Physiochemical parameter comparison

4.4.3.1 Parameter sensitivity analysis

In order to determine the most important temperature related parameters which give noticeable impact towards the battery performance, all of the six physiochemical parameters are individually tested. The sensitivity of these parameters towards the battery performance is studied by conducting a parametric sweep tests. Strictly speaking, several parameters could depend on each other, nevertheless, the single parameter sweep test is intended to verify and compare only two important parameters which are based on the work of Ye et al. (2012) and Bernardi and Go (2011). This test is carried out by reducing the fitted physiochemical parameters value by 50% and compare the simulated voltage curve that uses this new reduced value with the reference voltage curve. The effect given by each of the parameters on the simulated voltage curve is gauged based on the root mean square error (RMSE) as shown in Eqn. 4.74

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (V_{ref} - V_{test})^2}{N}} \quad (4.74)$$

Six repeated simulations are carried out to investigate the impact given by each of the physiochemical parameters on the voltage curve. Notable differences can be seen during discharge and at the early relaxation period at first and second pulse as shown in Fig. 4.21. From the calculated value of RMSE, the diffusion coefficient of the cathode is the main parameter which influences the overall voltage curve behaviour followed by its charge transfer coefficient as summarises in Table. 4.15. Since cathode potential predominantly governs the voltage curve, therefore, any changes with regards to its parameters will cause significant deviation as compared to the others physiochemical parameters from different battery components. These findings are consistent with those of Ye et al. (2012) and Bernardi and Go (2011) which stated that both diffusion and charge transfer coefficient at the cathode are the main parameters in dictating the behaviour of a battery voltage curve.

Based on this analysis, the two most dominant physiochemical parameters are altered to map the battery voltage performance under convection thermal control while keeping the battery temperature constant during the simulation which will be discussed in the next section. This is primarily to compare the deviation of these parameters if test conducted in the thermal chamber is assumed to be isothermal.

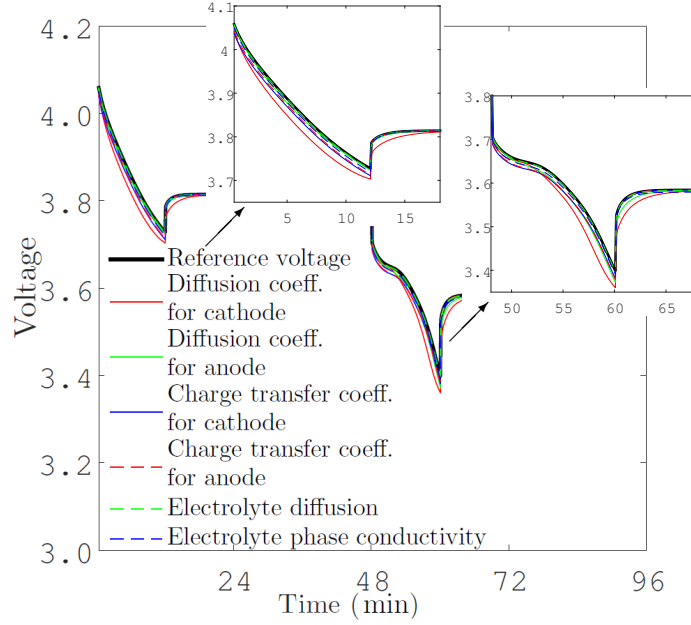


Figure 4.21: Simulated physiochemical parameters analysis

Table 4.15: Parameter change and calculated error for sensitivity analysis

Parameter	Initial value	New test value	Calculated error
Diffusion coefficient for anode (D_s^- , cm^2s^{-1})	4.572×10^{-12}	2.286×10^{-12}	6.5mV
Diffusion coefficient for cathode (D_s^+ , cm^2s^{-1})	6.013×10^{-12}	3.006×10^{-12}	18.1mV
Charge transfer coefficient for anode (k_{ct}^- , $\text{cm}^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$)	8.829×10^{-7}	4.414×10^{-7}	7.7mV
Charge transfer coefficient for cathode (k_{ct}^+ , $\text{cm}^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$)	8.776×10^{-7}	4.388×10^{-7}	8.8mV
Diffusion in electrolyte (D_e , cm^2s^{-1})	3.371×10^{-6}	1.685×10^{-6}	1.1mV
Electrolyte phase conductivity coefficient (κ , Scm^{-1})	1	0.5	5.2mV

4.4.3.2 Diffusion and Charge transfer coefficient of positive cathode

As described earlier, an appreciable error will be introduced particularly at low temperatures, if the battery thermal performance characterisation is carried out by using forced air convection in which the battery heating as a result of thermal imbalance is not taken into consideration. The error is attributed from the misinterpretation of the thermal chamber setting temperature which does not represent the actual battery temperature. Even if the actual battery temperature is measured and this effect compensated for, it is still inherently difficult to fit the physiochemical properties of the battery model if the battery temperature is not constant. The behaviour of the battery voltage is coupled to its temperature based on the Arrhenius equation. This equation mathematically necessitates the battery temperature to remain unchanged at the desired test temperature. This is the main reason why fitting of parameters are difficult even if the battery temperature is taken into account due to the fact that the Arrhenius equation only considers the deviation between reference temperature with the operating temperature.

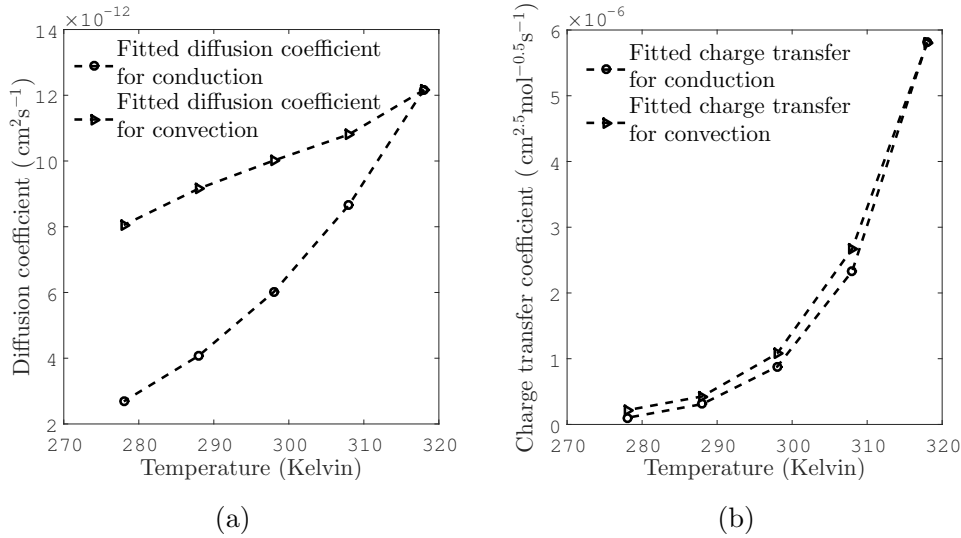


Figure 4.22: Physiochemical parameter obtained from simulation data for conduction and convection thermal control : (a) Diffusion coefficient, (b) Charge transfer coefficient

Fig. 4.22 (a) and (b) show the comparison of diffusion and charge transfer coefficient at cathode between conductive and convective thermal control respectively. These comparisons are built upon the two simulation data at different thermal conditions as described previously. Due to the heating effect which occurs during convective tests, both diffusion and charge transfer coefficient are larger as

compared to the value obtained from the conduction tests. This is primarily due to the temperature increase at this thermal conditions is compensated by increasing both of the parameters rather than changing the battery model temperature. Therefore allows the battery performance under convective environment to be assumed isothermal.

At high operating temperatures, the battery performances are quite similar albeit being operated at different thermal conditions. This is reflected by the relatively identical value of diffusion and charge transfer coefficient given from both thermal conditions. This implies that the convective environment can closely match the battery performance given by the conductive environment which in this case serves as an isothermal platform. On the other hand, larger deviations are manifested at low temperatures as a consequence of the battery heating. To compensate this effect from a battery model perspective, both parameters are adjusted while keeping the battery model temperature at a constant value that matches the isothermal temperature. This causes the value of the parameter to increase and deviate far from the reference value. The increased in the battery temperature especially at low ambient temperature is inevitable if the convection thermal control regulates the battery thermal boundary condition. This is because the battery heat generation exceeds the heat loss through convection, therefore, generates thermal imbalance which eventually causes the battery temperature to increase.

The largest deviation of the diffusion coefficient is recorded at the lowest temperature point which is at 5°C as shown in Fig. 4.22 (a). The difference is approximate to be about 56% based on the diffusion coefficient obtained under isothermal condition. On the other hand, the deviation of charge transfer coefficient is not significant which is about 2%. This suggests that data obtained from thermal chambers testing particularly at low temperatures, cannot be relied on if the testing is assumed to be isothermal. Nevertheless, at high temperatures, the data can be used, since its deviation from the conduction thermal control is not apparent. By comparing data from both thermal control, different activation energy and parameter are obtained as shown in Table 4.16 and 4.17 respectively.

Table 4.16: Fitted activation energy for physiochemical properties

Activation energy	Conduction data (J mol ⁻¹)	Convection data (J mol ⁻¹)
Solid phase diffusion, E_{act}^{Ds+} , E_{act}^{Ds-}	27737.3, 46495.2	8696.76, 46495.2
Exchange current density, E_{act}^{io+} , E_{act}^{io-}	74407.2, 45602.3	61382.8, 45602.3

Table 4.17: Fitted reference physiochemical properties for cathode from different thermal conditions

Parameter	Conduction data	Convection data
Cathode solid phase diffusion coefficient, ($D_s, cm^{-2}s^{-1}$)	6.013×10^{-12}	9.718×10^{-12}
Cathode charge transfer coefficient, ($k_{ct}, cm^{2.5}mol^{-0.5}s^{-1}$)	8.776×10^{-7}	1.225×10^{-6}

This quantitative analysis highlights the error caused by assuming an isothermal condition in a convective environment. In addition, it can also serve as a method to treat data obtained from tests conducted in a thermal chamber if an isothermal assumption is concerned. This can be done by re-adjusting the physiochemical parameters. Nevertheless, this still requires data obtained from an isothermal condition to form a relationship between the physiochemical parameters given from different thermal conditions. Eqn. 4.75 and 4.76 describe the relationship for diffusion and charge transfer coefficient respectively between data obtained from the conduction and convection thermal control. Both parameters are fitted based on the exponential fitting tools in Matlab. The quality of fitting is acceptable with R^2 value of 0.99.

The fitting of isothermal data for diffusion and charge transfer coefficient are made only based on the isothermal temperature of 25°C to 45°C. Since the physiochemical parameters behave in an exponential manner, the parameters of the isothermal temperature below 25°C are obtained by interpolating the fitted exponential equation. Hence, by having physiochemical parameters obtained under convective condition from high to low temperature and parameters obtained under isothermal condition from high to room temperature, a ratio between two thermal conditions can be formed. Fig. 4.23 (a) and (b) compare the diffusion and charge transfer coefficient obtained from an isothermal condition with the parameters obtained from the exponential fitted equation of the ratio between conduction to convection. It can be seen that the exponential fitted equation is able to match the data provided by the isothermal data. Hence, the isothermal performance can be predicted by using this relationship without having to conduct an experiment at the low isothermal temperature which is inherently difficult.

$$\frac{D_{s,conduction}^+}{D_{s,convection}^+} = \frac{(1.161 \times 10^{-16})e^{0.03638T}}{(5.837 \times 10^{-13})e^{0.009518T}} \quad (4.75)$$

$$D_{s,conduction}^+ = (D_{s,convection}^+)(1.989 \times 10^{-4})e^{0.0269T}$$

$$\frac{k_{ct,conduction}^+}{k_{ct,convection}^+} = \frac{(1.943 \times 10^{-19})e^{0.09761T}}{(3.861 \times 10^{-18})e^{0.08823T}} \quad (4.76)$$

$$k_{ct,conduction}^+ = (k_{ct,convection}^+)(0.0503)e^{0.0094T}$$

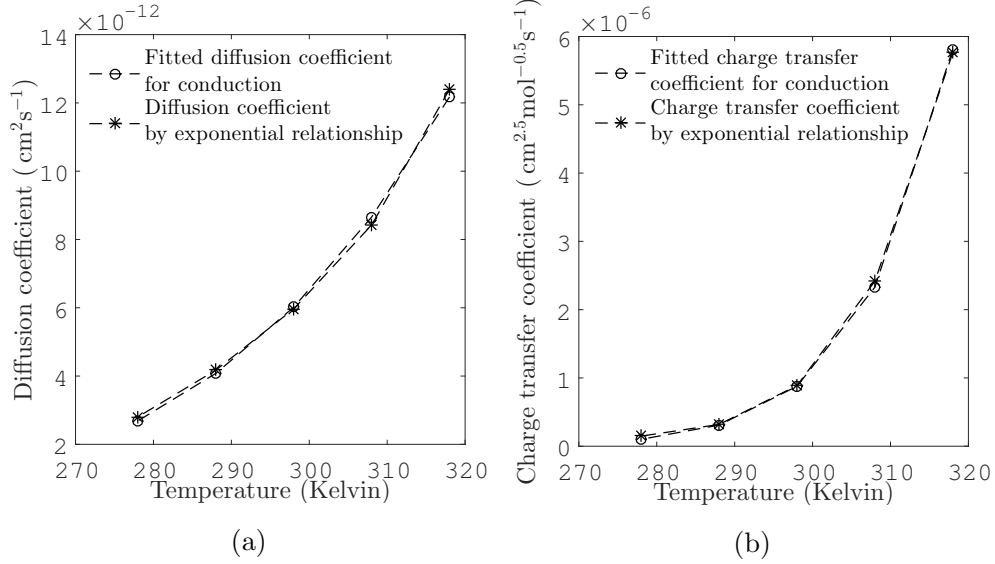


Figure 4.23: Physiochemical parameter comparison between the isothermal data and ratio of conduction to convection for : (a) Diffusion coefficient, (b) Charge transfer coefficient

4.4.3.3 Effect given by diffusion and charge transfer coefficient on battery performance

In a physics based battery model, the OCV is paramount which dictates the overall behaviour of the voltage curve. The OCV is then disintegrated into its respective anode and cathode potential as a function of its electrode stoichiometric. A stoichiometric profile of anode and cathode are generated during charge or discharge in which it is controlled by its diffusion coefficient depending on the applied current and the battery temperature. The stoichiometric gives a direct correlation to the individual electrode potential, and the difference between the cathode and anode

potential serves as the battery OCV. Fig. 4.24 (a) and (b) show the stoichiometric profile at high and low temperatures for anode and cathode respectively. These stoichiometric profiles are generated from the battery simulation of 10A discharge for 12 minutes at the temperature of 45°C and 5°C respectively. The stoichiometric value is calculated based on the ratio of the solid phase concentration at the particle surface to the maximum concentration at each electrode as shown in Eqn. 4.77 and 4.78 for anode and cathode respectively. The temperature during simulation is set to be constant. This is primarily to probe the effect of temperature towards the stoichiometric behaviour. During discharge, positive current density is applied to the anode while negative current density is applied to the cathode. This is to represent the movement of lithium ions from the anode to cathode.

$$stoi_{anode} = \frac{c^s(R)}{C_{anode}^{s,max}} \quad (4.77)$$

$$stoi_{cathode} = \frac{c^s(R)}{C_{cathode}^{s,max}} \quad (4.78)$$

The stoichiometric at anode decreases during discharge regardless of temperature because it loses concentration as a consequence of having negative flux boundary condition. On the other hand, the negative current density applied to the cathode changes the sign of the flux to positive. Therefore, causes its concentration to increase and subsequently drives the stoichiometric to a higher value. Eqn. 4.79 and 4.80 mathematically represent the boundary conditions for anode and cathode respectively. This gives an insight into different stoichiometric profile generated at high and low temperatures as shown in Fig. 4.24. It can be seen that at high temperatures, both the anode and cathode stoichiometric behave considerably linear as compared to its behaviour at low temperature. The high value of diffusion coefficient at high temperature causes the value of the flux to be smaller than its value at low temperature. This is because the diffusion acts as a denominator for the flux calculation; hence, its value is inversely proportional to the value of diffusion coefficient. Having a smaller value of flux causes the mass transfer from the anode to cathode during discharge due to concentration gradient to be less apparent as compared to the mass transfer at low temperature. This is reflected by the stoichiometric profile as shown in Fig. 4.24 (a).

$$\left. \frac{\partial c_s}{\partial x} \right|_{x=anode} = \frac{j_{Li}^{anode}}{-D_s a_s F} \quad (4.79)$$

$$\left. \frac{\partial c_s}{\partial x} \right|_{r=R}^{x=cathode} = \frac{-j_{Li}^{cathode}}{-D_s a_s F} \quad (4.80)$$

At high temperatures, the stoichiometric profile decreases linearly while at low temperature, the profile decreases exponentially. The behaviour of the stoichiometric profile is reversed at cathode whereby the stoichiometric profile increases linearly and exponentially at high and low temperatures respectively as depicted in Fig. 4.24 (b). This shows that although the discharge duration remains the same, more mass is taken out from the anode particularly at low temperatures because of the high value of flux due to low diffusion. Consequently, the OCV at low temperature will be lower than the OCV high temperature. The calculated OCV from the battery model at 5°C and 45°C is 3.76V and 3.81V respectively. Clearly, the different in temperature will result in the individual electrode to be different in terms SOC, although the discharge duration remains the same thus, indicating the importance of diffusion coefficient in dictating the OCV.

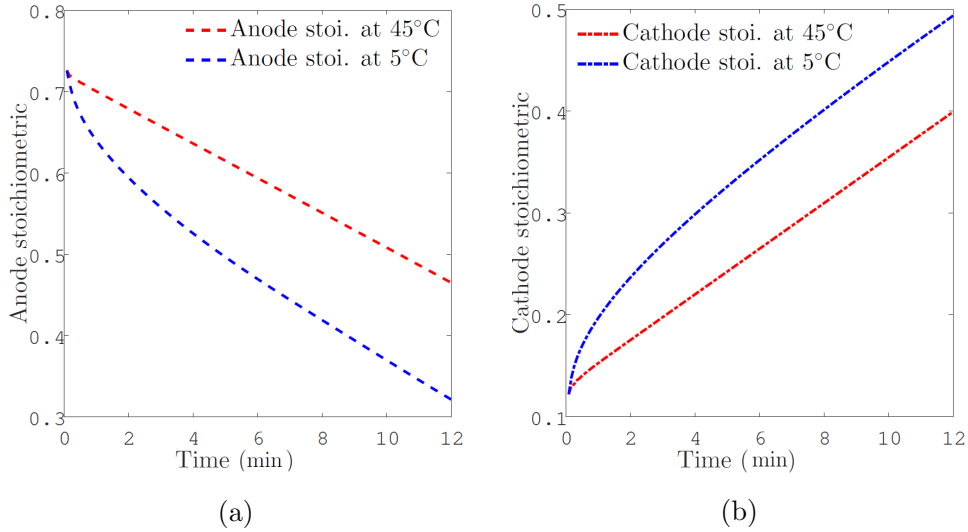


Figure 4.24: Comparison of stoichiometric generation due to temperature for : (a) Anode at 5°C and 45°C, (b) Cathode at 5°C and 45°C

The charge transfer coefficient obtained from the convective thermal control is slightly higher than the value given by the conductive thermal control as shown in Fig. 4.22 (b). The differences are not as significant as compared to the differences in comparing the diffusion coefficient. This is because the fitting process particularly for the temperature related parameter is initiated by regulating the diffusion coefficient due to its dominant effect as previously shown in the parameter sensitivity analysis. Moreover, the effect of diffusion is not only limited under the

electrical load or during charge/discharge. It is also important during relaxation because the diffusion dictates the concentration gradient which affects the dynamic behaviour of the terminal voltage when there is no external current.

$$k_{ct} = \frac{i_0}{F c_e^\alpha (c_{s,max} - c_{s,surface})^\alpha c_{s,surface}^\alpha} \quad (4.81)$$

The charge transfer coefficient which is responsible for controlling the rate of forward and backward reactions as a function of temperature, is directly related to the exchange current density as shown in Eqn. 4.81. The exchange current density is analogous to the rate constant used in chemical kinetics which is calculated based on the concentration of solid particle, electrolyte and temperature. Impact given by the charge transfer coefficient on the battery performance is rather limited to charge and discharge. During relaxation or when the external current is switched off, the reaction current density at anode and cathode is equal to zero. Since the reaction current density is inextricably linked to the exchange current density as shown in Eqn. 4.82, having zero value of reaction current density causes the effect which given by the charge transfer coefficient on the battery behaviour to be negligible. At this condition, the dynamic behaviour of the terminal voltage is mainly governed by the solid diffusion.

$$j_{Li} = a_s i_0 \left(\exp \left[\frac{\alpha_a F \eta_{total}}{RT} \right] - \exp \left[\frac{-\alpha_a F \eta_{total}}{RT} \right] \right) \quad (4.82)$$

Impact given by the charge transfer coefficient on the battery performance is paramount during charge/discharge. Low diffusion at low temperature causes the overpotential to be greater than the overpotential at high temperature as shown in Fig. 4.25 (a). During discharge, the amount of current entering at each electrode remains the same regardless of temperature as shown in Eqn. 4.83. Therefore at high temperature, the exchange current density needs to be higher to compensate the low value of overpotential. Conversely, the exchange current density at low temperature is significantly small as illustrated in Fig. 4.25 (b). However, this will be balanced by the high overpotential due to low temperature. Eqn. 4.84 shows the parameters which contribute to the calculation of the exchange current density.

$$\begin{aligned} \int_0^{\delta_n} j_{Li}^{High} &= \int_0^{\delta_n} j_{Li}^{Low} \\ \int_0^{\delta_n} i_0^{High} \sinh(\eta^{High}) &= \int_0^{\delta_n} i_0^{Low} \sinh(\eta^{Low}) \end{aligned} \quad (4.83)$$

$$\begin{aligned} \int_0^{\delta_n} k_{ct}^{High} c_e^{\alpha, High} (c_{s, max} - c_{s, surface}^{High})^\alpha c_{s, surface}^{\alpha, High} \sinh(\eta^{High}) \\ = \\ \int_0^{\delta_n} k_{ct}^{Low} c_e^{\alpha, Low} (c_{s, max} - c_{s, surface}^{Low})^\alpha c_{s, surface}^{\alpha, Low} \sinh(\eta^{Low}) \end{aligned} \quad (4.84)$$

It can be seen from the equation that the concentration of the solid phase, concentration of the electrolyte and the charge transfer coefficient govern the change of the exchange current density. Nevertheless, the effect given from the solid and electrolyte concentration at a different temperature on the exchange current density are not as significant as the effect given by the charge transfer coefficient. Fig. 4.26 (a) and (b) compare the variation of solid phase and electrolyte concentration across an electrode domain at different isothermal temperature. It is evident that the differences in concentration are not appreciable. Hence, the increased in solid phase concentration cannot offset the decreased in overpotential at high temperature. The same behaviour is observed at low temperature but in a reverse way. Therefore suggests that change of exchange current density on temperature is predominantly dictated by the charge transfer coefficient rather than the concentration of the solid and electrolyte phase.

4.4.3.4 Parameter fitting by temperature adjustment

Apart from only being able to regulate diffusion and charge transfer coefficient of the cathode for fitting data obtained from convection tests, temperature adjustment technique based on data fitted from conduction tests can also be used. This is achieved by changing the simulation temperature based on the average battery temperature obtained during convection tests. By allowing all of the six parameters to be changed simultaneously, the differences of diffusion and charge transfer coefficient for cathode between conduction and convection thermal control are significantly reduced as compared with the previous section as illustrated in Fig. 4.27 (a) and (b).

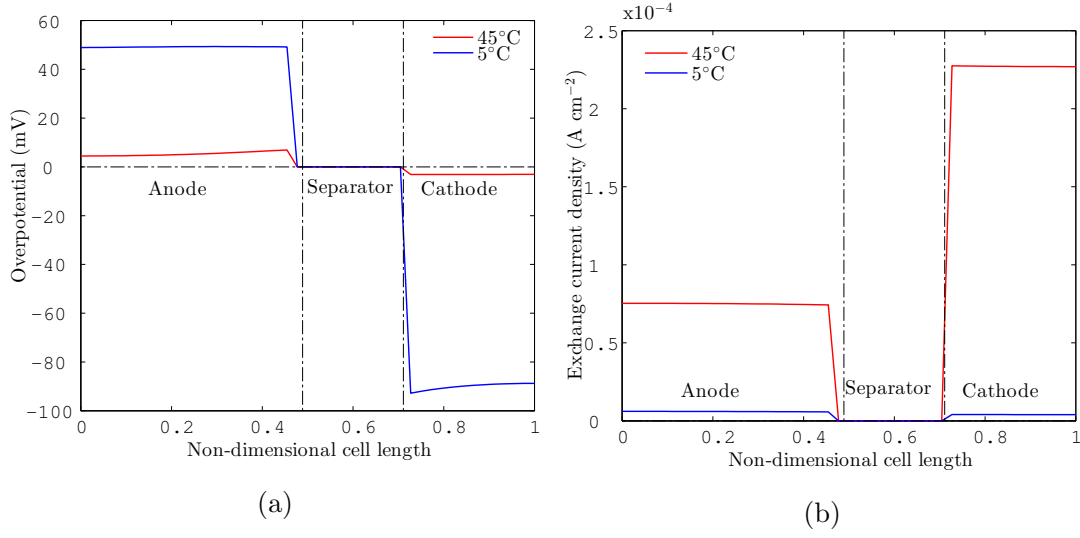


Figure 4.25: Comparison of : (a) Overpotential at 45°C and 5°C, (b) Exchange current density at 45°C and 5°C

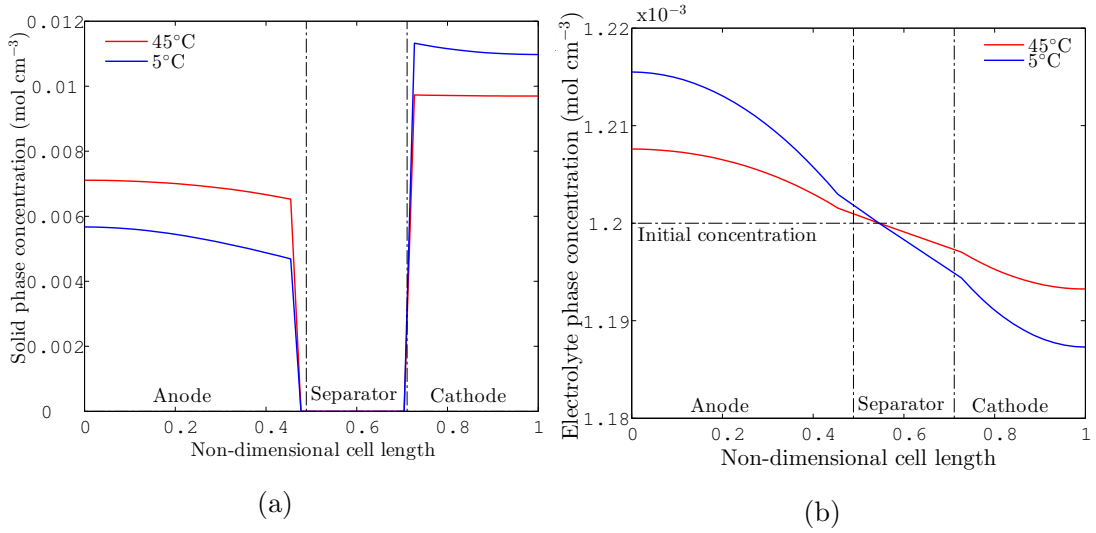


Figure 4.26: Comparison of : (a) Solid phase concentration at 45°C and 5°C, (b) Electrolyte phase concentration at 45°C and 5°C

More parameters involved in this fitting have caused the value of previous fitting (only two parameters) to be compensated. However, the major concern of this technique is that the temperature setting for the simulation does not represent the actual battery temperature as tabulated in Table 4.18.

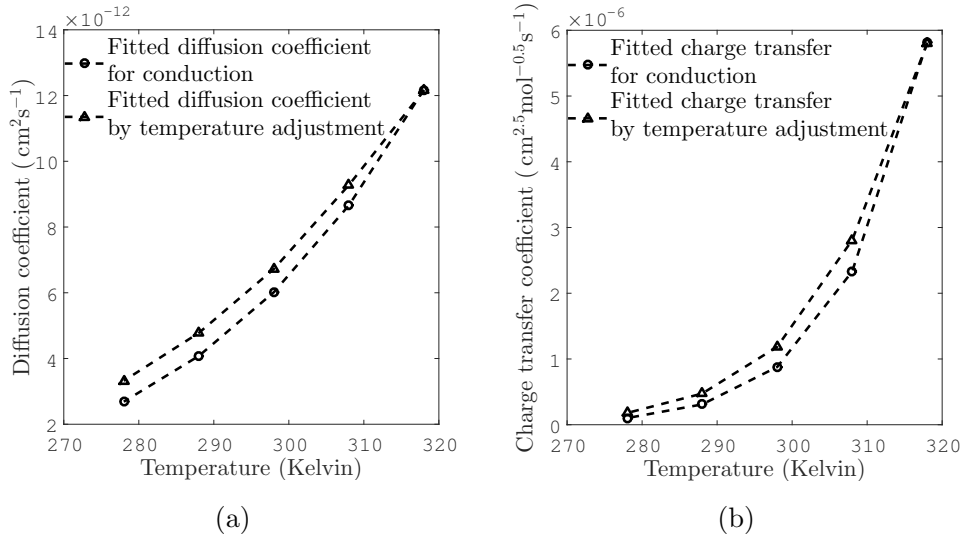


Figure 4.27: Comparison of diffusion and charge transfer coefficient by temperature adjustment

Table 4.18: Battery model temperature input for conduction and convection by allowing all physiochemical parameters to be changed

Temperature for conduction	Temperature for convection
45°C	45°C
35°C	37°C
25°C	28°C
15°C	19°C
5°C	10°C

4.4.4 Full discharge comparison

Figure 4.28 (a) and (b) compare the simulated voltage curve with the test data obtained under isothermal temperature of 45°C, 25°C and 5°C at 1C and 2C rate respectively. It can be seen that all of the simulated voltage can pick up the experimental data reasonably well. However, there is slight discrepancies particularly at low temperature. Table 4.19 compares the quality of the simulated data based on the RMSE. The simulated data conducted at low temperature yields the highest error, and the error is greater at high discharge rate as compared to low discharge rate. On the other hand, the simulated voltage curve at high temperature gives better accuracy for both discharge rate. The error at low temperature could be caused by the assumed value of the stoichiometric for anode and cathode which is

implemented in the battery model, do not match well when the overpotential is high especially at low temperature. Nevertheless, the capacity predicted by the model when the battery is at 0% SOC matches the experimental data reasonably well at all constant temperature.

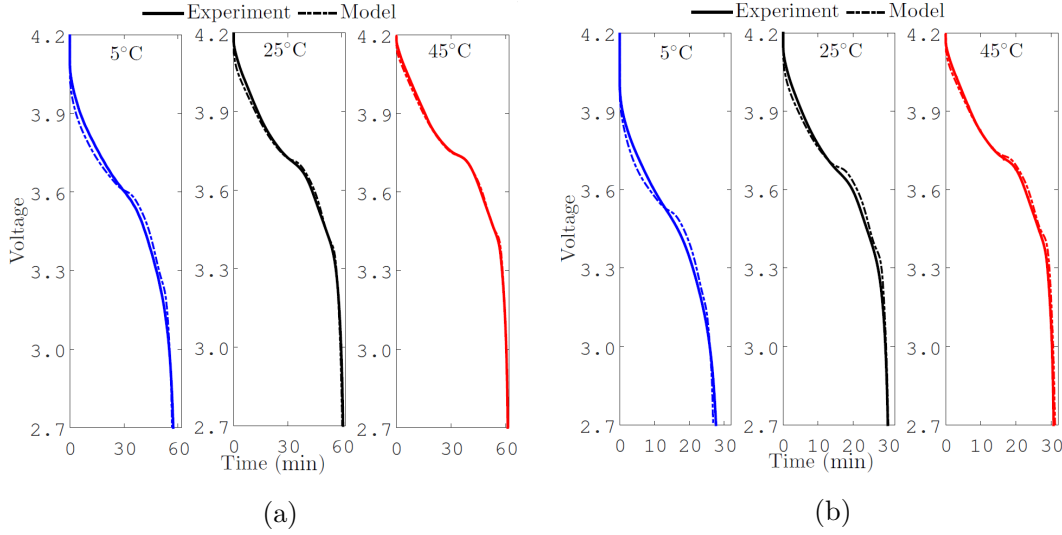


Figure 4.28: Full discharge comparison under isothermal condition : (a) 1-C rate, (b) 2-C rate

Table 4.19: Error comparison for 1C and 2C full discharge at different temperature

Temperature	1-C rate	2-C rate
45°C	14.1mV	18.7mV
25°C	22.2mV	32.3mV
5°C	47.6mV	58.4mV

High operating temperature results in a low value of overpotential. The low overpotential portrays a direct reflection of the battery behaviour towards its OCV. Hence, the characteristics given by the OCV such as its peaks and plateaus can be seen clearly from the simulated voltage curve at high temperature. The increased in overpotential is not primarily relied on the operating temperature, but it is also determined by the discharging rate.

High discharge rate causes the reaction current density to be greater than the reaction current density at the low discharge rate. This also results to high overpotential because more mass is transferred from anode to cathode and consequently the OCV at high discharge rate will be lower than the OCV at low discharge rate. The effect of the discharge rate on the model accuracy can be seen in Table 4.19

where the simulated voltage curve gives better accuracy at the low current rate.

4.4.5 Temperature prediction

4.4.5.1 Calculation of heat transfer coefficient

The temperature data from the battery performance test which was conducted in a thermal chamber can be used for calculating the heat transfer coefficient. This parameter is important especially in predicting the battery surface temperature and for heat removal calculation. To quantify the value of the coefficient, temperature during relaxation given from the two pulse discharge were used, as shown in Fig. 4.29. The dotted rectangular line shows the area which was considered in the calculation.

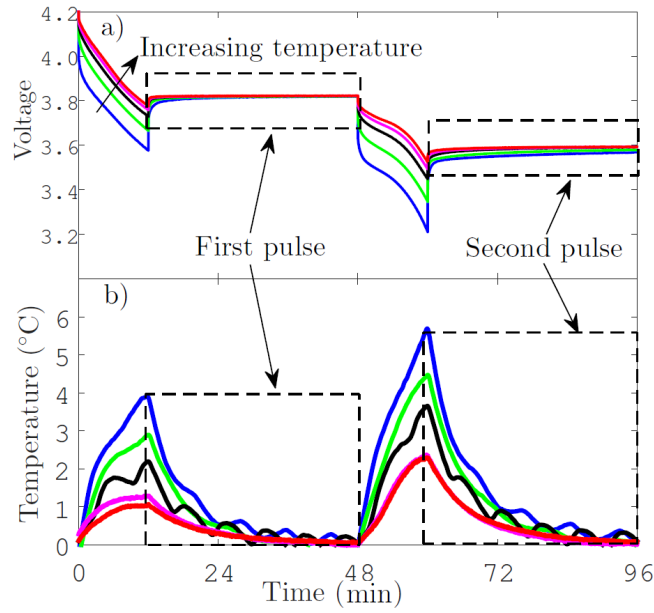


Figure 4.29: The regions for heat transfer coefficient calculation

By assuming the temperature in transverse and longitudinal direction are spatially uniform during the relaxation period, the convective heat transfer coefficient can be calculated by using the energy balance equation describes in Eqn. 4.85. Further derivation reduces the equation to a simple exponential form which is shown in Eqn. 4.86. The (τ) represents the characteristics of cooling time as shown in Eqn. 4.87. Therefore, by plotting the temperature drop during the relaxation period at different test temperatures, the heat transfer coefficient can be calculated by finding the gradient of the linearized temperature drop according to Eqn. 4.88. The slope equals to the characteristics of cooling time with the values shown in

Fig. 4.30 (a) and (b) at different test temperature given from the first and second pulse respectively.

$$(\rho C_p)(v_{vol}^{cell}) \frac{dT}{dt} = -hA_s(T - T_\infty) \quad (4.85)$$

$$T - T_\infty = e^{-\frac{t}{\tau}} \quad (4.86)$$

$$\tau = \frac{\rho C_p v_{vol}^{cell}}{hA_s} \quad (4.87)$$

$$\ln(\theta) = \frac{-hA_s}{\rho C_p v_{vol}^{cell}} t \quad (4.88)$$

Two regions were included in the calculation mainly to probe if there was any variability in cooling at different SOC. Fig. 4.30 (a) and (b) show linearized temperature during relaxation at 60% and 20% SOC respectively. On average, the value of characteristics cooling time given from the second relaxation period is slightly lower than the value given from the first relaxation period. The calculated characteristic cooling time from the second relaxation period is 491.9s while the characteristic cooling time from the first relaxation period is 556.2s. The variation in the characteristic cooling time is expected because the difference between the battery temperature with the ambient temperature during relaxation period is not identical at both relaxation period.

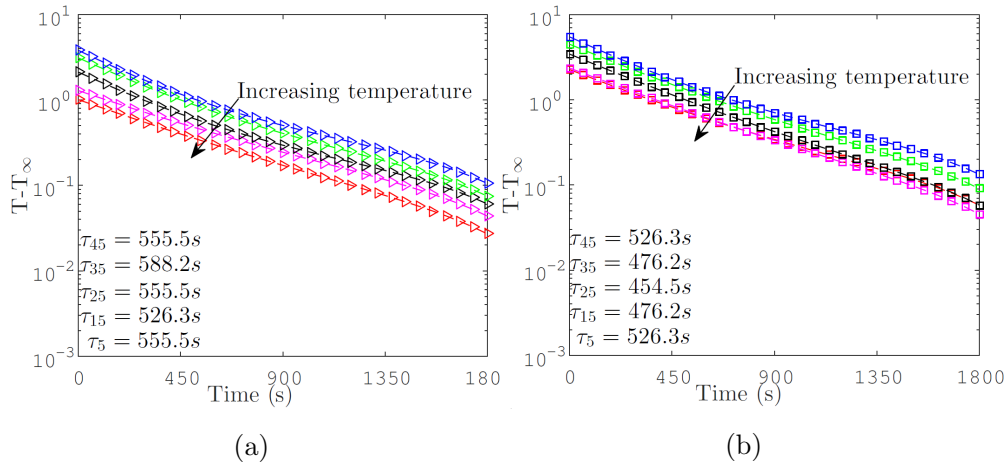


Figure 4.30: Linearisation of temperature evolution after current interruption based on : (a) Interruption after first pulse, (b) Interruption after second pulse

Technically, the lower the characteristics cooling time, the faster the temperature to drop or to reach the ambient temperature. Therefore the value of heat transfer coefficient given from the second pulse will be higher as a consequence of having higher temperature difference. However, since the fan inside the thermal chamber operates at the same constant speed, hence the forced convection will be the same albeit the setting environment temperatures inside the thermal chamber are different. The calculated heat transfer coefficient by using data from the first relaxation and second relaxation period are 20.26 and 22.91 $\text{Wm}^{-2}\text{K}^{-1}$ respectively. The average value of 21.58 $\text{Wm}^{-2}\text{K}^{-1}$ was used in the electrochemical-thermal model for the current work, and this value lies within the lower range of forced convection of gases given from Cengel (1998).

4.4.5.2 Surface temperature prediction using lumped capacitance thermal model

As a result of fitting the six physiochemical parameters by linearisation of the Arrhenius equation, the battery performance can be simulated with reasonable agreement from thermal and electrochemical aspect as illustrated in Fig. 4.31 (a) to (e) for different thermal chamber temperature. The simulation data are compared with the test data obtained from testing under the convection thermal control. This comparison yields maximum RMSE of 18.3mV and a maximum deviation of 64.1mV. On the thermal aspect, the maximum deviation is less than 1.5°C. This highlights the importance of having data under the isothermal condition which acts as a thermal reference. Therefore, the prediction of the battery performance can be made according to its surface temperature regardless the external thermal boundary conditions.

Due to the difficulty to model the convection condition given by the fan in the thermal chamber, it is desirable to assume the convection coefficient to be constant with the value of 21.58 $\text{Wm}^{-2}\text{K}^{-1}$ which is obtained from the heat transfer coefficient calculation. Moreover, since the sinusoidal behaviour of the temperature is mostly manifested during the relaxation period which does not affect the battery performance, it is still applicable to assume a constant rate of heat loss. The sinusoidal temperature variation is apparent, particularly at 25°C. However, the behaviour of the sinusoidal temperature has a considerably small pulse amplitude which can be neglected as depicted in Fig. 4.31 (c).

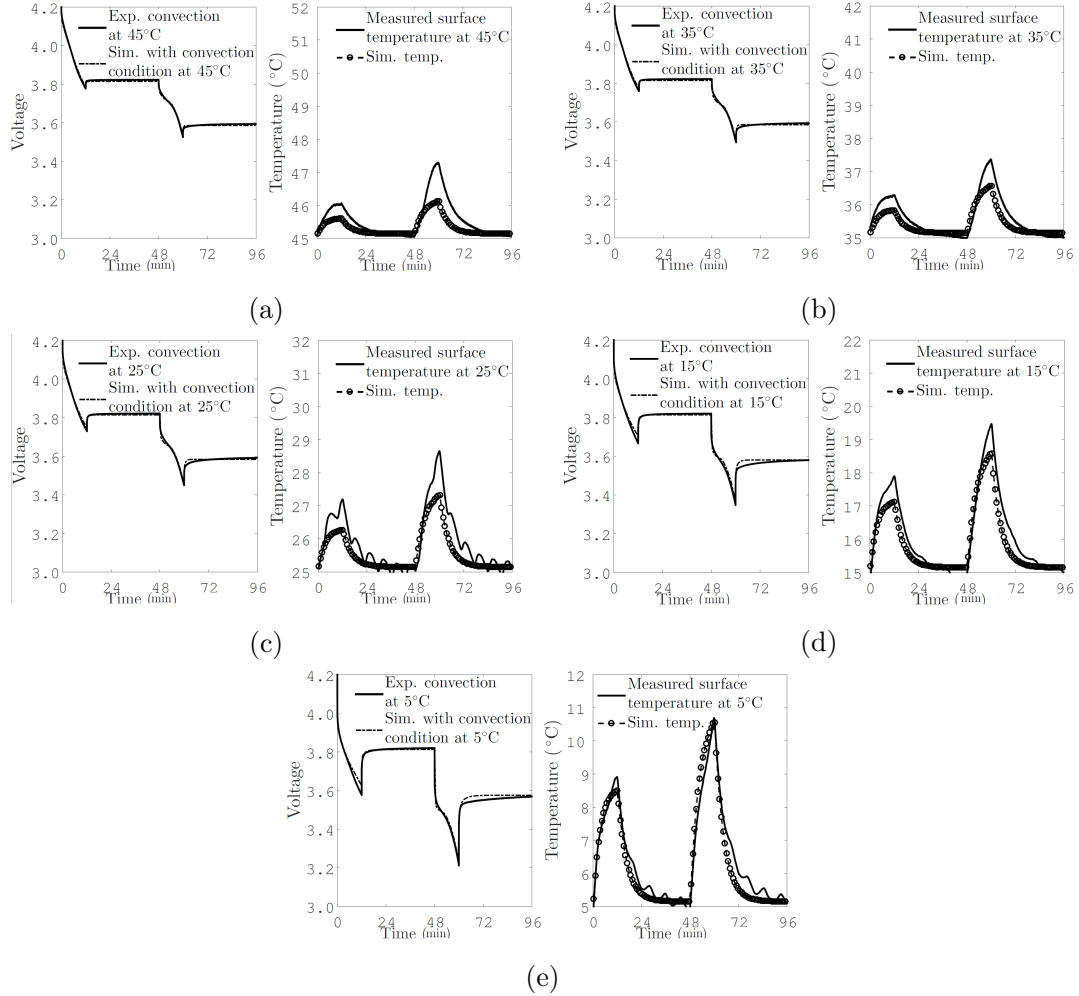


Figure 4.31: Comparison of simulated voltage curve along with temperature prediction with voltage obtained from convection thermal control at : (a) 45°C, (b) 35°C, (c) 25°C, (d) 15°C and (e) 5°C

4.4.5.3 Surface and internal prediction using dual uni-directional current battery model

It is inherently difficult to measure the internal temperature of a battery particularly at a battery pack level. As previously stated in the literature review, the conventional method of measuring the internal temperature by embedding a thermocouple inside of a battery will affect its electrochemical performance. Therefore to avoid this, the internal cell temperature is predicted by using a model that accounts for internal and surface temperature. The latter is validated by comparing the predicted temperature with the experimentally measured surface temperature.

The battery performances at all temperatures are simulated with the aim to replicate both thermal and electrochemical aspect on a surface level before its internal behaviour can be further estimated. Table 4.20 shows the comparison of RMSE and maximum deviation error for the prediction made using the lumped capacitance thermal model and the dual uni-directional current model by using the experimental data from the convection thermal control as a reference. The error calculation does not include relaxation period due to its comparatively long waiting time which could eliminate the impact on battery performance given by the thermal gradient. It can be seen that both models give the largest RMSE, particularly at low temperature. Nevertheless, the errors are still considered to be small based on the total battery operating voltage. In general, both models can yield a good agreement with the experimental data.

Some compelling findings which could unravel the effect of thermal gradient on the battery performance are shown on the right-hand side of the Table 4.20. Although both models can predict the surface temperature variations relatively similar, the resulting voltage curve as a consequence of using different thermal approach is relatively different. The voltage curve given by the lumped thermal capacitance model consistently over-predict the experimental data. These are reflected by the higher maximum error given by the model as compared to the dual uni-directional current model. On the other hand, the dual uni-directional current model demonstrates better accuracy due to its ability to take into account the internal and surface temperature. Fig. 4.32 (a) to (e) reveal the ability of this model to simulate the surface and predict the internal temperature which is caused by the convection thermal conditions and low thermal conductivity in the transverse direction at various thermal chamber temperature. It can be seen the model is able to pick up the surface temperature given from the experimental data reasonably good with a maximum

temperature difference of 1.5°C.

Previously in the lumped capacitance thermal model, the battery performance at a different temperature is dictated by its solid phase diffusion. However, by considering the surface and internal temperature, have caused the battery performance to be also governed by the local current. The dual uni-directional current model divides the battery into an external and internal layer. Since the external layer is exposed to the ambient, its temperature will be lower than the temperature of the internal layer, therefore, creating a thermal gradient. This causes the resistance of the external layer to be relatively higher than the resistance of the internal layer. Consequently, the internal layer discharges faster or operates at a relatively higher discharge rates. Therefore, when the discharge stops, the internal layer will be at lower SOC as compared to the SOC of the external layer albeit both layers experience the same discharge duration.

Each of the battery layers experiences constantly changing discharge rates depending on its effective temperature which eventually causes SOC imbalances. Since the layers are connected electrically in parallel, its overall electrochemical performance is dictated by the cell that has the lowest capacity or SOC. The dual uni-directional current model has the ability to take into account the effect of the local current and solid phase diffusion in predicting the battery performance as compared to lumped thermal capacitance model that only considers the solid phase diffusion. With these attributes, the battery performance can be predicted with better accuracy.

Table 4.20: Comparison of RMSE and maximum deviation between lumped thermal capacitance model and dual uni-directional current model

Temp.	RMSE for lumped thermal	RMSE for dual	Max. dev. lumped thermal	Max. dev. dual
45°C	8.1mV	8.1mV	17.8mV	16.2mV
35°C	10.1mV	10.1mV	26.6mV	26mV
25°C	12.2mV	12.6mV	39.4mV	38.9mV
15°C	18.2mV	20.8mV	46.4mV	43.7mV
5°C	21.6mV	27.7mV	64.1mV	61.4mV

At high ambient temperature, the predicted internal temperature is almost similar to its surface temperature. However, at low ambient temperature, the internal surface temperature is predicted to be up to 4°C higher than its surface temperature. This occurs due to the fact that the heat generated at low ambient

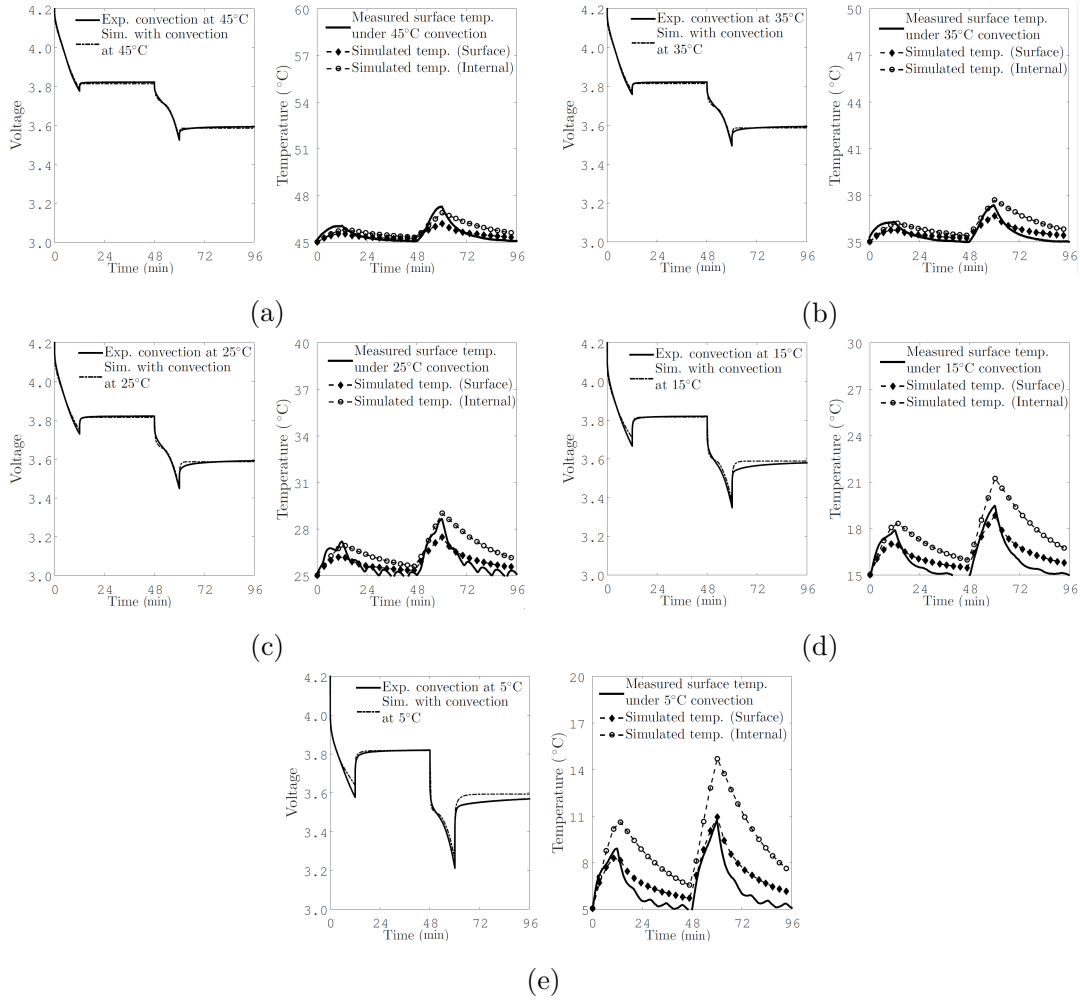


Figure 4.32: Prediction of voltage, surface and internal temperature by using dual uni-directional current battery model

temperature is significantly higher than the heat generated at high ambient temperature. When the rate of heat removal by the surface forced convection is constant, having high heat generation causes the heat to accumulate and low value of thermal conductivity in the transverse direction will exacerbate the thermal condition of the internal layers. This is not a concern for the layer on the surface because it is directly exposed to the convective environment; hence, the heat generated in this region can be directly transferred to the ambient. On the other hand, the internal layer accumulates heat at a higher rate than the rate of heat conducted to the surface due to poor cross-plane thermal conductivity, therefore, causes the internal temperature to be higher than the surface temperature.

Fig. 4.33 compares the deviation of surface temperature with its isothermal temperature and the difference between internal and surface temperature. It can be

seen that if an isothermal condition is concerned, the convective condition which is provided by testing inside a thermal chamber is definitely a poor choice of thermal control. This is because the surface temperature deviates significantly from its isothermal temperature, particularly at low ambient temperature. At this condition, the heat generation is greater than the heat generated at high ambient temperature, therefore, causes a larger deviation between internal and surface temperature.

The temperature increase could be suppressed by increasing the fan speed which ultimately enhances the heat transfer rate on the battery surface. Nevertheless, it is still challenging to keep the battery surface temperature relatively constant by employing the convective thermal control due to the fact that the battery heat generation is highly non-linear. These results indicate that the lower the ambient temperature, the greater the level of temperature non-uniformity or thermal gradient. Therefore necessitates more thermal discretization to probe the effect of thermal gradient on the battery performance.

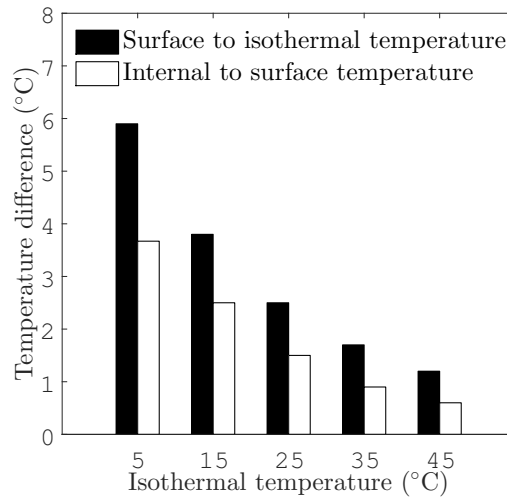


Figure 4.33: Histogram showing the comparison between internal and surface temperature at different isothermal temperature

It should be noted that although two regions are adequate for this work, much more would be needed to adequately describe the thermal gradients inside a cell at higher C rates or for more complicated load cycles. However, the purpose of this work is to show that the thermal gradients should never be ignored, not to comprehensively test how thermally discretised a model should be for a particular requirement.

4.4.6 Current deviation under thermal gradient

Due to the impact of the thermal gradient, the internal layer will be hotter as compared to the surface layer. Therefore causes larger currents to pass while the remaining current will pass through the colder region. These findings extend from Ye et al. (2012) confirming that the current deviation is determined by the local temperature of the layers where the internal layer always receives high current due to the rate of temperature increase is higher than the rate of temperature increase given by the external layer. The work was then extended by highlighting the impact given from thermal contact resistance between layers which caused the maximum temperature to increase and at the same time induced a thermal gradient as described by Ye et al. (2014). Nevertheless, the reported work did not demonstrate the interplay between thermal and electrochemical due to thermal gradient while the latter investigated the effect of thermal gradient only based on different thermal conditions which were adiabatic and convection without considering the effect of heat generation at various temperature. This study, therefore, integrates the investigation of an internal non-uniformity of thermal and electrical of a battery along with the typical temperature range experienced by the electric or hybrid vehicle.

The dual uni-directional current model predicts appreciable differences of current between the hotter and colder region as illustrated in Fig. 4.34 (a) for temperature region of 45°C to 5°C. At the early stage of discharge, the external current is divided evenly. Therefore, the amount of current entering each layer is identical. This is because the temperature difference between the layers at the early stage of discharge is not significant hence, the value of the local resistance for each layer is relatively equal. Nevertheless, this only occurs for a short period. When the difference in temperature is noticeable, the current starts to deviate. The layer with higher temperature experiences higher current than the ones with lower temperature. This is primarily due to the effect of low resistance which is generated when the temperature is high. Towards the end of discharge of the second pulse, the current of the hotter region decreases while the current at colder region increases. This is due to the resistance increasing rapidly at low SOC and the SOC of the hottest region dropping faster such that its resistance becomes higher than the resistance of the cold region although it is still hotter according to Zhang et al. (2013).

Interestingly, although the behaviour of the current for the internal region at all temperatures may be physically identical, the magnitude are distinct at different ambient temperature. This behaviour also applies for the current at surface

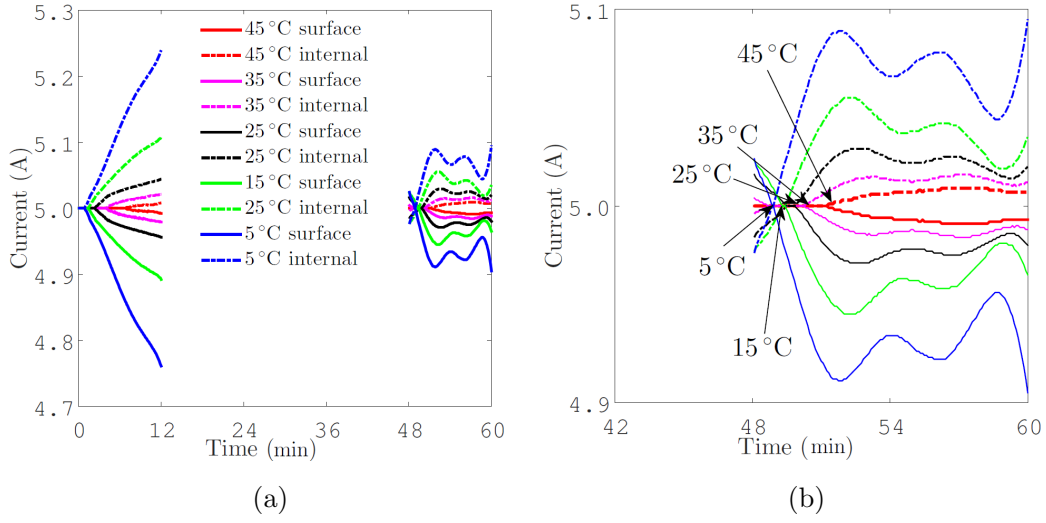


Figure 4.34: (a) Current deviation at different region, (b) Current deviation point at different temperature

region but in reversed manner. This phenomenon can be explained by the differences of the simulated temperature between the internal and surface region at each ambient temperature as illustrated in Fig. 4.35. It can be seen that at low ambient temperature, the temperature difference between internal and surface region is pronounced with the maximum temperature difference of 4°C while at high ambient temperature, the maximum temperature difference is approximately less than 1°C.

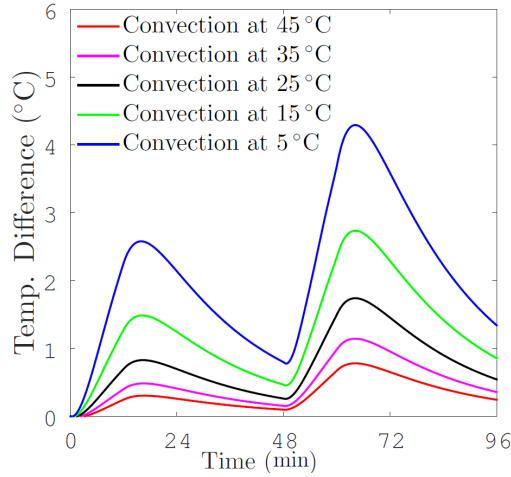


Figure 4.35: Temperature difference between surface and internal region

Significant thermal non-uniformities at low ambient temperature have induced the current of surface and internal layer to diverge at a different rate as compared to the rate of the current divergence at high ambient temperature. The change of the current over time are $21.4 \frac{mA}{min}$ and $1.5 \frac{mA}{min}$ at low and high ambient temperature respectively which is calculated based on the first discharge pulse. On

the other hand, the effect of the thermal gradient towards SOC non-uniformities has resulted in different crossover point of the current distribution which can be seen at the second discharge pulse as illustrated in Fig. 4.34 (b).

The change of the current distribution at the second discharge pulse is mainly caused by the effect of counter reacting between the potential drop and the local SOC non-uniformities. The current crossover for low temperature occurs at the early stage of the second discharge pulse, indicating that the battery is operated at low SOC. Conversely, the current crossover at high temperature happens relatively late as compared to low temperature which demonstrates that the battery is operated at higher SOC. The variation in current crossover is attributed to the different in overpotential at various temperature. High overpotential at low temperature causes the SOC to be lower than the SOC given by high temperature

For the 10 Amps and 24 minutes of total discharge time investigated here, the total ampere-hours throughput is 4Ah which should be equivalent to 2Ah from each region if the discharge occurs in a condition where both regions possess the same temperature. However further analysis shows that the internal region, consistently gives higher ampere-hours throughput and since the total charge is the same regardless of any temperature value, this causes the predicted ampere-hours throughput for the surface region to be comparatively lower as illustrated in Fig. 4.36.

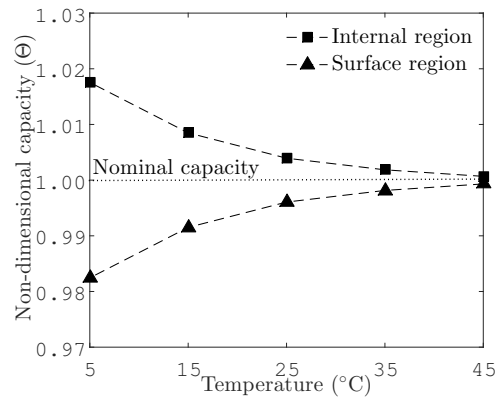


Figure 4.36: Non-dimensional capacity comparison between internal and surface region

This comparison is made by finding the ratio of the area under the curve given from each of the individual current plots to a reference capacity of 2Ah² which

²2Ah is the nominal capacity for 24 minutes discharge if there is no thermal gradient. Under the isothermal condition, the external current is evenly divided therefore each layer is discharged at 5Amps

is described by Eqn. 4.89. If there is no thermal gradient, the non-dimensional capacity of the internal and external layer should be at unity. However, due to the thermal gradient, the internal layer is over-utilised while the external layer is under-utilised. This deviation signifies that the layers operate at different SOC due to continuously changing of discharging rate. Although the difference in SOC between the region is not significant, it has been shown previously that the SOC inhomogeneity can become important if the cell is aggressively charged/discharged with high current over long periods of time as described by Fleckenstein et al. (2011).

$$\Theta = \frac{\sum \int I_i dt}{\int I dt} \quad (4.89)$$

4.5 Conclusion

The integration of the presented experimental and numerical works are generally to establish understanding on the limitation of the thermal chamber which provides thermal control by convection if the isothermal condition is concerned. If the thermal control or heat transfer is carried out mainly from the transverse direction, the transient thermal response will be poor due to the low value of Fourier number and high value of Biot number. This work shows the limitations of using forced air convection for cell testing, i.e. thermal chambers, particularly at low temperatures, and how such data should not be used to parameterise models that do not take into account internal heating effects and thermal gradients. Even fitting models which take these effects into account to this data will be difficult if the internal temperature profile is not known. The data gathered using conductive environment can be used to parameterise models that do not take into account internal heating effects and thermal gradients, as the cooling method is able to achieve conditions far closer to the isothermal conditions than forced air convection. The parameters fitted to this data can then be used in a model that does take into account internal heating effects, and thermal gradients to far better predict the performance of a battery under conditions where internal gradients are dominant particularly below the operating temperature of 25°C. The internal temperature is expected to be far higher than the measured surface temperature for more aggressive conditions.

This result is expected to be particularly useful for those conducting tests to understand and predict the performance of batteries in real world applications, especially to parameterize and validate models used in battery management systems for state and parameter estimation, especially SOC and internal temperature. The novelty of this work lies in the integration of the experiment data obtained from close to an isothermal condition with the physics based battery model for the purpose of investigating the differences of the physiochemical parameters at different external thermal condition. These differences indirectly highlight the error caused by different external thermal condition. Moreover, the work presented also gauges the limit of the use of thermal chamber in providing an isothermal condition.

Low order battery models are often fitted against data provided from a wide range of temperature testing for control engineer to use in BMS for prediction of SOC, SOH and cell temperature in a battery pack. This work demonstrates that both heating effect and thermal gradients must be taken into account, but that is for

applications up to 2C and between 45 to 5°C, such as an electric vehicle, a model with just two thermally discretised regions should be sufficient. More aggressive applications, such as hybrids would most likely require more complicated thermal discretisation. This work also suggests that data from thermal chambers should not be used to fit and parameterize these models without taking into account the heating effect and thermal gradients.

Chapter 5

Effect of conductive surface cooling/heating on batteries connected in parallel

5.1 Introduction : Internal temperature of a parallel connected battery

The specific objective of this experiment is to analyse the feasibility of getting an isothermal condition by enhancing the cooling/heating rate on the surface battery temperature. Furthermore, these results can be used to validate an electrochemical-thermal battery model in predicting the battery internal temperature. In pursuance of this, a dedicated thermal control system is utilised which allows the battery surface temperature to be controlled independently.

The direct temperature measurement in the battery core is desirable for validating a battery model which considers the prediction of the internal temperature. However, from an experimental point of view, the direct temperature measurement by means of installing a thermocouple inside a battery would not be a sensible approach if high C-rate operation and extreme operating temperature are concerned. Therefore this chapter presents an experimental technique to re-create the internal condition of a battery and furthermore measured the internal temperature at different operating temperature. The earlier part of this section explains the experimental procedure attempted for measuring the internal temperature. Sub-

sequently, coupled thermal-electrochemical model is used to described non-uniform behaviour. The analysis predicts the current distribution at different applied surface temperature.

5.2 Assumptions and experimental technique

Two 5Ah Kokam batteries were used and connected in parallel which is analogous to the method presented by Zhang et al. (2016) as illustrated in Fig. 5.1. The technique in measuring the internal temperature is conducted by securing several thermocouples between the two batteries with the aim to isolate the effect given from external thermal condition. The experiment system includes two independent surface temperature control mechanism and a Biologic HCP-1005 with 100A current booster to control the charge/discharge of the battery as shown in Fig. 5.1 (b).

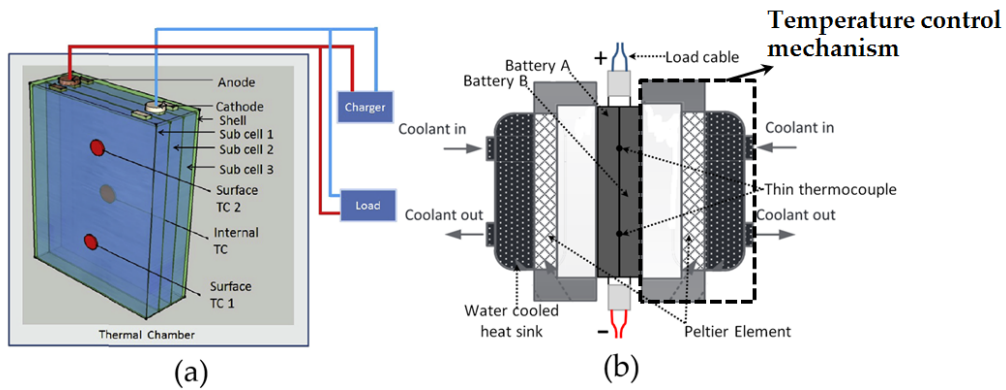


Figure 5.1: Experimental set-up for : a) Prismatic LiFePO₄-Graphite battery in parallel by Zhang et al. (2016), b) Two 5Ah Kokam battery connected in parallel with conductive surface temperature control

This method might not be an actual representation of the internal condition of a battery because the battery internal temperature is not measured at the 'core area' of the battery instead, the 'core area' is represented by a temperature between two batteries connected in parallel. However, by applying a firm pressure to keep the two batteries to be intact as illustrated in Fig. 5.1 (b), could potentially reduce the thermal interaction between the internal with the external thermal condition. This technique creates an artificial internal condition which could be closed to the actual internal condition of a battery without having to interfere the internal electrochemical process of the battery. Hence, the battery can be tested at high C-rate and wider temperature range.

The same charging protocol was applied after each discharge tests conducted at several constant surface temperature. This is to ensure the battery has the same SOC at the beginning of the discharge test. The protocol includes a constant current-constant voltage charging (CC-CV) at 25°C. The 100% SOC is obtained when the voltage level reaches 4.2V, and the current for constant-voltage charging is below 50mA. The battery was kept at the constant temperature provided by the conductive surface temperature control for at least 1 hour. This is to ensure that the battery reaches the thermal equilibrium condition before discharging can be performed.

In a parallel connected battery, the total capacity of the parallel string becomes the sum of the capacity of the individual battery. Hence, the total capacity of this parallel connected battery has doubled, from 5Ah to 10Ah. Previously, only one Kokam 5Ah battery was used, with discharging current of 10A. Therefore, to closely replicate the internal non-uniformity experienced by the single battery, the external current for the parallel connected batteries was increased to 20A. The increased of the external discharge current is primarily to make the heat generation of the parallel batteries to be comparable with the heat generation of the single battery. Nonetheless, this comparison cannot be used as a reference because the Biot number for a single battery is lower than the Biot number of two batteries connected in parallel. With the increase in the Biot number, the occurrence of the thermal gradient in the transverse direction is expected. The Biot number constitutes an indication of temperature uniformity of a solid body. As a result, a temperature gradient is likely to occur in a solid body that possesses a high Biot number. For that reason, although the heat generation for a single battery and parallel battery is relatively equal, the resulting non-uniform behaviour cannot be compared. Hence, the differences in battery performance are treated as an assessment for battery with different thickness and thermal conditions.

Because of the parallel connection, the total current is evenly divided according to the Kirchhoff's law. Therefore, each battery in the parallel string receives an equal amount of current which is relatively identical to the amount of current for a single 5Ah battery. However, the equal current distribution can only happen if both of the batteries have the same thermal condition. This is important because the battery temperature has a significant influence on its internal resistance. Therefore, by controlling the battery surface temperature by conduction, both battery surfaces can be at the same temperature, causing the internal resistance at each battery to be identical. Fig. 5.2 shows the physical comparison of a single battery

with the parallel connected battery. Two separate rectangular dotted lines in the figure represent the region of similarity with regards to the heat generation at the same given C-rate. Although the area of the parallel connected battery is relatively larger, the local heat generation is still comparable with the heat generation of a single battery because each of the cells in the parallel connected battery receives the same amount of current.

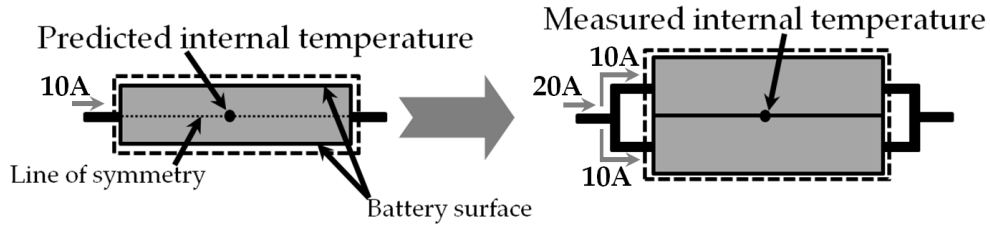


Figure 5.2: Physical comparison of a single battery with the parallel connected battery for internal temperature prediction/measurement

5.2.1 Set-up

This surface temperature control uses a total of six thermocouples. Four K-type thermocouples with the diameter of 0.2mm, are used to provide input to two PID controllers (Thermocouples on each battery surface). These controllers are responsible for regulating the amount of power required by the Peltier element to keep the battery surface temperature relatively unchanged. The Peltier element is attached to a copper plate by using a thermally conductive adhesive. The copper plate serves as a heat spreader or heat sink/source which provides a constant temperature surface as schematically shown in Fig. 5.1 (b). On the other hand, the measurement of the internal temperature is conducted by using two thin K-type thermocouples with the diameter of 0.075 mm. The fine thermocouple is chosen in this experiment to prevent damage on the battery surface. A uniform thermal contact between the battery surface and copper plate is achieved by clamping the parallel connected battery between the temperature control mechanism. If the diameter of the thermocouple which sits between the battery is thick, it will damage the battery surface. This could generate an internal short circuit and therefore causes the data collected to be unreliable.

Fig. 5.3 shows the location of the thin thermocouple and the battery arrangement from several views. Before placing the parallel connected battery on the surface temperature control rig, the batteries were partly wrapped by using Kapton

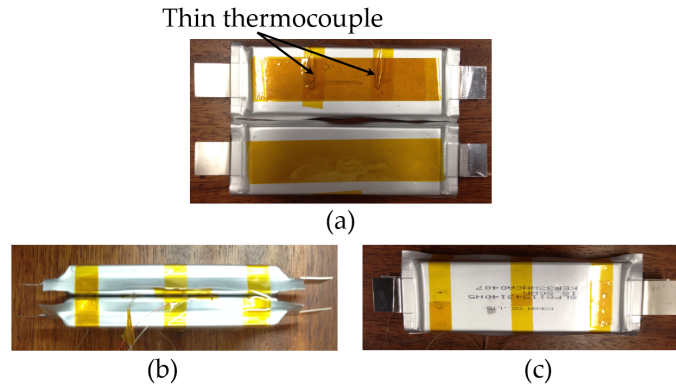


Figure 5.3: Arrangement of thermocouple : a) Two thin thermocouple to measure internal temperature, b) Top view of the connected batteries, c) Front view of the connected batteries

tape as illustrated in Fig. 5.3. This is to ensure the battery to be physically in parallel relative to the other battery and to create a single body for ease of handling before it can be firmly clamped on the surface temperature control rig.

5.2.2 Calibration of the internal temperature measurement

The heat generation at the internal region is accountable for the response to the internal temperature measurement. Calibrating the internal temperature by introducing an artificial heat generation is problematic because of the limited space at the periphery of the thermal control system. However, since the battery surface temperature can be independently controlled, the internal temperature measurement can be calibrated by applying different temperature at each of the battery surfaces. This eventually creates a temperature gradient along the transverse direction.

Following this method of calibration, the battery temperature was set at the constant temperature of 45°C and 5°C at each of the battery surfaces allowing an artificial thermal gradient to occur. Fig. 5.4 shows the temperature response at several thermocouple locations along the transverse direction. Two auxiliary thermocouples were placed at the edge of the battery surface to add more points for checking the temperature response as shown in Fig. 5.5 (a). Initially, the temperature along the transverse direction measured the lab temperature which was at 24°C . The Peltier element which is located at each of the battery surfaces receives a different amount of power because the target temperature at each battery surface is not identical. The two PID controller which were linked to each of the Peltier element

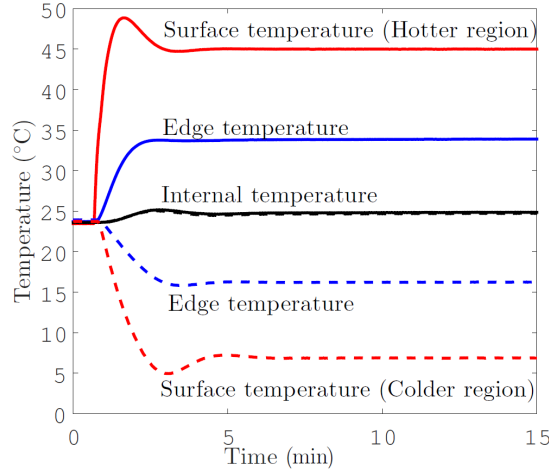


Figure 5.4: Temperature evolution at several location in the transverse direction at temperature gradient of 45°C/5°C

rectified the different amount of power required based on the thermocouple reading at each of the battery surfaces. This causes the surface temperature to overshoot slightly above the target temperature of 45°C and undershoot marginally under the target temperature of 5°C. On the contrary, these behaviour is not manifested at other location in the transverse direction. For instance, the edge temperature near to the hotter region increases exponentially while the edge temperature near the colder region decreases exponentially over time. The applied temperature gradient influences the behaviour of the edge temperature. A stark difference in temperature response is observed at the mid-point of the parallel connected battery. The temperature at this region just increases slightly above the lab temperature. Because the internal temperature is located at the mid-point of the parallel connected battery, its behaviour is dictated by the region which has the highest net temperature change. When both of the surface temperatures reach a steady state condition which is approximately after 5 minutes, a linear temperature gradient can be seen.

When a steady-state thermal condition has been reached, the temperature at various locations along the transverse direction will be unchanged. This condition is necessary for the calibration process. Theoretically, the internal temperature should indicate the average value of the two target temperatures applied on each of the battery surfaces. Therefore, some tuning is required to rectify the internal temperature reading if its value deviates from the average temperature of two battery surfaces. However, based on experimental data presented in Fig. 5.4, it seems that no temperature tuning is required. This is because the value of internal temperature at the steady-state condition is exactly 25°C which corresponds to the average

temperature given by the battery surface temperature combination of 45°C/5°C.

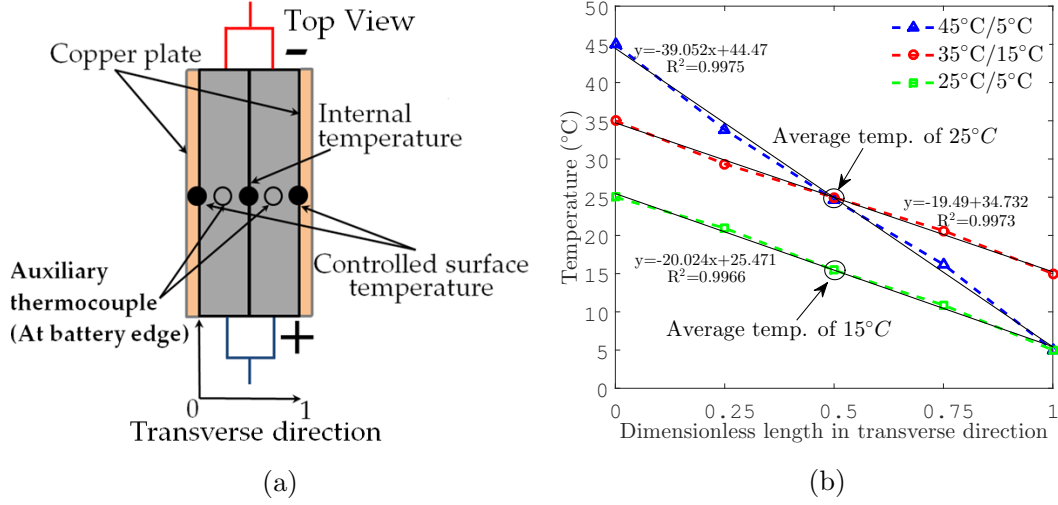


Figure 5.5: (a) Thermocouple location along the transverse direction (View from top), (b) Temperature gradient under steady-state condition at the average temperature of 25 °C and 15 °C (The circle represent the internal temperature)

To further investigate the response of the internal temperature, two additional temperature gradient cases with the combination of the surface temperature of 35°C/15°C and 25°C/5°C were applied. Fig. 5.5 (b) compares the temperature variation along the transverse direction under a steady-state thermal condition. The location of the measured temperature is represented in Fig. 5.5 (a). It can be seen that the internal temperature at each of the temperature gradient conditions reacts considerably well following a linear correlation. Moreover, the internal temperature can pick up the average value based on the different temperature applied on each of the battery surfaces. These results suggest that the internal temperature does not need any further tuning.

This calibration procedure is merely to examine the response of the internal temperature measurement by applying an artificial temperature on the battery external surfaces. However this method could be unsuitable to be used for calibrating thermocouple for measuring an actual internal battery temperature. The primary reason for this is that the physical condition for two batteries being clamped together is considerably different from the internal structure of battery which consists of several layered of active material. Nevertheless, this method could be useful for validating battery model that considers internal and surface temperature. By keeping the battery surface constantly reduces the effort for the battery thermal parameterisation.

5.3 Experimental results

Fig. 5.6 (a) compares the voltage curve at a different constant surface temperatures. It can be seen that the voltage drop at high constant surface temperature is relatively lower than the voltage drop at low constant surface temperature following the Arrhenius relationship. Although the total charge taken due to 20A pulse discharge remains the same at all temperature, the overpotential at low temperature is significantly higher than the overpotential at high temperature. This is the reason for the different rate of voltage polarisation at a different temperature. On the thermal perspective, higher overpotential creates higher battery heat generation thereby causing the battery temperature to increase at a higher rate which can be seen in Fig. 5.6 (b). These results are consistent with the results of pulse discharge of a single battery which have been previously discussed.

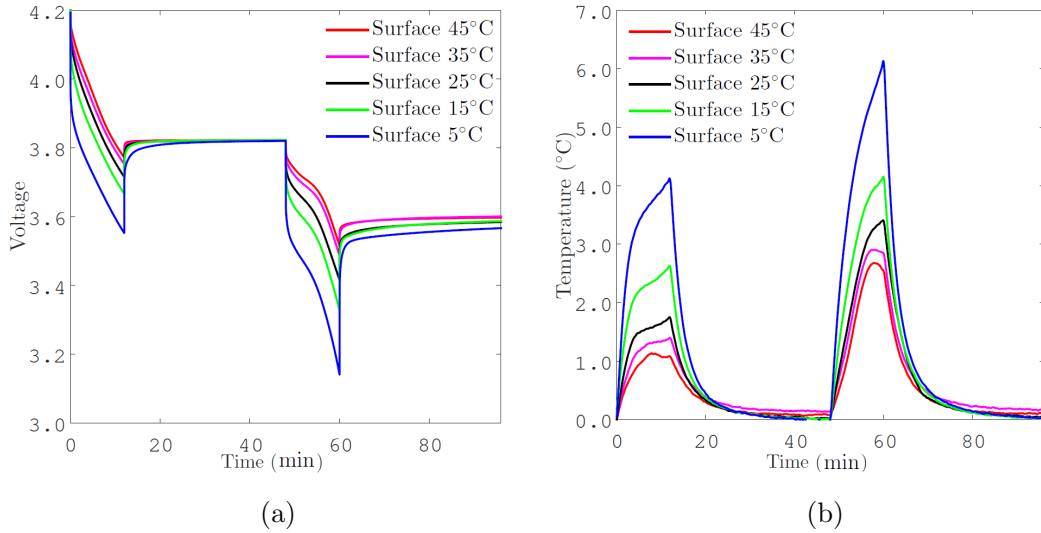


Figure 5.6: (a) Voltage curve under 20A pulse discharge for two 5Ah Kokam battery connected in parallel under a constant surface temperature, (b) Internal temperature increase

Although the surface temperature can be kept at a constant value, a significant internal temperature increase is observed particularly at the low constant surface temperature which can be seen in Fig. 5.6 (b). If an isothermal condition is gauged based on the battery surface temperature, clearly this method is not the right choice. During discharge, the PID controller which is responsible for regulating power required by the Peltier element only corrects disturbance on each of the battery surfaces, ensuring the surface temperature to be relatively constant, therefore, leaving the internal region to be thermally uncontrolled. From a thermal perspec-

tive, this condition divides the surface and internal region into two different thermal reservoir where the surface region resembles a heat sink and internal region as a heat source. Because the thermal conductivity in the transverse direction is significantly low, the rate of heat transfer from the heat source to heat sink is lower than the rate of heat generated at the internal region. This thermal imbalance causes the internal temperature to increase.

5.4 Modelling approach

The model which is executed for the parallel connected battery is analogous to the dual uni-directional current model which has been previously described. However, there is some difference particularly for the thermal boundary condition at the battery surface. The dual uni-directional current model adopts a Neumann boundary condition to represent the convection boundary condition. On the other hand, the model for the parallel connected battery with conductive surface temperature control employs a Dirichlet boundary condition to describe a fixed temperature as shown by Eqn. 5.1.

$$\begin{aligned} q_1^{Total} &= q^{Conduction} \\ T_1 &= T_{surface} \end{aligned} \tag{5.1}$$

$$\begin{aligned} q_2^{Total} &= q_2^c + q_2^j + q_2^r \\ \rho C_p^{eff} V_{half} \frac{dT_2}{dt} &= q_2^{Total} - k_y A_{conduc} \frac{(T_2 - T_1)}{dl} \end{aligned} \tag{5.2}$$

In this work, it is assumed that the heat generated at the battery surface is completely compensated by the conductive surface temperature control, therefore the foil which wraps the battery is ignored in the model. A fixed and constant surface temperature is applied to the node that represents the battery surface. The thermal interaction between the internal and surface region is constructed as such the surface region always acts as a heat sink while the internal region as a heat source as shown in Fig. 5.7. This is because the internal temperature is always higher than the surface temperature, therefore, creating a negative temperature gradient in the transverse direction with respect to the symmetric line. The temperature of the internal region is calculated based on Eqn. 5.2. This equation calculates the

thermal balance between the heat generation of the internal region and the heat transfer by conduction from the internal to the surface region.

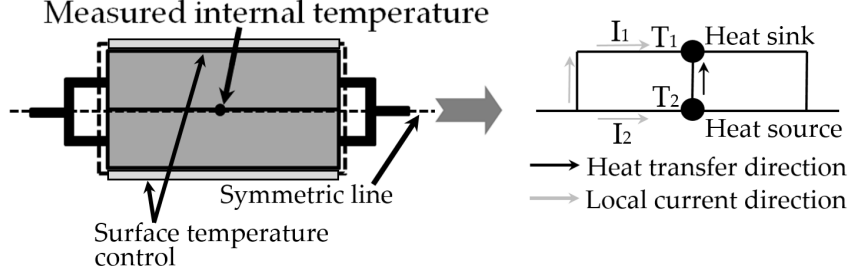


Figure 5.7: Schematic for battery modelling for two batteries connected in parallel with constant surface temperature

5.5 Results analysis : Modelling and experimental comparison

5.5.1 Pulse discharge comparison : Voltage, local current and internal temperature

With the experimental data, especially the internal temperature, it is interesting to evaluate the internal current distribution at a different SOC due to the applied constant surface temperature. The current distribution is caused by the different of temperature between the internal and surface region. Previously, the local current distribution and the battery internal temperature are predicted by using the voltage curve and battery surface temperature under the convection thermal condition as a reference. However, for the present investigation, where both of the battery surface temperatures are kept relatively unchanged, an additional reference can be used in predicting the current distribution of the surface and internal region. Therefore, the prediction of the local current will be more physically meaningful. The battery surface temperature, internal temperature and voltage curve are used as a reference for the electrochemical-thermal model validation. The architecture of the model is made as such the electrical/electrochemical aspect is arranged in parallel while the thermal aspect is arranged in series which is comparable to the electrical and thermal condition experienced in the actual parallel connected battery. This configuration causes the battery performance to be dependent on local temperature and current.

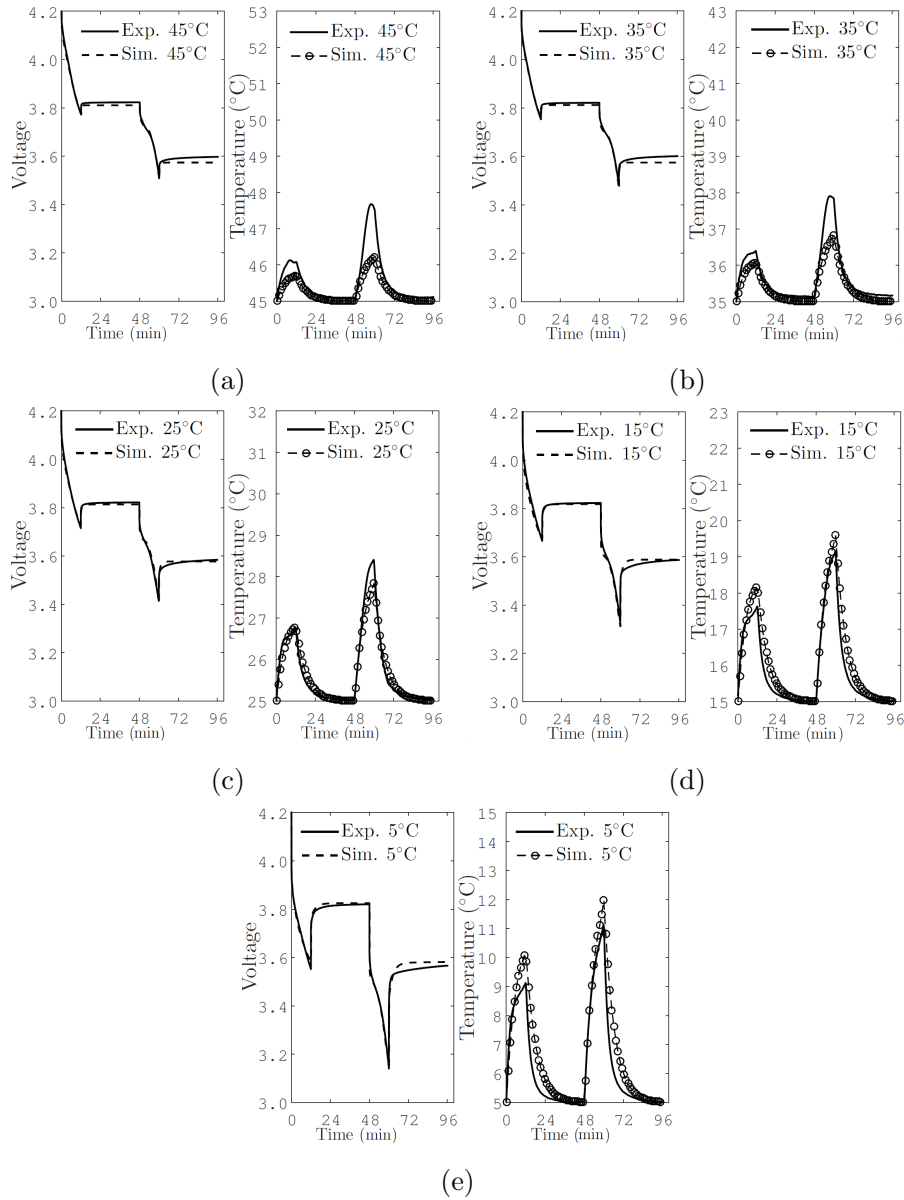


Figure 5.8: Comparison of voltage and internal temperature under pulse discharge between simulated data and experimental data obtained from surface conductive thermal control at : (a) 45°C, (b) 35°C, (c) 25°C, (d) 15°C and (e) 5°C

Fig. 5.8 (a) - (e) compare the voltage and internal temperature between the experiment and simulated data at constant surface temperature of 45°C to 5°C. The surface temperature is not presented in the figure because it is kept at a constant value. Quantitatively, the predicted voltage and internal temperature are in good agreement with the experimental data. A slight deviation can be seen for the temperature and voltage comparison at 45°C and 5°C respectively. The error can be associated with the effect of entropy. In this model, the entropy effect which influences the change of voltage with temperature especially during relaxation is

neglected. The prediction can be improved by adding the entropy coefficient at various SOC. However, this requires monitoring of the change of the open circuit voltage with the temperature at each SOC. Typically, a potentiometric tests are conducted to evaluate the dependency of the open circuit voltage with temperature as described by Eddahech et al. (2013).

Although the entropy is ignored, the model is still able to predict the voltage and internal temperature reasonably well. Additionally, the model can capture the relationship between the internal battery resistance with the applied constant surface temperature. This relationship causes the predicted internal temperature to be at a different rate depending on the applied temperature. The effect of entropy on the predicted internal temperature is negligible especially at the constant surface temperature of 25°C to 5°C. At this temperature range, the reversible heat generation due to entropy is significantly small as compared to the irreversible heat generation due to polarisation, therefore, results to a better internal temperature prediction.

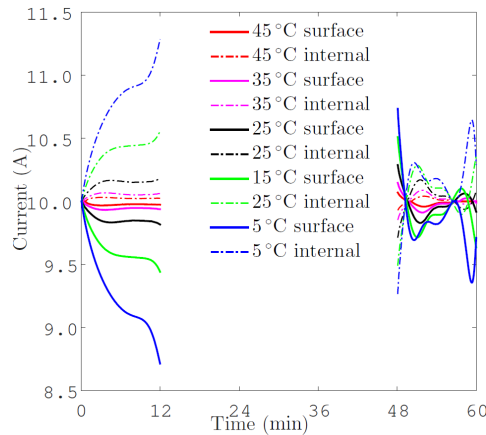


Figure 5.9: Current deviation at different region for constant surface temperature of 45°C to 5°C

As a result of the thermal gradient created from the controlled constant surface temperature, the internal layer is hotter than the surface temperature. Although the surface temperature is kept at a constant value, its local current varies because of the parallel configuration which describes by the Kirchhoff's current law. Therefore, if the resistance of each layer is not identical, the local currents will deviate causing each layer to be discharged at a different rate. Fig. 5.9 illustrates the deviation of current between the surface and internal region at various constant surface temperature. It can be seen that the current deviates at the onset of the first pulse discharge. This deviation is caused by the large temperature difference

between the surface and internal region. Because the temperature of the surface region is kept at a constant value, the resistance of this region is comparatively higher than the resistance of the internal region. Therefore, causing the internal region to experience higher current as compared to the surface region. As the discharge proceeds, the SOC of the internal region will be lower than the SOC of the surface region. The internal and external current behaviour are different at the end of discharge which is shown in the second pulse. This behaviour can be attributed to the counteracting of the local current with the SOC. At the second pulse, the difference of the SOC between the surface and internal region becomes appreciable. Therefore, to compensate this difference, the current at the internal region needs to reduce to allow the current of the surface region to increase.

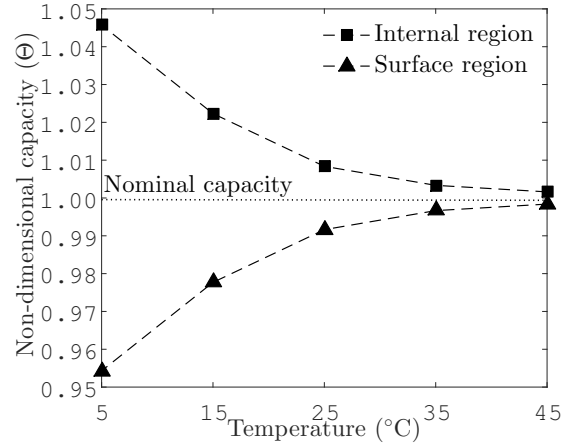


Figure 5.10: Non-dimensional capacity comparison between internal and surface region

The pulse discharge consists of 24 minutes of 20 Amps discharge current. Therefore, the total ampere-hours throughput is equivalent 8Ah. If both regions possess the same temperature, the amount of discharge energy at each region will be evenly divided, which is 4Ah for each region. The internal region is over-utilised particularly at the low constant surface temperature as shown in Fig. 5.10. This is due to the thermal gradient which causes the internal region to experience large currents. Conversely, as a result of the current distribution, the surface region is under-utilised. This comparison is made by obtaining the ratio of local current distribution of the internal and surface region to a reference capacity of 4Ah¹ which is described by Eqn. 5.3. The finite integration is replaced by the trapezoidal rule

¹4Ah is the nominal capacity for 24 minutes discharge if there is no thermal gradient. Under the isothermal condition, the external current is evenly divided therefore each layer is discharged at 10Amps

due to the highly non-linear behaviour of the local currents.

$$\Theta = \frac{\sum \int I_i dt}{\int I dt} \quad (5.3)$$

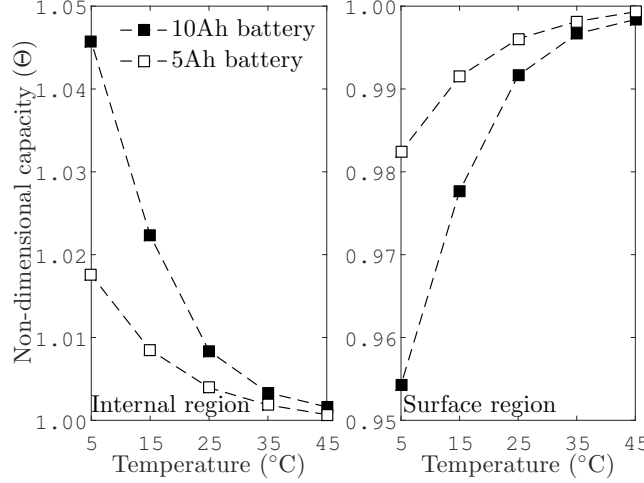


Figure 5.11: Non-dimensional capacity comparison for parallel connected battery-(10Ah) with single battery-(5Ah)

Fig. 5.11 evaluates the difference in capacity between the internal and the surface region for the single battery with 5Ah capacity and parallel connected battery with 10Ah capacity. This figure does not serve as a comparison, because the Biot number for each battery is different. The Biot number for the 10Ah battery is larger than the 5Ah battery by the factor of two. Therefore, this figure serves as an assessment for batteries with different thickness and different applied thermal condition. It can be seen that at high temperature, the deviation of the discharge throughput between parallel connected battery with single battery is not apparent. Nevertheless, the deviation is gradually increased as the operating temperature decreases. These phenomena can be associated with difference in temperature between internal and surface region.

Fig. 5.12 compares the temperature difference between internal and surface region for 10Ah and 5Ah battery. The trend of the temperature difference for 10Ah and 5Ah are analogous in which the temperature difference increases as the operating temperature decreases. However, the magnitude of temperature difference for 10Ah battery is significantly higher than 5Ah battery. Large temperature difference signifies that the battery experiences a thermal gradient at a higher magnitude as compared to a low temperature difference. This condition causes the local current

to be largely separated hence increasing the degree of over and under-utilisation of the discharge throughput for internal and surface region respectively.

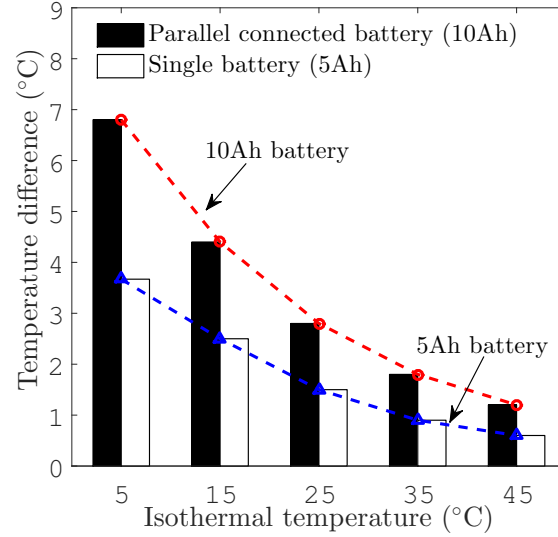


Figure 5.12: Histogram showing the difference between the internal and surface temperature for 10Ah and 5Ah battery

The difference in magnitude in the temperature difference between 10Ah battery with 5Ah battery is caused by the physical and external thermal factor. A Larger temperature gradient is expected to occur for 10Ah battery as compared to 5Ah battery. This is because the thickness of the 10Ah battery is two times greater than the 5Ah battery hence, each of the battery will have different Biot number. From a thermal perspective, the single battery is subjected to a convection condition whereby the air flow in the thermal chamber cools the heat generated at the battery surface. This condition is comparable to the external thermal condition experienced by the 10Ah battery. However, the rate of heat removal from the battery surface is greater for 10Ah battery which can be perceived as a battery with high cooling intensity imposed on its surface. Because the thermal conductivity in the transverse direction is poor, increasing the cooling intensity will promote greater temperature difference. This finding is in agreement with Ye et al. (2014) who found that by just increasing the heat transfer coefficient was not sufficient in reducing the overall temperature increase of a battery. This method was only effective in suppressing the temperature increase on the battery surface, not to narrow down the temperature difference between surface and internal region.

5.5.2 Full discharge comparison : Voltage, local current and internal temperature

Fig. 5.13 compares the simulated data with the test data for 2-C discharge from 100% to 0% SOC at different applied constant surface temperature. The simulated voltage curves are in good agreement with the test data. However, there is some discrepancy between the simulated data with the test data at the constant surface temperature of 5°C. This could be caused by the assumed value of the stoichiometric for anode and cathode which is used in the model, do not match well when the overpotential is high especially at low temperature. Nevertheless, the capacity predicted by the model when the battery is at 0% SOC matches the experimental data reasonably well at all constant surface temperature.

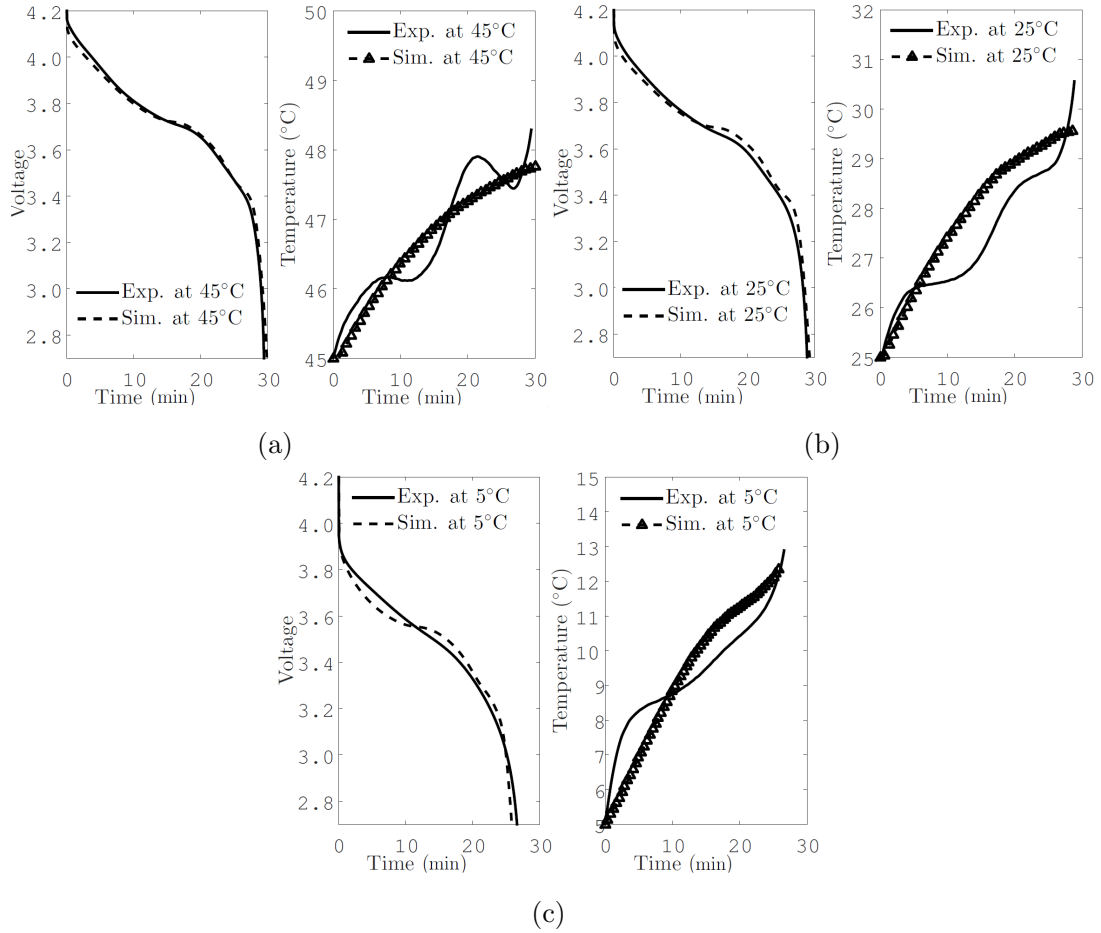


Figure 5.13: Comparison of voltage and internal temperature under full discharge between simulated data and experimental data obtained from surface conductive thermal control at : (a) 45°C, (b) 25°C and (c) 5°C

The internal temperature is predicted without considering the entropic

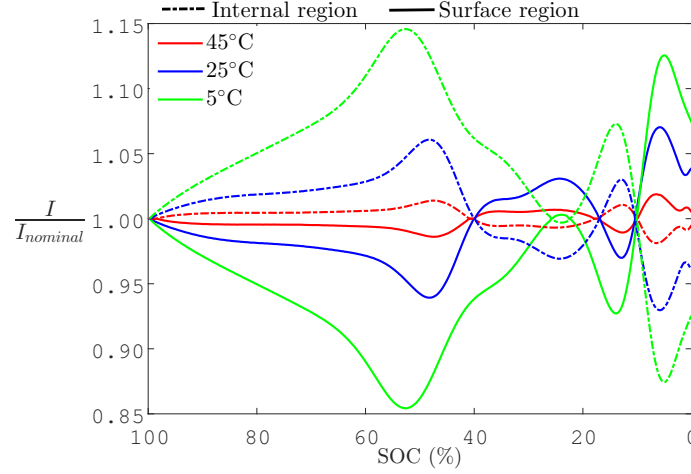


Figure 5.14: Comparison of local current distribution between the internal and surface region at constant surface temperature of 45°C, 25°C and 5°C

heat or reversible heat due to entropy. This simplification causes the model to be unable to capture the oscillations of temperature behaviour especially at the constant surface temperature of 45°C. At this condition, the reversible and irreversible heat generation are comparable. Technically, the irreversible heat is always positive while the entropic heat can be either positive or negative depending on the current polarity and the entropy coefficient at certain SOC. Therefore, the heat generated at 45°C increases and decreases causing the internal temperature to oscillate. Strong temperature oscillation is not manifested at 25°C and 5°C.

Additionally, at these temperature points, the internal temperature profile does not experience a gradual temperature drop. However, there is a period where the temperature increases monotonously. The period is relatively longer at the constant battery surface temperature of 25°C than at 5°C as illustrated in Fig. 5.13 (b) and (c) respectively. This temperature behaviour suggests that although the irreversible heat governs the overall heat generation, the entropic heat is also important at certain SOC, however, its impact on the internal temperature is relatively minimal. In general, the internal temperature predictions are in good agreement with the test data. The maximum error from the internal temperature prediction is approximately less than 2°C. This can be improved by adding the entropy coefficient at each SOC. However, this is beyond the scope of this study. The surface temperature is not presented in the figure because it is kept at a constant value.

Fig. 5.14 compares the current distribution for internal and surface region at a different constant surface temperature. The behaviour of the current deviation between the internal and surface region is analogous to the pulse discharge cases.

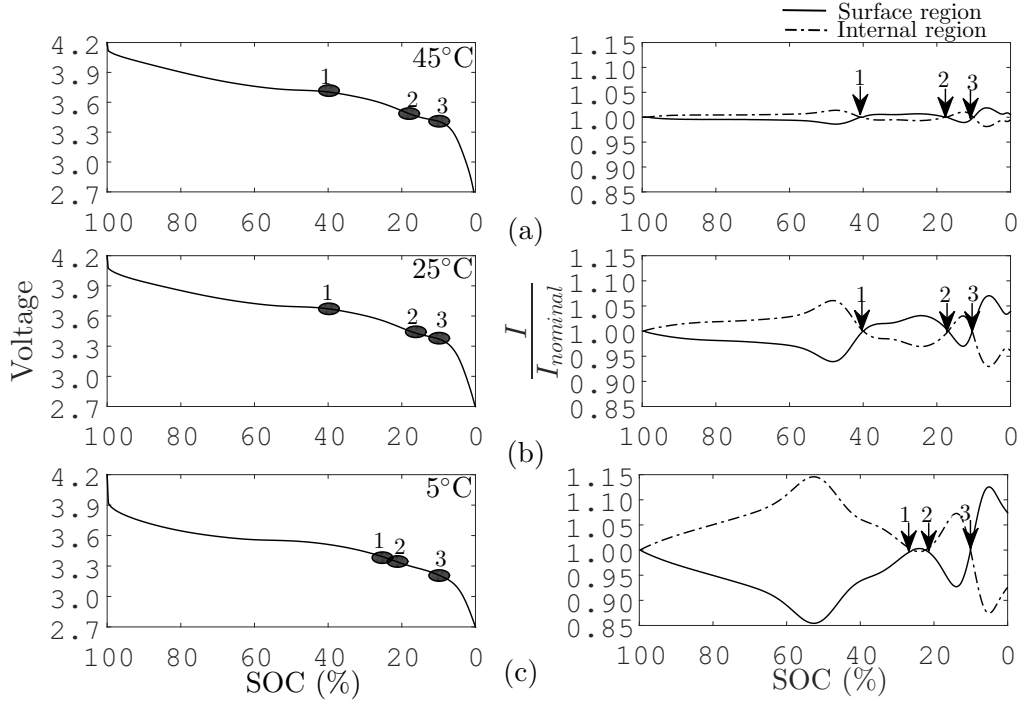


Figure 5.15: Current crossover points at different SOC for full discharge at : (a) 45°C, (b) 25°C and (c) 5°C

The largest current deviation is manifested at the constant surface of 5°C. This is expected because of the temperature difference between internal and surface region at 5°C, is the highest among all temperature points. It can be seen that there are several crossover points occur at various SOC. The crossover points indicate the point where the current of the internal region intersects the current of the surface region. The counteracting between local current and SOC is responsible for the occurrence of the crossover point. In general, the behaviour of the current distribution is consistent with those of Zhang et al. (2013) who found out where the current distribution reverses in the pattern because of the non-uniformity of the individual SOC which was caused by the uneven current distribution at the early stage of the discharge period. The variation of the current rate will eventually cause under-utilization of an active material for the surface region and over-utilization of an active material for the internal region.

The current crossover as shown in Fig. 5.14 occurs three times at all temperature. This finding is different with the finding of Zhang et al. (2013); Yang et al. (2016); Shi et al. (2016) which shows that the current crossover only occurs once during the full discharge. The differences could be due to the different of battery chemistry used by Zhang et al. (2013); Yang et al. (2016); Shi et al. (2016), which

was lithium iron phosphate (LFP). On the other hand, the battery chemistry used in the current study is nickel manganese cobalt (NMC). Each battery chemistry has distinct OCV which could possibly cause the difference in the current crossover. Fig. 5.15 (a) - (c) compares the point of occurrence of the current crossover at 45 to 5°C respectively. It can be seen that the crossover points at 45°C and 25°C happen at relatively similar SOC which are at the SOC of 40,18 and 10% for crossover point 1,2 and 3 respectively. On the other hand, the current crossover points at 5°C occur at the SOC of 25, 22 and 10%. Significant differences in the current crossover points particularly at low temperature is mainly due to the considerable current deviation which is caused by the large temperature difference between internal and surface region. High currents experienced by the battery at low temperature results to higher degree of utilisation of the active material. This has a direct implication on the OCV in which it drops to a lower SOC as shown in Fig. 5.15 (c).

5.6 Conclusion

In this chapter, a non-intrusive method in measuring the internal battery temperature is presented. This technique cannot be a representation of the internal temperature of a single battery. Furthermore, the feasibility of conducting this method is also limited to a battery with flat surfaces. However, it is apparent that this novel technique may be more flexible in terms of controlling the battery surface temperature and at the same time can be used to parameterise battery electrochemical-thermal model that accounts for the surface and internal temperature. This technique reveals that a battery constant surface temperature does not guarantee that the battery operates under isothermal condition. The internal temperature must be taken into consideration in order for the isothermal condition by just controlling the battery surface temperature to be valid.

Significant internal temperature increase is seen particularly at a low constant surface temperature which is caused by high amount of heat generated at low temperature and poor thermal conductivity in the transverse direction. These two aspects, cause the heat to accumulate at the middle of the parallel connected battery allowing the internal temperature to increase. This suggests that although the surface temperature is kept relatively constant, the resulting internal temperature variation causes the isothermal assumption to be invalid. On the other hand, the internal temperature increase and the voltage curve can be used for validating an electrochemical-thermal model which considers surface and internal temperature. Additionally, this method has indirectly evaluated the importance of entropy particularly for the internal temperature prediction. The behaviour of the measured internal temperature suggests that the entropy is important not only at low C-rate operation, but it also important in the temperature range of 45°C to 5°C.

The second part of this chapter explains the modelling architecture employed in predicting the internal temperature and local current deviation as results of the thermal gradient. The architecture of the model is similar to the dual unidirectional current model which has been previously described in the previous chapter. The main difference lies in the thermal boundary condition. The electrical aspect of the model is arranged in parallel while the thermal aspect is arranged in series. With this configuration, the local current can be predicted according to its effective temperature of the region. The deviation of the local current between internal and surface region is significant, especially at the low constant surface temperature.

The magnitude of the current deviation depends on the temperature difference between the regions. From this study, it can be concluded that the magnitude of the current deviation increases proportionally with the increase of the temperature difference between region. This is supported by the simulated data of the full discharge at three different constant surface temperature. From this simulation, the highest current deviation is given at the constant surface temperature of 5°C, with the value of 4.41% while the lowest current deviation is given at the constant surface temperature of 45°C, with the value of 0.16%.

Chapter 6

Conclusion and future work

6.1 Summary

This thesis evaluates the battery electrochemical and thermal performance at a various operating temperature and most importantly at a different thermal boundary condition by creating a specific thermal control system which closely matches the assumed thermal boundary condition experienced by the battery. The internal non-uniformity of the battery is inherently difficult to be measured. Therefore, a model has been used to predict this internal condition by using the measured parameters such as voltage and temperature as a reference for the model validation. To aid the validation exercise, a novel thermal control system has been created. The experimental rig can keep the battery surface and tab temperature as close to the desired temperature as possible, therefore, creating a thermally 'ideal' condition which could be perceived as a benchmark for performance comparison as a function of temperature. In addition to the experimental work, several modelling approaches have been studied.

6.2 Conclusion

The work presented in this thesis was conducted with the focus to tackle the specific objectives which were established in Chapter 1. Therefore, the conclusions of this thesis are organised in three sections based on each of the objectives.

6.2.1 Objective 1

To develop an experimental technique which can represent particular thermodynamics assumption for a broad temperature range relevant to automotive application

Analysis of the academic literature has revealed that the majority of work, particularly with regards to the investigation of the battery performance at different temperature, was designed based on the environment thermal boundary condition rather than the condition experienced on the battery surface. Therefore, from a modelling point of view, it is inherently difficult to reproduce the same behaviour as obtained in the experiment. This is because the actual thermal condition experienced by the battery is not identical with the thermal condition imposed on the battery model. If the battery temperature is measured, it is still problematic to use the data for fitting the parameter of the battery model because the surface temperature keeps on changing. This scenario thus provided the impetus for improving the external thermal boundary condition for battery testing.

A significant difference between the thermal conductivity in the longitudinal and transverse direction results in a different rate of heat transfer. Technically, a uniform temperature distribution can be expected if the heat transfer is controlled in the longitudinal direction. This condition is desirable to reduce thermal non-uniformity. Therefore, an isothermal condition can be assumed. However, due to the structure of the battery having different thermal resistance on the tab, the effect of ambient temperature also needs to be considered in the quest for obtaining an isothermal condition. Controlling the battery temperature from its tab merely improves the transient response of the temperature on the battery surface. During discharge, the battery surface temperature increases even at low C-rate discharge. Therefore, this method is not suitable for obtaining an isothermal condition. However, by integrating the conductive surface cooling/heating with the tabs temperature control, the battery temperature can be kept even closer to the desired tem-

perature even at low temperature where the heat generation is considerably high. Although the temperature of the battery tabs and surface are kept unchanged, it is no guarantee that this method can achieve a 'true' isothermal condition. This is because the internal battery temperature is unknown. Overall, the four point temperature control seems to be a viable option to achieve a thermal condition which is 'close' to the isothermal condition.

The ability to absorb heat generated by the battery instantaneously is necessary when keeping the battery temperature unchanged or obtaining an isothermal condition. The commonly used thermal/climate chamber which provides convective thermal control is unable to cope with the changing rate of heat generation of the battery. This inability is exacerbated at a low temperature causing the battery temperature to increase significantly. Clearly, the thermal chamber is not a good choice for evaluating the battery performance at various temperature if the isothermal condition is desired. Nevertheless, the thermal/climate chamber still can be used but only at high operating temperature because the heat generated by the battery at this temperature is small hence, the change in the battery temperature can be neglected. The comparison in battery performance at two different external thermal conditions suggests that thermal chamber are only acceptable at high test temperature if the isothermal condition is concerned. This has been shown by the deviation of physiochemical parameter particularly the diffusion coefficient at the positive electrode which is 4 times larger for test conducted by using the thermal chamber as compared to the 4 points temperature control rig at the target temperature of 5°C. Therefore, testing with the aim to obtain the battery parameters especially for low order model such as the electrical circuit model should be conducted at high temperature. Testing at this temperature can reduce the dependency of certain battery parameters to the temperature change hence reducing uncertainties in the fitting parameter process.

6.2.2 Objective 2

To explore techniques to address several thermal issues from a numerical perspective

A thermal model which is typically coupled to an electrochemical battery model is responsible for calculating the energy balance of the battery. This results in the change in temperature which depends on the rate of charge/discharge and the external thermal condition. The thermal model is not necessary if the model is validated

using test data obtained under isothermal conditions. A lumped capacitance thermal model is the simplest approach in calculating the energy balance to predict the temperature change. However, the applicability of this model to represent a solid body depends on its Biot number. The Biot number is determined based on the direction of the heat transfer. Therefore, the Biot number of a battery in the transverse direction is greater than in longitudinal direction because of the difference in thermal conductivity. Typically, the battery temperature is controlled from its surface. This condition causes the heat transfer to occur in the transverse direction. In this direction, a temperature gradient is expected to develop. Therefore, a lumped thermal model is not a good representation of a single battery because it cannot capture the internal temperature non-uniformity. The lumped thermal model only represents the surface temperature of the battery. However, this has been addressed by employing the lumped thermal model in a thermal network. This network physically represents the surface and the internal condition of the battery. The network is configured as such the thermal components are arranged in series while the electrochemical components are arranged in parallel. This configuration allows each region to generate heat at a different rate depending on its temperature and local current. By integrating the thermal information between the surface and internal region, deviation of current can be justified. It has been shown that, for two batteries connected in parallel, the current deviation can be up to 4% at low constant surface temperature and 0.1% at high constant surface temperature. This information could help engineers to build a better cooling architecture for a battery pack which not only suppress the temperature increase but also keep the thermal non-uniformity to be at minimum level. This modelling approach could closely portray the actual condition experienced in a battery. However, this model is numerically demanding especially if its electrochemical component is created from the physics-based approach.

6.2.3 Objective 3

To investigate the variation of the battery internal non-uniformities at different thermal boundary condition

A review of the academic literature focusing on the inherent non-uniformities of batteries particularly the internal current deviation has demonstrated that neither the internal temperature variation nor the external temperature variation is typically considered. Thus, the local current variation for two batteries connected in parallel is primarily caused by the individual battery having a different isothermal

temperature. In reality, this condition is surprisingly difficult to achieve. Therefore this oversimplification will cause an error in predicting the local current distribution. In this work, the local current distribution is predicted by using voltage curve and battery surface temperature as a reference. Results showed that the degree of current deviation is approximately proportional to the temperature difference between the regions. This phenomenon causes the active material at the hotter region to be over-utilised while the colder region to be under-utilised. The difference in utilisation of the active material between region will eventually cause SOC non-uniformity. However, the non-uniform behaviour is not significant at high operating temperature indicating that each region discharges at a relatively similar rate.

Battery performs better at high temperature due to improved kinetics particularly its diffusion. However, batteries connected in parallel string experiences different behaviour if one of the regions possess high temperature. This work, therefore, investigates the relationship of the local resistance with the temperature at each region. In a parallel configuration, when one of the regions operate at a relatively high temperature as compared to the other region, its local resistance will drop hence, causing more current to flow. The local resistance is inversely proportional to the temperature. Therefore, the region with high temperature will be discharged at a higher C-rate as compared to the region at low temperature. This high discharge rate causes the SOC of the hotter region to drop faster. Therefore, the remaining capacity of this region will be lower than the colder region. This behaviour cannot be captured by a battery model which adopts a lumped thermal model as its thermal coupling. At high temperature, a battery model with a lumped thermal coupling predicts improved battery performance due to the increase in diffusion coefficient. However, for a battery model that accounts for internal and surface temperature, the increase in temperature in one of the region causes the overall performance to drop due to the variation of the SOC.

For a battery model validation, the non-intrusive internal temperature measurement is perceived as an approach which can be used for a battery electrochemical-model that accounts for surface and internal temperature. Previously, for the 5Ah battery, the internal battery temperature is predicted by using the voltage curve and its surface temperature as a reference. With the predicted battery internal temperature, the distribution of the local current can be determined. However, the internal prediction could not be physically meaningful because the reference of the prediction is based only on the external condition. Therefore, an internal temperature measurement is necessary to predict the internal non-uniformities. The

non-intrusive internal temperature method provides data such as the surface temperature, internal temperature and voltage curve. With an additional test data, the internal prediction can be made more relevant. Assessment of the internal non-uniformities between 5Ah and 10Ah battery suggest that thicker battery is likely to experience a higher magnitude of local current deviation and higher temperature gradient. However, at a high test temperature, both batteries experience the same degree of current and temperature non-uniformity. These results suggest that the complexity of thermal condition in a battery is significantly reduced at high temperature. Therefore, at this condition, a lumped thermal model can be used although the battery is thick. On the other hand, low operating temperature requires more thermal discretization to capture the non-uniform behaviour.

6.3 Research Impact

The overall work highlights the difficulty of getting an isothermal condition from low to high ambient temperature. The rig is capable of keeping the battery temperature to be relatively unchanged with maximum deviation to be less than 1.5°C. Additionally, this work also suggests that there is no guarantee that isothermal condition can be achieved by only keeping the battery surface temperature to be constant during the discharge event. The internal temperature can vary especially at low constant surface temperature, indicating that the isothermal condition is not valid even though the battery surface temperature is kept constant.

It is inherently difficult to keep the battery temperature unchanged during discharge by using the common external thermal control which is normally based either on convection or by using thermal/climate chamber. The analysis suggests that an isothermal condition can be assumed only at high ambient temperature for the cases of low and moderate discharge rate. Furthermore, the analysis also recommends that a battery model should be parameterised at high ambient temperature, primarily to reduce thermal non-uniformity in the through plane direction.

From battery modelling point of view, the thermal discretisation of the battery model should consists on at least two points in the through plane direction. In this manner, it is possible to capture the current deviation due to thermal gradients especially at low ambient temperature.

6.4 Proposed Future Work

Even though this work has demonstrated the impact of the different thermal condition on the battery performance at a wide temperature range, further investigation is deemed necessary to complement the conclusion obtained from the current work. The following propositions are made for future work:

6.4.1 Entropy measurement

The battery model does not include the effect of entropy. It would be interesting if the entropic heat is added which can improve the temperature prediction. In general, the entropy measurement requires a very long period of testing because this measurement must be conducted in an equilibrium state. By using tabs temperature control as described in chapter 3, the testing duration could be significantly reduced because this method gives a better thermal transient performance. Therefore the time for the battery to reach thermal equilibrium will be faster.

6.4.2 Investigation for battery with different chemistry and form factor

In this study, only the battery thickness is varied for the assessment of current and temperature non-uniformity. The study could be expanded by conducting a test with different types of battery chemistry and battery with different form factor. The variations of these testing could therefore benefit the electric car maker especially in the areas of building a better battery pack. Combining the methodology presented in this thesis with more test data would create an engineering design rule specifically to address the concern of the cell to cell non-uniformities which is one of key problem for the BMS.

Bibliography

- The UK Low Carbon Transition Plan : National strategy for climate change. Technical report, 2009. URL <http://www.decc.gov.uk/>.
- Said Al-Hallaj and J. Robert Selman. Thermal modeling of secondary lithium batteries for electric vehicle/hybrid electric vehicle applications. *Journal of Power Sources*, 110(2):341–348, 2002. ISSN 03787753.
- F. An, J. Huang, C. Wang, Z. Li, J. Zhang, S. Wang, and P. Li. Cell sorting for parallel lithium-ion battery systems: Evaluation based on an electric circuit model. *Journal of Energy Storage*, 6:195–203, 2016.
- Davide Andrea. *Battery Management System*. Artech House, Massachusetts, 2010.
- Seongjun Bae, Hyeon Don Song, Inho Nam, Gil Pyo Kim, Jong Min Lee, and Jongheop Yi. Quantitative performance analysis of graphite-LiFePO₄ battery working at low temperature. *Chemical Engineering Science*, 118:74–82, 2014.
- Farid Bahiraei, Maryam Ghalkhani, Amir Fartaj, and Gholam-Abbas Nazri. A pseudo 3D electrochemical-thermal modeling and analysis of a lithium-ion battery for electric vehicle thermal management applications. *Applied Thermal Engineering*, 2017. doi: <http://dx.doi.org/10.1016/j.applthermaleng.2017.07.060>.
- Allen J Bard, Larry R Faulkner, New York, Chichester @bullet, Weinheim Brisbane, and Singapore E Toronto. *ELECTROCHEMICAL METHODS Fundamentals and Applications*. JOHN WILEY & SONS, INC., 2001.
- S. J. Bazinski and X. Wang. Thermal Effect of Cooling the Cathode Grid Tabs of a Lithium-Ion Pouch Cell. *Journal of the Electrochemical Society*, 161(14): A2168–A2174, 2014.
- S.J. Bazinski, X. Wang, B.P. Sangeorzan, and L. Guessous. Measuring and assessing the effective in-plane thermal conductivity of lithium iron phosphate pouch cells. *Energy*, 114:1085–1092, 2016.

- Dawn M. Bernardi and Joo Young Go. Analysis of pulse and relaxation behavior in lithium-ion batteries. *Journal of Power Sources*, 196(1):412–427, 2011.
- C R Birkl, E McTurk, M R Roberts, P G Bruce, and D A Howey. A Parametric Open Circuit Voltage Model for Lithium Ion Batteries. *Journal of The Electrochemical Society*, 162(12):A2271–A2280, 2015.
- K. Bourzac. Batteries : 4 big questions. *Nature*, 526(7572):S17–S17, 2015.
- Martin J. Brand, Markus H. Hofmann, Marco Steinhardt, Simon F. Schuster, and Andreas Jossen. Current distribution within parallel-connected battery cells. *Journal of Power Sources*, 334:202–212, 2016.
- Thomas Bruen and James Marco. Modelling and experimental evaluation of parallel connected lithium ion cells for an electric vehicle battery system. *Journal of Power Sources*, 310:91–101, 2016. ISSN 03787753.
- Yunus A. Cengel. *Heat Transfer A Practical Approach*. WCB/McGraw-Hill, 1998.
- Nalin A. Chaturvedi, Reinhardt Klein, Jake Christensen, Jasim Ahmed, and Aleksandar Kojic. Algorithms for advanced battery-management systems. *IEEE Control Systems Magazine*, 30(3):49–68, 2010. ISSN 08880611.
- S. C. Chen, C. C. Wan, and Y. Y. Wang. Thermal analysis of lithium-ion batteries. *Journal of Power Sources*, 140(1):111–124, 2005.
- Dennis W. Dees, Shigehiro Kawauchi, Daniel P. Abraham, and Jai Prakash. Analysis of the Galvanostatic Intermittent Titration Technique (GITT) as applied to a lithium-ion porous electrode. *Journal of Power Sources*, 189(1):263–268, 2009.
- Marc Doyle. Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell. *Journal of The Electrochemical Society*, 140(6):1526, 1993.
- S. J. Drake, D. a. Wetz, J. K. Ostanek, S. P. Miller, J. M. Heinzl, and A. Jain. Measurement of anisotropic thermophysical properties of cylindrical Li-ion cells. *Journal of Power Sources*, 252:298–304, 2014.
- Matthieu Dubarry, Arnaud Devie, and Bor Yann Liaw. Cell-balancing currents in parallel strings of a battery system. *Journal of Power Sources*, 321:36–46, 2016. ISSN 03787753.

- M. Ecker, T.K.D. Tran, P. Dechent, S. Kabitz, A. Warnecke, and D.U. Sauer. Parameterization of a Physico-Chemical Model of a Lithium-Ion Battery: I. Determination of Parameters. *Journal of the Electrochemical Society*, 162(9):A1836–A1848, 2015.
- Akram Eddahech, Olivier Briat, and Jean Michel Vinassa. Thermal characterization of a high-power lithium-ion battery: Potentiometric and calorimetric measurement of entropy changes. *Energy*, 61:432–439, 2013.
- Weifeng Fang, Ou Jung Kwon, and Chao-Yang Wang. Electrochemical-thermal modeling of automotive LI-ion batteries and experimental validation using a three-electrode cell. *International journal of energy research*, 34:107–115, 2010.
- Matthias Fleckenstein, Oliver Bohlen, Michael A. Roscher, and Bernard Bäker. Current density and state of charge inhomogeneities in Li-ion battery cells with LiFePO₄ as cathode material due to temperature gradients. *Journal of Power Sources*, 196(10):4769–4778, 2011.
- Christophe Forgez, Dinh Vinh Do, Guy Friedrich, Mathieu Morcrette, and Charles Delacourt. Thermal modeling of a cylindrical LiFePO₄/graphite lithium-ion battery. *Journal of Power Sources*, 195(9):2961–2968, 2010. ISSN 03787753.
- Joel C. Forman, Scott J. Moura, Jeffrey L. Stein, and Hosam K. Fathy. Genetic identification and fisher identifiability analysis of the Doyle-Fuller-Newman model from experimental cycling of a LiFePO₄ cell. *Journal of Power Sources*, 210:263–275, 2012.
- D Fouchard and J B Taylor. The molicec rechargeable lithium system : Multicell aspects. *Journal of Power Sources*, 21:195–205, 1987.
- Nandhini Ganesan, Suman Basu, Krishnan S. Hariharan, Subramanya Mayya Kolake, Taewon Song, Taejung Yeo, Dong Kee Sohn, and Seokgwang Doo. Physics based modeling of a series parallel battery pack for asymmetry analysis, predictive control and life extension. *Journal of Power Sources*, 322:57–67, 2016.
- Maryam Ghalkhani, Farid Bahiraei, Gholam-Abbas Nazri, and Mehrdad Saif. Electrochemical–Thermal Model of Pouch-type Lithium-ion Batteries. *Electrochimica Acta*, 247:569–587, 2017.
- Thomas Grandjean, Anup Barai, Elham Hosseinzadeh, Yue Guo, Andrew McGordon, and James Marco. Large format lithium ion pouch cell full thermal charac-

- terisation for improved electric vehicle thermal management. *Journal of Power Sources*, 359:215–225, 2017.
- Weijun Gu, Zechang Sun, Xuezhe Wei, and Haifeng Dai. A capacity fading model of lithium-ion battery cycle life based on the kinetics of side reactions for electric vehicle applications. *Electrochimica Acta*, 133:107–116, 2014.
- Meng Guo and Ralph E. White. Thermal Model for Lithium Ion Battery Pack with Mixed Parallel and Series Configuration. *Journal of The Electrochemical Society*, 158(10):A1166, 2011.
- Meng Guo and Ralph E. White. A distributed thermal model for a Li-ion electrode plate pair. *Journal of Power Sources*, 221:334–344, 2013.
- C. Heubner, M. Schneider, C. Lammel, U. Langklotz, and A. Michaelis. In-operando temperature measurement across the interfaces of a lithium-ion battery cell. *Electrochimica Acta*, 113:730–734, 2013.
- C. Heubner, C. Lammel, N. Junker, M. Schneider, and A. Michaelis. Microscopic in-operando thermography at the cross section of a single lithium ion battery stack. *Electrochemistry Communications*, 48:130–133, 2014.
- C. Heubner, M. Schneider, C. Lammel, and A. Michaelis. Local heat generation in a single stack lithium ion battery cell. *Electrochimica Acta*, 186:404–412, 2015.
- Hannah Hoag. Low-carbon electricity for 2030. *Nature Clim. Change*, 1(5):233–235, 2011.
- Kenneth Holmberg, Peter Andersson, and Ali Erdemir. Global energy consumption due to friction in passenger cars. *Tribology International*, 47:221–234, 2012.
- Ian A. Hunt, Yan Zhao, Yatish Patel, and J. Offer. Surface Cooling Causes Accelerated Degradation Compared to Tab Cooling for Lithium-Ion Pouch Cells. *Journal of The Electrochemical Society*, 163(9):A1846–A1852, 2016.
- Y. Inui, Y. Kobayashi, Y. Watanabe, Y. Watase, and Y. Kitamura. Simulation of temperature distribution in cylindrical and prismatic lithium ion secondary batteries. *Energy Conversion and Management*, 48(7):2103–2109, 2007.
- Y. Ji, Y. Zhang, and C.-Y. Wang. Li-Ion Cell Operation at Low Temperatures. *Journal of the Electrochemical Society*, 160(4):A636–A649, 2013. ISSN 0013-4651.

- Fangming Jiang, Peng Peng, and Yiqiong Sun. Thermal analyses of LiFePO₄/graphite battery discharge processes. *Journal of Power Sources*, 243: 181–194, 2013.
- Seunghun Jung and Dalmo Kang. Multi-dimensional modeling of large-scale lithium-ion batteries. *Journal of Power Sources*, 248:498–509, 2014.
- G Karimi and X Li. Thermal management of lithium-ion batteries for electric vehicle. *International journal of energy research*, 37:13–24, 2013. ISSN 0363907X.
- Gi-Heon Kim, Kandler Smith, Kyu-Jin Lee, Shriram Santhanagopalan, and Ahmad Pesaran. Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales. *Journal of The Electrochemical Society*, 158(8): A955, 2011. ISSN 00134651.
- Kokam. Kokam 31 Ah : SLPB (Superior Lithium Polymer Battery) Technical Specification. 2009. URL <http://enstroj.si/download.php?f=images/stories/Techspec-SLPB78216216H-31Ah-A1.pdf>.
- Julia Kowal, Arno Arzberger, Holger Blanke, and Dirk Uwe Sauer. How to determine the time for temperature equalisation in batteries and supercaps for reliable laboratory measurements. *Journal of Energy Storage*, 4:113–120, 2015.
- Karthikeyan Kumaresan, Godfrey Sikha, and Ralph E. White. Thermal Model for a Li-Ion Cell. *Journal of The Electrochemical Society*, 155(2):A164, 2008.
- Kyu Jin Lee, Kandler Smith, Ahmad Pesaran, and Gi Heon Kim. Three dimensional thermal-, electrical-, and electrochemical-coupled model for cylindrical wound large format lithium-ion batteries. *Journal of Power Sources*, 241:20–32, 2013.
- Zhe Li, Jianbo Zhang, Bin Wu, Jun Huang, Zhihua Nie, Ying Sun, Fuqiang An, and Ningning Wu. Examining temporal and spatial variations of internal temperature in large-format laminated battery with embedded thermocouples. *Journal of Power Sources*, 241:536–553, 2013.
- Chi Kai Lin, Yang Ren, Khalil Amine, Yan Qin, and Zonghai Chen. In situ high-energy X-ray diffraction to study overcharge abuse of 18650-size lithium-ion battery. *Journal of Power Sources*, 230:32–37, 2013.
- Languang Lu, Xuebing Han, Jianqiu Li, Jianfeng Hua, and Minggao Ouyang. A review on the key issues for lithium-ion battery management in electric vehicles. *Journal of Power Sources*, 226:272–288, 2013.

- Rajib Mahamud and Chanwoo Park. Spatial-resolution, lumped-capacitance thermal model for cylindrical Li-ion batteries under high Biot number conditions. *Applied Mathematical Modelling*, 37(5):2787–2801, 2013.
- Hossein Maleki, Said Al Hallaj, J. Robert Selman, Ralph B. Dinwiddie, and H. Wang. Thermal Properties of Lithium-Ion Battery and Components. *Journal of The Electrochemical Society*, 146(3):947, 1999. ISSN 00134651.
- So Miyatake, Yoshihiko Susuki, Takashi Hikiyara, Syuichi Itoh, and Kenichi Tanaka. Discharge characteristics of multicell lithium-ion battery with nonuniform cells. *Journal of Power Sources*, 241:736–743, 2013.
- K. A. Murashko, A. V. Mityakov, J. Pyrhonen, V. Y. Mityakov, and S. S. Sapozhnikov. Thermal parameters determination of battery cells by local heat flux measurements. *Journal of Power Sources*, 271:48–54, 2014. ISSN 03787753.
- Madhu Santosh K Mutyala, Jingzhou Zhao, Jianyang Li, Hongen Pan, Chris Yuan, and Xiaochun Li. In-situ temperature measurement in lithium ion battery by transferable flexible thin film thermocouples. *Journal of Power Sources*, 260:43–49, 2014.
- John Newman. *Electrochemical Systems*. John Wiley & Sons, Inc., Hoboken, New Jersey, third edition, 2004.
- John S. Newman and Charles W. Tobias. Theoretical Analysis of Current Distribution in Porous Electrodes. *Journal of The Electrochemical Society*, 109(12):1183, 1962.
- Carolyn R. Pals and John Newman. Thermal Modeling of the Lithium / Polymer Battery - I. Discharge Behaviour of a Single Cell. *Journal of The Electrochemical Society*, 142(10):3274–3281, 1995.
- Panasonic. Lithium Ion Batteries : Individual Data Sheet (Panasonic 830mAh, CGR17500). 2002. URL <http://www.batteryspace.com/prod-specs/4666.pdf>.
- C. Pastor-Fernandez, T. Bruen, W. D. Widanage, M. A. Gama-Valdez, and J. Marco. A Study of Cell-to-Cell Interactions and Degradation in Parallel Strings: Implications for the Battery Management System. *Journal of Power Sources*, 329: 574–585, 2016. ISSN 03787753.

- Justin Purewal, John Wang, Jason Graetz, Souren Soukiazian, Harshad Tataria, and Mark W. Verbrugge. Degradation of lithium ion batteries employing graphite negatives and nickel-cobalt-manganese oxide + spinel manganese oxide positives: Part 2, chemical-mechanical degradation model. *Journal of Power Sources*, 272:1154–1161, 2014.
- C. D. Rahn. *Battery System Engineering*. John Wiley & Sons, Ltd, 2013.
- Robert R. Richardson, Peter T. Ireland, and David A. Howey. Battery internal temperature estimation by combined impedance and surface temperature measurement. *Journal of Power Sources*, 265:254–261, 2014.
- Robert R. Richardson, Shi Zhao, and David A. Howey. On-board monitoring of 2-D spatially-resolved temperatures in cylindrical lithium-ion batteries: Part II. State estimation via impedance-based temperature sensing. *Journal of Power Sources*, 327:726–735, 2016.
- Jan Philipp Schmidt, Stefan Arnold, André Loges, Daniel Werner, Thomas Wetzel, and Ellen Ivers-Tiffée. Measurement of the internal cell temperature via impedance: Evaluation and application of a new method. *Journal of Power Sources*, 243:110–117, 2013.
- Z. Shen, L. Cao, C. D. Rahn, and C.-Y. Wang. Least Squares Galvanostatic Intermittent Titration Technique (LS-GITT) for Accurate Solid Phase Diffusivity Measurement. *Journal of the Electrochemical Society*, 160(10):A1842–A1846, 2013.
- Wei Shi, Xiaosong Hu, Chao Jin, Jiuchun Jiang, Yanru Zhang, and Tony Yip. Effects of imbalanced currents on large-format LiFePO₄/graphite batteries systems connected in parallel. *Journal of Power Sources*, 313:198–204, 2016.
- Kandler Smith and Chao-Yang Wang. Power and thermal characterization of a lithium-ion battery pack for hybrid-electric vehicles. *Journal of Power Sources*, 160(1):662–673, 2006.
- Li Song and James W Evans. Measurements of the thermal conductivity of lithium polymer battery composite cathodes. *Journal of the Electrochemical Society*, 146(3):869–871, 1999.
- Li Song, Yufei Chen, and James W Evans. Measurements of the Thermal Conductivity of Poly (ethylene oxide) -Lithium Salt Electrolytes. *Journal of the Electrochemical Society*, 144(11):3797–3800, 1997.

- Neil S. Spinner, Corey T. Love, Susan L. Rose-Pehrsson, and Steven G. Tuttle. Expanding the Operational Limits of the Single-Point Impedance Diagnostic for Internal Temperature Monitoring of Lithium-ion Batteries. *Electrochimica Acta*, 174:488–493, 2015.
- Rob Spurrett, Carl Thwaite, Adam Holland, David Lizius, and Geoff Dudley. Modeling of Highly-Parallel Lithium-Ion Batteries. *Space Power, Proceedings of the Sixth European Conference*, (502):685–691, 2002.
- Marie-therese Von Srbik, Monica Marinescu, Ricardo F Martinez-botas, and Gregory J Offer. A physically meaningful equivalent circuit network model of a lithium-ion battery accounting for local electrochemical and thermal behaviour , variable double layer capacitance and degradation. *Journal of Power Sources*, 325:171–184, 2016.
- Rengaswamy Srinivasan. Monitoring dynamic thermal behavior of the carbon anode in a lithium-ion cell using a four-probe technique. *Journal of Power Sources*, 198: 351–358, 2012.
- Rengaswamy Srinivasan, Bliss G. Carkhuff, Michael H. Butler, and Andrew C. Baisden. Instantaneous measurement of the internal temperature in lithium-ion rechargeable cells. *Electrochimica Acta*, 56(17):6198–6204, 2011.
- Peyman Taheri, Scott Hsieh, and Majid Bahrami. Investigating electrical contact resistance losses in lithium-ion battery assemblies for hybrid and electric vehicles. *Journal of Power Sources*, 196(15):6525–6533, 2011.
- Peyman Taheri, Maryam Yazdanpour, and Majid Bahrami. Transient three-dimensional thermal model for batteries with thin electrodes. *Journal of Power Sources*, 243:280–289, 2013.
- Yannic Troxler, Billy Wu, Monica Marinescu, Vladimir Yufit, Yatish Patel, Andrew J. Marquis, Nigel P. Brandon, and Gregory J. Offer. The effect of thermal gradients on the performance of lithium-ion batteries. *Journal of Power Sources*, 247:1018–1025, 2014.
- C. Veth, D. Dragicevic, and C. Merten. Thermal characterizations of a large-format lithium ion cell focused on high current discharges. *Journal of Power Sources*, 267:760–769, 2014.
- Qian Wang, Bin Jiang, Bo Li, and Yuying Yan. A critical review of thermal management models and solutions of lithium-ion batteries for the development of pure

- electric vehicles. *Renewable and Sustainable Energy Reviews*, 64:106–128, 2016. ISSN 13640321.
- Qingsong Wang, Ping Ping, Xuejuan Zhao, Guanquan Chu, Jinhua Sun, and Chunhua Chen. Thermal runaway caused fire and explosion of lithium ion battery. *Journal of Power Sources*, 208:210–224, 2012.
- Zhang Wenwei, Zhang Xingjuan, Wang Chao, Yu Guangfeng, and Yang Chunxin. Experimental and Computational Research on the Thermal Conductivities of Li/SOCl₂ Batteries. *Journal of the Electrochemical Society*, 161(5):A675–81, 2014. ISSN 0013-4651.
- Ralph E. White, B. E. Conway, and J. O. Bockris. *Modern Aspects of Electrochemistry*. Springer, US, Boston, MA, 1983.
- Billy Wu. *Fuel Cell Hybrid Electric Vehicle Powertrain Modelling and Testing*. PhD thesis, Imperial College London, 2014.
- Billy Wu, Vladimir Yufit, Monica Marinescu, Gregory J. Offer, Ricardo F. Martinez-Botas, and Nigel P. Brandon. Coupled thermal-electrochemical modelling of uneven heat generation in lithium-ion battery packs. *Journal of Power Sources*, 243:544–554, 2013.
- Mao Sung Wu, K. H. Liu, Yung Yun Wang, and Chi Chao Wan. Heat dissipation design for lithium-ion batteries. *Journal of Power Sources*, 109(1):160–166, 2002.
- Mao Sung Wu, Chang Yen Lin, Yung Yun Wang, Chi Chao Wan, and C. R. Yang. Numerical simulation for the discharge behaviors of batteries in series and/or parallel-connected battery pack. *Electrochimica Acta*, 52(3):1349–1357, 2006. ISSN 00134686.
- Meng Xiao and Song-Yul Choe. Dynamic modeling and analysis of a pouch type LiMn₂O₄/Carbon high power Li-polymer battery based on electrochemical-thermal principles. *Journal of Power Sources*, 218:357–367, 2012.
- Jingzhi Xun, Rui Liu, and Kui Jiao. Numerical and analytical modeling of lithium ion battery thermal behaviors with different cooling designs. *Journal of Power Sources*, 233:47–61, 2013.
- Naixing Yang, Xiongwen Zhang, Binbin Shang, and Guojun Li. Unbalanced discharging and aging due to temperature differences among the cells in a lithium-ion battery pack with parallel combination. *Journal of Power Sources*, 306:733–741, 2016.

- Yonghuang Ye, Yixiang Shi, Ningsheng Cai, Jianjun Lee, and Xiangming He. Electro-thermal modeling and experimental validation for lithium ion battery. *Journal of Power Sources*, 199:227–238, 2012.
- Yonghuang Ye, Lip Huat Saw, Yixiang Shi, Karthik Somasundaram, and Andrew A O Tay. Effect of thermal contact resistances on fast charging of large format lithium ion batteries. *Electrochimica Acta*, 134:327–337, 2014.
- J. Yi, U. S. Kim, C. B. Shin, T. Han, and S. Park. Three-Dimensional Thermal Modeling of a Lithium-Ion Battery Considering the Combined Effects of the Electrical and Thermal Contact Resistances between Current Collecting Tab and Lead Wire. *Journal of the Electrochemical Society*, 160(3):A437–A443, 2013. ISSN 0013-4651.
- Cheng Zhang, Kang Li, and Jing Deng. Real-time estimation of battery internal temperature based on a simplified thermoelectric model. *Journal of Power Sources*, 302:146–154, 2016.
- G. Zhang, C. E. Shaffer, C.-Y. Wang, and C. D. Rahn. In-Situ Measurement of Current Distribution in a Li-Ion Cell. *Journal of the Electrochemical Society*, 160(4):A610–A615, 2013.
- G. Zhang, L. Cao, S. Ge, C.-Y. Wang, C. E. Shaffer, and C. D. Rahn. In Situ Measurement of Radial Temperature Distributions in Cylindrical Li-Ion Cells. *Journal of the Electrochemical Society*, 161(10):A1499–A1507, 2014a. ISSN 0013-4651.
- Jianbo Zhang, Bin Wu, Zhe Li, and Jun Huang. Simultaneous estimation of thermal parameters for large-format laminated lithium-ion batteries. *Journal of Power Sources*, 259:106–116, 2014b.
- Zhuqian Zhang, Li Jia, Nan Zhao, and Lixin Yang. Thermal modeling and cooling analysis of high-power lithium ion cells. *Journal of Thermal Science*, 20(6):570–575, 2011. ISSN 10032169.
- Rui Zhao, Sijie Zhang, Jie Liu, and Junjie Gu. A review of thermal performance improving methods of lithium ion battery: Electrode modification and thermal management system. *Journal of Power Sources*, 299:557–577, 2015. ISSN 03787753.
- Cong Zhu, Xinghu Li, Lingjun Song, and Liming Xiang. Development of a theoretically based thermal model for lithium ion battery pack. *Journal of Power Sources*, 223:155–164, 2013.

Chen-Xi Zu and Hong Li. Thermodynamic analysis on energy densities of batteries.
Energy & Environmental Science, 4(8):2614, 2011.

Appendices

```

1  clear all
2  close all
3  clc
4  format short
5  %% Battery Dimension Parameters
6  sxn=40.9e-4;           %Length for -ve electrode
7  sxs=25.4e-4;           %Length for seperator
8  sxp=25.5e-4;           %Length for +ve electrode
9  XL=sxp+sxs+sxn;        %Total length of a cell
10 MaxP=45;               %Nodal in a cell (X-direction)
11 XP=MaxP-1;
12 Dx=XL/XP;
13 GdNeg=round((sxn/Dx)+1);
14 GdSep=round((sxs/Dx)+1);
15 GdPos=round((sxp/Dx)+1);
16 MaxN=GdNeg;
17 MaxS=GdNeg+GdSep-1;
18 XS=MaxS-1;
19 XN=MaxN-1;
20 Ln=0:Dx:sxn;
21 if max(size(Ln))==MaxN
22     Ln=0:Dx:sxn;
23 elseif max(size(Ln))<MaxN
24     Ln=0:Dx:sxn+Dx;
25 elseif max(size(Ln))>MaxN
26     Ln=0:Dx:sxn-Dx;
27 end
28 Lp=0:Dx:sxp;
29 if max(size(Lp))==(MaxP-MaxS+1)
30     Lp=0:Dx:sxp;
31 elseif max(size(Lp))<(MaxP-MaxS+1)
32     Lp=0:Dx:sxp+Dx;
33 elseif max(size(Lp))>(MaxP-MaxS+1)
34     Lp=0:Dx:sxp-Dx;
35 end
36 XL=max(Ln)+sxs+max(Lp);
37 %% Simulation Parameters

```

```

38 t_sim=1800;           %Time of simulation
39 Dt=5;                 %Time step
40 Dt_log=5;             %Data logging time step
41 iter=t_sim/Dt;        %Number of simulation cycle
42 for t=1:iter          %Input current
43     I(t)=10.00;
44 end
45 SOC(1)=100;           %SOC
46 Tsim=45;              %Battery temperature
47 Tref=298.15;
48 Tl=Tsim+273.15;
49 pn=1.99;              %Bruggemann coefficient -ve electrode
50 ps=1.87;              %Bruggemann coefficient seperator
51 pp=2.01;              %Bruggemann coefficient +ve seperator
52 esn=0.455;           %Volume fraction in -ve electrode
53 esp=0.545;           %Volume fraction in +ve electrode
54 %% Physiochemical Parameters
55 CsP=27765.60485;      %Solid diffusion positive (OR)
56 CsN=46542.61997;      %Solid diffusion negative (OR)
57 ioTP=74482.82512;     %Exchange current density (OR)
58 ioTN=45648.00129;     %Exchange current density (OR)
59 CeT=11772.21737;      %Electrolyte diffusion (OR)
60 JeT=45477.55814;      %Electrolyte conductivity (OR)
61 %% Battery Physical Parameters
62 A=8400;               %Electrode plate area
63 Rf=20;
64 %% Battery Parameters (Solid)
65 Dsnn=4.57232e-12;      %Diffusion coeff in -ve electrode
66 Dspp=6.01358e-12;      %Diffusion coeff in +ve electrode
67 kctN=8.82947e-7;       %Charge transfer coefficient negative
68 kctP=8.77665e-7;       %Charge transfer coefficient positive
69 csmaxN=16.1e-3;        %Maximum Li concentration in -ve electrode
70 csmaxP=23.9e-3;        %Maximum Li concentration in +ve electrode
71 stoiFN=0.726;          %Stoichiometric 100 SOC for -ve electrode
72 stoiFP=0.122;          %Stoichiometric 100 SOC for +ve electrode
73 stoiZN=0.033;          %Stoichiometric 0 SOC for -ve electrode
74 stoiZP=0.820;          %Stoichiometric 0 SOC for +ve electrode

```

```

75 Rsn=0.70e-4;           %Rad. for Li particle in -ve electrode
76 Rsp=0.90e-4;           %Rad. for Li particle in +ve electrode
77 MaxR=17;               %Maximum nodal in particle
78 R=MaxR-1;
79 Drn=Rsn/R;
80 Drp=Rsp/R;
81 aan=(3*esn./Rsn); %Specific surface area of -ve electrode
82 aap=(3*esp./Rsp); %Specific surface area of +ve electrode
83 On=1;                   %Solid phase -ve conductivity
84 Op=0.1;                 %Solid pahse +ve conductivity
85 Oen=On*esn;             %Eff. electronic conduc. for -ve electrode
86 Oep=Op*esp;             %Eff. electronic conduc. for +ve electrode
87 %% Battery Parameter (Electrolyte)
88 De=3.37e-6;             %Diffusion coeff in electrolyte
89 eep=0.340;              %Volume Fraction in +ve electrode
90 ees=0.500;              %Volume Fraction in seperator
91 een=0.330;              %Volume Fraction in -ve electrode
92 F=96485.3415;
93 tr=0.363;
94 Rg=8.314299999999999;
95 %% Parameters Setting
96 stoi=zeros(2,MaxP);
97 U=zeros(2,MaxP);
98 cn=zeros(MaxR,MaxN);
99 c0n=zeros(1,MaxR*MaxN);
100 cp=zeros(MaxR,(MaxP-MaxS+1));
101 c0p=zeros(1,MaxR*(MaxP-MaxS+1));
102 cnn=zeros(1,MaxR*MaxN);
103 csn=zeros(MaxR,MaxN);
104 cnp=zeros(1,MaxR*(MaxP-MaxS+1));
105 csp=zeros(MaxR,(MaxP-MaxS+1));
106 cs=zeros(MaxR,MaxP);
107 crn=zeros(MaxR,MaxN);
108 crp=zeros(MaxR,(MaxP-MaxS+1));
109 ce=zeros(1,MaxP);
110 cel=zeros(1,MaxP);
111 jLin=zeros(MaxR,MaxN);

```

```

112 jrn=zeros ( 1 ,MaxR*MaxN) ;
113 jLiRn=zeros ( 1 ,MaxN) ;
114 jLip=zeros (MaxR, ( MaxP–MaxS+1)) ;
115 jrp=zeros ( 1 ,MaxR*(MaxP–MaxS+1)) ;
116 jLiRp=zeros ( 1 ,MaxP–MaxS+1) ;
117 jn1=zeros (MaxR,MaxN) ;
118 jp1=zeros (MaxR, ( MaxP–MaxS+1)) ;
119 jn2=zeros (MaxR,MaxN) ;
120 jp2=zeros (MaxR, ( MaxP–MaxS+1)) ;
121 jLi=zeros ( 1 ,MaxP) ;
122 Z2n=zeros ( 1 ,MaxR*MaxN) ;
123 Z2p=zeros ( 1 ,MaxR*(MaxP–MaxS+1)) ;
124 Asn=zeros (MaxR*MaxN,MaxR*MaxN) ;
125 bsn=zeros (MaxR*MaxN, 1) ;
126 Asp=zeros (MaxR*(MaxP–MaxS+1),MaxR*(MaxP–MaxS+1)) ;
127 bsp=zeros (MaxR*(MaxP–MaxS+1), 1) ;
128 Ae=zeros (MaxP,MaxP) ;
129 be=zeros (MaxP, 1) ;
130 Ace=zeros (MaxP,MaxP) ;
131 bce=zeros (MaxP, 1) ;
132 Acs_neg=zeros (MaxN,MaxN) ;
133 bcs_neg=zeros (MaxN, 1) ;
134 Acs_pos=zeros (MaxP–MaxS+1,MaxP–MaxS+1) ;
135 bcs_pos=zeros (MaxP–MaxS+1, 1) ;
136 io=zeros ( 1 ,MaxP) ;
137 kef=zeros ( 1 ,MaxP) ;
138 Kdef=zeros ( 1 ,MaxP) ;
139 je=zeros ( 2 ,MaxP) ;
140 jsn=zeros ( 2 ,MaxN) ;
141 jsp=zeros ( 2 ,MaxP–MaxS+1) ;
142 js=zeros ( 2 ,MaxP) ;
143 etha=zeros ( 2 ,MaxP) ;
144 ethadif=zeros ( 2 ,MaxP) ;
145 ethael=zeros ( 2 ,MaxP) ;
146 ethaact=zeros ( 2 ,MaxP) ;
147 etotal=zeros ( 2 ,MaxP) ;
148 jLiBV=zeros ( 1 ,MaxP) ;

```

```

149 check=zeros(1,MaxP);
150 U_log=zeros((t_sim/Dt_log):MaxP);
151 c_log=zeros((t_sim/Dt_log):MaxP);
152 ce_log=zeros((t_sim/Dt_log):MaxP);
153 je_log=zeros((t_sim/Dt_log):MaxP);
154 js_log=zeros((t_sim/Dt_log):MaxP);
155 V_log=zeros(1,(t_sim/Dt_log));
156 Tl_log=zeros(1,(t_sim/Dt_log));
157 etha_log=zeros((t_sim/Dt_log):MaxP);
158 ethadif_log=zeros((t_sim/Dt_log):MaxP);
159 ethael_log=zeros((t_sim/Dt_log):MaxP);
160 etotal_log=zeros((t_sim/Dt_log):MaxP);
161 OCV_log=zeros(1,(t_sim/Dt_log));
162 jLi_log=zeros((t_sim/Dt_log):MaxP);
163 T_log=zeros((t_sim/Dt_log):MaxP);
164 I_log=zeros((t_sim/Dt_log):MaxP);
165 stoi_log=zeros((t_sim/Dt_log):MaxP);
166 time_log=zeros(1,(t_sim/Dt_log));
167 t=1;
168 t_log=1;
169 t_log_loop=1;
170 %% Initial Condition (Solid)
171 %Initial condition -ve electrode
172 for j=1:MaxR
173     for i=1:MaxN
174         stoi(1,i)=stoiZN+(stoiFN-stoiZN)*SOC(1)./100;
175         a1n = 0.06929;
176         b1n = 0.005336;
177         c1n = 0.009271;
178         a2n = 0.09137;
179         b2n = 0.02094;
180         c2n = 0.02244;
181         a3n = 0.1991;
182         b3n = 0.02;
183         c3n = 0.1761;
184         a4n = 0.08659;
185         b4n = 0.8768;

```

```

186         c4n = 0.2858;
187         a5n = 58.78;
188         b5n = -0.1442;
189         c5n = 0.06212;
190         a6n = -0.06336;
191         b6n = 0.3784;
192         c6n = 0.132;
193         a7n = 0.1856;
194         b7n = 0.3752;
195         c7n = 0.2402;
196         aagn=a1n*exp(-((stoi(1,i)-b1n)/c1n).^2);
197         bbgn=a2n*exp(-((stoi(1,i)-b2n)/c2n).^2);
198         ccgn=a3n*exp(-((stoi(1,i)-b3n)/c3n).^2);
199         ddgn=a4n*exp(-((stoi(1,i)-b4n)/c4n).^2);
200         eegn=a5n*exp(-((stoi(1,i)-b5n)/c5n).^2);
201         ffgn=a6n*exp(-((stoi(1,i)-b6n)/c6n).^2);
202         gggn=a7n*exp(-((stoi(1,i)-b7n)/c7n).^2);
203         U(1,i)=aagn+bbgn+ccgn+ddgn+eeegn+ffgn+gggn;
204         cn(j,i)=stoi(1,i)*csmatN;
205     end
206 end
207 [c0n(1,:)]=vec2mat(cn(:,:),1);
208 %Initial condition +ve electrode
209 for j=1:MaxR
210     for i=MaxS:MaxP
211         stoi(1,i)=stoiZP+(stoiFP-stoiZP)*SOC(1)./100;
212         a1p = 5.658;
213         b1p = -0.4546;
214         c1p = 0.7131;
215         a2p = 2.569;
216         b2p = 0.4839;
217         c2p = 0.4452;
218         a3p = 0.02509;
219         b3p = 0.5315;
220         c3p = 0.05809;
221         a4p = 0.2814;
222         b4p = 0.7765;

```

```

223         c4p =      0.05625;
224         a5p =      1.329;
225         b5p =      0.7643;
226         c5p =      0.2348;
227         aagp=a1p*exp(-((stoi(1,i)-b1p)/c1p).^2);
228         bbgp=a2p*exp(-((stoi(1,i)-b2p)/c2p).^2);
229         ccgp=a3p*exp(-((stoi(1,i)-b3p)/c3p).^2);
230         ddgp=a4p*exp(-((stoi(1,i)-b4p)/c4p).^2);
231         eegp=a5p*exp(-((stoi(1,i)-b5p)/c5p).^2);
232         U(1,i)=aagp+bbgp+ccgp+ddgp+eegp;
233         cp(j,i-(MaxS-1))=stoi(1,i)*csmxP;
234     end
235 end
236 [c0p(1,:)]=vec2mat(cp(:,:),1);
237 %% Initial Condition (Electrolyte)
238 %Initial Condition
239 for i=1:MaxP
240     ce(1,i)=0.0012;
241 end
242 %% Guess Reaction Current Density (jLi)
243 if I(1)>0
244     %Guess value for -ve JLi
245     for j=1:MaxR
246         for i=1:MaxN
247             jLin(j,i)=0.3;
248         end
249     end
250     [jrn(1,:)]=vec2mat(jLin(:,:),1);
251     %Guess value for +ve JLi
252     for j=1:MaxR
253         for i=1:(MaxP-MaxS+1)
254             jLip(j,i)=-0.3;
255         end
256     end
257     [jrp(1,:)]=vec2mat(jLip(:,:),1);
258 elseif I(1)==0
259     %Guess value for -ve JLi

```

```

260         for j=1:MaxR
261             for i=1:MaxN
262                 jLin(j,i)=0;
263             end
264         end
265         [jrn(1,:)] = vec2mat(jLin(:,:),1);
266         %Guess value for +ve JLi
267         for j=1:MaxR
268             for i=1:(MaxP-MaxS+1)
269                 jLip(j,i)=0;
270             end
271         end
272         [jrp(1,:)] = vec2mat(jLip(:,:),1);
273     end
274     I_check=zeros(1,iter);
275     while t<=iter
276         %% Current sign change
277         if t~=1
278             if I_check(t)~=1
279                 if I(t)>0 && I(t-1)<=0
280                     %Guess value for -ve JLi
281                     for j=1:MaxR
282                         for i=1:MaxN
283                             jLin(j,i)=0.3;
284                         end
285                     end
286                     [jrn(1,:)] = vec2mat(jLin(:,:),1);
287                     %Guess value for +ve JLi
288                     for j=1:MaxR
289                         for i=1:(MaxP-MaxS+1)
290                             jLip(j,i)=-0.3;
291                         end
292                     end
293                     [jrp(1,:)] = vec2mat(jLip(:,:),1);
294                     I_check(t)=1;
295                 elseif I(t)==0
296                     %Guess value for -ve JLi

```

```

297         for j=1:MaxR
298             for i=1:MaxN
299                 jLin(j,i)=0;
300             end
301         end
302         [jrn(1,:)] = vec2mat(jLin(:,:),1);
303         %Guess value for +ve JLi
304         for j=1:MaxR
305             for i=1:(MaxP-MaxS+1)
306                 jLip(j,i)=0;
307             end
308         end
309         [jrp(1,:)] = vec2mat(jLip(:,:),1);
310         I_check(t)=1;
311     end
312 end
313 end
314 %% Calculation of Cs (Solid Lithium Concentration)
315 Dsn=Dsn*exp((CsN/Rg)*((1./Tref)-(1./Tl)));
316 Dsp=Dsp*exp((CsP/Rg)*((1./Tref)-(1./Tl)));
317
318 for j=1:MaxR
319     rn(j)=(j-1)*Drn;
320 end
321 for j=1:MaxR
322     rp(j)=(j-1)*Drp;
323 end
324
325 Z0n=(3*Dsn*Dt)/(2*(Drn.^2));
326 Z0p=(3*Dsp*Dt)/(2*(Drp.^2));
327 Z1n=(Dsn*Dt)/(2*(Drn.^2));
328 Z1p=(Dsp*Dt)/(2*(Drp.^2));
329 for j=1:MaxR
330     for i=((MaxN-1)*(j-1))+j : ((MaxN-1)*j)+j
331         Z2n(i)=(2*Dsn*Dt)/(4*(Drn)*rn(j));
332     end
333 end

```

```

334 for j=1:MaxR
335     for i=((MaxP-MaxS)*(j-1))+j : ((MaxP-MaxS)*j)+j
336         Z2p(i)=(2*Dsp*Dt)/(4*(Drp)*rp(j));
337     end
338 end
339 for j=1:1
340     for i=((MaxN-1)*(j-1))+j : ((MaxN-1)*j)+j
341         Asn(i,i)=1+(2*Z0n);
342         Asn(i,i+MaxN)=-2*Z0n;
343         bsn(i,1)=(Z0n*c0n(1,i+MaxN))+((1-(2*Z0n))*c0n(1,i))
            +(Z0n*c0n(1,i+MaxN));
344     end
345 end
346 for j=2:MaxR-1
347     for i=((MaxN-1)*(j-1))+j : ((MaxN-1)*j)+j
348         Asn(i,i)=1+(2*Z1n);
349         Asn(i,i+MaxN)=-Z1n-Z2n(i);
350         Asn(i,i-MaxN)=-Z1n+Z2n(i);
351         bsn(i,1)=((Z1n+Z2n(i))*c0n(1,i+MaxN))+((1-(2*Z1n))*
            c0n(1,i))+((Z1n-Z2n(i))*c0n(1,i-MaxN));
352     end
353 end
354 for j=MaxR:MaxR
355     for i=((MaxN-1)*(j-1))+j : ((MaxN-1)*j)+j
356         Asn(i,i)=1+(2*Z1n);
357         Asn(i,i-MaxN)=-2*Z1n;
358         bsn(i,1)=((Z1n)*c0n(1,i-MaxN))+((1-(2*Z1n))*c0n(1,i)
            )+((Z1n)*c0n(1,i-MaxN))-(((4*Drn*jrn(1,i))./(aan*
            Dsn*F))*(Z1n+Z2n(i)));
359     end
360 end
361 [Lsn,Usn] = lu(Asn);
362 ysn = Lsn\bsn;
363 xsn = Usn\ysn;
364 cnn(1,:)=xsn;
365 [csn(:,:)] = vec2mat(cnn,MaxN);
366 for j=1:1

```

```

367     for i=((MaxP-MaxS)*(j-1))+j:( (MaxP-MaxS)*j)+j
368         Asp(i,i)=1+(2*Z0p);
369         Asp(i,i+(MaxP-MaxS+1))=-2*Z0p;
370         bsp(i,1)=(Z0p*c0p(1,i+(MaxP-MaxS+1)))+(1-(2*Z0p))*
            c0p(1,i)+(Z0p*c0p(1,i+(MaxP-MaxS+1)));
371     end
372 end
373 for j=2:MaxR-1
374     for i=((MaxP-MaxS)*(j-1))+j:( (MaxP-MaxS)*j)+j
375         Asp(i,i)=1+(2*Z1p);
376         Asp(i,i+(MaxP-MaxS+1))=-Z1p-Z2p(i);
377         Asp(i,i-(MaxP-MaxS+1))=-Z1p+Z2p(i);
378         bsp(i,1)=((Z1p+Z2p(i))*c0p(1,i+(MaxP-MaxS+1))
            +((1-(2*Z1p))*c0p(1,i))+((Z1p-Z2p(i))*c0p(1,i-(
            MaxP-MaxS+1))));
379     end
380 end
381 for j=MaxR:MaxR
382     for i=((MaxP-MaxS)*(j-1))+j:( (MaxP-MaxS)*j)+j
383         Asp(i,i)=1+(2*Z1p);
384         Asp(i,i-(MaxP-MaxS+1))=-2*Z1p;
385         bsp(i,1)=((Z1p)*c0p(1,i-(MaxP-MaxS+1)))+(1-(2*Z1p))
            *c0p(1,i)+((Z1p)*c0p(1,i-(MaxP-MaxS+1)))-(((4*
            Drp*jrp(1,i))./(aap*Dsp*F))*(Z1p+Z2p(i)));
386     end
387 end
388 [Lsp,Usp]=lu(Asp);
389 ysp=Lsp\bsp;
390 xsp=Usp\ysp;
391 cnp(1,:)=xsp;
392 [csp(:,:)] = vec2mat(cnp,(MaxP-MaxS+1));
393 for j=1:MaxR
394     for i=1:MaxN
395         cs(j,i)=csn(j,i);
396     end
397 end
398 for j=1:MaxR

```

```

399     for i=MaxS:MaxP
400         cs(j,i)=csp(j,i-(MaxS-1));
401     end
402 end
403 rcdn(:,:)=vec2mat(jrn,MaxN);
404 for j=MaxR:MaxR
405     for i=1:MaxN
406         jLiRn(1,i)=rcdn(j,i);
407     end
408 end
409 rcdp(:,:)=vec2mat(jrp,(MaxP-MaS+1));
410 for j=MaxR:MaxR
411     for i=1:(MaxP-MaS+1)
412         jLiRp(1,i)=rcdp(j,i);
413     end
414 end
415 for i=1:MaxN
416     jLi(1,i)=jLiRn(1,i);
417 end
418 for i=MaxN+1:MaxS-1
419     jLi(1,i)=0;
420 end
421 for i=MaxS:MaxP
422     jLi(1,i)=jLiRp(1,i-(MaxS-1));
423 end
424
425 for i=1:MaxN
426     stoi(1,i)=cs(MaxR,i)/csmN;
427     a1n = 0.06929;
428     b1n = 0.005336;
429     c1n = 0.009271;
430     a2n = 0.09137;
431     b2n = 0.02094;
432     c2n = 0.02244;
433     a3n = 0.1991;
434     b3n = 0.02;
435     c3n = 0.1761;

```

```

436     a4n =      0.08659;
437     b4n =      0.8768;
438     c4n =      0.2858;
439     a5n =      58.78;
440     b5n =     -0.1442;
441     c5n =      0.06212;
442     a6n =     -0.06336;
443     b6n =      0.3784;
444     c6n =      0.132;
445     a7n =      0.1856;
446     b7n =      0.3752;
447     c7n =      0.2402;
448     aagn=a1n*exp(-((stoi(1,i)-b1n)/c1n).^2);
449     bbgn=a2n*exp(-((stoi(1,i)-b2n)/c2n).^2);
450     ccgn=a3n*exp(-((stoi(1,i)-b3n)/c3n).^2);
451     ddgn=a4n*exp(-((stoi(1,i)-b4n)/c4n).^2);
452     eegn=a5n*exp(-((stoi(1,i)-b5n)/c5n).^2);
453     ffgn=a6n*exp(-((stoi(1,i)-b6n)/c6n).^2);
454     gggn=a7n*exp(-((stoi(1,i)-b7n)/c7n).^2);
455     U(1,i)=aagn+bbgn+ccgn+ddgn+eegn+ffgn+gggn;
456 end
457
458 for i=MaxS:MaxP
459     stoi(1,i)=cs(MaxR,i)/csmxp;
460     a1p =      5.658;
461     b1p =     -0.4546;
462     c1p =      0.7131;
463     a2p =      2.569;
464     b2p =      0.4839;
465     c2p =      0.4452;
466     a3p =      0.02509;
467     b3p =      0.5315;
468     c3p =      0.05809;
469     a4p =      0.2814;
470     b4p =      0.7765;
471     c4p =      0.05625;
472     a5p =      1.329;

```

```

473     b5p =      0.7643;
474     c5p =      0.2348;
475     aagp=a1p*exp(-((stoi(1,i)-b1p)/c1p).^2);
476     bbgp=a2p*exp(-((stoi(1,i)-b2p)/c2p).^2);
477     ccgp=a3p*exp(-((stoi(1,i)-b3p)/c3p).^2);
478     ddgp=a4p*exp(-((stoi(1,i)-b4p)/c4p).^2);
479     eegp=a5p*exp(-((stoi(1,i)-b5p)/c5p).^2);
480     U(1,i)=aagp+bbgp+ccgp+ddgp+eegp;
481 end
482 %% Calculation of Ce (Electrolyte Concentration)
483 Dee=(De)*exp((CeT/Rg)*((1./Tref)-(1./Tl)));
484
485 Den=Dee*(een.^pn);    %Eff. Diff. coeff in elect. -ve
486 Des=Dee*(ees.^ps);    %Eff. Diff. coeff in elect. seperator
487 Dep=Dee*(eep.^pp);    %Eff. Diff. coeff in elect. +ve
488
489 Deen=((Den*Dt)/(2*een*(Dx^2)));
490 Dees=((Des*Dt)/(2*ees*(Dx^2)));
491 Deep=((Dep*Dt)/(2*eep*(Dx^2)));
492
493 if I(t)>0
494
495     midn=round((max(size(Ln)))/2);
496     Ln1=Ln(midn)/2;
497     Ln2=Ln(midn)+((Ln(MaxN)-Ln(midn))/2);
498     arN1=trapz(Ln(1:midn),jLi(1:midn));
499     arN2=trapz(Ln(midn:MaxN),jLi(midn:MaxN));
500     midptn=((arN1*Ln1)+(arN2*Ln2))/(arN1+arN2);
501
502     midp=round((max(size(Lp)))/2);
503     Lp1=Lp(midp)/2;
504     Lp2=Lp(midp)+((Lp(MaxP-MaxS+1)-Lp(midp))/2);
505     arP1=trapz(Lp(1:midp),jLi(MaxS:MaxS+midp-1));
506     arP2=trapz(Lp(midp:MaxP-MaxS+1),jLi(MaxS+midp-1:MaxP)
507         );
508     midptp=((arP1*Lp1)+(arP2*Lp2))/(arP1+arP2);

```

```

509     a1=XL-midptn;
510     a2=XL-(Ln(MaxN)+sxs+midptp);
511     a3=midptn+((a1-a2)/2);
512     a4=round((a3/Dx)+1);
513
514     elseif I(t)==0
515         a4=25;
516     end
517
518     for i=1:1
519         Ae(i,i)=1+(2*Deen);
520         Ae(i,i+1)=-2*Deen;
521         be(i,1)=(Deen*ce(1,i+1))+((1-(2*Deen))*ce(1,i))+(Deen*ce
            (1,i+1))+(((1-tr)/(een*F))*jLi(1,i));
522     end
523     for i=2:MaxN-1
524         Ae(i,i)=1+(2*Deen);
525         Ae(i,i+1)=-Deen;
526         Ae(i,i-1)=-Deen;
527         be(i,1)=(Deen*ce(1,i+1))+((1-(2*Deen))*ce(1,i))+(Deen*ce
            (1,i-1))+(((1-tr)/(een*F))*jLi(1,i));
528     end
529     for i=MaxN:MaxN
530         ce(1,i)=((Deen*ce(1,i-1))+(Dees*ce(1,i+1)))/(Deen+Dees)
            ;
531         Ae(i,i)=1;
532         be(i,1)=ce(1,i);
533     end
534     for i=MaxN+1:a4-1
535         Ae(i,i)=1+(2*Dees);
536         Ae(i,i+1)=-Dees;
537         Ae(i,i-1)=-Dees;
538         be(i,1)=(Dees*ce(1,i+1))+((1-(2*Dees))*ce(1,i))+(Dees*ce
            (1,i-1));
539     end
540     for i=a4:a4
541         ce(1,i)=0.0012;

```

```

542     Ae(i,i)=1;
543     be(i,1)=ce(1,i);
544 end
545 for i=a4+1:MaxS-1
546     Ae(i,i)=1+(2*Dees);
547     Ae(i,i+1)=-Dees;
548     Ae(i,i-1)=-Dees;
549     be(i,1)=(Dees*ce(1,i+1))+((1-(2*Dees))*ce(1,i))+(Dees*ce
        (1,i-1));
550 end
551 for i=MaxS:MaxS
552     ce(1,i)=((Deep*ce(1,i+1))+(Dees*ce(1,i-1)))/(Dees+Deep)
        ;
553     Ae(i,i)=1;
554     be(i,1)=ce(1,i);
555 end
556 for i=MaxS+1:MaxP-1
557     Ae(i,i)=1+(2*Deep);
558     Ae(i,i+1)=-Deep;
559     Ae(i,i-1)=-Deep;
560     be(i,1)=(Deep*ce(1,i+1))+((1-(2*Deep))*ce(1,i))+(Deep*ce
        (1,i-1))+(((1-tr)/(eep*F))*jLi(1,i));
561 end
562 for i=MaxP:MaxP
563     Ae(i,i)=1+(2*Deep);
564     Ae(i,i-1)=-2*Deep;
565     be(i,1)=(Deep*ce(1,i-1))+((1-(2*Deep))*ce(1,i))+(Deep*ce
        (1,i-1))+(((1-tr)/(eep*F))*jLi(1,i));
566 end
567
568 [Le,Ue]=lu(Ae);
569 ye=Le\be;
570 xe=Ue\ye;
571 ce1(1,:)=xe';
572
573 kctNn=kctN*exp((ioTN/Rg)*((1/Tref)-(1./Tl)));
574 kctPp=kctP*exp((ioTP/Rg)*((1/Tref)-(1./Tl)));

```

```

575
576 for i=1:MaxN
577     io(1,i)=kctNn*F*((cel(1,i))^0.5)*((csmxn-cs(MaxR,i))
        ^0.5)*((cs(MaxR,i))^0.5);
578 end
579 for i=MaxS:MaxP
580     io(1,i)=kctPp*F*((cel(1,i))^0.5)*((csmxp-cs(MaxR,i))
        ^0.5)*((cs(MaxR,i))^0.5);
581 end
582 %% Calculation of Je (Electrolyte Charge Conservation)
583 Chec=exp((JeT/Rg)*((1/Tref)-(1./Tl)));
584
585 for i=1:MaxN
586     kef(1,i)=((1)*(15.8)*cel(1,i))*exp(-13472*(cel(1,i))
        .^1.4)*(een^pn)*Chec;
587 end
588 for i=MaxN+1:MaxS-1
589     kef(1,i)=((1)*(15.8)*cel(1,i))*exp(-13472*(cel(1,i))
        .^1.4)*(ees^ps)*Chec;
590 end
591 for i=MaxS:MaxP
592     kef(1,i)=((1)*(15.8)*cel(1,i))*exp(-13472*(cel(1,i))
        .^1.4)*(eep^pp)*Chec;
593 end
594
595 for i=1:MaxP
596     Kdef(1,i)=(2*Rg*Tl*(kef(1,i))*(tr-1))/F;
597 end
598
599 for i=1:1
600     Ace(i,i)=1;
601     bce(i,1)=0;
602 end
603 for i=2:MaxP-1
604     Ace(i,i-1)=(kef(1,i-1))./(Dx^2);
605     Ace(i,i)=(-2*kef(1,i))./(Dx^2);
606     Ace(i,i+1)=(kef(1,i+1))./(Dx^2);

```

```

607     bce(i,1)=(((−Kdef(1,i−1))./(Dx^2))*log(ce(1,i−1)))
        +(((2*Kdef(1,i))./(Dx^2))*log(ce(1,i)))−(((Kdef(1,i
        +1))./(Dx^2))*log(ce(1,i+1)))−jLi(1,i);
608 end
609 for i=MaxP:MaxP
610     Ace(i,i)=(−2*kef(1,i))./(Dx^2);
611     Ace(i,i−1)=2*(kef(1,i−1))./(Dx^2);
612     bce(i,1)=(((−Kdef(1,i−1))./(Dx^2))*log(ce1(1,i−1)))
        +(((2*Kdef(1,i))./(Dx^2))*log(ce1(1,i)))−(((Kdef(1,
        i−1))./(Dx^2))*log(ce1(1,i−1)))−jLi(1,i);
613 end
614
615 [Lce,Uce] = lu(Ace);
616 yce = Lce\bce;
617 xce = Uce\yce;
618 je(1,:) = xce';
619 %% Calculation of Js (Solid Charge Conservation)
620 jLisNN=je(1,MaxN)+U(1,MaxN)+((Rg*Tl)./(0.5*F))*log(ce1(1,
        MaxN)./(2*aan*io(1,MaxN)))−(Rg*Tl/F)*log(cs(MaxR,MaxN)./
        cs(1,MaxN))−(Rg*Tl/F)*log(ce1(1,MaxN)./0.0012);
621 jLisPP=je(1,MaxS)+U(1,MaxS)+((Rg*Tl)./(0.5*F))*log(ce1(1,
        MaxS)./(2*aap*io(1,MaxS)))−(Rg*Tl/F)*log(cs(MaxR,MaxS)./
        cs(1,MaxS))−(Rg*Tl/F)*log(ce1(1,MaxS)./0.0012);
622
623 Oeff_n=Oen./(Dx^2);
624 Oeff_p=Oep./(Dx^2);
625
626 for i=1:1
627     Acs_neg(i,i)=−2*Oeff_n;
628     Acs_neg(i,i+1)=2*Oeff_n;
629     bcs_neg(i,1)=jLi(1,1)−(2*I(t)/(Dx*A));
630 end
631 for i=2:MaxN−1
632     Acs_neg(i,i)=−2*Oeff_n;
633     Acs_neg(i,i+1)=Oeff_n;
634     Acs_neg(i,i−1)=Oeff_n;
635     bcs_neg(i,1)=jLi(1,i);

```

```

636 end
637 for i=MaxN:MaxN
638     Acs_neg(i,i)=1;
639     bcs_neg(i,1)=jLisNN;
640 end
641
642 [Lcs_neg,Ucs_neg]=lu(Acs_neg);
643 ycs_neg=Lcs_neg\bcs_neg;
644 xcs_neg=Ucs_neg\ycs_neg;
645 jsn(1,1:MaxN)=xcs_neg';
646
647 for i=1:1
648     Acs_pos(i,i)=1;
649     bcs_pos(i,1)=jLisPP;
650 end
651 for i=2:(MaxP-MaxS+1)-1
652     Acs_pos(i,i)=-2*Oeff_p;
653     Acs_pos(i,i+1)=Oeff_p;
654     Acs_pos(i,i-1)=Oeff_p;
655     bcs_pos(i,1)=jLi(1,(MaxS-1)+i);
656 end
657 for i=(MaxP-MaxS+1):(MaxP-MaxS+1)
658     Acs_pos(i,i)=-2*Oeff_p;
659     Acs_pos(i,i-1)=2*Oeff_p;
660     bcs_pos(i,1)=jLi(1,(MaxS-1)+i)-(2*I(t)/(Dx*A));
661 end
662
663 [Lcs_pos,Ucs_pos]=lu(Acs_pos);
664 ycs_pos=Lcs_pos\bcs_pos;
665 xcs_pos=Ucs_pos\ycs_pos;
666 jsp(1,1:(MaxP-MaxS+1))=xcs_pos';
667
668 for i=1:MaxN
669     js(1,i)=jsn(1,i);
670 end
671 for i=MaxS:MaxP
672     js(1,i)=jsp(1,i-(MaxS-1));

```

```

673 end
674 %% Reaction Current Density by Butler–Volmer
675 for i=1:MaxN
676     etha(1,i)=js(1,i)-je(1,i)-U(1,i);
677     ethadif(1,i)=(Rg*Tl/F)*log(cs(MaxR,i)./cs(1,i));
678     ethael(1,i)=(Rg*Tl/F)*log(ce1(1,i)./0.0012);
679     etotal(1,i)=etha(1,i)+ethadif(1,i)+ethael(1,i);
680 end
681 for i=MaxS:MaxP
682     etha(1,i)=js(1,i)-je(1,i)-U(1,i);
683     ethadif(1,i)=(Rg*Tl/F)*log(cs(MaxR,i)./cs(1,i));
684     ethael(1,i)=(Rg*Tl/F)*log(ce1(1,i)./0.0012);
685     etotal(1,i)=etha(1,i)+ethadif(1,i)+ethael(1,i);
686 end
687 for i=1:MaxN
688     jLiBV(1,i)=(aan*io(1,i))*(exp((0.5*F*etotal(1,i))./(Rg*
        Tl))-exp(-(0.5*F*etotal(1,i))./(Rg*Tl))));
689 end
690 for i=MaxS:MaxP
691     jLiBV(1,i)=(aap*io(1,i))*(exp((0.5*F*etotal(1,i))./(Rg*
        Tl))-exp(-(0.5*F*etotal(1,i))./(Rg*Tl))));
692 end
693
694 if I(t)>0
695     %Cell Voltage
696     V(1)=(js(1,MaxP))-(js(1,1))-((Rf*I(t))./A);
697 elseif I(t)==0
698     %Cell Voltage
699     V(1)=U(1,MaxP)-U(1,1);
700 end
701
702 %OCV
703 OCV(1)=U(1,MaxP)-U(1,1);
704
705 if I(t)>0
706     %% Discharging Mode %%
707

```

```

708     for i=1:MaxP
709         if abs((jLiBV(1,i))-(jLi(1,i)))<=0.001
710             check(1,i)=1;
711         elseif abs((jLiBV(1,i))-(jLi(1,i)))>0.001
712             check(1,i)=0;
713             for i=1:MaxP
714                 jLi(1,i)=jLi(1,i)+((jLiBV(1,i)-jLi(1,i))
715                     /(100));
716             end
717         end
718     end
719     for j=1:MaxR
720         for i=1:MaxN
721             jn1(j,i)=jLi(1,i);
722         end
723     end
724     [jrn(1,:)]=vec2mat(jn1(:,:),1);
725
726     for j=1:MaxR
727         for i=1:(MaxP-MaxS+1)
728             jp1(j,i)=jLi(1,i+(MaxS-1));
729         end
730     end
731     [jrp(1,:)]=vec2mat(jp1(:,:),1);
732
733     if sum(check(1,1:MaxP))==MaxP
734
735         total_jLi_neg=A*trapz(Ln(1,1:MaxN),jLi(1,1:MaxN));
736         total_jLi_pos=A*trapz(Lp(1,1:(MaxP-MaxS+1)),jLi(1,
737             MaxS:MaxP));
738
739         if abs(abs(total_jLi_neg)-((I(t)/(1))))<=0.01
740             current_dist_neg=1;
741         elseif abs(abs(total_jLi_neg)-((I(t)/(1))))>0.01
742             for i=1:MaxN
743                 jLi(1,i)=jLi(1,i)-((abs(total_jLi_neg)-(I(t)

```

```

                                /(1))/100);
743     for j=1:MaxR
744         for i=1:MaxN
745             jn2(j,i)=jLi(1,i);
746         end
747     end
748     [jrn(1,:)] = vec2mat(jn2(:,:),1);
749     current_dist_neg=0;
750 end
751 end
752
753 if abs(abs(total_jLi_pos)-(I(t)/(1)))<=0.01
754     current_dist_pos=1;
755 elseif abs(abs(total_jLi_pos)-(I(t)/(1)))>0.01
756     for i=MaxS:MaxP
757         jLi(1,i)=jLi(1,i)+((abs(total_jLi_pos)-(I(t)
                                /(1))/100);
758     for j=1:MaxR
759         for i=1:(MaxP-MaxS+1)
760             jp2(j,i)=jLi(1,i+(MaxS-1));
761         end
762     end
763     [jrp(1,:)] = vec2mat(jp2(:,:),1);
764     current_dist_pos=0;
765 end
766 end
767
768 if current_dist_neg+current_dist_pos==2
769     %% Saving parameters
770     if t_log_loop==Dt_log/Dt
771         c_log(t_log,:)=cs(MaxR,:);
772         U_log(t_log,:)=U(1,:);
773         stoi_log(t_log,:)=stoi(1,:);
774         ce_log(t_log,:)=ce1(1,:);
775         je_log(t_log,:)=je(1,:);
776         js_log(t_log,:)=js(1,:);
777         etha_log(t_log,:)=etha(1,:);

```

```

778         ethadif_log(t_log,:) = ethadif(1,:);
779         ethael_log(t_log,:) = ethael(1,:);
780         etotal_log(t_log,:) = etotal(1,:);
781         jLi_log(t_log,:) = jLi(1,:);
782         OCV_log(t_log) = OCV(1);
783         V_log(t_log) = V(1);
784         I_log(t_log,:) = I(t);
785         time_log(t_log) = t * Dt;
786         t_log_loop = 0;
787         t_log = t_log + 1;
788         figure (2)
789         plot(time_log, V_log, '—')
790         xlim([0 t_sim])
791         ylim([2.7 4.3])
792         xlabel('Time(Seconds)');
793         ylabel('V');
794         grid on;
795         grid minor;
796     end
797 %% Update Parameters
798     for j = 1:MaxR
799         for i = 1:MaxN
800             crn(j,i) = cs(j,i);
801         end
802     end
803     [c0n(1,:)] = vec2mat(crn(:,:), 1);
804     for j = 1:MaxR
805         for i = 1:(MaxP - MaxS + 1)
806             crp(j,i) = cs(j, i + (MaxS - 1));
807         end
808     end
809     [c0p(1,:)] = vec2mat(crp(:,:), 1);
810     ce(:, :) = ce1(:, :);
811     U(1,:) = U(1,:);
812     stoi(1,:) = stoi(1,:);
813     js(1,:) = js(1,:);
814     je(1,:) = je(1,:);

```

```

815         etha(1,:)=etha(1,:);
816         ethadif(1,:)=ethadif(1,:);
817         ethael(1,:)=ethael(1,:);
818         ethaact(1,:)=ethaact(1,:);
819         etotal(1,:)=etotal(1,:);
820         V(1)=V(1);
821         OCV(1)=OCV(1);
822         t=t+1;
823
824         if I(t)<=0
825             I_check(t)=0;
826         end
827
828         t_log_loop=t_log_loop+1;
829         progressbar(t/(t_sim/Dt));
830         if V(1)>4.3 | V(1)<2.7
831             msgbox('Out of Limit')
832             break
833         end
834     end
835 end
836 elseif I(t)==0
837     for j=1:MaxR
838         for i=1:MaxN
839             jLin(j,i)=0;
840         end
841     end
842     [jrn(1,:)]=vec2mat(jLin(:,:),1);
843
844     for j=1:MaxR
845         for i=1:(MaxP-MaxS+1)
846             jLip(j,i)=0;
847         end
848     end
849     [jrp(1,:)]=vec2mat(jLip(:,:),1);
850
851     %% Saving parameters

```

```

852         if t_log_loop==Dt_log/Dt
853             c_log(t_log,:)=cs(MaxR,:);
854             U_log(t_log,:)=U(1,:);
855             stoi_log(t_log,:)=stoi(1,:);
856             ce_log(t_log,:)=ce1(1,:);
857             je_log(t_log,:)=je(1,:);
858             js_log(t_log,:)=js(1,:);
859             etha_log(t_log,:)=etha(1,:);
860             ethadif_log(t_log,:)=ethadif(1,:);
861             ethael_log(t_log,:)=ethael(1,:);
862             etotal_log(t_log,:)=etotal(1,:);
863             jLi_log(t_log,:)=jLi(1,:);
864             OCV_log(t_log)=OCV(1);
865             V_log(t_log)=V(1);
866             I_log(t_log,:)=I(t);
867             time_log(t_log)=t*Dt;
868             t_log_loop=0;
869             t_log=t_log+1;
870             figure (2)
871             plot(time_log,V_log,'—')
872             xlim([0 t_sim])
873             ylim([2.7 4.3])
874             xlabel('Time(Seconds)');
875             ylabel('V');
876             grid on;
877             grid minor;
878         end
879         %% Update Parameters
880         for j=1:MaxR
881             for i=1:MaxN
882                 crn(j,i)=cs(j,i);
883             end
884         end
885         [c0n(1,:)] = vec2mat(crn(:,:),1);
886         for j=1:MaxR
887             for i=1:(MaxP-MaxS+1)
888                 crp(j,i)=cs(j,i+(MaxS-1));

```

```

889         end
890     end
891     [c0p(1,:)] = vec2mat(crp(:, :), 1);
892     ce(:, :) = ce1(:, :);
893     U(1, :) = U(2, :);
894     stoi(1, :) = stoi(2, :);
895     js(1, :) = js(2, :);
896     je(1, :) = je(2, :);
897     etha(1, :) = etha(2, :);
898     ethadif(1, :) = ethadif(2, :);
899     ethael(1, :) = ethael(2, :);
900     ethaact(1, :) = ethaact(2, :);
901     V(1) = V(2);
902     OCV(1) = OCV(2);
903     t = t + 1;
904
905     if I(t) ~ 0
906         I_check(t) = 0;
907     end
908
909     t_log_loop = t_log_loop + 1;
910     progressbar(t / (t_sim / Dt));
911     if V(2) > 4.3 | V(2) < 2.7
912         msgbox('Out of Limit')
913         break
914     end
915 end
916 end

```
