Effects of non-uniform temperature distribution on degradation of lithium-ion batteries

Gabriel M. Cavalheiro

Follow this and additional works at: https://louis.uah.edu/uah-theses

Recommended Citation
Cavalheiro, Gabriel M., "Effects of non-uniform temperature distribution on degradation of lithium-ion batteries" (2019). Theses. 305. https://louis.uah.edu/uah-theses/305

This Thesis is brought to you for free and open access by the UAH Electronic Theses and Dissertations at LOUIS. It has been accepted for inclusion in Theses by an authorized administrator of LOUIS.
EFFECTS OF NON-UNIFORM TEMPERATURE DISTRIBUTION ON DEGRADATION OF LITHIUM-ION BATTERIES

by

GABRIEL M. CAVALHEIRO

A THESIS

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering in The Department of Mechanical and Aerospace Engineering to The School of Graduate Studies of The University of Alabama in Huntsville

HUNTSVILLE, ALABAMA

2019
In presenting this thesis in partial fulfillment of the requirements for a Master of Science in Mechanical and Aerospace Engineering degree from The University of Alabama in Huntsville, I agree that the Library of this University shall make it freely available for inspection. I further agree that permission for extensive copying for scholarly purposes may be granted by my advisor or, in his/her absence, by the Chair of the Department or the Dean of the School of Graduate Studies. It is also understood that due recognition shall be given to me and to The University of Alabama in Huntsville in any scholarly use which may be made of any material in this thesis.

[Signature]
(student signature)  
11/12/19
(date)
THESIS APPROVAL FORM

Submitted by Gabriel Marcilio Cavalheiro in partial fulfillment of the requirements for the degree of Master of Science in Physics and accepted on behalf of the Faculty of the School of Graduate Studies by the thesis committee.

We, the undersigned members of the Graduate Faculty of The University of Alabama in Huntsville, certify that we have advised and/or supervised the candidate on the work described in this thesis. We further certify that we have reviewed the thesis manuscript and approve it in partial fulfillment of the requirements for the degree of Master of Science in Physics.

Sheng 11/12/19

(Date)

Committee Chair

E. V. 11/12/19

H. N. 11/12/19

Department Chair

W. D. 11/12/19

College Dean

D. A. 11/13/19

Graduate Dean
ABSTRACT
The School of Graduate Studies
The University of Alabama in Huntsville

Degree Master of Science in Engineering College/Dept. Mechanical and Aerospace Engineering

Name of Candidate Gabriel Marcilio Cavalheiro

Title Effects of Non-Uniform Temperature Distribution on Degradation of Lithium-ion Batteries

The effects of non-uniform temperature distribution on degradation of Lithium-ion (Li-ion) batteries are investigated in this study. A Li-ion battery stack consisting of five 3 Ampere hour (Ah) pouch cells connected in parallel was tested for 2215 cycles and compared with a single baseline cell. The behaviors of temperature distribution, degradation, and current distribution of the stack were characterized and discussed. Results supported the hypothesis that non-uniform temperature distribution causes non-uniform and accelerated degradation. All cells in the stack experienced higher temperature rise and degraded faster than the baseline cell. In particular, capacity retention of the middle cell in the stack decreased to 50.7% after 2215 cycles while the baseline cell capacity retention was still 87.8%. Resistance of cells in the stack experienced non-uniform but similar pattern of variation with cycling. The resistances remained stable in early cycles, then experienced a rapid increase, and then became stable again. The middle cell resistance increased abruptly in the last 20 cycles before failure. Current distribution behaviors of the stack also changed significantly during cycling, which was consistent with cell resistance behaviors. The middle cell experienced much higher discharge current (C rate) than average, suggesting its accelerated degradation can be attributed to the synergized effects of higher local temperature and higher local current. Differential voltage analysis suggested
that growth of solid-electrolyte-interface (SEI) on the anode is the primary mechanism for accelerated degradation of the middle cell in the stack.
ACKNOWLEDGMENTS

The work presented in this thesis would not have been possible without the guidance and assistance of many special people. Not in any order of importance, I would like to thank each one of you for all the support and cheer presented during my time preparing my thesis and doing my research.

First, I would like to thank Dr. Guangsheng Zhang for all the knowledge shared with me and the guidance provided, awakening the passion for research inside me. Second, I would like to thank my co-workers Shan Huang and Takuto Iriyama for all the countless hours spent in the lab and outside too, sharing knowledge, laughs and assistance. Third, I would like to thank my family who gave me the education that made me who I am today and also supported me in my life choices, even though not always agreeing with it. I would also like to thank my girlfriend Kristen for the unconditional support given and all the hours of complaint that she had to hear, and even being hundreds of miles away she made me feel comfortable and gave me courage to continue this step of my life.

Lastly I would like to thank my committee members Dr. George Nelson and Dr. Keith Hollingsworth for their time and advice. Also would like to send special thanks to Hernando that helped me setting up a few experiments.
# Table of Contents

List of Figures .................................................................................................................. viii

List of Tables ..................................................................................................................... xi

Chapter I ................................................................................................................................. 1

1. Introduction ..................................................................................................................... 1

2. Motivation ....................................................................................................................... 4

3. Hypothesis ....................................................................................................................... 5

4. Summary and Goals ....................................................................................................... 6

Chapter II ............................................................................................................................... 8

1. Experimental Setup ....................................................................................................... 8

   1.1 Experimental System Design .................................................................................. 8

   1.2 Experimental Li-ion Cells Screening and Stack Assembly .................................... 10

   1.3 Test Protocol ........................................................................................................... 12

2. Results and Discussion ................................................................................................. 14

   2.1 Non-Uniform Temperature Distribution in the Stack .............................................. 14

   2.2 Non-Uniform Degradation of Li-ion Cells in the Stack .......................................... 15

   2.3 Interaction between Temperature Distribution and Current Distribution ............... 20

   2.4 Non-Uniform SOC Distribution ............................................................................. 25
List of Figures

Figure 1.1: Projection of annual global light-duty vehicle sales ............................................. 2
Figure 1.2: Architecture of a cell with composite electrodes [12]............................................ 3
Figure 1.3: Non-uniform temperature distribution in a small cylindrical cell [37] ............. 6
Figure 2.1: Schematic of a single Li-ion cell with natural convection cooling. ............... 9
Figure 2.2: Schematic of a 5 Li-ion cell stack with natural convection cooling. ............. 9
Figure 2.3: (a) Picture of a single cell placed vertically for symmetric cooling during cycling test; (b) Picture of the 5-cell stack thermally insulated on the sides and placed vertically to promote symmetric and one dimensional heat transfer condition; (c) 3D schematic of the 5-cell stack. ................................................................. 12
Figure 2.4: (a) Representative temperature rise during discharge of baseline cell and 5-cell stack in cycle 200. (b) Representative spatial distribution of temperature rise inside the 5-cell stack at different stage of discharge in cycle 200. ............................................. 14
Figure 2.5: (a) Capacity retention of baseline cell, 5-cell stack and individual cells in the stack during cycling from cycle 1 to cycle 2215. (b) Capacity retention of baseline cell, 5-cell stack and individual cells in the stack during cycling from cycle 2185 to cycle 2215. ........................................................................................................ 16
Figure 2.6: (a) Comparison between baseline cell and cells in the stack during discharge phase in cycle 1 and cycle 2215. (b) Variation of DC resistance with cycle number. ..... 17
Figure 2.7: (a) Variation of temperature rise at the end of discharge with cycle number. (b) Variation of non-uniform temperature distribution in the stack at the end of discharge with cycle number. .............................................................................................................. 19

Figure 2.9: (a) Normalized local currents of cell 1 in the stack during discharge in different cycles. (b) Normalized local currents of cell 3 in the stack during discharge in different cycles...................................................................................................................................................................... 22

Figure 2.10: (a) Variation of relative current of cell 1 (side cell) and cell 3 (middle cell) with cycle number at beginning of discharge. (b) Variation of relative current of cell 1 (side cell) and cell 3 (middle cell) with cycle number at end of discharge ....................... 24

Figure 2.11: (a) SOC of cells in the stack during discharge in cycle 1300. (b) SOC difference between cell 3 and cell 1 during discharge in different cycles. .............................. 25

Figure 3.1: Sample analysis of dV/dQ method. [79] .................................................................................................................. 31

Figure 3.5: dV/dQ curves for Stack at different sample cycles. ......................................................... 35

Figure 3.6: Cathode capacity retention from dV/dQ analysis for different cycles and cells. .................................................................................................................................................. 38

Figure 3.7: Lithium inventory loss from dV/dQ analysis for different cycles and cells. . 38

Figure 3.8: Anode capacity retention from dV/dQ analysis for different cycles and cells. .................................................................................................................................................. 39

Figure A.1: Characteristic cooling time estimation ................................................................. 45

Figure B.1: UOC at different SOC levels and temperatures......................................................... 48

Figure B.2: Entropic coefficient estimation ............................................................................. 48

Figure B.3: (a) Irreversible heat generation both in baseline cell and stack. (b) Reversible heat generation both in baseline cell and stack. ................................................................. 49
Figure B.4: Total heat generation rate. .......................................................... 50
List of Tables

Table 1.1: Comparison of commercially relevant rechargeable battery technologies [11]. 2
Table 2.1: Cycling test protocol ........................................................................................................ 13
Table 3.1: dV/dQ Analysis of Baseline. ............................................................................................. 36
Table 3.2: dV/dQ Analysis of Cell 1. .................................................................................................. 36
Table 3.3: dV/dQ Analysis of Cell 3. .................................................................................................. 37
Table 3.4: dV/dQ Analysis of Stack ................................................................................................... 37
Table A.1: Parameter used for heat transfer coefficient estimation and Biot number calculation. ........................................................................................................ 45
Chapter I

1. Introduction

The history of batteries could date back to the first century BC by the discovery of the so-called “Baghdad Battery”, clay pots found by archeologists in Baghdad, Iraq that contained an iron rod encased in copper and used to be filled with acidic substance [1, 2]. Luigi Galvani also famously demonstrated the animal electricity, as he claimed it, in 1700s [2, 3], in which a frog leg held by a brass hook moved when touched with an iron scalpel. After Galvani’s discovery, scientists at that time started developing batteries based on frog legs [4]. But it was only in 1800 that the first electrochemical storage device to truly be considered a battery was created by Alessandro Volta which was called the Voltaiic Pile [5]. It was considered the first true battery because it was the first device to produce continuous electricity and a stable current [6]. Since then, battery research and development became increasingly more important and relevant as the uses for electricity and battery grew.

Lithium-ion batteries (LIBs) have been developed since 1970s and were commercialized only in early 1990s [7]. But they have been used in a wide range of applications, from cellphones to electric vehicles (EVs) [8, 9]. In particular, LIB technology has enabled the revolutionary development EV industry since 2010 [10]. It is projected that by 2040, more than 60 million EVs will be sold annually, accounting for
54% of all new light-duty vehicle sales globally [11] representing a larger portion of the market than internal combustion engines as shown in Figure 1.1.

![Figure 1.1: Projection of annual global light-duty vehicle sales [11].](image)

Table 1.1 shows comparison between Li-ion batteries and other rechargeable batteries. It can be seen that Li-ion batteries stand out due to their high specific energy, wide range of operating temperature and cell voltage.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Electrolyte</th>
<th>Cell voltage (V)</th>
<th>Specific energy (Wh/kg)</th>
<th>Operating temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb/acid</td>
<td>Sulfuric acid (aq.)</td>
<td>2.04</td>
<td>30</td>
<td>-25 to +50</td>
</tr>
<tr>
<td>Ni/Cd</td>
<td>Alkali hydroxide (aq.)</td>
<td>1.3</td>
<td>50</td>
<td>-40 to +60</td>
</tr>
<tr>
<td>Ni/MH</td>
<td>Alkali hydroxide (aq.)</td>
<td>1.35</td>
<td>65</td>
<td>-20 to +60</td>
</tr>
<tr>
<td>Li ion</td>
<td>LiPF6 (organic solvents)</td>
<td>3.6</td>
<td>150 to 270</td>
<td>-30 to +60</td>
</tr>
<tr>
<td>Li polymer</td>
<td>Li salt (polyethyleneoxide)</td>
<td>3</td>
<td>140</td>
<td>60 to 100</td>
</tr>
</tbody>
</table>
It is important to look at the internal components of a Li-ion cell to have a better understanding of the electrochemical device used in this work.

As seen in Figure 1.2, a Li-ion cell is mainly composed of four components:

- Electrodes: The electrodes allow lithium ions to move in and out of their structures with a process called intercalation or deintercalation. The anode (negative electrode) have intercalated lithium ions when charged that deintercalate during discharge and migrating to the cathode (positive electrode). During the charging process the reverse occurs, the intercalated ions in the cathode deintercalate and migrate to the anode [14]. Usually the anode material is graphite and the cathode material is LiCoO₂ (Lithium Cobalt Oxide), LiFePO₄ (Lithium Iron Phosphate), LiMn₂O₂ (Lithium Manganese Oxide), or LixMnyCzo₂ (Lithium Nickel Manganese Cobalt Oxide).

Figure 1.2: Architecture of a cell with composite electrodes [13].
• Separator: The separator is a porous membrane that is responsible for physical separation of the anode and cathode. While this membrane act as an electrical insulator, avoiding short circuit, it promotes ion transport between cathode and anode [15].

• Current Collectors: As the name implies, the current collector is the component that collect the current from the electrodes and transfer to the tabs of the battery where the load will be applied. Usual materials are copper and aluminum. The materials are different from each other due to the different corrosion environments that they are subjected to [16].

• Electrolyte: The electrolyte is the transport medium for the ions to commute between anode and cathode.

2. Motivation

Even though LIBs have undergone extensive research and development, great challenges still exist for EV batteries, notably cycle life, cruise range, recharging time, cost, and safety according to DOE’s roadmap [17]. This work addresses the degradation challenge [17-24].

Degradation includes capacity degradation and power degradation [25]. Capacity degradation reduces usable energy of Li-ion batteries. Power degradation reduces power output and energy conversion efficiency as well as increasing recharging time and heat generation. Together, the capacity degradation and power degradation would reduce Li-ion battery life and performance while increasing lifetime cost and risk of thermal runaway [26].
### 3. Hypothesis

Several previous studies [12, 24, 27-31] have shown that Li-ion batteries degrade much faster at higher operating temperatures; e.g., ~ twice as fast at 45°C than that at 25°C [24]. In Saxton’s 2012 survey [29], faster capacity loss of Nissan LEAF EVs in climatically hot areas like the state of Arizona demonstrated practical consequences as a result of this phenomenon. Considering that EV batteries are required to operate at temperatures up to 52°C [17], accelerated degradation of the LIB at higher temperatures exacerbates the challenge of extending battery life. Higher temperature accelerates capacity and power degradation through electrolyte decomposition, SEI (solid electrolyte interface) layer growth, decomposition of binder, and other mechanisms [17, 18, 20-22, 32].

Some in situ diagnostic studies [33-38] showed that temperature distribution inside Li-ion cells is non-uniform during operation. It is due to very low thermal conductivity of battery materials, only ~1 Wm^{-1}K^{-1} [39, 40] in the direction of battery thickness. As shown in Figure 1.3 [38], a temperature difference up to ~5°C across a small thickness of 7 mm was observed in a relatively small cylindrical cell (diameter 18 mm, height 65 mm) with a capacity of 1.6 Ah during 4.8 A constant current discharge. This non-uniform temperature distribution was not only observed at cell level, it was also observed at module level through a stack of cells [41, 42].
Based on the above mentioned findings that Li-ion batteries degrade much faster at higher temperatures, and that a non-uniform temperature distribution exists inside a Li-ion cell during operation, it was hypothesized that non-uniform temperature distribution in large-format LIBs causes non-uniform degradation and leads to faster overall degradation than smaller cells under similar operating conditions. Experiments were designed as follows to verify the hypothesis and quantify the effects.

4. Summary and Goals

There are a few studies on the effects of non-uniform temperature distribution on performance of Li-ion batteries, such as cell resistance [12, 43], current distribution in parallel-connected cells [44, 45] and available discharge energy [45]. But all these studies
are short term performance tests. There are no reported experimental studies on the effects of non-uniform temperature distribution on degradation during extensive cycling.

This study aims to fill the gap through long term cycling studies of a Li-ion battery stack consisting of five pouch cells connected in parallel. Temperature, capacity retention, internal resistance, current and state of charge (SOC) of each cell in the stack are measured and compared during 2215 cycles of 1C charge and discharge over a period of more than 11 months. The results are compared with a single baseline Li-ion cell subjected to the same cycling protocol.

By experimentally quantifying the effects of non-uniform temperature distribution on degradation, this work would be useful for understanding degradation behaviors of both Li-ion battery modules and large-size single cells in which the temperature distribution is not uniform.

The goals of this study include:

- Quantify the temperature non uniformity developed in the 5-cell stack.
- Quantify and compare degradation of individual cells in the stack and the baseline cell.
- Observe and understand how the behavior of each cell changes during cycling.
- Understand mechanisms of the non-uniform degradation.
Chapter II

1. Experimental Setup

1.1 Experimental System Design

As schematically shown in Figure 2.1 & 2.2, two sets of experimental systems are designed. One system is for characterization of a single pouch Li-ion cell as a baseline cell. The baseline cell is connected to a battery tester for cycling tests. It is positioned in a way that both sides can be directly cooled by ambient air during test. A micro temperature sensor is placed on the cell surface to monitor its temperature during testing. The other system is for characterization of a stack that consists of five Li-ion cells connected in parallel. The five cells are of the same type as the baseline cell. The 5-cell stack is also connected to a battery tester for the cycling tests. Each of the five cells is connected to a shunt resistor for measurement of individual cell current (I_1, I_2, I_3, I_4, I_5) while the total stack current (I_total) is measured by the battery tester. The five cells are stacked so that only the two side cells (cell 1 and cell 5) can be cooled by ambient air. In this configuration, non-uniform temperature distribution would develop from the middle cell to side cells during the test. Micro thermocouples, six in total, are placed between the cells and on the side cells’ surfaces to monitor temperature distribution through the stack thickness. Comparison of thermal and degradation behaviors between the baseline cell and the 5-cell stack would enable investigation of how the non-uniform temperature distribution influences degradation.
Figure 2.1: Schematic of a single Li-ion cell with natural convection cooling.

Figure 2.2: Schematic of a 5 Li-ion cell stack with natural convection cooling.
1.2 Experimental Li-ion Cells Screening and Stack Assembly

Commercial Li-ion pouch cells with nominal capacity of 3 Ah (Tenergy 30107-0) were used in this study. Dimensions of the cell are 102 mm (L) x 50 mm (W) x 5.4 mm (T), not including tabs. Each cell weighs 60 grams. A total of 80 cells were screened by measuring their weight (OHAUS Ranger 3000 scale), high frequency resistance (HIOKI 3561 Battery HiTester) and discharge capacity (Arbin Battery Tester LBT21084). Six cells with similar high frequency resistance (6.7 ± 0.3 mΩ) and 1C discharge capacity (3.27 ± 0.03 Ah) were chosen. One of them was used as the baseline cell and the other five were used for the stack.

The chosen cells were then prepared for the test by soldering 16 AWG wire (Store House) to the positive tab of each cell and 14 AWG wires (Store House) to the negative tab of each cell. The negative wire was subsequently welded to a small resistor (2 mΩ) shunt resistor (PRC PLV7AL) used to measure the individual current of each cell in the stack and also to simulate the same conditions for the baseline cells, the small value of the resistor was chosen so there would be a minimal interference of the resistance of the resistor to the experimental results. The wires from all the cells were trimmed in a manner that the high frequency resistance of the whole cell including the wires and the shunt was within ± 0.5 mΩ from each other. All the exposed wire was insulated with Kapton tape.

Assembly of the 5-cell stack was done by stacking the cells and adding T type thermocouples (OMEGA 5TC-TT-T-30-72) to the surface of each cell in the stack and securing them in place with Kapton tape and electrically insulating tape (3M Scotch Vinyl Electrical Tape Super 88). The geometrical middle of both main surfaces of each cell was marked and then the 0.5mm thick thermocouples were attached using the electrically
insulating tape as seen in Figure 2.3 (a). After all the thermocouples were added, the 5 cells that were going to compose the stack started being stacked one by one and at the end they were wrapped with the same electrically insulating tape to ensure the mechanical stability of the stack. Due to the small diameter of the thermocouple and also the high deformability of the cell pouch material, the contact between each cell surface was ensured, guaranteeing the contact necessary for the conduction to properly happen.

The temperature distribution would be non-uniform in both through-plane direction and in-plane direction [35, 46]. To ensure the measured temperatures are representative of distribution through stack thickness, which is the focus of this work, the stack was thermally insulated with expanded polystyrene foam on all the sides except the faces of the external cells, and measuring tips of the thermocouples were aligned in the centers of cell surfaces.

The prepared cells can be seen in Figure 2.3. Note that both the single cell and the 5-cell stack were placed vertically for symmetric cooling from two sides of the main surface.
Figure 2.3: (a) Picture of a single cell placed vertically for symmetric cooling during cycling test; (b) Picture of the 5-cell stack thermally insulated on the sides and placed vertically to promote symmetric and one dimensional heat transfer condition; (c) 3D schematic of the 5-cell stack.

1.3 Test Protocol and Measurement Uncertainty

The baseline cell and the 5-cell stack were independently connected to and controlled by a multi-channel battery tester (Arbin Instruments LBT21084). The battery tester was also used to measure individual cell current (through shunt resistors) and temperatures (through micro thermocouples). All the data was recorded at 1 Hz. Voltage and overall current measurement accuracy is 0.02% of full range (± 5V, ± 30 A) for the battery tester, which translates to voltage measurement uncertainty of 2 mV and current measurement uncertainty of 12 mA. The currents of individual cells in the stack were obtained from Ohm’s Law, \( I=V/R \), in which \( V \) was voltage drop across shunt resistors and measured by the battery tester (accuracy of 0.02%), and \( R \) was resistance of shunt resistor (accuracy of 0.5%). Therefore, the overall accuracy for individual cell current measurement was 0.5004%, translating to measurement uncertainty of 23 mA for a measured current of 4.6 A, which was the highest during the tests. The T type
thermocouples used in this work have error of 1 °C according to the manufacturer (OMEGA), and temperature measurement unit of the battery tester has an error of 2 °C according to the manufacturer (Arbin). Therefore, the overall temperature measurement uncertainty can be calculated to be 2.2 °C. Considering that temperature difference across the 5-cell stack thickness is of more concern, it is worth noting that the maximum difference between readings of the six thermocouples in the stack at thermal equilibrium (after 24 hours of rest) was smaller than 0.1 °C.

Both the baseline cell and the stack were cycled using the same charging protocol: 1C constant current (CC) charging to 4.2 V and then constant voltage (CV) charging until current drops to C/20. After a rest period of 30 minutes, the cells were then discharged at constant current of 1C to 2.8 V. After a rest of 10 minutes, the cells were charged again for another cycle. Note that the rest time before charging was set short, only 10 minutes, to simulate actual use of Li-ion batteries in which they would be recharged soon after being discharged. Both the baseline cell and the 5-cell stack were tested at room temperature (25 ± 6 °C). The relatively large variation in ambient temperature was due to the long duration of the cycling test (more than 11 months) and occasional operation of a large heat-generating environmental chamber in the laboratory. Table 2.1 summarizes the schedules of each testing.

Table 2.1: Cycling test protocol

<table>
<thead>
<tr>
<th></th>
<th>Charge</th>
<th>Discharge</th>
<th>Cooling condition</th>
<th>Rest after charge</th>
<th>Rest after discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline cell</td>
<td>CC-CV (3 A, 4.2 V max, 0.15 A cutoff)</td>
<td>CC (3 A, 2.8 V cutoff)</td>
<td>Natural convection</td>
<td>30 min</td>
<td>10 min</td>
</tr>
<tr>
<td>5-cell stack</td>
<td>CC-CV (15 A, 4.2 V max, 0.75 A cutoff)</td>
<td>CC (15 A, 2.8 V cutoff)</td>
<td>Natural convection</td>
<td>30 min</td>
<td>10 min</td>
</tr>
</tbody>
</table>
2. Results and Discussion

2.1 Non-Uniform Temperature Distribution in the Stack

Figure 2.4 (a) shows the rise of local temperatures, calculated as the difference between temperature at current time and temperature in the beginning of discharge, in the 5-cell stack and surface temperature of the baseline cell during 1C discharge in a representative cycle.

![Figure 2.4: (a) Representative temperature rise during discharge of baseline cell and 5-cell stack in cycle 200. (b) Representative spatial distribution of temperature rise inside the 5-cell stack at different stage of discharge in cycle 200.](image)

As expected, the stack experienced a much higher temperature rise than the baseline cell. This can be attributed to a much smaller ratio of cooling area to volume of heat generation for the stack. Between 500 seconds and 900 seconds into discharge, the temperature rise slowed down for the stack and the temperature even decreased slightly for
the baseline cell. This can be attributed to the variation of entropic heat generation rate with SOC. The entropic heat generation rate can be negative in some SOC ranges, thus slowing the temperature rise for cells in the stack or decreasing the temperature for the baseline cell.

Figure 2.4 (a) also shows that the middle cell (cell 3) experienced higher temperature rise than the side cells (cell 1 and cell 5) or the cells between them. This is because the middle cell has to overcome higher thermal resistance to dissipate heat to the ambient. It confirms that temperature distribution becomes non-uniform as discharge proceeds. The development of a non-uniform temperature distribution is more clearly shown in Figure 2.4 (b), in which the spatial temperature distribution at different stages of discharge is plotted. By the end of discharge, the surface temperature of cell 3 became nearly 5 °C higher than that of cell 1 and the difference would become larger with cycling.

2.2 Non-Uniform Degradation of Li-ion Cells in the Stack

Capacity retention, calculated as the discharge capacity divided by the initial discharge capacity, is used to compare degradation of different cells. Testing of the 5-cell stack was stopped after 2215 cycles when the stack’s average capacity retention suddenly dropped to 76%.

Figure 2.5 (a) shows capacity retention of the baseline cell, the 5-cell stack average, and each cell in the stack during 2215 cycles. Figure 2.5 (b) shows detailed capacity retention during the last 30 cycles. It is clear that all five cells in the stack degraded faster than the baseline cell. After 2215 cycles, the baseline cell still had 87.8% capacity retention, but cells in the stack had capacity retention of no more than 83.8%. In particular,
the middle cell capacity retention was only 74% after 2200 cycles and further dropped to 50.7% after 2215 cycles.

![Figure 2.5: (a) Capacity retention of baseline cell, 5-cell stack and individual cells in the stack during cycling from cycle 1 to cycle 2215. (b) Capacity retention of baseline cell, 5-cell stack and individual cells in the stack during cycling from cycle 2185 to cycle 2215.](image)

Figure 2.6 (a) compares 1C discharge voltage curves between the baseline cell and cells in the stack in cycle 1 and cycle 2215. The faster and non-uniform degradation of cells in the stack than baseline cell is consistent with results in Figure 2.5. It is interesting to note that the initial part of discharge curves of cycle 1 and cycle 2215 almost overlap for the baseline cell but they are very different for cells in the stack. This suggests a much larger increase of internal resistance for cells in the stack than that for the baseline cell.
Figure 2.6 (b) shows variation of Direct Current (DC) resistance of each cell during cycling. The DC resistance RDC is calculated according to equation (1):

$$R_{DC} = \frac{U_{OC} - V_{10s}}{I_{10s}}$$

(1)

in which $U_{OC}$ is cell open circuit voltage, $V_{10s}$ is cell voltage at ten seconds into discharge, and $I_{10s}$ is cell current at ten seconds into discharge [45, 47-49]. DC resistance of the baseline cell increased only ~25% after 2215 cycles, but resistance of cells in the stack increased 50%-80%. The resistance of cell 3 surged an additional 140% in the last 20 cycles. It is interesting to note that resistance of the baseline cell did not show obvious increase until after 1300 cycles, while resistance of cell 3 in the stack started to increase rapidly after only 500 cycles.

It is also interesting that the resistance of cell 3 reached a peak near 1300 cycles, then reduced a little and leveled off before the final surge. Other cells in the stack
experienced a similar pattern in variation of resistance, but the rapid increase started in later cycles, suggesting slower degradation for the outer cells than the middle cell. Such non-uniform degradation is also consistent with the trend of non-uniform temperature distribution. After 1700 cycles, resistance of all cells in the stack reached stable values. It is worth noting that higher internal resistance of Li-ion cells suggests not only capacity degradation but also power degradation. Capacity degradation leads to less usable energy while power degradation leads to reduced power performance and longer recharging time.

The faster degradation of cells in the stack can be attributed to higher temperature during cycling than the baseline cell. The much faster degradation of the middle cell than that of side cells in the stack can be attributed to the non-uniform temperature distribution within the stack. These results are consistent with previous studies on single cell cycling at different temperatures [12, 28, 31]. They clearly support the hypothesis that non-uniform temperature distribution causes non-uniform and accelerated degradation.

Figure 2.7 (a) shows variation of the maximum temperature rise during discharge with cycle number. The maximum temperature rises of the baseline cell changed little during cycling, but that of cells in the stack showed an obvious increase after 1000 cycles and then stabilized after 1700 cycles. The trend is consistent with the variation of cell resistance shown in Figure 2.9.
Figure 2.7: (a) Variation of temperature rise at the end of discharge with cycle number.
(b) Variation of non-uniform temperature distribution in the stack at the end of discharge with cycle number.

Figure 2.7 (b) shows variation of temperature difference with cycle number, calculated as the difference between the highest temperature (T3) and the lowest temperature (T1) in the 5-cell stack at the end of discharge. It can be seen that the temperature difference kept increasing until it reached a stable value after about 1300 cycles. This is also consistent with the variation of cell resistance during cycling in Figure 2.6 (b). Cell 3 resistance reached peak value at 1300 cycles and then slightly decreased while the resistance of cell 1 started to catch up. The larger increase of maximum temperature rise and temperature non-uniform temperature distribution in the stack, in comparison with baseline cell, could have contributed to the non-uniform and accelerated degradation.
2.3 Interaction between Temperature Distribution and Current Distribution

A recent study [45] showed that an artificially created non-uniform temperature distribution would cause non-uniform current distribution in parallel-connected Li-ion cells during discharge primarily by influencing cell resistance. In the present study, non-uniform temperature distribution developed naturally in the 5-cell stack during discharge and the non-uniform temperature distribution became larger with cycling, as shown in Figures 2.4 & 2.7. The cell resistance also increased and became non-uniform with cycling, as shown in Figure 2.6 (b). Therefore, it can be expected that current distribution would be non-uniform and the distribution behaviors would change with cycling. To investigate this, the current distribution in several cycles with similar ambient temperature (25 ± 2 °C) were analyzed. The results are shown in Figures 2.8-2.10, with Figure 2.8 focusing on comparison between cells in the stack while Figures 2.9 & 2.10 focus on the effects of cycling.

Figure 2.8 shows the normalized current distribution (current of each cell divided by the average current which is 3 A) in the stack during discharge in cycles representing different stages of the cycling test. The current distribution behaviors changed significantly during cycling. At the early stage of cycling, cycle 72, the current distribution was uniform and stable until near the end of discharge. As cycling proceeded, the current distribution became non-uniform, shown in cycle 763, cycle 999 and cycle 1300. In particular, the local current of cell 3 was obviously lower than that of other cells at the beginning of discharge but became much higher near end of discharge. Such wavy variation of current distributions can be attributed to the difference in cell resistance and capacity consumption.
Figure 2.8: Normalized current distribution during discharge ($I_n/I_{\text{Average}}$) in different cycles with similar ambient temperature ($25 \pm 2 \, ^{\circ}\text{C}$). (a) cycle 72; (b) cycle 763; (c) cycle 999; (d) cycle 1300; (e) cycle 1900; (f) cycle 2200. Experimental data points are fitted by 9th order polynomial for clarity of trend.
rate according to prior studies on current distribution measurement [45, 50-52]. Cell 3 had higher resistance than other cells in the stack at the beginning of discharge between cycle 500 and 1300, as shown in Figure 2.6 (b), so its current would be lower than other cells at initial stage of discharge. Such lower initial current means slower reduction in SOC and higher open circuit voltage than the other cells at later stages of discharge. The higher open circuit voltage then would drive higher current. Therefore, the current of cell 3 increased and eventually became much higher than the currents of the other cells near the end of discharge in those cycles. As cycling further proceeded to cycle 1900, the current distribution became more uniform and stable again because resistances of other cells started to catch up with cell 3, as shown in Figure 2.6 (b). By cycle 2200, cell 3 resistance started to surge, so the current distribution became similar as cycle 1300 again.

Figure 2.9: (a) Normalized local currents of cell 1 in the stack during discharge in different cycles. (b) Normalized local currents of cell 3 in the stack during discharge in different cycles.
Figures 2.9 shows normalized local current of cell 1 and cell 3 during discharge in different cycles. It is interesting to note that cell 1 current behaviors changed little with cycling but cell 3 current behaviors changed significantly. At initial stage of cycling (cycle 457 and earlier), cell 3 current was quite stable during the whole discharge. But by cycle 1300, cell 3 current fluctuated between 85% and 150% of average current. In cycle 2215, the fluctuation was from 55% to nearly 140% of average current.

The large variation of cell 3 current behaviors with cycling can be attributed to its much faster degradation and larger temperature rise than other cells in the stack.

Figures 2.10 shows local current of cell 1 and cell 3 at the beginning and the end of discharge in each cycle relative to that in cycle 1. The effects of cycling on the current distribution behaviors can be clearly seen. In particular, the cell 3 current at beginning of discharge started to decrease around cycle 500, reached a minimum around 1300 cycles, then increased until near 1600 cycles and nearly leveled off before sudden decrease in the last cycles. Comparison between Figure 2.15 and Figure 2.6 (b) shows that the trend of the cell 3 current variation agreed very well with its resistance variation, suggesting that variation of the current distribution at the beginning of each discharge was primarily driven by the resistance variation. The cell 3 current at the end of discharge showed an opposite pattern but the changes occurred at a similar stage of cycling.
Figure 2.10: (a) Variation of relative current of cell 1 (side cell) and cell 3 (middle cell) with cycle number at beginning of discharge. (b) Variation of relative current of cell 1 (side cell) and cell 3 (middle cell) with cycle number at end of discharge

It is worth noting that higher discharge C rate also accelerates Li-ion cell degradation. Therefore, the higher current of cell 3 near the end of discharge could also contributed to its faster degradation than other cells. It suggests that non-uniform temperature distribution causes accelerated degradation of the middle cell in a stack through not only higher temperature but also higher local current (up to 1.5 times of average current during 1C discharge).

It is also worth noting that cell temperature and current are correlated. The stack configuration promotes a higher temperature in the middle cell than outer cells. This enhanced temperature would cause the resistance to drop [53, 54] during discharge, which could cause a higher current. This higher current, in turn, promotes a higher temperature. Such positive feedback could further accelerate degradation of a stack with parallel connected cells.
2.4 Non-Uniform SOC Distribution

Prior studies [50, 51] on current distribution measurement show that non-uniform current distribution would cause non-uniform SOC distribution. Figure 2.11 (a) shows the SOC change of each cell in the stack during discharge in cycle 1300 and Figure 2.11 (b) shows the difference between cell 3 and cell 1 during discharge in different cycles. SOC distribution was indeed not uniform during discharge, in particular SOC of cell 3 was obviously higher than other cells during discharge in cycle 1300. The SOC difference between cell 3 and cell 1 reached up to 7% during discharge in cycle 1300. It is interesting to note that the SOC difference pattern experienced dramatic change with cycling. The difference was small and stable in early cycles until around 500 cycles, then became larger and larger until cycle 1300, then became smaller again. Such variation is consistent with variation of current distribution and resistance as discussed earlier.

![Figure 2.11](image)

Figure 2.11: (a) SOC of cells in the stack during discharge in cycle 1300. (b) SOC difference between cell 3 and cell 1 during discharge in different cycles.
Chapter III

1. Degradation Mechanisms

1.1 SEI Layer

An important aspect of a Li-ion cell is the Solid Electrolyte Interphase (SEI) layer. It occurs in the first charging cycle of the battery, when the thermodynamically unstable electrolyte solution at low and very high potentials starts to reduce on the anode surface (usually graphite in the anode) and form the SEI layer [55]. This layer is permeable for lithium ions, but rather impermeable for the other components of the electrolyte, resulting in the protection of the electrolyte from further reduction and also the prevention of corrosion on the charged electrode [27].

Although this layer is beneficial for the cell in general, as stated before, it can also be harmful. The SEI formation on the anode is responsible for the release of gases from the electrolyte decomposition, especially at high temperatures and State of Charge (SOC). This can cause the cell to swell over time, increasing the impedance and losing both capacity and power available [27]. This electrolyte decomposition is also responsible for transforming the active lithium into inactive lithium, further decreasing the cell capacity [56, 57].

The growth of the SEI layer is also responsible for the decrease of the accessible surface area. A study shows that an SEI layer thicker than 10 Angstrom is sufficient to render the cell electron transfer from the anode via tunneling impossible [58], raising again
the impedance, and leading to power fade. This process is accelerated in cell operating conditions of high temperature and high SOC [27, 59].

Pinson and Bazant [60] showed a single particle model, based on empirical trends rather than mathematical models, able to predict commercial Li-ion cells lifetime due to SEI layer formation in graphite anodes. The results were similar to other published experimental results.

The main debate over this topic solution has been focused on new anode materials that can promote not only a high energy density and specific capacity but also small volumetric change, limiting the SEI layer cracking due to the inflation and deflation of the anode during intercalation and deintercalation [61]. This cracking can cause further SEI decomposition and formation, amplifying the effects explained before.

Another area studied to minimize the effects of degradation due to SEI layer is the electrolyte composition. Ramasubramanian et al. [62] suggests that SEI growth rate, structure, composition, and resistance significantly depend upon the electrolyte composition. They show, through equations of diffusion of ions in SEI grain boundaries, that the diffusion in SEI layers are of utmost importance to understand and improve Li-ion cells performance.

1.2 Binder

Capacity fade can also be observed due to the decomposition of the binder, material that is responsible for the link between the electrode and the current collector, and also for the maintenance of the physical structure of the electrode.
The binder materials can react at elevated temperatures and elevated SOC with the charged anode to form LiF [63, 64]. This reactivity can contribute to degradation in the form of loss of lithium and loss of mechanical stability.

Current efforts to solve this issue is to develop binder materials that are not fluorinated, and reduce the heat [65]. Besides the complication of the cell degradation, commonly used binder materials are harmful for the environment, therefore research in water soluble binders are also a tendency in this subject [66].

1.3 Current Collector

Another mechanism that can cause overpotentials, impedance rise, and inhomogeneous distribution of current and potential is the current collector corrosion. Copper and aluminum are widely used in the industry as current collectors, but they are naturally subjected to corrosion: aluminum to pitting corrosion and copper to environmentally assisted cracking. A study showed that while the aluminum corrosion might not be affected by the cell environment, copper was shown to be susceptible to environmental cracking at or near the lithium potential [16].

A high potential in the anode (Low SOC) and over discharge are the most common reasons for current collector corrosion which by itself enhances other degradation mechanisms, since corrosion products that exhibit poor electronic conductivity cause larger overpotentials and favor inhomogeneous current and potential distributions, and thus, lithium plating, a mechanism that will be soon explained [27].

One of the main advances in the current collector subject is the development of carbon nanotubes current collectors, enabling not only current collectors with better
adhesion and mechanic durability, but also lower contact resistance when compared to usual metallic current collectors [67]. Besides those benefits, the lightweight nature of carbon promotes a higher specific energy for Li-ion cells with carbon nanotube current collector when compared to usual metallic current collector Li-ion cells.

1.4 Lithium Plating

One of the biggest degradation mechanisms that the EV industry is currently facing is lithium plating. Lithium plating occurs during the charging process, and two processes are responsible for it: Lithium interaction into active materials and anode Lithium plating [68, 69], shown as follows:

\[ xLi^+ + xLi_6C_6 + xe^- \rightarrow Li_{6+x}C_6 \]  
\[ yLi^+ + ye^- \rightarrow yLi \]

Li\(^+\) ions commute from the cathode to the anode and intercalate quickly into the anode active material. The deposited Li metal forms dendrites in the surface of the anode, easily reacting with the electrolyte, consuming active lithium and electrolyte, and also causing the loss of electrical contact of some deposited Li with the anode [68, 69]. Not only this mechanism is responsible for capacity and power fade but it is also a safety concern as the dendrites grow over time, they can puncture the separator and causing a short circuit. It is a challenge for the EV industry because it is accelerated at low temperature conditions and high C-rate charging, which directly limits the fast charging possibilities until further development in this research area.

Recent topics showed that rather than a physical composition change to overcome this lithium plating issue, heating Li-ion cells to higher temperatures is promising solution.
Wang et al. [70, 71] reported a self-heating Li-ion battery (SHLB) structure to preheat Li-ion cells before charging at sub-zero temperatures to avoid lithium plating. More recently, based on the SHLB structure, Yang et al. [72] further enhanced the self-heating temperature to 60 °C and demonstrated 6C extreme fast charging without lithium plating. Li et al. [73] reported that a high current charge-discharge cycling promoted heating in the deposited lithium dendrites from a degraded cell. The high current cycling treatment was able to migrate the lithium from the dendrites, smoothening the metal surface. Such lithium dendrite healing was also reported through external heating of the electrode as opposed to high current heating [74].

2. Differential Voltage Analysis

As stated before, there are many degradation mechanisms that affect the capacity and power of a Li-ion cell. However, they can be divided into three main categories: cathode degradation, anode degradation and SEI formation. To quantitatively assess the degradation of the cell, we can use the dV/dQ curve analysis, which is obtained from the differentiation of the charge/discharge curve (voltage–capacity curve). The analysis of battery degradation using dV/dQ curves has been reported for LiNi$_{1-x}$Co$_x$Al$_y$O$_2$/graphite [75], LiNi$_{1-x}$Co$_x$Mn$_y$O$_2$/hard carbon [76], and LiCoO$_2$/graphite batteries [77].

The dV/dQ curve of the full cell exhibits three peaks, the first two of which reveal the signatures from the cathode, while the last peak is contrition from the anode. Therefore, the distance between the first two peaks (denoted as Q$_{AB}$) can be used to quantify the change of cathode capacity, while the change of anode capacity can be calculated from the evolution of the width of the third peak (denoted as Q$_{CD}$) [78]. The loss of Li$^+$ inventory in
the cell can be generally represented by the voltage offset between the cathode and the anode potential curves. $Q_{BC}$ indicates the voltage slippage between anode and cathode, providing information of Li$^+$ loss [79]. $Q_{AB}$ and $Q_{CD}$ provide a metric of electrode material loss within only a portion of each electrode's full voltage window.

Li et. al. [80] applied this method in a clear and concise manner in the study of cell degradation mechanisms and hence this paper will be the basis for the differential voltage analysis in this work. The method works by analysing the distance in the X axis between the local peaks and valleys of the graph. Figure 3.1 shows how the analysis is done.

Figure 3.1: Sample analysis of dV/dQ method. [80]

Sample cycles were used to analyse the degradation evolution during the cycling process. The same cycles as those used in chapter II, Figures 2.8. For this method, the occurrence of 3 peaks in the curve is necessary and due to the fluctuation of the data given by the shunt resistor, a 9th polynomial fitting was introduced to be able to identify those peaks. Figures 3.2-3.5 show the dV/dQ curves for each critical cell and cycles.
Figure 3.2: dV/dQ curves for Baseline at different sample cycles.
Figure 3.3: $dV/dQ$ curves for Cell 1 at different sample cycles.
Figure 3.4: dV/dQ curves for Cell 3 at different sample cycles.
Figure 3.5: dV/dQ curves for Stack at different sample cycles.
The value of the local maximums and minimums were precisely identified using origin’s quick peak tool. The values were obtained for each case and were then compared to the first cycle in order to calculate the capacity retention for each component of this method. The results can be seen in Table 3.1-3.4 and Figures 3.6-3.8.

Table 3.1: dV/dQ Analysis of Baseline.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Q_{AB} (Ah)</th>
<th>Q_{AB} Retention (%)</th>
<th>Q_{BC} (Ah)</th>
<th>Q_{BC} Retention (%)</th>
<th>Q_{CD} (Ah)</th>
<th>Q_{CD} Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.99</td>
<td>100.00</td>
<td>1.06</td>
<td>100.00</td>
<td>0.25</td>
<td>100.00</td>
</tr>
<tr>
<td>72.00</td>
<td>0.99</td>
<td>99.16</td>
<td>1.03</td>
<td>97.60</td>
<td>0.25</td>
<td>98.20</td>
</tr>
<tr>
<td>763.00</td>
<td>0.92</td>
<td>92.61</td>
<td>0.99</td>
<td>93.17</td>
<td>0.22</td>
<td>89.05</td>
</tr>
<tr>
<td>999.00</td>
<td>0.90</td>
<td>90.68</td>
<td>0.98</td>
<td>92.70</td>
<td>0.21</td>
<td>83.36</td>
</tr>
<tr>
<td>1300.00</td>
<td>0.90</td>
<td>90.87</td>
<td>0.97</td>
<td>91.40</td>
<td>0.21</td>
<td>84.77</td>
</tr>
<tr>
<td>1900.00</td>
<td>0.88</td>
<td>88.22</td>
<td>0.97</td>
<td>91.24</td>
<td>0.19</td>
<td>75.14</td>
</tr>
<tr>
<td>2200.00</td>
<td>0.85</td>
<td>85.88</td>
<td>0.96</td>
<td>91.07</td>
<td>0.18</td>
<td>72.99</td>
</tr>
<tr>
<td>2215.00</td>
<td>0.86</td>
<td>86.18</td>
<td>0.97</td>
<td>91.39</td>
<td>0.19</td>
<td>73.24</td>
</tr>
</tbody>
</table>

Table 3.2: dV/dQ Analysis of Cell 1.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Q_{AB} (Ah)</th>
<th>Q_{AB} Retention (%)</th>
<th>Q_{BC} (Ah)</th>
<th>Q_{BC} Retention (%)</th>
<th>Q_{CD} (Ah)</th>
<th>Q_{CD} Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.01</td>
<td>100.00</td>
<td>1.02</td>
<td>100.00</td>
<td>0.29</td>
<td>100.00</td>
</tr>
<tr>
<td>72.00</td>
<td>1.00</td>
<td>98.51</td>
<td>1.03</td>
<td>101.37</td>
<td>0.27</td>
<td>94.24</td>
</tr>
<tr>
<td>763.00</td>
<td>0.93</td>
<td>91.94</td>
<td>0.97</td>
<td>95.21</td>
<td>0.26</td>
<td>88.24</td>
</tr>
<tr>
<td>999.00</td>
<td>0.92</td>
<td>90.42</td>
<td>0.96</td>
<td>94.24</td>
<td>0.25</td>
<td>86.04</td>
</tr>
<tr>
<td>1300.00</td>
<td>0.89</td>
<td>87.50</td>
<td>0.95</td>
<td>93.26</td>
<td>0.25</td>
<td>85.37</td>
</tr>
<tr>
<td>1900.00</td>
<td>0.84</td>
<td>83.00</td>
<td>0.91</td>
<td>89.60</td>
<td>0.23</td>
<td>80.56</td>
</tr>
<tr>
<td>2200.00</td>
<td>0.82</td>
<td>80.63</td>
<td>0.90</td>
<td>87.89</td>
<td>0.23</td>
<td>78.78</td>
</tr>
<tr>
<td>2215.00</td>
<td>0.82</td>
<td>81.46</td>
<td>0.90</td>
<td>87.91</td>
<td>0.23</td>
<td>80.67</td>
</tr>
</tbody>
</table>
Table 3.3: dV/dQ Analysis of Cell 3.

<table>
<thead>
<tr>
<th>Cycle (Ah)</th>
<th>$Q_{AB}$ (Ah)</th>
<th>$Q_{AB}$ Retention (%)</th>
<th>$Q_{BC}$ (Ah)</th>
<th>$Q_{BC}$ Retention (%)</th>
<th>$Q_{CD}$ (Ah)</th>
<th>$Q_{CD}$ Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>1.05</td>
<td>100.00</td>
<td>1.04</td>
<td>100.00</td>
<td>0.30</td>
<td>100.00</td>
</tr>
<tr>
<td>72.00</td>
<td>1.00</td>
<td>95.52</td>
<td>1.04</td>
<td>99.87</td>
<td>0.28</td>
<td>90.66</td>
</tr>
<tr>
<td>763.00</td>
<td>0.92</td>
<td>88.02</td>
<td>0.99</td>
<td>95.62</td>
<td>0.25</td>
<td>82.20</td>
</tr>
<tr>
<td>999.00</td>
<td>0.90</td>
<td>86.28</td>
<td>0.99</td>
<td>95.79</td>
<td>0.23</td>
<td>75.16</td>
</tr>
<tr>
<td>1300.00</td>
<td>0.85</td>
<td>80.68</td>
<td>0.97</td>
<td>93.18</td>
<td>0.21</td>
<td>67.69</td>
</tr>
<tr>
<td>1900.00</td>
<td>0.83</td>
<td>79.27</td>
<td>0.91</td>
<td>87.80</td>
<td>0.22</td>
<td>74.10</td>
</tr>
<tr>
<td>2200.00</td>
<td>0.72</td>
<td>68.92</td>
<td>0.82</td>
<td>79.02</td>
<td>0.19</td>
<td>62.88</td>
</tr>
<tr>
<td>2215.00</td>
<td>0.48</td>
<td>46.25</td>
<td>0.57</td>
<td>54.59</td>
<td>0.10</td>
<td>31.37</td>
</tr>
</tbody>
</table>

Table 3.4: dV/dQ Analysis of Stack

<table>
<thead>
<tr>
<th>Cycle (Ah)</th>
<th>$Q_{AB}$ (Ah)</th>
<th>$Q_{AB}$ Retention (%)</th>
<th>$Q_{BC}$ (Ah)</th>
<th>$Q_{BC}$ Retention (%)</th>
<th>$Q_{CD}$ (Ah)</th>
<th>$Q_{CD}$ Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>5.02</td>
<td>100.00</td>
<td>5.28</td>
<td>100.00</td>
<td>1.41</td>
<td>100.00</td>
</tr>
<tr>
<td>72.00</td>
<td>5.00</td>
<td>99.66</td>
<td>5.16</td>
<td>97.76</td>
<td>1.37</td>
<td>97.23</td>
</tr>
<tr>
<td>763.00</td>
<td>4.64</td>
<td>92.44</td>
<td>4.86</td>
<td>92.14</td>
<td>1.27</td>
<td>89.99</td>
</tr>
<tr>
<td>999.00</td>
<td>4.56</td>
<td>90.97</td>
<td>4.83</td>
<td>91.53</td>
<td>1.22</td>
<td>86.74</td>
</tr>
<tr>
<td>1300.00</td>
<td>4.36</td>
<td>87.00</td>
<td>4.80</td>
<td>90.97</td>
<td>1.15</td>
<td>81.79</td>
</tr>
<tr>
<td>1900.00</td>
<td>4.16</td>
<td>83.02</td>
<td>4.55</td>
<td>86.26</td>
<td>1.14</td>
<td>80.74</td>
</tr>
<tr>
<td>2200.00</td>
<td>3.96</td>
<td>78.97</td>
<td>4.40</td>
<td>83.36</td>
<td>1.05</td>
<td>74.49</td>
</tr>
<tr>
<td>2215.00</td>
<td>3.72</td>
<td>74.22</td>
<td>4.15</td>
<td>78.58</td>
<td>0.96</td>
<td>68.23</td>
</tr>
</tbody>
</table>
Figure 3.6: Cathode capacity retention from dV/dQ analysis for different cycles and cells.

Figure 3.7: Lithium inventory loss from dV/dQ analysis for different cycles and cells.
Figure 3.8: Anode capacity retention from dV/dQ analysis for different cycles and cells.

We can observe a trend among all the cells where the anode had the highest degradation, followed by the cathode and lastly by the loss of lithium. Vetter et. al. [27] suggests that high temperatures and high SOC contributes to electrolyte decomposition, the decomposition products build up “protective layers” that cover the electrode’s surface which increase the SEI growth. The electrolyte decomposition causes the loss of active lithium, explaining the trend in the loss of lithium inventory analysis, where the baseline only had a 9% loss of lithium inventory, while cell 1 had 12% loss and cell 3 had 45% loss.
This could confirm that the high temperature experienced by the stack and especially by the middle cell caused an accelerated SEI growth and lithium consumption.

When looking at the anode degradation, we can observe that the baseline cell had a slightly higher degradation than cell 1 with 27% and 20% respectively. The higher degradation in the anode for the baseline cell could be explained by the lower charging temperature which could have induced lithium plating.

The trend was also clear for the cathode degradation of the cells, where the baseline had 14% degradation, cell 1 had 19% degradation and cell 3 had 54% degradation. The main factor for the cathode degradation, especially in LiCoO₂ based cells is the electrochemical oxidation, which could be accelerated by higher cycling temperature [81].
Chapter IV

1. Conclusion

To investigate the effects of non-uniform temperature distribution on degradation of Li-ion batteries, a Li-ion battery stack consists of five 3 Ah pouch cells connected in parallel was tested for 2215 cycles. Temperature, capacity retention, internal resistance, current, and SOC of each cell in the stack were measured and compared. The results were also compared with a single baseline cell going through same cycling test. A thorough dV/dQ analysis was made with the goal of finding the roots of the degradation and maybe link it to possible degradation mechanisms. Based on the measurement results and analysis, the following conclusions can be made.

- The temperature of cells in the stack during discharge increased almost 4 times higher than that of baseline cell. The temperature distribution in the stack became non-uniform during discharge.
- All the cells in the stack degraded faster than the baseline cell and the middle cell in the stack degraded most rapidly. This finding supports the hypothesis that non-uniform temperature distribution causes non-uniform and accelerated degradation.
- Resistance of the cells in the stack experienced non-uniform increase with cycle number which is consistent with degradation rate, but all the resistances showed similar pattern of increase. They remained stable in early cycles, then experienced a rapid increase, and became stable again before a sudden increase of the middle
cell resistance. Such variation can be attributed to the non-uniform degradation of cells in the stack.

- Current distribution in the stack also became non-uniform and their behaviors changed significantly with cycling. The change can be attributed to variation of cell resistance.
- Non-uniform current distribution led to non-uniform SOC distribution and could also contribute to the fast degradation of the middle cell in the stack.
- Differential voltage analysis suggested that growth of SEI on the anode is the primary mechanism for accelerated degradation of the middle cell in the stack.

2. Future Work

While the results above have supported the hypothesis that non-uniform temperature distribution causes non-uniform and accelerated degradation through quantitative cycling test, further research is needed to better understand the effects. For example, the degradation mechanisms behind the rapid increase of cell resistance followed by restabilization need to be understood, but lack of full details of chemistry in the commercial cells used in this study prevented such understanding. Comparable tests on cells with well-defined chemistry, as well as post-mortem analysis [28, 82], need to be done. In addition, higher discharging C rate or stronger cooling could exacerbate the non-uniformity of temperature distribution due to higher heat generation or heat transfer rate, which could cause more dramatic non-uniform degradation. At lower ambient temperatures or higher charging C rate, lithium plating would play an important role in degradation [71, 83-85] and the higher temperature of middle cells would mitigate lithium
plating induced degradation. In such cases, the effects of non-uniform temperature distribution on degradation could be very different from this study and deserve further investigation. This research will motivate the development of novel and practical thermal management to mitigate the degradation while improving performance and safety.
Appendix A

In this appendix, the cooling coefficient of a single cell is estimated using lumped capacitance method. To estimate the cooling coefficient, the characteristic cooling time (time constant) needs to be firstly estimated by plotting the surface temperature rise in log scale versus time after discharge and then fitting the curves according to:

\[ T - T_\infty = (T_i - T_\infty)e^{-\frac{t}{\tau}} \]  \hspace{1cm} (4)

Where \( T \) is the final temperature, \( T_\infty \) is the ambient temperature, \( T_i \) is the initial temperature and \( \tau \) is the characteristic cooling time. Following previous works that used this method [38, 86], the curve fittings are performed in the time range of 100 s to 600 s, to avoid the mixing effect right after discharge and larger error at later times due to smaller temperature difference. After retrieving the value of \( \tau \) the convection cooling coefficient can be estimated using:

\[ h = \frac{mc_p}{\tau A_s} \]  \hspace{1cm} (5)

Where \( h \) is the cooling coefficient, \( m \) is the mass of the pouch cell, \( c_p \) is the specific heat of the pouch cell and \( A_s \) is the cell surface area. The necessary parameters to estimate the heat transfer coefficient are shown in Figure A.1 and Table A.1.
Figure A.1: Characteristic cooling time estimation

Table A.1: Parameter used for heat transfer coefficient estimation and Biot number calculation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposed Area</td>
<td>$A_s$</td>
<td>0.0102</td>
<td>m$^2$</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>$c_p$</td>
<td>1000</td>
<td>Jkg$^{-1}$K$^{-1}$</td>
</tr>
<tr>
<td>Mass</td>
<td>$m$</td>
<td>0.06</td>
<td>kg</td>
</tr>
<tr>
<td>Characteristic Cooling Time</td>
<td>$\tau$</td>
<td>701</td>
<td>s</td>
</tr>
<tr>
<td>Heat Transfer Coefficient</td>
<td>$h$</td>
<td>8.39</td>
<td>Wm$^{-2}$K$^{-1}$</td>
</tr>
<tr>
<td>Characteristic Length</td>
<td>$L_C$</td>
<td>0.0027</td>
<td>m</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$k$</td>
<td>1</td>
<td>Wm$^{-1}$K$^{-1}$</td>
</tr>
</tbody>
</table>
Inputting the parameters from table A.1 in equation (5), we have that the heat transfer coefficient for a single cell used in this study is approximately 8.39 Wm\(^{-2}\)K\(^{-1}\). This analysis can be used if the Biot number is smaller than 0.1, which implies that the heat conduction inside the body is much faster than the heat convection away from its surface, and temperature gradients are negligible inside of it. For this purpose, the Biot number was calculated according to its definition:

\[
Bi = \frac{Lc h}{k} \quad (6)
\]

Inputting parameters from table A.1 in equation (6) we get that the Biot number for this system is 0.0227 which is smaller than 0.1 and thus this analysis can be considered valid.
Appendix B

In this Appendix, the heat generation of both the baseline and the stack are estimated for cycle 200. The heat generation was divided between the reversible and irreversible heat generation. All the calculations were done based on Huang et al. [54]

By neglecting mixing heat generation which is much smaller than irreversible and entropic heat generation, the heat generation rate $q_{gen}$ during discharging of a Li-ion cell can be estimated:

$$q_{gen} = q_{gen,irr} + q_{gen,rev} = I(U_{OC} - V) - IT \left(\frac{dU}{dT}\right)$$  \hspace{1cm} (7)

Where $I$ is current, $V$ is cell voltage, $U_{OC}$ is open-circuit voltage, $T$ is absolute temperature with unit of K, and $\left(\frac{dU}{dT}\right)$ is entropic coefficient. The term $I(U_{OC} - V)$ represents irreversible heat generation rate $q_{gen,irr}$ and the term $IT\left(\frac{dU}{dT}\right)$ represents reversible heat generation rate $q_{gen,rev}$.

For the data acquisition of $U_{OC}$, a single fresh cell was charged to 100% SOC, and discharged in 10% SOC steps until the cell reached 0% SOC, between every 10% SOC discharge the temperature would be set to 20, 30 and 40 °C t steps and the cell would rest two hours to ensure that the $U_{OC}$ would be stable and the data would be collected. The data can be seen in Figure B.1.
Figure B.1: $U_{OC}$ at different SOC levels and temperatures.

The estimation of $\left(\frac{dU}{dT}\right)$ was done by using the slope of the $U_{OC}$ vs Temperature graphs for each SOC. The slope of each SOC curve represents the entropic coefficient and can be seen in Figure B.2.

Figure B.2: Entropic coefficient estimation.
With the data about the variation of the open circuit voltage with temperature and SOC obtained, the irreversible heat generation $q_{\text{gen,irr}}$ was calculated, it is shown in Figure B.3 (a). The reversible heat generation $q_{\text{gen,rev}}$ was calculated and is shown in Figure B.3 (b).

Figure B.3: (a) Irreversible heat generation both in baseline cell and stack. (b) Reversible heat generation both in baseline cell and stack.

Figure B.3 (a) shows a relatively constant irreversible heat generation rate throughout discharge until the very end where there is an abrupt increase. However, for the reversible heat generation rate shown in Figure B.3 (b), it is visible that the rate is high during the beginning of discharge and negative between 500 and 1000 seconds, after that negative period there is an increase until 3000 seconds when it starts decreasing until the end of discharge.
The total heat generation $q_{\text{gen}}$ can be simply calculated as the sum of both heat generations as shown in equation (7). Figure B.4 shows the total heat generation during discharge. The trend of total heat generation is consistent with the thermal behavior of the cells as seen in Figure 2.4 (a).

Figure B.4: Total heat generation rate.
References


[29] Saxton, T., 2012, "Plug In America’s LEAF Battery Survey ".


[34] Fleckenstein, M., Bohlen, O., Roscher, M. A., and Bäker, B., 2011, "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), pp. 4769-4778.


