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Characterization and Degradation Analysis of Commercial Lithium-Ion Batteries for eVTOL Applications

A Thesis Presented for the
Master of Science
Degree

The University of Tennessee, Knoxville

Preston Matthew Young

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Abstract

Electric vertical take-off and landing (eVTOL) aircraft are gaining more attention for their potential to relieve traffic congestion in urban areas. Lithium-ion batteries are the most common choice for eVTOL systems thanks to their relatively high energy and power densities. These batteries have seen large amounts of research and development over the past decade thanks to their usage in electric vehicles (EVs) and consumer electronics such as cellphones and laptops. However, the demands placed on the lithium-ion batteries that will be used in eVTOL aircraft are much more stringent, requiring further research on how these cells would behave in such an application. The power demands of an electric aircraft during vertical take-off and landing would require fast discharge rates of around 10-25C. The safety demands of batteries used in aircraft would be very stringent with thermal runaway being a major area of concern. Recently, additional concern surrounding EV performance in cold weather has been increasing and eVTOL systems would face similar challenges.

Despite this rising attention, little research has been done to analyze how current state-of-the-art lithium-ion batteries would behave in an eVTOL application. This study tests the performance of three commercial cells chosen for their high discharge power, providing important data on cell performance and degradation under high c-rates. The cells are tested for up to 500 cycles over four different ambient conditions: 20°C with natural convection and 20°C, 0C, and -10°C with forced convection cooling. A characterization test, comprising of a 1C battery capacity determination (BCD) and electrochemical impedance spectroscopy (EIS), was performed at beginning of life and after every 50 cycles to track cell degradation. Distribution of relaxation times (DRT) is employed to deconvolute the over-potentials of different processes in the cell. Changes in the DRT spectra are used to identify degradation mechanisms within the cell, including SEI growth/decomposition, lithium plating, and

electrode degradation. The results of these endurance tests provide much needed information on battery performance in eVTOL conditions.

Additionally, accelerating rate calorimetry (ARC) testing was performed on a few of the cells to study their thermal runaway characteristics, and a new battery test stand was developed which rapidly controls the temperature of the cells, laying the groundwork for further study of lithium-ion battery's applicability to eVTOL systems.

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Nomenclature

Ah	Ampere-hours
ARC	Accelerating Rate Calorimetry
BOL	Beginning of Life
CC	Constant Current
CCCV	Constant Current, Constant Voltage
CPU	Heat Capacity Unit
CtCv	Cell to Cell Variations
DCIR	Direct Current Internal Resistance
DRT	Distribution of Relaxation Times
ECM	Equivalent Circuit Model
EESCL	Electrochemical Energy Storage and Conversion Laboratory
EIS	Electrochemical Impedance Spectroscopy
EOL	End of Life
EV	Electric Vehicle
eVTOL	Electric Vertical Take-off and Landing
GEIS	Galvanostatic Electrochemical Impedance Spectroscopy

HFR	High Frequency Resistance
HWS	Heat-Wait-Seek
IR	Infrared
IR	Internal Resistance
LAM _{NE}	Loss of Active Material of the Negative Electrode
LAM _{PE}	Loss of Active Material of the Positive Electrode
LCO	Lithium Cobalt Oxide
LFP	Lithium Iron Phosphate
LIB	Lithium Ion Battery
LLI	Loss of Lithium Inventory
LMO	Lithium Manganese Oxide
NCA	Lithium Nickel Cobalt Aluminum Oxide
NE	Negative Electrode
NMC	Lithium Nickel Manganese Cobalt Oxide
PE	Positive Electrode
PEI	Positive Electrolyte Interphase
PEIS	Potentiostatic Electrochemical Impedance Spectroscopy
PWL	Piece-wise Linear
RBF	Radial Basis Functions
RC	Resistive-Capacitive (circuit element)
SEI	Solid Electrolyte Interphase

SOC	State of Charge
SOH	State of Health
TEC	Thermoelectric Cooler
THT	Thermal Hazard Technology
UAM	Urban Air Mobility
UTSI	University of Tennessee Space Institute

Chapter 1

Introduction

1.1 Growing Need for eVTOL Batteries

Traffic congestion is becoming increasingly problematic in urban centers. In 2019 alone, Americans spent an average of 99 hours sitting in traffic, resulting in 88 billion dollars in lost productivity nationally. This congestion issue will only worsen with the trend of growing urbanization [33]. One potential solution to alleviate congestion is to exploit the airspace above population centers with flying vehicles capable of carrying both passengers and cargo, a concept known as Urban Air Mobility (UAM) [17]. In 2016, Uber Elevate [13] released a white paper describing how on-demand urban air transportation could be accomplished with a network of electric vertical take-off and landing (eVTOL) aircraft. An image of one potential Uber Elevate design is shown in Figure 1.1. eVTOLs provide significant advantages over current aircraft, such as greater mobility in urban environments, zero operational emissions, decreased noise pollution, and no requirement for fixed routes. Since the release of this paper, eVTOL systems have received increasing attention and now hundreds of these aircraft systems are under development [26].

However, difficult challenges still need to be solved before these aircraft can be seen carrying passengers overhead, namely meeting the power and energy demands of an eVTOL's mission profile. Multiple studies have been performed analyzing aircraft configuration, mission parameters, and payload to better understand the power demands and challenges of eVTOL applications [33, 2, 20]. Ayyaswamy et al, modeled three different aircraft configurations



Figure 1.1: Uber Elevate rendering of a potential eVTOL design [12].

(multicopter, tilt rotor, and vectored thrust) and concluded that the flight time would be limited to under 40 minutes with a range of less than 200 km [2]. To increase range and flight time, hybrid power systems could be utilized with batteries supplying the needed power during the lift and hover phases. During the low power cruise phase, an onboard generator or fuel cell can power the aircraft and simultaneously charge the battery system [26].

Lithium-ion batteries (LIBs) are commonly selected to provide power for eVTOL systems thanks to their promising high energy and power densities. These batteries are widely used in personal electronics, power tools, and electric vehicles (EVs) and have been the subject of countless studies exploring new materials and characterizing LIB performance. However, the majority of these studies are focused around EVs and applications that do not demand nearly as much power as eVTOLs. A better understanding of LIB performance under high-power applications is needed before eVTOLs can take flight [33]. In this work, three commercial lithium-ion batteries are tested under high rate discharges over a range of different ambient temperature conditions to study how state of the art cells perform and degrade in a high-power eVTOL setting.

1.2 Background in Lithium-Ion Batteries

1.2.1 Electrode Naming Convention

In electrochemical systems, the cathode is the electrode in which the reduction reaction takes place and electrons are gained. The anode is the electrode in which the oxidation reaction takes place and electrons are lost. Under discharging conditions, electrons flow from the negative electrode to the positive electrode. Therefore, the negative electrode is the anode and the positive electrode is the cathode. When charging, current flow reverses and the locations of the anode and cathode swap with the negative electrode being the cathode and vice versa. However, it is customary in battery literature to refer to each electrode as if the battery is discharging regardless of cell state. So the positive electrode (PE) is always the cathode and the negative electrode (NE) is always the anode. In this work, this naming convention is followed unless otherwise stated.

1.2.2 Lithium-Ion Battery Construction

Lithium-ion batteries are electrochemical energy storage devices that utilize the movement of lithium ions between the anode and cathode to store energy and provide power to electrical systems. They are comprised of five main components: cathode, anode, electrolyte, separator, and current collectors, shown in [Figure 1.2](#). The cathode (positive electrode) is a lithium metal oxide which donates lithium ions to the system. Commonly used battery chemistries are lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium nickel cobalt aluminum oxide (NCA), and lithium nickel manganese cobalt oxide (NMC), to name a few. Each of these cathode materials provide the battery with different electrochemical characteristics.

The anode (negative electrode) is predominantly made out of graphite. Electrode materials are made into a fine powder, blended with solvents and binders, and pasted onto the current collectors which lead to the tabs outside the cell. Aluminum and copper are commonly selected as the current collector material for the cathode and anode respectively. The electrolyte is a mixture of lithium salt and organic solvents which is flooded between the two electrodes and allows for the movement of lithium ions. The separator is a plastic film commonly made from polyethylene or polypropylene, which is permeable to lithium ions. This is placed between the electrodes, preventing them from touching and causing an internal short circuit while still allowing for ion transport [\[37\]](#). These components are stacked and rolled for use in coin, cylindrical, pouch, and prismatic cells. [Figure 1.3](#) shows cylindrical and pouch formats.

1.2.3 Lithium-Ion Principals and Definitions

Working Principal

Batteries convert chemical energy to electrical power by pushing ions through an external circuit. This is accomplished through the movement of positively charged lithium ions between the electrodes in the cell. As the cell is charged, ions move from the cathode to the anode through the electrolyte and separator. Lithium ions enter the graphite anode through a process called intercalation, where the ion species is inserted into the lattice structure of the carbon anode [\[5\]](#). Likewise, during discharge ions move from the anode into the

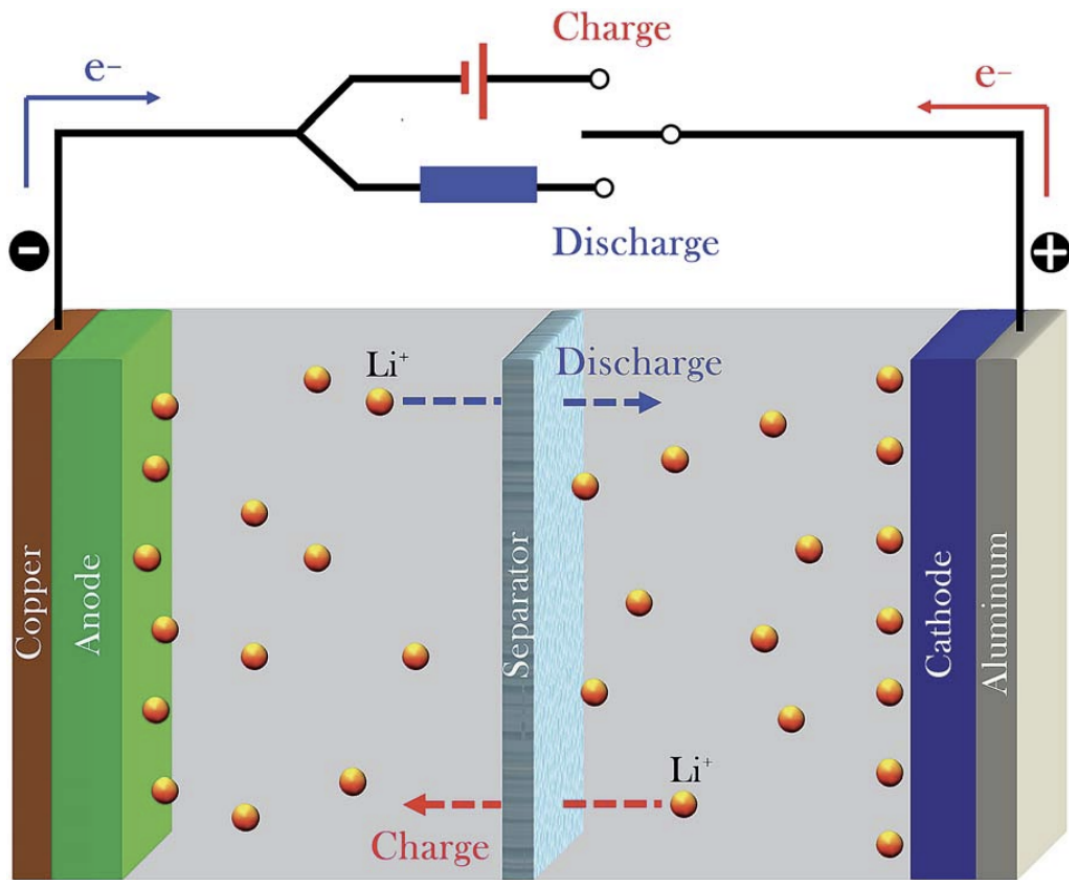


Figure 1.2: Schematic of the working mechanism of a lithium-ion battery [22].

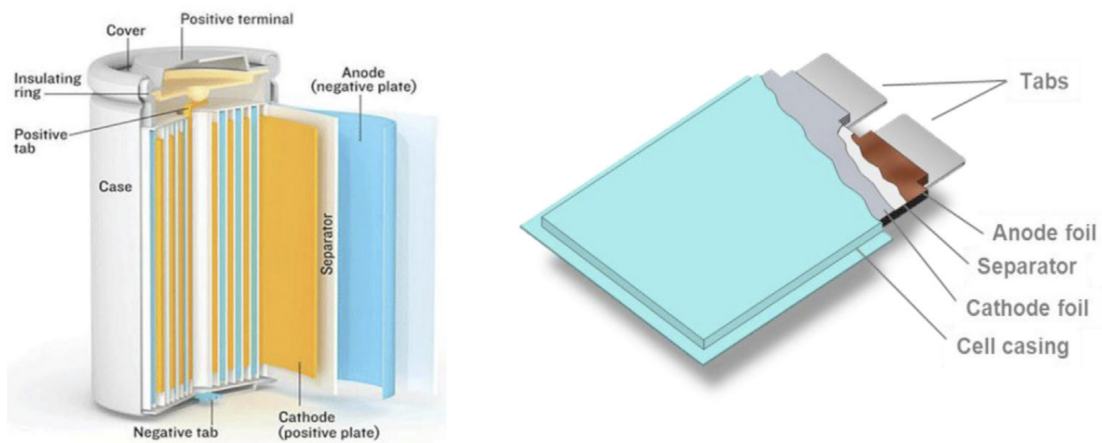


Figure 1.3: Cylindrical and pouch cell configurations [37].

cathode. This movement can be seen in [Figure 1.2](#). As the ions move through each material and across interfaces, an impedance resists that movement. Every process in a battery, electrical and electrochemical, has an associated impedance, which has a direct effect on battery performance.

After assembly, formation cycles are performed on lithium-ion cells which forms passivation layers between each electrode and the electrolyte. These layers play a crucial role in the performance and cyclability of the battery and are known as the solid electrolyte interphase (SEI) and the positive electrolyte interphase (PEI) for the anode and cathode respectively. As the cell is cycled, the SEI layer can both grow and breakdown, resulting in degradation. While both passivation layers are important to battery function and contribute to degradation, the SEI layer plays a larger role and is most commonly referred to in the literature.

Capacity

Batteries are commonly rated by their capacity, which is a measure of the total charge that can be obtained from a fully charged battery expressed in the unit of Ampere-hours (Ah) [5]. Discharge capacity is specified by the manufacturer for specific conditions as both current and temperature can affect available capacity.

Charge and Discharge Protocols

The most common method for charging cells is through the constant current, constant voltage (CCCV) scheme. In this method the cell is charged at a constant current to the upper voltage cut-off. Then the voltage is held constant at this value, trickle charging the cell until the current reaches a given current cut-off value. To discharge the cell, a constant current (CC) approach is common, where the cell is discharged at a constant current until the voltage reaches the lower cut-off. Selected cut-off voltages depend on cell chemistry but 4.2 V is a common upper limit and 3.0 or 2.5 are common lower limits.

C-Rate

C-rate is a commonly used metric when discussing charge and discharge currents for batteries. One C is the current in Amperes equal to the capacity of the cell in Ampere-hours.

Multiples of the C rate are used to express larger or smaller currents. For example, a 2.0 Ah cell discharged at a current of 1C (or 2.0 Amps) will be fully discharged in approximately one hour. The same cell discharged at 2C (or 4.0 Amps) will be fully discharged in approximately 30 minutes.

State of Charge

State of charge (SOC) is a commonly-used term to discuss the amount of charge a battery contains at any given moment. It can be expressed in Ah or as a percentage of the total battery capacity [5]. SOC is useful in battery discussion as instantaneous cell performance can be drastically affected by the charge currently stored in the battery.

State of Health

State of health (SOH) is a term used to reflect the degradation of the cell and the current performance as compared to the cell at beginning of life (BOL). SOH is not a defined measurement that can be taken from a cell but instead encompasses many battery characteristics which can experience degradation: capacity, power, internal resistance (IR), self discharge rate, etc. Many investigations into SOH mainly refer to the capacity retention as the cell degrades. It is common for cell end-of-life (EOL) to be defined as when the cell is only capable of delivering 80% of the capacity as it was at BOL.

Thermal Runaway

As lithium-ion batteries rise in popularity, so too are fire safety concerns. If the battery's internal temperature rises too high, then materials in the cell will break down, and violent exothermic reaction can take place. This is known as thermal runaway [16]. Large amounts of heat and flammable gases can be released, generating large fires and even explosions. Thermal runaway can be triggered by a number of battery abuses including the following: external heating, internal ohmic heating, punctures, physical damage, and internal short circuits. These abuses can lead to SEI decomposition, electrolyte decomposition, separator decomposition, and side reactions between the electrodes and electrolyte. All of these contribute to heat release and thermal runaway. A schematic of thermal runaway for a LCO

cell is shown in [Figure 1.4](#). As EVs become more popular and increasing public attention is being given to fires in EVs, thermal runaway mitigation and prevention is an important area of research.

1.3 Characterization Methods of LIBs

1.3.1 Degradation Modes and Mechanisms.

As lithium-ion batteries degrade, their ability to store energy and provide power are reduced. Degradation is caused by cycling, high or low temperatures, and their storage conditions. A complex system of physical and chemical mechanisms cause degradation. Sets of degradation mechanisms are clustered into degradation modes, which ultimately lead to one of two effects on the cell: capacity fade and power fade [7]. Three degradation modes are commonly reported in the literature:

- **Loss of lithium inventory (LLI):** Lithium ions are consumed in parasitic reactions and are no longer available for cycling between the anode and cathode, leading to capacity fade. These reactions include SEI and PEI growth, lithium plating, decomposition reactions, etc. [7]
- **Loss of active material of the negative electrode (LAM_{NE}):** Negative electrode active mass is no longer available for lithium insertion caused by particle cracking, loss of electrical contact, blocking of active sites by surface layer growth, etc. This leads to both capacity and power fade [7].
- **Loss of active material of the positive electrode (LAM_{PE}):** Positive electrode active mass is no longer available for lithium insertion caused by particle cracking, loss of electrical contact, structural disordering, etc. This leads to both capacity and power fade [7].

Each degradation mode is caused by a multitude of individual degradation mechanisms within the cell. These mechanisms have been extensively studied in the literature and are verified through postmortem analysis. These degradation mechanisms include SEI

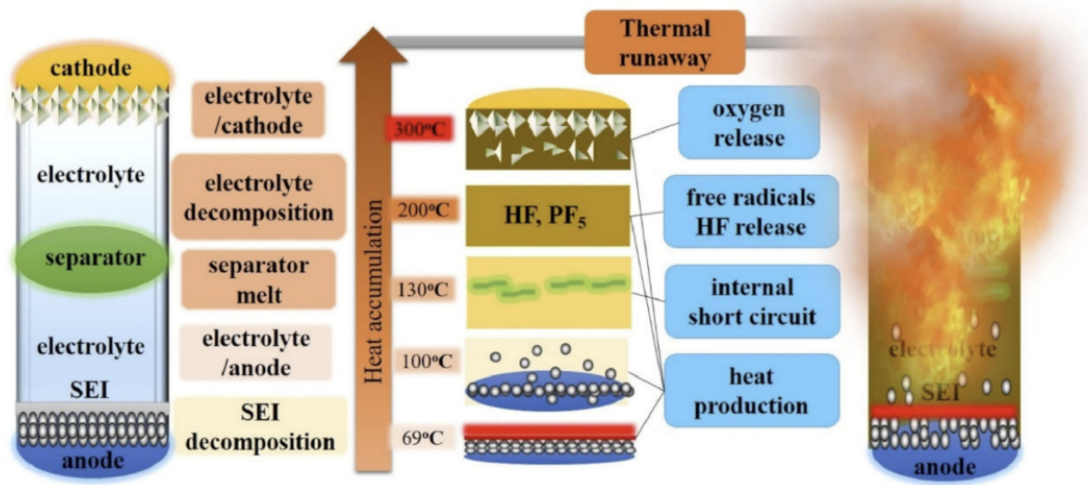


Figure 1.4: A schematic of thermal runaway processes in lithium cobalt oxide (LCO)/graphite cell [16].

formation, SEI decomposition, particle cracking, lithium plating, dendrite formation, binder decomposition, and contact loss. A diagram of the degradation mechanisms is presented in [Figure 1.5](#). Additionally, the physical and chemical degradation mechanisms can be caused by time, high or low temperature, state of charge, current load, etc. [Figure 1.6](#) shows the cause and effect relationships of degradation in the cells starting with the root cause, then the degradation mechanisms and degradation modes, and ultimately the final effect on the cell.

1.3.2 Postmortem Analysis

Postmortem analysis involves disassembly of the cell to analyze the materials inside. This can provide important insights into the degradation of the cell materials although it requires the destruction of the cell. Because of this, it is common to disassemble cells at both BOL and EOL for a better understanding of the changes in the electrode material. Due to the reactive nature of the electrolyte and to avoid unwanted changes to the cell materials, great care must be taken during the disassembly process, so that the cell components are maintained to a very similar state as they were operating in the cell.

The first step of disassembly is to discharge the cells to a defined SOC as the charge contained in the cell can effect the results. A lower SOC is desirable for disassembly as it lowers the energy contained in the cell, reducing the risk of thermal runaway. For this reason, some studies lower the cell voltage all the way to 0 V for safety. However, discharging the cell outside of the voltage window can cause undesirable material changes that are not due to ageing. Therefore, it is most common to discharge the cell to 0% SOC with a discharge down to the lower cut-off voltage. Different methods have been used to reach a consistent SOC including slow (C/20) discharges to the cut-off voltage and holding the cell at the cut-off voltage for extended periods of time [\[29\]](#).

Once the cell is set to the desired SOC, the lithium-ion cell is disassembled in a chemically inert environment such as an argon filled glove box. Great care should be taken to prevent external and internal short circuits. Ceramic tools or tools with non-conductive coatings can be used, and the cell should be cut in a place where the electrode layers will not be damaged and cause an internal short. The cutting process is different for cylindrical, pouch, and prismatic cells, but, in general, the cell can be cut with a rotary tool or ceramic scissors.

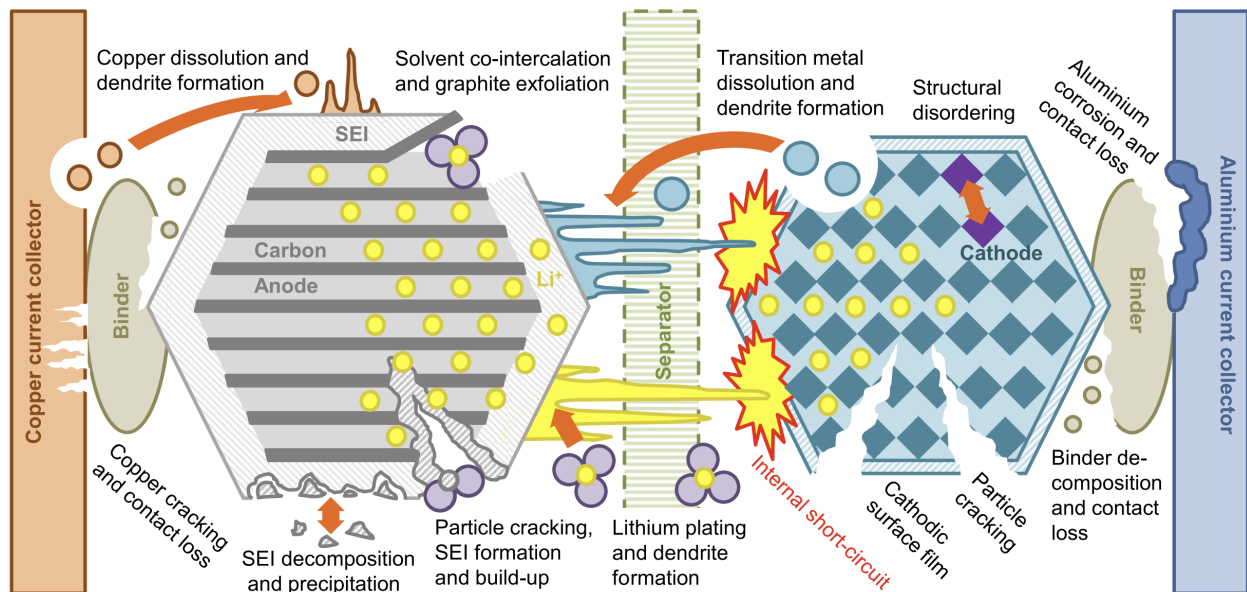


Figure 1.5: Degradation mechanisms of lithium-ion cells [7].

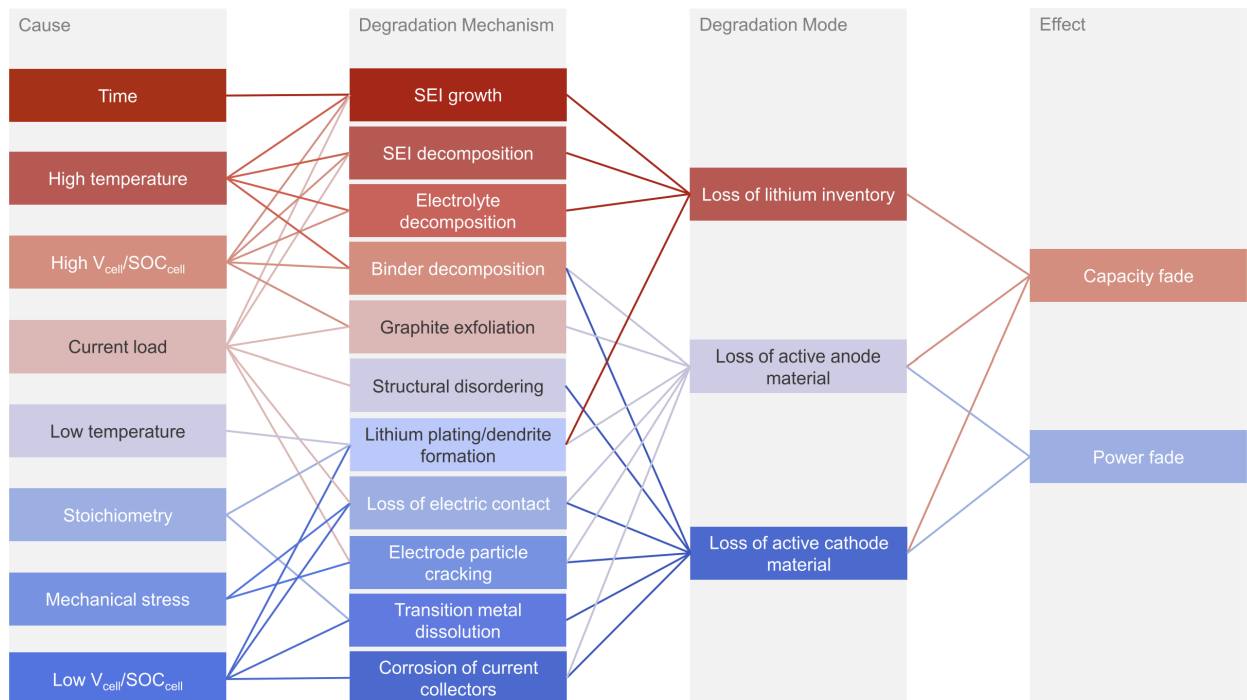


Figure 1.6: Cause and effect of degradation mechanisms and associated degradation modes [7].

During cutting, drops of electrolyte can be recovered for analysis. Once the cell casing is opened, the jelly roll can be removed and cell components can be separated and washed with an electrolyte solvent [29].

A simple visual inspection of cell electrodes can provide some insight into degradation mechanisms. The most common things to see are a grey film on the negative electrode indicating lithium plating (Figure 1.7) or electrodes that are non-uniformly lithiated (Figure 1.8). It may also be possible to see large cracks or delaminations in the material.

These recovered cell materials can also undergo physical-chemical characterization. Many different methods have been used in the literature including scanning electron microscopy, x-ray diffraction, Raman spectroscopy, and transmission electron microscopy.

1.3.3 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a widely-used, non-destructive technique for the characterization of electrochemical systems. Two modes of EIS can be used to measure cell impedance. Potentiostatic EIS (PEIS) applies a sinusoidal voltage to the cell of a certain amplitude and frequency, measuring the gain and phase shift of the cell's response. In Galvanostatic EIS (GEIS) a sinusoidal current is applied. This EIS measurement is repeated for a number of frequencies in the kHz to mHz range which allows this technique to capture the effects of cell processes with different time constants.

The measured impedance is plotted in a Nyquist plot where the negative imaginary part of the impedance is plotted against the real part, allowing for parameterization of the resistance, capacitance, and inductance of the cell processes. An idealized graphical representation of a Nyquist plot for a commercial lithium-ion battery is shown in Figure 1.9. The higher frequencies, where the Nyquist plot is below the real axis, represent the inductive behavior of the system. This is attributed to the geometry of the cell windings and the connections to the measurement device. Where the plot crosses the real axis is known as the high frequency resistance (HFR), which is a measure of all the ohmic resistances, including electrolyte, active material, current collectors, and electrical contacts. After the HFR, one or two arcs can be seen, representing the electrochemical processes occurring inside the cell, which combine resistive and capacitive effects. These processes represent ion movement through various cell



(a) Pristine



(b) Lithium Plated

Figure 1.7: Visual inspection of a (a) pristine graphite anode and a (b) lithium plated anode [19].

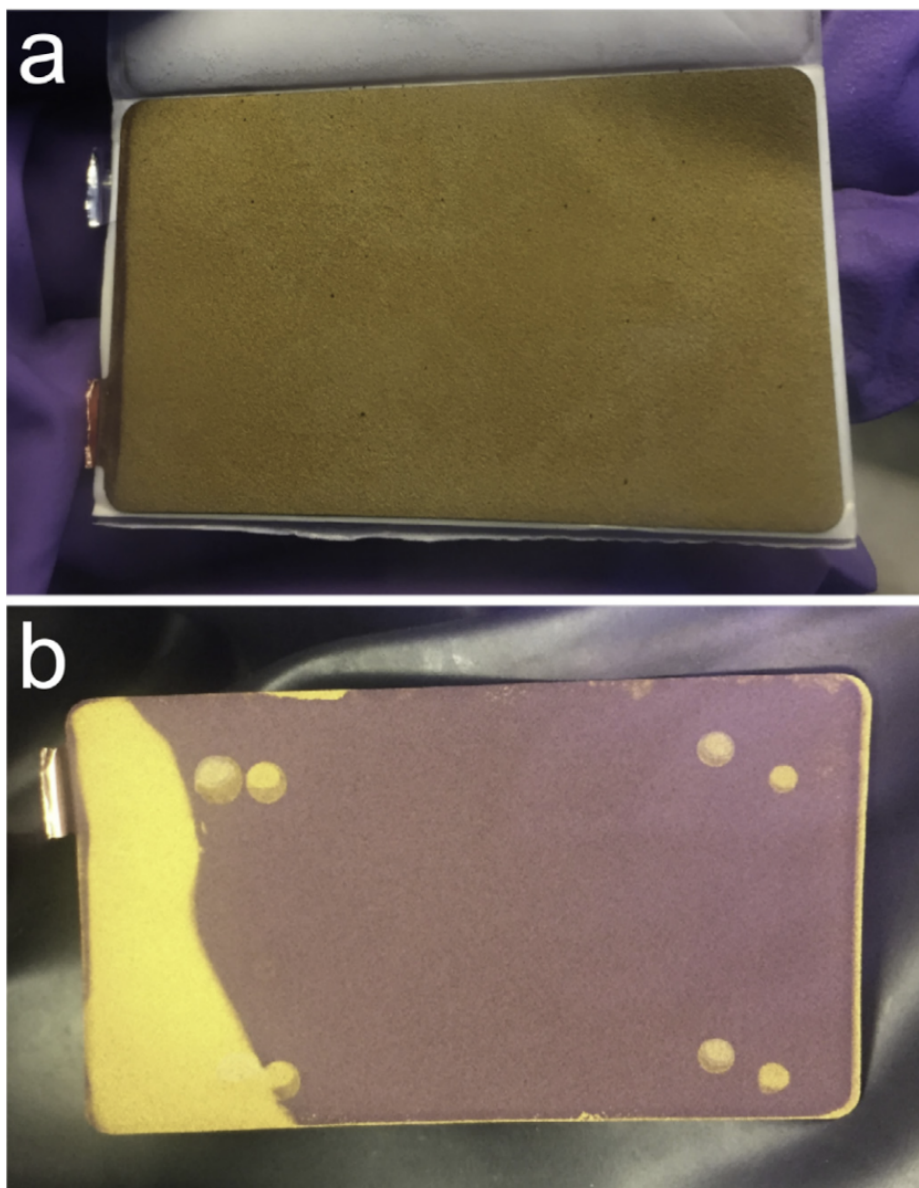


Figure 1.8: Visual inspection of non-uniform lithiation on the graphite negative electrodes: (a) uniformly lithiated and (b) non-uniformly lithiated [7].

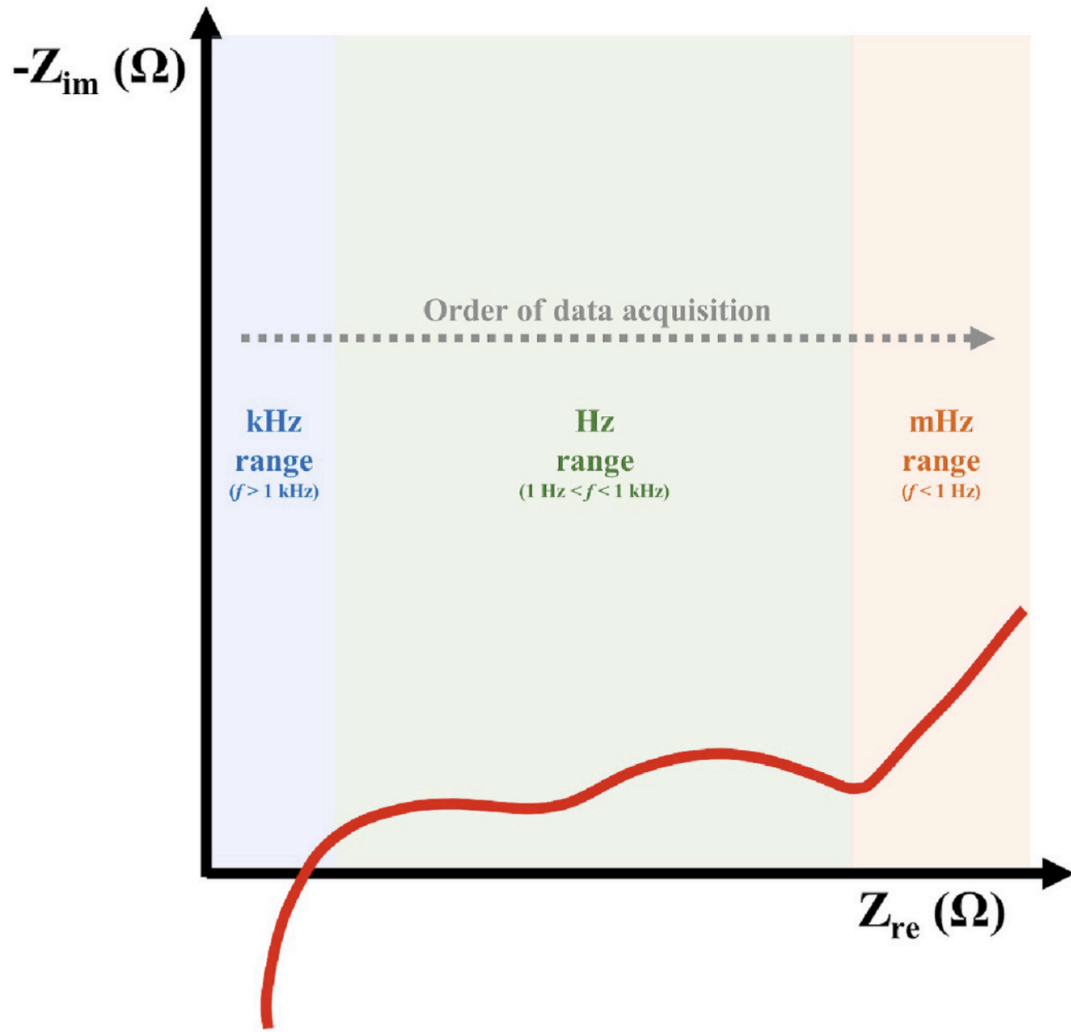


Figure 1.9: Graphical representation of a Nyquist plot from an EIS measurement of a lithium-ion battery [24].

interfaces. The low-frequency tail represents lithium-ion diffusion in the cell, particularly in the active material of the electrodes [24].

While examining the impedance and shape of the Nyquist plot can provide insights into cell performance, it can be useful to create models of the cell for study and prediction of cell performance. To this end, equivalent circuit models (ECM) can be created based on the Nyquist impedance. Typically ECM's are created with a resistor representing the HFR, resistive-capacitive (RC) circuit elements representing the arcs, and a Warburg element for the diffusion tail. A simple Randles model is comprised of a resistor and RC element and shown in Figure 1.10 with a Warburg element. ECM's can become more accurate and complex with additional resistive and inductive elements. One such example is shown in Figure 1.11 [36].

1.3.4 Distribution of Relaxation Times

Distribution of Relaxation Times (DRT) is an analysis technique which can be performed on EIS data enabling for the deconvolution of the impedance from the frequency domain into the time domain. The resulting data is a distribution of peaks with varying gains and time constants. Peak fitting algorithms can be employed to analyze the DRT data [27]. Thus, electrochemical processes in the batteries can be separated by time constants to be individually identified and analyzed.

Calculation of DRT

Many methods exist for the calculation of DRT. In general, the experimental EIS data Z_{exp} is fitted to a model Z_{DRT} , which is obtained from the following Fredholm integral of the first kind:

$$Z_{DRT}(f) = R_{\infty} + \int_0^{\infty} \frac{g(\tau)}{1 + i2\pi f\tau} d\tau \quad (1.1)$$

Where R_{∞} is the HFR and $g(\tau)$ is a function that describes the time relaxation characteristics of the electrochemical system. Equation 1.1 can be thought of as an equivalent Voigt circuit, made up of a resistor and an infinite number of RC circuit elements [30],

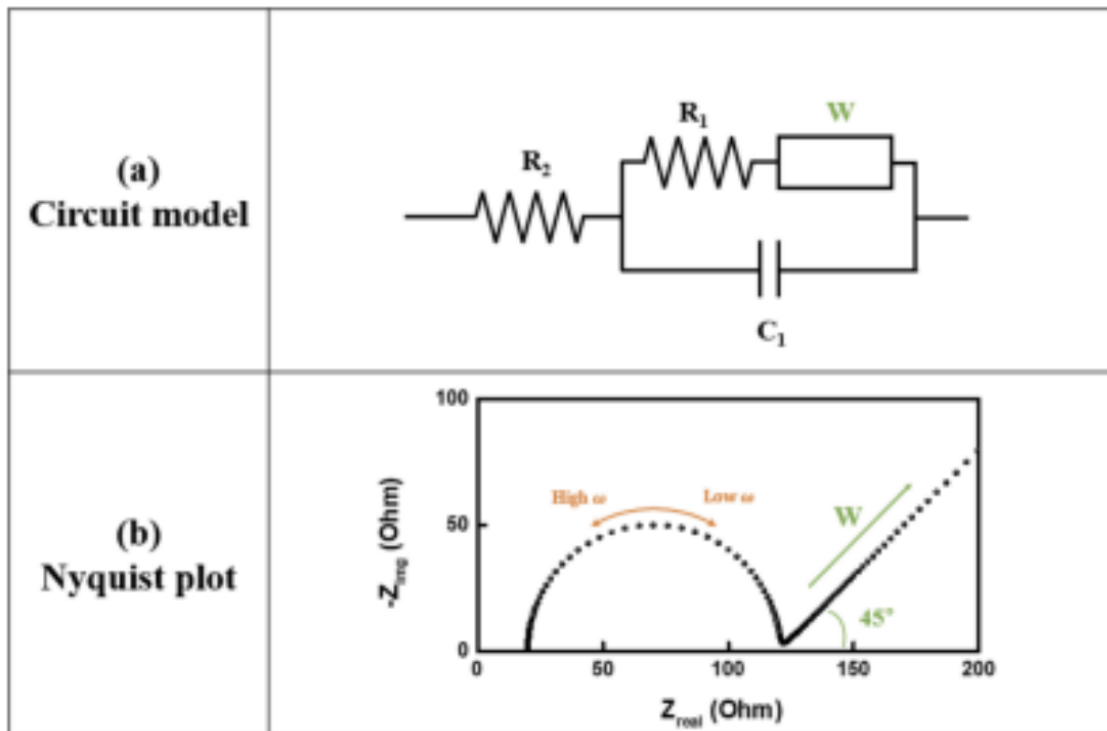


Figure 1.10: An example of a Randles cell model with a Warburg element and the resulting Nyquist plot [36].

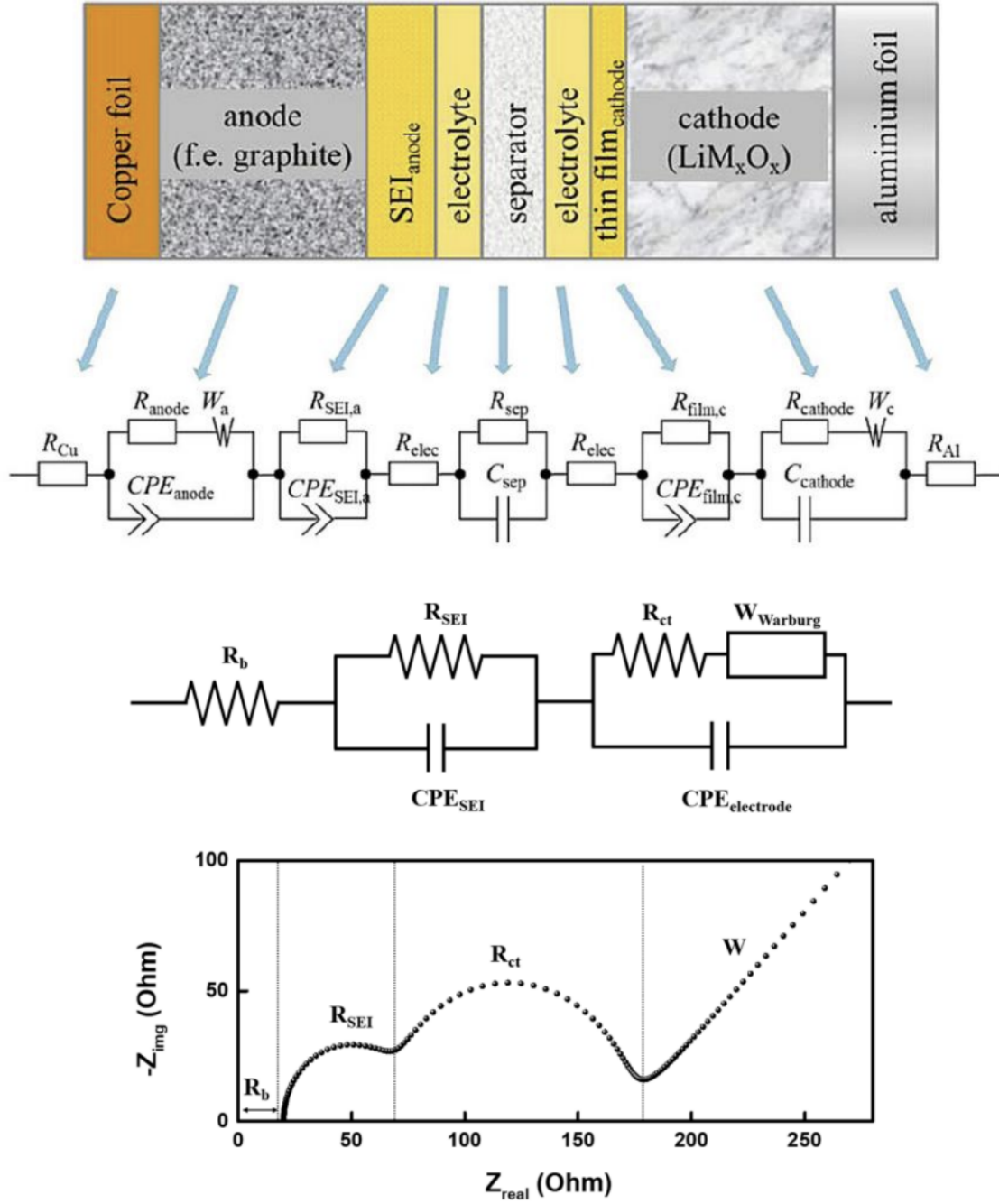


Figure 1.11: Diagram of a typical lithium-ion cell and a more complex ECM representing the shown Nyquist plot [36].

similar to the ECM's discussed above. Because frequency data is generally collected in the logarithmic scale, for the purposes of DRT Equation 1.1 can be rewritten as:

$$Z_{DRT} = R_{\infty} + \int_{-\infty}^{\infty} \frac{\gamma(\ln\tau)}{1 + i2\pi f\tau} d\ln\tau \quad (1.2)$$

Where $\gamma(\ln\tau) = \tau g(\tau)$ [30].

Fredholm integral equations are generally inverse ill-posed problems, as multiple solutions exist, and not all of these solutions are meaningful. Therefore, the solution space is constrained to positive values and a regularization technique is employed to reduce the number of possible solutions. Many approaches have been used for this deconvolution problem, including applications of Fourier transforms, neural networks and probabilistic deconvolution methods. Even the iterative Van-Cittert and Gold algorithms commonly used in image processing and the sparse-spike deconvolution technique used in seismology have been applied to DRT. However, the most common method involves discretizing the integral by applying Tikhonov L2-regularization to a linear optimization algorithm [27].

Wan et al. show the importance in selection of the basis for discretizing $\gamma(\ln\tau)$ to reduce the approximation error in DRT calculation. Generally, the $\gamma(\ln\tau)$ Voigt circuit is estimated using a piece-wise linear (PWL) approximation, which assumes the $\gamma(\ln\tau)$ is linear between each consecutive timescale. In their work, Wan et al. propose a DRT based on radial basis functions (RBF). They show that applying an RBF approximation is comparable to the PWL discretization method and improves on PWL discretization when EIS data collection is incomplete. Furthermore, RBF discretization can reduce convergence time [30]. Additionally, Wan et al. developed a MATLAB GUI toolbox for the calculation of DRT which is used in this work.

Internal Process Identification with DRT

As distribution of relaxation times allows for the deconvolution of processes inside the cell, it becomes important to identify what these processes are inside the cell. Many studies have been involved with attributing peaks to specific cell processes by varying both temperature and SOC to test how the DRT spectra changes. Then each peak is attributed to a certain

cell process accordingly [19]. An example of temperature and SOC's effect on DRT can be seen in Figure 1.12. When studying full cells, it is impossible to identify different processes at the anode and cathode, because the leads are connected to the positive and negative electrodes. To study just the anode or cathode side of the cell, 3-electrode cells can be created by including a reference electrode in the cell, or half cells can be created by using lithium metal as the counter electrode [18]. For example, EIS could be performed on an anode half-cell to study the effects of the SEI without the effects of the PEI. The results of these DRT studies show a general consensus on the process attributions of these peaks. Figure 1.13 shows the time constants where processes can be expected in the DRT spectra. Generally, DRT is used to study the following four main processes:

- **Particle-Particle Interactions:** These processes are the effect of the interfaces between electrode material particles. It includes the movement of lithium across electrode grain boundaries and the contact resistance between the electrodes and metal current collectors. This peak shows almost no variation with SOC, only a small variation with temperature change, and generally occurs with time constants below 10^{-3} s [19, 27].
- **Passivation Layers:** Also referred to as the SEI layer, this peak encompasses the process of transporting Lithium ions through the passivation layers on the negative electrode (SEI) and the positive electrode (PEI). Also included in this range are the effects of the electrolyte interfaces. These peaks are sensitive to temperature change but not to SOC and generally occur around 10^{-3} - 10^{-2} s [19, 27].
- **Charge Transfer Processes:** These peaks include the lithium ion's movement into and out of the electrode, the intercalation of ions into the electrodes, and the effects of the double layer. These processes generally show up as two or more peaks, are sensitive to high and low SOC, and generally occur in the ranges of 10^{-2} and 10^0 s [19, 27].
- **Diffusion Processes:** These processes relate to the diffusion of ions inside the solid material of the electrodes. They are also sensitive to SOC and low temperature. Diffusion is the slowest of the processes and occurs at time constants higher than 10^0 s [19, 27].

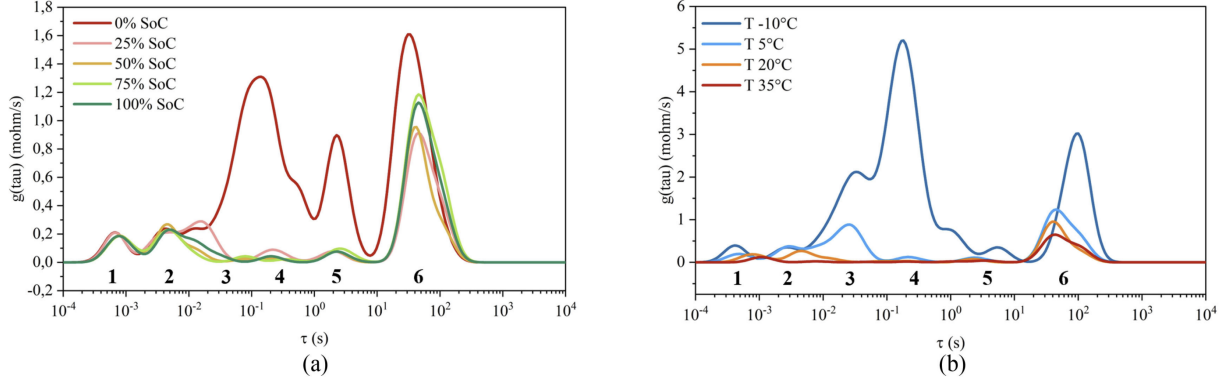


Figure 1.12: DRT profiles of a large NMC pouch cell. (a) DRT profiles at 20°C and different SOC levels. (b) DRT profiles at 50% SOC and different temperatures. This cell shows six peaks corresponding to: 1) particle-particle interactions, 2) passivation Layer, 3-4-5) charge transfer processes, and 6) diffusive processes. [19].

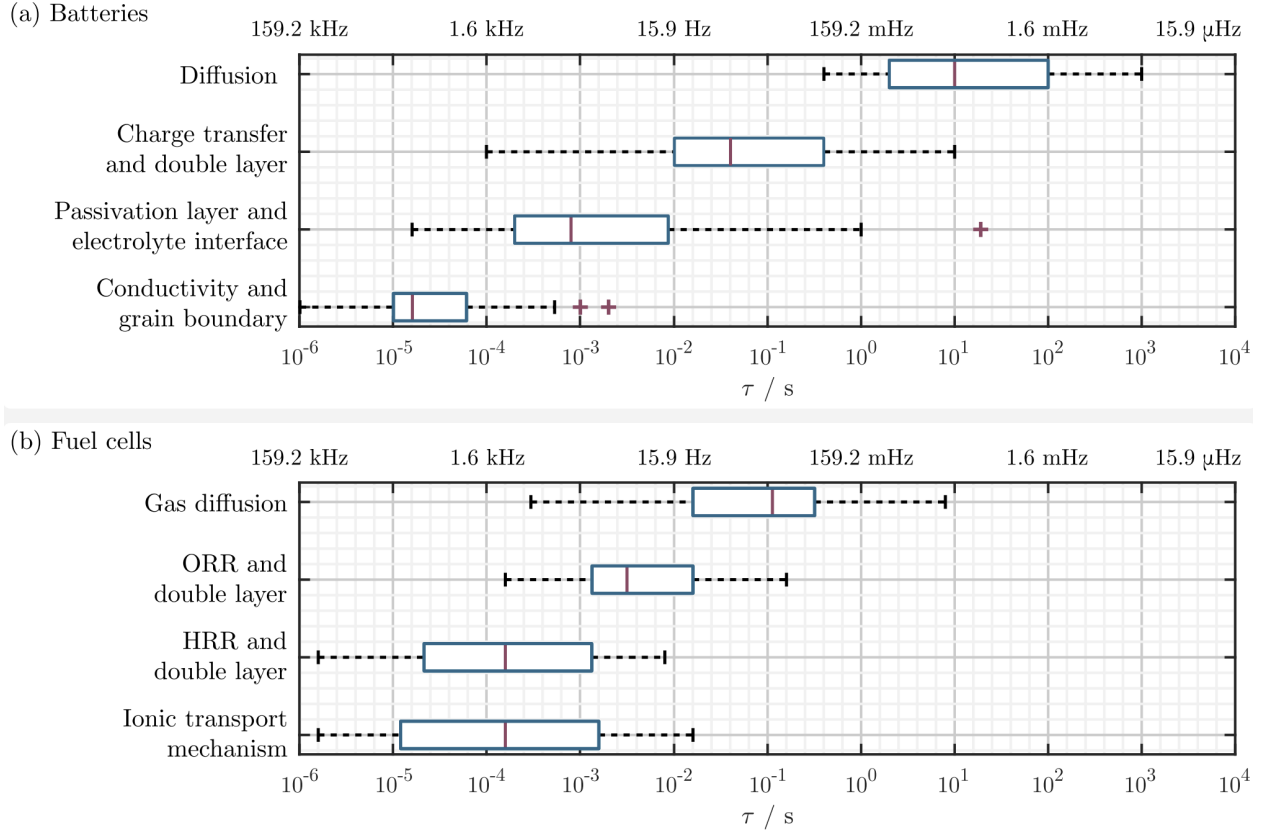


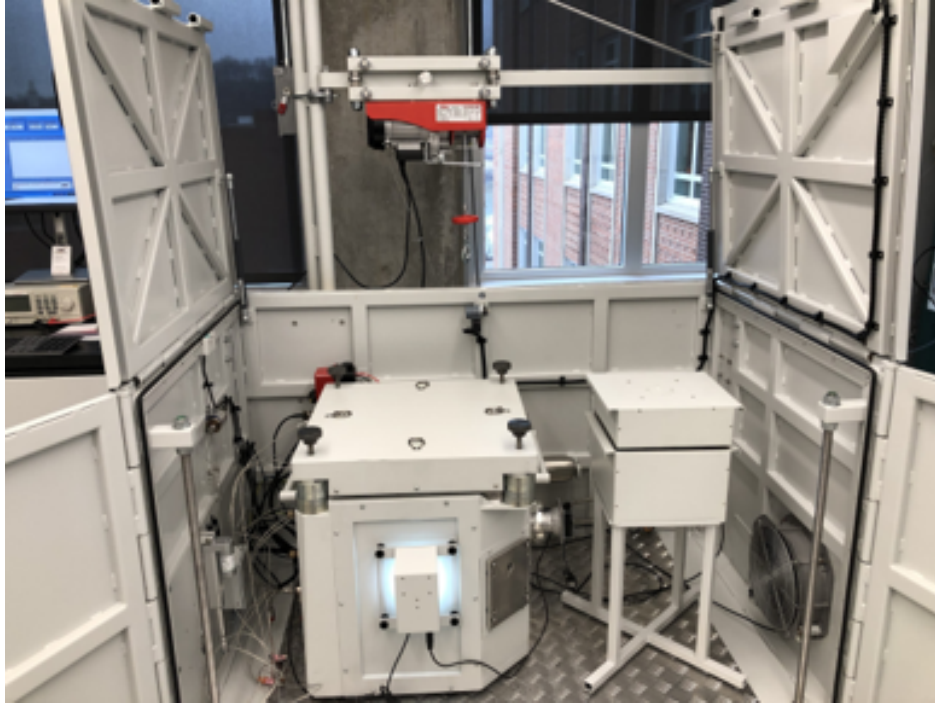
Figure 1.13: Time constants of internal processes for (a) batteries and (b) fuel cells [27].

Other studies have used DRT to analyze changes in peak processes during degradation studies to identify degradation mechanisms within the cell. Iurilli et al. analyzed commercial cylindrical cell degradation. The team disassembled some of the cylindrical cells and manufactured half-cells from the anode and cathode material. They also created full coin cells from the extracted material. The cells were cycled to induce degradation. SEI growth/decomposition, lithium plating, cathode and anode degradation, and diffusion process degradation was identified in the DRT spectra and verified through postmortem analysis [18]. Another study by Chen et al. induced lithium plating in batteries by cycling them in low temperature conditions with over-discharge. They found that lithium plating tends to reduce the size of the charge transfer peak and shift it to faster time constants [9]. Applications of DRT to understanding cell performance and degradation is still an ongoing topic of research.

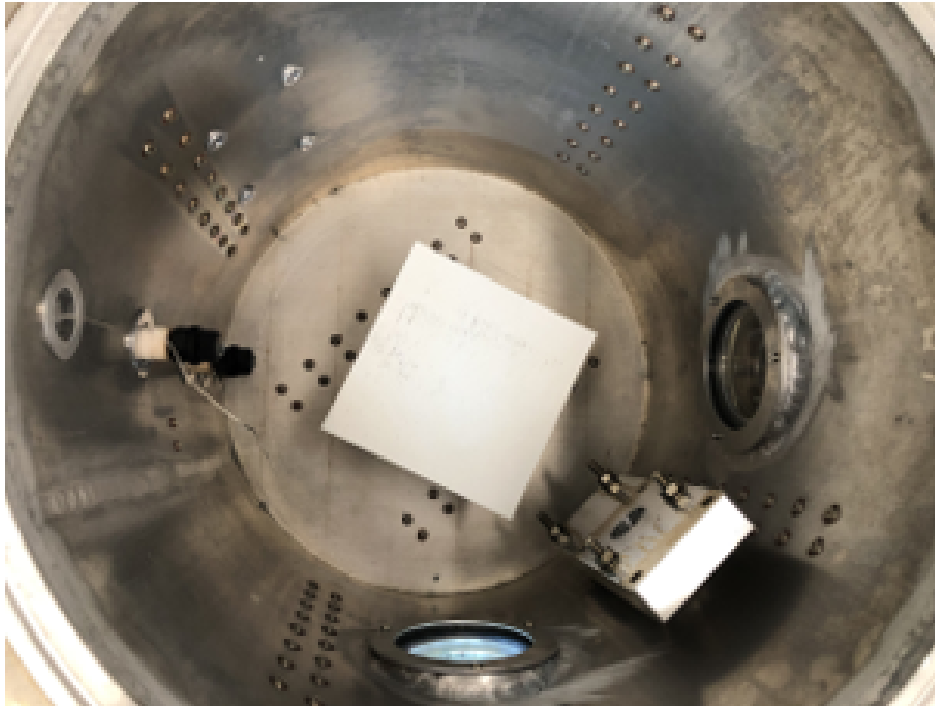
1.3.5 Accelerating Rate Calorimetry

Understanding and mitigating thermal runaway is important to the safety of lithium-ion batteries. One of the most popular methods to study thermal runaway is with an accelerating rate calorimeter (ARC). An ARC system from Thermal Hazard Technology (THT) is shown in Figure 1.14. The most common ARC test method is known as the “heat-wait-see” (HWS). In this test, a cell is loaded into the ARC with a thermocouple attached and isolated from the floor and walls, usually by suspending the cell from the lid or a bracket. Then the ARC heats up by preset temperature steps, usually 5°C. After heating, the ARC waits to allow the cell temperature to equilibrate with the environment. Then the ARC uses the thermocouple attached to the cell to search for any self heating in the cell due to exothermic side reactions. If the thermocouple reads the cell’s temperature increasing within a sensitivity of 0.02°C/min, then the ARC’s heaters will match the temperature rise of the cell and track it all the way up to 300°C creating an adiabatic environment during self heating and thermal runaway. If no temperature rise is detected during the seek phase, then the ARC will heat the cell up by 5°C more and repeat the process. Typical temperature curves for the ARC test are shown in Figure 1.15.

THT’s ARC is a versatile machine with extra options to improve functionality. Cells can be placed in a sealed canister to take pressure measurements throughout thermal runaway. A



(a)



(b)

Figure 1.14: Images of the Accelerating Rate Calorimeter with (a) Image of a THT ARC with two sizes of calorimeters: the larger “EV+” (left) and smaller “standard” (right). (b) Image inside of the EV+ calorimeter.

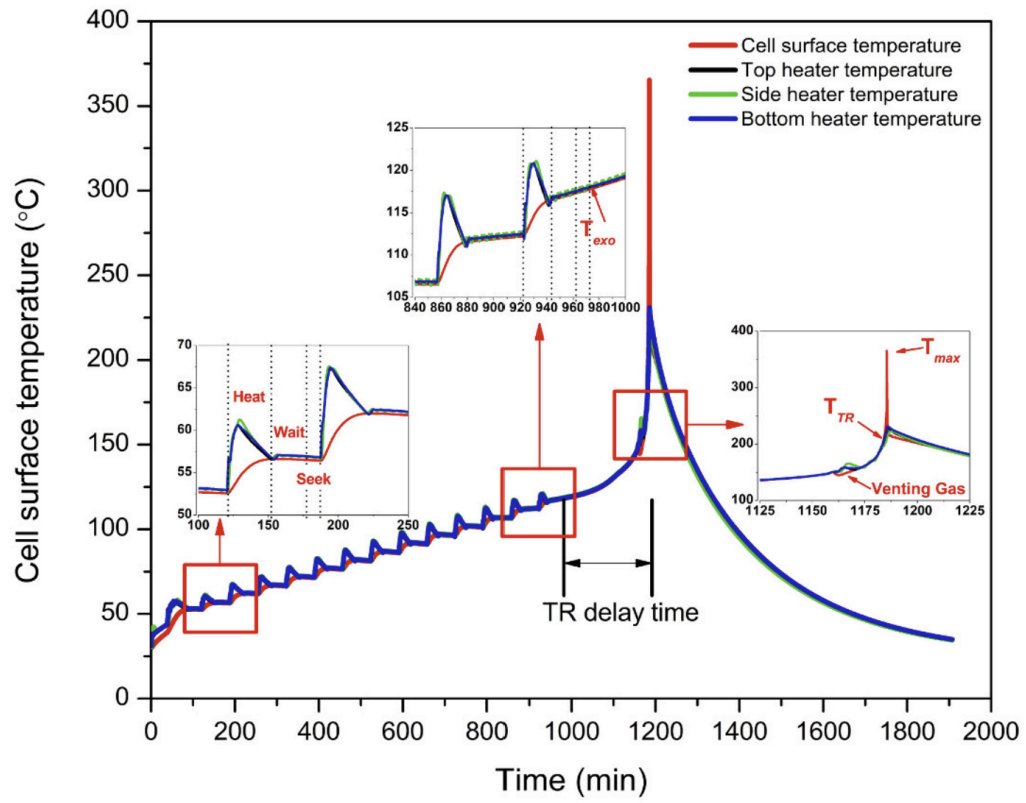


Figure 1.15: Typical temperature curves for an ARC test following the heat-wait-seek strategy [34].

gas collection system may be attached to the canister so that exhaust gases can be collected for analysis after the test. The ARC has a window allowing for videos to be captured of the burning cell with an option to replace the regular camera with an Infrared Camera (IR). A nail penetration tester can be attached for the study of mechanical damage including puncture and crushing. Electrode leads go through the ARC for electrochemical testing or overcharging. A heat capacity unit (CPU) can be attached to measure the heat capacity of a battery. A large amount of information can be learned from ARC testing, including heat energy released, onset temperature, peak temperature, and self heating rate, which is vital to understanding lithium-ion safety and model development.

Thermal runaway is a growing topic of research, aided by the ARC system. Studies have been performed to characterize the thermal runaway behavior of commercial LIBs. Said et al. tested commercial 18650 cells in both adiabatic and non-adiabatic conditions using an ARC system and oven heating respectively. It was found that battery SOC had a profound effect on thermal runaway. Fully charged batteries saw more severe thermal runaway characteristics with shorter times to induce self-heating and higher maximum temperatures up to 522°C. Cells at 0% SOC would experience self-heating but it did not lead to thermal runaway for the batteries tested [23]. Other ARC tests have focused on preventing thermal runaway. Zhang et al. used changes in cell voltage to trigger cooling of the cell, preventing thermal runaway while retaining cell function. It was found that the cell voltage dropped around 130°C and by rapidly cooling the battery with liquid nitrogen at this voltage drop or at 130°C, thermal runaway can be prevented with around 20% capacity degradation [35]. Dong et al. applied EIS measurements to ARC testing and found that analysis of three different indicators in the EIS spectra could provide a reliable early warning of dangerous conditions and could be used to prevent thermal runaway [11].

1.3.6 Cell to Cell Variations

Other characteristics of lithium-ion batteries that need to be understood are the differences between seemingly identical cells known as cell to cell variations (CtCv). These variations are caused by slight manufacturing differences during the creation of active material, binding electrode material to the current collectors, stacking the layers together, or cell assembly [4].

At the battery level, CtCv can be seen as variations in capacity, resistance, degradation, and thermal runaway.

Baumhöfer et al. cycled 48 identical cells under the same testing conditions and found a significant spread in the capacity degradation throughout the lifetime of the cell as shown in [Figure 1.16](#). Rüther et al. performed generalized DRT analysis on 92 identical Panasonic NCR 18650B cells and identified CtCv within the internal processes of the batteries. Additional statistical analysis showed that the variations did not often follow a normal distribution, but was better fitted with lognormal, gamma, and logistic distributions. They concluded that cell-to-cell variations do not follow a normal distribution, as is commonly assumed [\[28\]](#). Zhang et al. studied CtCv in lithium-ion battery thermal runaway and showed how 9 identical 18650 cells had vastly different onset temperatures, peak temperatures, and time from the onset of self-heating to the peak of thermal runaway [\[34\]](#) as shown in [Figure 1.17](#). Statistical understanding of cell to cell variations is important for battery applications and safety, especially when building a battery pack or module.

1.4 Motivation for LIB Analysis in eVTOL Applications

Over the past decade, lithium-ion battery technology has seen remarkable improvement thanks to the boom of electric vehicles and subsequent research. However, this research has been focused on EV applications with lower discharge rates, whereas eVTOLs have uniquely different operating conditions and battery requirements. With eVTOL battery research still being scarce, there is a need for experimental work into LIBs with eVTOL applications [\[33\]](#). Prior LIB degradation studies analyzing the effect of high discharge C-rates have focused on discharge rates of 3C or less [\[15, 25, 1\]](#) with some studies going up to 6C [\[21, 32\]](#). Only a few studies have examined cell performance at discharge rates higher than 10C. Fleischhammer et al. cycled commercial 18650 cells with 16C discharge but the study focused on thermal runaway and safety, concluding that thermal runaway characteristics depended on the type of degradation, with lithium plating causing a significant increase in self heating [\[14\]](#). Another study by Dixit et al. cycled cells at an eVTOL-based discharge profile including a 45s 15C discharge pulse followed by a long C/3 discharge. These tests were carried out with lab scale,

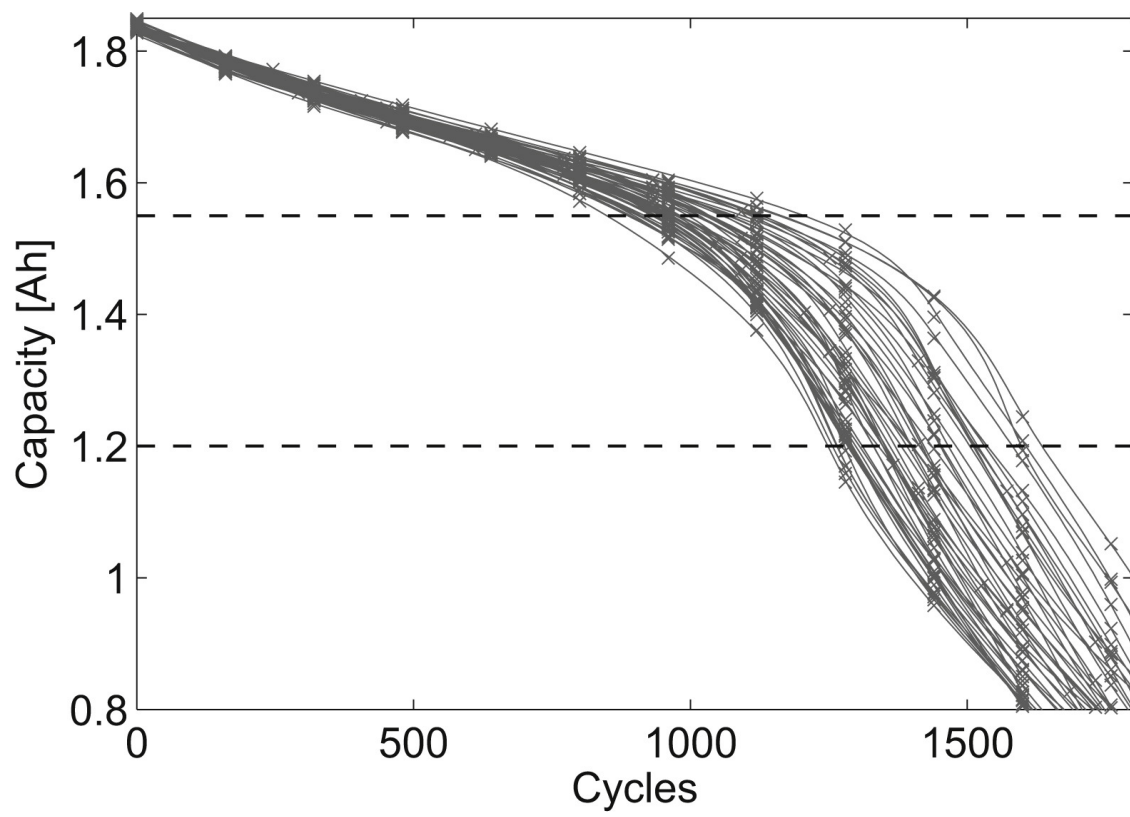


Figure 1.16: CtCv in capacity fade from 48 identical cells [3].

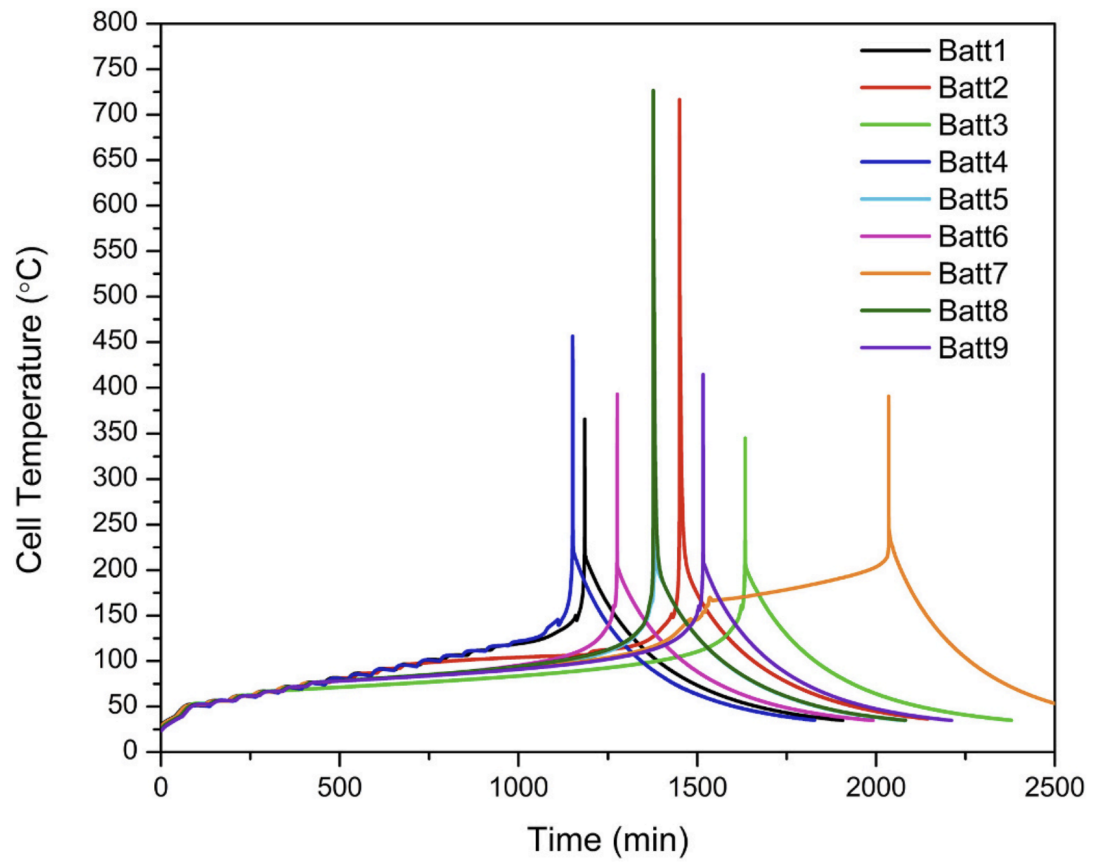


Figure 1.17: Variations in battery ARC testing for 9 identical cells [34].

single-layer pouch cells with capacities under 100 mAh and showed that the cells could not sustain the high-rate discharge pulses for extended cycling [10]. This review of numerous studies highlights the need for better understanding of cell performance under the high rate discharges that will be experienced by eVTOL batteries.

Additionally, cell performance in cold temperatures is an important consideration for eVTOLs as they could experience conditions as cold as -40°C [2]. Studies performed on cells in cold environments have shown that EV batteries cycled at -20°C have 60% of the available capacity as it does at room temperature [20]. However, the thermal demands of eVTOL batteries need to be further studied. The high discharge rates of eVTOL will cause large amounts of self-heating with the potential to cause large temperature changes during discharge. While self-heating could potentially help the cell performance at cold temperatures, if the temperature becomes too high, it could lead to thermal runaway.

Further testing is needed to understand LIB performance and thermal management requirements for eVTOL applications. Compared to EVs, eVTOLs have much more demanding power requirements of around 10-25C. With this increase in power comes increasing cooling demands, presenting a unique challenge for eVTOL battery pack design. Additionally, eVTOLs will fly all around the globe, potentially at high altitudes, exposing the batteries to a wide range of environments at both hot and cold temperatures. More research is required to understand battery performance under eVTOL applications before they can be seen flying overhead.

Chapter 2

LIB Degradation and Characterization Methodology

2.1 Battery Selection

Three different commercial lithium-ion batteries designed for high power applications were selected as the main cells in this study. The Molicel P28A is an 18650 cylindrical cell with a capacity of 2.8Ah and a rated maximum discharge current of 12.5 C. The other two cells are pouch cells designed for drone racing, selected for their high power capability. The Tattu R-Line 2.0 Ah pouch cell and the Race Day Quads (RDQ) 2.2 Ah pouch cell rated for discharge bursts of up to 120C and 80C respectively were also selected for this study. Initial high rate discharges were run on the cells to identify the maximum continuous discharge c-rate they were capable of, which partly determined the discharge c-rate for the endurance tests. Each individual cell was given a six character designation comprised of a three character cell type identifier and a three character number. Examples for the Molicel 18650, Tattu 2.0 Ah pouch, and the RDQ 2.2 Ah pouch are "Mol001", "Tat001", and "RQ2001", respectively. The batteries tested and their properties are listed in [Table 2.1](#).

Table 2.1: Battery properties

Cell Name	Molicel P28A	Tattu R Line 2.0	Race Day Quads 2.2
Manufacturer	Molicel	Grepow	Race Day Quads
Type	NCA 18650 cylinder	LCO Pouch	LCO Pouch
Capacity (Ah)	2.8	2.0	2.2
Rated Max C Rate	12.5	120	80
Mass (g)	46	47.7	54.8
Endurance Test C Rate	10	25, 40	23

2.1.1 Pack Disassembly

The pouch cells used in this study are sold in packs of four or six cells connected in series in order for the voltage to be high enough for drone racing. These packs were disassembled to test individual cells. The pack wrapping was removed and the current and voltage leads cut. Inside the pack, each cell was glued to each other with their tabs spot-welded together in series. These tabs were cut and the cells were separated from each other. Photographs from the disassembly of a four-cell Tattu battery pack can be seen in [Figure 2.1](#).

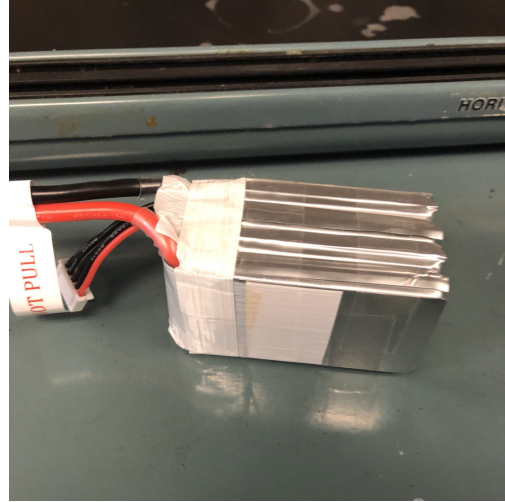
2.2 Endurance Test Protocol

The batteries in this study were tested for degradation in a variety of environmental conditions, set in an environmental chamber. The cells were cycled with a 1C CCCV charge protocol to 4.2V with a cutoff voltage of 100mA. After a 15 minute rest, the cells were discharged under constant current at 10C, 25C, and 23C for the Molicel, Tattu, and RDQ respectively, to the cut-off voltage for each cell as per manufacturer guidelines: 2.5V for Molicel and 3.0V for the pouches. After discharge, the cells were allowed to rest for 30 minutes to re-equilibrate with the environmental temperature before charging. The endurance tests lasted for up to 500 cycles or when the cells failed to cycle with characterization tests occurring in between every 50th cycle.

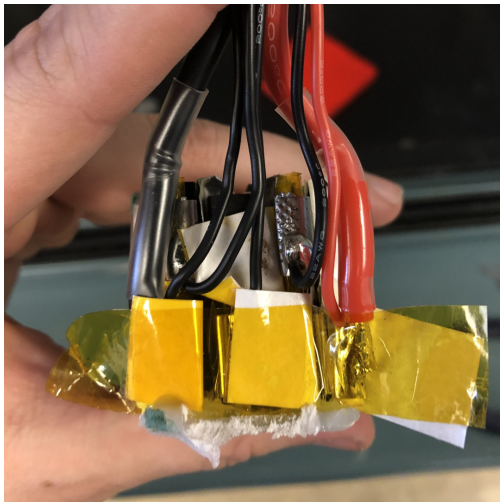
Four endurance tests were performed on each cell type under various thermal conditions: 20°C with natural convection (NC), 20°C with forced convection (FC), 0°C with force convection, and -10°C with forced convection. During the forced convection tests, airflow was supplied to the cells via a 90 mm PC cooling fan powered by a 12V power supply. The fan was mounted above the cell and pointed at a 45° angle towards the cell from about 3cm away supplying around 48.2cfm of airflow to the cell surface. A 3D printed cell and fan holder was used in the test and is shown in [Figure 2.2](#). Thermocouples were attached to each cell and measured the cell's surface temperature. The endurance test set-up is shown in [Figure 2.3](#).



(a) Tattu Pack



(b) Un-wrapped Tattu Pack



(c) Tattu Pack Wiring



(d) Four Separated Tattu Cells

Figure 2.1: Disassembly of a four-cell Tattu battery pack

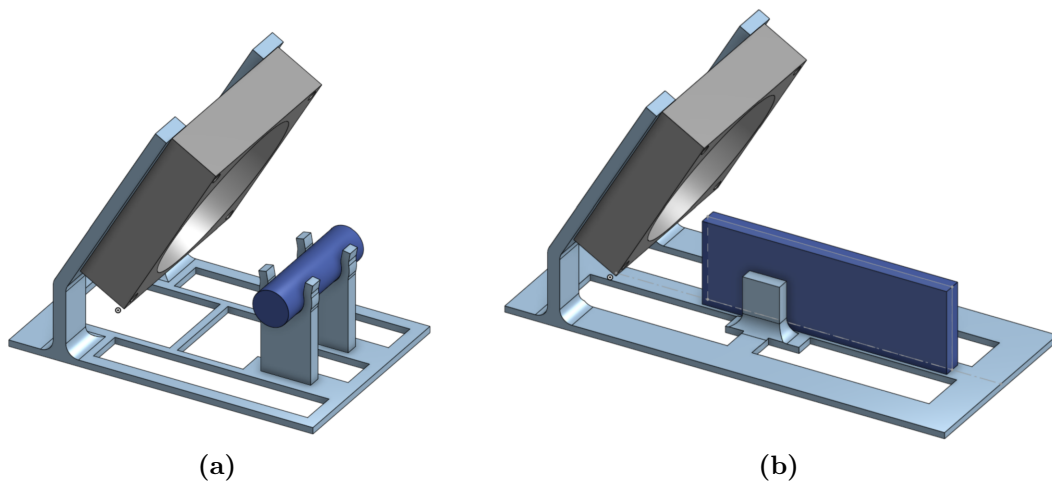


Figure 2.2: CAD model of the endurance test cell holders



Figure 2.3: Setup for the endurance tests inside of the environmental chamber.

2.3 Characterization Test Protocol

Characterization tests were performed at beginning of life (BOL), end of life (EOL), and every 50 cycles on a Biologic potentiostat. In order to capture the degradation effects of cycling under each thermal condition, cells were removed from the environmental chamber and characterized at room temperature after reaching thermal equilibrium. Characterizations included two tests: a battery capacity determination (BCD) and an EIS performed at every 10% state of charge (SOC). Each EIS was performed with a voltage perturbation of 15mV over a frequency range of 10KHz to 100mHz and with 10 data points per decade. The BCD test was a 1C charge-discharge cycle measuring cell capacity in mAh. The cell was then charged back to 100% SOC where an EIS was performed. The cell was discharged in steps of 10% of the measured capacity with an EIS being performed at each step for a total of 11 EIS measurements taken from 100% to 0% SOC. The cell was allowed to rest for 15 minutes after every charge and discharge step. Voltage profiles for the BCD and EIS at every 10% SOC are displayed in [Figure 2.4](#).

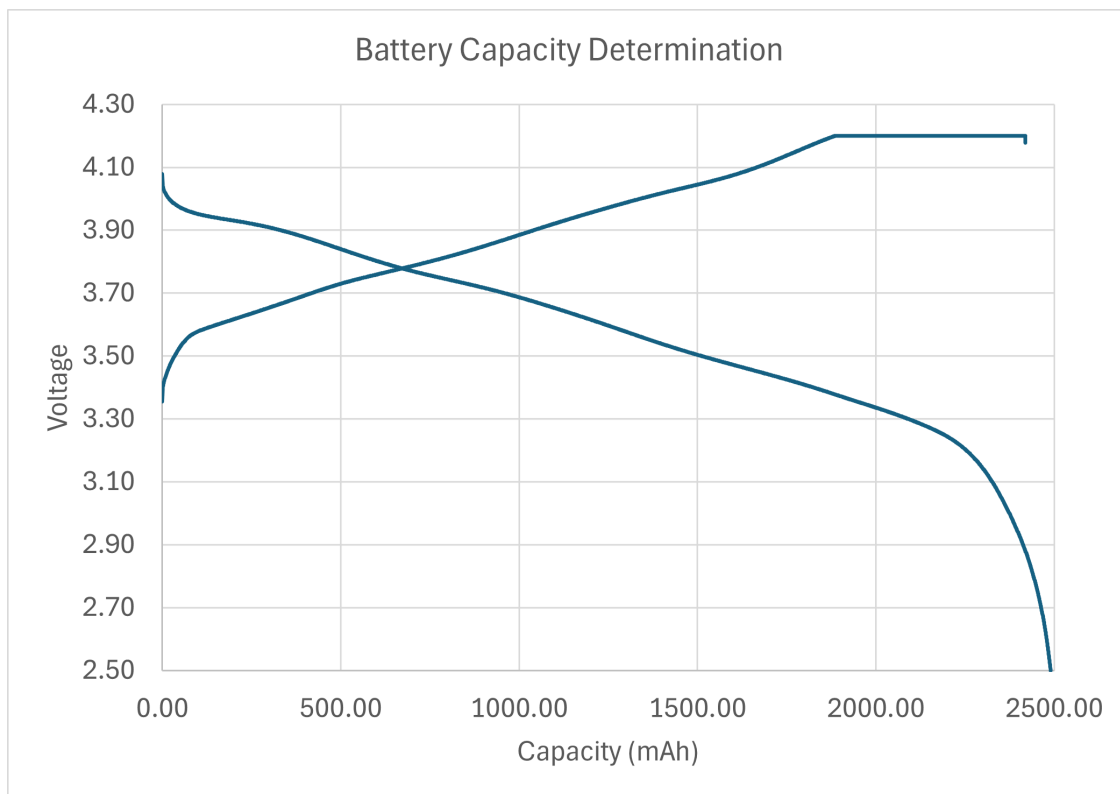
Additionally, one pristine cell of each type was characterized under temperature conditions ranging from 20°C to -35°C inside of an environmental chamber. These tests provide insights into the performance of the cells over a range of temperatures.

2.4 Post-Processing Methods

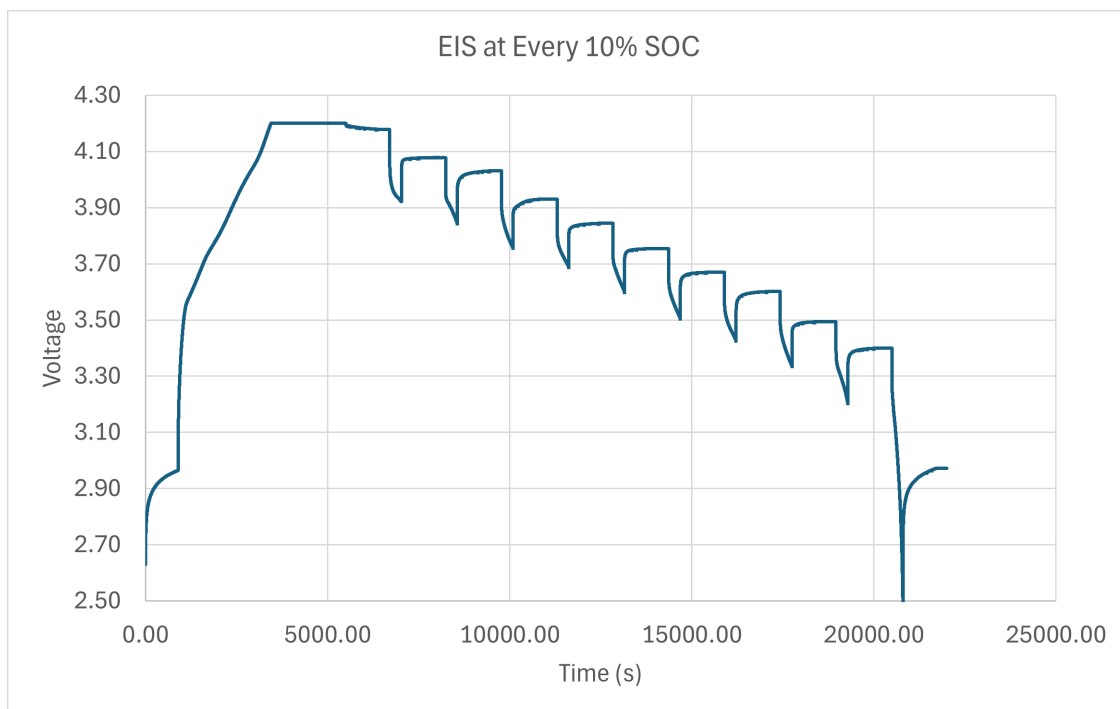
Three main MATLAB scripts were created for processing the data collected in this study. One processes the cycling data collected by the Arbin. Another performs DRT on the EIS data collected by the Biologic and fits Gaussian distributions to the subsequent peaks. The last displays the impedance peaks in a heat map to better identify the trends in cell degradation.

2.4.1 Cycle Data Processing

The Arbin captures a multitude of different data points each second, making a robust post-processing method imperative to understanding cell performance and degradation. The data files generated by the Arbin are converted to text files for MATLAB to read. The



(a)



(b)

Figure 2.4: Example data plots from the characterization test showing (a) the battery capacity determination and (b) voltage profile for performing EIS at every 10% SOC.

MATLAB script is built with a set of "for" loops that allows it to process all the data for each cell designation entered by the user.

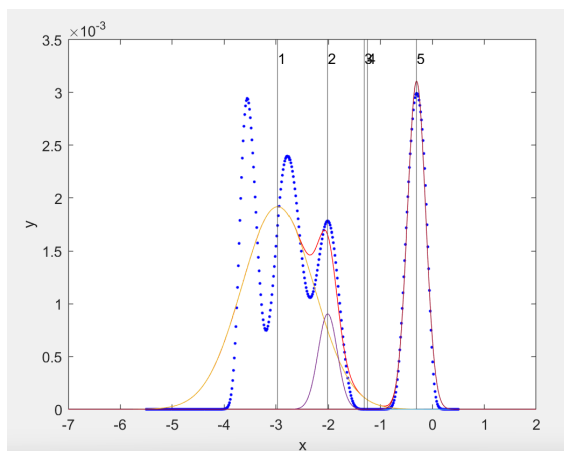
For each cell, the script inputs the text files for each set of fifty cycles, and stores all the cycle data for the cell in a single matrix. The script then parses through the data and stores each individual cycle in a structure variable. Then the data points most relevant to battery performance such as current, voltage, temperature, capacity, and energy are stored in their own class for easy access, such that the variable "voltageData.cycle42" contains just the voltage data for cycle 42.

For many variables, only one data point is used to represent the entire cycle such as discharge capacity, discharge energy, maximum discharge temperature, and average voltage. These data points are pulled from the cycle data so that cell performance can be compared with cycle number. Finally, discharge capacity is compared with nominal capacity as reported by the manufacturer to derive a % capacity number, the main value used to track cell degradation. The script also collects the capacities for the BCD test collected by the Biologic, then the relevant data is plotted and saved in Excel files. All figures are then closed and variables erased, repeating this process for the next cell.

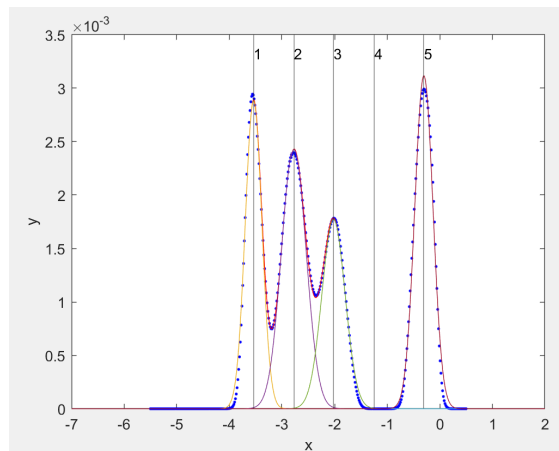
Due to the long-term nature of endurance testing, some of the tests were interrupted by power outages. In this case, it was identified by how many cycles each test was cut-short by, and cycling was resumed to reach 50 cycles. The post-processing script was written to handle these files cut short by power outages.

2.4.2 DRT Post-Processing

The impedance data from the characterization tests with EIS at every 10% SOC is all stored in one file from the Biologic. So the MATLAB script first parses this data into each individual EIS test and stores in in an Excel file. This file is then used to perform DRT using the "DRT Tools" created by Wan et. al. [30], creating the distribution of peaks and gains for each %SOC. Gaussian peaks are then fitted to the DRT peaks using MATLAB's Gaussian "fit" function. This function requires initial guess values to run, and as the peaks change with SOC and cycle number the initial guess values need to change. To expedite this process, the GUI in [Figure 2.5](#) was created to allow the user to adjust the initial guess values and



(a) Unacceptable DRT Fit



(b) Acceptable DRT Fit

Peak Number	A	B	C
1	0.00548	-3.46	0.1146
2	0.00448	-2.8	0.1146
3	0.002	-2	0.2
4		-1.25	
5	0.00213	-0.35	0.197

Recalculate Fit

Accept Fit?

(c) Gaussian Fit Initial Guesses GUI

Figure 2.5: Example GUI for Gaussian fitting of DRT from MATLAB

re-calculate the DRT until the fit is acceptable. Each Gaussian peak is then integrated to estimate the impedance of the peak in Ohms.

This same MATLAB script also performs DC internal resistance (DCIR) on the voltage profile of the 10% SOC discharge pulses. In this test, a 1C current is applied to discharge the cells and after 10% of the SOC is removed, this current is interrupted and the cell allowed to rest. Through the voltage changes of applying and interrupting current, the DC resistance of the cell can be analyzed. The initial voltage drop when current is applied represents the internal resistance of the fast processes within the cell (occurring within 1 second), and is approximately equal to the sum of the HFR and each integrated peak. When the current is interrupted and the cell allowed to recover over a period of 15 minutes, this voltage change represents all the processes inside the cell including the fast processes and the slower diffusion. The technique of DCIR through both current application and current interrupt provides an easy measurement for the cell's resistance, commonly used in industry and in thermal models. Additionally, by comparing both measurements, an estimation for the diffusion resistance inside the cell can be made.

2.4.3 Heat Map Generation

The third main MATLAB script created for this work is used to compile the results of the DRT peak fitting into heat maps, comparing peak resistance with %SOC and either cycle number or temperature. This script goes through the characterization tests for each cell, pulling the integrated impedance data that was saved by the DRT post-processing script. The resistances for each peak is then plotted as a heat map. The changes in the time constants is also plotted to aid in identification of changes within the cell. As a single process in the cell can be represented by multiple peaks, multiple peaks are combined into the same heat maps. Options in this script allow it to handle processing multiple cells at a time, to set limits on the color scale so for easier comparison between cells, and to display impedance results vs %SOC and temperature.

Chapter 3

Endurance Testing Results

3.1 Characterization Testing at Various Temperatures

Pristine cells of each battery type tested in this study underwent characterization tests with ambient temperature conditions of 20°C down to -20°C or until they failed to safely charge. A failed charge condition was taken to be when the voltage over potential from a charge current of 1C jumped the cell voltage above the cut-off voltage of 4.2 V. This would cause the CCCV charge protocol to switch to constant voltage too early, allowing the charge current to rise beyond the set point of 1C. The Molicel and RDQ underwent successful cycles at -20°C, while the Tattu cell failed. These results determined that the coldest endurance test would occur at -10°C so that all three cells could be tested.

As expected, available capacity is drastically reduced with decreasing temperature. The results for each cell is displayed in [Table 3.1](#). The Molicel lost about 5% capacity for every 10°C decrease in temperature, ending with 76.9% capacity at -20°C. The Tattu was not affected by temperature changes above 0°C as much, losing around 2.5% capacity from 20°C to 0°C. However, the Tattu lost 5% of its capacity from 0°C to -10°C, retaining 89.5% of the rated capacity. The RDQ is similar to the Tattu and only saw a minor loss from 20°C to 10°C, but at 0°C and below it saw major losses in capacity retaining only 71.4% of rated capacity at -20°C. The differences in these trends could be explained by cell chemistry. The Molicel is NCA and experiences a consistent capacity loss with each 10°C step, while the LCO pouches show a fairly stable capacity above 0°C, but then drop off quickly below 0°C.

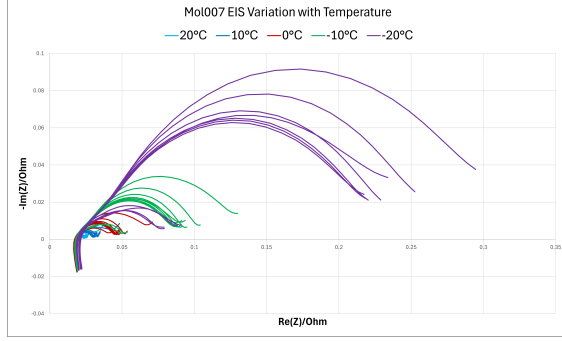
Table 3.1: Battery capacities at various temperatures

	Molicel		Tattu		RDQ	
Rated Cell Capacity	2.8 Ah		2.0 Ah		2.2 Ah	
	Measured Capacity (Ah)	Percent Rate Capacity	Measured Capacity (Ah)	Percent Rate Capacity	Measured Capacity (Ah)	Percent Rate Capacity
20°C	2.631	94.0	1.935	96.7	2.211	100.5
10°C	2.543	90.8	1.918	95.9	2.189	99.5
0°C	2.399	85.7	1.881	94.1	2.107	95.8
-10°C	2.284	81.6	1.789	89.5	1.909	86.8
-20°C	2.154	76.9	-	-	1.571	71.4

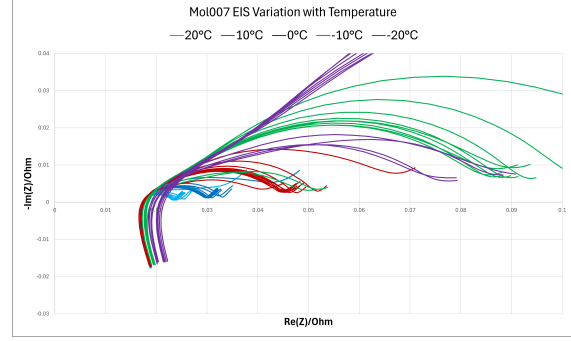
The EIS spectra and subsequent DRT analysis of these characterizations can provide insights into the cell behavior at cold temperatures. Every cell shows drastic increases in impedance as the temperature decreases, as seen in the Nyquist plots for each cell. Further DRT analysis is used to deconvolute the polarization effects providing information of how the processes change within the cell. [Figure 3.1](#) shows Nyquist plots and internal process changes with decreasing temperature for the Molicel. In (a) and (b) it is most noticeable how drastically the impedance increases with decreasing temperature. This impedance change begins to exponentially increase between 0 and -10°C. The change in HFR is smaller, ranging from 0.017 ohms to 0.021 ohms at 20°C and -20°C respectively. At colder temperatures, from 0°C to -20°C, the charge transfer region of the Nyquist plot begins separating into two distinct semi-circles as the slower processes become more distinct from the faster ones. Additionally, at -10°C, the Nyquist plot begins spreading out with the changing %SOC. Then at -20°C, a large jump can be seen at 60% for both the HFR and the slower half of the Nyquist.

These observations from the Nyquist plots are expanded upon in the DRT heat maps. All the peaks show increasing resistances with colder temperatures. Both peak 1 and peak 2, attributed to particle-particle interactions and the passivation layers respectively, show little to no dependence on SOC. Both the HFR and the combined charge transfer processes of peaks 3, 4, and 5 show a strong dependence to SOC at -10°C and -20°C.

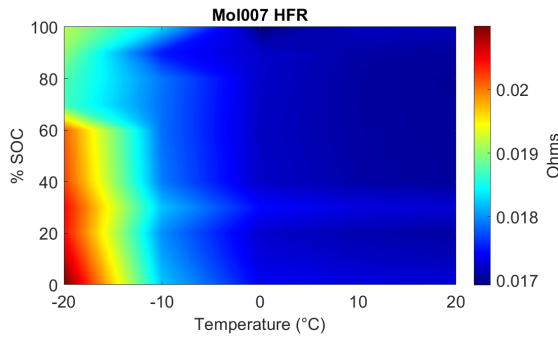
The characterization results at various temperatures for the Tattu and RDQ cells show similar results to the Molicel and are displayed in [Figure 3.2](#) and [Figure 3.3](#), respectively. Both cells show drastic increases in impedance with decreasing temperature. The HFR also increases a small amount similar to the Molicel. These cells show how, at cold temperatures, the HFR and slower charge transfer processes are dependant on %SOC. The Tattu, however, shows a much more gradual increase in impedance from 100% SOC to 0% SOC at cold temperatures, while the RDQ shows a large jump around 70% SOC, similar to the Molicel. This EIS and DRT analysis over a wide range of temperatures and %SOC can aid in understanding cell performance and identifying limiting conditions for cells. For example, limiting the tested cells SOC window to 100% - 70% when at -10°C and below would likely aid cell performance and prevent excess degradation due to the cold.



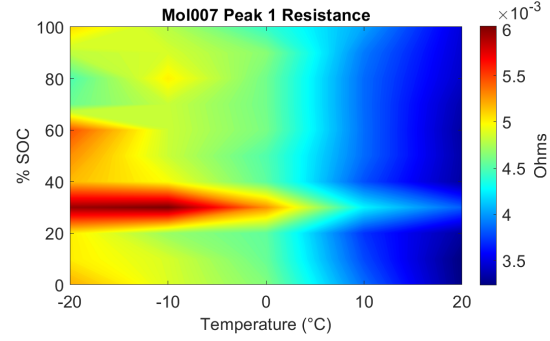
(a)



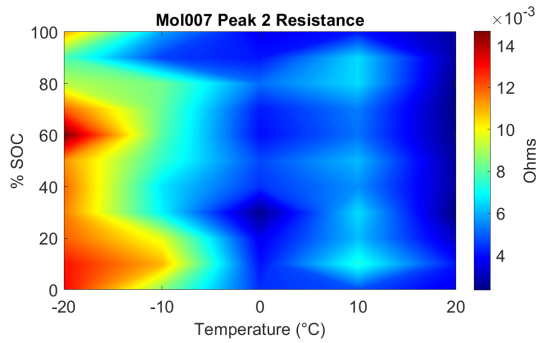
(b)



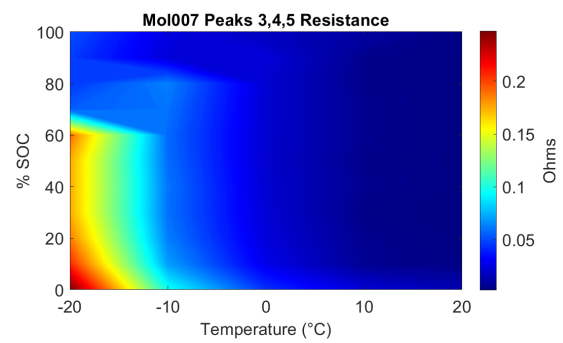
(c)



(d)

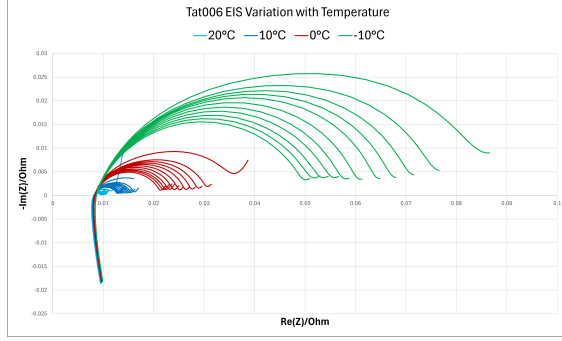


(e)

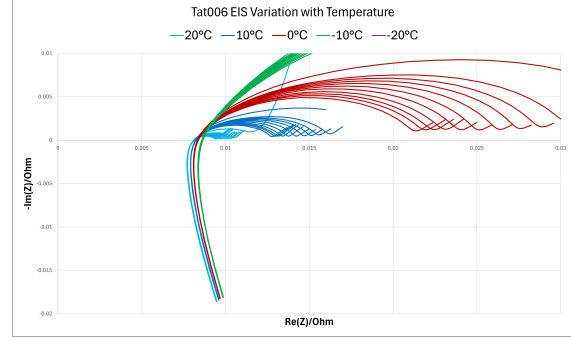


(f)

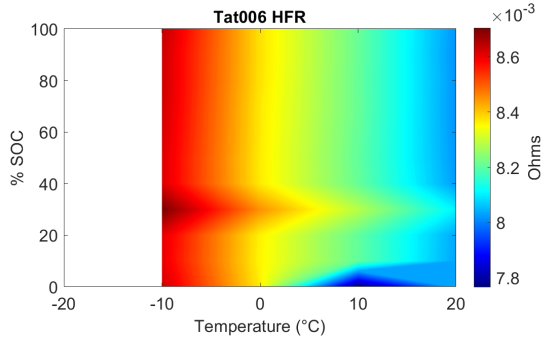
Figure 3.1: Molicel characterization results under various temperature conditions. (a) Nyquist impedance plot for all temperature conditions. (b) Zoomed in version of "a" showing more detail for the warmer temperatures. Variation of (c) HFR, (d) peak 1, (e) peak 2, and (f) peaks 3, 4, and 5 resistances with respect to temperature and %SOC.



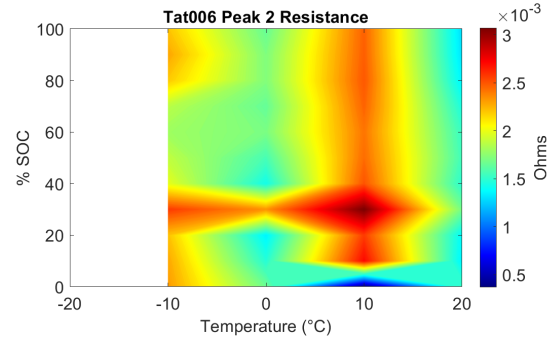
(a)



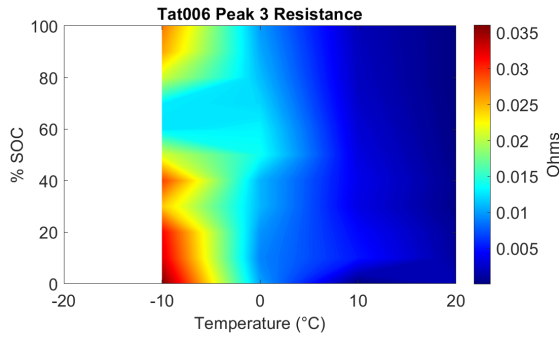
(b)



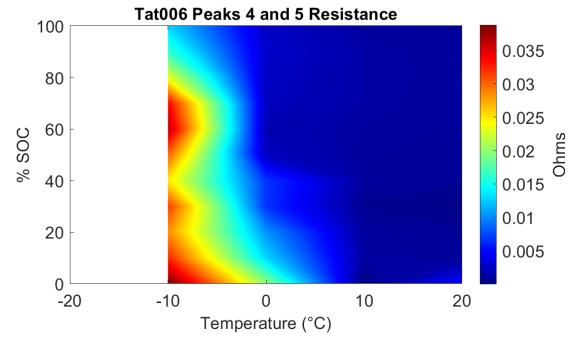
(c)



(d)

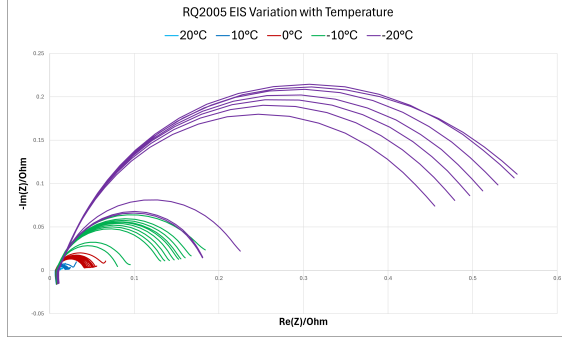


(e)

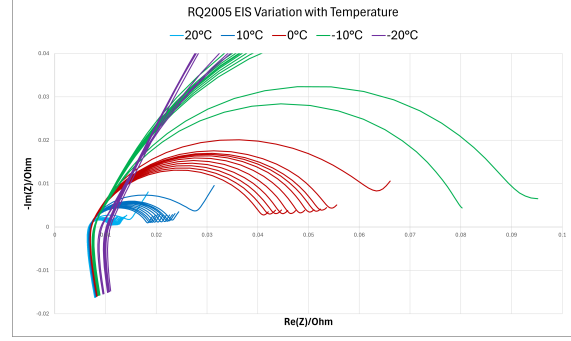


(f)

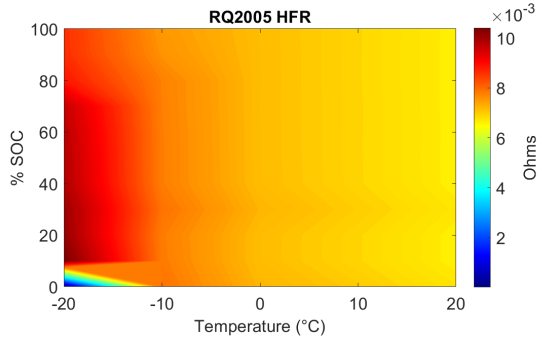
Figure 3.2: Tattu characterization results under various temperature conditions. (a) Nyquist impedance plot for all temperature conditions. (b) Zoomed in version of "a" showing more detail for the warmer temperatures. Variation of (c) HFR, (d) peak 2, (e) peak 3, and (f) peaks 4 and 5 resistances with respect to temperature and %SOC.



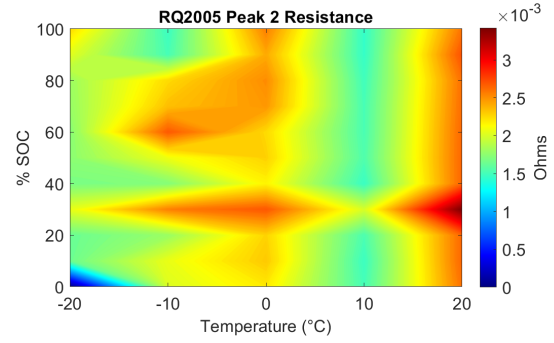
(a)



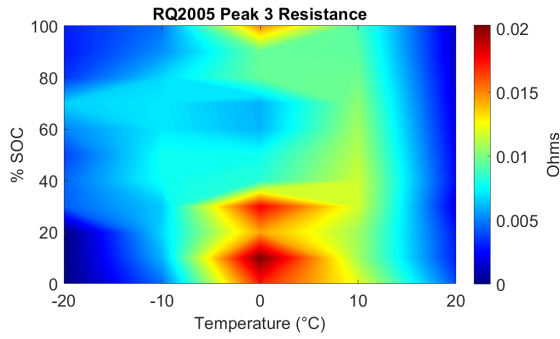
(b)



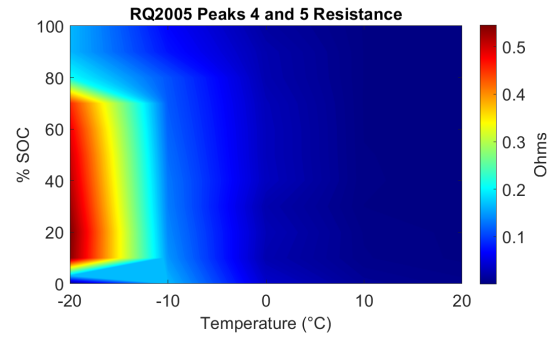
(c)



(d)



(e)



(f)

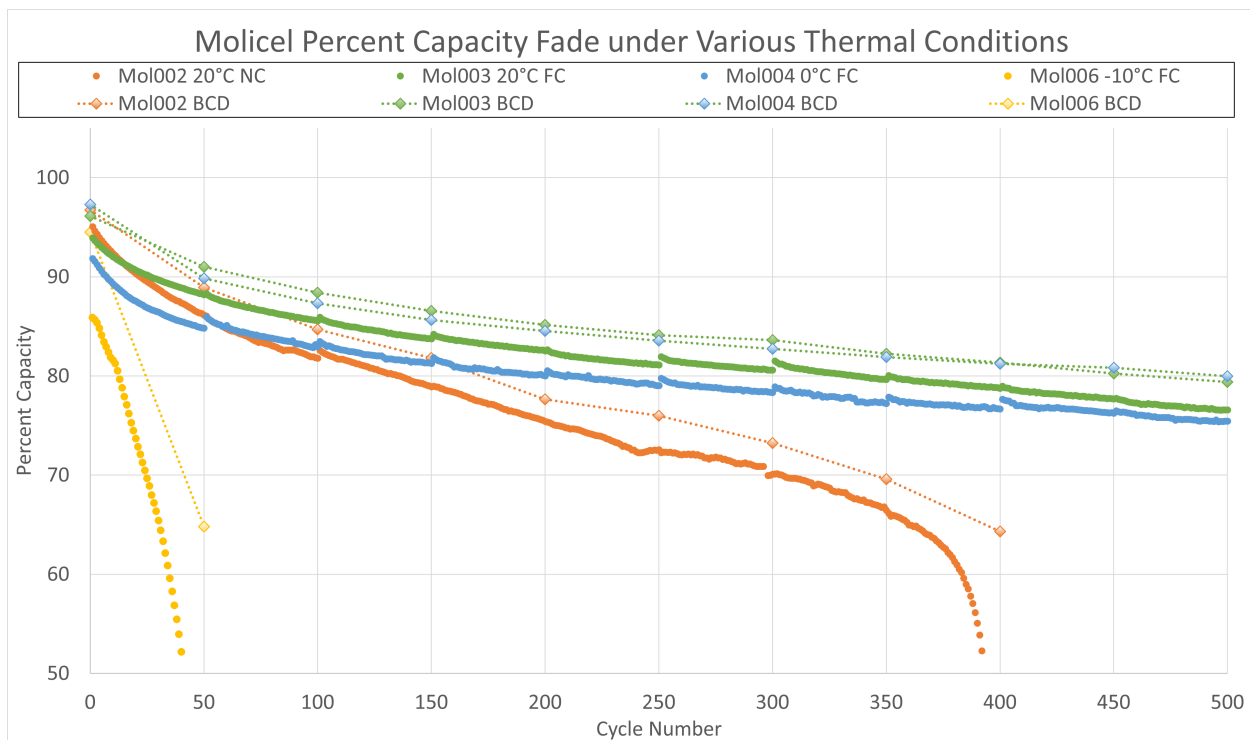
Figure 3.3: RDQ characterization results under various temperature conditions. (a) Nyquist impedance plot for all temperature conditions. (b) Zoomed in version of "a" showing more detail for the warmer temperatures. Variation of (c) HFR, (d) peak 2, (e) peak 3, and (f) peaks 4 and 5 resistances with respect to temperature and %SOC.

3.2 Endurance Testing at High C-Rate and Various Temperature Boundary Conditions

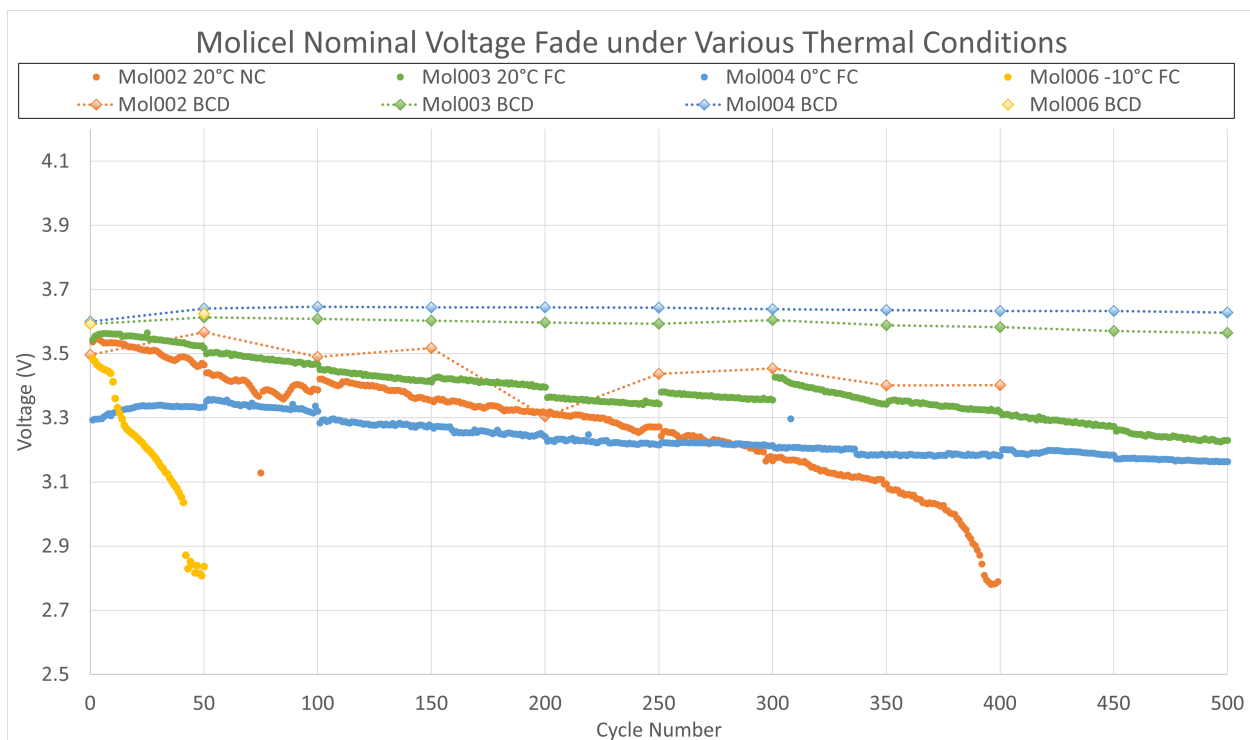
Four endurance tests were performed on the studied cells. For each test, the cells were charged under CCCV protocol at 1C and discharged at 10C, 25C, or 23C for the Molicel, Tattu, and RDQ, respectively. ET1 held the cells at room temperature (20°C) with natural convection. ET2 held the cells at 20°C with 90mm PC fans supplied force convection cooling. ET3 held the cells at 0°C with forced convection cooling. ET4 held the cells at -10°C with forced convection. Every cell was characterized at BOL, every 50 cycles, and at the end of the test, with the tests lasting up to 500 cycles or when the cell could no longer complete cycles at the high rate. One additional Tattu cell was included in ET1 with a discharge current of 40C because initial testing showed that the Tattu was capable of such high discharge rates. This test was performed to identify the effects of such high rates on degradation but was not continued for the rest of the endurance testing because it required a special cycling channel capable of such high currents.

3.2.1 Capacity and Voltage Fade

The discharge capacity and voltage fade results for the Molicel, Tattu, and Race Day Quads can be seen in [Figure 3.4](#), [Figure 3.5](#), and [Figure 3.6](#). Each plot shows the results from the high discharge rate cycling and the 1C BCD testing, displayed as solid data points or diamonds connected with a dotted line, respectively. This figure shows how the cell is degraded during the endurance test and how that degradation is manifested under lower rates. Each capacity measurement is normalized to the rated cell capacity from the manufacturer to better compare cell performance with manufacturer expectations. Many of the cells start at capacities lower than 100%, which is expected as many manufacturer's report capacity measurements with rates less than 1C. The voltage plots show the "nominal voltage" of the cells during discharge. For the purposes of this test, nominal voltage is taken to be the average voltage throughout the entire discharge.

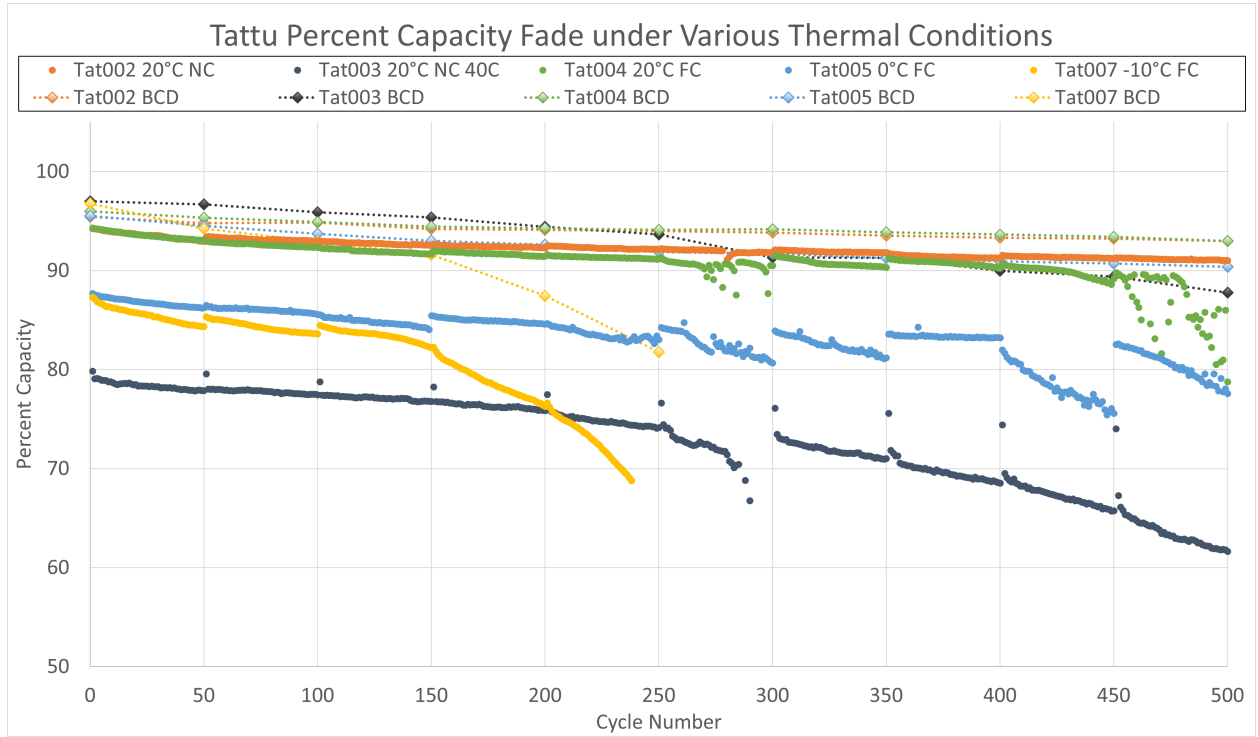


(a)

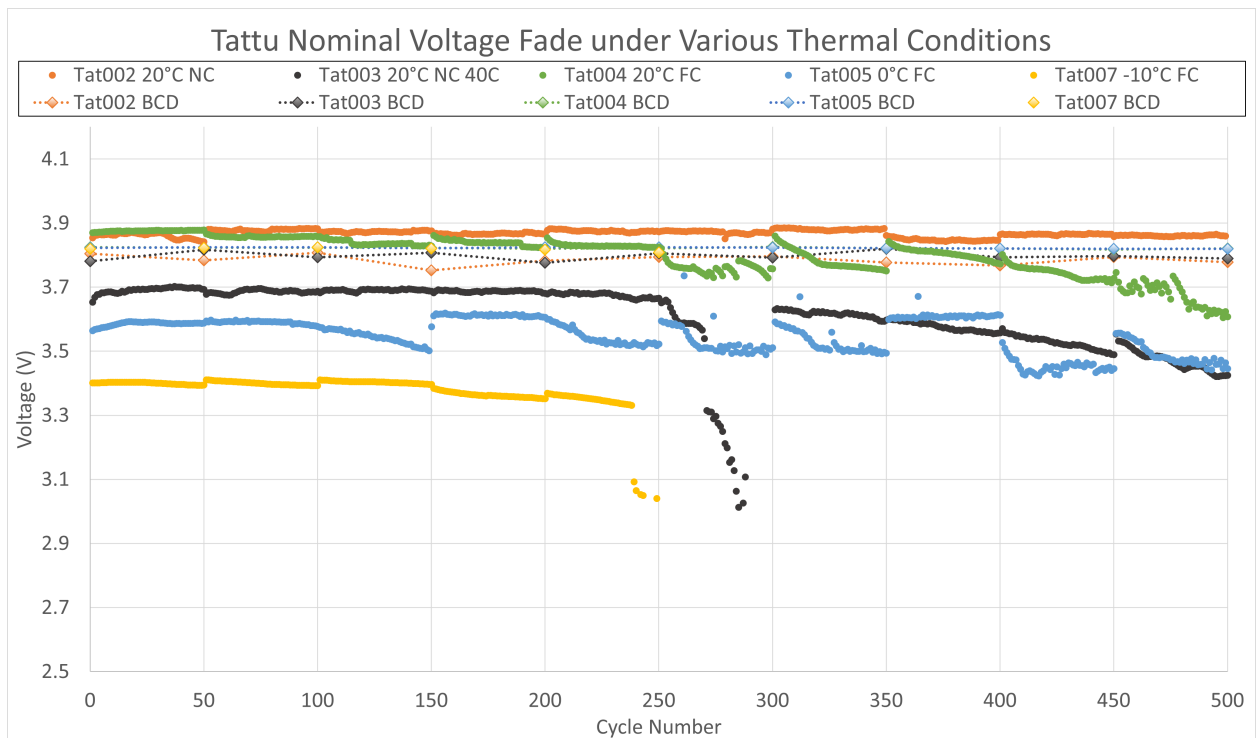


(b)

Figure 3.4: MoliceL (a) capacity and (b) nominal voltage fade for 10C discharge at various ambient temperature conditions

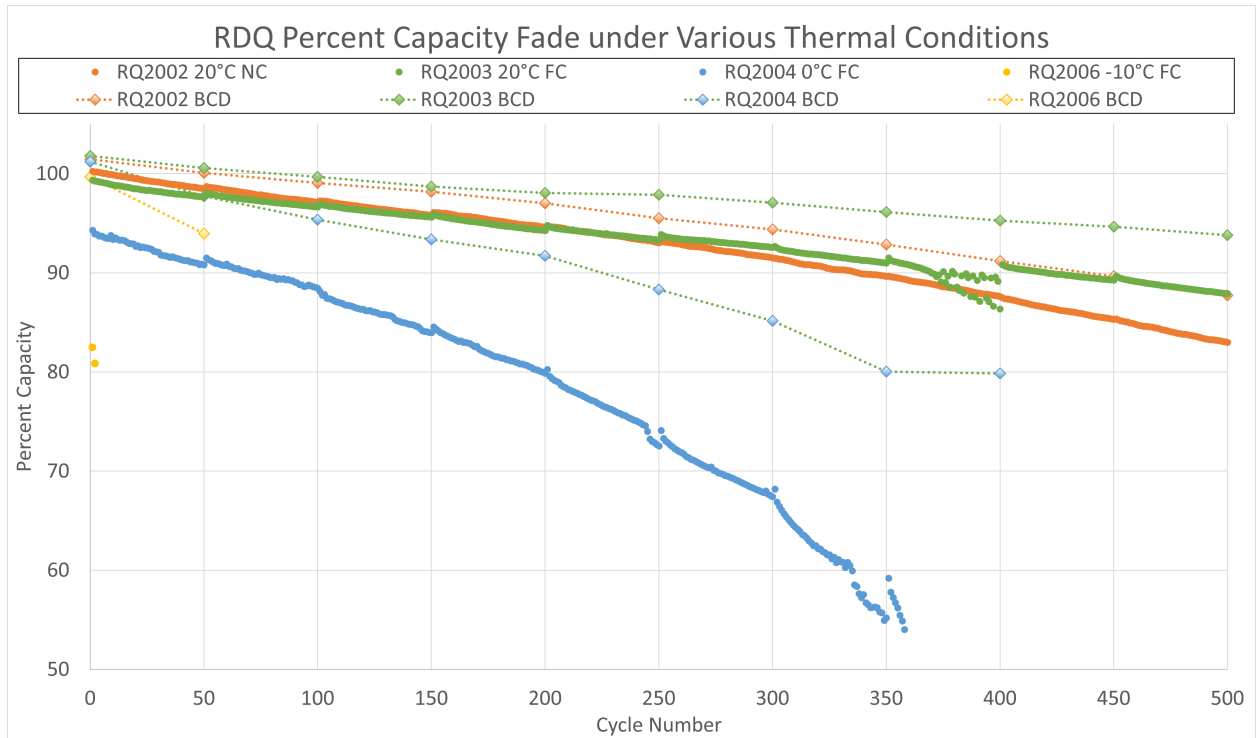


(a)

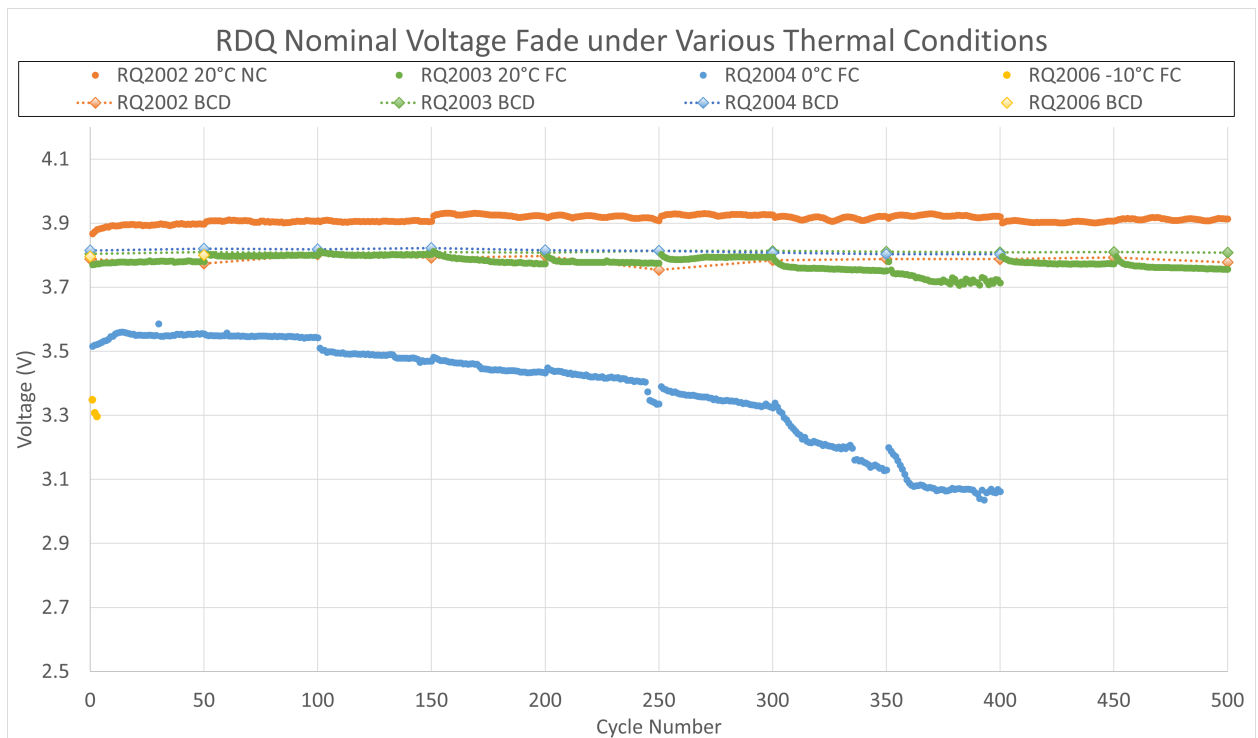


(b)

Figure 3.5: Tattu (a) capacity and (b) nominal voltage fade for 25C and 40C discharges at various ambient temperature conditions



(a)



(b)

Figure 3.6: Race Day Quads (a) capacity and (b) nominal voltage fade for 23C discharge at various ambient temperature conditions

Temperature plays a major role in cell performance and degradation. To track cell temperature, a thermocouple was taped onto the surface of each cell. The average charge and discharge peak temperatures throughout the endurance tests for each cell is displayed in [Table 3.2](#).

The Molicel showed good degradation performance with adequate temperature control. Both forced convection at 20°C and at 0°C survived 500 cycles with 75% capacity retention normalized to the rated cell capacity. The cell's performance at 0°C was strikingly similar to 20°C with forced convection. At 0°C, the cold temperature reduced the available capacity by about 3%. The BCD results for these tests show almost identical capacity fade throughout the 500 cycles. Performance at 0°C could have been aided by the large heating caused by high rate discharge. For the two tests the average peak discharge temperature was fairly similar at 55°C and 47°C. However in ET1, with no cooling applied to the cell, the Molicel failed to reach 400 cycles. In this case the large levels of heating without cooling caused the cell to reach an average temperature of 79°C, inducing greater degradation. As the cell began to fail near 400 cycles, the increased resistances from degradation raised the cell temperature even further, reaching up to 95°C. Alternatively, in ET4 at -10°C, the Molicel failed within 50 cycles despite a large level of self-heating during discharge, reaching an average peak temperature of 44°C. The capacity degradation at 1C from the BCD tests track well with the capacity fade seen during the high rate cycling.

In general, the Tattu shows excellent capacity retention throughout the endurance testing. However, some cells appear to have troubles with continual cycling. ET1 showed great performance with almost no capacity loss throughout 500 cycles, but during ET2 and ET3, the cells showed large levels of capacity fade during each 50 cycle section, especially towards higher cycle numbers. This capacity loss is not reflected in BCD tests, and after each characterization the capacity recovers. This implies that some level of degradation in the cell is recoverable through either extended rest periods or a few low-rate cycles. This behavior is also not seen in the cells from endurance test one or four, so cell-to-cell variations or some other outside factor could play a role, but further testing would be needed to identify the cause.

Table 3.2: Average peak temperatures reached by each cell under charge and discharge.

Cell Designation	Test Conditions	Peak Charge Temperature (°C)	Peak Discharge Temperature (°C)
Mol002	20°C NC	27.4	78.9
Mol003	20°C FC	20.2	55.2
Mol004	0°C FC	4.64	47
Mol006	-10°C FC	-6.59	44.1
Tat002	20°C NC	23.3	45.6
Tat003	20°C NC 40C	24.6	54.6
Tat004	20°C FC	20.8	44.36
Tat005	0°C FC	3.61	35.7
Tat007	-10°C FC	-9.69	27.7
RQ2002	20°C NC	24.9	44.1
RQ2003	20°C FC	19.8	42.4
RQ2004	0°C FC	1.39	26.9
RQ2006	-10°C FC	-9.27	21.2

At 20°C with both natural and forced convection, the Tattu shows very similar performance and reached a discharge temperature of 46°C and 44°C respectively, with nearly identical capacity loss in the BCD tests. At 0°C, the cell begins to show increasing levels of degradation. The reversible capacity fade during each 50 cycle step is much worse for this cell, increasing with cycle number. Additionally, the 1C capacity fade is higher with 2% less capacity than the cells at 20°C. However, at 0°C the cell provides 10% less starting capacity than at 20°C. The available capacity at -10°C is surprisingly similar to the cell at 0°C, but the cell at -10°C experience the most degradation by far, failing before 250 cycles. Of the three cells tested, the Tattu showed the best performance at -10°C.

The initial testing of the Tattu cells showed that the battery was capable of much higher C-rates. So in ET1 a Tattu cell was tested with a discharge rate of 40C and still survived to 500 cycles. At such a high C-rate the available capacity was reduced by 15%. This cell degraded more than the ones at 25C and ended with a BCD 6% less than its 25C counterpart. The 40C testing of the Tattu cell was not continued to the other endurance test to focus on 25C testing, which is more relevant to eVTOL.

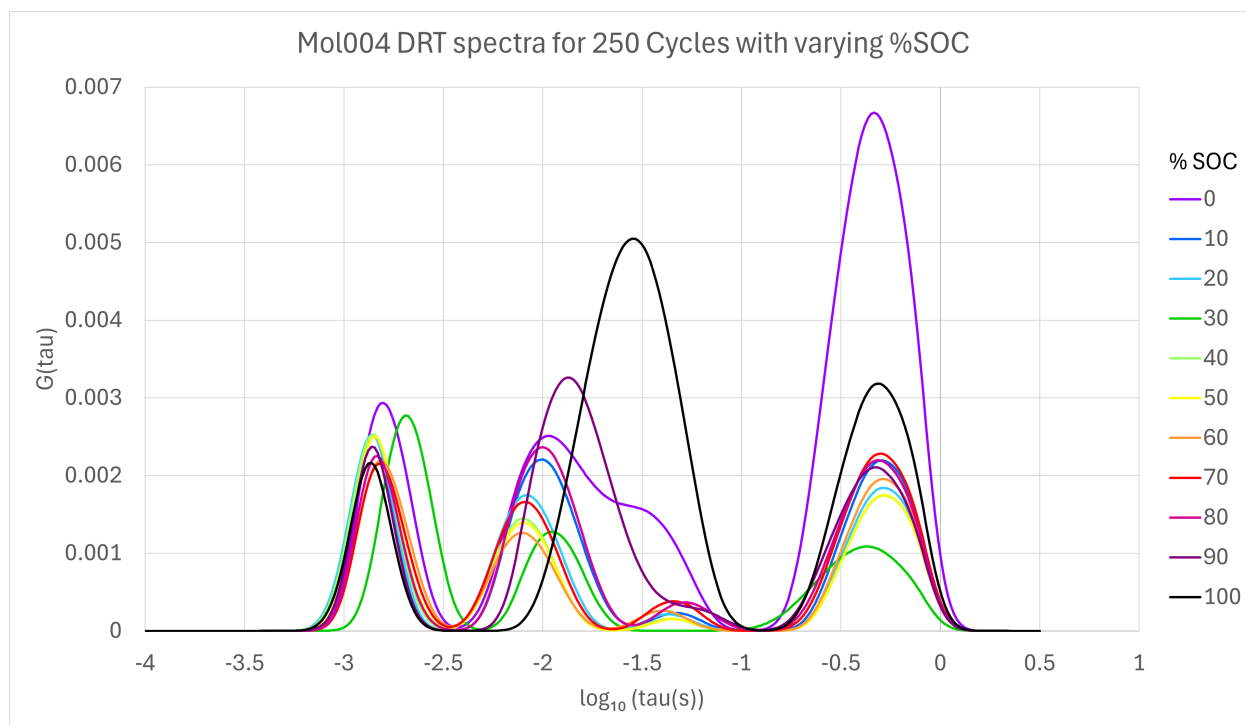
The RDQ cell shows a gradual capacity fade at 20°C with both natural and forced convection. ET2 with forced convection shows the best degradation results, reaching 500 cycles with 88% capacity retention. With natural convection, increased capacity fade occurred, with the cell reaching 500 cycles at 83% capacity retention. The RDQ degradation performance quickly drops off with decreasing temperatures. At 0°C, much higher rates of capacity fade can be seen with the cell failing at around 360 cycles, and at -10°C, the cell only cycled twice before failing. The BCD tests show how the 1C capacity degradation of all the cells compares, with the test at 0° having the most degradation.

The cell voltages show a similar story as the capacities. Colder temperatures reduce cell voltage and thus power output. Additionally, as the cell degrades, the discharge voltage also reduces. However, the voltage at 1C discharge during the BCDs does not appear to be affected by the cell degradation and remains fairly consistent for the entirety of endurance testing.

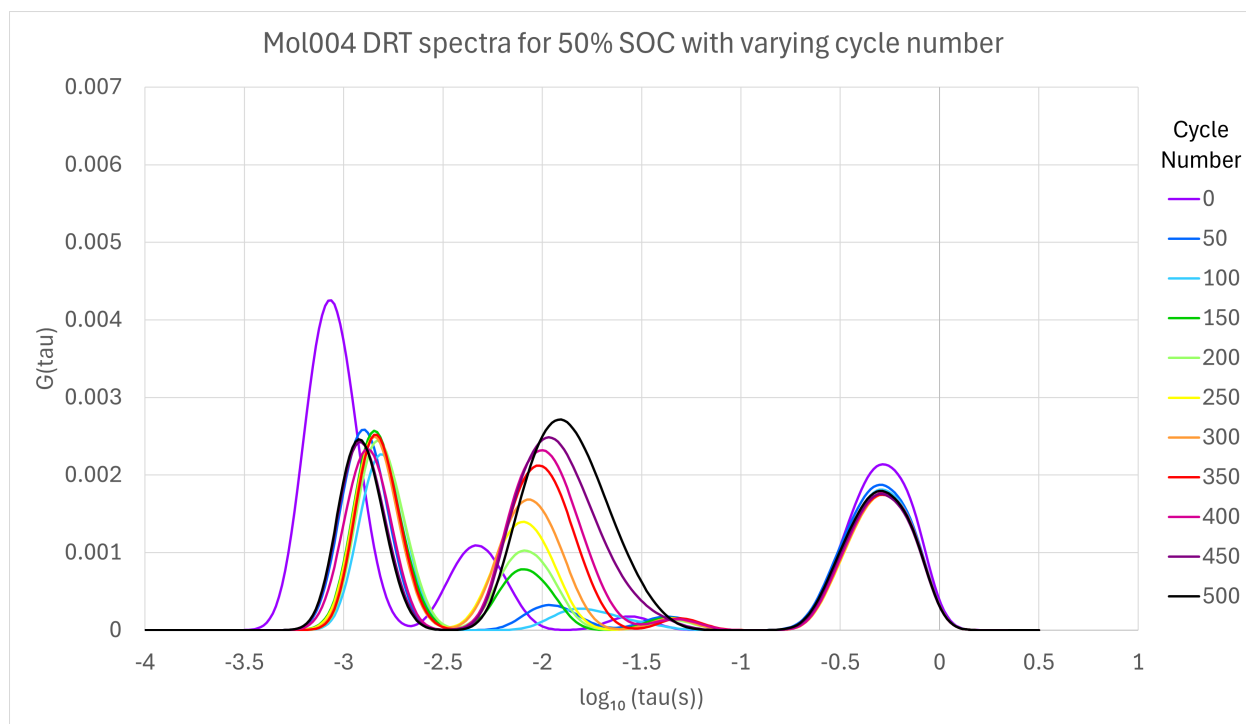
3.3 Distribution of Relaxation Times

DRT analysis is performed on the gathered EIS data in order to separate the polarization effects. The changes in the DRT peaks with respect to SOC and cycle number can be used to indicate degradation within the cell [18, 9]. As an example, DRT results from the MoliceL cycled at 0°C show how the DRT spectra can change with both %SOC and cycle number. Figure 3.7 presents DRT spectra at 250 cycles with varying %SOC, and at 50% SOC with varying cycle number. As SOC is varied, the peak attributed to the passivation layers ($10^{-2.5}$ - $10^{-1.5}$ s) and those attributed to the charge transfer processes ($10^{-1.5}$ - 10^0 s) also vary. This is consistent with findings in the literature [30, 19, 28, 27, 18] as these processes can depend on lithium ion concentrations within the cell. Changes in DRT peaks with cycle number are indicative of electrochemical/physical changes within the cell, i.e. degradation. In Figure 3.7 the peak attributed to the passivation layers increases with cycle number, indicating some degradation in the SEI or PEI.

In order to better visualize these changes in the DRT spectra, each peak is fitted with a Gaussian peak-fitting algorithm, integrated to estimate the impedance, and plotted in a color heat map against %SOC and cycle number. Visualizing the DRT peaks in a heat map allows for analysis of the large data sets and identifying trends in the cell's degradation. From the existing literature, three cell processes are expected to be captured in the DRT, appearing as 3 to 5 peaks. Multiple peaks could represent the same physical processes at different locations in the cell [19, 18, 9]. Likewise, the cells in this study most commonly show 4 peaks, but depending on how the processes change with SOC and cycle number 3 or 5 peaks are possible. For example, in Figure 3.7 (a), the middle two peaks are clearly distinct from 0% to 90% SOC. However, the speed of this process changes with SOC, and at 100% SOC, the peaks blend together. In situations like these, the peak-fitting algorithm still places two peaks in that space, but it is impossible to know with certainty what contributions each peak makes. While great care was taken during the peak fitting process to accurately represent the trends in the DRT, the resulting integrations and heat maps should be taken as qualitative in nature.



(a)



(b)

Figure 3.7: Example DRT spectra variation with respect to (a) %SOC and (b) cycle number for the Molicel cycled with 10C discharge at 0°C with forced convection.

Despite this limitation, the DRT peak heat maps are still a useful tool for identifying trends in the cell processes. In this study, five peaks were tracked in the DRT. However due to cell characteristics, four peaks were most commonly seen. [Figure 3.7](#) shows typical DRT spectra for the cell with peaks 1,2,3, and 5 clearly visible. Another peak sometimes appears for the Molicel in the 10^{-1} area, referred to as peak 4. For the pouch cells, three or four peaks are seen with peak 1 set to zero and peak 4 coming and going as it moves around and merges with peaks 3 and 5. Throughout all the testing, the peak tracking was consistently applied for each cell so that the changes in the cell could be tracked as accurately as possible and compared to other cells.

As certain processes can be represented by multiple peaks in the DRT, the resistances of certain peaks were added and displayed together to best represent the trends in each process's impedance. In this study's naming conventions, particle-particle interactions are represented by peak 1 for the molicel and peak 2 for the pouch cells, the passivation layers are represented by peak 2 in the molicel and peak 3 for the pouch cells, and the charge transfer processes are represented by peaks 3, 4, and 5 for the molicel and peaks 4 and 5 for the pouch cells.

[Figure 3.8](#) shows the DRT peak impedances with respect to %SOC and cycle number for endurance tests 1, 2, and 3. Endurance test 4 is not included here and will be discussed later because the cells failed so quickly. Mol002 failed early in ET1 due to excessive heating, the consequences of which can be seen in the DRT heat maps. As the cell aged, increased resistance can be seen in all the peaks, especially between 300 and 400 cycles. The increase in peak 1 towards the end of cycling indicates some degradation in the particle-particle interactions which is not seen in the other endurance tests. High temperature is known to be a main contributor to SEI growth and decomposition [7]. Peak 2 shows increases in resistance towards the end of cycling, indicating this degradation mechanism. The charge transfer processes of peaks 3, 4, and 5 show higher impedance with increasing cycle number, especially at the SOC extremes. This “U” shape is expected for these electrochemical processes. As more ions are intercalated into an electrode, the resistance should increase. The same shape is seen in the Mol003 of ET2, however the higher temperatures of ET1 caused increased degradation.

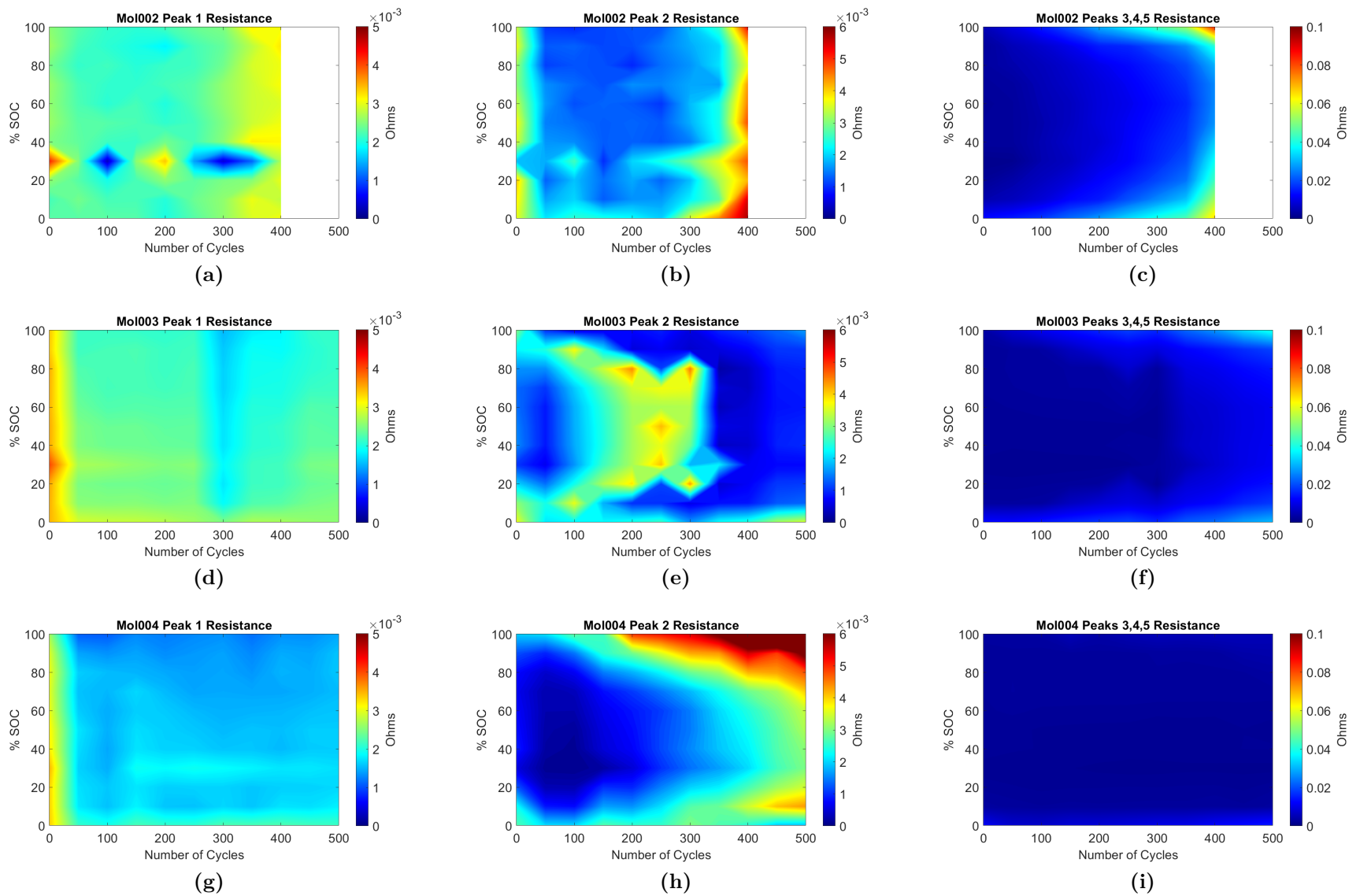


Figure 3.8: MoliceL DRT peak heat maps.

The Molicel showed the best performance in endurance test 2 at 20°C with forced convection cooling, which is reflected in the DRT. Peak 1 shows little to no degradation in both ET2 and ET3, indicating that this process is mainly affected by high temperatures. This peak does show larger resistances at beginning of life than it does during the rest of the endurance test, which is seen in endurance tests 2, 3, and 4. This shape is also seen in peak 2 of endurance test 1. This initial decrease in resistance during cycling could indicate some more formation of processes in the cell. Peak 2 shows no trends of increasing resistance with SOC or cycle number, but does show higher resistances in the middle of the endurance tests, which is believed to be impedance captured from peak 3, as a hole of the same shape is missing from the peaks 3, 4, and 5 heat maps.

At 0°C in ET3, peak 2 shows large increases in impedance, especially with high %SOC and high cycle number. This increase is attributed to lithium plating on the anode because cold temperatures are known to contribute to lithium plating [7]. Peaks 3, 4, and 5, show much less impedance rise than in ET1 and ET2. Chen et al. showed that lithium plating causes a reduction in the charge transfer peaks [9], which would explain the low impedance of peaks 3, 4, and 5 in the Mol004.

The DRT results for the Tattu cells are shown in [Figure 3.9](#). The DRT trends for the Tattu are less conclusive than the Molicel, which is expected as the Tattu experienced less degradation. In all the tests, the charge transfer processes of peaks 4 and 5 show no degradation, with cycle number and high impedance only occurring at 0% SOC. Peak 3 shows the most degradation and is attributed to SEI growth/decomposition. The cause of the reversible capacity loss during concurrent cycling as seen in Tat004 and Tat005 is unknown, but could be related to peak 3 because Tat002 shows very little peak 3 impedance. The cause of this behavior may be attributed to cell-to-cell variations, which is outside the scope of this study.

The RDQ heat maps shown in [Figure 3.10](#) are similar to those of the Tattu cell. The cells at 20°C both displayed a small, gradual capacity fade. The DRT of these cells show little correlation to cycle number. At 0°C, the RDQ cell showed significant degradation and failed around 360 cycles. Again, no trends are seen in the particle-particle interactions of peak 2.

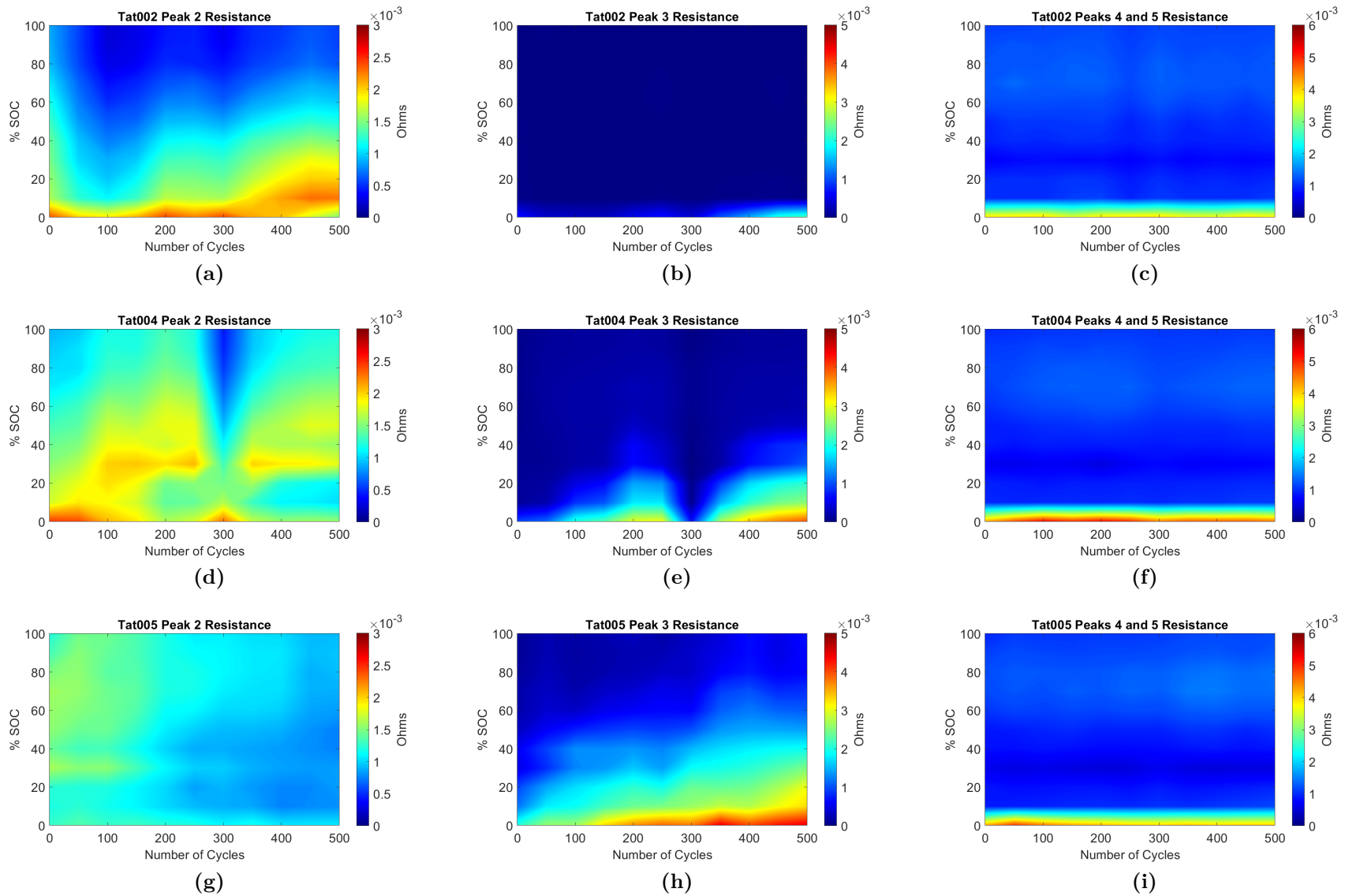


Figure 3.9: Tattu DRT peak heat maps.

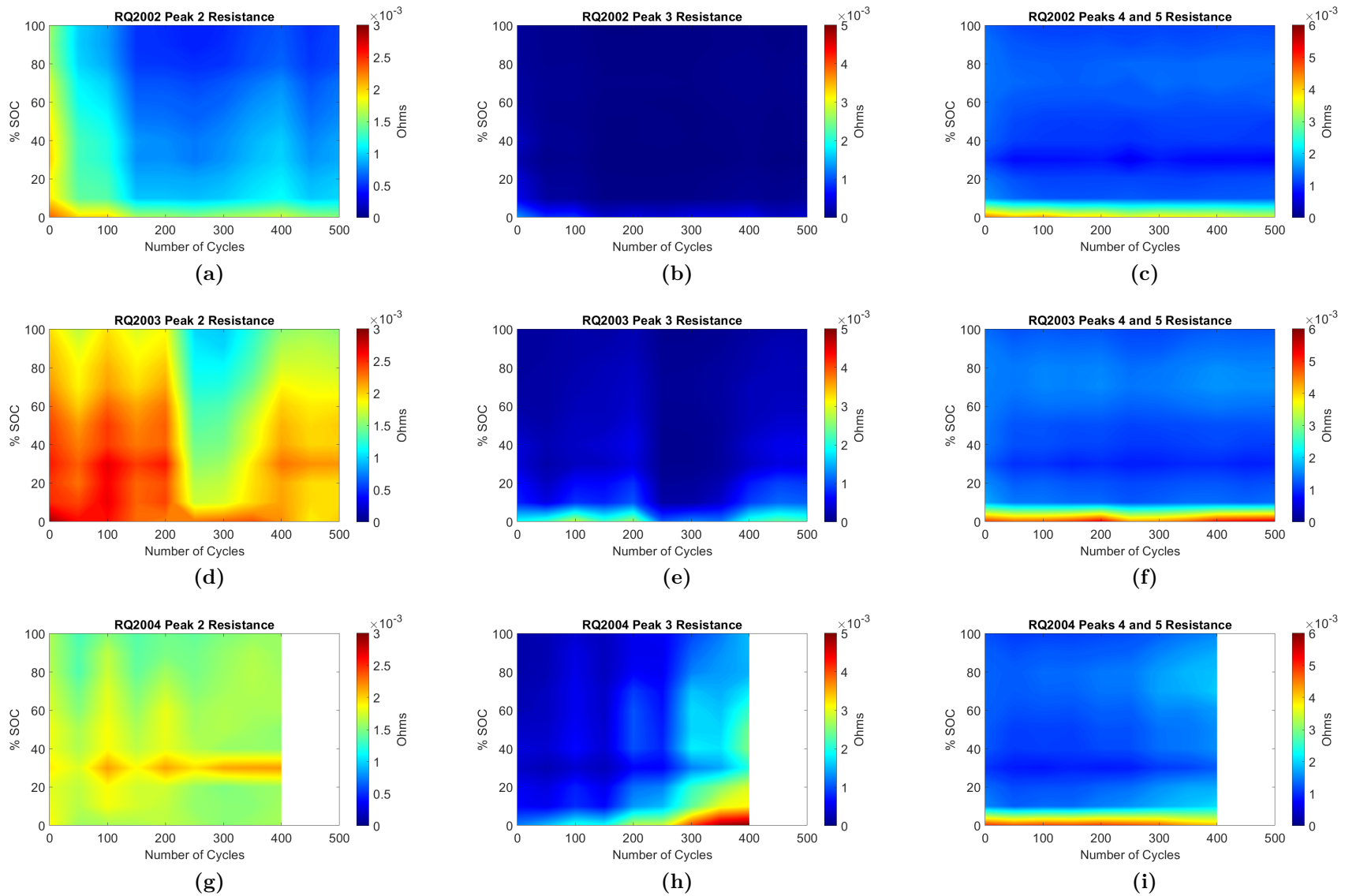


Figure 3.10: Race Day Quads DRT peak heat maps.

Peak 2 however, shows a large increase in impedance with increasing cycle number, especially at low SOC. By cycling the cell at cold temperatures, lithium plating is expected. The charge transfer processes of peaks 4 and 5 also show decreasing impedance, also alluding to lithium plating.

The Tattu was the only cell to cycle well at -10°C . The heat maps for this test are displayed in [Figure 3.11](#). Again, the most degradation for the Tattu cell is seen in the passivation layers of peak 3 due to SEI degradation. However, the charge transfer processes of peaks 4 and 5 show decreasing impedance with cycle number, which has been correlated with lithium plating by Chen et al [\[9\]](#). The Molicel and Race Day Quads however failed within 50 cycles and not enough EIS data was gathered to identify degradation trends in the cells.

DRT is a useful tool for tracking cell performance and identifying degradation mechanisms in lithium-ion batteries. The particle-particle interactions only showed signs of degradation for the Molicel that became too hot. High cell temps can lead to electrolyte and binder decomposition [\[7\]](#). The literature surveyed for this thesis indicates that little research has been done examining the effects of electrolyte and binder decomposition on the DRT spectra, but these degradation processes could affect the particle-particle interactions. More research would be needed on particle-particle interactions and DRT to verify this. The passivation layers showed increased signs of degradation due to both high and low temperatures. High temperatures are known to cause SEI growth/degradation while low temperatures tend to cause lithium plating. The charge transfer peaks showed increasing degradation with cycle number. High current loads are known to cause electrode particle cracking and affect lithium intercalation[\[7\]](#). The charge transfer resistances reduce in colder temperatures, which is known to correlate to lithium plating [\[9\]](#).

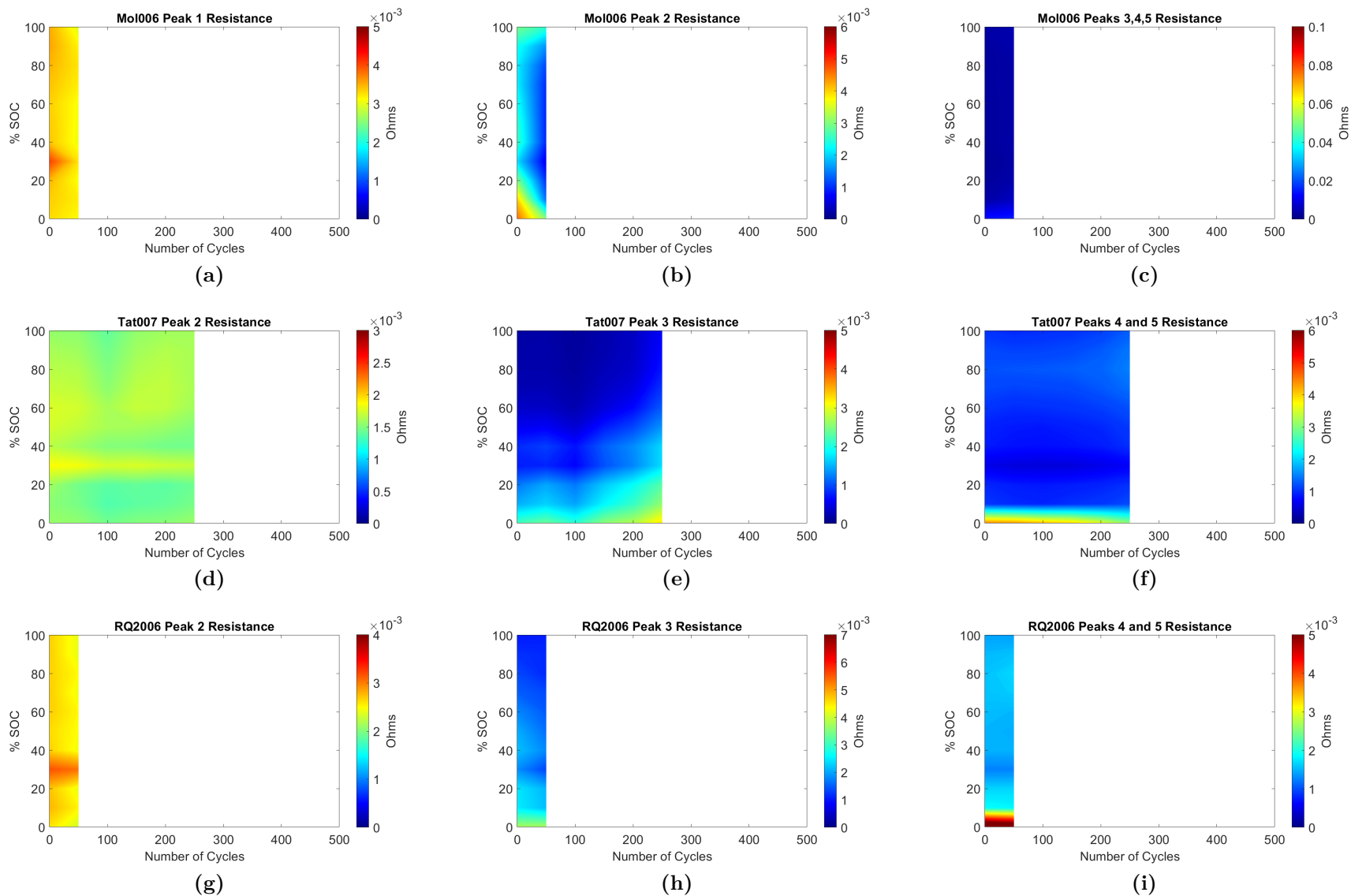


Figure 3.11: Endurance Test 4 DRT peak heat maps.

Chapter 4

Study of Thermal Runaway Through ARC Testing

Recently, the Electrochemical Energy Storage and Conversion Laboratory (EESCL) acquired an Accelerating Rate Calorimeter (ARC) from Thermal Hazard Technology (THT). As discussed in [Chapter 1](#), this equipment allows for the study of thermal runaway by burning the cell in an adiabatic environment to measure energy released, nail penetration testing, crush testing, collection of off-gases for analysis, collecting pressure data during the thermal runaway event, and measuring the heat capacity of cells, among other studies. These types of studies are vitally important to understanding cell safety in all applications and are especially important for aircraft. With the ARC installed, initial testing has been performed on the Molicel P28A for safety analysis.

4.1 Calibration and Drift Checks

4.1.1 Calibration

During the “Seek” mode of the ARC test, the system is looking for a change in cell temperature greater than $0.02^{\circ}\text{C}/\text{min}$. A precise calibration ensures the accuracy of the measurement. The ARC is calibrated by placing the thermocouple on a small calibration sample and running a test up to 310°C . The test involves heating the ARC by 50°C steps,

followed by a 40 minute wait period, where the offset between the thermocouple and calorimeter is determined. This offset is determined for a range of temperatures between 50°C and 300°C. During the calibration, the thermal mass inside the calorimeter should be similar to the mass during the thermal runaway test. The bracket used to suspend the cell inside the calorimeter was included during calibration. The ARC calibrates to a sensitivity of 0.01°C/min so that the calibration is setup to be more precise than that of a test. At each step, if the change in temperature of the sample has a magnitude greater than 0.01°C/min, then the ARC will heat slightly more and try again.

4.1.2 Drift Check

A drift check is performed after a calibration to ensure that the calibration is accurate enough for testing. In this test the thermocouple is attached to a larger drift sample and the sensitivity is set back to 0.02°C/min. The drift check is performed similarly to the calibration, with heating by 50°C steps starting from 50°C up to 300°C. The calibration is considered a success if the magnitude of the rate of change in temperature at each 50°C step is less than 0.02°C. The calibration and drift samples and example calibration data are shown in figure [Figure 4.1](#)

4.2 Molicel P28A ARC Testing

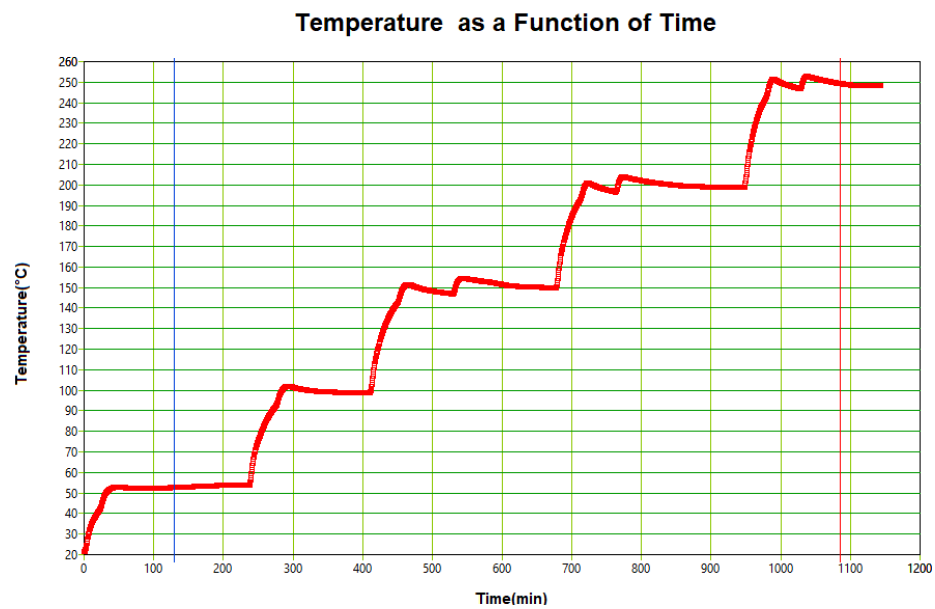
The Molicel was selected for the first tests in the ARC due to its low cost relative to the Tattu and RDQ pouch cells. Both heat capacity and heat-wait-see (HWS) tests were performed.

4.2.1 Molicel Heat Capacity

To determine the Molicel's heat capacity, the plastic wrap is removed from the cell and a resistive heating element is taped onto the cell's can. Three cells are bundled together with the heating element at the center. The thermocouple is taped to the outside of the cell with the heating element attached. This bundle is suspended inside either of the two



(a)



(b)

Figure 4.1: Calibration Samples and Data. (a) Image of calibration (left) and drift (right) samples. (b) Example data for a calibration test.

calorimeters and the heating element wires connected to the heat capacity unit (CPU). An example bundle (without the cell wrapping removed) and the CPU is shown in [Figure 4.2](#). A CPU test is started at room temperature. When the ARC system enters “Seek” mode, the CPU begins heating the cells. The calorimeter then heats at the same rate as the cell, keeping an adiabatic environment. The cell is linearly heated to the endpoint temperature, usually set to 60°C to avoid accidental thermal runaway.

The results from the CPU test are evaluated in THT’s post-processing software “ARCCALPLUS”. The user selects the linear range of the data and the software calculates an equation for the cell’s heat capacity. The Molicel was found to have a heat capacity of 0.8-0.86 J/g°C over the range of 27°C to 60°C. Images of the temperature profile during the CPU test and the curve fit of the CPU data are shown in [Figure 4.3](#). The heat capacity for the Molicel was calculated to be...

$$CPU_{Mol} = 2.65551e^{-5} * T^2 - 4.88559 * T + 0.792282 \quad (4.1)$$

The heat capacity measurement is important to understand and model the thermal behavior of the cell, as well as evaluate the thermal runaway results from HWS testing in the ARC.

4.2.2 Molicel Thermal Runaway

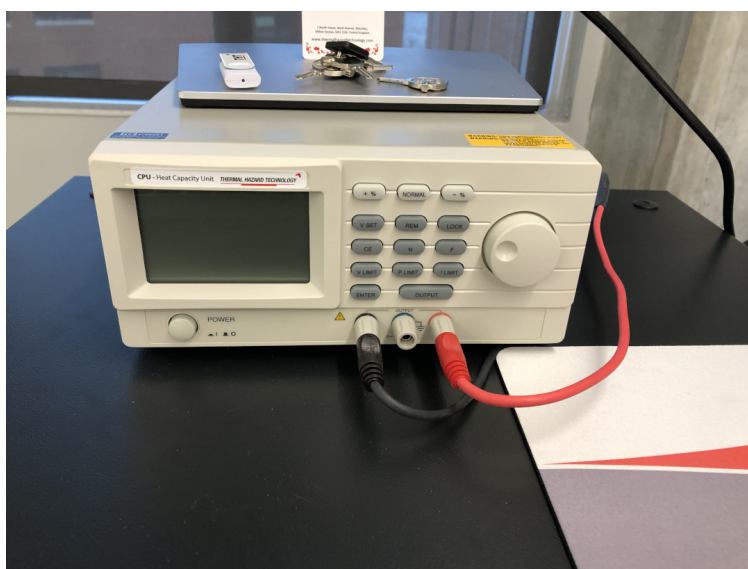
A couple of Molicel P28A’s were burned in the ARC under HWS protocol. The cells were charged to 100% SOC, had their wrapping removed, and were suspended via steel wire from a bracket inside the ARC. The thermocouple was attached to the cell using metal tape with fiberglass tape wrapped around the cell holding it all together as seen in [Figure 4.4](#) and loaded into the ARC. The HWS tests were performed starting at 50°C, with a temperature step of 5°C, and a wait time of 30 minutes between each heating. In the first test, the cell reacted with enough force to shear the steel wire suspending it in the ARC. The cell fell to the floor of the ARC, detaching the thermocouple and likely lowering the measured maximum temperature from what the cell actually experienced. In the second test more wire was



(a)



(b)

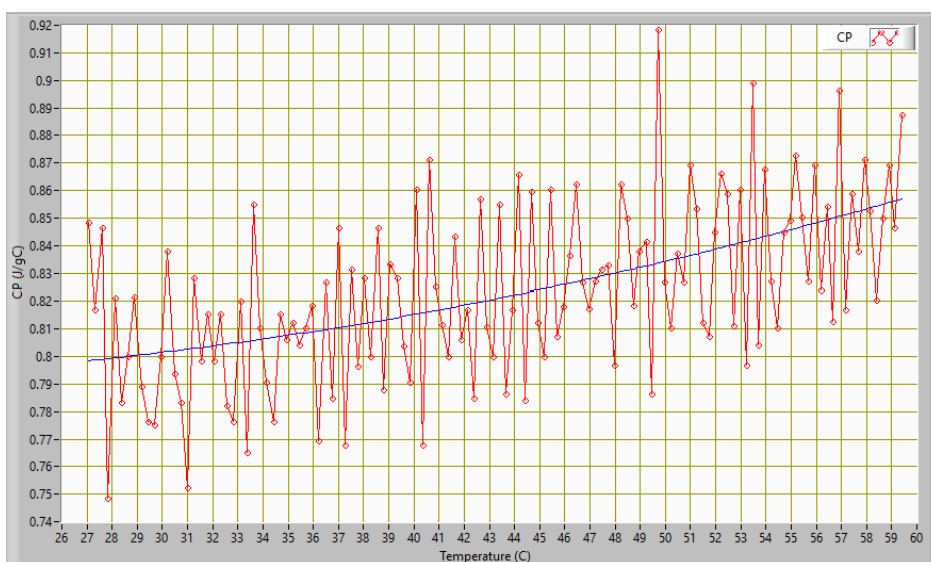


(c)

Figure 4.2: CPU unit and cell bundle. (a) Molice with CPU resistive heater attached, (b) bundle of three Molice cells for a CPU test, (c) CPU unit used for ARC testing.



(a)



(b)

Figure 4.3: CPU data for the Mollicel. (a) Heating profile during the CPU test (b) heat capacity curve fit over the raw data from the CPU test



Figure 4.4: Molicel 18650 set up for a thermal runaway test.

used to suspend the cell and it remain suspended and attached to the thermocouple. The aftermath of these two tests are shown in [Figure 4.5](#).

From the cells' temperature profiles, displayed in [Figure 4.6](#), a couple important data points can be identified, shown in [Table 4.1](#). Exothermic onset occurred at 77.9°C and 67.84°C as the cells began self-heating. In the second test, this first stage of heating eventually ran out of power and the cell stopped rising in temperature. The ARC identified this, and re-entered heating mode, to seek the 2nd exothermic onset temperature, which occurred at 84.1°C. These onset temperatures have important implications to thermal runaway safety and correlate to excess degradation. In endurance test 1, the MoliceL had maximum discharge temperatures ranging from 70°C at the beginning of the test to 95°C at the end, with an average temperature of 78.9°C. These temperatures are high enough to cause irreversible exothermic reactions within the cell, increasing degradation. The exothermic rate at this temperature is low and did not send the MoliceL into thermal runaway during the endurance tests, but it was enough to increase degradation. Another point on the temperature profiles shows a small but sharp decrease in temperature around 110°C before continuing with exothermic heating. This shape in the temperature profile indicates the cell is venting gases that have been built up, causing the temperature to slightly drop before continuing with thermal runaway.

The final data point of interest in the temperature profile is the maximum temperature reached by the cell. In this test, the second cell burned was measured to reach 699.5°C during the thermal runaway event. The first cell reached 388.1°C, but it sheared the wire suspending it and disconnected from the thermocouple, so it is impossible to know if the thermocouple recorded the maximum temperature that the cell experienced. However, Zhang et al. analyzed cell to cell variations in 18650 cylindrical cells and found large variations of maximum temperature ranging from 345.1°C to 726.7°C, which is a larger variation than in these two tests [34]. Nonetheless, conclusions will not be made from the first cell's peak temperature. In both tests, large amounts of material were expelled from the cells including fine-powdery ash and large pieces of current collector foil, amounting to around 25g for each cell. Safety and thermal runaway studies such as these will prove invaluable in designing safe eVTOL systems by providing thermal runaway data caused by over-heating, nail penetration,



(a)



(b)



(c)



(d)

Figure 4.5: Aftermath of thermal runaway test on Molicel P28A showing (a) the burned cell of test 1 and the sheared hanging wires, (b) the inside of the ARC after test 1 with the cell sitting on the floor, (c) the burned cell of test 2 still hanging from the bracket with the thermocouple attached, and (d) the inside of the ARC after test 2

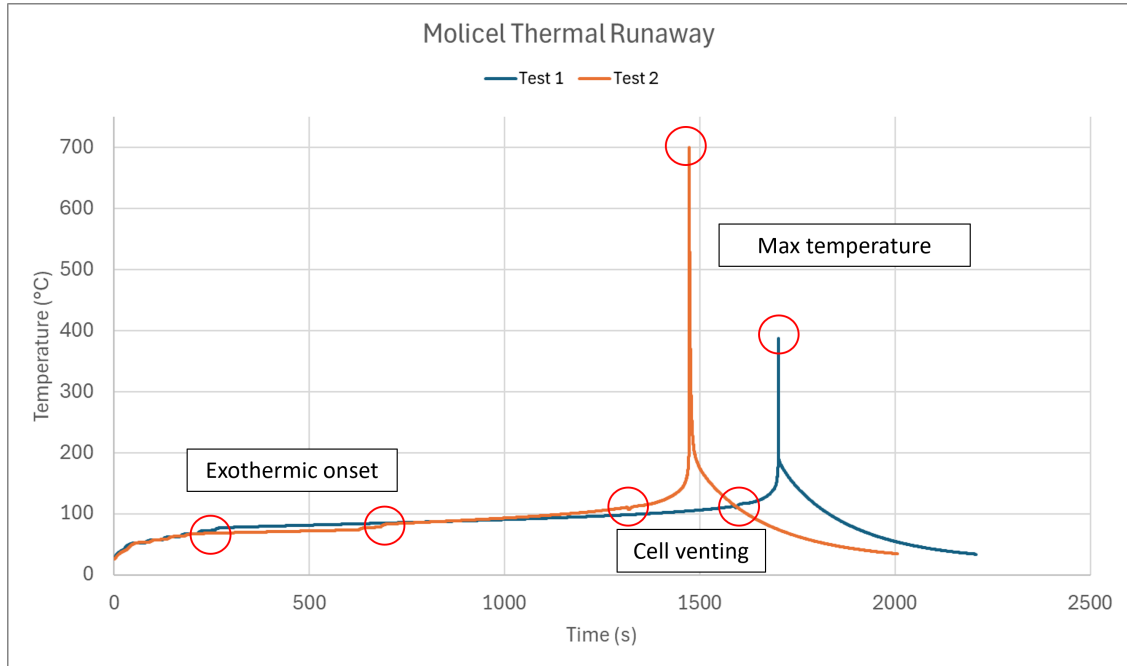


Figure 4.6: Temperature profiles for Molice thermal runaway.

Table 4.1: Molice thermal runaway results for the first two tests

Molice Thermal Runaway		
	Test 1	Test 2
Mass (g)	44.5	44.6
CPU (J/gK)	0.85	0.85
Onset Temp (°C)	77.9	67.84
2nd Onset Temp (°C)	-	84.05
Cell Venting Temp (°C)	112	109.8
Maximum Temp (°C)	388.1*	699.5
Final Mass (g)	17.5	19.1
Expelled Mass (g)	27	25.5

crushing, overcharge, and high currents, measuring heat capacity for thermal modeling, and identifying exothermic onset temperature to better inform pack design and cooling requirements.

Chapter 5

Related and Future Work

5.1 Pairing EIS and DRT Analysis with ARC Studies

Continuing to understand thermal runaway and the safety implications of lithium-ion batteries is vitally important to the long term success of EV and eVTOL systems. But much is still unknown about the thermal runaway process. Distribution of relaxation times analysis of electrochemical impedance spectroscopy data provides useful insights into the processes occurring in the cell and could be applied to better understand the processes leading up to thermal runaway. The groundwork has been laid for the following two potential areas of research which apply DRT analysis to ARC studies: an analysis of cell-to-cell variations in both the DRT spectra and the thermal runaway characteristics of identical cells to find any correlations between the two that may contribute to more violent thermal runaway, and performing EIS measurements on cells inside the ARC as they are heated and approach thermal runaway. Both studies could be performed at the same time.

5.1.1 Analysis of Cell Processes and Thermal Runaway Cell-to-Cell Variations

As previously discussed in [Section 1.3.6](#), cell-to-cell variations (CtCv) can play a major role in degradation and thermal runaway. Additionally, CtCv have been identified in the DRT spectra, as processes inside the cells can also vary. The cause of these variations is usually

attributed to manufacturing or storage inconsistencies [28, 34], but any correlation that may exist between the variations in the DRT spectra and the variations in cell performance or thermal runaway have not been identified. Statistical analysis of CtCv in both the DRT spectra and thermal runaway may reveal correlations between certain cell process variations with more violent thermal runaway, which would provide greater insights into cell safety.

5.1.2 EIS and DRT Analysis During a Thermal Runaway ARC Test

Another line of research which could be pursued in the future is performing EIS testing and DRT analysis on cells in the ARC during a thermal runaway test. Dong et. al. performed a similar experiment in which EIS data was taken during a HWS ARC test, in order to identify if a change in the EIS spectra could be an early warning of thermal runaway [11]. They showed that changes in high and intermediate frequencies can be used as early warnings to thermal runaway, and allow time to stop the cell before it catches fire. Figure 5.1 shows the changes in the EIS spectra due to heating in the ARC. However, up to this point no DRT analysis has been performed on EIS data leading up to thermal runaway, which could provide insight into how the cell processes change approaching thermal runaway.

Both of these studies could be performed at the same time. Each cell could initially undergo a characterization test at BOL and then be charged to the selected SOC for ARC testing, and testing in a HWS test while having EIS performed. The ground work for these studies has already been laid. In conjunction with Dr. Peng Zhao's lab at the University of Tennessee Space Institute (UTSI) and with the help of Liwen Zhang, an initial test was performed to connect a potentiostat with a cell in the ARC with a simple LabVIEW executable to trigger EIS every 5°C. The cell was charged to 50% SOC and did not experience thermal runaway. Heating the cell caused exothermic reactions within the cell, but these reactions did not have enough energy to cause flame. The physical connections between the potentiostat and the cell created significant noise, rendering the captured EIS unusable. These EIS spectra had large inductance behavior that covered up to charge transfer regions due to the long wires used to connect the cell to the potentiostat. However, the EIS was successfully triggered

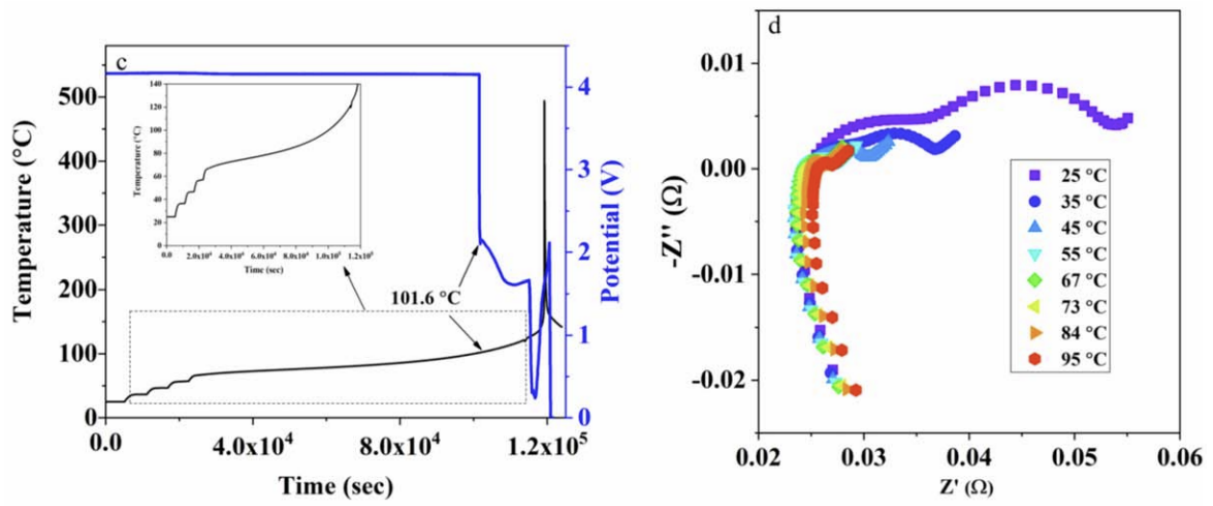


Figure 5.1: Changes in EIS during an ARC test [11].

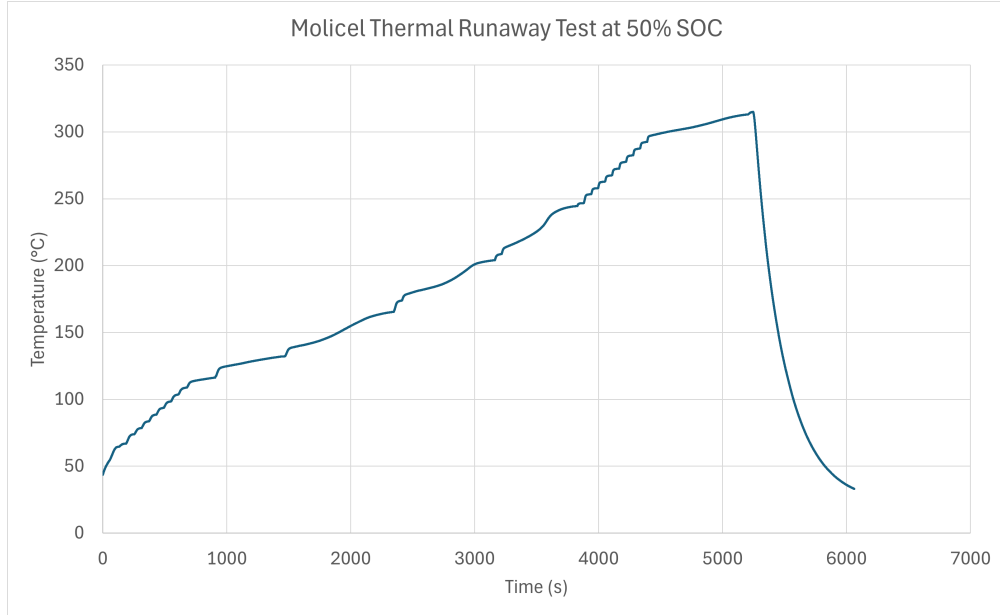
during an ARC test. The results from this test are displayed in [Figure 5.2](#). Continued research is being conducted to improve the connection between the potentiostat and a cell inside the ARC, as well as improve the controls between the ARC and the potentiostat.

5.2 Design of a Rapid Temperature Controlling Lithium-Ion Battery Test Stand

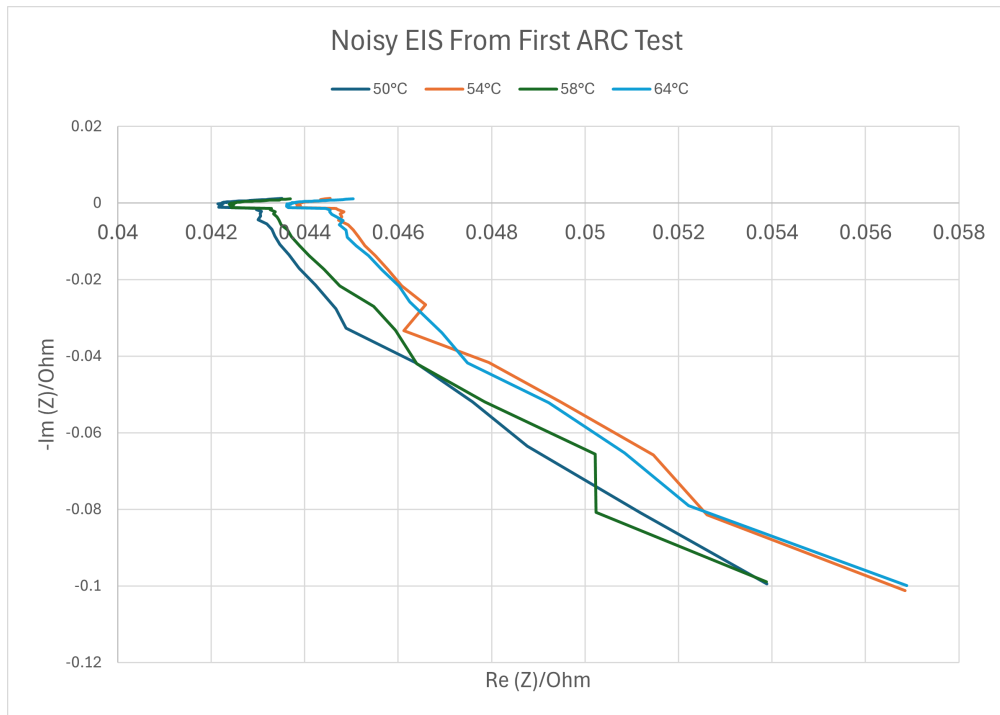
For degradation studies on lithium ion batteries, it is standard practice to cycle the cells at a single temperature controlled by an environmental chamber, with both charging and discharging occurring under the same conditions [18, 9, 7, 6, 31, 32, 8]. It is also commonly accepted in the literature that one of the main degradation mechanisms due to low temperature cycling is lithium plating occurring during charging [20, 9, 6], but degradation studies charging and discharging cells at different temperatures have not been performed. As more attention is placed on EV and eVTOL performance in cold temperatures, the need arises for understanding how degradation is affected by both charge and discharge temperatures independently.

Degradation studies are inherently challenging due to the time it takes to put the batteries through a large number of cycles. Each endurance test of 500 cycles in this study took around three-and-a-half months to complete, with a 15-minute rest after charging and a 30-minute rest after discharging. A degradation study performed in an environmental chamber with different temperatures for charging and discharging would require drastically more time. For example, an environmental chamber could take up to an hour and a half to change temperature and allow time for the cell to re-equilibrate with the environment. Adding two extra hours of rest for every cycle adds about a month and a half of waiting time to a 500 cycle test. Thus, a new test stand is required for performing such degradation studies which can quickly change the temperature of the cell between the charge and discharge steps.

The designed test stand (U.S. Provisional Patent Application No. 63/668,509) utilizes thermoelectric coolers (TEC) to pump heat away from the battery into a circulated coolant via the Peltier effect. When current is applied to the TEC, heat is pumped from one side to



(a)



(b)

Figure 5.2: Initial results from performing EIS during ARC heating. (a) Temperature evolution of a Molicel charged to 50% SOC inside the ARC and (b) Noisy EIS at different temperatures during an ARC test.

the other. Reversing the direction of current also reverses the direction of the heat pump. A TEC can generally create a temperature difference of about 30°C from one side to the other. However, it also generates some heat through ohmic heating and will quickly increase in temperature if not cooled itself. Coolant fans, heat sinks, and liquid coolant are commonly used for this application. For this application a chilled coolant loop is utilized to remove heat from the TEC and battery.

This test stand is comprised of two identical halves controlling the temperature of the cell between them, show in [Figure 5.3](#). Each half is built from an aluminum block that sits on the cell acting as a heat sink. A row of TEC's sits on the block, with an aluminum water cooling block on the other side. A 3D printed bracket holds the layers together. A pouch cell is placed in between the two aluminum blocks, cooling the largest faces of the cell. Additional aluminum flanges can be added to the cooling blocks to provide for heat transfer between the cell edges and the heat sinks. Thermal paste is used between every interface in the test stand to promote heat transfer. Coolant lines are connected to the water cooling blocks, which circulates glycol-water through a chilled water bath. Because the TEC's can pump heat in either direction, they act as a control interface between the water bath and the battery, capable of both heating or cooling the cell.

The prototype is designed to hold the cell at different temperatures during charge and discharge and is controlled via a LabVIEW VI connected to an Arduino MEGA and a TC-08 thermocouple logger. The Arduino reads analogue data from a Hall-effect current sensor and the cell voltage to determine the state of the cell. The "charging" state occurs after the cell is either fully discharged or during charging. The "discharging" state signifies a battery is fully charged or actively discharging. The TC-08 reads the temperature of thermocouples attached to the cell, streaming it to the VI. A simple temperature controller takes the measured cell temperature and the desired cell temperature, and then sets a cooling power value from -1 to 1. The Arduino sends this value as a PWM signal to a DC motor controller which powers the TECs. A 12V DC power supply provides power to the motor controllers. The test stand is surrounded with thermal insulation and placed inside a LiPo fire bag as shown in [Figure 5.4](#) to contain any potential thermal runaway events and prevent heat exchange between the test stand and the lab.

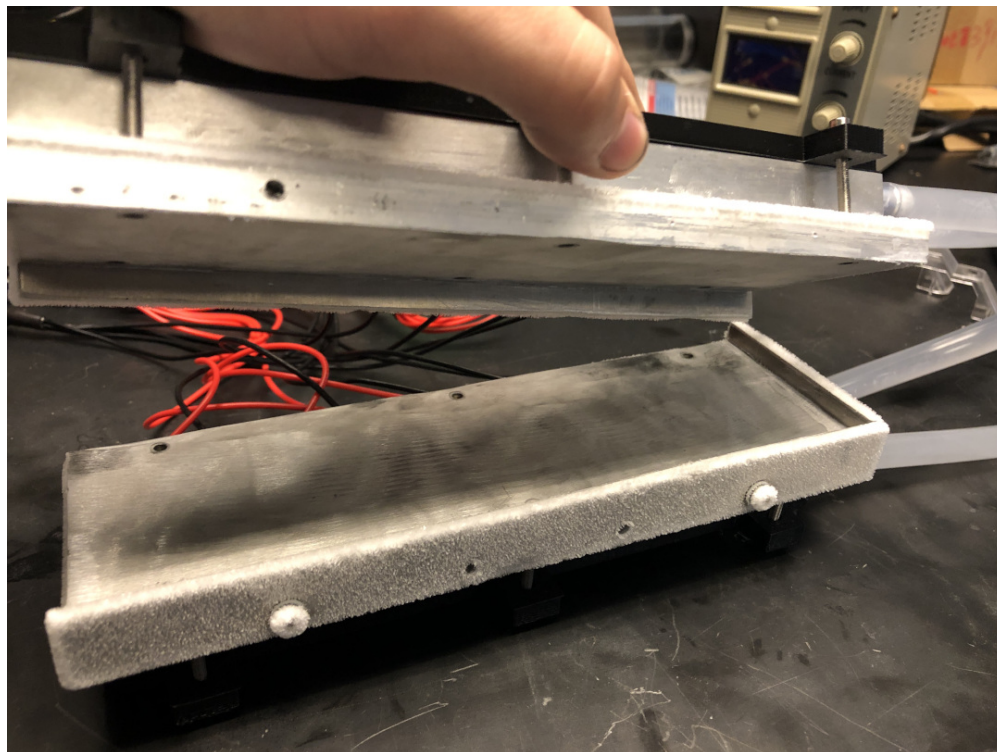
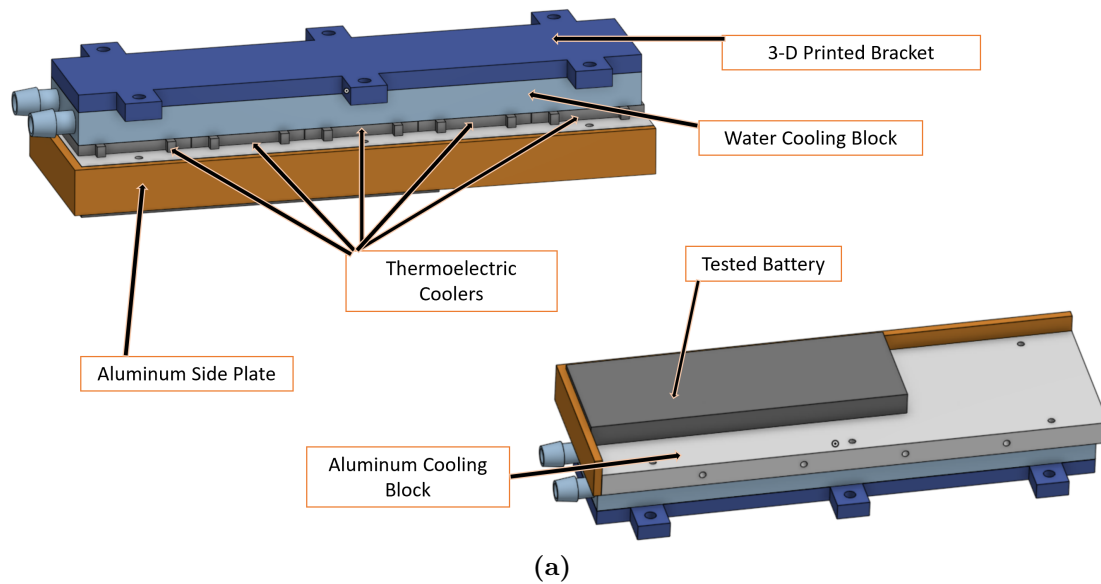
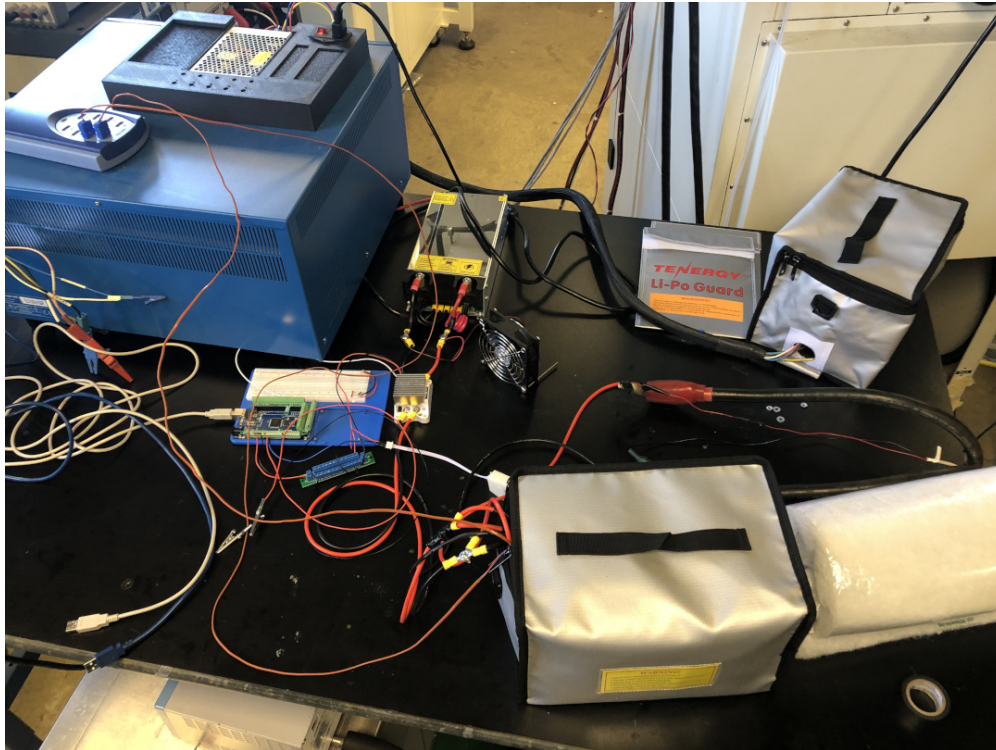
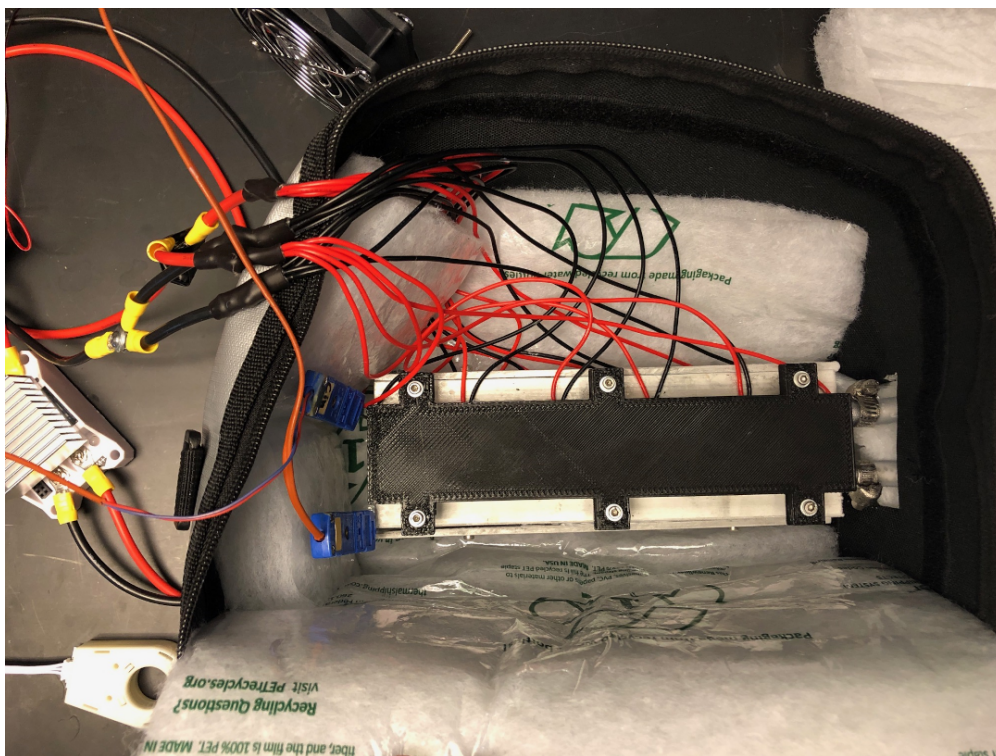


Figure 5.3: Design of battery test stand prototype. (a) CAD design of rapid temperature controlling test stand showing each component (b) The initial prototype opened to show where the cell goes. Icing can be seen on the outside of the test stand as it is held at -20°C .



(a) Test stand setup



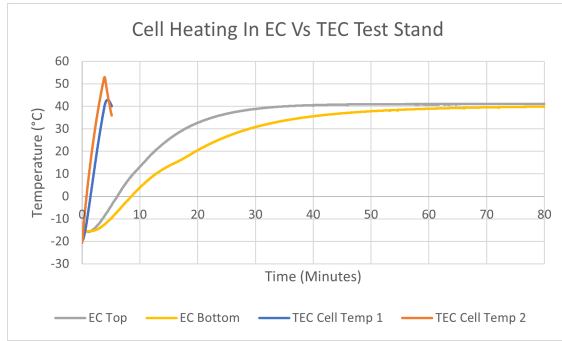
(b) Test stand in a bag

Figure 5.4: (a) Prototype setup of the battery test stand and (b) the test stand inside of a LiPo fire bag and thermal insulation.

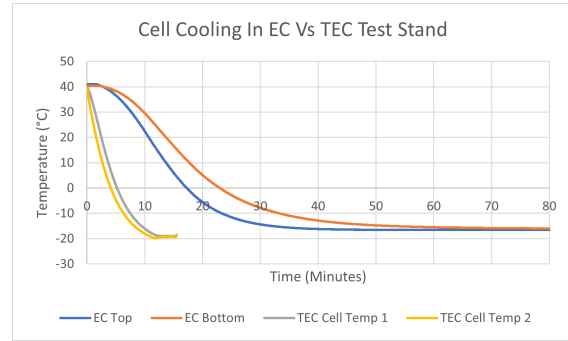
The coldest temperature attainable by the test stand is determined by the temperature of the water bath. With a 5°C water bath, a cell temperature of -20°C is possible. Initial testing compared the time it takes to swing the temperature of a 6.5Ah pouch cell between -20°C and 40°C. Two thermocouples were placed on the edges of the pouch cell inside of the TEC test stand. Thermocouples were placed on two batteries inside of the environmental chamber, one on the top rack and one on the bottom rack of the chamber. The cell in the test stand was heated from -20°C to 40°C in 5 minutes and cooled from 40°C to -20°C in 12 minutes. The environmental chamber, however, took approximately an hour to both heat and cool the battery as shown in [Figure 5.5](#). Thus, using this designed test stand to perform a 500-cycle endurance test, with charge and discharge occurring in different temperatures, would decrease test time by a month and a half, when compared to using an environmental chamber.

Another test demonstrated how the software uses voltage and current measurements to set the temperature of the cell during cycling. [Figure 5.6](#) shows data collected from the test stand as a cell went through a 1C charge and discharge. The measurements from the Arduino are imprecise. The voltage is higher than the cell's actual voltage, and the current has a large amount of noise. However, the trends in this data are enough to identify cell state and control the temperature. During CCCV charging, when the cell is at 4.2V and current is falling to 0.1 amps, the Hall effect sensor has trouble identifying when current actually stops and the noise causes the temperature control to oscillate a few times between the two set points. Nonetheless, the prototype functions acceptably well in its current state, and improving the micro controllers, sensors, and control software would make it a very useful tool for battery testing. Additionally, a new cell holder could be designed for the test stand to control the temperature of cylindrical cells.

The designed test stand has multiple advantages over environmental chambers. Not only can the test stand change the temperature of cells faster than an environmental chamber, it can do so automatically as the cell cycles. Additionally, the test stand reads all the necessary data from the cell and does not require any communication with the battery cycling equipment, making it easy to install on any battery-testing setup. In traditional test setups with environmental chambers, multiple cells are cycled in the same chamber. This is efficient



(a) Heating Curves



(b) Cooling Curves

Figure 5.5: (a) Heating and (b) cooling curves for the prototype test stand and environmental chamber.

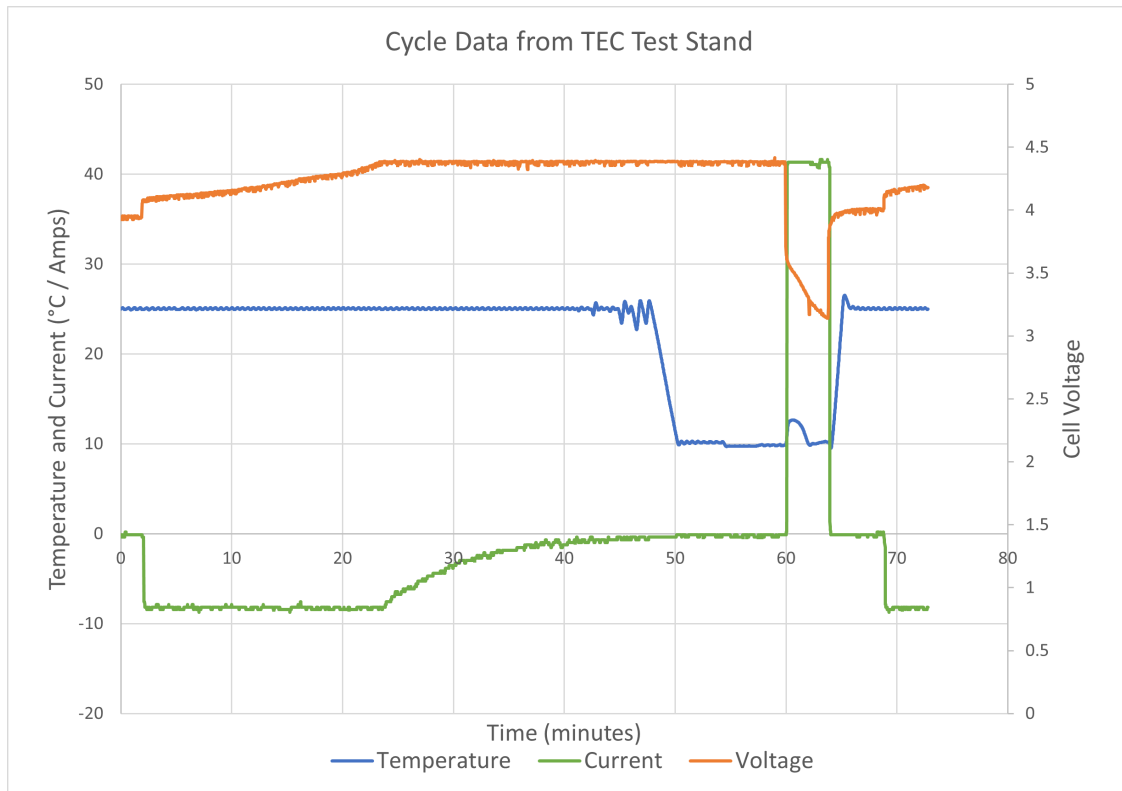


Figure 5.6: Voltage, current, and temperature curves from the test stand.

when the temperature is kept constant throughout the study, but when the temperature needs to change in response to the cell state, having multiple cells in the same chamber is no longer feasible. This test stand controls the temperature for individual cells and could run multiple tests in parallel with further development.

5.3 Future Work in Lithium-Ion Batteries for eVTOL Applications

Many questions still remain concerning the behavior of lithium ion batteries under the high rate discharges that will be experienced under eVTOL requirements. The effect of cell to cell variations is vitally important to module design and needs to be studied for each cell type selected for an aircraft. New methods for cooling the battery packs in such weight-limited applications need to be researched and developed. Additionally, the information gained by studying state-of-the-art commercial cells can be applied to developing new high-rate lithium ion batteries specific for eVTOL applications.

Chapter 6

Conclusions

In this work, state-of-the-art commercial lithium-ion batteries were tested under the demanding requirements which could be seen for eVTOL applications. Molicel P28A 18650's, Tattu 2.0 Ah pouches, and Race Day Quads 2.2 Ah pouches were cycled for up to 500 cycles under various thermal conditions with 10C, 25C, and 23C discharge currents respectively. The cells were cycled in an environmental chamber under 20°C with natural convection and 20°C, 0°C, and -10°C with forced convection. A characterization test including a battery capacity determination and EIS at every 10% SOC was performed at BOL and after every 50 subsequent cycles. Additional characterization tests were performed on pristine cells at various temperatures down to -20°C. Distribution of relaxation times performed on the EIS data showed how internal processes in the cell changed over %SOC and cycle number or temperature.

The results of this study show that state-of-the-art, commercial lithium ion batteries are capable of the high rate discharges required by eVTOL applications for up to 500 cycles while retaining 80% capacity or more, depending on ambient conditions and cell type. Power fade is also an important consideration for eVTOL batteries. As the cells degrade with increasing cycle number, the average discharge voltage under high rate conditions tends to drop similar to the capacity fade. However, this voltage fade is not reflected in the open circuit voltage measurements or the 1C discharge voltage. Power fade due to the cell degradation could have a profound impact on eVTOL aircraft systems.

Distribution of relaxation times is a powerful tool for understanding cell performance. Characterization tests performed at various temperatures show how cell process resistance is affected and can be used to aid in identification of acceptable operating ranges. DRT is additionally applicable to analyzing the degradation of LIB's without destruction of the cell. In these cells, the DRT signatures of particle-particle interactions degradation, SEI growth/decomposition, lithium plating, and electrode decomposition can be seen. By pairing comprehensive characterization testing with endurance studies, a deeper understanding of cell performance and process degradation within commercial batteries is achieved. This type of analysis will be vitally important when scaling batteries into a pack for eVTOL applications.

Thermal runaway and safety analysis of lithium ion batteries is needed for eVTOL batteries to ensure a safe aircraft. Heat capacity and impedance measurements can lead to thermal models of cells and packs and help design thermal management systems. Further degradation testing on the TEC test stand will provide insight into the best thermal management strategies for cells with regards to both charge and discharge temperature.

The cells chosen for this study were designed for high power applications and are among the closest batteries commercially available for meeting eVTOL requirements. The Molicel is a general purpose high power 18650 cell, while the pouch cells tested are designed for drone racing and are capable of very high power output. However, commercial cells have not yet been designed specifically for large scale eVTOL aircraft systems. In order for eVTOL systems to take off, next generation batteries need to be designed for these aircraft. Analysis of current state of the art batteries using advanced characterization methods can aid in the design of the LIB's necessary for eVTOL.

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