

IMPERIAL COLLEGE LONDON



THERMAL CHARACTERISATION AND PERFORMANCE OF CYLINDRICAL LITHIUM-ION BATTERIES

PhD Thesis

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Statement of Originality

I hereby declare that the work in this thesis is my own, and where appropriate the work of others, including any work generated by artificial intelligence, has been acknowledged and referenced.

Mohamed Waseem Marzook

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Abstract

Lithium-ion cells are a key piece of technology in the world today, used in a variety of applications from electric vehicles to mobile phones. Most applications use multiple cells in a battery pack. Choosing the right cell for a given application can be critical to achieving an optimised battery pack. However, a lack of information from cell datasheets makes choosing an optimum cell a challenge. This thesis aims to assess potential methods of making the comparison of cells easier.

The Cell Cooling Coefficient (CCC) is a thermal metric designed to define the heat rejection capability of lithium-ion cells. Experiments presented in this thesis successfully measure the CCC value for base cooled cylindrical cells. While modelling work, highlighted potential issues caused by the heat generation profile of the cell, making the CCC non-constant, with the impact of real experimental losses impacting the measurement of the CCC, resulting in the application of the CCC being restricted to use as a standardised comparison for cell thermal performance.

Following this, a study benchmarking the performance of six cylindrical cells has been performed aiming to assess the viability of selecting cells based on standardised conditions. Through a series of tests covering a range of electrical loads and different cooling systems, it is demonstrated that the conditions of testing can impact percentile-based ranking by over 20%, proving that cells must be tested under application-specific conditions to enable the correct choice of cell.

Finally, an experimental lifetime study is performed on two commercial cells, comparing base cooling, side cooling and standardised conditions, under automotive-relevant cycles. It is found that side cooling is the better cooling system for both beginning and end of life, with standardised conditions being unrepresentative of either. Concluding that cells should be tested for life performance under application-relevant conditions, to choose the best cell.

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Laura Bravo Diaz, Alastair Hales, Mohamed Waseem Marzook, Yatish Patel, Gregory Offer, **Measuring Irreversible Heat Generation in Lithium-Ion Batteries: An Experimental Methodology**. *J. Electrochem. Soc.* (2022). doi:10.1149/1945-7111/ac5ada.

Conference Presentations

‘The Cell Cooling Coefficient: A Design Tool to Optimise Thermal Management of Lithium-ion Cells in Battery Packs’ - A. Hales, R. Prosser, L. Bravo Diaz, G. White, Y. Patel, G. J. Offer, and M. W. J. Marzook, *240th Electrochemical Society Meeting, Online, 2021*

Posters

‘Cell Cooling Coefficient, thermal gradients and their implications on degradation’ - M. Waseem Marzook, Shen Li, Alastair Hales, Cheng Zhang, Gregory Offer and Monica Marinescu, *Advanced Battery Power Conference, Muenster, Germany, 2022*

‘The Effect of Test Conditions on the Performance of Cylindrical Cells’ - M. Waseem Marzook, James Eaton, Gregory Offer and Monica Marinescu, *Advanced Battery Power Conference, Aachen, Germany, 2023*

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List of Acronyms

3D	3-Dimensional
ABS	Acrylonitrile butadiene styrene
AC IR	Alternating Current – Internal Resistance
AMB	Ambient
BoL	Beginning of Life
BMS	Battery Management System
CC	Constant Current
CCC	Cell Cooling Coefficient
CCCV	Constant Current followed by Constant Voltage
CID	Current Interrupt Device
Conv.	Convection Boundary Condition
CP	Constant Power
CPCV	Constant Power followed by Constant Voltage
C-rate (C)	Capacity rate, defines the current (A) with respect to the nominal capacity (Ah) of a cell
DC	Drive Cycle
DC IR	Direct Current – Internal Resistance
DC IRT	Direct Current – Internal Resistance – Tested in this work
DTA	Differential Thermal Analysis
DTV	Differential Thermal Voltammetry
E-rate (E)	Energy rate, defines the power (W) with respect to the nominal energy (Wh) of a cell
EV	Electric Vehicle

FF	Fast Charge – Fast Discharge Cycle
FS	Fast Charge – Slow Discharge Cycle
GITT	Galvanostatic Intermittent Titration Technique
Gr-Si	Graphite and Silicon blended anode
HPPC	Hybrid Power Pulse Characterisation
I	Current (A)
IR	Internal Resistance
LAM	Loss of Active Material
LFP	Lithium Iron Phosphate Cathode
LIB	Lithium-Ion Battery
LLI	Loss of Lithium Inventory
PTC	Positive Temperature Coefficient Device
RPT	Reference Performance Test
Nat. Conv.	Natural Convection
NCA	Nickel Cobalt Aluminium Cathode
NEDC	New European Driving Cycle
NMC	Nickel Manganese Cobalt Cathode
OCV	Open Circuit Voltage
SEI	Solid Electrolyte Interphase
SF	Slow Charge – Fast Discharge Cycle
SOH	State of Health
SOC	State of Charge
SS	Slow Charge – Slow Discharge Cycle
TC	Thermocouple

TMS	Thermal Management System
WLTP	Worldwide Harmonised Light Vehicle Test Procedure

List of Symbols

A	Area (m ²)
E_{DC1}	Output Energy for cell under drive cycle 1 (W)
h	Heat transfer coefficient (W/m ² K)
I	Current (A)
k	Thermal conductivity (W/mK)
l	length (m)
P_1	Baseline power for synthetic drive cycle (W)
P_2	Peak power for synthetic drive cycle (W)
$\dot{q}$	Specific heat rate (W/m ²)
$\dot{Q}$	Heat rate (W)
$\dot{Q}_{fin}$	Heat flow rate through cooling fin (W)
$\dot{Q}_{ins}$	Heat flow Rate through insulation (W)
$\dot{Q}_{loss}$	Heat flow rate of losses (W)
$\dot{Q}_{LR}$	Heat flow ratio of losses to total heat (W)
$\dot{Q}_{tot}$	Heat generation rate (W)
r	Ratio of gradient and y-intercept for linear heat generation (1/m)
R	Electrical resistance of the cell (Ω)
R_c	Thermal resistance of the cell (K/W)
R_f	Thermal resistance of the cooling fin (K/W)
R_i	Thermal resistance of the insulation (K/W)
T	Temperature (K)
T_a	Temperature of ambient (K)

T_c	Temperature of cooling (K)
T_{DC1}	Maximum temperature of cell under drive cycle 1 (K)
T_1	Temperature of insulated surface of cell (K)
T_2	Temperature of cooled surface of cell (K)
ΔT	Temperature difference (K)
x	Displacement though length (m)

Chapter 1: Introduction

1.1 Context

Lithium-ion cells have been a hugely popular area of research over the last two decades, due to their wide range of uses from portable electronics to medical devices. The global climate crisis has brought forth the need to reduce global carbon emissions. This has facilitated a meteoric rise in popularity of electric vehicles (EVs) and stationary energy storage, identified as key technology to achieving net zero carbon emissions. This in turn has propelled lithium-ion manufacturing and research significantly.¹

In the automotive industry vehicle manufacturers are in a race to achieve the most optimised battery packs. Targeting battery packs that give the most range and lifetime, for the least mass, volume, and cost. Designing and building a battery pack is not a trivial task,² there are numerous choices, such as the cell, cooling system and electrical connection, which can significantly impact the performance and efficiency of the pack.³ The most critical choice is that of the cell.

Cylindrical cells are a popular form factor for EVs, used by Tesla, Lucid and Rivian, in their vehicles. They have the advantage of being produced in standardised sizing, allowing easy upgradability and supply chain flexibility. Each cell size offers a range of choice between different manufacturers and their models.⁴ Choosing the optimum cell for a particular application can be a challenging process. However, the standardised sizing of cylindrical cells helps to limit comparisons to electrical, thermal and lifetime performance (excluding cost), as the geometry can be fixed.

1.2 Background

1.2.1 Fundamentals

A lithium-ion battery is a rechargeable electrochemical battery that uses lithium to store electrical energy as chemical energy. It does this by transferring lithium between a positive and negative electrode.⁵ Lithium-ions (Li^+) are able to intercalate in and de-intercalate out of the electrodes⁶, able to move between the electrodes via an ionically conductive liquid, known as the electrolyte, which the electrodes are immersed in.⁷ Intercalation is a process by which metallic ions can be hosted within the structure of another compound by accepting an electron.⁸

While within the structure, the metallic ions can diffuse deeper into the structure allowing the entire bulk of the structure to host lithium, not just the surface.⁹ The electrolyte is typically a combination of solvents, lithium salts and additives, all aimed at achieving a highly ionically conductive liquid, that is stable and long-lasting.⁷ It is typically not possible to prevent the electrolyte from reacting with the electrodes, however when they react they form a boundary layer on the electrodes that prevent further reaction. Thus, the components in the electrode are carefully tailored, alongside designed formation cycles, to form layers that have specified structures and compositions, this layer is often referred to as the solid electrolyte interphase (SEI). The SEI layer is precisely designed by battery manufacturers so that provides little resistance to lithium intercalation/de-intercalation, and has high cycling, chemical and thermal stability.¹⁰

The final three key features of a lithium-ion battery are the positive and negative current collectors, and the separator.¹¹ The separator is an ionically porous material that allows Li^+ ions to flow through freely, but physically separates the two electrodes to prevent them from shorting. The current collectors are thin metal foils that are attached to the electrodes, they facilitate the flow of electrons to and from the electrodes to complete the electrical circuit. The positive current collector is typically made of aluminium, and the negative current collector, copper. The components of a typical lithium-ion battery are shown by a simplified diagram in Figure 1. It is typical to refer to a single lithium-ion device as either a cell or battery, since for the latter it is comprised of multiple electrodes. However, in automotive or energy storage applications a single device is not enough, the battery packs used in these applications contain 100s to 1000s of individual lithium-ion devices. Thus, in this thesis, a single contained device containing a stack of electrodes will be referred to as a lithium-ion cell and a collection of these contained cells will be referred to as a lithium-ion battery pack.

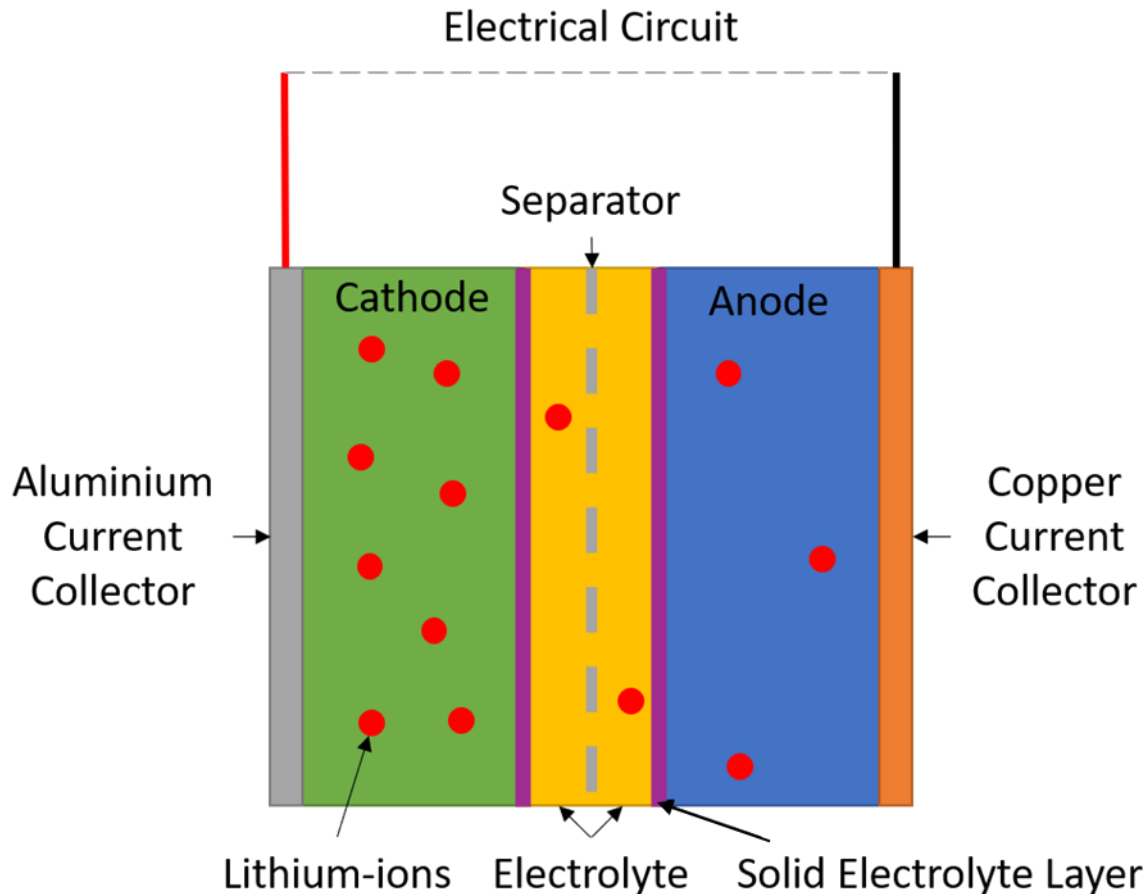


Figure 1: Simplified schematic of the inner structure of a single set of electrodes in a lithium-ion cell. The schematic highlights a representation of a discharged cell, the components of the cell have been simplified for clarity. A more accurate representation of a cell is shown in Figure 9.

A lithium-ion cell is able to release energy because, while it is discharging, the lithium-ions stored in the negative electrode, or anode, want to move to the positive electrode, or cathode, due to it having a lower Gibbs free energy when in the cathode structure.¹² This means that as long as the electrical circuit is complete, such that electrons can flow between the electrodes, and there is a potential difference between the two electrodes, Li^+ ions will be released from the anode structure (along with an electron) and flow to and intercalate into the cathode structure (accepting an electron), until the potential difference between the electrodes goes to zero. When charging, although electrochemically the terms anode and cathode should switch between the negative and positive electrode, it is typical when referring to lithium-ion cells to stick to the discharging terminology, where the negative electrode is the anode and the positive the cathode. Thus, while charging, an external potential is required to drive the lithium-ions back to the anode structure, entering a higher energy state.⁵

The amount of electrical energy a cell can store is typically defined using the term capacity given in Ah or energy in Wh. This defines how many amps or watts can be drawn continuously for an hour. For example, a 5 Ah cell can be discharged from fully charged at 5 A for 1 hour, or 0.5 A for 10 hours. The amount of energy a lithium-ion cell can store is largely dependent on how much lithium the electrodes can store. This is affected not only by the total volume of the electrodes but the specific capacity of the materials. The specific capacity of the electrodes is not only dependent on the material chemistry but also the particle size and porosity in the electrode.¹³

1.2.2 Cell Chemistries

While all lithium-ion cells utilise the transfer of Li^+ ions, the material compounds for the two electrodes can affect everything from the capacity to lifetime. When comparing different materials, specific capacity density is used, this can be gravimetrically or volumetrically. This section will briefly cover the most relevant chemistries for the present automotive market.

Anodes

The most popular anode used for lithium-ion cells is graphite. This is for a multitude of reasons, the foremost being, low cost, ease of availability, good thermal and chemical stability, and good reversibility during lithium intercalation.¹⁴ Fully intercalated graphite becomes LiC_6 , thus one lithium-ion is able to be stored for every six carbon atoms. However, with the need to push energy densities even higher, the present generation of cells has moved past pure graphite electrodes. Another anode material that has immense potential is silicon, theoretically it can achieve a significantly higher specific capacity compared to graphite, fully intercalated it becomes $\text{Li}_{12}\text{Si}_5$. However, it experiences large changes in volume during intercalation, making it much more unstable for lifetime performance.¹⁵ In compromise, lithium-ion cell manufacturers have opted to blend small percentages of silicon particles into graphite, to create a blended electrode. This allows them to make use of the boost in specific capacity of the silicon and use the graphite to help constrain the silicon particles. The Si percentages are typically kept low, as the introduction of the silicon particles can still negatively impact the lifetime performance.¹⁶

Cathodes

NMC

NMC is an abbreviation for a nickel, manganese, and cobalt cathode. The NMC cathode has a layered structure with a chemical formula of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, where $x + y + z = 1$.¹⁷ This is

one of the most popular chemistries of choice for the automotive industry, due to its high lithium storage capability. The ratios of the three rare metals can be adjusted to alter certain properties of the electrode. Higher ratios of nickel improve the specific capacity but lower the lifetime stability. Although cobalt helps improve stability, due to sustainability of sourcing the metal and cost, ratios are typically kept low.¹⁸

NCA

NCA is an abbreviation for a nickel, cobalt, and aluminium cathode. The NCA cathode is another layered structure with a chemical formula of $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, where $x + y + z = 1$. NCA offers very similar performance to NMC,¹⁹ with high nickel content giving it good capacity density, however the loss of manganese helps improve the lifetime stability of the electrode, while the aluminium helps improve thermal stability.²⁰ These factors have allowed NCA, along with NMC, to become two of the most popular chemistries for high energy (long-range) battery packs.

LFP

LFP is an abbreviation for a lithium iron phosphate cathode. The LFP cathode is an olivine structure with a chemical formula of LiFePO_4 . This cathode material offers very good lifetime stability at low cost, due to the cheaper more attainable elements.²¹ It has a flatter voltage curve compared to NCA and NMC, resulting in more consistent power delivery. This chemistry also offers better thermal stability compared to the two Ni based chemistries, making it inherently safer.²² The one drawback it has against the Ni based cathodes is a lower specific capacity. These attributes have made it the chemistry of choice for low cost, low-mid range battery packs, in the automotive space.

1.2.3 Form Factors

There are 3 main types of lithium-ion cells, pouch, prismatic and cylindrical formats.²³ All three formats have been used to make electric vehicle battery packs, each having their own advantages and benefits.

Pouch

Structurally a pouch cell is the simplest format for a lithium-ion cell. Alternating stacks of double sided positive and negative electrodes are stacked on top of one another and connected in parallel to terminating tabs. The tabs can be positioned anywhere around the stack, resulting in either both tabs along one edge, or one at each end of the stack. The stack is vacuum sealed in a polymer casing filled with electrolyte.²⁴ This type of cell offers minimal protection for the

cell, but has the highest energy densities, since almost all of the volume and mass is made of the active electrode material.²⁵ The lack of protection of the cell structure means that typically added protection is required in the pack structure when using these cells in battery packs.³

Prismatic

A prismatic cell is typically comprised of a stack or roll of electrodes housed in a cuboidal metal container. Typically, the container is like a box, with the majority being one continuous piece, and the top attached on at the end. The electrode can either be inserted in as a stack or a flattened electrode roll, sometimes multiple rolls are used.²⁶ This means that not only does it have the added weight of the metal casing, but also loses some volume utilisation in the corners of the container. This reduction in energy density, comes with a significant improvement in safety. Alongside the protection that the metal casing provides, it also contains a safety vent to release gas in the event of overpressure, preventing potential explosions.²⁷

Cylindrical

As the name suggests a cylindrical cell is an electrode stack stored in a cylinder. Akin to AA and AAA batteries, cylindrical cells come in a variety of standardised sizes, with terminals at either end of the cylinder. Two of the most common sizes are known as 18650 and 21700, where these names denote the size, the first 2 digits indicate the diameter in mm, and the next 2 the height in mm. The majority of cells in these two sizes are made the same way. Starting with a stainless steel cylinder with no top, a single stack of double-sided anode and cathode is wound into a tight roll, known as a jelly roll, and inserted into the cylinder.²⁸ The negative tab from the jellyroll is welded to the inside of the base of the can via a gap in the centre of the roll. The cylinder is filled with electrolyte and with the positive tab welded to a positive cap, the cap is crimped into the top of the cylinder,²⁹ this can be seen in Figure 2.³⁰ This results in the entire cell body and base being electrically negative, with only the top cap being positive. The top cap has inherent isolation between the central button and outer rim to prevent shorting the positive and negative via the cylinder body. Additionally, the top cap houses a couple of in-built safety devices, these include a safety vent (similar to prismatic cells),³¹ positive temperature coefficient (PTC) device, and current interrupt device (CID). The purpose of these devices will be explored in more detail in Section 1.2, but the relatively small size of these cells and the numerous safety devices, result in the cylindrical format being the safest of the three from factors.

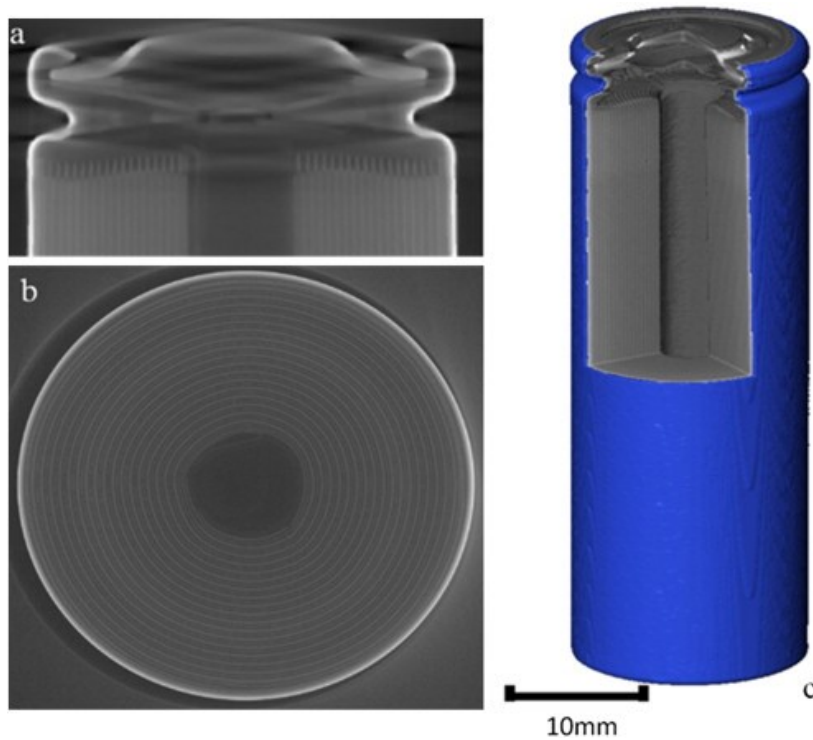


Figure 2: 3D rendering of cylindrical cell. Recreated from Ref. ³⁰(permission given).

1.2.4 Cell Mechanics

The electro-thermal mechanics of a lithium-ion cell makes their operation more complicated than typical electrical devices.

Voltage

The voltage of a cell is dependent on a multitude of variables, the foremost of which is the lithiation state of the two electrodes. As the electrodes transfer lithium from one to the other (depending on charge or discharge) the potential of each electrode changes independently, thus the potential difference between the two varies.³² The state of lithiation (how much lithium is intercalated) of the electrodes is often referenced by a parameter known as the state of charge (SOC). Each electrode is not designed to be fully lithiated or de-lithated, as this can cause irreversible damage to the cell.³³ Thus, cell manufacturers balance the electrodes and set maximum and minimum SOC's via voltage limits.³⁴ This is because the SOC is not something that can be directly measured from the cell, but the voltage can. The problem with defining these states via the voltage is the complex kinetics of a lithium-ion cell, which does not behave like a zero-resistance voltage source.

Resistance

Storing energy in a lithium-ion battery and recapturing it does not come without cost. Although the energy cycle efficiency is very high for lithium-ion cells it is not 100%. There are several mechanisms in a lithium-ion cells that give it resistance, either for the movement of ions or electrons.³⁵ The categories of the different resistances are described in this section.

Ohmic

The ohmic resistances in the cell refers to the instantaneous resistances that activate as soon as a load is applied (charge or discharge). This comes largely from the resistance of the current collectors and tabs to electron flow, and the resistance of the electrolyte to ion flow.³⁶ Typically, these resistances are altered by temperature, where higher temperatures reduce the electrolyte resistance but increase the electrical resistance. Since the electrolyte resistance is normally much larger than the electrical resistance, the ohmic resistance of the cell usually reduces with increasing temperature.³⁷

Diffusion

Diffusion resistances in the cell build up over a longer time scale compared to the ohmic resistances. Primarily it refers to the resistance caused by the diffusion of lithium-ions in the electrode structure, as they move to and from the surface into the bulk of the material.³⁸ This means that you can establish differences in concentration of lithium in various parts of the electrode. The longer or more aggressively that ions are forced to flow, the larger the concentration gradient can be.³⁹ This changes the diffusion rate of lithium, thus the diffusion resistance. This means that this resistance is dependent on time and current, as well as temperature. Additionally, as the electrodes get closer to being fully lithiated or de-lithiated, it is harder to diffuse ions in and out, so the resistance increases near 0 and 100% SOC.⁴⁰

Double Layer Capacitance

The double layer capacitance is the name given to a phenomenon that occurs at the electrode-electrolyte interface. As Li^+ ions travel to the surface of the electrode, rather than intercalate into the bulk of the electrode structure, which takes time and energy, they can form a layer on the surface of the electrode.⁴¹ This layer of positive ions can now apply a repelling force on new incoming ions, this resistance is the double layer capacitance. Similar to the diffusion resistances this resistance is dependent on time and temperature.⁴²

Charge Transfer

The charge transfer resistance is the resistance to transferring charge, in this case the Li^+ ion, from one electrode to the other, through the electrolyte.⁴³ This includes the intercalation and de-intercalation of lithium in and out of the electrodes, as well as the faradaic reactions to release electrons. The charge transfer resistance is heavily dependent on temperature⁴⁴ and the SOC.⁴⁵

Overpotential

Since lithium-ion cells have resistance, Ohm's law states that if current is applied, there must be a subsequent voltage drop for this resistance, this is known as the overpotential. Since $V=IR$, the overpotential is not only dependant on current but also any variables that affect resistance, primarily temperature. The overpotential causes the voltage to drop during discharge and increase during charge.⁴⁶ This means that while charging or discharging the cell the voltage profile of the cell is not equal to the potential difference between the electrodes, this potential difference is often represented by the open circuit voltage (OCV). The OCV represents what the resting voltage of the cell would be at any point, if the external current was removed. The accumulation of overpotentials, on top of the OCV, from the various cell resistances can be seen in Figure 3.⁴⁷ A key point to note is that some of the resistance is built up over time (e.g. diffusion),⁴⁸ thus the overpotential can persist even after an external load is removed. This leads to a voltage relaxation towards the OCV, as all the concentration gradients and dynamic processes relax to equilibrium.⁴⁹

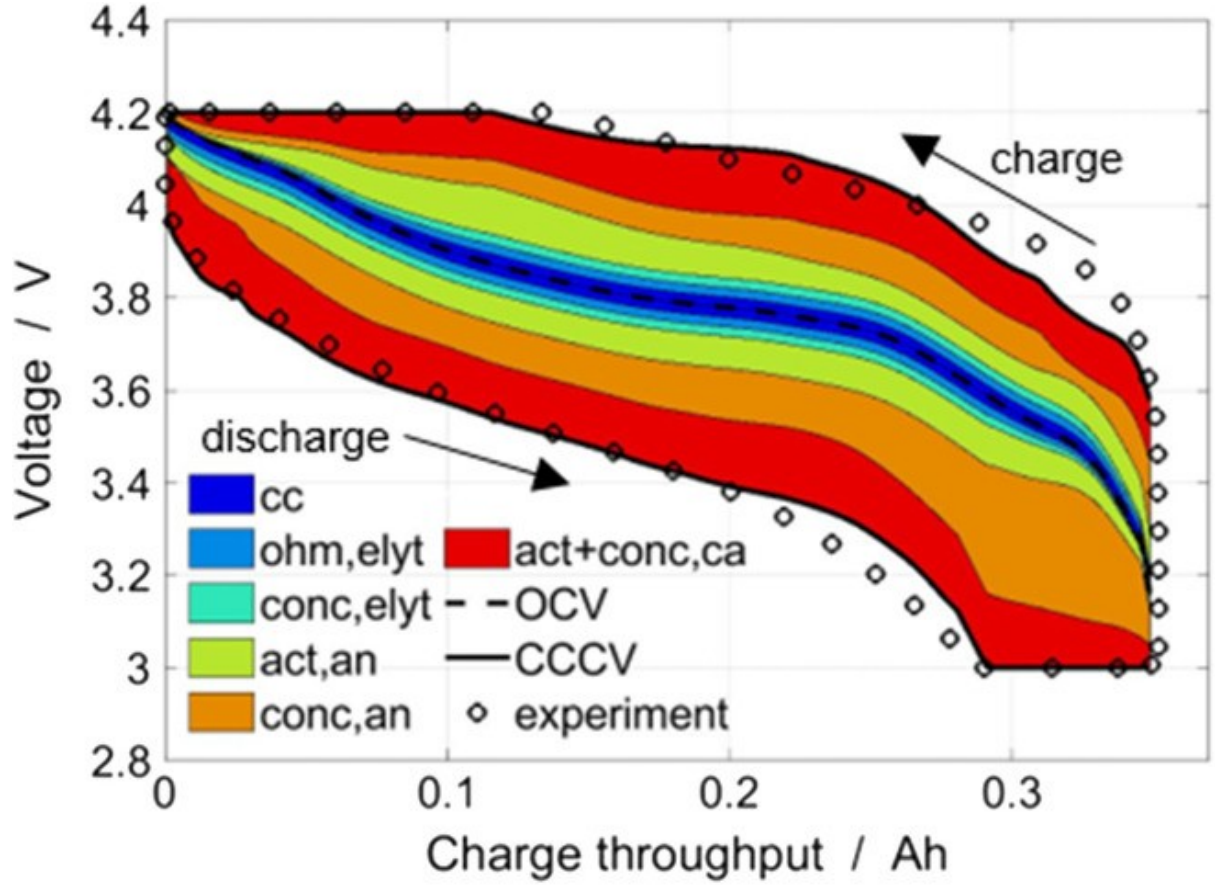


Figure 3: Representation of the stack up of overpotential caused by various resistances; **cc** – current collectors, **ohm,elyt** – ohmic resistance of the electrolyte, **conc,elyt** – diffusion resistance in the electrolyte, **act,an** – activation energy of the charge-transfer resistances of the anode, **conc,an** – diffusion resistance in the anode, and **act+conc,ca** – charge-transfer and diffusion resistance in the cathode. Recreated from Ref. ⁴⁷.

The overpotential also affects both the current and the power depending on if the load is based on power or current. These effects lower the energy efficiency of the cell, as it increases the amount of energy (or power) needed to charge the cell (due to the higher voltage) and decreases the amount of energy (or power) that can be delivered back by the cell (due to the lower voltage). Further to this, because the safe operating limits of the cell are defined through voltage limits, the overpotential results in reaching these voltage limits earlier, before the potential difference of the electrodes can get there.⁵⁰ This in turn affects the starting and ending SOC and capacity of the cell, with the capacity of the cell reducing with current and increasing with temperature. Ultimately this means that the capacity and energy of a lithium-ion cell is dependent on a several factors, most crucial of which are current and temperature. For this reason, cell manufactures typically offer the capacity of the cell as a nominal value, determined from a specified rate charge and discharge, at a given temperature, all chosen by the manufacturer.⁵¹

Heat Generation

As established, lithium-ion cells have internal resistance, these resistances represent energy being lost to inefficient processes, much of this energy is released as heat. Additionally, there are thermodynamic processes that can absorb or create heat. This means that some of heat sources can be reversible and others irreversible.^{52,53} Below is an overview of the meaningful sources of reversible and irreversible heat in a lithium-ion cell.

Irreversible Heat Sources⁵⁴

- Electrode diffusion
- Electrolyte diffusion
- Ion mixing
- Ohmic heat
- Solid electrolyte interphase (SEI) layer

Reversible Heat Sources⁵⁵

- Entropic heat
- Faradaic reactions

The entropic heat in the cell comes from the entropy changes as the electrode materials go through phase changes.⁵⁶ This occurs as the level of lithiation in the electrode changes, altering the structure. This process is reversible thus if a phase transition is exothermic in one direction it will be endothermic in the other. This is similar for the faradaic reactions, which include the redox reactions that release and accept the electrons for the transfer of charge.

A consequence of multiple heat sources in the cell is the fact that the amount of heat generated depends on multiple factors. The strongest factor is current: the higher the current, the greater ohmic heating, thus the more heat is generated.⁵⁷ As mentioned, the overall resistance of a cell reduces with increasing temperature thus so does the heat generation.⁵⁴ Cell heat generation is also related to the SOC of the cell, the entropic heat changes as the electrodes go through phase changes and the irreversible heat increases as the electrodes move towards either extreme of lithiation.⁵⁸ The duration of the applied current also plays a role in the amount of heat generated by a cell, due to the effect time and current has on resistance. Interrupted current loads⁵⁹ and realistic dynamic load cycles⁶⁰ can lead to significantly different amounts of generated heat. Due to the dependence on so many different factors cell heat generation profiles can be difficult to determine. The complexity of the heat profile is made worse by the interplay between many

of these factors while charging or discharging. Since the cell is generating heat its temperature increases, which reduces the resistance, reducing the heat generation, if the cell is undergoing a power-based load this drop in resistance, reduces the overpotential, increasing the current, which of course increases the heat generation. This constant interplay and trade-off makes the heat generation profile complex and difficult to predict. It is crucial to understand as much as possible about the heat generation and subsequent temperature profiles, as the temperature can have a substantial impact on the lifetime performance and safety of lithium-ion cells.

Inhomogeneity

While it is obvious that a lithium-ion cell is a 3-dimensional object, it is important to consider how this impacts the uniformity of the cell. Current will always flow down the path of least resistance; this means the current flow through the electrodes is generally not perfectly homogeneous.⁶¹ Current flow can focus around the tabs, depending on their location, as well as regions of the cell that are warmer (due to lower resistance). The asymmetry of thermal properties can result in natural thermal gradients within a cell, which can be exacerbated by the thermal boundary conditions imposed on the cell, this can be seen in Figure 4. Inhomogeneous current and temperature profiles will lead to inhomogeneous heat generation and SOC.⁶² These inhomogeneities make it significantly more complicated to define and understand the cell's state.

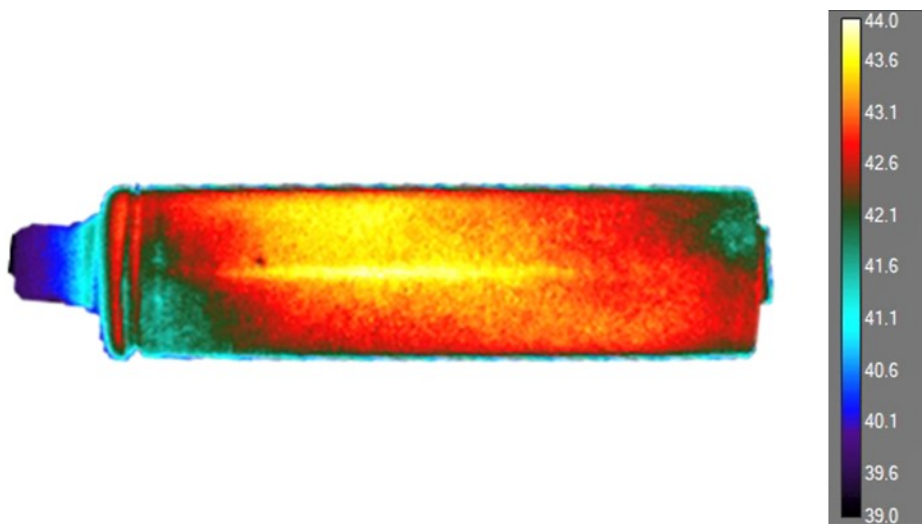


Figure 4: Thermal image of a 18650 cylindrical cell undergoing a 1 C discharge.

1.2.5 Testing Lithium-ion Cells

Capacity and Energy Rates

Since lithium-ion cells come in a variety of shapes and sizes, as well as energy densities of the electrodes, it is often useful to test cells in a way that keeps them comparable given differences in capacity or energy. For example, there is little insight to be gained from comparing a 5 A continuous current discharge between a 5 Ah cell to a 50 Ah cell, other than the obvious fact that one has 10 times the capacity compared to the other. It is of more value to compare the cells at a rate that is based upon their capacity or energy, since even for use in applications the cells would be combined into packs of similar total energy. This is why cells are often tested using capacity rates (C-rate) or energy rates (E-rates), these define the current or power, respectively. The C-rate defines the current relative to the nominal capacity of the cell or pack.⁶³ A C-rate of 1 C defines the current that discharges the cell completely in 1 hour, i.e., 1 C for a 5 Ah cell is 5 A, and 2 C for a 7.5 Ah cell is 15 A. This means that a given C-rate on any cell will discharge it in the same length of time, regardless of its capacity. The E-rate is the same where it defines the power based on the nominal energy of the cell.

Constant Current, Power, & Voltage

When characterising lithium-ion cells, it is common to use a constant current (CC) or power (CP) loads, this helps standardise tests and makes scientific analysis easier. When charging a cell, it is common to use a CC-CV protocol, this stands for constant current and constant voltage. It involves using a constant current to charge the cell until it reaches the maximum voltage limit, once there the cell is held at this voltage, while the current decays as the overpotential reduces. The constant voltage is ended once either a set amount of time has passed or the current drops below a threshold value, this makes it possible to mitigate against the overpotential caused by the charge current without taking the cell over its safe voltage limit.⁶⁴ This protocol is useful for charging a cell quickly maximising the amount of energy put in.

Application Loads

In almost all real applications of these cells the discharge load demanded of the cells will be based on power. This means that while fully charged the cells will discharge with a lower current than when they are almost fully discharged (due to the difference in voltage), with the inverse occurring during charge. This can affect the heat generation and capacity/energy output of the cell. Most scientific research is performed using current driven loads, mostly because it makes scientific analysis and understanding much easier, removing the variable of a changing

current. It is however important to keep in mind how conclusions may change when assessing based on power and energy. Another major consideration is that while charging can usually be constant current/power, real discharge loads are usually highly irregular. Automotive drive cycles can vary rapidly with peaks of upwards of 2C with an average of C/3.⁶⁵ The link between time of load and resistance means that real dynamic cycles will behave differently to constant current equivalents. Further to this, automotive discharge loads can have charge pulses due to regenerative braking, this affects both the resistance build up and the amount of capacity/energy extracted over the course of the discharge.⁶⁶ The automotive industry uses standardised drive cycle designed to replicate real driving profiles, to get a more accurate assessment of performance compared to CC or CP cycles. The worldwide harmonised light vehicles test procedure (WLTP) is one of these cycles.⁶⁷

1.2.6 Safety

The safety of lithium-ion cells is a major concern in the automotive sector. The significant amount of energy stored in EV battery packs and their close proximity to consumers, mean that it is critical that they remain as safe as possible. The danger that lithium-ion cells present is that of fire and explosion. This is because under certain circumstances they can release their stored energy very rapidly, resulting in significant heat release.⁶⁸ One way they can do this is through a short circuit, this can be internal or external to the cell.⁶⁹ Lithium-ion cells have very low resistances, typically the larger the cell the lower the resistance, cylindrical cells can have resistances in the 10s of mΩ, with large pouch and prismatic cells in the order of 1/10 of a mΩ. Cells have voltages of around 3 V, this can lead to short circuit currents of 300-30,000 Amps, this will lead to significant heat generation in not only the cell but whatever is causing the short circuit. While this can be a very rapid and significant release of energy, this is not the primary mechanism that leads to lithium-ion fires. Most lithium-ion fires occur because they can go into a state known as thermal runaway. Thermal runaway is an event where the cell starts rapidly generating its own heat, in an uncontrollable chain reaction that leads to ignition of the electrolyte and eventually electrodes.⁷⁰ The liquid electrolytes used in lithium-ion cells are extremely volatile and once they start breaking down, can start an exothermic chemical chain reaction that cannot be stopped. This is what makes lithium-ion fires so dangerous, part of the chemical reaction produces oxygen, this makes it almost impossible to put lithium-ion fires out, they are completely self-sustaining.⁷¹ Since this reaction produces significant quantities of gas, sometimes the cell can reach critical overpressure before catching fire, this can result in a sudden and rapid explosion of the cell casing. The breakdown of the electrolyte is typically

triggered by elevated temperatures, this can be from a short circuit or simply overheating the cells. As a cell progresses through its lifetime it can also become more prone to a thermal runaway event,⁷² the mechanisms of which will be described in more detail in Section 2.5 Long Term Life.

As safety is such a critical concern, cell manufacturers often fit various safety devices to cells to try and reduce the likelihood of thermal runaway and explosion. The most common of which is a safety vent, which is an overpressure seal, designed to blow in the event of overpressure allowing gases to vent from the cell, before the pressure in the cell can reach a critical point for explosion.⁷³ In pouch cells these vents are designed into a section of the seam of the polymer casing, in prismatic cells a vent is often placed at the top of the cell between the two terminals. For cylindrical cells the vent is designed into the positive cap. The positive cap of a cylindrical cell is often fitted with other safety devices to help prevent cell failure and thermal runaway. The most common are Positive Thermal Coefficient (PTC) and Current Interrupt devices (CID).^{73,74} The PTC is a composite material that logarithmically increases in electrical resistance as the temperature rises, this will inhibit current flow through the cell if it exceeds a certain temperature. This device can 'reset' once the temperature drops back down, but will have often increased in resistance from its original value.⁷⁴ The CID is a pressure disc within the positive cap that disconnects if the internal pressure gets too high, severing the electrical connection through the cap.⁷⁵

These safety devices are not perfect and have been proven to fail in some scenarios. The PTC can fail if the voltage across it is too high, caused by a high number of cells in series.⁷⁶ The safety vents can fail if the gas build up is unable to reach the vent fast enough.⁷³ Thus, the presence of these devices do not allow for the thermal performance of these cells to be ignored, but they provide a useful safety net.

1.3 Research Objectives & Questions

The research presented in this thesis will attempt to find and assess the best ways to choose the optimal cylindrical cells and cooling systems for use in battery packs. Cylindrical cells are chosen due to their standardised sizing, ease of procurement, and the simplification of comparison, mentioned previously. Cell datasheets are often the starting point for cell comparisons. However, they provide only basic information that is insufficient to choose the best cell, and often misleading.⁷⁷ Furthermore, they usually provide no information to

characterise the thermal performance of a cell. This information is required to design the cooling system and thermal management strategy for a pack. Finally, the choice of cell and cooling system can significantly impact how long the cell lasts before it is inoperable. Ensuring cell and cooling choices are made with information on the lifetime performance of the cell is critical.

The work in this thesis will attempt to solve these problems by answering the following research questions:

1. Are there a suitable thermal metrics that can be applied to cylindrical lithium-ion cells that can help characterise their thermal performance for cell selection?
2. Can datasheet performance metrics be trusted to provide a fair and accurate assessment of a lithium-ion cell, such that the most optimal cell can be selected for a specific application?
3. How is the lifetime performance of cylindrical lithium-ion cells affected by application-relevant* testing, and can standardised* testing give comparable lifetime performance?

* In this context, application-relevant testing is defined by conditions that are reflective of typical lithium-ion applications, thermally this involves, cooling systems that can be applied in a battery pack, and electrically, this involves dynamic, non-constant drive cycles, based on power loads. Whereas standardised testing is defined by conditions typically used for cell datasheets, involving convective cooling using an ambient temperature, and constant, non-dynamic cycles based on fixed current loads.

1.4 Thesis Structure

Chapter 1: Introduction – This chapter gives context for the work in this thesis, a background on lithium-ion batteries, as well as a description and identification of the research questions this work aims to answer.

Chapter 2: Literature Review – This chapter reviews the relevant literature, beginning with a review of cell thermal properties, how they can be measured, and finally an assessment on suitable metrics for cell datasheets. Then cell datasheets and standardised conditions are reviewed, followed by a look into cylindrical battery packs to assess typical cooling systems and electrical connections. Finally, the degradation mechanisms, influencing variables and assessment of health, of lithium-ion cells are investigated.

Chapter 3: The Cell Cooling Coefficient of Base Cooled Cylindrical Cells – This chapter assesses the CCC as a thermal metric and its application to cylindrical cells. Two experimental rigs are

developed and presented to measure the CCC of a base cooled cylindrical cell under two different electrical connections. Two models are developed to investigate measurement problems with the CCC. A 3D MATLAB model is used to assess how real losses impact the measurement of the CCC. A 1D steady state heat transfer model is derived to analyse the fundamental nature of the CCC and its behaviour for a lithium-ion cell. Finally, this chapter uses the results from the models to create updated guidelines for how the CCC should be measured and how it can be used for lithium-ion cells.

Chapter 4: The Effect of Test Conditions on Benchmarking Cylindrical Lithium-ion Cells – This chapter focuses on experimentally assessing the validity of datasheets and standardised testing, for making cell comparisons. It outlines and presents the results of an experiment undertaken on a selection of cylindrical lithium-ion cells, to test if the cooling and current load can influence the performance ranking of cells. A series of drive cycles is tested on the cells, and linear relationships fit to changes in power of the load. This allows for the prediction of performance to any potential pack size for these cells.

Chapter 5: Impact of Cooling on Cell Lifetime Performance – This chapter experimentally explores the degradation performance of cylindrical lithium-ion cells under application relevant cycles. The cells are aged under application-relevant conditions (side and base cooling) and standardised conditions. Differential voltage analysis and post-mortem disassembly of the cells are used to assess the degradation mechanisms that afflicted these cells, to understand how to extend life.

Chapter 6: Conclusion – This chapter summarises the key conclusions from the work in this thesis, along with any key areas of future work of interest.

Chapter 2: Literature Review

Some of this literature review is based on the author's internally submitted Early Stage Assessment, as well as “M. W. Marzook, Alastair Hales, Yatish Patel, Gregory Offer, Monica Marinescu, **Thermal evaluation of lithium-ion batteries: Defining the cylindrical cell cooling coefficient**, *Journal of Energy Storage*, Volume 54, 2022, 105217, ISSN 2352-152X, <https://doi.org/10.1016/j.est.2022.105217>.”, and “M. Waseem Marzook, James Eaton, Mohammad Amin Samieian, Yatish Patel, Gregory Offer, Monica Marinescu, **The Effect of Test Conditions on the Relative Performance of Cylindrical Lithium-ion Cells**, *Journal of Energy Storage*, Volume 105, 2025, 114485, ISSN 2352-152X.”, and “M. Waseem Marzook, Gregory Offer, Monica Marinescu, **Understanding the Cell Cooling Coefficient: A Fundamental Heat Transfer Model of Lithium-ion Batteries**, *to be submitted*.”

2.1 Introduction

This section reviews the available scientific research attempting to answer the research questions and assess any relevant gaps in knowledge. This will help identify which areas of research warrant further investigation to help answer the research questions, as well as helping to narrow the scope of the research questions so that targeted research studies can be defined. The relevance of the reviewed topics approximately aims to follow the order of the research questions defined in the previous section.

2.2 Thermal Properties

2.2.1 Cell Thermal Properties

The composite nature of the structure of lithium-ion cells lead to anisotropic conductivities.⁷⁸ Each component of the cell has a different thermal conductivity and heat capacity.⁷⁹ The thermal conductivity varies by several orders of magnitude between components such as the separator and current collectors.⁸⁰ This makes the conductivity in the plane of the electrodes much higher than through the electrodes.⁸¹ An example of the range of thermal conductivities for the components of a lithium-ion cell is shown in Table 1.

Table 1: Example of the component thermal conductivities of a lithium-ion cell. Taken from LIB A in Ref. ⁸²

Component	Negative Current Collector	Positive Current Collector	Separator	Anode	Cathode	Casing
Conductivity (W/mK)	398	238	0.34	1.58	1.04	238

The internal structure of cylindrical cells results in complex thermal pathways and heat generation profiles within these cells. The anisotropic conductivity heavily favours the axial direction with cells having over an order of magnitude higher axial conductivity compared to radial.⁸³ The high relative resistance of the positive safety cap in cylindrical cells can lead to skewed thermal profiles with a high concentration of localised heat generated at the top of the cell.³⁰

2.2.2 Variation in Thermal Properties

Further to the inherent anisotropic nature of the thermal properties, the thermal properties of a cell can be variant during operation. There are a number of studies that explore and measure the variance in properties such as thermal conductivity and heat capacity with the SOC of a cell. Bazinski et al. (2015) showed that for a LFP pouch cell the heat capacity, through-electrode plane thermal conductivity are shown to vary with temperature and slightly with SOC, respectively.⁸⁴ In follow up work in 2016 they measured and modelled the in-electrode plane thermal conductivity to show similarly weak trends with SOC.⁸⁵ Yu et al. (2023) and Kovachev et al. (2021) showed similar minor trends with SOC for NMC cylindrical and pouch cells, respectively.^{86,87} Overall these works all demonstrate differences of around less than 10% across the SOC range of a cell, thus in practice they are small enough that they can be ignored when making assessments and comparisons of cell performance in applications.

Variations in thermophysical properties can be much more significant with ageing. Marconnet et al. (2024) showed significant degradation of thermal conductivity (up to 25% reduction from BoL) in NCA pouch cells, after 8200 full equivalent cycles at 50°C, at temperatures at or below 25 the reduction is observed to be less than 10% from the BoL value.⁸⁸ Kovachev et al. (2021) saw reduction in thermal conductivity of up to 20% in aged NMC pouch cells, however this was only for cells under no compression, cells under realistic and high compression loads, experienced significantly lower reduction in thermal conductivity, noticeable but negligible.⁸⁷

Spitthoff et al. (2023) found reductions in thermal conductivity ranging from around 20% up to 65% from BoL in pouch cells around 70% SOH, degraded under various conditions covering clamping, temperature and electrolyte wetting.⁸⁹ It is clear from these studies that age can have a significant impact on the thermal properties of cells, capturing and understanding these changes could be important to effectively designing a battery pack cooling system, ensuring it remains effective and does not get overloaded at EoL. The key to assessing the change in thermal properties in cells is accurately measuring them, however this is far from a trivial process.

2.2.3 Measuring Thermal Properties

There are numerous methods used to determine the thermal properties of cells, however the composite structure and complex geometry make this the process challenging. Measurements can be made on the individual materials within a cell.⁹⁰ This can produce a detailed view of the thermal paths within the cell, but presents significant limitations. Bazinski et al. (2015) demonstrated that neglecting to account for the electrolyte in the electrodes can underestimate the thermal conductivity by 50%.⁸⁴ Shi et al. (2018) found that ignoring interfacial resistances between the layers in the battery cell leads to around 8% error in modelling of the cell.⁹¹

For this reason, individual material thermal properties are unsuitable for the calculation of a datasheet-ready thermal metric. Instead, bulk measurements would be preferable. Such measurements have been used to assess the effective thermal properties of the cell, which are often anisotropic and, as such, must be measured in various directions. Literature presents several techniques to make measurements of anisotropic conductivities and heat capacity. Drake et al. (2014) used external adiabatic heating and thermocouples.⁹² Murashako et al. (2017) and Murashako et al. (2020) used heat flux measurements to obtain high accuracy values.^{93,94} White et al. (2022) developed novel methods to accurately measure the thermal conductivity and diffusivity of lithium-ion cells, however the conditions required for these measurements require carefully designed experimental rigs.⁹⁵ While it has been demonstrated that passive thermal properties such as thermal conductivity, conductance, heat capacity and Biot number can be determined, a battery cell acts as a heat source.

Therefore, the additional creation of heat generation maps is needed, to be used along standard heat equations.^{96,97} Internal thermal gradients coupled with the temperature dependence of internal resistance lead to non-uniform heat generation profiles dependent on the boundary conditions and internal current flow, making the heat diffusion equations harder to solve

analytically. Fully developed electro-thermal coupled models can solve these equations, however for cell comparison from a datasheet, displaying these properties without the heat generation profiles would not allow for a useful comparison. Thus, a new thermal metric that includes the effect of heat generation of the cell is needed.

2.2.4 Cell Cooling Coefficient

The cell cooling coefficient (CCC) is a thermal metric designed specifically for cells, intended to address the problem of accounting for the heat generation.⁸² The CCC defines the amount of heat a cell can reject from a cooled surface for a given thermal gradient, measured in W/K. The CCC is effectively a thermal conductance for a cell that is generating and transferring its own heat. The thermal gradient and heat generation of a cell are measured while it generates its own heat, without the use of any external heating. Since the heat generation profile of a cell is dependent on the boundary conditions and will change based on which surfaces are being cooled, a CCC value is defined for a given cooling approach. This produces multiple CCC values for a single cell, one for each of its common cooling surfaces.

A square wave current pulse allows the cell to generate its own heat without changing the SOC. To accurately measure the heat generation of a cell while it is being cooled, the cell is insulated on all sides except the cooled surface, where it is cooled through a conduction fin controlled with Peltier elements. The heat generation is measured through the fin, whose cross-sectional area is designed to be thermally restrictive enough to accurately measure the heat flow along it. Once the cell reaches steady state thermal conditions the heat flowing through the fin is equal to the heat generated by the cell. The thermal gradient is defined by the difference between the temperature at the hottest point on the surface of the cell and the cooled surface, the heat flow divided by the thermal gradient equates to the CCC. Figure 5 illustrates a standard temperature and current profile for a CCC test (regions 1 and 2).⁸²

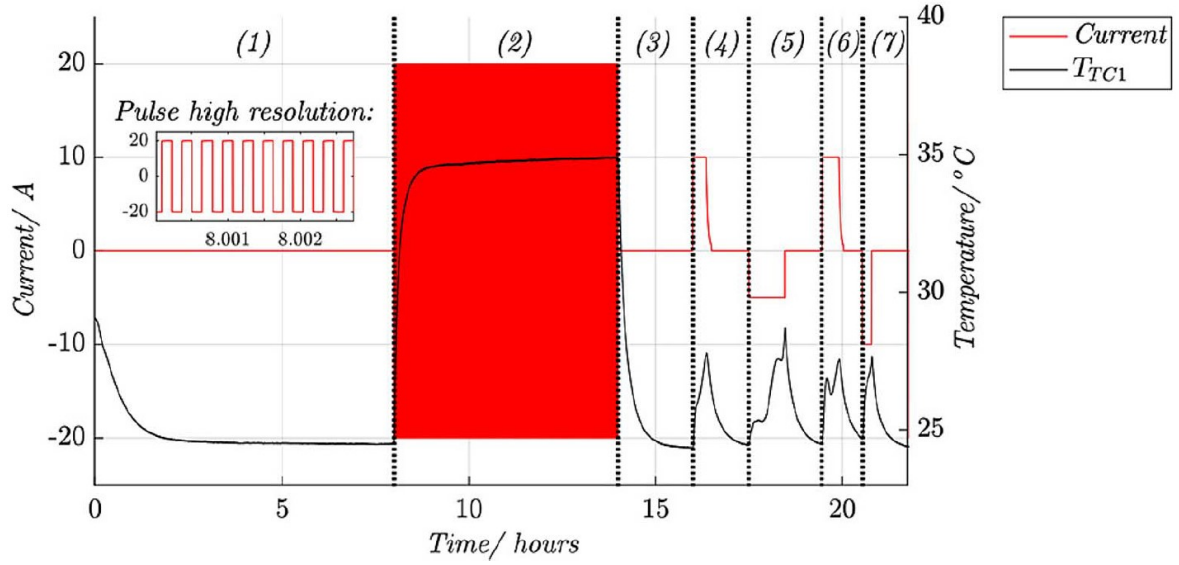


Figure 5: CCC current profile and temperature (regions 1 & 2). Recreated from Ref. ⁸²

The CCC has been proven and measured for tab cooling and single surface cooling of pouch cells.^{82,98} Figure 6 presents a diagram highlighting how CCC_{tabs} and CCC_{surf} were defined. For tab cooling, the heat flow through both tabs was summed and the two thermal gradients from the tab to centre were averaged. CCC_{surf} was defined for cooling of a single surface, so that the thermal gradient was the difference from one surface to the other.

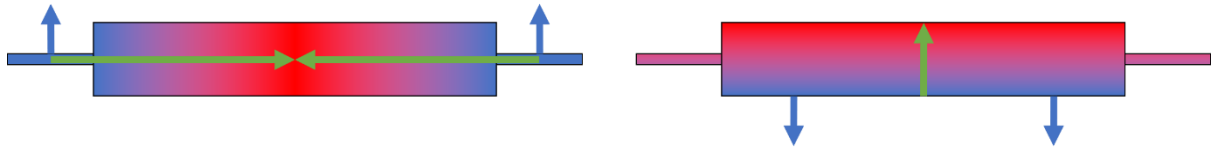


Figure 6: CCC for tab (left) and surface (right) cooling for pouch cells. Arrows indicating the heat flow (blue) and thermal gradient (green) for CCC calculation. $CCC = \text{heat flow/thermal gradient}$

The CCC of a pouch cell was shown to be independent of current, state of charge (SOC), heat generation, and cell and cooling temperature. It facilitated the comparison of two geometrically dissimilar pouch cells under both cooling schemes, highlighting the value of this new thermal metric for cell and cooling surface comparison.^{82,98} The CCC has proven to be useful in aiding cell design to optimise thermal performance.⁹⁹ By comparing the CCC of pouch cells when varying design choices such as the number of electrode layers and tab thickness, the cell design can be optimised to achieve the thermally most performant cell. Using the CCC in this way can help cell manufactures make critical decisions to help improve the thermal performance of their cells. The CCC has also been applied to surface cooling a prismatic LFP cell and coupled with a 3-D electro-thermal equivalent circuit network model, to highlight cell and pack

improvements.¹⁰⁰ Spitthoff et al. (2023) demonstrated how the CCC can be used to assess the evolution of thermal properties in ageing pouch cells, highlighting how it correlated well with changes in thermal conductivity.

Although a promising solution, the CCC has yet to be proven on cylindrical cells and the fundamental concept must be improved; the measurement and calculation of the CCC is currently flawed. The first attempt at measuring the surface cooling CCC for pouch cells generated the results presented in Figure 7. In contrast to measurement of CCC_{tabs} , the CCC_{surf} results displayed an inversely proportional dependence on the cell heat generation.^{82,98} This was described to be a result of measurement errors caused by heat losses. The calculation of the CCC, previously worked out by averaging the results, was altered to an extrapolation, to $Q = 0W$, a situation in which there would be no losses. However, as this is a point of no heat generation, this value may no longer represent the CCC but simply a thermal conductance. Thus, a CCC value obtained in this manner may no longer be representative of the cell in operation.

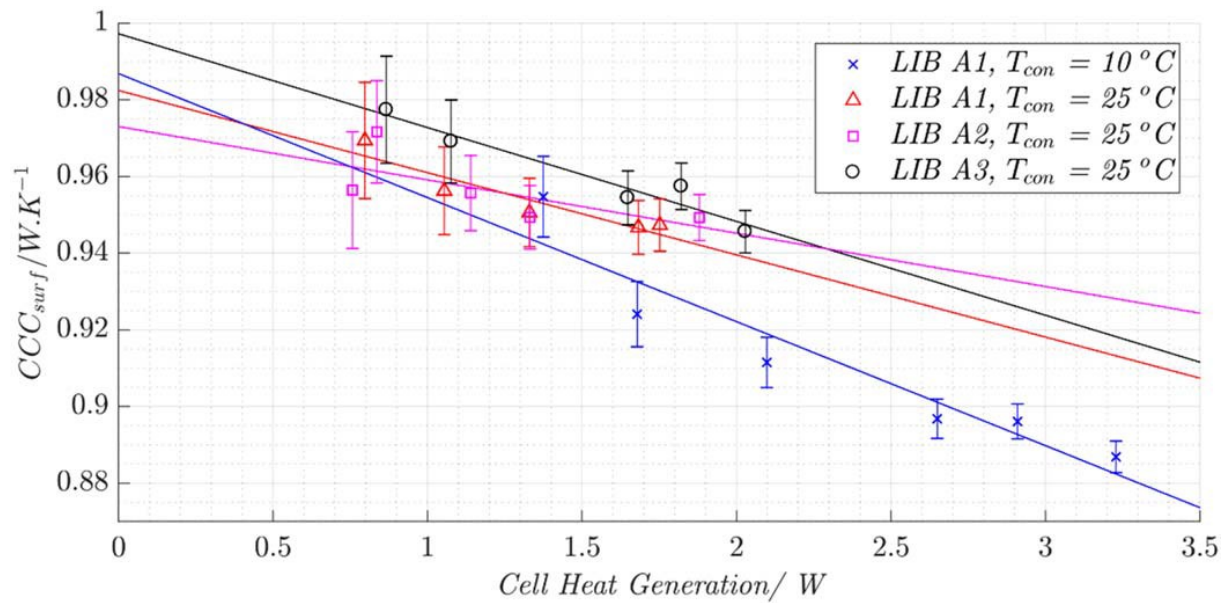


Figure 7: CCC_{surf} vs. measured heat generation for a 5Ah Kokam pouch cell for cooling on one surface at temperature T_{con} . LIB A1-3 represent data from 3 of the 5Ah Kokam cells tested under identical conditions. Recreated from Ref. ⁹⁸.

The work that followed, focusing on cell design optimisation, proposed a new surface cooling CCC rig aiming to solve the problems of the first one.⁹⁹ Thermal control of the busbars connected to the cell tabs was added with the aim of eliminating the thermal gradient and ensuing minimal heat flow away from the tabs. The CCC_{surf} results generated from this rig showed less variation with cell heat generation than in the original rig.

The CCC has never been proven beyond the single cell scale. It provides a powerful tool to compare different cells to one another, but if it is to be used as a cell selection tool in an industrial setting, its validity at pack level must be evaluated. The CCC at cell and module level must be compared, and a set of rules must be determined for how to upscale cell values to pack-relevant values. Ultimately, one problem remains with using the CCC for cell selection; that it is only one half of the thermal description of a cell, the other being the cell heat generation. One can envision a scenario where cell A has a 10% better (higher) CCC compared to cell B, but cell B produces 15% less heat at the required operating point. In this scenario, cell A would be incorrectly chosen for the application, if solely based on the CCC. To fully capture an approximation of the thermal performance of a lithium-ion cell both the CCC and a heat generation metric are required.

A standardised heat generation metric that captures the relevant resistances in the relevant operating intervals would complement the use of CCC. A related study demonstrates how extensive testing can help create heat generation maps across multiple conditions, that can be used in conjunction with the CCC to aid cell selection.¹⁰¹

2.3 Cell Specification Sheets and Standardised Testing

One of the ways in which cells can be down-selected prior to testing is by using the information provided in the cell datasheet.¹⁰² These datasheets usually contain basic information for the cell, which can help make initial comparisons of different cells, such as maximum charge and discharge currents, nominal capacity and energy, voltage limits, 1 kHz AC internal resistance, size, weight, tested under standardised conditions (constant current loads and convective cooling boundary conditions). While the information provided in datasheets can help filter out some poor solutions, this information can often be misleading. Cell manufacturers seem to rarely follow any international testing standards for defining cell characteristics on datasheets, which leads to no consistency in definitions across datasheets between different cells and manufacturers.⁷⁷ This makes attempting like-for-like comparisons almost impossible, and when testing multiple cells under a single standard, capacities can vary from the value given in cell datasheets.¹⁰³ For example, the listed maximum discharge rate has no standard definition and is often not achievable with simple ambient cooling, requiring an aggressive active cooling method to ensure the cell does not overheat. A potential reason for this is the international standards, where there is a different standard defined for each potential use of a lithium-ion battery, each with its own definitions for testing standards and rates (IEC 62660, IEC 62133,

UNECE R100, etc.).¹⁰⁴ Cell manufacturers may not use any of these standards as their cells may be designed for many potential applications. Furthermore, many standards are defined based on the manufacturer's specification not the other way around.

An additional challenge is that all information in a datasheet is based on constant current testing in ambient air conditions; given how dependant cell performance is to test conditions, it is possible that under the required conditions some cells may perform better relative to their performance under the standardised conditions. For example, as has been established, the resistance of a cell has several dependencies causing its value to change significantly under different conditions; thus, comparing cells based on a single value of their resistance under the relatively extreme standard conditions (1kHz at 100% SOC) may give an unrepresentative result. Furthermore, the temperature and pressure of ambient air conditions can significantly impact electrical and thermal performance of a cell,¹⁰⁵ as well as differences caused by non-constant ambient conditions that may be present in real applications.¹⁰⁶

In recent years, websites and services have started to offer lithium-ion databases (Battery Archive¹⁰⁷, ENPOLITE¹⁰⁸, etc.) that compile repositories of available cell data. This can be very useful for comparing many different cells tested under various conditions. However, only existing data is included, meaning that some cells are not represented with comprehensive datasets. In addition to these websites, there are companies, such as Batemo¹⁰⁹, that aim to test cells on the market comprehensively and provide extensive cell performance metrics than what is available on the datasheet. These sites may provide some or all this information for free. Since their tests are done with no specific application in mind, they are standardised, i.e. under set load types, electrical connections, and thermal conditions. Thus, the only way that remains, to compare cells for specific applications, is through the resource-consuming benchmark testing of all cells using the targeted conditions. Thus, comparisons must be made based on the results of these standardised tests.

No published work to date has assessed whether such tests are suitable for cell selection, and whether comparisons of cells made under standard conditions continue to hold when the same cells are tested under more realistic conditions. Importantly, one would want to avoid a scenario in which the down-selection of cells based on information from these standard tests leads to the removal of a cell that would have been optimal for the application.

2.4 Cylindrical Cell Battery Packs

Cylindrical cells are used in a wide variety of battery packs from portable electronics to large automotive battery packs. They have been used by the likes of Bosch, Tesla and Lucid. Battery packs containing these cells can range from a handful of cells to 1000s of cells connected in various configurations of series and parallel. Having large numbers of cells connected in series and parallel makes it crucial to ensuring maximum homogeneity across all the cells. This means designing efficient cooling systems that can keep temperatures uniform across all cells, along with highly consistent electrical connections that ensure current uniformity throughout the pack.

2.4.1 Thermal Management of Cylindrical Packs

The main cooling strategies used in cylindrical packs are side, base, terminal and immersion cooling.¹¹⁰ Side cooling involves cooling the side surface of the can. This can be applied to varying degrees of surface contact. Typically, 100% surface cooling would be done with direct cooling using a fluid medium such as air or a liquid coolant but can additionally be done with solids and foams. The lower percentage contacts are indicative of indirect cooling, using serpentine cooling fins that snake through a pack, contacting strings of cells.¹¹¹ These fins can be straight contacting minimal areas of each cell or can be bent to contact larger portions of the surface. Similarly, cooling fins can be machined to contact varying percentages of the side surface of the cell. The large variability in the level of cooling allows for freedom based on the required application. High power packs can opt for higher percentage coverages to maximise the cooling power, and lower power packs can gain better space efficiency by having a lower contact area. Cells in a surface cooled pack can alternate orientation between series strings, or all aligned in orientation. This makes side cooling completely flexible in how electrical connections can be made. The main drawbacks with surface cooling are packing, weight and cooling efficiency. Since either fins or fluid need to fit in between the cells, they cannot be packed as densely as they can in the other cooling systems. Liquid cooling can have issues with weight especially if used to directly cool the cells, also requiring sealing of any fluid compartments to avoid leaks. Finally, this cooling scheme makes use of the cell's radial conductivity which is significantly worse than axial direction, making it an inefficient way to cool a cylindrical cell, though it offers the most surface coverage.¹¹²

Base cooling involves cooling the negative base of the cell, typically done with a simple flat cooling plate. All the cells in the pack are lined up in a single orientation on a cooling plate.

The cells can be packed as densely as is safe since the cooling system does not need to go in between the cells. Furthermore, cells can be stacked on the opposite side of the same cooling plate. This makes base cooling one of the most space efficient cooling schemes. The main drawbacks with base cooling are the low thermal contact area and the electrical connection. Though base cooling allows for the utilisation of the cell's high axial conductivity (explained further in Section 1.5), the contact area is relatively small, limiting the amount of heat flow possible.¹¹³

Dual-Terminal cooling involves cooling both ends of the cell by directly or indirectly cooling the busbars and cell terminals of the pack. This cooling method makes maximum use of the axial conductivity without the electrical limitations of base cooling. This type of pack can be assembled with all the cell in alignment or with them alternating. Direct cooling can be done with significantly less fluid compared to surface or immersion cooling. Identical to base cooling, the packing factor is high for this cooling scheme. Studies on the cell-level have proven that cooling both terminals can lead to lower thermal gradients than both base and 100% surface cooling.^{112,114} The key drawback of dual-terminal cooling is the complexity associated with cooling both terminals of the same pack, without shorting or leaking fluid, as well as the complexities associated with covering or immersing the cell's safety vent.

Immersion cooling involves fully immersing the pack in fluid, offering the maximum cooling potential with all the surfaces of the cells being cooled.¹¹⁵ This can be with a static fluid,¹¹⁶ using natural convection and its own thermal mass to maintain the pack temperature, or actively pumped and cooled. The fluid must be dielectric to prevent shorting of the cells through the coolant. The biggest drawbacks are leak prevention and weight, where the trade-off may only be worthwhile for extremely high-power applications.¹¹⁷

2.4.2 Electrical Connections of Cylindrical Packs

The electrical connection of the cell can impact the electrical performance and the thermal boundary conditions. This is especially true for cylindrical cells due to their small thermal mass, but also the small area to make available for making electrical connections. When the cooling system allows the cells to alternate orientation connections can be made at both ends of the cell. This offers a range of potential connection methods. Tabs and busbars can be welded to the terminals of the cell using spot, ultrasonic or laser welding.¹¹⁸ Alternatively, individual wires or ribbons can be ultrasonically welded from the cell terminal to central busbars.

When the cells are unable to alternate orientate, the negative connection is commonly made at the top of the cell where the shoulder of the can is electrically connected to the negative tab, this can be seen in Figure 2. By making the connection at the top of the cell, the current must flow down the can into the internal negative tab, adding extra electrical resistance to the cell. Additionally, the small area of the shoulder limits the options for electrical connection, with only ultrasonic wire and ribbon bonding and high precision laser welded tabs being a possibility.¹¹⁹ Wire bonding offers the unique ability to fuse each cell individually, greatly boosting pack safety. However, since they are intended for fusing, they can have high relative resistances.¹²⁰ For higher power applications ribbons can be bonded, or tabs can be welded, making a much lower resistance connection.

2.5 Long Term Life

Lithium-ion cells do not last indefinitely, with time and usage their ability to store and deliver energy reduces. The more cycles a cell performs the more degraded it can become, but lithium-ion cells degrade even when they do nothing. Calendar ageing is the term given to the degradation experienced by a cell when it is not being used.¹²¹ There are 3 levels of defining the degradation in lithium-ion cells, the most in-depth of which are the degradation mechanisms.¹²² Degradation mechanisms are the fundamental processes that affects the performance of a cell, while these are the best description of the degradation of the cell, they can be very difficult to determine for an ageing cell.¹²³ The next level of description is known as degradation modes, these group more generally the impacts of the mechanisms, with modes being easier to measure and determine compared to the mechanisms.¹²⁴ The final and most general descriptions of degradation are capacity and power fade. Capacity fade is a reduction in the total capacity of the cell and power fade is an increase in internal resistance of the cell, reducing the cell's capability to deliver power.¹²⁵ These are the easiest to measure and provide useful information on the state of the cell, but they do not offer any insight into how or why the degradation occurred. The three levels of definitions can be seen in Figure 8.¹²⁶

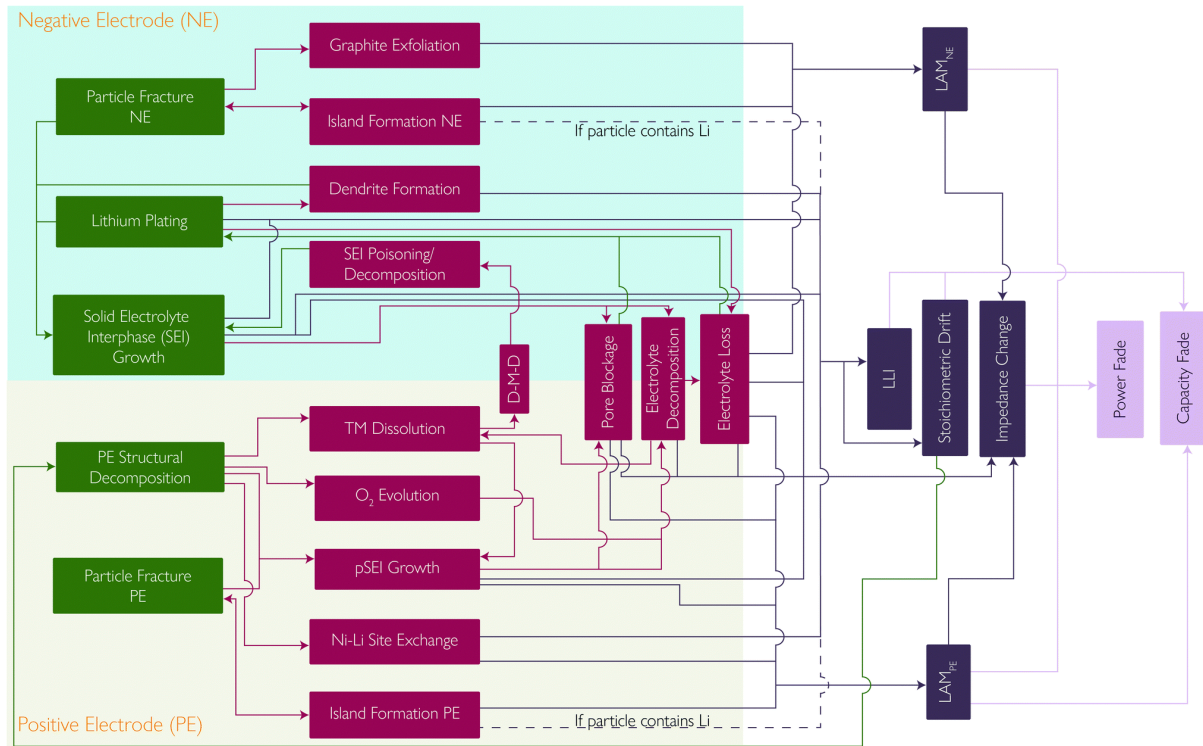


Figure 8: Diagram of the different degradation mechanisms, and how they can be categorised down into degradation modes, and further down to capacity and power fade. Recreated from Ref. ¹²⁶.

2.5.1 Degradation Mechanisms & Modes

Degradation Modes

Degradation modes group the impacts of the degradation mechanisms into three categories: resistance increase, the loss of lithium inventory (LLI) and the loss of active material (LAM).¹²⁷ Resistance increase, similar to power fade, characterises increases to any of the cell's internal resistances. LLI characterises any loss in cyclable lithium, this can be via mechanisms that use up lithium via side reactions, or trap lithium such that it is no longer available for intercalation. LAM characterises any loss of active sites for lithium intercalation, this is usually separated further into anode and cathode LAM. Both LLI and LAM contribute towards capacity fade,¹²⁸ with resistance increase contributing to power fade. For the analysis of degradation from experiments, while degradation mechanisms require complex modelling and validation to determine their impact, degradation modes can be determined from degraded OCV curves, which is much less intensive.¹²⁹

Degradation Mechanisms

A Li-ion cell has many degradation mechanisms affecting the different materials within, a schematic of most of these can be seen in Figure 9.¹³⁰ Processes such as lithium plating, SEI cracking/dissolution/formation, and electrolyte and binder decomposition, can all result in

LLI.¹³¹ Processes such as electrode fracture/cracking, solvent co-intercalation, metal dissolution, phase transition and structural disordering, can all result in LAM.¹³² Some of these same processes can also result in resistance increase, such as electrolyte decomposition, SEI growth and metal dissolution, with additional processes such as electrode porosity changes and current collector corrosion all increasing various resistances in the cell.¹³³ A few key mechanisms will be explored in further detail.

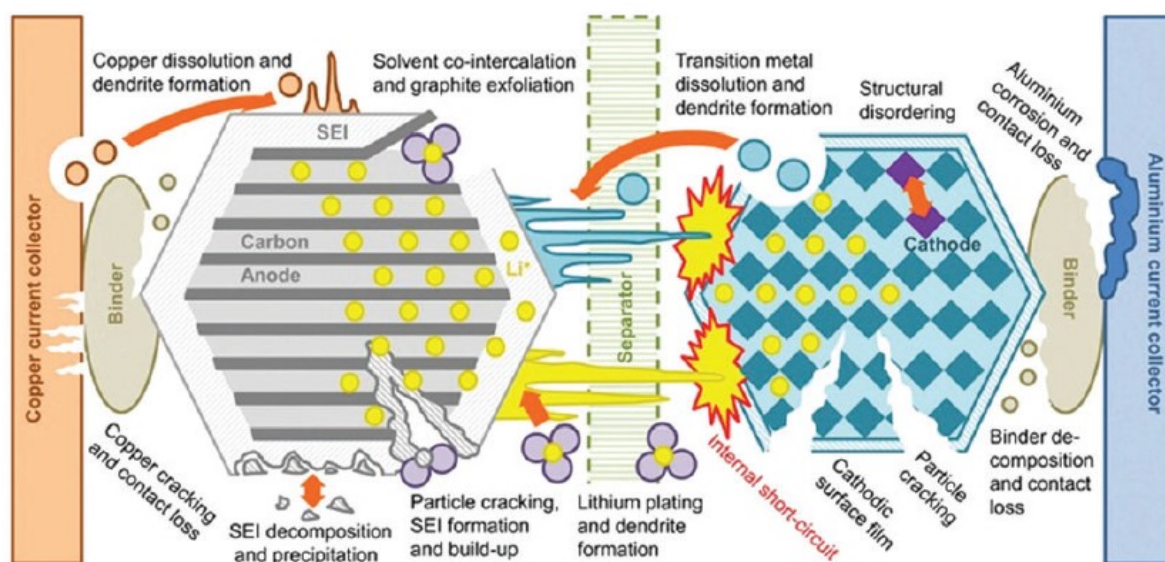


Figure 9: Schematic of the various mechanisms of degradation within a Li-ion cell and coupling between them. Recreated from Ref. ¹³⁰.

SEI Growth, Cracking and Formation

SEI growth involves the thickening of the SEI layer, this can occur with time and results in the resistance caused by the SEI layer increasing.¹³⁴ This can be accelerated by high temperature, increasing the reaction rate between the electrolyte and electrode.¹³⁵ The SEI can also crack and break away from the electrode, this can occur due to the thermal, mechanical, or electrical cycling of the electrode.¹³⁶ When this occurs, the electrolyte will react with the newly exposed electrode forming new SEI, this consumes lithium, resulting in LLI.

Particle Cracking

Mechanical stress can be induced in both electrodes from electrical cycling, caused by the insertion and removal of lithium-ions in and out of the structure, resulting in constant expansion and contraction of the materials.¹³⁷ This stress coupled with that coming from thermal cycling can result in cracks forming and propagating.¹³⁸ This can cause parts of the electrode to break away from the bulk of the material, disconnecting it from the current collectors, this makes these sites inaccessible for lithiation, resulting in LAM.¹³⁹ If the electrode that breaks away is

lithiated, then the lithium stored inside it is no longer able to take part in the cell's cycling, resulting in LLI.

Lithium Plating

Lithium plating is a mechanism that can occur at the anode, where at high charge rates, low temperatures or high SOC, it can become more thermodynamically favourable for the Li^+ ions to form lithium metal on the surface of the anode instead of intercalating into the anode.¹⁴⁰ This lithium is still capable of eventually intercalating into the anode or stripping back into ions to go back to the cathode during discharge.¹⁴¹ In this case the lithium plating is reversible and does not cause any degradation of the cell.¹⁴² However, the layer of lithium metal formed is prone to reacting with the electrolyte, this consumes the lithium and electrolyte, removing this lithium from the cyclable inventory, resulting in LLI.¹⁴³ The lithium metal can also break away from the electrode (possibly breaking some SEI with it), electrically disconnecting it from the current collectors, resulting in LLI.

The most dangerous possibility with lithium plating is that of dendrite growth. This is when plated lithium starts to grow out from the electrode. This is possible because regions of plated lithium become the path of least resistance for new Li^+ ions travelling to the anode. Thus, plated lithium is prone to continually plating on top of itself growing out towards the cathode, these are called dendrites.¹⁴⁴ These dendrites are dangerous because they can pierce through the separator and reach the cathode, short circuiting the cell. Extreme levels of plating can even take the cell into thermal runaway.¹⁴⁵

Transition Metal Dissolution

Transition metal dissolution is a mechanism that affects the transition metals in the cathode structure. It occurs through side reactions with the electrolyte that cause some of the metals in the cathode to dissolve into the electrolyte.¹⁴⁶ This weakens the cathode structure which can lead to particle cracking and cause LAM in the cathode. These metallic ions can deposit on the anode and grow into a dendrite, with the same safety risks as a lithium plating dendrite.¹⁴⁷

Electrolyte Consumption & Decomposition

Many of the prior mechanisms involve reactions with the electrolyte. This consumes the electrolyte which can lead to localised or bulk dry-out,¹⁴⁸ increasing the resistance of the cell. Further to this, high temperatures can lead to the decomposition of the electrolyte on its own, often forming byproducts with lithium, leading to LLI.¹⁴⁹

2.5.2 Variables Affecting Degradation

Temperature

Extreme temperatures, high or low, can affect most of these degradation processes, leading to accelerated ageing of the battery.¹⁵⁰ Electrolyte and binder decomposition, SEI growth and metal dissolution are all accelerated by high temperatures, with processes such as lithium plating accelerated by low temperatures.¹³³ Large internal thermal gradients within a cell or battery pack can lead to imbalances in current flow and result in accelerated degradation.^{151,152} The direction of the thermal gradient could be just as important as the magnitude, Hunt et al. (2016) discovered that for pouch cells, tab cooling results in a lower degradation rate compared to surface cooling. This was attributed to the thermal gradient developing parallel to the electrode layers helping minimise current imbalance, though the cell was hotter overall.¹⁵¹ However, Zhao et al. (2019) revealed that the internal thermal difference under tab cooling were significantly lower than under surface cooling.¹⁵³ Thus it is hard to separate the effect of the lower magnitude from that of the direction of the gradient. For cylindrical cells, with only two effective electrode stacks, all thermal gradients are parallel to the electrode layer. Therefore, when comparing different cooling schemes, the overall temperature difference may be the most important factor in identifying the best cooling scheme to minimise degradation.

SOC & Voltage Window

The voltage and SOC window can have a significant impact on the life of a cell. High voltages can accelerate degradation mechanisms such as transition metal dissolution¹⁵⁴ and electrolyte decomposition,¹⁵⁵ as well as, charging to high SOC's increasing the likelihood of lithium plating. Even cycling in low SOC and voltage windows has been shown to be detrimental to the lifetime of cells, due to factors such as electrode stress.¹⁵⁶ Cycling within the full voltage maximises the stress cycle on the electrodes as the cycles between extreme states of lithiation. Reducing the voltage and SOC window away from the maximum and minimum can significantly improve the life of a cell.¹⁵⁷

Charge & Discharge Loads

Current Magnitude

As mentioned, high charge rates can increase the likelihood of lithium plating.¹⁵⁸ In general, high currents in both charge and discharge increase the stress on both electrodes leading to more electrode particle and SEI cracking. Since higher currents result in higher overpotentials, when cycling between fixed voltage limits, it will result in changes to the cycled SOC window.

This reduction in the SOC window can offset the detrimental effects of the higher rate. Additionally, since high currents will lead to significant heat generation it is impossible to decouple the effects of current and temperature. These dependencies lead to contradictory results in literature.^{159–161}

Irregular Loads

Most studies on degradation are performed using constant current loads, even though it is well understood that power based irregular drive cycles are more relevant to most applications. There is likely a significant difference in degradation between constant current cycling and irregular loads. Even between a synthetic drive cycle (designed to represent real driving) and real driving data, there has been shown to be degradation differences.¹⁶²

Path Dependence

Both experimentally¹⁶³ and in simulations¹⁶⁴, lithium-ion cells have been shown to experience significant degradation path dependence, denoting the fact that the cycle-life of the cell is not only dependent on the present thermal and electrical conditions, but also on its history. This is because degradation mechanisms can result in chain reactions and compound on one another, so it is not possible to add the effects of one cycle to another.

2.5.3 State of Health Estimation & Identification

Electrical Data

Capacity and Resistance

The simplest way to assess the state of health of an aged cell is through a measurement of the remaining capacity in the cell.¹⁶⁵ However, since it is likely that an ageing cell will experience both capacity and power fade, the capacity of the cell under its usage cycle is often being reduced by increased resistance, this capacity is often referred to as the usable capacity. It is common to assess the capacity fade during a separate reference performance test (RPT) using a low-current charge or discharge, to minimise the impact of the increased resistance.¹⁶⁶ This gives a value of capacity typically referred to as the available capacity of the cell. The reduction in the available capacity as the cell degrades is typically used to define the capacity fade of the cell. RPTs can often include other specialised cycles, designed to gather other metrics such as the OCV or resistances of the cell, such as HPPC (hybrid pulse power characterisation) and GITT (galvanic intermittent titration technique).¹⁶⁷ Resistance tracking from these cycles is typically used to assess power fade.

Differential Voltage & Capacity

A more complex analysis technique is differential voltage or capacity. This involves differentiating the voltage vs capacity of the cell, from a pseudo-OCV curve, often using the same low-current charge or discharge used for available capacity assessment.¹⁶⁸ Both the differential voltage and capacity of a lithium-ion cell display peaks and troughs corresponding to when the electrodes go through different phase changes¹⁶⁹. Modelling and experimentation have brought understanding to the features of these curves.¹⁷⁰ As the cell ages, different mechanisms can shift and alter the shape of these features, allowing for the analysis of degradation modes, and some mechanisms.¹⁷¹

Thermal Data

SOH estimators that involve measurements from temperature sensors include differential thermal analysis (DTA)¹⁷² and differential thermal voltammetry (DTV)¹⁷³. A single temperature measurement per cell is sufficient for either, but high accuracy measurements at high sampling rates are required for differential analysis. Additionally, DTA and DTV are performed over standard cycles and may not be viable for noisy load scenarios. As a cell incurs power fade, its resistance increases, resulting in more heat generated for the same current load. Through the use of models, the evolution of a cell's heat generation has been used to estimate SOH.¹⁷⁴

2.5.4 Realistic Degradation Studies

The complexities of real cycling conditions make it difficult to separate interconnected variables, to highlight and analyse their impact (current, SOC, temperature, etc.). For this reason, research on realistic cycles and cooling are uncommon, but few exist. Luo et al. (2023) modelled an LG M50T 21700 cylindrical cell in PyBaMM to explore the impact of reduced SOC windows and temperature on degradation.¹⁷⁵ Modelling the cell thermally, including four degradation models, SEI growth, lithium plating, particle cracking and LAM. This model reiterated common understanding that low temperatures promote lithium plating and high temperatures SEI growth, highlighting a theoretical optimal range for this cell of 25-35 °C. The model indicates a negative feedback loop between SEI growth and lithium plating mechanisms where LLI from SEI growth reduces the maximum lithiation state of the anode, preventing lithium plating. It also highlights a positive feedback loop between LAM and particle cracking, where LAM leads to increased interfacial current densities, increasing mechanical stress, promoting particle cracking. The model shows that for the degradation mechanisms that have been modelled, lower SOC's lead to reduced degradation, however the lack of degradation of the silicon in the model, means this outcome may not be true for the real cell. An important

highlight of this work is that clogging of pores in the anode can result to knee points in degradation. Although though there are degradation mechanisms missing from the model in this work, that cloud the results and may leave some feedback and coupling mechanisms hidden, it is still very useful to know that anode clogging may be one cause of knee points in degradation that is commonly seen in experimental studies.

Micari et al. (2022) performed an experimental degradation study supplemented by a degradation model, covering the degradation of a 63 Ah LMO-NMC/graphite prismatic cell designed for automotive applications.⁶⁷ The cell is degraded under the WLTP class 3B drive cycle, an automotive drive cycle standard designed to replicate real driving conditions to benchmark the fuel economy and performance of passenger vehicles. Using a representative drive cycle to degrade the cells should help replicate the degradation mechanisms and pathways that may occur in real applications. Unfortunately, the compression and cooling condition are less representative, the cell is tested without compression and under a convective thermal condition (in a thermal chamber). In an automotive battery pack these cells would be under compression and have very different thermal conditions, with most surfaces being adiabatic due to being sandwiched between other cells, and possibly one surfaced cooled via a cooling system. Nevertheless, the use of the WLTP cycle makes this study more application-focused than most. In this study a single cell is cycled under a 1 C CC charge and the WLTP cycle (converted into current for a BMW i3) between 4.12 and 3.1 V at 25 °C for an equivalent of 8 years of driving (+4000 cycles). The experimental results of cycling under the WLTP cycle showed 11% capacity degradation for this cell for the 8 years of cycling. The authors use incremental capacity analysis to suggest that the degradation can be attributed to LAM in the anode and LLI. The authors couple this result with calendar ageing data to create a lifetime model to predict the degradation of this cell, under different temperatures and distance travelled per year. Their model predictions show that increasing the number of km's travelled per year reduces the number of years the cell will last. It also indicates that 15 °C offer improved life and 35 °C reduced life. However, the temperature dependence on degradation is purely based on calendar ageing, with no insight as to how temperature impacts the cycle ageing of the cell,

Keil & Jossen (2017) performed an experimental ageing study on an 18650 format NCA cylindrical cell, attempting to explore the impact of dynamic driving loads and regenerative braking on ageing.¹⁷⁶ The authors converted the US06 highway driving profile for a 100 km passenger vehicle, into current, limiting it to 5.5 A. They used 4 variations of this current cycle, one with max regenerative braking, one limited to 2 A, another limited to 1 A, and the final one

with no regeneration. Similar to the previous study, tests were performed in an unrepresentative convection condition. Further to variations in regeneration, the authors tested under different temperatures (40, 25, 10 °C), cycle depth (2, 4, 6 repeats of US06 cycle), charging voltage (4.1, 3.9, 3.7 V), and a constant current equivalent. Results show that 25 °C is the least degrading for this cell, with 10 °C being the most degrading. Furthermore, the temperature is most impactful in the high voltage window, and least impactful in the lowest voltage window. The impact of increasing regenerative braking is shown to improve life and is seen to be most impactful at higher voltage windows, and lower temperatures. This is seen via less degradation per full equivalent cycle (FEC), however if the regenerative charge throughput is discounted from the conversion to FEC, the impact of the different levels of regeneration almost entirely disappears. The authors use this to conclude that the improvements in degradation are a result of reduced cycle depth, resulting in less lithium plating during the CC charge between drive cycles. However, I would argue that the comparison neglecting the regeneration throughput is more relevant for automotive, as it better represents distance travelled of a vehicle. Thus, the data shows that for these cells and cycles, increased regenerative power has no considerable impact on reducing the degradation per distance travelled. Results of their more significant cycle depth variations highlight that increased cycle depth increases the cell degradation. Finally, their results indicate that constant current equivalent discharges can effectively represent the degradation of the drive cycles. It is useful to keep in mind that this result may only hold true under convective cooling conditions and that under real cooling systems the degradation may deviate.

Buare & Dubarry (2019) performed an experimental study on an 18650 NCA cylindrical cell to determine the impact on degradation of standardised drive cycles (DST, FUDS, NEDC) vs real driving profiles.¹⁶² Cells were screened to remove outliers, and tested under the three standardised drive cycles previously mentioned, and two cycles based on real driving data; one derived from a single commute, and the other comprised of a range of different commutes. All tests were performed in the full voltage window under convection boundary conditions. The results show a large difference between the two real data cycles, with none of the standardised cycles able to replicate the degradation of the real data cycle that most closely matched the average discharge of the standardised cycles (single commute). The authors conclude that the average discharge and charge capacity during discharge are important metrics to assess the degradation of a cycle, with real traffic being highlighted as a critical influence to the lifetime of a cell. An important note from this study is that all cells displayed knee points in capacity

degradation, and the authors highlight that neither capacity fade or resistance increase tracking can predict the onset of a knee point. They do highlight the potential for degradation mode analysis to predict knee points, by showing that all cells had a ratio of LAM (negative): LLI above 1 as they transitioned into the knee point, concluding that the knee points were a result of irreversible lithium plating.

Although there have been studies that look at realistic load cycles and others that investigate realistic cooling systems, there is no literature that compares the degradation of cells under both realistic loads and cooling at the same time. Given the established impact of these variables on degradation, and the cross dependencies between these variables, it follows that testing under realistic cycles and cooling will have an impact on the lifetime of a cell, that has yet to be explored.

2.6 Conclusions

This literature review highlighted some key research gaps related to the three research questions. The key findings and gaps related to the research questions are summarised in the following three sub-sections.

2.6.1 Research Question 1

The CCC has been identified as a thermal metric with a high potential for use on cell datasheets, with its ability to capture information about the cell's thermal conductivity and heat generation, under applied conditions. However, there are still questions surrounding the consistency of its measurement, and how successfully it can be applied to cylindrical cells and their cooling systems.

2.6.2 Research Question 2

Cell datasheets have been shown to lack consistency and comparability, making cell comparisons challenging. Furthermore, standardised conditions have been proven to produce differing performance compared to more application relevant loads and cooling. No existing research has sought to prove if comparing cells under standard conditions leads to a different outcome than if compared under more realistic application relevant conditions. It cannot be determined via literature whether the ways in which different cells respond to the difference in conditions will be large enough to impact the outcome of such comparisons.

2.6.3 Research Question 3

Base and side cooling have been identified as two key cooling systems in cylindrical battery packs, it is also highlighted that electrical connections are typically made at one end of a cylindrical cell, utilising the shoulder, requiring high precision welding techniques. These conditions would be expected to have significant impact on the lifetime of cells, however it has yet to be determined how these cooling systems compare when tested under realistic electrical connections and loads profiles.

Chapter 3: The Cell Cooling Coefficient of Base Cooled Cylindrical Cells

The work presented in this chapter is based on “M. W. Marzook, Alastair Hales, Yatish Patel, Gregory Offer, Monica Marinescu, **Thermal evaluation of lithium-ion batteries: Defining the cylindrical cell cooling coefficient**, *Journal of Energy Storage*, Volume 54, 2022, 105217, ISSN 2352-152X.”, as well as, “M. Waseem Marzook, Gregory Offer and Monica Marinescu, **Understanding the Cell Cooling Coefficient: A Fundamental Heat Transfer Model of Lithium-ion Batteries**, *to be submitted*.

Dr Alastair Hales assisted with the design of the experimental rig for the tab welded cells.

3.1 Introduction

The cell cooling coefficient (CCC) has been identified as a potentially useful thermal metric for characterising the thermal performance of lithium-ion cells, offering benefits over typical thermal metrics such as thermal conductivity, describing thermal performance inclusive of a cell’s internal heat generation. This offers it the potential to be used to define a cell’s thermal characteristics without the need for a model. However, it has yet to be applied to the cylindrical form factor of lithium-ion cells. Additionally, there are many unanswered questions around the validity of the metric and its potential application.

The work presented in this chapter begins with a refinement of the calculation process, based on experimental measurements, for the CCC. This is followed by the description of the first CCC rig for cylindrical cells, designed to assess the CCC for base cooling, with tab welded electrical connections. The CCC for base cooling (with tab welded connections) is measured on two commercially available cells, one 21700 and one 18650 cell. The CCC is then used to assess and compare the heat rejection capability of both cells. Following this work, an updated rig is presented which uses a wire bonded electrical connection, which is more relevant to base cooled pack applications. Problems with the consistency of measurements result in the development of models to assess the CCC at a fundamental level. A 3D MATLAB model is used to assess the impact of perpendicular and inline losses on a base cooled heat generating cylinder. Following this, a 1D steady state heat transfer model is used to gain analytical

solutions to the CCC under various ideal and real conditions. Finally, guidelines for the future measurement and usage of the CCC are presented.

3.2 The First Cylindrical CCC Measurements

3.2.1 Re-defining CCC Measurements

The CCC is defined by, the amount of internal heat rejected from a cell's cooled surface(s) ($\dot{Q}$), divided by the temperature difference from the cell's cooled surface(s) to the hottest point of the cell (ΔT), in steady state, as shown in Eq. 1.

$$CCC = \dot{Q} / \Delta T \quad \text{Eq. 1}$$

The CCC is a cell-level thermal metric and can be thought of as a material property for a cell. It should be noted that the CCC is a different characteristic from the heat transfer coefficient, which defines the heat transfer between a cooling medium and surface. It can more closely be compared to an effective thermal resistance for a body (cell), defining the ratio of heat flow to thermal difference. However, instead of external heat passing through the body, the CCC describes a system where heat is generated within the body and fully rejected from a specified surface(s). The anisotropic nature of thermal conductivity, diffusivity, and heat generation in a cell result in the CCC being defined separately for each combination of surfaces that are cooled (dual-tab, single tab, dual-surface, single surface, base, etc.). There are four published articles on the topic, identifying, defining and measuring CCC values for different types of cells and surfaces of cooling. These works cover dual-tab⁸² and single surface^{98,99} cooling of pouch cells, as well as single-sided surface cooling for prismatic cells¹⁰⁰.

The CCC measurement method involves constant current pulsing a cell at 1 Hz in a setup with controlled thermal boundary conditions where the temperature is measured at various positions around the cell. Once the cell reaches steady state thermal conditions the value of CCC is calculated through the measured heat rejection and temperature difference as per Eq. 1. This test is done at multiple current magnitudes and cooling temperatures, with the calculated CCC values plotted on a graph of CCC against heat generation (assumed to be equal to heat rejection), as shown in Figure 7. In these works, the plot of CCC versus measured heat generation is used to quantify the correlation between the two variables, where a horizontal line is associated with no correlation. A dependency of the CCC on the measured heat generation, i.e. a non-horizontal plot, is assumed to indicate a correlation between the two, which, in turn, is assumed to be caused by limitations in the experimental procedure, such as

difficulties in managing heat loss, accurately measuring heat flow, and measuring accurate cell thermal differences. The test rig designed to determine CCC_{tab} was found to lead to no observable correlation,⁸² while the first proposed method to determine CCC_{surf} was found to lead to correlations, due to the non-zero slopes of the lines in Figure 7.⁹⁸ The correlation in these results was described to be due to heat losses in the experimental rig, thus to eliminate this from the determined value, the CCC was extrapolated back to zero heat generation, $Q = 0$ W, where heat losses are zero. A more complex test rig for CCC_{surf} allowed for improved thermal control over the cell, thus eliminating the apparent correlation between CCC and heat generation.⁹⁹ Both of these solutions result in a CCC derivation process that is more complicated than was originally intended.

According to Eq. 1 the CCC is the slope on a Q vs. ΔT plot. If the CCC of a given cell is constant, then all experimentally measured heat generation values should lie on a single line on a plot vs. ΔT , and the CCC value for the considered cooling scheme is the gradient of the linear fit of $Q = f(\Delta T)$. Figure 10 re-illustrates the pouch cell data shown in Figure 7,⁹⁸ together with the results from the other two publications on CCC,^{82,99} in the alternative way proposed above.

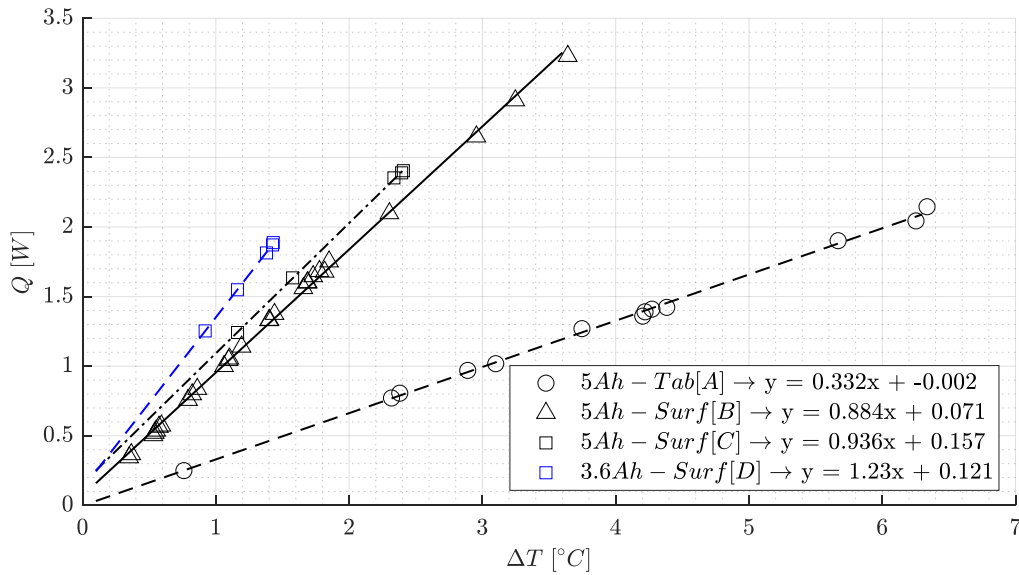


Figure 10: Previously presented CCC data displayed on a plot with different axes: Q vs. ΔT . Data obtained from the following references: A. [82], B. [98], C & D. [99]. Recreated from Ref. 177

For zero measured temperature gradient there is no heat flow through the cell, indicating that $\{0,0\}$ is a point that must lie on the linear fit. However, two of the lines that best fit the data have, in fact, significant non-zero Y-intercepts. This is possibly caused by the limited temperature range for which these results were obtained, leading to a significant extrapolation

from the dataset down to zero. This error results in an important new criterion for accurate CCC measurement: **experimental data must cover a sufficient thermal range for the cell and cooling system**, this means the data should start at low temperature differences and have a range of points leading up to the maximum realistic ΔT that keeps the cell within safe operation for the cooling system, both electrically and thermally.

3.2.2 Experimental Setup & Procedure

The CCC for base cooling of cylindrical cells (CCC_{Base}) is approximated as the heat rejected from the base of the cell divided by the measured temperature difference between the top and base of the cell. The CCC_{Base} is determined for two cells of different sizes. Firstly, an LG INR21700 M50T cell is considered, a high energy cell with a silicon doped graphite anode and an NMC811 cathode and a nominal capacity of 5 Ah. Secondly, a Samsung INR18650 30Q cell is evaluated, considered a mixed power and energy cell, with a silicon doped graphite anode and an NCA cathode and a nominal capacity of 3 Ah.

Cell Connection

A typical base cooled cylindrical cell has its external negative electrical connection at the top shoulder of the cell instead of at the base of the cell, to avoid hindering the cooling path. This choice of connection allows all cells to be oriented in the same direction in a pack. Connecting to the shoulder of a cylindrical cell requires sophisticated and expensive welding techniques, such as laser or ultrasonic welding, due to the relatively small surface area available for contact. This type of connection cannot be done cheaply or quickly, even for a single cell. These types of welding equipment can be expensive to purchase or use; and will require the design and manufacture of custom rigs to hold the cell and connections in place for welding. In this experiment, a more traditional tab connection is used instead, at the base of the cell, allowing for an easier measurement of CCC_{Base} . A tab is spot welded as closely to the edge of the base as possible in order to minimise its effect on the cooling path. This connection is expected to yield the theoretical maximum for the CCC measurement for base cooling because the heat generation of the negative connection is as close as possible to the heat sink, allowing for the shortest heat conduction path out of the cell. Moving the connection up to the top of the cell would shift this heat to the furthest point away from cooling, increasing the temperature gradient in the cell, whilst marginally increasing heat generation, thus lowering the CCC.

CCC Rig Design

A schematic of the rig is illustrated in Figure 11. As is the case for the previous CCC measurement rigs,^{82,98,99} the experimental rig is designed to restrict all thermal pathways except for the one of interest, attempting to create adiabatic boundary conditions on all surfaces not being actively cooled. The cooling path, in this case the brass rod, is designed to develop a significant measurable temperature gradient along its length when heat flows from the cell. This rig is additionally designed to measure the axial heat losses from the cell, via the placement of an additional thermocouple (TC), denoted as number 11 in Figure 11, in the insulation below the positive end of the cell, which is expected to be the hottest point on the cell, as well as additional TCs positioned along the Ni tabs connecting the cell (numbers 8, 9 and 10 in Figure 11). Real images of the experimental rig can be found in Appendix A.1.

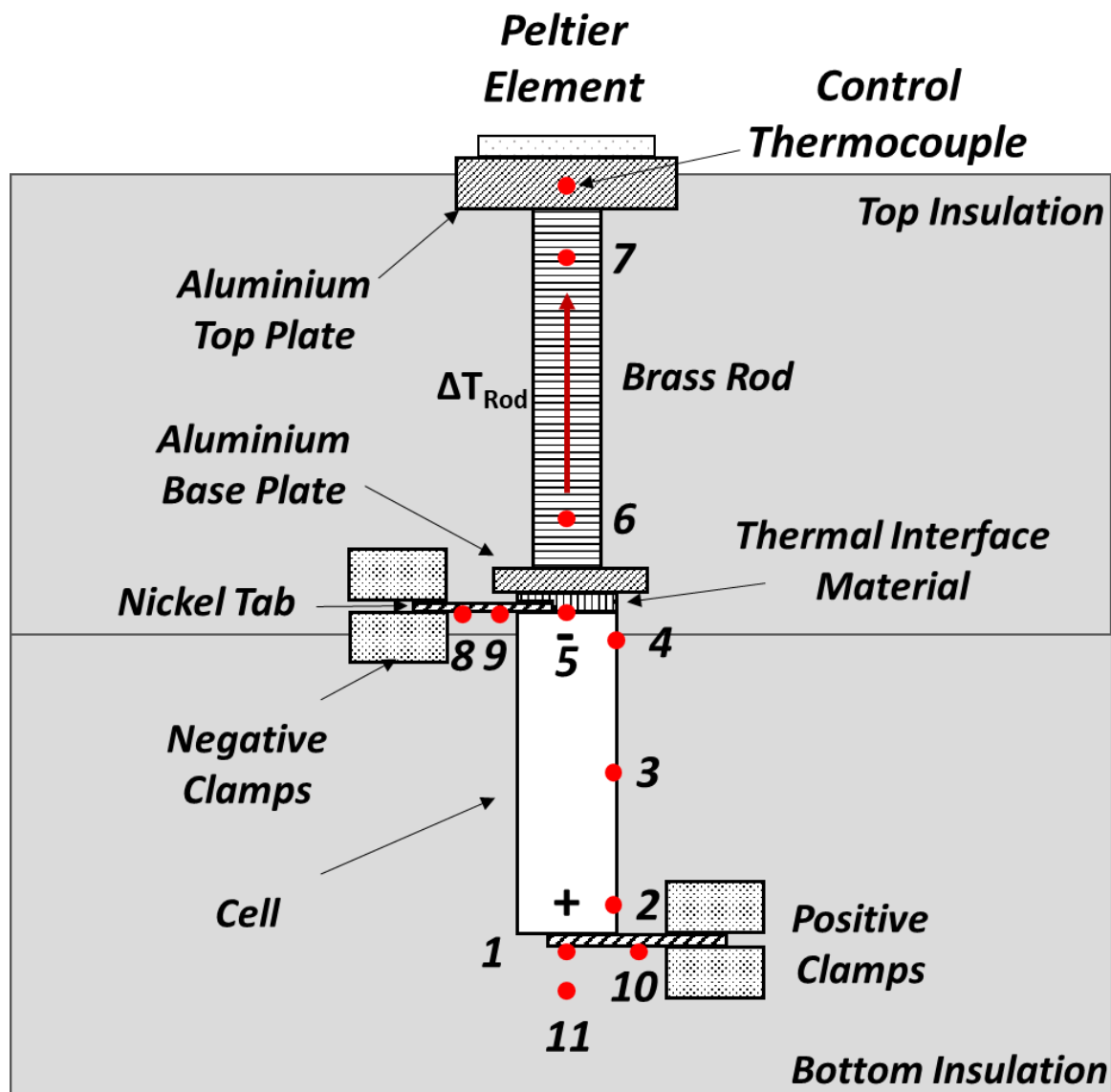


Figure 11: Schematic of the CCC base cooling rig. All non-cooled surfaces are surrounded by insulation to create an adiabatic boundary condition. The base is cooled via a cooling fin designed to be thermally restrictive enough to generate a measurable thermal difference when heat flows through it. A 4.9N weight sits on top of the cooling fin to keep it secured to cell. This rig includes the measurement of axial losses at both ends of the cell (via numbers 8, 9, 10 & 11). The red dots denote placement of thermocouples. Not to scale. Recreated from Ref. ¹⁷⁷

The cooling fin comprises two aluminium plates, denoted as ‘Top’ and ‘Base’ in Figure 11, that are bonded to a brass rod of dimensions 6 mm in diameter and 100 mm in length. The heat flow through the cooling fin is measured through two TCs, number 6 and 7, positioned 60 mm apart. A 40 x 40 mm Peltier element in contact with the aluminium top plate maintains the temperature of the plate using PID control to keep the temperature of the aluminium top plate constant. The electrical connection uses 8 x 0.15 mm (width x thickness) Ni tabs, spot welded using a Sunkko 709AD+ resistance welder. The negative Ni tab is positioned and welded at the edge of the base so that it minimises the obstruction to the cooling path. The Ni tabs are clamped between two brass blocks. Two ring terminated leads, one carrying current and the other one sensing voltage, are secured to each set of brass blocks in order to make a connection with the battery cycler, a Bio-Logic BCS-815.

All but one of the TCs used are k-type and are secured to the cell with MG Chemicals thermal epoxy (thermal conductivity – 1.22 W/mK). TC number 5 is a flat leaf k-type thermocouple, 0.1mm in thickness, sandwiched between two layers of TGlobal thermal interface material (thermal conductivity – 12 W/mK), each 0.5 mm thick. This arrangement helps minimise the effect of this TC on the cooling path via the fin. A 4.9 N weight is placed on top of the fin, resulting in a pressure of 14 kPa at the base of the cell. The weighted fin applies pressure vertically on the set-up, ensuring good thermal contact between the fin and the base of the cell.

For the calculation of CCC, the temperature difference is taken as that between TC 1 and 5. TC 2, 3 and 4 are positioned 10, 35 and 60 mm along the length of the cell, respectively, to monitor the temperature profile along the surface. This rig has three axial loss paths, two through the positive end and one through the negative. Losses through the insulation at the positive end are measured through TCs 1 and 11, which are 10 mm apart. Losses through the Ni tabs are measured through TC 1 and 10, and TC 8 and 9, which are 14 and 8 mm apart, respectively.

The 18650 cell is tested using the same experimental rig, with some slight changes. The axial loss TCs are removed, as they were already measured to be sufficiently low enough when the 21700 was tested. Additionally, TCs 2, 3 and 4 are positioned 10, 30 and 50 mm along the length of the cell, respectively (distances measured from the base of the cell).

Standard CCC Procedure & Calculation

The cell is charged and discharged via square wave current pulses, causing it to generate heat. During pulsing, the mean current is 0 A, to prevent any net change in State of Charge (SOC). Current pulsing at 1 Hz is performed for 6 hours to allow the cell and experimental rig to thermalise, this can be seen in region 2 shown in Figure 5. Once the cell reaches thermal steady state, it generates a relatively constant amount of heat throughout the experiment. The experimental rig is kept in a Binder KB400 thermal chamber at constant ambient temperature. The set point temperature for the Peltier element is the same as the value set for the thermal chamber; it is controlled using a PID controller in order to maintain a constant temperature, despite the cell generating heat. Six pulsing experiments of increasing current amplitudes are performed, with a 90-minute rest after each set of pulses at a constant current amplitude. These six pulsing sets are designed to generate a sufficient range of temperature gradients across the cell to allow for a sufficient spread in the Q vs. ΔT plot, and thus a good baseline for a linear fit when calculating CCC. Each set of pulses are performed at a set operating point, where the operating point is defined by a pre-determined combination of SOC and ambient temperature values. Table 2 shows the combinations of current, SOC and ambient cooling temperatures used for testing the LG M50T. The current amplitudes are selected such that they ensure that the dataset for each operating point includes a sufficient range of axial thermal differences for the cell, so that it can be used to find a reliable CCC for the specific operating point. Alternatively, all the data from multiple operating points can be combined to find an overall CCC for a cell.

Table 2: Combinations of experimental conditions tested for both LG M50T cells. For 50% SOC all combinations were tested. For 25% and 75% SOC only, the grey highlighted combinations were tested.

		T(°C)		
		10	20	30
I (A)	3.75			
	5			
	6.25			
	7.5			
	8.75			
	10			

The ΔT and Q for the CCC plot is determined from temperature differences between the thermocouples, while the cell is at steady state. The cell ΔT is determined from the difference between TCs 1 and 5, as described in the previous section. The Q is determined using the heat conduction equation, using the thermal difference between TCs 6 and 7, the conductivity of the brass rod (123 W/mK), the cross-sectional area of the rod (based of the 6 mm diameter), and the distance between TCs 6 and 7 (60 mm).

3.2.3 Results & Discussion

21700 Measurements

Current, Temperature & SOC Variation

To obtain a CCC with high confidence, it is important that the measured temperature gradient on the cell is large enough (>0.5 °C). The smallest temperature gradient is seen at the lowest current amplitude with the highest ambient temperature. At the opposite extreme, the highest current amplitude was chosen such that the cell temperature does not evolve above the safe operating temperature, even when operating at the highest ambient temperature. The maximum operating temperature allowed for these tests is 60 °C.

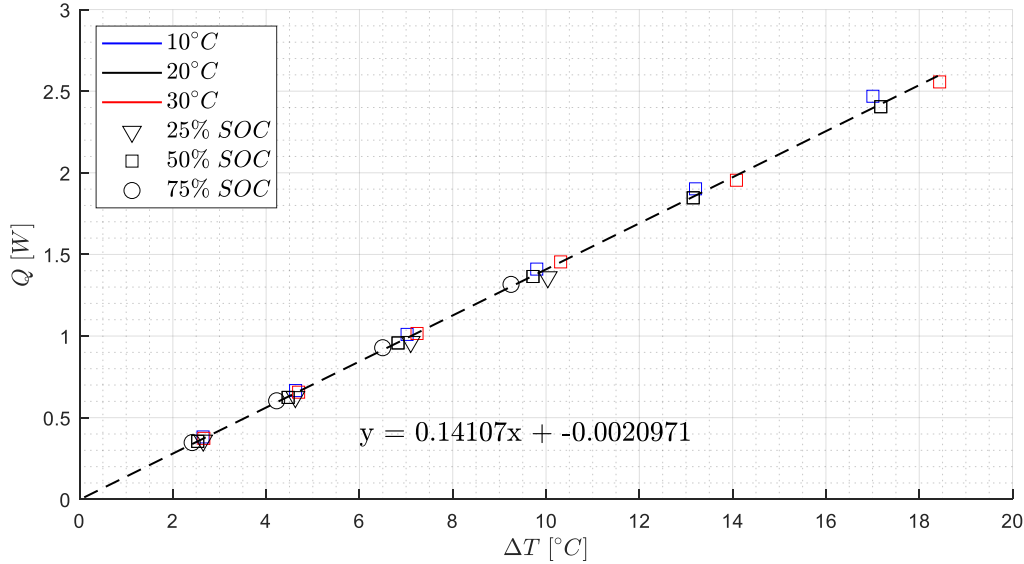


Figure 12: Measured heat generation versus measured temperature gradient for the LG M50T cell under base cooling, exhibiting a strong linear correlation that enables the calculation of $CCC_{base} = 0.141 \text{ W K}^{-1}$ with high confidence. The symbols correspond to each of the 26 pulsing sets, at six current amplitudes (between 3.75 A and 10 A), three SOC (between 25% and 75%), and three cooling (and ambient) temperatures (between 10 °C and 30 °C). Recreated from Ref. ¹⁷⁷

Figure 12 shows the results of 18 pulsing sets, corresponding to all the combinations shown in Table 2, covering six currents at three cooling temperatures all performed at 50% SOC. Additionally, it shows 8 pulsing sets, corresponding to the 4 combinations shown in blue in

Table 2, performed at 25% and 75% SOC. The line of best fit has a negligible y-intercept, indicating that the range of temperature gradients in these tests is sufficiently large to yield a $CCC_{base} = 0.141 \text{ W/K}$ value with an error of approximately $\pm 1.5\%$. Minor trends are visible in the data, firstly that the CCC is reduced for the experiments in which the ambient temperature is higher. Secondly that the CCC is decreasing as the SOC of the cell reduces. A possible explanation for this, is that the saturation and thickness of the electrodes is affecting the effective thermal conductivity and/or the heat generation profile of the cell.⁹⁰ However, as will be shown in the following section, all these variations are less than the variation between setups and cells, thus there are no key insights to be gained from examining the individual CCC values of each SOC and temperature.

The LG M50T does not appear to show any significant relationships with any of the three variables (I, T & SOC). However, further work would be needed to prove this is the case for more extreme conditions. Similarly, cells other than the LG M50T would need to be similarly checked, as different compositions of electrodes and electrolyte may cause a stronger variation of CCC with these variables.

Setup & Cell Variation

To test the repeatability of the CCC measurements across experiments and cells, a second LG M50 cell was tested. Figure 13 shows the results from testing both cells under identical conditions, 10 ° C at 50% SOC.

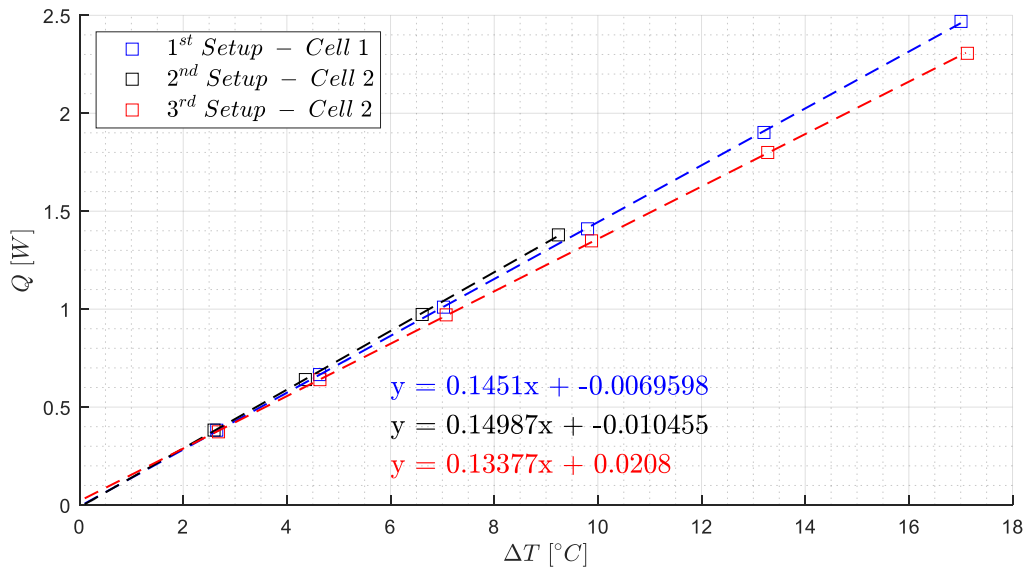


Figure 13: Measured heat generation versus measured temperature gradient for the LG M50T cell under base cooling, giving a CCC range of 0.134 - 0.150 W K^{-1} . The colours correspond to different setups and cells, each performing 6 pulsing sets, at six current amplitudes (between 3.75A and 10A), except for setup 2 which only performed the first 4 pulsing sets due

to an electrical fault. All tests are performed at 50% SOC and 10 °C cooling and ambient temperature. Recreated from Ref. 177

Setup 2 was later identified to suffer from electrical noise affecting both the voltage and thermocouple readings, caused by the fin contacting the negative tab. The problem was rectified in setup 3. While the electrical short may have affected the measurement of CCC in setup 2, the ensuing error is relatively small (3% higher than setup 1 and 12% higher than setup 3). The variation between the two cells, setup 1 (cell 1) and setup 3 (cell2), is $\pm 4\%$ from the mean. The variation is considered low enough to indicate that the rig is suitable for the accurate measurement of CCC (within $\pm 10\%$).

LG M50T CCC_{Base}

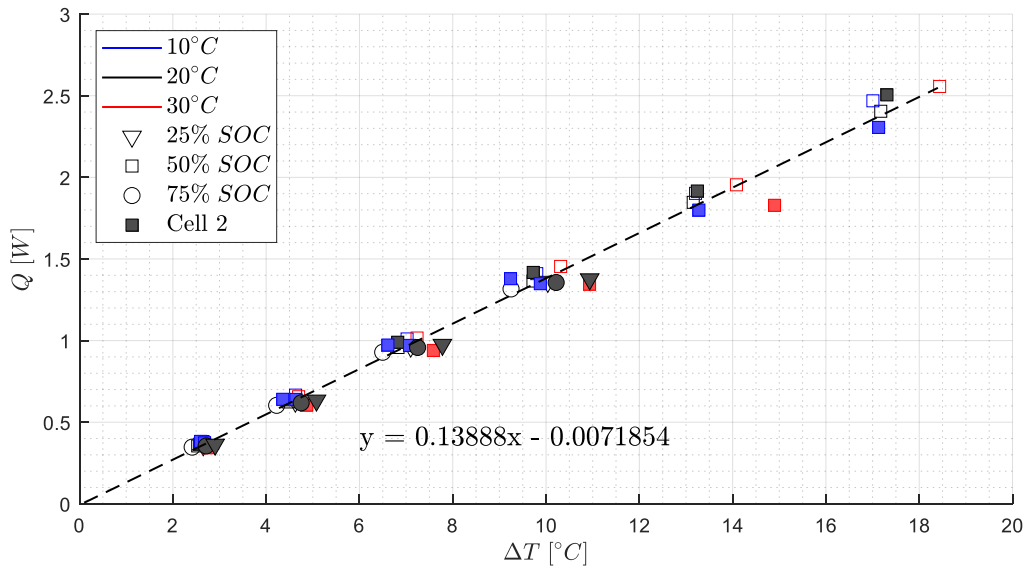


Figure 14: Measured heat generation versus measured temperature gradient for the LG M50T cell under base cooling, giving a CCC of 0.139 W K^{-1} . The symbols and colours correspond to each of the 51 pulsing sets, at six current amplitudes (between 3.75 A and 10 A), three SOC's (between 25% and 75%), three cooling (and ambient) temperatures (between 10°C and 30°C), and two LG M50T cells. Recreated from Ref. 177

Figure 14 shows all data gathered for LG M50T cells 1 and 2, with a line of best fit for the full dataset. The CCC_{Base} for the LG M50T is **0.139 W/K $\pm$ 2.8%**, where the error margin is calculated based on the 95% confidence bounds of the fit, to account for the spread.

The heat flow in the identified loss paths is calculated using the estimated thermal resistance of the individual loss paths and the thermal differences recorded by the TCs. The percentage of heat flowing through the loss paths compared to the heat flowing through the fin was calculated as 1.5% loss from the positive end, including losses through the tab and insulation; and 1.5% gain at the negative end, through the tab. This indicates that 1.5% of the heat measured through the fin is not generated by the cell, instead originating in the negative clamps

and tab, before conducting into the cell. The proportion is low and should have minimal effect on the measured CCC which as such can be assumed accurate.

Pouch Cell Comparison

A comparison between the CCC values for cylindrical cells and those for pouch cells is meaningful, but not straightforward. CCC for base cooled cylindrical cells is most similar in concept to single tab cooling for pouch cells (that have tabs at either end). Previous CCC work has measured CCC values for dual tab cooling of pouch cells, one of these cells is the Kokam 5 Ah (SLPB11543140H5).⁸² This Kokam cell is comparable to the LG M50T, with similar NMC chemistry and capacity. The Kokam cell has dimensions of 142.5 x 43 x 11.7 mm (L x W x T), with tabs at either end of its length. Under dual tab cooling, the steady state thermal profile of the cell was found (in previous work) to be approximately uniform across the cell's width and thickness, as confirmed via experimental measurements from surface thermocouples and via the output of a 3-D electro-thermal equivalent circuit model, described and validated for the Kokam 5Ah cell by Zhao et al. (2018).¹⁷⁸ A thermal gradient was found to develop along the length of the cell. The CCC was defined by the heat flow out of both tabs, divided by the thermal difference from the tabs to the centre of the cell (measured at the surface). Under single tab cooling it is expected that the thermal difference should approximately double for the same heat flow, with a single tab needing to extract heat from the entire length of the cell instead of just half. This thermal difference would be expected to be from one tab to the other, doubling the characteristic length. It is important to note that this is a rough approximation due to many interconnected phenomena affecting the heat flow and generation. However, in terms of order of magnitude estimation, the CCC value for dual tab cooling will be halved and used for comparison. This Kokam cell has a dual-tab cooling CCC of 0.332 W/K,⁸² a single tab cooling CCC for this cell would be approximated to be 0.150 W/K. This value is only 8% higher, and thus marginally better, than the cylindrical LG M50T cell. Based on these numbers, a reasonable assumption may be that the two cells are thermally similar. However, the characteristic length of the cell impacts the value of the CCC considerably, thus making it an essential property for understanding any comparison between cells with different form factors. The Kokam cell's characteristic length is 150% greater than that of the LG M50T (113 mm for the Kokam cell, discounting the tabs, versus 70 mm for the LG M50T), thus one might expect the Kokam cell should have a lower CCC than the LG M50T. The similar CCC values for the two cells suggest that the structure of the Kokam cell is more efficient for tab heat rejection, compared to the structure of the LG M50T for rejecting heat through its base.

18650 Measurements

The choice between pouch or cylindrical cells will often be based upon several other more influential factors (e.g., configuration, safety, energy/power densities, pack construction). However, the decision between different cylindrical cells, in their various capacities and sizes, may be significantly less rigid and could come down to factors like thermal performance. As part of this work, another popular cylindrical cell form factor is tested, the 18650. Figure 15 shows the CCC plot for a set of CCC_{Base} data gathered for a 3 Ah Samsung INR18650-30Q cell, under six different currents, ranging from 1 C to 3.5 C, and three ambient temperatures, 10, 15 and 20 °C. All results are gathered from a single cell at 50% SOC, with the 20 °C repeat data simply a repeated test of the same cell, where the cell was removed from the rig and subsequently inserted back in. The same nickel tabs and connection position as for the 21700 cell are used, with the cell tested in the same experimental rig. Given that the setup is identical to that in Figure 11, losses are expected to be of a similar magnitude to the M50T tests, and thus assumed to have minimal effect on the calculated CCC.

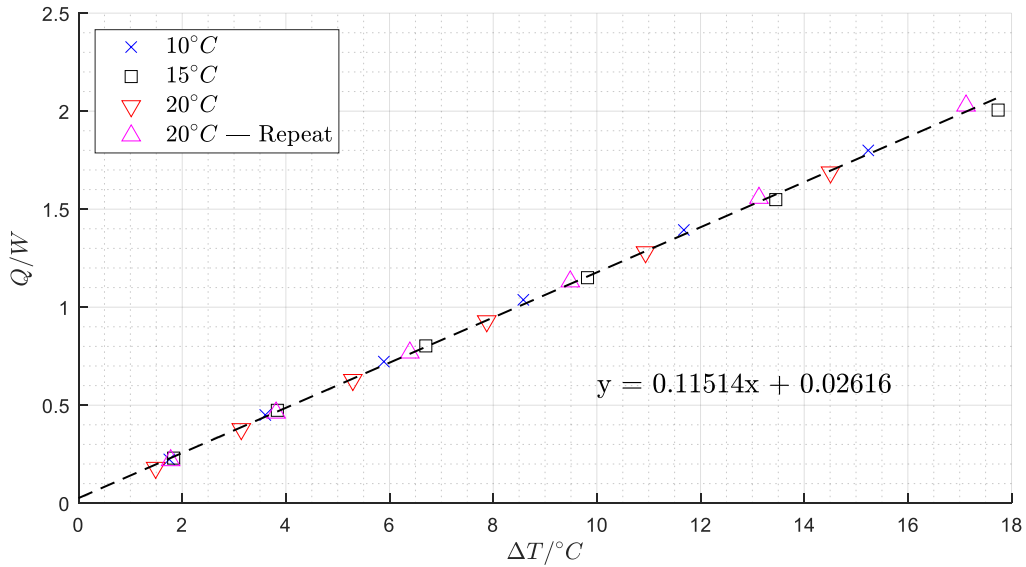


Figure 15: Measured heat generation versus measured temperature gradient for the Samsung 30Q cell under base cooling, giving a CCC of 0.115 W K^{-1} . The symbols and colours correspond to each of the 24 pulsing sets, at six current amplitudes (between 3A and 10.5A, in increments of 1.5A), three cooling (and ambient) temperatures (between 10°C and 20°C), and one repeated test at 20°C. All tests were performed at 50% SOC. Recreated from Ref. ¹⁷⁷

The data points lie on a line of fit with small scatter, showing that the data is consistent. The y-intercept is relatively low, indicating a sufficient thermal range for the results to be trustworthy. This line gives a CCC_{Base} of **$0.115 \text{ W/K} \pm 1.5\%$ for the Samsung 30Q**. The two measures of a successful CCC test – the spread of data across a linear fit and the low y-intercept – indicate that this dataset is significantly more consistent than the results from the LGM50; no

dependence on ambient temperature and no apparent change in data with a repeat are visible. It could be assumed that the lack of dependency of this data could translate to a consistent and horizontal dataset on the original plot for the CCC (CCC vs. Q).⁸²

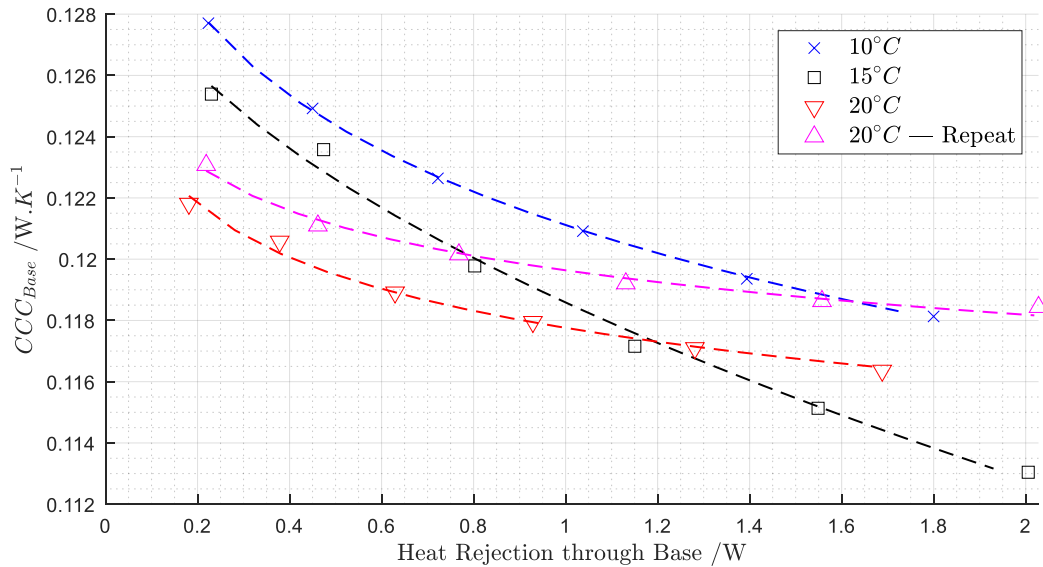


Figure 16: CCC versus measured heat rejection for the Samsung 30Q. Representing the same data displayed in Figure 15 using the old CCC representation. Recreated from Ref. ¹⁷⁷

Figure 16 shows the same data plotted using the original representation from Hales et al.⁸² It is clear that the data does not sit on a single horizontal line on this plot, each set of six currents has its own heat rejection dependence, with no clear dependence on ambient temperature and a significant effect of a repeat, visible in the two 20 °C tests. The CCC value can only be obtained by calculating the mean of the dataset, yielding a value of 0.120 W/K $\pm$ 6%. This CCC_{Base} value is about 4% higher than the value obtained above using the improved method. It is hypothesised that the difference between these two values is a result of relatively small difference between the absolute temperature of cooling provided by the Peltier element and the temperature of the ambient air in the chamber. This temperature difference results in small steady state heat flows within the rig/cell that affects the measured values of Q and ΔT by a fixed amount. This is hypothesised to affect each individually calculated CCC value shown in Figure 7, while appearing as a shift in the data on Figure 6 (the non-zero y-intercept). As a result, the difference in temperatures does not affect the fixed relationship between Q and ΔT (gradient) across multiple values of Q . This indicates that adopting the new CCC plotting procedure helps reduce the uncertainty in determining the CCC value. Figure 16 leaves room for significant interpretation of the results and how best to determine a singular CCC value, i.e., extrapolate to 0 W, extrapolate to ∞ W, mean of the data, whereas using Figure 15 removes

this, as it simply requires the line of best fit for the data. Additionally, using a line of best fit generates a singular CCC value that conforms to all of the data, as opposed to generating individual CCC values for each data point and attempting to find a singular answer.

18650 vs 21700 comparison

Comparing the 18650 to the 21700 cell only based on their CCC value is not an accurate representation of their thermal performance in a pack. The 18650 cell is found to have a CCC_{Base} value 16% lower than that of the 21700 cell, meaning that it can transfer 16% less heat when at the same temperature difference. However, the 18650 has a base area 36% smaller than the 21700 through which heat can be transferred during base cooling. Thus, it may be useful to compare heat flux as opposed to total heat flow out of the base of the cells. The ratio $CCC/area$ (CCC'') is proposed as an additional tool in this comparison, using the heat flux divided by the temperature difference, as shown in Eq. 2.

$$CCC'' = \frac{CCC}{Area} = \frac{\dot{Q}}{Area \Delta T} = \dot{Q}'' / \Delta T \quad Eq. 2$$

This metric has units of $W K^{-1} m^{-2}$, identical to the surface heat transfer coefficient (h). However, these two metrics are fundamentally different as h defines the heat flux between two bodies across a 2-D surface for a given temperature difference between the two bodies, whereas the CCC'' defines the possible heat flux (of internally generated heat) from a 3-D body through selected 2-D surfaces for a given temperature difference across the 3-D body. The value of the CCC'' for the two cells tested is shown in Table 3.

Table 3: CCC_{Base} , CCC''_{Base} and $CCC_{GN,Base}$ comparison of 21700 and 18650 cells

Cell	CCC_{Base} [W/K]	Base Area [m ²]	CCC''_{Base} [W/m ² K]	Length/Area a [m ⁻¹]	$CCC_{Base} * Length/Area$ ($CCC_{GN,Base}$) [W/mK]
21700	0.139	3.46x10 ⁻⁴	401	202	28.1
18650	0.115	2.54x10 ⁻⁴	452	256	29.4

According to this new criterion, the value of the CCC'' , the 18650 is superior to the 21700. These values predict that, when using multiple cells, as is the case in a pack, the 18650 cells can reject 13% more heat than the 21700 cells for the same temperature gradient across the cell and the same cooling area of the thermal management system. While the geometry plays a role in this outcome, differences in the internal structure of the two cells are also expected to affect it. This particular 18650 cell is known to have two internal negative tabs, while the 21700 has only one; there may also be differences in electrode and current collector thicknesses, which is

expected from the cells having different power/energy densities, as well as the different electrode chemistries (NMC for the 21700 and NCA for the 18650).

Influence of Internal Composition and Structure

The effect of these internal differences can be accounted for by calculating a CCC normalised for geometry, shown by Eq. 3

$$CCC_{GN} = \frac{\dot{Q}/A}{\Delta T/l} = CCC \times \frac{l}{A} \quad \text{Eq. 3}$$

where $\dot{Q}$ is the heat transferred through the cooled surface, $\Delta T/l$ is the temperature gradient from the hottest point to the cooled surface, with ΔT being the difference in temperature and l being the distance between these two points, and A is the cross-sectional area of the cooled surface. CCC_{GN} has units of W/mK, identical to thermal conductivity (k). However, k defines the heat flux flowing through a 1-D body for a given temperature gradient (K/m) across the length of the body, whereas CCC_{GN} defines the heat flux of internally generated heat rejected from a 1-D body for a given temperature gradient across the length of the body. Comparing the values of CCC_{GN} , the 18650 is only 5% better than the 21700. This value predicts that, were the two cells of the same size, there would only be a 5% difference in CCC between them. Any further differences can be assumed to be the result of the cells' geometry.

Geometrical Influence

An estimate of what the CCC for an 18650 with the same internal components and structure as the LG M50T 21700 can be calculated by taking the CCC_{GN} for the 21700 and multiplying it by the area/length for an 18650. A CCC of 0.115 W/K is obtained for an 18650 sized LG M50T, a value 21% lower than that of the CCC for the real 21700 sized LG M50T. When the CCC is normalised to the cooling area of the cells, a value of 452 W/m²K indicates a 7% better CCC" for an 18650 sized LG M50T versus the 21700 sized LG M50T. This analysis is strictly valid only if the value of CCC_{GN} is independent of cell size. These numbers suggest that the CCC favours the 21700 geometry, and the CCC" favours the 18650. This would mean that in a battery pack, a group of 18650 cells are easier to cool (because they are shorter) compared to a group of 21700. However, per cell, each 21700 would be able to reject more heat (because they have a better base area to height ratio) than each 18650.

Heat Generation

The thermal performance of these cells cannot be compared without considering their heat generation. The heat generation of a lithium-ion cell, however, depends on multiple factors. A

recent study demonstrates how extensive testing can help create heat generation maps across multiple conditions, that can be used in conjunction with the CCC to aid cell selection.¹⁰¹ However, for the purpose of simply comparing heat generation in the two cells, a single set of conditions was chosen; the heat generation was estimated at 1 Hz from the CCC experiments, at 50% SOC and 20 °C. Even though at this frequency not all the heat generated will be ohmic, an estimate for heat generation can be found by using the overpotentials from the voltage data ($V=IR$) during the pulsed CCC experiments, estimating heat generation through Joule heating ($Q=I^2R$). The effective R value can be used to estimate heat generation at different currents. The effective internal resistance values extracted are 20 mΩ and 25 mΩ, for the 18650 and the 21700 cell respectively. According to these values, the following predictions can be made:

Under Equal C-Rate – [$Q = C^2R$ (21700: C=5 A, 18650: C=3 A), $\Delta T = Q/CCC$]

- The 21700 cell would produce 250% more heat
- The 21700 cell would have a 180% larger temperature difference along its length

Under Equal Current – [$Q = I^2R$ (I=5 A), $\Delta T = Q/CCC$]

- The 21700 cell would generate 25% more heat.
- The 21700 cell would have a 3% larger temperature difference along its length

Both comparisons indicate that this 18650 is thermally superior in all scenarios, because the 21700 cell is 25% more resistive than the 18650 cell according to the measured 1 Hz resistance. However, the CCC of the 18650 cell is only 21% worse than that of the larger cell. In a battery pack, the 21700 compensates for its poorer thermal behaviour by its higher energy density.

The CCC value of a cell has been demonstrated to be a key piece of thermal information,⁹⁹ despite currently missing from data sheets. The raw CCC indicated that the 21700 is superior, however much of its advantage was found to be the result of geometry, namely its larger base area. Once heat generation is accounted for, the 18650 considered in this study becomes the better cell, in terms of its capability to reject its own heat through its base. How much heat a cell will generate under realistic conditions is also almost impossible to work out from a typical cell data sheet, although there is normally a 1 kHz AC resistance value which can be used for simple calculations, like those above. The above analysis highlights the importance of accounting for factors such as cell geometry, heat generation and capacity when making comparisons between different cells.

3.3 Base Cooled CCC with Industrially Relevant Electrical Connections

While the experiments in the previous section successfully demonstrated the CCC on cylindrical cells, due to limited access to industry standard welding techniques, the electrical connection method used was unrealistic for base cooling. For a cylindrical cell, the electrical connections can significantly impact their thermal boundary conditions. Large tabs welded to the cell like that of the base cooled CCC measurements, provide an excellent thermal path into and out of the cell. While tab connections at the positive and negative end of the cell can be common for side or convection cooled cylindrical cell packs, it is not a connection method that can be used for base cooled packs. In a base cooled cylindrical pack the cells would typically be aligned in parallel, perpendicular to the base plate (negative terminal in thermal contact with the base plate), with both positive and negative electrical connections made at the top of the cell (e.g., Lucid Air 2022, Rivian R1T 2022). This is possible due to the construction of these cylindrical cells, where the can (which is part of the cell negative terminal) wraps over the top edge of the positive cap to form a shoulder. Connecting the cell in this way is not ideal as it increases the resistance slightly as the current needs to flow down the cell can to reach the internally welded negative tab at the base of the cell. Using precise welding techniques, such as laser or ultrasonic welding, it is possible to make electrical connections that utilise this thin shoulder. Ultrasonic wire bonding is one suitable connection technique; it involves bonding a short and thin wire (typically 100-800 microns in diameter) from the cell to the busbar to make the electrical connection (e.g. Tesla Model 3 2019). Wire bonding cylindrical cells for base cooling negatively affects the electrical resistance of the system. The wires, typically used for fusing, have a relatively high electrical resistance compared to tabs, due to the much smaller cross-sectional area. Additionally, it is possible that the change in the location of the negative terminal connection will impact the thermal profile of the cell, and subsequently the CCC.

3.3.1 Experimental Rig

A new test rig was created to measure the CCC for base cooling with a wire bonded electrical connection, on the LG M50T, the same commercially available 21700 cylindrical cell tested in the previous base cooled CCC study. The wire bonded rig uses the same fin, but different insulation and electrical connections, compared to the original rig.¹⁷⁷ The fin can be re-used as it is still compatible with the base of the cell. The insulation needed to be re-designed because the electrical connections are in a different location and are different in design, as there are no

longer tabs to connect to. A bespoke housing holds two 25 mm x 25 mm x 1 mm (width x length x thickness) aluminium busbars to the cell and protects the wire bonds. The housing is 3D printed out of carbon fibre blended nylon and the aluminium contacts glued into the housing. The housing sits on the shoulder of the cell, covering 3 mm of the cell surface. The housing is glued to the cell to secure it. The same ring-terminal banana leads, as the previous rig, are bolted through two holes in each of the aluminium contacts to route the electrical connection outside the insulation. The wire bonding is achieved using a Hesse Wire Bonder Bondjet BJ955/959 with 300-micron aluminium wire, with a wire length of approximately 5 mm. A schematic of this rig is shown in Figure 17, alongside a photo of the rig during setup, and a photo of the aluminium contacts held to the cell by the custom holder.

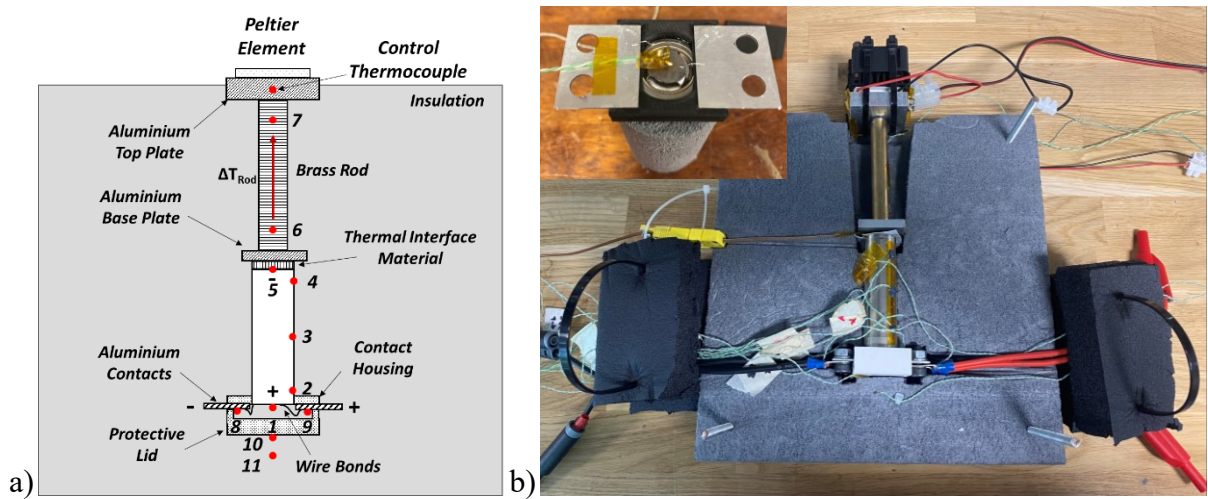


Figure 17: a) Schematic of the CCC base cooling rig for the Wire Bonded electrical connection. The red dots denote placement of the thermocouples. Not to scale. b) Photo of rig setup with front insulation removed - image of cell top embedded in the top left corner.

The measurement of cell and fin temperature differences is identical to the previous rig, shown in 3.2.2 Experimental Setup & Procedure. Five thermocouples measure the full axial thermal difference of the cell (TC 1-5), two measure the fin thermal difference (TC 6-7), and four thermocouples are positioned around cell to measure heat losses away from the cell (TC 8-11). For the calculation of the CCC, TC 6 and 7 measure the fin thermal difference, and TC 1 and 5 measure the cell's axial thermal difference. This rig has more complex loss paths at the positive end compared to the previous rig, these are shown in Figure 18. Each aluminium contact can transfer heat between the cell through the wires and the housing. The top of the housing also loses heat to the insulation. The positive contact losses are measured by TC 1 and 9. The negative contact losses are measured by TC 1 and 8. The insulation loss is determined from the difference between TC 10 and 11 which are 10 mm apart. Comparing the cell

overpotential drops during pulsing (difference between the peak voltage in the charge pulse and the min voltage in the discharge pulse, divided by the change in current), a rough estimate of the ohmic resistance can be determined, to assess the impact of the wire bonded connection compared to the previous tab welded one. The tab welded LG M50T cells had an average ohmic resistance of 29.5 m Ω at 20 °C and 50% SOC; under the same conditions, the wire bonded cells have an average series resistance of 33.25 m Ω . This is a 12.5% increase in ohmic resistance caused by the wire bonds and cell can.

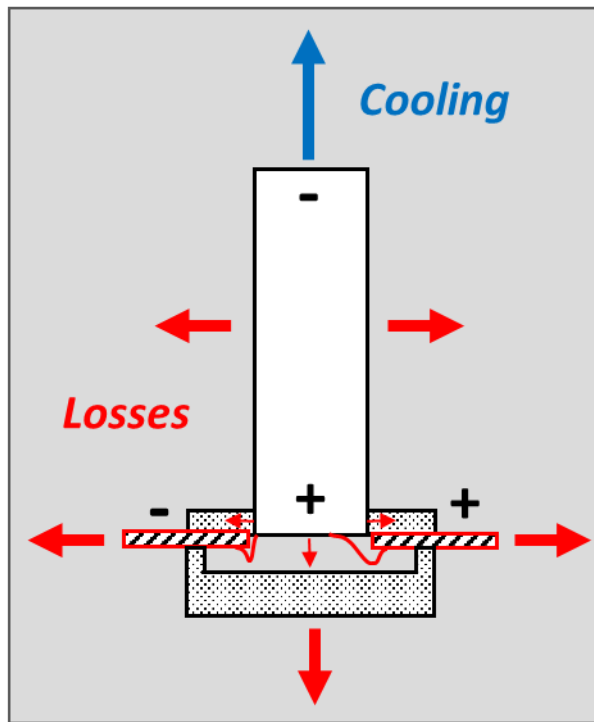


Figure 18: Schematic highlighting the heat flow paths out of the cell. The cooling is shown in blue, with the undesirable heat loss paths shown in red.

3.3.2 Experimental Results

The CCC measurements made for the LG M50T cell are shown in Figure 19, it can be seen that there is a significant spread to the results. The first round of pulsing tests from this test rig gave CCC results that were far lower than expected, with further analysis showing significant thermal differences through the loss paths at the positive end, most transmitting a small amount of heat back into the cell from the terminals. This means that the cell is being slightly heated through the electrical connections, rather than slightly cooled, as it was in the tab cooled experiments.¹⁷⁷ Attempts to resolve this “issue” involved re-bolting the banana leads, and changing the electrical current flow setup. The original electrical setup used two banana leads per terminal, one carrying current and the other measuring voltage. A second setup was used

instead, that involved stacking the banana plugs so that the current split down both cables, moving the voltage measurement to the banana plug stack. The rig was re-setup and adjusted several times using the same LG M50T cell. Each minor setup change or re-setup seemed to greatly impact the measured CCC, these minor changes included, adding insulation to the banana plug cables, thickening the insulation housing the cell, and replacing the banana plug cables. The results of all the tests are presented in Figure 19. The difference between the smallest and largest measured CCC was over 75%. These results are significantly outside the acceptable measurement accuracy for the CCC of $\pm 10\%$.¹⁷⁷

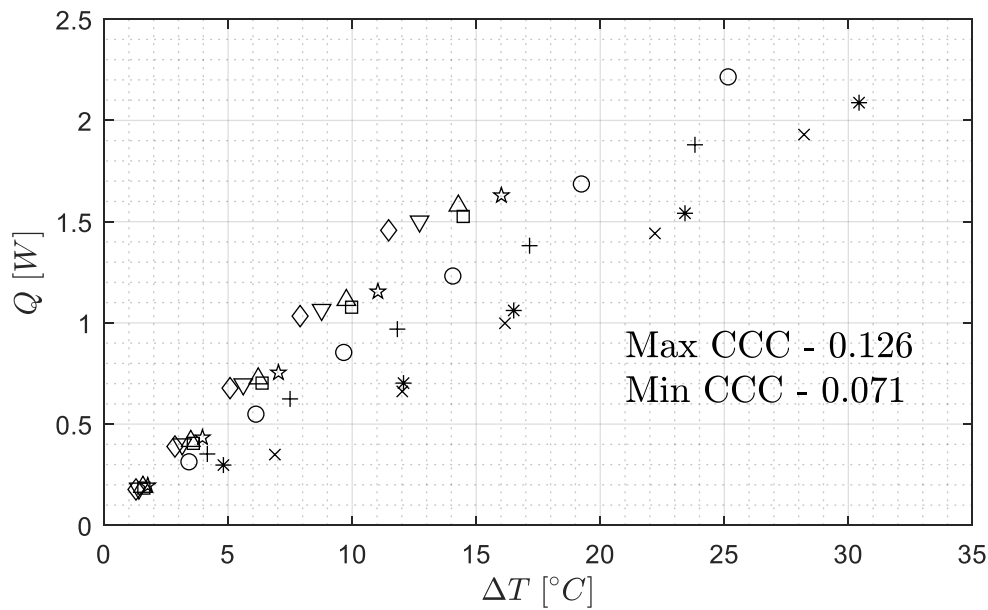


Figure 19: Initial CCC results for base cooled LG M50T with a wire bonded electrical connection. Markers differentiate between 7 different pulsing runs of the cell, each with small changes to the setup.

To help understand why these setup changes affect the measured CCC so significantly, we need to understand the CCC from a more fundamental perspective, thus assessing what variables affect the CCC value and what variables can affect the measurement of it. This is difficult to do with experiments, due to the difficulty in isolating variables and achieving perfect conditions. Real insulation will always allow some amount heat flow, and the heat generation of the cell is highly coupled to a variety of variables such as the cell temperature, current, and SOC. The best way to assess the CCC is through a model, where each variable can be isolated independently to assess its potential impact on the heat transfer of the system and perfectly adiabatic boundaries can be created to isolate heat flows.

3.4 Modelling the CCC using the Fundamental Heat Transfer Equation

3.4.1 Model Goals

This work aims to understand the CCC as a fundamental thermal property of a heat-generating body, in particular a battery cell. This should help improve our ability to design and build CCC rigs that can generate consistent results. The goal is not to model the cell and system that has been used for experiments, but to understand more fundamentally how different aspects of the system affect the subsequent heat transfer. Thus, instead of a complex thermo-electric 3D lithium-ion cell model, a simplified heat transfer model is used to explore the CCC for a generic heat generating body.

This work will aim to answer the following questions:

- In a perfect system with no losses:
 - **What is the CCC, as it has been defined, and is it related to any standard thermal metrics?** (The relationship between the CCC and standard thermal metrics will help improve the conceptual understanding of what the CCC represents)
 - **What variables of the body or system define the CCC value?** (This will help prove if the CCC is truly constant for a given lithium-ion cell under a defined cooling system)
 - **How can the CCC of a body be improved?** (This can help identify ways to improve the CCC of a cell via its design)
- In a real system, with losses:
 - How do losses perpendicular to cooling affect the measurement of the CCC? (This understanding will help design better CCC measurement rigs)
 - How do losses in-line to cooling affect the measurement of the CCC? (This understanding will help design better CCC measurement rigs)
 - Can losses be accounted for in the measurement of the CCC, using simple equations and experimentally measurable variables? (If possible, losses that are unavoidable in real experiments can be mitigated against)
 - **Is it possible to define a real CCC, that can account for system heat flows?** (If possible, it improves the ability for battery engineers to use the CCC to predict performance in applied battery packs)

- How low must losses be kept by the experimental set up and operating conditions to maintain an accurate CCC measurement? (This will help further standardise the measurement of the CCC)

3.4.2 Perpendicular Losses (3D MATLAB Model)

It is expected that perpendicular losses are significantly less impactful to the CCC than inline losses, due to heat transfer understanding on how perpendicular losses should impact inline thermal differences.⁹⁶ To assess this assumption, a simple steady state heat transfer model of a cylinder is created in MATLAB using the in-built thermal solver in the Partial Differential Equation Toolbox. A model is best suited to assess this assumption as it can create perfect adiabatic boundary conditions, to help isolate the impact of the heat flow directions. Creating an adiabatic condition in a real experiment is extremely difficult. The reference geometry and conductivity is based on the LG M50T cell (70 mm – height, 21 mm – diameter, 14 W/mK – approximate bulk conductivity), however when geometrical and conductivity changes are explored these values are varied significantly.

Initially, the body is assumed to have a uniform conductivity and uniform heat source throughout its geometry. The boundary conditions and heat source are set up to represent a CCC_{Base} experiment, where the base of a cylinder is cooled while the cylinder body generates heat, all other surfaces should be insulated. This is replicated by applying a heat transfer coefficient of $3200 \text{ W/m}^2\text{K}$ to one of the circular faces (face 1) of the cylinder, shown in Figure 20, with the other circular face (face 2) and the curved face (face 3) placed under adiabatic conditions. The ambient temperature for the convection boundary conditions is 25°C , and 2 W of total heat is applied uniformly across all the elements of the body. The CCC is defined by the heat flowing through the cooled face (face 1) divided by the axial thermal difference between the two circular faces (average of face 2 – average of face 1). To assess the impact of perpendicular losses, the heat transfer coefficient applied to face 3 is increased, while keeping face 2 adiabatic, until the CCC is affected by 100%. This will be compared to the effect caused by in-line losses where the heat transfer coefficient of face 2 is increased while face 3 remains adiabatic. All the equations for these calculations are given in the Appendix A.2.



Figure 20: Diagram of cylinder used for model with the faces labelled 1-3.

The results of the model are shown in Figure 21. This plot shows that both the in-line and the perpendicular losses can significantly impact the CCC, both improving the measured CCC as the percentage of losses increase. However, the magnitude of loss required to impact the CCC by 100% is much higher for the perpendicular surface compared to the in-line one. The CCC is thus less sensitive to perpendicular losses. Changing the magnitude of the heat generated by the cell does not affect these results, but changes to the geometry and the value of conductivity of the body affect the position of the perpendicular dependence curve, while the in-line curve remains unaffected by these changes. Increasing the length, shifts the perpendicular curve to the left, increasing the perpendicular losses for the same level of insulation. Increasing the conductivity of the body shifts the perpendicular curve to the right, reducing the perpendicular losses for the same level of insulation. The in-line dependence curve is changed only when the heat source or the conductivity is assumed non-uniform. Applying a linearly varying heat source, conductivity, or altering the body to be a multi-body cylinder with different conductivities creates a shift in the in-line (and perpendicular) curves. Having higher heat generation or conductivity shifts both curves to the right reducing both in-line and perpendicular losses for the same level of insulation.

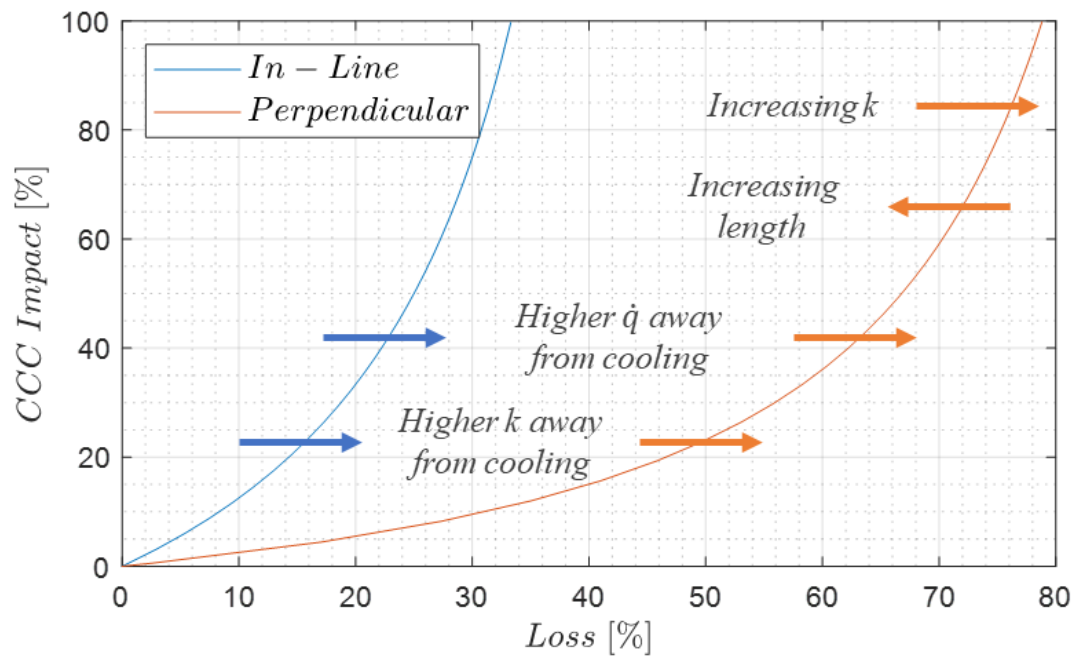


Figure 21: 3-D model results showing the impact on the CCC measurement of the percentage of heat losses leaving the perpendicular or in-line surfaces, when cooling one of the circular faces of a cylindrical body. Arrows indicate the variables that can affect these curves.

These results suggest that it could be difficult to account for the impact of losses in real experiments, as these curves have multiple dependencies, on variables that are not easily

determined via experimentation. For a given cell, conductivity and geometry can be considered fixed, at least at beginning of life. The remaining variable to consider is the profile of heat generation in the cell. Since the CCC is defined independently for each cooling system, the heat generation profile of a cell may remain constant with increasing current, for a given cooling system. However, the thermal coupling of heat generation in a lithium-ion cell may result in a time-dependent heat generation profile, changing as losses impact the steady state temperatures across the cell. Thus, it is likely not possible to generate a fixed version of this plot for a real cell.

In conclusion, perpendicular losses affect the CCC less than in-line losses but must be kept low nonetheless, as their impact on the measurable CCC of a body cannot be quantified, using information gained from simple experiments. It is difficult to recommend a value to stay below, for perpendicular losses, due to the wide range of conductivity and geometries available for lithium-ion cells. However, previous CCC rigs have managed to keep losses below 10% of the total heat, thus this seems a reasonable recommendation. This conclusion significantly affects the success of designs for cooling systems that would expect moderate levels of perpendicular cooling, such as surface cooling where the tabs are perpendicular to cooling. In such cases, the CCC would not be able to predict quantitative performance, contrary to what has been suggested in previous works.⁹⁸ Despite this, the CCC still remains useful for qualitative comparison of cells or cooling, if developed into a recognised standard. Cells can be tested under defined standards for each cooling method, offering a fixed comparison point, where cells can be fairly compared to one another based on their thermal performance, via the CCC.

3.4.3 1-D Steady-State Heat Transfer Model with Heat Source

Model Setup and Equations

Having established that in-line losses have a more significant impact on the value measured for the CCC compared to perpendicular losses, this section is focused on formulating fundamental analytical equations for the CCC of a body, considering in-line losses only. These equations will help improve our understanding of the CCC as a thermal metric and possibly result in an equation that can be used to compensate for the more significant in-line losses. By setting the boundary conditions of all surfaces that are perpendicular to the cooling direction adiabatic, the heat flow in the system becomes 1-dimensional. Thus, using the 1-D steady state heat diffusion equation with heat source term is appropriate. The boundary conditions are set to replicate a single sided cooling scenario, where the hottest point is on the face of the body that

is opposite to where the cooling is applied. Simplifying the model to 1-D means that the thermal conductivity and heat generation of the body along the other two axes are considered uniform in all other directions except x , along the central axis of the cell. Thus, in reference to this model, all “inline” heat flows and thermal differences discussed are assumed in the direction of x (axial for a cylindrical cell).

The spatial distribution of the heat generated in the body is given by $q(x)$. The spatial distribution of the thermal conductivity of the body is given by $k(x)$. Both q and k are kept independent of temperature. A schematic of the model can be seen in Figure 22. The insulated boundary at $x=0$, is modelled as an ideal boundary where the thermal resistance of the insulation is $R_0=R_i=\infty$, and the ambient air temperature is $T=T_a$, thus allowing for losses inherent to realistic experimental setups to be accounted for. The cooled boundary is modelled with a thermal resistance of the cooling fin given by $R_L=R_f$ and a temperature of the Peltier cooling plate set point of $T=T_c$.

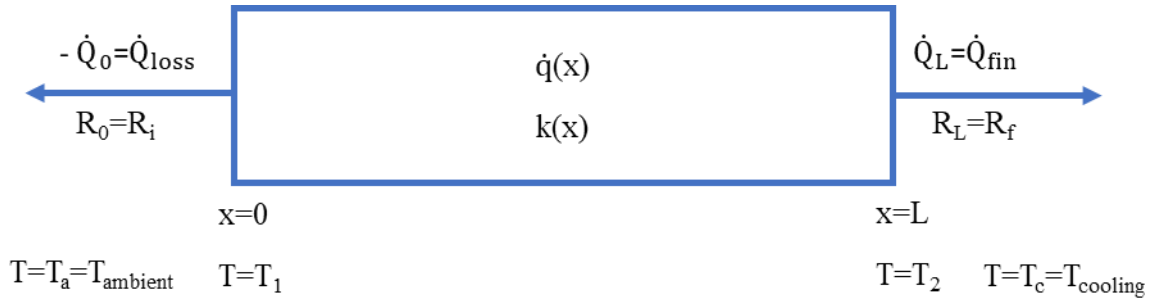


Figure 22: Model Schematic of the 1D system used for generating the expression for CCC corresponding to one-sided insulation of a battery cell.

The 1-D steady state heat diffusion equation and its integrals are displayed in Eq. 4, Eq. 5, and Eq. 6.

$$\frac{d}{dx} \left(k(x) \frac{dT}{dx} \right) = -\dot{q}(x) \quad \text{Eq. 4}$$

$$\frac{dT}{dx}(x) = \frac{1}{k(x)} \left[- \int_0^x \dot{q}(x) dx + C_1 \right] \quad \text{Eq. 5}$$

$$T(x) = \int_0^x \frac{1}{k(x)} \left[- \int_0^x \dot{q}(x) dx + C_1 \right] dx + C_2 \quad \text{Eq. 6}$$

Solution

Integrating and solving for the integration constants, using the following (ideal) boundary condition, result in Eq. 7 and Eq. 8:

- At $x = 0$, $Q = 0$, $dT/dx = 0$, $T = T_l$, corresponding to the insulated surface

$$\frac{dT}{dx}(x) = \frac{-1}{k(x)} \left[\int_0^x \dot{q}(x) dx \right], C_1 = 0 \quad \text{Eq. 7}$$

$$T(x) = \int_0^x \frac{-1}{k(x)} \left[\int_0^x \dot{q}(x) dx \right] dx + T_l, C_2 = T_l \quad \text{Eq. 8}$$

The CCC equation can be determined from its definition, shown in Eq. 9. Eq. 8 can be solved at $x=L$, where $A \int_0^L \dot{q} dx = \dot{Q}_{fin}$, as the heat out through $\dot{Q}_{fin}$ must be equal to the total heat generated. The resulting equation is given below in Eq. 10.

$$CCC = \frac{\dot{Q}_{fin}}{T_1 - T_2} \quad \text{Eq. 9}$$

$$CCC = \frac{A \int_0^L \dot{q} dx}{\int_0^L \frac{1}{k(x)} \left[\int_0^x \dot{q}(x) dx \right] dx} \quad \text{Eq. 10}$$

This equation shows that the fundamental CCC of a body is only dependent on its heat generation profile, thermal conductivity, and geometry. In steady state, there is no dependence on the thermal resistance of the cooling fin, ambient temperature, or the temperature of cooling. This justifies the use of high thermal resistance cooling fins in CCC experiments. The fact that the CCC is dependent on the integrals of $\dot{q}$ demonstrates the importance of measuring the CCC only once the thermal profile of the cell and testing rig have fully stabilised.

Exploration of the effect of system parameters on the value of the Fundamental CCC

Heat Generation Profiles

It is well established that the heat generation of lithium-ion cells is inhomogeneous (spatially) during typical operation.⁵² As current will always follow the path of least resistance, it is expected that there will be current and temperature inhomogeneity within the electrodes of a cell. Both lead to spatial variability of the internal heat generation of the cell.⁵⁷ Modelling work has shown that internal current profiles follow internal temperature profiles.¹⁷⁸ Thus it would be expected for internal heat generation to follow expected temperature profiles, i.e., for the cooling system in this model, temperature would be hotter on one side and colder on the other,

so it can be expected that the heat generation would be similar. At low currents, all three, current, temperature and heat generation profiles, would be expected to be approximately homogeneous, assuming the natural current path within the cell is homogenous.

To explore the impact of the heat generation profile in this model, the CCC equation from Eq. 6 is evaluated for constant thermal conductivity, and varying $\dot{q}$. The simplest heat generation profile is one that is uniform with x , $\dot{q}(x) = c$. In this case, the equation for the CCC becomes:

$$CCC = kA \frac{2}{L} = \frac{2}{R_c} \quad \text{Eq. 11}$$

The variable c cancels out of the equation, leaving the CCC independent of the heat generated by the body, and dependent on the thermal resistance of the cell (R_c) only. The thermal conductance of a body is the reciprocal of the thermal resistance; in its simplest form, the CCC is twice the thermal conductance of the body. As the body generates and rejects its own heat, rather than passively transmitting heat, the CCC is an equivalent to thermal conductance for heat generating bodies.

For a heat generation profile that is linear in x , such that $\dot{q}(x) = mx + c$, the equation for CCC becomes:

$$CCC = kA \frac{mL + 2c}{\frac{mL^2}{3} + cL} \quad \text{Eq. 12}$$

CCC is now dependent on the coefficients of the internal heat generation profile (m, c). For an equal amount of total heat generation, a linearly increasing profile along x , $m > 0$, increases the CCC, while a linearly decreasing profile, $m < 0$, reduces the CCC, compared to uniform heat generation.

This conclusion becomes relevant when considering different types of cells and cooling strategies. A cylindrical cell under base cooling is expected to have a $m < 0$ profile, due to the large concentration of heat in the positive cap, whereas a pouch cell under surface cooling could have a $m > 0$ profile, as the colder electrode layers may produce more heat than the hotter ones. By having more of the total heat generated at the cooled end of the cell ($m > 0$) the heat has a shorter path to leave the cell, thus the thermal difference reduces for the same heat transfer through the cooled boundary. The CCC thus remains dependent on c , which controls the magnitude of the heat generation rate. Experimental data⁸² contradicts this, where the CCC has been measured as roughly constant even with varying magnitudes of heat generation rate. This implies that there is a scenario where m and c both vary in such a way that the CCC is constant.

This occurs if their ratio is constant with respect to the total heat generation. Substituting $r=m/c$ in Eq. 12 gives:

$$CCC = kA \frac{rL + 2}{\frac{rL^2}{3} + L} \quad \text{Eq. 13}$$

The CCC is now only dependent on r and as long as r remains constant as the total heat generation rate of the cell varies (i.e., with current) the CCC will remain constant. Physically this implies that the ratio between the heat produced by the hot side of the cell and that produced by the cold side remains the same, no matter how much heat is produced by the cell overall. As explained, a fixed r is required for the CCC to remain constant with heat generation, however in experiments the CCC is not perfectly constant. It is plausible that slight trends in CCC with heat generation in experimental data may be caused by variations in r .

The dependence of the CCC on the shape of the heat generation profile is concerning given that Li-ion cells can have complex heat profiles due to the heavy dependencies on variables such as temperature, current and SOC. This means that it is likely that the CCC of a cell does not remain constant while a cell is transiently charging or discharging, during normal operation. This may prevent the CCC from being used to predict the thermal performance of cells in normal operation. However, this should not impact the measurement of the CCC, since it is defined at steady state, for a single cooling system, which should result in a roughly constant r over the range of measurements.

Even though this analysis has been done for simple linear q profiles, the trends should still apply to more complex q profiles, that may be expected in real operation of a cell. This model suggests that the CCC of a cell should remain constant as long as r remains fixed. Unfortunately, there is not guarantee that this will be the case for all lithium-ion cells. Thus, for the best measurement of the CCC, experimental data must be obtained for a full thermal operating range, so that the data covers all possible heat generations and thermal differences, to help assess any potential trends of the CCC with varying heat generation, for the tested cell and cooling system.

Conductivity

To explore the impact of inhomogeneous conductivities Eq. 10 will be evaluated keeping $\dot{q}$ constant. A linearly varying function of $k=mx+c$ will be used to explore its impact on the CCC. The CCC is given by Eq. 14, showing the dependency on both the gradient and magnitude of conductivity.

$$CCC = \frac{m^2 AL}{mL + c \ln\left(\frac{c}{mL + c}\right)} \quad \text{Eq. 14}$$

As with a constant conductivity, increasing the magnitude of conductivity increases the CCC. In contrast to heat generation, for an equivalent total thermal conductivity, a linearly increasing conductivity profile ($m > 0$) reduces the CCC, and a linearly decreasing profile ($m < 0$) increases the CCC, compared to uniform conductivity. Practically this means that if there is a thermal bottle neck in the cell, it is best to cool the surface closest to it.

Geometry

The impact of geometry on the CCC is relatively intuitive, as it follows the same principles that govern the heat transfer for passive elements. To keep the thermal difference low, i.e., the CCC high (Eq. 9), the cross-sectional area needs to be increased and the characteristic length reduced, as inferred from Eq. 11. The geometry of the body governs the CCC through the ratio of A/L , thus increasing this ratio improves the CCC. This dependency can be used to evaluate the expected base cooling performance of some popular cylindrical cell sizes, under the assumption that their thermal conductivity and heat generation does not vary significantly from cell to cell. The predicted relative values of CCC are shown in Table 4.

Table 4: Comparison highlighting the impact of geometry on the CCC_{Base} of popular cylindrical cell sizes.

Cell Format	A/L Ratio [mm]	CCC Impact
18650	3.9	1.0
21700	4.9	1.26
4680	20.8	5.33
46120	13.8	3.54

This table shows that the 4680 format is expected to perform over five times better under base cooling compared to a 18650 cell; the 46120 performs worse than the 4680, but significantly better than the 21700 or 18650 formats.

Real Solution for Non-Ideal Boundary Conditions

To understand the CCC in real systems, where there are unavoidable losses, the model is also solved for a real insulated boundary condition at $x=0$. For simplicity, the conductivity is assumed uniform, i.e. constant with x .

Using the following boundary conditions, Eq. 4, Eq. 5, and Eq. 6, become Eq. 15 and Eq. 16.

- At $x = 0$, $T = T_1$, $Q = -Q_{loss}$, corresponding to the insulated surface. Applying this to Eq. 6, gives $C_2 = T_1$.
- At $x = L$, $T = T_2$, $Q = Q_{fin}$, corresponding to the cooled surface. Applying this to Eq. 6, using $C_2 = T_1$, gives $C_1 = \frac{1}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L}$

$$\frac{dT}{dx}(x) = -\frac{1}{k} \int_0^x \dot{q}(x) dx + \frac{1}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L} \quad Eq. 15$$

$$T(x) = -\frac{1}{k} \int_0^x \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{x}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L} x + T_1 \quad Eq. 16$$

Applying Fourier's Law at the two boundaries gives solutions for T_1 and T_2 , allowing Eq. 16 to be solved, given in Appendix A.3. These solutions can be used to generate a general solution for the CCC under realistic boundary conditions at the two ends of the body. The solution depends on the thermal resistances at the boundaries, making it too complex to allow an intuitive understanding of how losses affect the value of the CCC compared to its value under ideal boundary conditions. Thus, an equation for the CCC that compares it to the ideal CCC (Eq. 11), will be considered instead. This equation, displayed in Eq. 17, is solved for uniform heat generation and conductivity with $T_a = T_c$, and is arranged in the format that allows the solution for the in-line losses to be obtained from the plot in Figure 21. The derivation of Eq. 17 is given in Appendix A.4.

$$\frac{1 - \frac{\dot{Q}_{loss}}{\dot{Q}_{tot}}}{1 - 2 \frac{\dot{Q}_{loss}}{\dot{Q}_{tot}}} = \frac{CCC_{Real}}{CCC_{Perf}} \quad Eq. 17$$

From Eq. 17 and Figure 21, the CCC ratio ($CCC_{Measured}/CCC_{Ideal}$) is the value read on the y-axis for a given Loss % on the x axis given by the loss ratio $\dot{Q}_{LR} = \dot{Q}_{loss}/\dot{Q}_{tot}$ on the In-line curve, where $\dot{Q}_{loss}$ is the total steady state heat flow from the loss surface of interest, and $\dot{Q}_{tot}$ is the total steady state heat flow leaving all surfaces of the body. This gives the following relationship: $y = 1 - \dot{Q}_{LR}/1 - 2\dot{Q}_{LR}$. This proves that there is a fixed relationship between these two ratios that is unaffected by any other variables, as long as both heat generation and conductivity are uniform throughout the length of the cell. This relationship shows that, as $\dot{Q}_{loss}$ goes to zero, the CCC tends towards its ideal value ($y \rightarrow 1, CCC_{Measured} \rightarrow CCC_{Ideal}$). As $\dot{Q}_{loss}$ tends to half of the total heat generated within the cell, $\dot{Q}_n \rightarrow 0.5$ and $y \rightarrow \infty$. This occurs due to the definition of the CCC, at a loss ratio $\dot{Q}_{LR} = 0.5$, where half of the heat is being lost from the insulated side, the same amount of heat ejected at the cooled side. In this scenario the heat

flowing through the cooled face, required by the definition of CCC (Eq. 9), is half of the total heat. Since the same amount of heat leaves both sides of the body, the system is symmetrical about the mid-point length of the cell, $x=L/2$. The thermal difference is thus zero in the CCC definition, thus rendering the CCC infinite, in a real scenario where both ends of the cell are cooled, the CCC definition would be changed to define the thermal difference between the two ends to the middle of the cylinder.

Understanding this limiting case helps reveal why changes away from the assumption of uniformity of heat generation and conductivity, such as the linear profiles considered above, affected the relationship between in-line losses and the measured CCC. Skewing the heat generation or conductivity profiles towards one side of the body shifts the point of thermal inflection away from the cell midpoint at $x=L/2$; thus, a different split of heat flow is needed to retrieve the case of $CCC \rightarrow \infty$ given by $T_1 - T_2 = 0$. The heat generation and conductivity of real lithium-ion cells is expected to be non-uniform, meaning that the real relationship, between the losses and measured CCC, will likely not be equal to this homogenous solution. Additionally, as mentioned previously, the thermal coupling between the temperature and heat generation throughout the cell likely means that it is not possible to experimentally generate a fixed version of Figure 21. In the absence of such a plot for a given cell, heat losses in the experimental rig for measuring the CCC need to be kept as low as possible.

Figure 23 displays model results, for the solution to Eq. 16 given in Appendix A.3, (for an M50-like body, height = 70 mm, diameter = 21 mm, uniform conductivity = 15 W/mK, uniform heat generation ranging from 0 to 2 W of total heat, ambient and cooling temperature = 20 °C, fin thermal resistance = 5 K/W). The thermal resistance of the insulation is varied to highlight the impact of losses on the thermal profile of a body and their impact on the CCC values that would be obtained from measurements. Figure 23a shows the temperature profiles for the body when generating 2 W of total heat, it displays that as losses increase, overall temperatures throughout the body reduce, with the temperature at $x=0$ reducing the most and the location of the maximum temperature shifting inward of the body. At a loss ratio $\dot{Q}_{LR} = 0.2$ (20%), the temperature at the insulated boundary is 7°C lower than in the case of no loss, while the maximum temperature point has shifted away from $x = 0 \text{ mm}$ to $x = 15 \text{ mm}$.

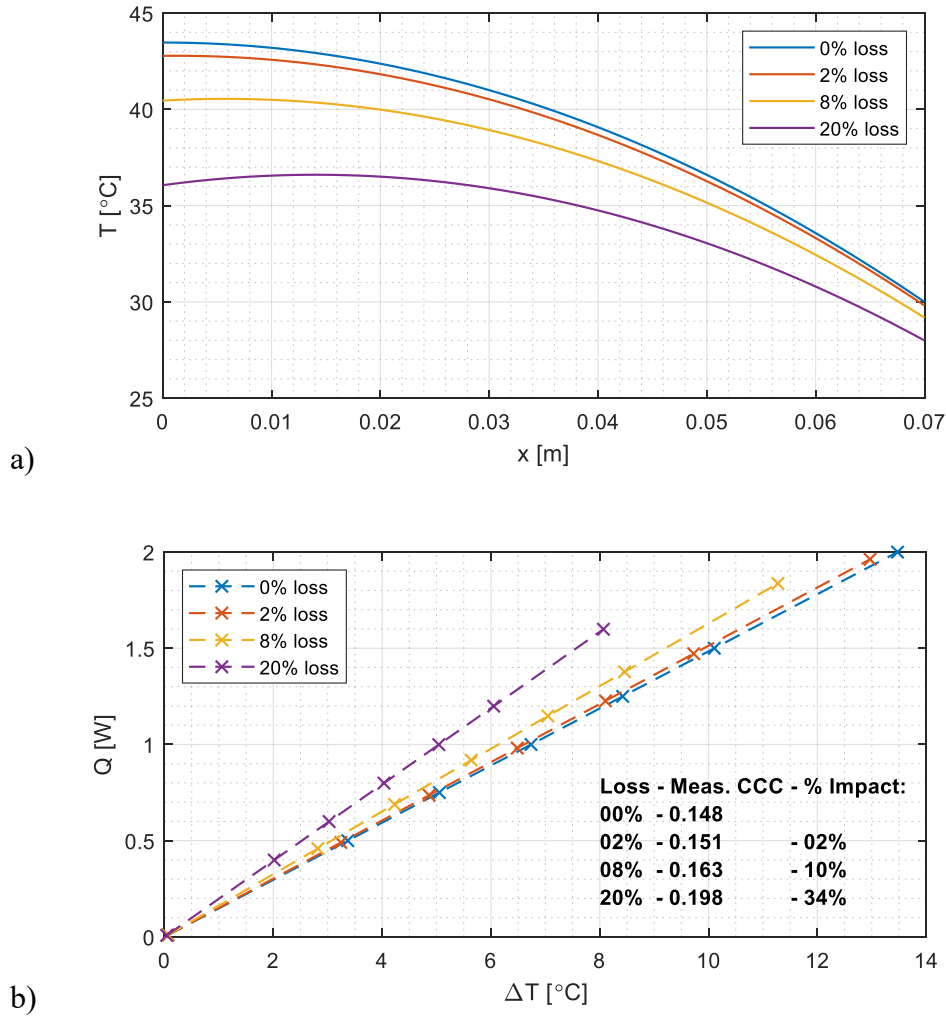


Figure 23: Results from the 1D model with realistic boundary conditions displaying (a) the impact of in-line losses on the thermal profile of a body, when generating 2 W of heat, and (b) the subsequent measurement of the CCC of such body, across a range of heat generation from 0-2 W (b).

Figure 23b displays the impact of such in-line losses on the measurements for a CCC experiment. It can be seen that, as the losses increase, so does the measured CCC, increasing the gradient of the Q vs ΔT dependence. The threshold for an accurate CCC measurement has been defined, early in this chapter, as 10% error. For the characteristics of this body, this limit results in a maximum acceptable 8% loss for an accurate measurement of the CCC. As the value of the acceptable loss percentage depends on the degree of non-uniformity of the conductivity and heat generation profiles of the cell, this value is expected to change from cell to cell.

Impact of cooling in experiments

While it is clear that the performance of the cooling system does not directly impact the CCC of a body, it can affect the amount of heat that flows through the insulated boundaries. The lower the thermal resistance is between the coolant and the cooled surface of the body, the less

heat escapes through the insulated boundaries. This improves the accuracy of CCC measurements. This is an important conclusion for any measurement of the CCC. In typical CCC measuring rigs,¹⁷⁹ cooling fins with a high thermal resistance are used, this helps generate thermal differences that are large enough to accurately measure the heat flow. The thermal control point for the Peltier element in these cooling fins is attached to the block directly below the Peltier element, as can be seen in Figure 17a. This ensures that the cooling system is stable and capable of reacting quickly to temperature changes. Reducing the thermal resistance of these fins will negatively affect the ability to measure the heat flow over the same distance. However, this thermal resistance problem can be overcome by changing the location of the control thermocouple for the Peltier cooling. Moreover, since the CCC measurement is made at steady state, it is not necessary for the cooling system to be fast responding. Thus, by heavily damping the PID settings, the control point can be moved instead to the block that is nearest to the cell's cooled surface. This significantly worsens the control system's response time but moves the constant temperature boundary very close to the cell surface. This change should reduce the heat losses through the insulated surfaces of the cell, improving the accuracy of the CCC measurement. Such a setup has the added advantage of increasing the range of conditions that can be tested, it allows the cell to be pulsed at higher currents before it reaches the thermal safety cut-off. The previous control scheme would result in the cell's cooled surface being several degrees above the control temperature, during the highest current pulses, due to the temperature difference through the cooling fin. The new control system proposed will keep the cooled surface of the cell at the control temperature, allowing for higher magnitude current pulses before safe thermal limits are exceeded.

Mismatch Between Ambient and Cooling Temperatures

In CCC experiments and the equations shown above it is assumed that the ambient temperature and the cooling temperature are equal. Under experimental conditions, a mismatch between the two is inevitable, given the finite capability of any thermal control system. Below, the consequences of a non-ideal cooling thermal control system are considered. Changing T_c to be 10 °C above T_a , for constant r and linear $q(x)$, predicts the measurements given in Figure 24.

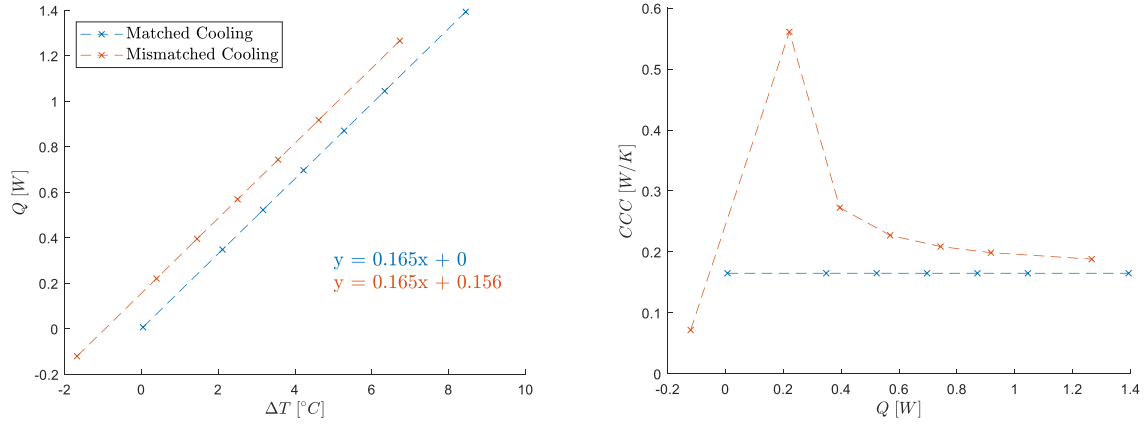


Figure 24: Difference in CCC between $T_c = Amb$ and $T_c = Amb + 10$. New plot (left) and old plot (right).

The left plot shows that the mismatch causes a shift in the dependence between the heat dissipation and thermal difference, causing a non-zero y-intercept, but leaving the CCC unchanged. The plot on the right shows the results in the previous CCC representation; the mismatch alters the individually calculated CCC values. This further justifies the use of the new representation proposed in this work, and the interpretation of CCC as the slope of Q vs ΔT , rather than $Q/\Delta T$. These results also strongly indicate that a mismatch between the ambient and cooling set points may be the leading cause of a non-zero y-intercept in real experiments.^{177,179}

3.4.4 Experimental Implications

The models proposed and solved here give insight into the experimental problems described in the Experimental section. The geometrical complexity of the loss paths, shown in Figure 18, make it difficult to accurately assess the magnitude of the losses, however the relative magnitude of the losses between the different test can be assessed by comparing the thermal differences in the loss paths. This comparison indicated that the loss ratio was varying significantly from one experiment to the next. This led to the varying CCC values obtained. After inspecting the rig, a few areas of improvement were identified:

- The electrical cables were replaced, as they were deteriorating causing fluctuating connection resistance.
- A new cell was wire bonded with two wires per terminal, to reduce the heat generated by the connection.
- Extra insulation was added around the rig to further reduce both inline and perpendicular losses.

- The 4-wire cable set up was chosen, over the 2-wire set up, as it resulted in the smallest thermal differences at the face of the cell where losses were measured.

The corresponding results for this new setup are shown in Figure 25. The results are significantly more consistent, generating good results across the temperature range, which had not been achievable with the original setup. The thermal differences at the loss end are now halved, from 2-3 °C to 1-1.5 °C, indicating decreased losses through that surface.

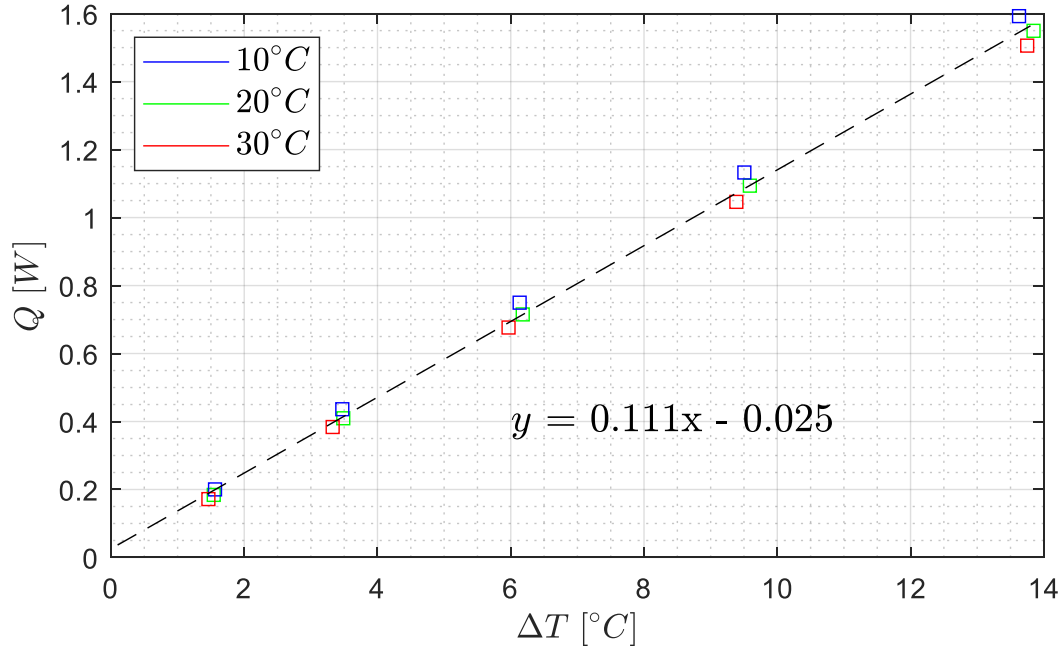


Figure 25: CCC results for M50T after rig and setup improvements.

The experimentally calculated CCC has a value of **0.111 W/K ± 3%** for a wire bonded LG M50T. This is 20% lower than the tab welded CCC. The drop in thermal performance can be explained using the insight from the model. The wire bonds are not only more resistive than the tabs, but they also focus additional heat generation at the positive (insulated) end of the cell. This has a similar effect to a linearly decreasing heat generation in the cell ($m < 0$), in Eq. 12, which reduces the CCC, compared to uniform heat generation, as it moves heat further away from the cooling. Since this type of electrical connection is more representative of real applications, than a tab welded connection, this lower value of CCC is more representative for base cooling, than the value of the tab welded CCC_{Base} found in 3.2.3 Results & Discussion. It can be hypothesised that reducing the electrical resistance of the electrical connection would improve the CCC; thus more/thicker wires, ribbon welding, or laser welded tabs should all help improve the thermal performance of base cooled cylindrical cells in applications.

3.5 CCC Measurement Guidelines

Using the insights gained from this work, new guidelines can be suggested for making accurate and consistent measurements of the CCC.

- Keep all losses as low as possible.
- Ensure that the heat flow through electrical connections is managed to maintain minimal losses.
- The constant temperature boundary condition point for cooling should be as close to the cell as possible.
- The cell should be measured under realistic conditions, i.e. under pressure, as much as possible.
- Reliable, consistent, and realistic electrical connections must be used.

3.6 How can the CCC be used?

The new understanding that the model has provided means that it is necessary to re-assess how the CCC can be used. Its dependence on the heat profile and losses means that the CCC in real applications is different from that measured in the bespoke rig in the lab. The CCC of a cell is a variable property with many dependencies. However, the CCC still is a relevant and useful component of a cell's thermal information that is currently unknown for many cells. By strictly defining the measurement criteria, a fixed CCC for each cell can be defined that allows for comparisons across different cells, at a consistent and known operating point, making the measurement of the CCC similar to typical thermal metrics. While it is not possible to use this to accurately predict behaviour when the electrical and thermal boundary conditions change, it does allow for cell and cooling comparisons and provides a useful starting point for understanding the thermal behaviour of a lithium-ion cell. Highlighted below is a list of ways the CCC can and cannot be used.

The CCC can be used to:

- Choose the best cooling system for a cell.
- Compare cells for cell selection.
- Give a starting point for understanding the thermal performance of a cell.

The CCC cannot be used to:

- Predict thermal differences in applications.
- Model the heat transfer of cells.

- Compare cells when a combination of cooling systems may be used (*new CCCs would need to be measured*).
- Compare cells when using unusual/bespoke electrical connections (*new CCCs would need to be measured*).

3.7 Conclusions

The work in this chapter presents a new way to calculate and display the CCC. Heat flow is plotted against the temperature difference measured across the cell, to display a linear relationship where the gradient of the line of best fit is CCC of the cell. The new method simplifies significantly the calculation of CCC for both pouch and cylindrical cells, decreasing the uncertainty in the determined CCC values compared to the previous method.⁹⁸ It is shown that CCC experiments must cover the complete thermal range of the cell being tested, to help ensure useful and accurate measurements are made.

A successful experimental rig for determining the CCC of base cooling for cylindrical cells is proposed. A tab welded connection is used at both the positive cap and negative base of the cell. Although not the industry standard for base cooling, this type of connection allows optimal performance of the cell under base cooling, due to negative terminal heat generation being at the closest position to cooling rather than the furthest away (when connected at the shoulder), giving a theoretical maximum CCC_{Base} for the cell. The proposed CCC procedure for the CCC_{Base} of a 21700 cell gives consistent results across multiple currents, SoCs and ambient conditions. This consistency indicates that a single value of CCC_{Base} per cell is required to describe its thermal performance.

This work displays how the CCC provides valuable thermal information that, combined with additional metrics, enables the thermal comparison of different cells for down selection during pack design. The CCC_{Base} of the 18650 cell tested is 16% lower than that of the larger 21700 cell, indicating that the latter is superior. However, when dividing the CCC_{Base} by the cooled area of the bases, the 18650 cell is found to reject 13% more total heat for the same size cooling area. Furthermore, the 18650 cell would also generate less heat for the same C rate, as its resistance at 1 Hz was 20% lower. The 21700 would therefore generate 250% more heat and have a 180% larger thermal difference along its axial length for an equal C rate. The comparison between form factors is not fair, as the 18650 was a hybrid cell and the 21700 was an energy cell. A hybrid cell has its electrodes and internal structure designed to provide a balance between energy storage and power delivery, whereas an energy cell is designed to maximise its

energy storage capability, sacrificing power delivery and possibly thermal performance. Nevertheless, this comparison demonstrates the equal importance of understanding heat generation alongside the CCC when designing a cell or down selecting a cell for a particular application.

A second CCC rig is developed to measure the CCC of base cooled cylindrical cells using wire bonded electrical connections. While this is a more application-relevant connection, initial attempts at measuring the CCC revealed inconsistencies with the measurement of the CCC. CCC values varied by up to 75% due to small changes to the rig and setup. To help diagnose the root cause of this variation, two models are developed so that the potential variables impacting the CCC measurement could be varied independently to assess their impact.

One of the models developed for this study uses the one-dimensional steady state heat transfer equation to explore the meaning and capabilities of the CCC cell property at a fundamental level. Identifying difficulties in conducting experimental CCC measurements, this work uses this simple model to identify the variables that impact the CCC of a body and its measurement with real losses. Solving the model under perfect boundary conditions, the CCC is shown to be equivalent to twice the thermal conductance of a body, if its thermal conductivity and heat generation are uniform. If the heat generation is non-uniform, the CCC becomes dependant on the shape of the heat profile, where it is improved when more heat is generated nearest the cooled face. Similarly, if the thermal conductivity is non-uniform, the CCC is dependent on its profile and is improved when cooling is nearest the region of lowest conductivity. The dependence of the CCC on the shape of the heat profile means that the CCC is likely non-constant as a cell charges/discharges through its SOC window. Conversely, the CCC is constant during the measurement of the CCC, since it is measured under conditions where the cell is under a fully developed and stable internal thermal profile, and at constant SOC and current.

To explore the impact of real losses, the model was solved also with real boundary conditions. The results showed that, for a homogeneous body, there is a fixed relationship between the losses in-line to cooling and their impact on the measurement of the CCC ($y = 1 - \dot{Q}_{LR} / 1 - 2\dot{Q}_{LR}$, where $\dot{Q}_{LR}$ is the ratio of heat loss to total heat, and y is the ratio of the measurable CCC and its ideal value). This relationship changes if either the heat generation or conductivity is inhomogeneous. These findings highlight the importance of driving losses as low as possible when making measurements of the CCC. A simple three-dimensional model in MATLAB was used to confirm that, while losses perpendicular to cooling can impact the measurement of the

CCC, their impact is significantly lower than that of losses in-line. The knowledge that the CCC of a cell is impacted by losses means that the CCC of a cell in application will likely be different to that of the CCC measurement in a bespoke testing rig in the lab.

The knowledge from these models was used to create updated guidelines for measuring the CCC that focus on minimising losses and ensuring that conditions are realistic for intended applications. These guidelines should help create a strict operating point for measuring the CCC, allowing for consistent comparisons between cells and cooling. The models also enabled a list of recommendations to be created about how the CCC can and cannot be used. Since the CCC is dependent on the specific boundary conditions and is variable as a cell cycles through its SOC, the CCC cannot be used to accurately predict thermal behaviour in real applications. However, the CCC provides relevant thermal information than is currently unobtainable from the information on cell datasheets, providing a useful standardised comparison point for choosing the best cells or cooling system.

Chapter 4: The Effect of Test Conditions on Benchmarking Cylindrical Lithium-ion Cells

The work presented in this chapter is based on “M. Waseem Marzook, James Eaton, Mohammad Amin Samieian, Yatish Patel, Gregory Offer, Monica Marinescu, **The Effect of Test Conditions on the Relative Performance of Cylindrical Lithium-ion Cells**, *Journal of Energy Storage*, Volume 105, 2025, 114485, ISSN 2352-152X.”

James Eaton provided the following contributions to the work presented in this chapter: i) assisted with the conceptualisation and design of the experimental rigs and procedures ii) assisted with performing the experiments, iii) assisted with the thermal data analysis and fitting of the drive cycle equations, and iv) assisted the review of the journal article before submission. Dr Mohamed Amin Samieian assisted with improvements to the visualisation of Figure 31 and Figure 34 in this work.

4.1 Introduction

The previous chapter established that the CCC requires strict standardised conditions to be an impactful thermal metric for the comparison of cell thermal performance. However, it is well understood that cell performance is highly dependent on several variables, such as, current, temperature, SOC, and degradation. Real applications of cells in battery packs, such as automotive, require cells to perform under conditions that would be considered far from “standard”, using specific cooling systems, and variable current loads. This highlights an important concern with the standardised testing of lithium-ion cells – Are cell performance comparisons made under standardised conditions true when cells are used in application? Can choosing a cell based on performance assessed under standardised tests, lead overlooking a cell that may have been superior for the application conditions?

In this chapter, an overview of the aims of this study will be presented followed by a detailed description of the test procedure and experimental setup. Six commercially relevant 21700 cylindrical cells are tested under base cooling and natural convection, for an array of loads. A percentile-based ranking system is used to assess the cells thermal and electrical performance

under the different loads and cooling. Part of the array of loads is a series of drive cycles with increasing baseline and peak powers. The performance from these drive cycles is assessed to investigate the translatability of both thermal and electrical performance across the ranging power levels.

4.2 Aims

This work aims to assess the following question:

Does the cell that performs best under standardised conditions, perform the best under application-focused conditions?

If this statement is false, then cell datasheets cannot be trusted for the selection of cells for any application that deviates from the standardised conditions the cells are tested under. This will be assessed via testing of the validity of using datasheet specifications and standardised experiments for the down-selection and performance prediction of cylindrical lithium-ion cells. To this end, a test procedure is created to cover a range of tests for different types of performance, e.g. power capability, usable energy, thermal performance, under realistic conditions, such as constant power, irregular load profiles and different types of cooling. Multiple 21700 cylindrical cells of varying energy densities are chosen, and predictions are made using the available information on their datasheets. The cells are compared across the different tests and conditions, with the key focus being on relative changes in performance between cells under different types of tests and cooling conditions. This study aims to assess the translatability of cell performance from one set of specific conditions to another.

4.3 Test Procedure

The standardised sizing of cylindrical cells leads to specific design considerations when designing cylindrical packs. Since a high energy (5 Ah) 21700 cell has the same dimensions as a high power (4 Ah) 21700 cell, it is possible to create packs of the same size with different capacities, and packs of different sizes with the same capacity. As a result, for a given power load on the pack, the corresponding load on individual cells can vary significantly. For example:

- For packs of equivalent dimensions, i.e., with the same total number of cells, undergoing the same load, the average cell-level current is identical between packs, irrespective of cell capacity.

- For packs of equal capacity, i.e., with a different number of cells, the average C-rate of the individual cells will be the same in both packs, and therefore current will be different depending on capacity, where C-rate is the capacity rate, defined by the current (A) with respect to the nominal capacity (Ah) of a cell.

The tests in this work are chosen to represent a range of applications and scenarios, shown in Table 5. Most of the tests focus on discharge comparisons. Although fast charging is actively pursued by the industry, many of the chosen cells have a datasheet maximum charge around 1 C. Due to safety considerations, the cells were not taken significantly outside manufacturing specification. Four conditions/characteristics were identified to be of interest:

1. The resistance of the cell: understanding the resistance of a cell is crucial to understanding the heat that would be generated when the cell is under load. The resistance test is designed to test if an ohmic resistance measurement made at a frequency more relevant to most applications differs from the 1kHz (i.e., 1 ms period) resistance given on cell datasheets. For this test the resistance of the cell is calculated from the voltage drop during a current interrupt from 1 C, taken at 1 s after the current has been switched off, at 10% SOC intervals.
2. The cell performance for constant current discharge: the continuous current discharge tests are designed to act as a reference for cell performance, while also emulating the performance in applications imposing constant loads for significant lengths of time.
3. The cell performance for high current cycling: the high-rate cycling is designed to test the cells' performance under extreme current rates, in terms of their ability to continue to provide usable capacity and their heat retention, when discharged at a high rate following fast charges.
4. The cell performance for a (synthetic) power-controlled drive cycle: the pulsed simplified drive cycle is designed to test the cells under a profile relevant to automotive applications, in which batteries may experience low average discharge rates with high-rate peaks for short periods of time.

Table 5 - list of all tests carried out, all cells use the same voltage limits of 4.2V and 2.5V.

Purpose	Main test	Detailed test
1: Resistance – Determine resistance over a relevant time scale.	1 C 10% Discharge Pulse	1. C/2 CCCV charge – 4.2 V, $I < 250$ mA 2. 1 C CC Discharge – 6 min or 2.5 V 3. Rest – 10 min 4. Loop back to Step 2. until 2.5 V is reached
2: Standard Rate Continuous Current Discharge – Moderate load continuous current comparison of capacity and temperature for same C-rate or same current.	1 C Discharge	1. C/2 CCCV charge – 4.2 V, $I < 250$ mA 2. 1C CC Discharge – 2.5 V
	5 A Discharge	1. C/2 CCCV charge – 4.2 V, $I < 250$ mA 2. 5A CC Discharge – 2.5 V
3: High-Rate Continuous Cycling – High-rate continuous load comparison for fixed number of cycles.	1 C Charge 2 C Discharge x10	1. 1C CC Charge – 4.2 V 2. 2C CC Discharge – 2.5 V Repeated for 10 total cycles
4: Pulsed Simplified Drive Cycle – Drive cycle equivalent of the 5 A discharge test.	4.9 A mean drive cycle	1. C/2 CCCV charge – 4.2 V, $I < 500$ mA 2. Drive cycle – See Figure 26

The charge for Test 3 in Table 5 does not contain a CV hold, as the aim of the test is to determine the impact of high rate cycling between the cell's voltage limits, including any historic effects that build up from cycle to cycle, a CV hold would suppress the impact of these effects, thus has not been included. The drive cycle for Test 4 in Table 5 follows the profile shown in Figure 26. The profile created has 3 sections: rest, baseline, and peak; this was deemed the simplest profile to still contain all the fundamental features of a drive cycle. The cycle is as follows: 0 W for 6 s, 27 W (P_1) for 8.25 s and 36 W (P_2) for 0.75 s, as shown in Figure 26, repeated until the lower voltage cut-off, 2.5 V, is reached. The cycle period was chosen to be $\frac{1}{4}$ of a minute so that the peak remained a short pulse. The power values were chosen as they equate to an average current of 4.9 A, this gives it an equivalency with the 5A discharge. Further details on how this drive cycle was created are given in 4.5.3 Performance under Pulsed Simplified Drive Cycles, along with the results and analysis of numerous variations of P_1 and P_2 .

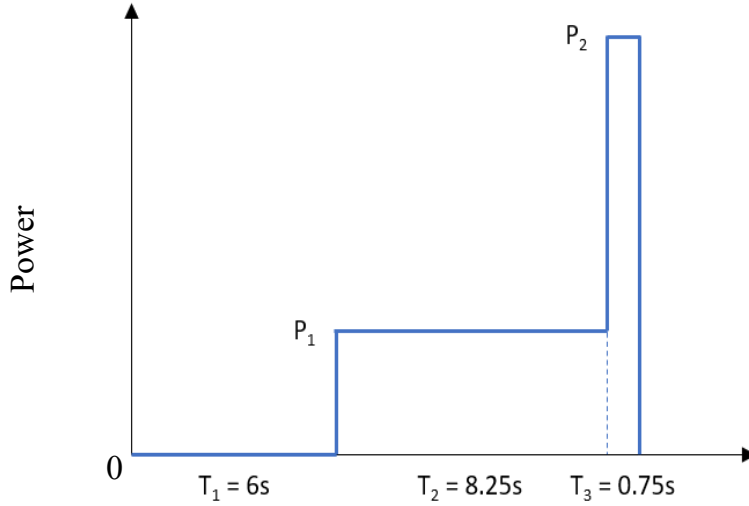


Figure 26 – Generic drive cycle power profile, where the values of P_1 and P_2 can be varied independently. Recreated from Ref. ¹⁸⁰

All tests carried out used an upper voltage limit of 4.2 V and a lower voltage limit of 2.5 V as the voltage cut offs. Before every discharge test, the cells were allowed to rest for 2 hours. Each test was carried out in a partially insulated natural convection condition and under base cooling (defined in detail in the following section), in order to compare the effect of the specified cooling approach. The analysis in this study focuses solely on cell level performance under the two significantly different applied boundary conditions; the performance of the cooling systems themselves is not the subject of study. The natural convection tests were carried out on the same cells following their base cooled tests; therefore, it is noted that the cells are minimally degraded between the two cooling tests. All the comparisons are made at beginning of life, therefore degradation and potential impacts to long-term life are not considered here and remain the subject of future work.

4.4 Experimentation

4.4.1 Experimental Setup

The experimental rigs for this study were carefully designed to create pack relevant conditions. The cylindrical cells are connected electrically via ultrasonic wire bonding at the positive cap and top shoulder (negative terminal) of the cells. This is one of the industry standard connection methods used in cylindrical cell packs with base cooling. A small 3D printed ABS mount was designed to hold two laser-cut aluminium terminals (1mm thickness) near the cells; this mount was glued to the top of the cells. The cells were stripped of their plastic coating to allow for

wire bonding. Panel mount 4mm banana plug sockets were attached to the aluminium terminals, to allow connection to the cell cycler. Two 300 μm wire bonds were ultrasonically bonded, using a Hesse Bondjet BJ955/959, from each aluminium terminal to the positive cap and negative shoulder, resulting in 4 wires in total, as shown in Figure 27.



Figure 27 - Top view of a wire bonded cell before being placed in the test rig. Recreated from Ref. ¹⁸⁰

The cell was then secured in a 3-D printed ABS test rig which clamped the base of the cell to a thin 3mm aluminium plate through a layer of thermal interface material (0.5 mm thick, thermal conductivity – 3.2 W/mK), shown in Figure 28. The test rig was then secured to a separate 3 D printed ABS base, shown in Figure 28a. For the natural convection tests, the base held an empty volume; for the base cooled tests, the base housed a water-cooled block (40 x 40 x 12 mm – L x W x H) that contacted the thin aluminium plate through a layer of thermal interface material (0.5 mm thick, thermal conductivity – 6 W/mK). The thermal interface material between the cell and the aluminium plate has a lower conductivity than the one between the aluminium plate and the water block, because this layer was required to be harder so that the base of the cell does not push through and electrically contact the aluminium plate. Figure 28 shows the test rig, base, and cooling block with the thermistor positions on the cell identified as red circles, as well as an isometric view, for clarity.

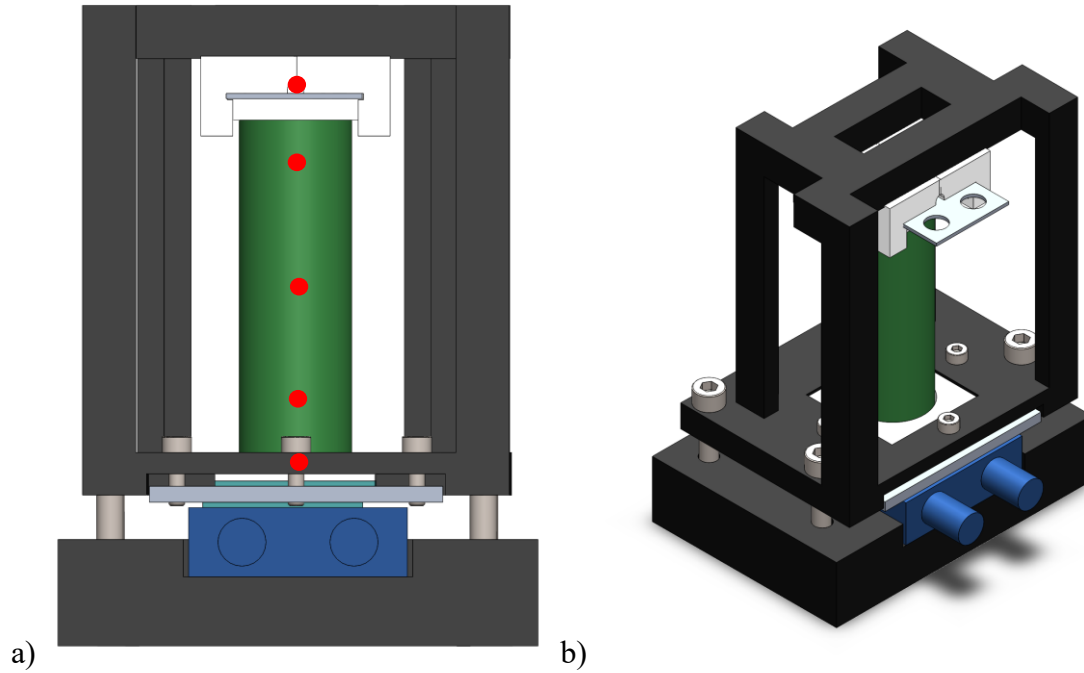


Figure 28: Side profile (a) and isometric view (b) of the cell test rig, shown here without insulation for clarity. The thermistor positions are shown in red. Recreated from Ref. ¹⁸⁰

Insulation was cut and placed along the four open sides of the test rig, out of Armacell Armaflex AF sheet type O insulation (32 mm thick). The whole structure was placed in an insulated box, shown in Figure 29 (lid removed in the image). The box is made out of Rapid Styrofoam (50 mm thick), cut to create a box (350 x 230 x 160 mm – L x W x H), leaving an internal cavity (250 x 130 x 160 mm), which is split by a cut piece of the Armaflex insulation to create two subsections, each large enough for a single rig, i.e. a box for two cells tested simultaneously. The cables and water hoses exit the box via cut-outs in the front, where any remaining gaps were filled with the Armaflex insulation. The box was then placed in a Binder KB53 set to 25 °C and 60% fan speed, which maintains a constant ambient temperature (± 0.5 °C). The box prevents the airflow from affecting the thermal boundary of the cells inside. The base cooling water was pumped and thermally controlled using a ThermoFisher Scientific Arctic A10-AC200 refrigerated circulator, the temperature was set to 25 °C, and the pump speed to high. These settings result in the water block effectively operating as a 25 °C constant temperature boundary condition, verified by a thermistor placed in between the water block and aluminium plate.

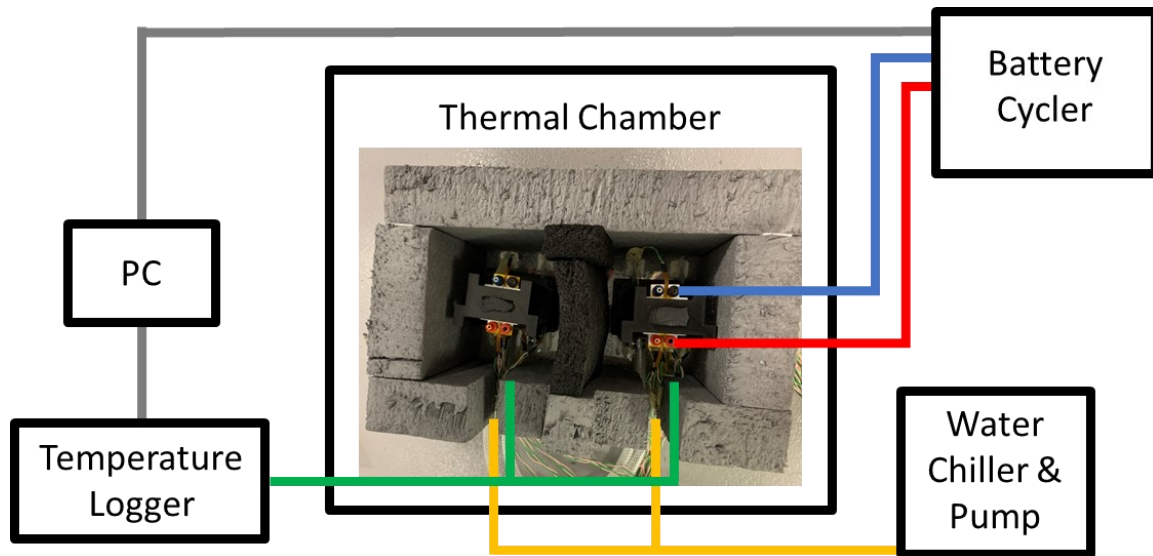


Figure 29 – Experimental test setup, depicts insulation box created to test two cells simultaneously, and the connections between the rigs and auxiliary systems. Recreated from Ref. ¹⁸⁰

This setup results in a high resistance heat conduction path from the top of the cell via the electrical connections, with almost no air flow over the top and sides of the cell, giving minimal cooling via natural convection. Under base cooling, the cell has a low resistance conduction path to the cooling fluid. Under natural convection cooling, the thermal mass of the aluminium plate is expected to absorb a small amount of heat, but only be able to transfer away relatively small amounts of this heat via weak natural convection cooling, as there is no forced air flow. This setup ensures that the surfaces of the cell are well insulated from the ambient air, with the exception of the base. This is done in order to emulate the thermal insulation they would experience when operating inside a battery pack. The two cooling scenarios created are: insulated sides with base cooling, and insulated sides with base convective cooling. The second scenario aims to test the effect of the base cooling only, by leaving all other thermal conditions the same. The removal of the base cooling leaves the minimal natural convection in the trapped air pocket to be the dominant heat transfer mode. Every cell had five NTC thermistors (Semitec 103JT-050, 10 k Ω , accuracy 1%) glued to it with thermal epoxy (MG Chemicals 8329TFS). Their positions are shown as red dots in Figure 28 and tabulated in Table 6; distances are given from the base of the cell upwards.

Table 6 - thermistor locations

1	Positive Cap
2	Can – Top – 55mm
3	Can – Middle – 35mm
4	Can – Bottom – 15mm
5	Cell Base

The cells are cycled using a BioLogic BCS-815 (Accuracy – Voltage [$\pm 0.01\%$ of value ± 0.3 mV], Current [$< 0.05\%$ of value ± 3 mA]), and the thermistors (Accuracy – Resistance [1%]) are measured using a 16-bit ADC connected to an Arduino Uno, calibrated at 25 °C and 45 °C, diagrammatically depicted in Figure 29. The use of this equipment means that the measured values of voltage, current, charge passed, and temperature are highly accurate, and unlikely to affect the outcomes of this work. Although no repeats are performed in this study, the cells are all of commercial quality, thus the BoL performance of these cells is expected to be very consistent, with cell-to-cell variation unlikely to change any of the outcomes from this work.

4.4.2 Cell Information & Datasheet Predictions

Six 21700 cylindrical cells of varying energy densities and chemistries were chosen. Their key datasheet parameters are listed in Table 7. The T48P, as it has been named in this work (Tesla-4.8Ah-Panasonic), was taken from a 2018 Tesla Model 3 Long Range with approximately 3000 miles driven i.e., approximately 10 equivalent full cycles, given a specification full range of 300 miles. This cell, along with the Murata VTC6A-AM, have no datasheet parameters as we were unable to acquire datasheets for these cells, thus they must be excluded from the following datasheet comparison. For the purposes of setting C-rates for these two cells, their capacities are estimated to their nearest equivalent cell, the VTC6A-AM to the VTC6A, and the T48P to the 48X.

Table 7 - Datasheet parameters for six cells

	Energy			Power		
	M50T	48X	T48P	VTC6A-AM	VTC6A	P42A
Manufacturer	LG Chem	Samsung	Tesla	Murata	Murata	Molicel
Capacity (mAh)	4850	4800	4800	4100	4100	4200
Energy (Wh)	17.61	17.47	-	-	14.76	15.5
Chemistry	NMC	NCA	-	-	NCA	NCA(M)
Max Discharge Current (A)	14.55	18	-	-	40	45
Std Discharge Current (A)	0.97	4.8	-	-	4.0	-
Max Charge Current (A)	3.395	18	-	-	9.0	8.4
Std Charge Current (A)	1.455	1.584	-	-	4.5	4.2
Temperature Limit (°C)	55	60	-	-	60	60
1kHz AC IR (mΩ)	25	13	-	-	5-15	10
C-Rate [1C] (A)	4.8	4.8	-	-	4.1	4.2

Using the information gained from the datasheets, shown in Table 7, predictions for which cells will perform best in each test are given in Table 8. The most relevant datasheet information for each test is given in the third column, displayed in descending order of relevance. Based on this information the best power cell, best energy cell and the best overall cell are determined, if possible. As shown in Table 8, it is not always clear which cells should be chosen as the optimal ones, especially when sacrifices in one characteristic result in gains in another. Choosing a “winner” is particularly difficult for the standard continuous load comparisons, where it is impossible to make a prediction on whether the loss in capacity will lead to sufficient gains in thermal performance for the power cells vs the energy cells. Additionally, it may often

depend on the details of the application requirements as to whether capacity or thermal performance is more important. A key point to note is that while a clear distinction has been made between power and energy cells, there is no true line that separates these definitions, instead all cells lie on a continuous scale trading higher energy density for higher power capability. Coupling this with the identical geometry of these cells, there is no reason not to make cross comparisons between “power” and “energy” cells, hence an overall best cell is also assessed.

Table 8 - Expectations of the best cells for each test based on information available in the cell datasheet, shown in Table 7

Test	Details	Relevant datasheet info	Best Energy Cell	Notes	Best Power Cell	Notes	Best Cell	Notes
1. Resistance	1 C 10% Pulse	1. AC IR	48X	Lower AC IR than the M50T	P42A	VTC6A could be better given the wide range of AC IR	P42A	Lowest overall AC IR
2. Standard Continuous Load	1 C Discharge	1. Max Discharge I 2. Capacity	48X	Higher max discharge current limit for slightly less capacity than the M50T	P42A	Highest max discharge current with better capacity than VTC6A	N/A	Cannot judge if capacity will counteract thermal performance between the power and energy cells
	5 A Discharge	1. Capacity 2. Max Discharge I	M50T	Highest capacity	P42A	Higher capacity than VTC6A	N/A	
3. High-Rate Continuous Cycling	1 C Charge 2 C Discharge 10 times	1. Max Discharge I 2. Max Charge I 3. AC IR	48X	Higher max charge current than the M50T	VTC6A	Higher max charge current than P42A	VTC6A	Test is sufficiently high rate that power cells would be expected to win
4. Pulsed Simplified Drive Cycles	Increasing CP drive cycles	1. Energy 2. Max Discharge I 3. AC IR	48X/ M50T	Cannot judge if the 48X's higher max discharge current will make up for its reduced energy. The M50T may be better for the early DCs, due to its higher energy.	P42A	Highest max discharge current and lowest AC IR, with higher energy than VTC6A	48X – P42A	Early DCs will favour the high energy cells. As the DC power increases, the power cells will become favoured.

4.5 Results and Discussion

4.5.1 Resistance test

The purpose of this test is to generate a value of cell resistance that is more relevant to many applications compared to the resistance at 1 kHz frequency. Typical automotive cycles have discharge profiles with pulses lasting from around a second to a minute, with continuous loads during charging. For this reason, it is important to assess the value of the resistance response of the cell at times longer than the 1 ms of the 1 kHz AC IR. The resistance was extracted from 1 C pulses of 6 min duration at 1 s after the pulse end. The resistance of a cell is expected to significantly vary with frequency, it is expected that 1 kHz is too high a frequency to be relevant for most applications. It is well understood that the resistance of a lithium-ion cell is dependant of the timescale of the measurement.³⁵ A 1 s resistance may capture more elements (with time scales up to 1 s) of a cell's resistance that will be active during application loads. The measured resistance value was found to be relatively consistent across the SOC range, while it increased, as expected, at the extreme states of charge (SOC).¹⁸¹ Additionally, the difference between the resistances calculated for the two cooling methods was within error of the equipment. Thus, the base cooled resistance values that were measured have been averaged across the SOC range and denoted as DC IRT (the tested internal resistance). These measured values are displayed in Figure 30 alongside the stated 1 kHz AC resistance value from the datasheet (AC IR). The datasheet for the P42A is the only one that includes a DC IR value, namely for a 10 A, 10 second pulse. The value given is 16 m Ω , displayed in Figure 30 as DC IR.

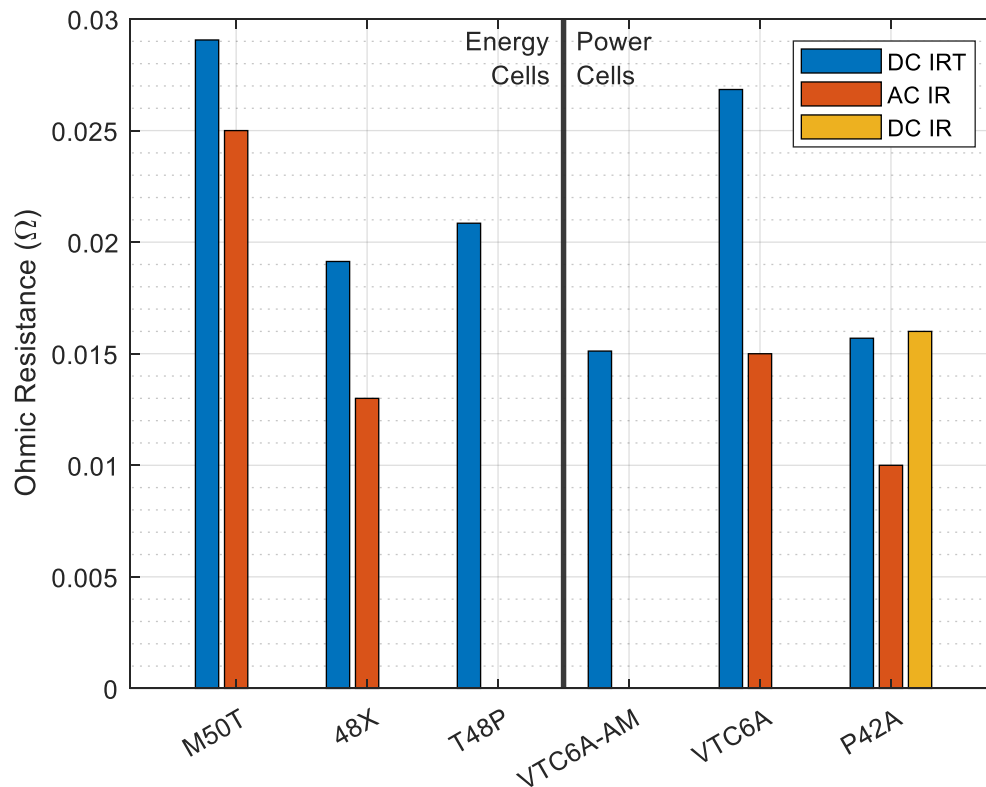


Figure 30 – Chart showing the measured resistance at 1s after pulse application, for 1C discharge pulses of 6min duration (DC IRT) against the datasheet 1kHz resistance (AC IR) for all 6 cells. The P42A also lists a DC IR resistance (16mΩ). Recreated from Ref. ¹⁸⁰

For almost all cells the DC IRT measured in this test is higher than the quoted AC IR, as expected given the longer time scales of the current pulses used in this test. The predicted best energy cell was the 48X, because its datasheet AC IR is much lower than that of the M50T, excluding the T48P, for which there is no information. The 48X does have the lowest DC IRT, 34% lower than the M50T and 10% lower than the T48P. The predicted best power cell was the P42A, however the VTC6A-AM has a 5% lower DC IRT value. This could not be predicted because no datasheet for the VTC6A-AM was available. Although across all the cells a lower AC IR is reflective of a lower DC IRT, they do not scale together. The difference between the two values ranges from 16% to 80% higher for the DC IRT compared to the AC IR. This helps highlight how misleading the AC IR information can be in making quantitative comparison between cells. Cells such as the VTC6A are significantly more resistive at lower frequencies, whereas cells such as the M50T perform similarly across both these time scales.

The P42A's measured DC IRT value (15.7 mΩ) is almost identical to the datasheet DC IR value given. Thus, if this metric is standardised and adopted by other manufacturers, it can help provide a significantly more relevant resistance value for these cells. These results show the

need for further work to study the relationship between resistance values at various time scales, so that the most relevant resistance or set of resistances can be used on cell datasheets.

4.5.2 Performance under Various Electrical Loads and Cooling

The performance of the six different cells under the two cooling systems will be compared across (i) standard continuous load discharge (at 1C and 5A), (ii) the high-rate continuous cycling and (iii) a drive cycle. To make testing easier a drive cycle may be converted to an average current to test a simpler continuous load; this will be presumed to be “equivalent”. The drive cycle used for this analysis has a mean current (in time) of 4.9A, which is aimed to provide a comparison against the 5A continuous load, to test the truth of this equivalency. Section 4.5.3 contains analysis of multiple additional drive cycles aiming to assess how translatable performance is across varying levels of power for a specified electrical load and cooling condition. The key performance metrics to be compared across these cells and tests are: the usable capacity under the load (for the high rate cycle test, this is from the final discharge), the maximum cell temperature recorded (occurring at the end of discharge), and the maximum temperature difference across the surface of the cell (occurring at the end of discharge). The highest performing cell for this test will have the highest available capacity and/or the lowest maximum temperature and temperature difference. Although the cells do not reach critically unsafe temperatures, lower maximum temperatures and gradients are desirable, as it is assumed that lower temperatures will be indicative of better long-term performance, i.e., lower rate of degradation.⁵³ Temperature profiles of the VTC6A under 1C discharge for both cooling conditions are included in Appendix B.1, to present an example of the temperatures analysed in these tests.

However, comparing the absolute values of these performance metrics across the different sets of conditions may not be feasible. For example, cells under base cooling are expected to have lower absolute values of temperature than under natural convection cooling, since the former condition represents active cooling. This makes the comparison of how well each cell performs under the two cooling systems difficult. Cell 1 may reach a maximum of 30 °C in one of the base cooled tests and 50 °C when in the natural convection condition under the same load, while Cell 2 may reach 25 °C in the first test and 55 °C in the second. In this situation, Cell 1 has an apparent improved performance in terms of maximum temperature reached over Cell 2 when under natural convection. These types of performance changes need to be captured, to make accurate assessments of comparative cell performance.

Percentile-based Ranking System

The aim of this work is to assess whether different application-relevant test conditions result in different outcomes in terms of which cells perform best. Thus, the most important aspect to consider is the comparative placement of each cell under each set of test conditions, rather than the quantitative comparison of the results from each test. Thus, the absolute results will not be presented in this work but is available in the following Zenodo database (<https://doi.org/10.5281/zenodo.7385979>). Due to the limited number of cells tested, a percentile-based ranking system is used to rank the cells by two key types of performance: capacity and surface temperature. This percentile-based ranking will help highlight even subtle changes in the comparative performance of the cells, as the cooling and load changes. Each metric, capacity, maximum surface temperature, and maximum surface temperature gradient, is calculated using Eq. 18, evaluated separately for each electrical load test and cooling condition, where the cells are ranked in order for each metric and the metric values for the best and worst cells are based on the resulting order for that metric. The score for each cell and performance criterion is a value between 0 and 100, normalised for that performance metric and test: 100 is the score for the best cell in that test and 0 is the score for the worst performing cell, for each metric separately. For example, a score of 80 for capacity in the 1C discharge test under base cooling indicates that the particular cell has a capacity ranked in the 80th percentile of cells tested under base cooling for the 1 C discharge test. Maximum temperature and temperature difference are scored separately, then averaged into a single “thermal score”. This system is devised to be robust for the case in which many different cells are tested and/or different weighting are more appropriate to be given to thermal versus capacity performance.

$$\text{Score}_{\text{Cell X}} = \frac{\text{Metric Value}_{\text{Cell X}} - \text{Metric Value}_{\text{Worst Cell}}}{\text{Metric Value}_{\text{Best Cell}} - \text{Metric Value}_{\text{Worst Cell}}} \times 100 \quad \text{Eq. 18}$$

Graphical Comparison of Rankings Across All Test Types

Figure 31 combines the calculated capacity and thermal ranking scores for all six cells for each of the three continuous load tests and the drive cycle, under the two cooling schemes, where a higher score on either axis represents a better ranking. The ranking region of each cell is shaded and labelled by the colour clouds. This plot helps to visualise comparative rank changes caused by the cooling method applied (regular thickness vs bold symbols) and the type of current load (marker shape). It is important to highlight the region in the bottom right of the plot, where the M50T and T48P cells clearly swap positions, depending on the cooling and type of current. As

an example, under a 5A load in the natural convection condition, the M50 has an overall better ranking compared to the T48P, with a 20% better thermal rank for only a 5% worse capacity rank. However, for the same load under the base cooling condition, the T48P has the all-around better ranking with a 20% better thermal rank and a marginally better capacity rank. Beyond the particularities of each cell's performance, there are three general key messages from this plot:

- The ranking of each cell changes significantly with the condition under which it is tested (illustrated by the large colour cloud) and the rank cloud overlaps with that of other cells, indicating that the relative positions change quantitatively when the test conditions change.
- The ranking region has a different shape for each cell, showing that individual cells vary differently for the same changes in operating conditions.
- Moving from one set of test conditions to another the ranking order of the best performing cells changes, thus achieving the goal to prove that the best performing cell under one set of conditions may not be the best performing cell under another set of conditions.

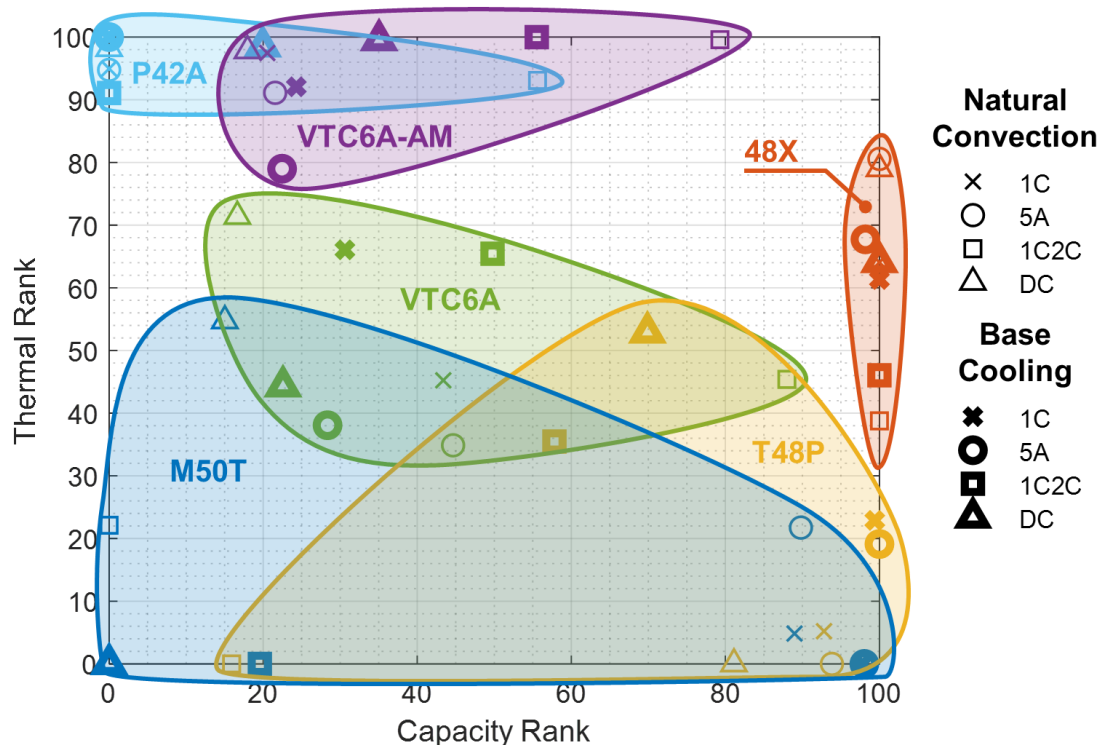


Figure 31: Thermal rank vs capacity rank for the six cylindrical cells tested. The range of each cell is shown by a coloured cloud: light blue for P42A, purple for VTC6A-AM, green for VTC6A, dark blue for M50T, yellow for T48P and red for 48X.

The display includes the results of eight experiments: 1C discharge, 5A discharge, 1C charge – 2C discharge cycle and a drive cycle (4.9A mean), each under both natural convection and base cooling. Recreated from Ref. ¹⁸⁰

Looking closely at Figure 31 there are no obvious trends, i.e. no cell becomes definitively better or worse under base cooling; under some load types a cell improves and under others its performance worsens. Particular features of individual cells are worth noting:

- The T48P is the only cell that has a definite improvement to its rankings under base cooling, however under the drive cycle it trades off its capacity slightly for a significant improvement in its thermal rank.
- The 48X performs best amongst the energy cells.
- The VTC6A-AM performs best amongst the power cells.
- In general, the power cells are clustered in the top left of the map, showing better thermal rankings, and energy cells generally fall in the bottom right, with better capacity rankings.
- For two cells that are closely matched on the map, such as the M50T vs T48P, the best cell is highly dependent on the particular set of test conditions. For continuous loads, the M50T and T48P perform very similarly, trading places with the changes in cooling. For the drive cycle, the performance of the M50T is significantly more limited, dropping to become one of the worst cells under this load, while the T48P's performance remains competitive.

The absolute performance changes are well understood, cooling can affect the internal temperature of a cell, impacting the cell resistance, thus changing both the temperature rise and final capacity extractable. Similarly, different loads can impact both the temperature and final capacity output of a cell due to differences between a cell's resistance at various time scales, a cell typically has lower resistance at shorter time scales compared to longer ones, thus drive cycles are often able to extract more capacity and cause less temperature rise. What may not be as well understood is how the impact of these effects differs from one cell to another. Physically, this can come from differences in the different elements that make up a cell's resistance. Two cells could have similar ohmic resistances but very different diffusion resistances, due to factors such as electrode and current collector thickness, position of internal tabs, electrolyte composition, and electrode composition and structure. In this case, when comparing between different loads, the cell with higher diffusion resistance, would display a much greater improvement in its performance in a drive cycle versus a continuous load, compared the other cell. Similarly, cells may have different responses to changes in temperature

due their internal composition and structure. One cell's resistance may be less impacted by increasing temperature compared to another, due to internal composition. Alternatively, one cell may have an internal structure that favours one cooling system over another (potentially seen by the T48P which performed very well under base cooling), by having a different base/can thickness, or different number and/or position of internal tabs. These examples highlight the multitude of ways the differences between cells can impact how they respond to changes in load and cooling, stressing the importance of comparing cells under the conditions that reflect the desired application.

4.5.3 Performance under Pulsed Simplified Drive Cycles

The goal of this set of experiments is to determine if cell performance can be translated across varying baseline and peak power. For this purpose, a simplified synthetic profile was created instead of using standardised drive cycles (WLTP, NEDC, Artemis, etc.), so that the peak and average powers, as well as their ratio, could be altered independently. The profile created has 3 sections: rest, baseline, and peak; this was deemed the simplest profile to still contain all the fundamental features of a drive cycle. The cycle is as follows: 0 W for 6 s, P_1 (W) for 8.25 s and P_2 (W) for 0.75 s, as shown in Figure 26, repeated until the lower voltage cut-off, 2.5 V, is reached. The cycle period was chosen to be $\frac{1}{4}$ of a minute so that the peak remained a short pulse. There are a total of 15 drive cycles with different P_1 and P_2 values, as listed in Table 9. The duty cycle of this drive cycle was derived from the standard WLTP drive cycle, chosen because it is the automotive standard for the UK and Europe.⁶⁷ The duty cycle is derived by: converting the WLTP class 3 (version 5) cycle into power for an example Vehicle X (table of values shown in Appendix B.2), replacing negative power with zeros (i.e., no regenerative braking), normalising the cycle against the maximum power, and separating out the cycle into 3 sections based on the percentile of power (bottom 0.1% (rest), 0.1-60% (baseline) and 60-100% (peak)). The duration of each step was created based on the percentage of time occupied by each of the 3 sections. The ratio of P_1 to P_2 in the WLTP drive cycle is the same as DC2, 3.6 – 13.5 W, based on the mean of the baseline and peak power. Starting from DC2 the rest of the values of P_1 to P_2 were created using a matrix of 5 values of P_1 (3.6, 9, 18, 27 & 36 W) and 4 values of $P_2 - P_1$ (3.6, 9.9, 18 & 36 W). The matrix uses $P_2 - P_1$ as metric instead of values of P_2 because the peak power is considered as an addition to the baseline power. To save test time not all combinations of potential drive cycles are tested, however tests cover low, medium and high combinations to for end-to-end coverage of the test matrix.

Table 9 - Power values of P_1 and P_2 , in W, for drive cycles 1 to 15

		P_1				
		3.6	9	18	27	36
$P_2 - P_1$	3.6	DC1	DC4	DC7		
	9.9	DC2	DC5	DC8	DC10	DC13
	18	DC3	DC6	DC9	DC11	DC14
	36				DC12	DC15

Drive Cycles Under Natural Convection

The simplified drive cycle profile developed for this work (Figure 26), based on the WLTP duty cycle, is intended to replicate in a simplified way the load conditions of real drive cycles. The inclusion of very brief large peak loads makes cell resistance a significant factor for these tests compared to the continuous load conditions, thus greatly affecting both the overpotentials and the heat generated by the cell, both which can limit the performance. The performance metrics for this test is limited to usable energy of the drive cycle (total discharge energy throughput at the end of the drive cycle) and maximum temperature reached (occurring at the end of the drive cycle), since trends across the 15 sets of cycles are examined, instead of scoring each cycle against each other. The thermal difference does not provide substantially new information that is not already indicated by the maximum temperature. Unlike in Section 4.2, energy is used instead of capacity, because these drive cycles use constant power loads rather than constant current. These drive cycles are loads designed to be application-oriented; for real applications, energy is a more useful metric than capacity. For the previous cycles, the use of energy delivered in discharge is less pertinent, as cell performance was compared under constant current loads, where capacity is typically compared over energy. The cell resistance under constant load remains relatively constant, only changing with SOC. In contrast, under drive cycles, the load contains a frequency component, thus it is important to capture this transient resistance behaviour by using energy as a metric.

Figure 32 displays the results of all 15 drive cycles under the natural convection condition, in terms of the usable energy dissipated during discharge and the maximum cell surface temperature reached. Each drive cycle number corresponds to a particular combination of P_1 and P_2 values, as shown in Table 9. General trends can be seen, such as a reduction in the usable energy per cycle and an increase in the maximum surface temperature as the power of

the drive cycles increases. There is a clear separation between the energy and power cells with regards to the usable energy of the drive cycles, with the energy cells delivering more energy than the power cells for low power cycles, with the gap reducing as the power increases. When considering the maximum surface temperature, all cells operate similarly for the low power drive cycles, while as the power increases the energy cells reach significantly hotter temperatures compared to the power cells. From DC13 on, both the M50T and T48P cells fail to complete the drive cycle without their surface temperature increasing beyond the 60 °C safety limit.

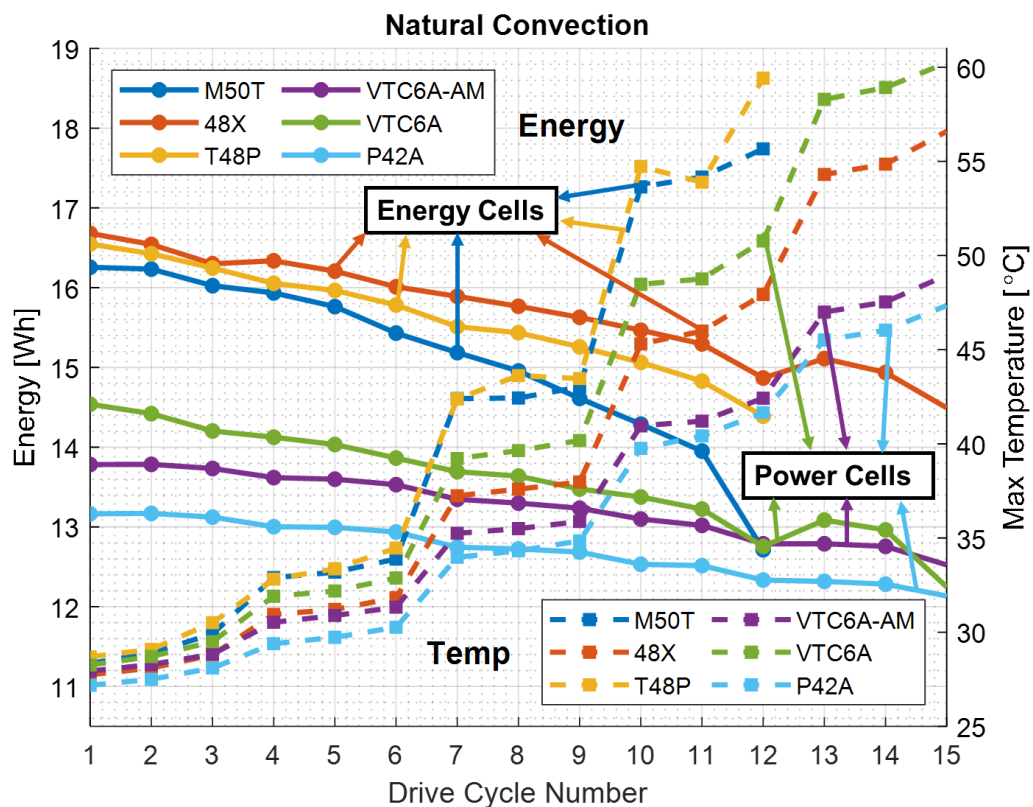


Figure 32 – Usable energy in discharge and cell surface maximum temperature reached for DC1-DC15 drive cycles, as defined in Table 9, under the natural convection condition. Energy and Power cells are defined as per Table 7, based on the cell datasheet. Recreated from Ref. ¹⁸⁰

Further analysis of Figure 32 indicates that the 48X is very clearly the best energy cell, delivering the most usable energy of any cell for all 15 drive cycles, while at the same time operating with a significantly lower maximum surface temperature than the other two energy cells (M50T and T48P). The best power cell is the VTC6A-AM, even though the VTC6A delivers more usable energy for 13 out of 15 of these drive cycles. This latter apparent benefit is due to the VTC6A consistently operating hotter than the 48X. In conclusion, there is no reason to choose the VTC6A over the 48X. The VTC6A-AM, while producing slightly less

usable energy than the VTC6A, operates with significantly lower maximum temperatures, giving it a tangible benefit over the 48X.

Drive Cycles Under Base Cooling

The results for the 15 drive cycles under the base cooling condition are shown in Figure 33. The three most notable changes under base cooling compared to the natural convection tests are:

- The T48P operates significantly better thermally, performing akin to the 48X, but still delivering less energy.
- The VTC6A-AM and P42A now perform near-identically thermally, thus the increased energy delivery of the VTC6A-AM makes it the clear winner amongst the power cells.
- Although both the M50T and the T48P can now complete DCs 13-15, the M50T delivers less energy than every other cell, falling below the power cells.

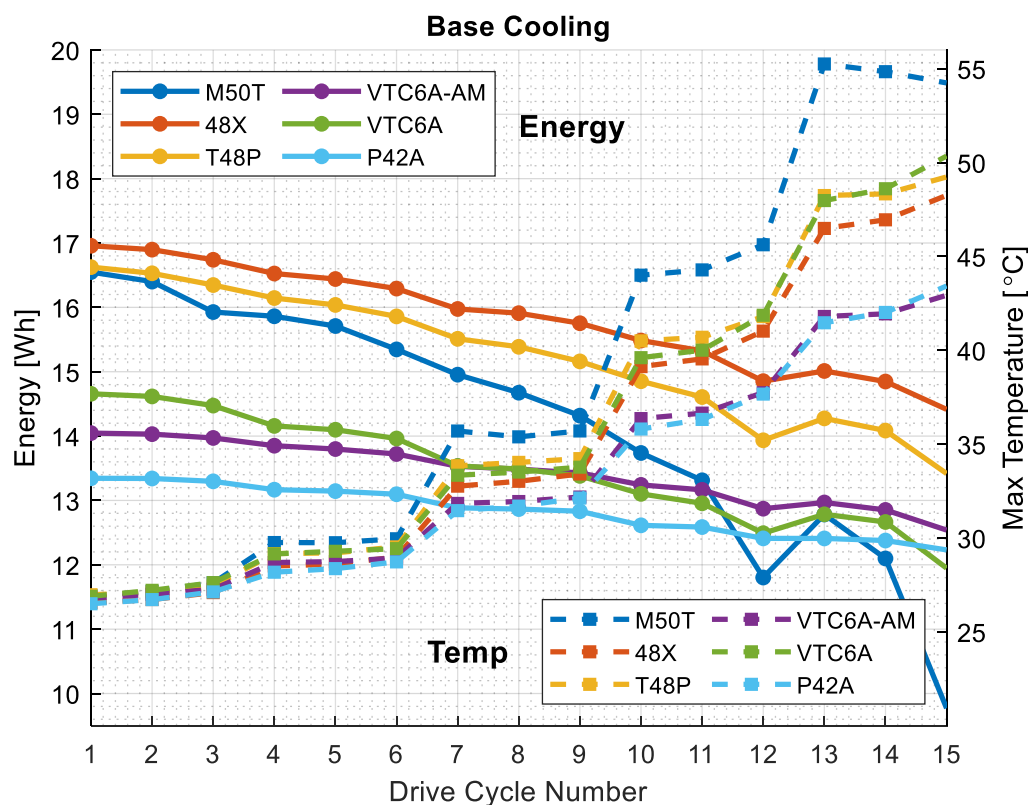


Figure 33 – Usable energy in discharge and cell surface maximum temperature reached for DC1-DC15 drive cycles, as defined in Table 9, under base cooling. Recreated from Ref. ¹⁸⁰

Linear Trends in Cell Performance during Drive Cycles

The use of a simplified profile for the drive cycle testing means that performance can be tracked across the different values of P_1 and P_2 in terms of their effects on usable energy and maximum

cell surface temperature. It was found that a linear equation (Eq. 19) can be fit to the trends in both maximum surface temperature and usable energy delivered, giving a good agreement to experimental data ($r^2 > 0.95$). The constant f_0 corresponds to the magnitude of the usable energy or maximum surface temperature when linearly extrapolated to the virtual drive cycle characterised by $P_1 = 0$ and $P_2 = 0$. In this extreme region, the dependence of these characteristics on P_1 and P_2 may be non-linear, leading to a f_0 value that is theoretically impossible (e.g., a T_0 value below ambient). For this purpose, f_0 is obtained from the equation corresponding to the DC 1 dependence (Eq. 20) as the low P limit, and substituted into Eq. 19, yielding Eq. 21 as the optimum fit for the available data for all DCs. This translation of the equation ensures that the fitted constant remains within the range of tested data, and not representative of an extrapolated impossible point, while also making it clearer which values of P_1 and P_2 are extrapolations below the tested data. The goodness of the fits to Eq. 4 is described in Appendix B.3.

$$f(P_1, P_2) = f_0 + bP_1 + p(P_2 - P_1) \quad \text{Eq. 19}$$

$$f_{DC1} = f_0 + 3.6b + 3.6p \quad \text{Eq. 20}$$

$$f(P_1, P_2) = f_{DC1} + b(P_1 - 3.6) + p(P_2 - P_1 - 3.6) \quad \text{Eq. 21}$$

The values for all the fitted parameters are given in a table in Appendix B.4. The fitted values are graphically represented in Figure 34, where each cell is positioned in terms of its energy loss per unit of power and maximum usable energy (Figure 8a) and its surface temperature increase per unit of power and maximum usable energy (Figure 8b). The cell surface maximum temperatures obtained in DC 1 are all similar, such that the values for T_{DC1} are not useful for differentiation between cells. As P_1 and P_2 increase, the energy delivered in discharge reduces and the maximum surface temperature rises, hence the values for b and p are negative for the energy equation and positive for the temperature equation. A high value of E_{DC1} and near zero values of all 4 b and p parameters characterise a cell that has a high energy output with minimal loss in energy, and a minimal increase in temperature as the load power increases. Given these criteria, high E_{DC1} and near zero values of all b and p indicate a more desirable cell; this target location is indicated by the * icon in the top right of each plot.

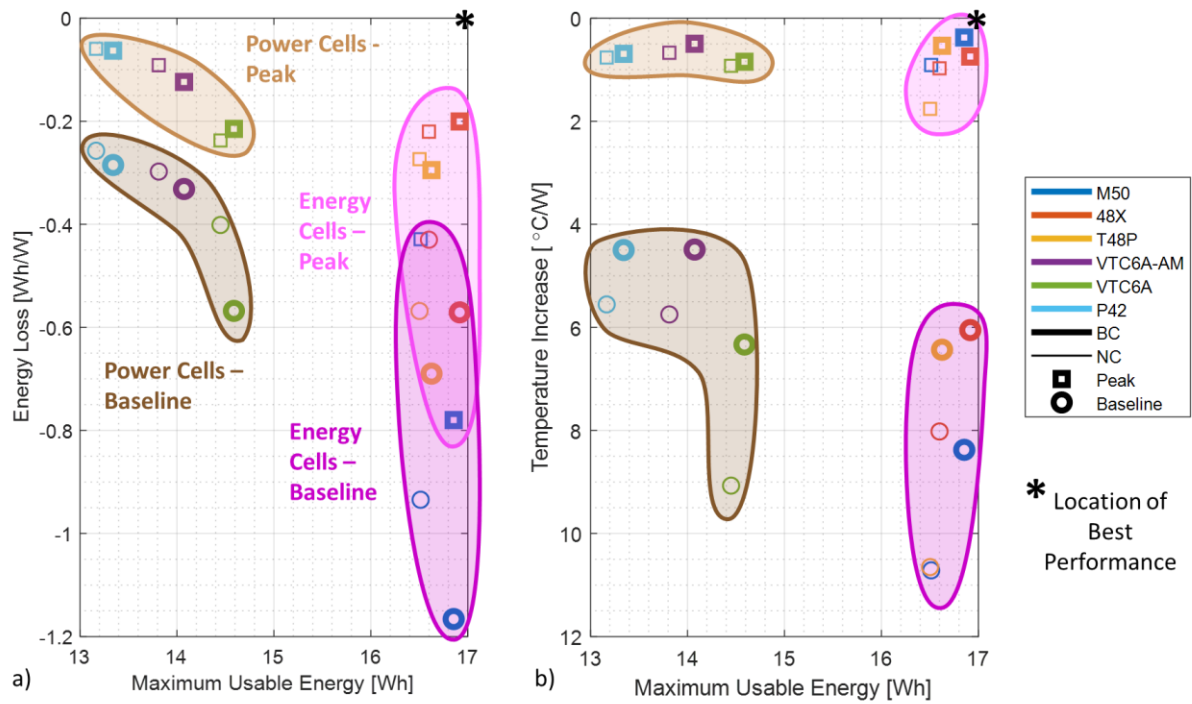


Figure 34: Fitted baseline (b) and peak (p) parameters for both (a) the energy and (b) the temperature variation of Eq. 21 plotted against maximum usable energy (E_{DC1}). Shaded regions highlight the groupings of the energy cells (pink) vs the power cells (brown), and the baseline (circles) vs the peak (squares) parameters. The thicker markers highlight the base cooled variables and the thinner markers the natural convection variables. Recreated from Ref. ¹⁸⁰

As expected, the parameter values in Figure 34 further support the conclusions from the analysis of the data in Figure 32. Figure 34 allows a clearer visualisation of the differences between baseline vs peak power, power vs energy cells, and base cooling vs natural convection. This plot helps to visualise the fundamental cell characteristics that drive a cell's performance under a peak load vs a more continuous load, and how these characteristics can change with cooling. Key takeaway points are summarised below.

Compared to peak power, baseline power:

- Significantly reduces the usable energy per watt of power increase.
- Dominates the increase in maximum temperature per watt of power increase.

Compared to power cells, energy cells:

- Start with higher maximum usable energy.
- Lose usable energy faster with increasing baseline and peak power.
- Increase in maximum temperature faster with baseline power.

Compared to natural convection, base cooling:

- Increases the rate at which cells lose usable energy with increasing baseline power.
- Reduces the rate at which cells increase in maximum temperature with increasing baseline power.

Analysis of the parameters shown in Figure 34 confirm the VTC6A-AM as the best power cell, and the 48X as the best energy cell for all of the drive cycles tested (their values are closest to the top right corner of both plots). Just as the M50T dropped below the power cells in usable energy for the last few drive cycles in base cooling, it is hypothesised that, once base and/or pulse power is large enough, the VTC6A-AM may deliver more energy than the 48X. Since the base and pulse power are independent of each other, there is no fixed cross-over point for the cell performance. For example, starting at a given drive cycle, e.g. DC6, it is possible to keep increasing only the pulse power, to a point where the VTC6A-AM is predicted to output more energy than the 48X. The same can be achieved by increasing only the base power, thus giving a completely different “cross-over” drive cycle. To demonstrate the potential use of these equations in battery pack design, a worked example is given in the following section.

The most significant outcome of these tests is that it is shown that performance can be translated, linearly, across the varying baseline and peak powers of the drive cycles. This seems to contradict the previous section where it is shown that performance cannot be translated from one test to another. However, there is a significant difference between the types of loads shown in Figure 31 and the way in which they affect cell performance. For these drive cycles the fundamental profile and timescales are kept the same. Since performance is tracked only across a range of varying power, for each cooling condition separately, a relationship can be established; the previously shown lack of predictive power from one test performance to another is represented by the individual fits achieved for each cell under each condition.

Procedure for the Use of Drive Cycle Performance Equations

This is an example procedure of how the relationships derived in the previous section between cell performance metrics (usable energy and maximum cell surface temperature) and power requirement in the drive cycle can be used to select cells for an application, together with information on the pack size and cooling method. For simplicity, there are several factors that are ignored here: the effects on energy utilisation and bulk temperature increase of putting the cells into packs, the effect of pack weight on power requirements and/or delivery, and the effect of cooling on power requirements and/or delivery. This section is designed to serve as an example of how these equations could be used, no weight should be given to the quantitative outcomes of this section.

A motorsport battery pack is required to complete a drive cycle with a baseline power of 50kW and a pulse power of 250kW without exceeding 70 °C, based on the base drive cycle profile presented in this work (Figure 26). The number of cells used in this pack determines the cell-level power requirement: the fewer cells used, the higher the cell-level power required. The ratio of base power to pulse power remains the same, independently of the number of cells used; in this example $P_1:P_2 = 1:5$ (Eq. 22). A fixed ratio of P_1 and P_2 has a single cross-over point for usable energy, thus this point can be calculated to compare the best power cell (A: VTC6A-AM) against the best energy cell (B: 48X). At this point, the same amount of energy will be delivered by either cells, A and B, when the energy variation of Eq. 21 written for the two cells is equal for a given ratio $P_1:P_2$, thus yielding Eq. 23.

$$5P_1 = P_2 \quad \text{Eq. 22}$$

$$P_1 = \frac{E_{DC1,A} - E_{DC1,B} - 3.6(p_A + b_A) + 3.6(p_B + b_B)}{(5 - 1)(p_B - p_A) + b_B - b_A} \quad \text{Eq. 23}$$

Figure 35 shows the predicted values of usable and maximum pack energy values for pack configurations with 850 to 1200 cells, calculated using Eq. 4-6 and using the parameters fitted for the VTC6A-AM and 48X performances. Plots showing predicted values of usable cell energy and configurations ranging from 500 to 5000 cells are presented in Appendix B.5. Using Figure 35 both cells and cooling systems can be compared against one another.

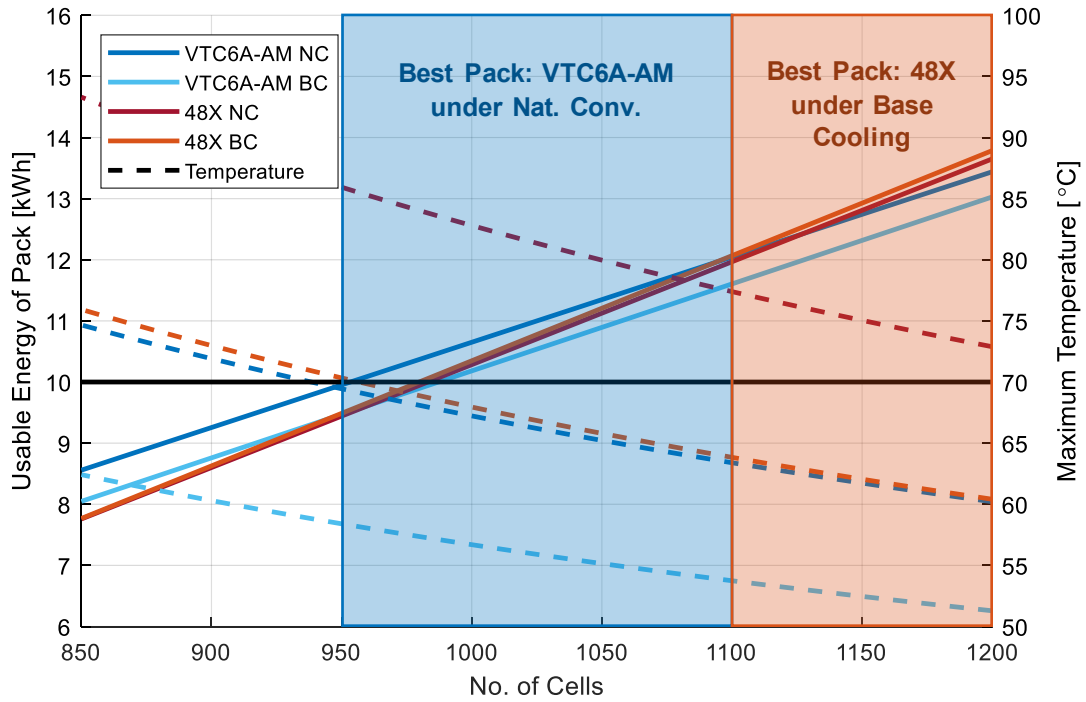


Figure 35: Predicted usable pack energy and maximum cell surface temperature against the number of cells used in the pack, for 4 pack types: made with cells VTC6A-AM or 48X, cooled by natural convection or base cooling. The black solid line shows both the 10 kWh energy requirement and the 70 °C temperature limit. The blue shaded region shows the pack size for which the VTC6A-AM with natural convection cooling is the best choice. The red shaded region shows the pack size for which the 48X with base cooling is the best choice. Recreated from Ref. ¹⁸⁰

To further the analysis of this example, a pack for a hybrid powertrain may have a usable energy requirement of 10 kWh. It can be seen from Figure 35 that it is not possible for the pack to contain fewer than 950 cells to meet this energy requirement. Only the VTC6A-AM with natural convection cooling is able to achieve this requirement in the smallest pack configuration. This configuration is also predicted to operate only marginally within the temperature limit. The other 3 configurations, VTC6A-AM with base cooling, 48X with natural convection and 48X with base cooling, require at least 980 cells to meet the energy requirement. The configuration of the VTC6A-AM with natural convection remains the optimal solution for packs with up to 1100 cells; for larger packs the 48X with base cooling becomes the optimal solution. Conversely, for an example pack for a fully electric powertrain that may have the higher energy requirement of 50 kWh, the 48X with base cooling is the optimum choice. The exact number of cells for these cross-over points between any cell A and B can be calculated by dividing the total pack power by the calculated cell-level power cross-over point given by Eq. 23.

As mentioned at the start of this section no significance should be given to the quantitative analysis in this section, this is due to both base and pulse powers considered for this motorsport example being significantly higher than what has been tested in the previous section, leading the need to use significant extrapolation for the analysis. However, a cross-over point was observed for the M50T, and the performance remained linear in this region, thus it is deemed appropriate to make these extrapolations. Furthermore, the goal of this analysis was fulfilled, in that it demonstrates how experimental expressions obtained from the bespoke tests performed in this section can be used for cell selection for pack design, by determining the trade-offs that exist between power and energy cells, while considering the effect that cooling has on the optimal cell for an application. If this analysis were to be performed realistically, the cells would first need to be tested at power levels that cover the region shown in Figure 35 (850 cells – base power up to 59 W, peak power up to 295 W), so that the fits for the equations would be accurate in the region of interest.

4.5.4 Recommendations for Cell Testing for Performance Benchmarking

It is clear from Figure 31 that performance in one test cannot simply be translated to performance predictions for another, thus undermining the usefulness of standardised testing under a unique set of conditions. In contrast, by successfully fitting the performance results from a series of drive cycles of increasing power, it is possible to translate performance across different power and duty levels for a defined load type and cooling condition. These outcomes combined with the awareness that it is not always possible to test individual cells under conditions that exactly match the desired application, lead to our key recommendations for benchmarking of cells for use in packs:

- 1. Cells should be tested under thermal conditions that attempt to closely mimic the thermal boundary conditions that the cell would be subjected to in the pack, including the choice of thermal management and electrical connection method.**
- 2. Cells should be tested under load cycles that are as close to the desired application as possible. At a minimum, the cycle must contain similar “features” to the load seen in application.**

The electrical connection method is specified to be application-relevant in point 1 as this can impact not only the electrical performance but also impact the thermal boundary condition of the cell. To expand on point 2, the cells should be tested under constant load only if this is reflective of their use in the application. Conversely, if the application subjects the pack to a

noisy drive cycle, the cells should be tested with a cycle that contains rests, peaks, and average loads, preferably with similar frequencies to the application load. Finally, if the application features regeneration in the discharge drive cycle, such instances should also be reflected in the test load cycle.

It can be concluded that cell performance should not be compared without a specific application in mind. If a general comparison, however, is required, a range of tests should be performed covering the following conditions:

1. All potential cooling methods
2. Multiple different types of loads ranging from constant current cycles to drive cycles
3. A range of current/power levels, determining trends, where possible

Testing of this scale can be very costly on resource and time, it would be conceivable to use this effort to develop and validate a battery model for each cell, that could predict the performance of the cell under different conditions. Unfortunately, realistic test conditions will often lead to the performance of a cell being driven by differences in inhomogeneity, this can be internal thermal gradients, or current and SOC gradients within the electrodes. This means that only a 3D model, capable of modelling cell inhomogeneity, would be capable of accurately predicting a cell's performance under the required conditions. Parameterising and validating a model of this complexity would also be very costly both on resource and time. Furthermore, it would likely require running similar tests to those described in this section to ensure the model is properly validated. As an example, you could not expect a lumped 1D battery model, parameterised under convection tests and constant loads, to accurately predict the performance of the same cell under base cooling and a drive cycle. Therefore, the effort required to build a robust battery model could be greater than that of simply testing the cell under the desired condition. It would, of course, be a worthwhile endeavour, if cells are needed to be consistently tested and compared under new conditions, in this case battery models could help save valuable testing time and resource. Nevertheless, the testing guidelines described in this section should still be followed to help accurately parameterise and validate battery models capable of predicting real-world performance.

4.6 Conclusions

This chapter tested six commercial 21700 cells (three energy and three power cells) under a comprehensive testing programme, designed to subject the cells to different current loads and

cooling conditions. The conditions were chosen to reflect two types of potential battery packs, one with active liquid cooling and one without. The cells were tested under two cooling strategies (natural convection and base cooling) and four different types of loads (constant current discharge, constant C-rate discharge, high-rate constant C-rate cycling, and a simplified set of drive cycles). While it is well understood that BoL performance, characterised by cell usable capacity and maximum surface temperatures/gradients, changes significantly across the different cooling and load types, the percentile-based ranking analysis performed in this study, illustrates that the cells change their ranking compared to one another depending on these conditions. Differences in cooling are shown to affect ranking by up to 20%, and differences in load type can affect ranking by up to 98%. This means that some cells perform better under one combination of cooling and load type, and others perform better under a different combination. Importantly, this proves that the assumption that the cell that performs best in standardised conditions will perform best under the real application, is false. These observations are essential to considerations around the creation and improvement of standardised testing, which should strongly differentiate between different types of applications. The possibility to translate performance from one simplified drive cycle to another one of a different load power level was also reported in this study; results were successful, indicating a possible avenue for establishing sets of tests that enable a translation of cell performance across multiple load intensities.

The cell's internal resistance has the biggest impact on the capacity/energy and temperature performance of the cell at BoL. Existing research has established that experimental testing aspects such as the electrical connection, thermal boundary conditions, and electrical load profile, can impact the resistance of a cell, and thus its performance. It is not well understood how these changes to resistance can vary from one cell to another, and whether the difference in resistance response between cells can result in differing ranking of cell performance. This work has successfully shown that there is a difference in resistance response between cells, and it is large enough to cause changes to cell performance rankings. These differences will likely be driven by fundamental cell characteristics such as, electrode and current collector thicknesses, internal tab position and quantity, casing thickness and conductivity, etc. None of these characteristics would be given on a typical cell datasheet, so that assessments could be made prior to any testing.

It is concluded that cell specification sheets and standardised cell benchmarks cannot be exclusively relied upon for the selection of cells, due to test conditions that are not relevant to most real applications.

For accurate benchmarking of cells for pack applications, it is recommended that:

Cells should be tested:

- **under thermal boundary conditions that closely reflect the desired application,**
- **with electrical connections achieved through methods and with materials similar to those used in the application**
- **under power or current load profiles that represent the desired duty cycle**

This work is most impactful to battery pack engineers and manufacturers, as well as researchers running cell level testing for pack applications or models. This work helps stress the importance of running bespoke, relevant testing to choose the best cell and generate more application-relevant cell-level results. However, further work is required to ensure that these findings hold true for all other lithium-ion chemistries and form factors.

Chapter 5: Impact of Cooling on Cell Lifetime Performance

5.1 Introduction

The previous chapter demonstrated that test conditions are of extreme importance to lithium-ion cell testing at beginning of life (BoL). Although the BoL performance of cells is of significant importance, the lifetime performance of cells is often of even greater importance. Especially in the automotive industry, achieving warranty targets of 8 to 10 years is crucial to vehicle manufacturers. Degradation studies are typically performed under standard cooling conditions and constant current loads. It would be expected for application-focused cooling and loads to perform differently at BoL, thus they should perform differently under ageing as well.

This chapter outlines a lifetime performance study comparing the two most popular cylindrical cooling systems, base, and side cooling. The aims of the experiment are explained and followed by a description of the experiment. Two commercially relevant 21700 lithium-ion cells are cycled under a few combinations of application-oriented cycles and the two cooling systems, along with convection cooling as reference. The BoL performance of the cells under the different combinations of conditions are analysed to make predictions of the lifetime performance. The capacity fade and resistance increase of the cell is tracked via reference performance tests (RPT) up to a generic cut-off of 80% available capacity. To further the understanding of the degradation, a selection of the cells is disassembled for visual analysis, coupled with differential voltage analysis.

5.2 Aims

The aims of this study are summarised below:

1. **Is Side Cooling better than Base Cooling for life performance?**

Side and base cooling are the two most popular cooling systems used in automotive cylindrical cell battery packs (e.g. Tesla, Lucid, Rivian).¹⁸² A key aim of this study is to assess if one of these cooling systems is better for the life performance of cylindrical cells under automotive relevant conditions. Predicting which cooling system is better is not simple. Preliminary tests could give the BoL electrical and thermal performance. However, the degradation will be

impacted by the inhomogeneity within the cell, and without developing high fidelity electro-thermal models with degradation the answer can only be gained from experimentation.

2. What variables influence this result?

- a. **Charge vs Discharge Rate** - Is one cooling system better than the other for both extreme charges and discharges?

It is important to assess if the rate of the charge or discharge impacts which cooling system is better. Fast charge rates are important to consumer automotive, and fast discharge rates for high performance vehicles. Thermodynamic differences between charge and discharge as well as Peltier effects from the dissimilar metals welded together, could result in heat flow differences between charge and discharge that may be better suited to one of the cooling systems.

- b. **Cell Design** - Does a cell with a better internal structure for base cooling result in a longer life under that cooling system?

The internal structure of the cylindrical cell could have a significant impact on which cooling system is most effective. Parameters such as the can and base thickness, and the number of internal tabs at each terminal could determine which cooling system is best. While it can be hypothesised that cells with more internal negative tabs may be better at base cooling, modelling would be required to accurately assess the true impact to the internal temperature.

5.3 Experimental Setup

This study aims to assess the degradation difference between base cooling and side cooling, exploring if this difference is dependent on factors such as the cell energy density, physical design, and the rates of the charges and discharges. A key goal of this study is to ensure that the results of the experiment are relevant to industry. As demonstrated by the work in Chapter 4: The Effect of Test Conditions on Benchmarking Cylindrical Lithium-ion Cells, the experimental test conditions and load profiles can make a big impact on BoL performance. It is expected that these BoL performance differences will impact the lifetime performance of the cells. Therefore, the experimental rigs and test procedures designed for these experiments aimed to closely replicate automotive base and side cooled applications. To contrast both these highly application relevant setups, an additional cooling system and rig will be tested, which will involve convection cooling and spring-loaded standardised 21700 holders, this setup will aim to highlight potential problems with testing life performance in unrepresentative test rigs.

5.3.1 Cell Choice

The most ideal choice of cells would be two identical cells, where the only difference between them is physical, such as the number of internal tabs. However, it is important that the cells tested are commercially relevant, such cells do not exist. Thus, the two commercially available cylindrical cells used for this study are the Samsung INR21700-50S and the Molicel INR21700-P45B. These cells relatively similar with the required physical differences, these similarities and differences can be seen in Table 10. The cells have similar chemistries (confirmed via analysis of BoL differential voltage curves), but differ in their energy and power density, as well as physical construction. These differences aim to answer the following questions:

1. Are higher power cells less impacted by the type of cooling?
2. Are cells that contain more negative tabs better at base cooling compared to side cooling?

Table 10: Cell Information

	Samsung 50S	Molicel P45B
Capacity (mAh)	5000	4500
Upper Voltage (V)	4.2	4.2
Nominal Voltage (V)	3.6	3.6
Lower Voltage (V)	2.5	2.5
Maximum Continuous Charge Rate (A)	6	13.5
Maximum Continuous Discharge Rate (A)	45	45
Maximum Temperature (°C)	80	80
Mass (g)	72	70
Dimensions (Ø x H mm)	21.25 x 70.62	21.55 x 70.15
Chemistry*	NCA/Gr-Si	NCA/Gr-Si
Positive Tabs*	1	2
Negative Tabs*	1	3
Adhesive between jellyroll and can	Yes	No

5.3.2 Cooling and Experimental Rigs

Side and Base Cooling

The goal of this experiment is to assess industrially relevant base cooling against side cooling; thus, the experimental rigs were designed such that they were identical between the two cooling systems. For this reason, both setups use single sided wire-bonded electrical connections. Custom 3D printed polycarbonate arches are used to support 2 aluminium terminal blocks above the top of the cell. Two 300-micron aluminium wires are bonded between each terminal block and the cell (top button for positive and shoulder for negative). These arches, terminal blocks and wire bonds are identical between the two cooling setups. The base cooling setup has three copies of the cell rig bolted into a single water block (via the arches). The water block is a standard 12 x 40 x 240 mm water cooling block. The side cooling setup has each rig and cell bolted and adhered to an individual ABS base block with one side plate attached through the arches to three copies of the rig. The side cooling plates are custom cut by Trumony Aluminium Limited, to a standard very similar to industry. Both cooling setups use 3 cells to a single cooling plate for two reasons, most critically it is so that the plates are not overloaded by the heat from the cells, preliminary testing showed that with 3 cells per plate, the thermal impact from one cell to another is minimal. The second reason is that this study uses 3 repeats per test combination, by using 3 cells per plate, all 3 cells on a plate can be a repeat of each other. The cell to cooling plate thermal and mechanical connection is achieved through the use of a thermally conductive structural epoxy (Parker Lord TC2002) which contains 100-micron glass beads to maintain consistent bond gaps. Images of the rigs can be seen Figure 36.



Figure 36: Images of the custom base (left) and side (right) cooled rigs.

To record the cell surface temperatures, k-type thermocouples and Pico loggers are used. Since each plate contains 3 identical repeats, only the centre cell on each plate is fully instrumented, the other two cells have one thermocouple attached to the middle of the cell can (35 mm from the base). For both base and side cooling the fully instrumented cell contains 3 thermocouples along the height of the can (positioned at 10, 35 and 60 mm from the base), with the side cooling cell also containing another thermocouple at 35mm approx. 90° from the other 3. This setup allows for the measurement of axial (height) gradients in both setups, as well as radial gradients for side cooling. A diagram of the instrumentation can be seen in Figure 37.

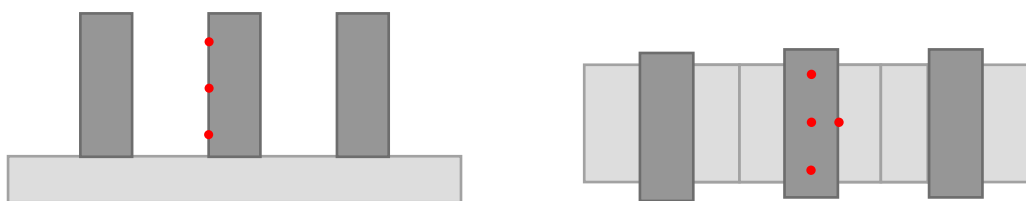


Figure 37: Diagram of thermocouple instrumentation for the base (left) and side (right) cooled rigs.

A ThermoFisher Scientific Arctic A10-AC200 refrigerated circulator is used to pump and maintain 25 °C water through the plates. Two of these systems are used, one for all 6 base plates and another for all 6 side plates, this ensured that the same pumping force was used for each type of plate, and there is no bias of flow towards the plate type that has the lower pressure drop. All the actively cooled setups are separated into boxes and immersed in vermiculite. This provides insulation around each cell, and acts as a safety control in the event of thermal

runaway. These boxes are kept in a large Espec BPL-3 thermal chamber, which maintains a steady 25 °C ambient condition around the rigs, this can be seen in Figure 38.



Figure 38: Complete setup for all base and side cooled tests.

Convection

The purpose of the convection tests is to mimic the ‘typical’ setup for cylindrical cell testing and act as a reference for the other two cooling systems. Thus, this cooling setup uses standardised spring loaded 21700 cylindrical cell holders. The cells in the holders are tested in a Binder KB53 thermal chamber, which provides a consistent 25 °C ambient temperature, this setup can be seen in Figure 39. The internal fan in the chamber is set to 60% to circulate the air in the chamber, this minimises the thermal gradient in the chamber, reducing any bias between cells directly in front of the fan. As no surface thermal gradients are expected along these cells, due to the uniform cooling, only one thermocouple is attached to each cell (in the middle, 35 mm from the base).

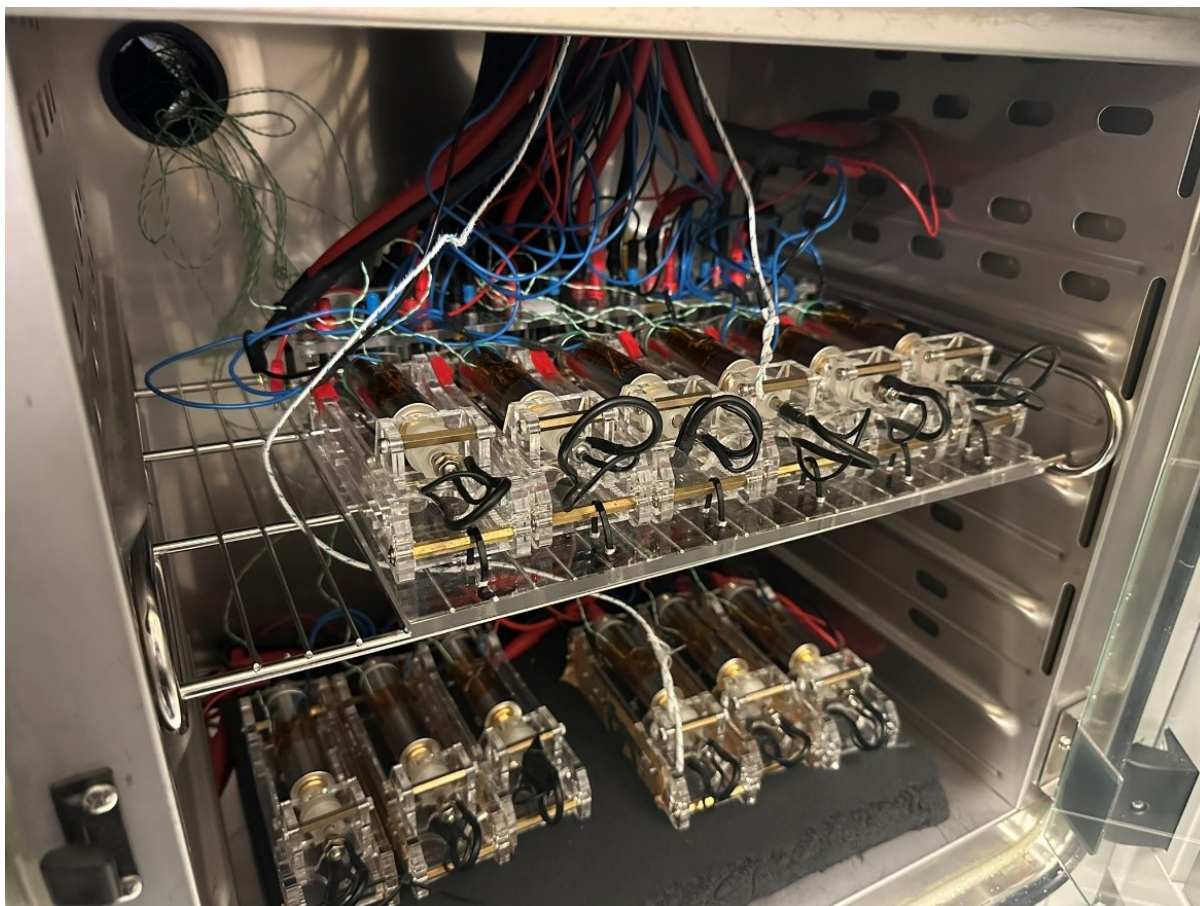


Figure 39: Complete setup for convection cooled tests.

5.3.3 Procedures and Test Matrix

Degradation Cycle Procedure

As mentioned, a key aim of this study is to ensure application relevance, to achieve this the degradation cycle for this study is based on power instead of current, uses a slightly reduced voltage window, and uses a ‘drive cycle’ discharge. The details of this cycle are described in Table 11. The drive cycle discharge follows a similar simplified profile to that in Chapter 4: The Effect of Test Conditions on Benchmarking Cylindrical Lithium-ion Cells, with changes to the timing and the addition of regenerative charge pulses. For both the drive cycle discharge and CP-CV charge, there are two rates; slow – a representative passenger automotive rate, and fast – an accelerated high-power version, designed to push the cell to and past its limits. While the discharge rates are well within the recommended rates for both cells, the fast charge rate is outside of the recommended rate for both cells. This is chosen due to the low charge limit on the Samsung cell, it is deemed unfair to charge within the limit of one cell and outside the limit for the other. The voltage limits have been chosen as 4.15 to 2.7 to achieve approximately 95% capacity utilisation on the slow rates. The discharge is triggered by the cruise step (step 3)

reaching the lower voltage cut-off, if the acceleration pulse (step 2) reaches the cut-off the step is simply skipped. This is an effort to somewhat mimic power de-rating as the SOC gets low, where the peak power would be limited for a vehicle. The end of charge is triggered by reaching the time limit on the CV hold.

Table 11: Degradation Cycle Parameters. The drive cycle discharge is described by a loop of steps 1-4, where the time for each step is indicated in the square brackets. Approx. E-Rate is defined in reference to a nominal energy of 18 Wh, where an E-Rate of 1 equals 18 W.

Discharge till 2.7 V	Slow	Fast
1 – Rest [18 s] (W)	-0.1	-0.1
2 – Accel. [3 s] (W)	-42	-100
3 – Cruise [36 s] (W)	-4	-50
4 – Brake [3 s] (W)	34	80
Average Power (W)	6.23	39.03
Approx. E-Rate	1/3	2
Charge till 4.15 V	Slow	Fast
Power (W)	9	54
CV Time	30 min	15 min
Approx. E-Rate	1/2	3

Reference Performance Tests

The reference performance test (RPT) for this study occurs every 50 cycles and involves a C/10 charge and discharge in the full voltage window of the cell, the discharge has a short 10 sec pause at 3.6 V to get an ohmic resistance measurement. Every 100 cycles a longer RPT containing a charge and discharge GITT (galvanostatic intermittent titration technique) protocol is also performed, the analysis of which will be left for future study. Due to data management constraints the test procedures are run continuously for approximately 18 days, at which point the test is stopped and restarted, due to the loss of the running cycle counter and the order in which the procedure is built into the BaSyTec. This results in both the main and longer RPT being performed at every restart, giving the main RPT a frequency of once every 18 days and/or 50 cycles. The longer RPT has a frequency of once every 18 days and/or 100 cycles.

Matrix of Tests

Even though the cells in this study are commercially available and have very minimal cell-to-cell variation in BoL performance, at EoL there can be significant variation in performance. For this reason, each combination of cooling and load rates has 3 repeats. With 3 cooling systems, and a fast and slow rate for both charge and discharge, giving 4 possible rate combinations, there are 12 possible combinations of cooling and charge-discharge rate. Table 12 shows which combinations of tests have been chosen for this study. The SS (slow charge – slow discharge) rate combination acts as the automotive reference for this study, while the FF (fast charge – fast discharge) rate combination is predicted to be the most intense and fastest degrading, since the high currents are expected to apply maximum stress on the electrodes as well as cause the highest internal temperatures, both of which should result in accelerated degradation. For these reasons both cells will do both these combinations under all cooling systems.

Table 12: Matrix of Test Conditions. X markers indicate chosen tests, O markers indicate tests that have been added following the completion and analysis of other tests. Rate combination nomenclature is based on a description of charge then discharge, i.e., FS indicates a combination of the fast charge and the slow discharge.

Rate Combination	Samsung 50S			Molicel P45B		
	Base	Side	Conv	Base	Side	Conv
FF	X	X	X	X	X	X
FS	X	X	O			O
SF	X	X				
SS	X	X	X	X	X	X

5.4 Results and Discussion

5.4.1 Beginning of Life Analysis

Temperature and Energy Analysis

To ensure that the cooling and rate combinations have the desired BoL performance impact, the gross discharge energy and temperature performance of the initial degradation cycles have been analysed. The gross discharge energy is the total energy discharged during the drive cycle discharge, without subtracting the extra energy required to compensate for the regenerative charge pulses. This is deemed the more appropriate metric as it represents the potential range

of the vehicle, if the cells are to be used in an EV pack. The temperature is taken at the peak for the entire cycle, so this can be either at the end of charge or discharge depending on which is hotter. The results of this analysis can be seen in Figure 40.

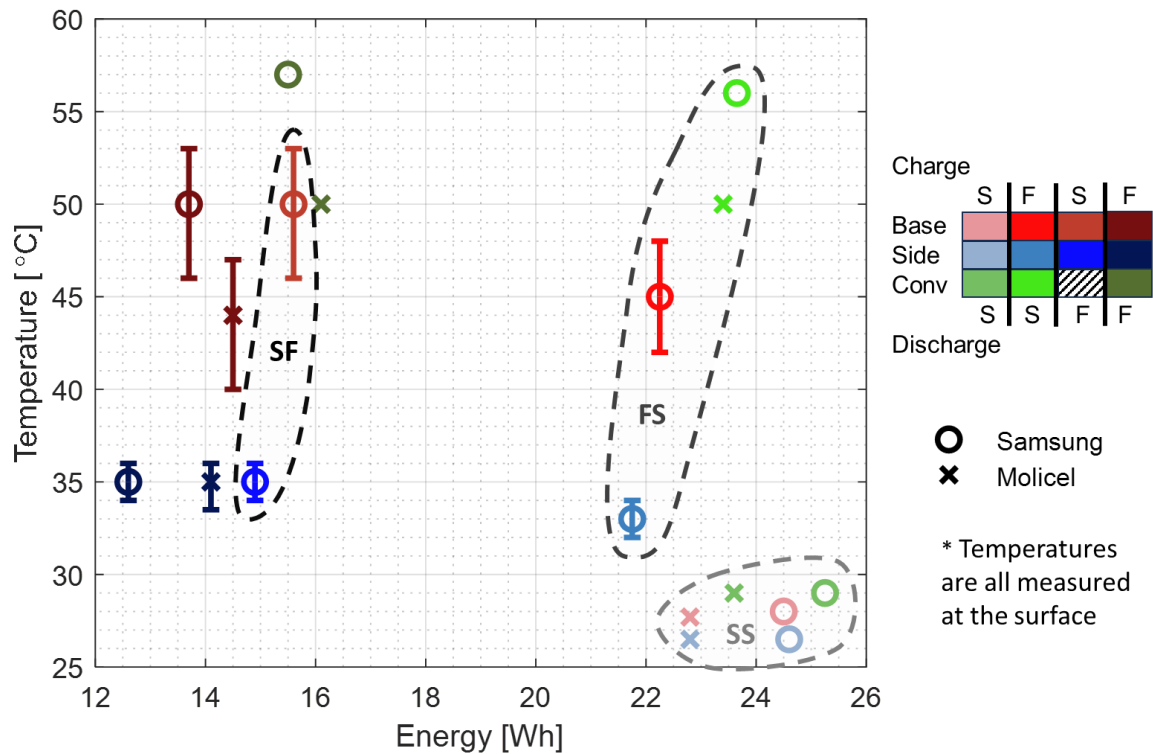


Figure 40: Beginning of Life performance plot for both Samsung and Molicel under the 3 cooling types (base, side, and convection), and the 4 rate combinations (SS, FS, SF and FF, where S – slow, F – fast, defined by Table 11 and Table 12). Average surface temperature is plotted against gross discharge energy. The error bars demonstrate the minimum and maximum cell surface temperatures recorded at the end of the charge/discharge (whichever was hottest, discharge was always hotter than charge).

The key points to note from this plot:

- SS appears relatively agnostic of the cooling, with only a slight difference in temperature between the base and side cooling. There is a slight energy gain for the convection cooling, but this will likely be caused by the difference between the lower ohmic resistance of the spring-loaded rig and the higher resistance of the wire bonds in both the base and side cooled rigs.
- The fast discharge appears to have a much larger impact on the usable energy compared to the fast charge, partially due to its higher average E-rate, with around a 40% reduction in the output energy caused by the fast discharge compared to around a 10% reduction caused by the fast charge. This is likely due to the CV hold in the charge minimising the impact of the current difference. (This will be investigated further in the following section)

- Convection cooling is the least effective cooling system and side cooling is the most effective. Base cooling, while better than convection for average temperature, displays large surface temperature gradients, indicating high levels of thermal inhomogeneity, which could prove detrimental for life performance.
- The Samsung cell delivers more energy than the Molicel for both SS and FS rates, but the Molicel delivers more under FF rates. This is expected due to the difference in capacity and resistance between the cells.
- For the FF rate the Molicel is superior to the Samsung under convection and base cooling, delivering more energy at lower peak temperatures. For side cooling the Molicel still delivers more energy but both cells have equal temperature performance, this is likely due to a combination of the Molicel being better suited for base cooling with its three negative tabs, and the Samsung being better suited for side cooling with its adhesive improving thermal contact between the jellyroll and can.

Analysis of BOL Cyclable State of Charge Window

To investigate the large difference in discharge energy, the SOC window of the cells needs to be analysed for each rate combination. Although all the tests use the same voltage cut-offs, the subsequent overpotential drops caused by the different current magnitudes result in the cells reaching these voltage cut-offs at different SOC's depending on whether a fast or slow rate is used. This means that the fast charge will likely reach a lower SOC than the slow charge, and the fast discharge will end at a higher SOC than the slow discharge. Further to this, the cell and cooling will impact these overpotentials, the more energy dense Samsung 50S has a higher internal resistance so may be more affected by the rate difference than the Molicel. The average cell temperature will impact these overpotentials, therefore the cooling systems that are less effective like base or convection cooling can end up with lower overpotentials and thus a larger SOC window.

To accurately determine the effect of the rate combination, cell, and cooling on the cyclable SOC window, an accurate cell model would be required to predict the resulting SOC's, alternatively it could be determined experimentally by allowing the cell to rest for a significant period after a representative charge and discharge in the cycle. This will allow for the determination of the OCV voltage at the top and bottom of the cycle, thus the SOC. The degradation procedure does not contain any significant rests in the cycle to ascertain the true OCV, however it does contain 15 minutes of rest between every charge and discharge. The voltages at the end of these rests can be used to gain a rough idea of the OCV/SOC window of

the cycles. Although it could be possible to fit curves to the rests to estimate a more accurate OCV, that level of accuracy is not required for this analysis. To go alongside these rough OCV values, the net discharge capacity of the drive cycle can be used to further indicate how much of the total cell capacity is being cycled. Figure 41 presents both these 15-minute resting voltages and net discharge capacity (normalised against the nominal cell capacity) of each rate combination, cell, and cooling.

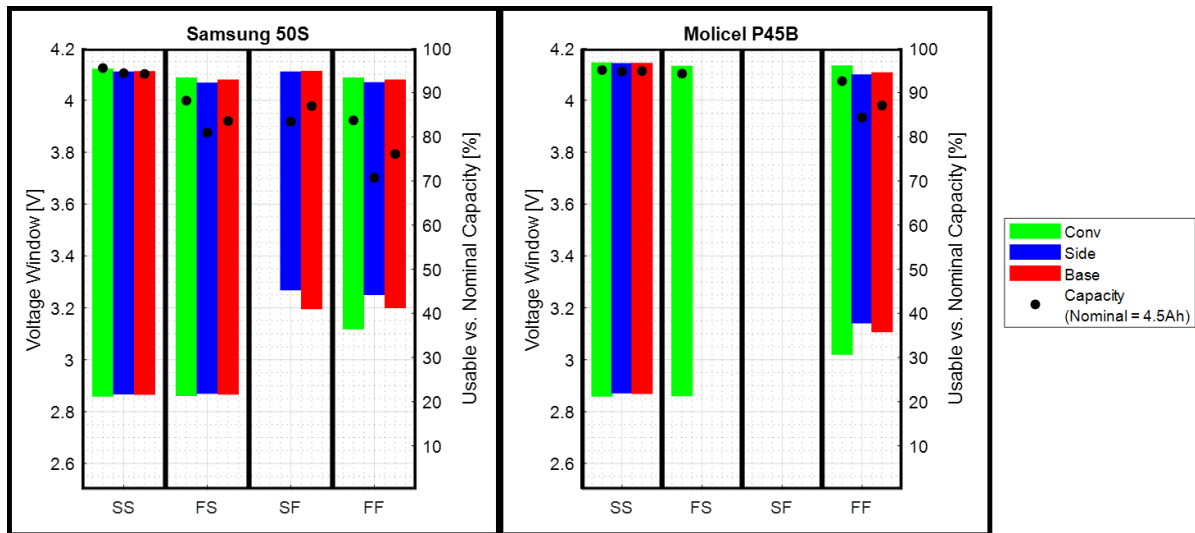


Figure 41: Beginning of Life Depth of Discharge Plot. Estimated pseudo-OCV voltage window (determined at the end of the 15 min rest post charge and discharge) for each rate (x axis) and cooling (colour) combination. The usable capacity normalised against the nominal capacity is also shown using the black markers and right axis, to aid the assessment of the cyclable window. The rate combination labels follow the naming convention established in Table 12. Repeats perform almost identically so the spread is not shown here.

Analysing the SS rate it can be seen (via the differences in voltage window and usable capacity) that although the convection rig has a visible impact to the output energy of discharge, its impact to the cyclable SOC window is very minor for the Samsung cell and almost negligible for the Molicel. It appears that increases or decreases to ohmic resistance have a greater impact to energy in and out than they do to capacity. This is because a change in ohmic resistance impacts the voltage throughout the voltage range, constantly impacting the power, current and energy. Alternatively, the ohmic resistance will only affect the capacity through the voltage cut-offs, and since the voltage curves are inherently steep and only a small proportion of capacity exists in the region of the cell voltage limits, the impact is relatively small. One point to note is that the reduced voltage window (4.15 to 2.7 V), as designed, only removes a small portion of capacity, with around 95% of nominal capacity still being delivered in the cycle.

Moving onto the FS rate the impact of the fast charge on the SOC window can be analysed. It can be seen that the lower voltage values are identical to that of SS, confirming that the end of

discharge point is unchanged by the faster charge rate. Although the charge steps contain CV holds, differences in the resting voltage after charge are to be expected. The time-based CV hold cut-offs mean that differences in CP rate and changes in the thermal distribution within the cell (caused by different cooling) can affect the final current and/or SOC reached when the charge ends. For the Samsung the upper voltages have reduced by just under 50 mV, and the usable capacity has dropped by around 5 to 15%, this matches the drop in output discharge energy shown in Figure 40. The identical lower voltages, triggered here by the cruise step of the slow rate drive cycle hitting the lower voltage limit, infer that this reduction in usable capacity comes off the top of the SOC window, meaning the fast charge leaves the cell roughly 5-15% lower in its SOC window, depending on the cooling. As mentioned, the magnitude of this reduction is dependent on the cooling, with the apparent trend tied to the cell temperature; convection being the hottest, has the least reduction, and side cooling being the coldest, has the most reduction. For the Molicel this rate is only tested on convection cooling, but it can be seen that the impact of the fast charge is minimal.

Now comparing the SF rate for the Samsung, the upper voltages are identical to SS, indicating that the end of charge/start of discharge SOC is identical to SS. The impact of fast discharge on the lower voltages is significant, raising the lower voltage by around 300-400 mV. In contrast, the usable capacity is marginally greater than that of the FS rate. This means that the fast discharge causes less of a reduction to the SOC window than the fast charge, this is in stark contrast to the output discharge energy which was impacted more significantly by the fast discharge than the charge. The causes of this difference between energy and capacity are parallel those listed out previously for why ohmic resistance is more impactful to energy compared to capacity. The high rates of this discharge result in large overpotentials, this results in larger currents which trigger early cut-off of the cycle due to voltage limits, but also less effective regen, as for the same power pulse, less current and therefore capacity is recovered. This highlights the importance of comparing energy as well as capacity when examining the rate capability of cells.

Finally, the combination of the fast charge and discharge into the FF rate appears to compound the two individual effects. For the Samsung cell, this leads to usable capacities ranging from around 85% of nominal for convection down to 70% of nominal for side cooling. This is a significant reduction in the usable SOC window from the 95% capacity of the SS rate. The Molicel shows a similar cooling trend but with a significantly smaller impact, ranging from just over 90% to around 85%. Given that it is already noted that the fast charge has very

minimal impact on the usable capacity (for convection), it is likely that most of this reduction comes from the fast discharge.

These unwanted changes to the SOC window are inherent to making rate changes when testing Li-ion cells. This coupling between the current/power and the usable SOC window can make it difficult to separate the impact on life caused by high currents against those caused by SOC window. It would have been possible to use a capacity-based limit to end discharge instead of a voltage limit. While this would potentially remove this coupling between current and SOC, it would have its own between the current and voltage, which will have its own implications to and evolution with degradation. Voltage limited cycling is at least more relevant to automotive applications. In a similar way, it is impossible to decouple the impact of high currents and temperature, as increasing the current will always increase the heat generation, even with the most effective cooling system possible, the thermal resistance in the cell will lead to elevated internal temperatures, this coupling can be seen in Figure 40. While this may make analysis complicated from a scientific perspective, from the perspective of this study, this coupling exists when the cells are used in application, thus the increased temperature and reduced SOC window with higher C rates are an inherent coupling occurring when increasing the power rate of cells and packs, making it a crucial component to this comparison.

Predictions

Using the analysis of the BoL data, shown in Figure 40 and Figure 41, and trends seen in literature, the following predictions can be made (listed from most degrading to least degrading, the criteria for which will be described at the start of the following section):

Cooling Comparison

Prediction: Convection > Base > Side

Convection is predicted to be the most degrading cooling system, as it results in the highest average temperature and largest cyclable SOC window, both of which will be detrimental to life performance.¹⁴⁷ Base cooling is predicted to be the next as it still results in high temperatures with very large surface thermal gradients, which should negatively impact life. Side cooling is predicted to be the least degrading as it results in the lowest average temperatures and thermal gradients, as well as the lowest cyclable SOC window, all of which should be beneficial to extending life performance.

Rate Combination Comparison

Prediction: FF > FS > SF > SS

The FF rate is predicted to be the most degrading as it uses extreme current loads resulting in high temperatures, both of which are expected to negatively impact life performance. This may be counteracted by the reduction in the usable SOC window, which would improve life, it is unclear as to whether this would offset the impact of the high currents and temperatures. The FS rate is predicted to be more degrading than the SF rate as fast charging is expected to be worse for life than fast discharging, due to the fast charge being outside the manufacturer's limit for both cells. Furthermore, while both the fast charge and fast discharge remove similar amounts of the SOC window, the fast charge removes it from the high voltage portion and fast discharge removes it from the low voltage. Due to the silicon component of the anode, it is expected that this de-utilisation of SOC from the low voltage region will help improve life by reducing the silicon utilisation.^{16,129} Finally, the SS rate is predicted to be the least degrading due to its low currents and temperatures. Although this type of cycling spans the largest cyclable SOC window, it is not expected that this would offset the impact of the current and temperature. It is expected that the most detrimental portion of the SOC window, for lifetime, is already removed by the reduced voltage window, in both high and low voltage ranges, compared to the datasheet recommendations.

Cell Comparison

Prediction: Samsung > Molicel

Making a prediction for the comparisons of the cells is challenging as very little information is available to provide evidence of their lifetime performance. However, assuming they have very similar lifetime performance, the Samsung may perform worse than the Molicel, as it generally operates at a hotter temperature across the range of tests. The exception to this is for the FF-side cooling test, where both cells operate at similar temperature, but the Molicel uses significantly more of its SOC window. For this test it is expected that the Molicel may perform worse than the Samsung.

5.4.2 Cycling Analysis

To track the degradation of the cells, the available capacity of the cells is determined using the C/10 charge from the RPT. There are many metrics to track Li-ion degradation, against cycle number, capacity throughput, or full equivalent cycles. For this study, the degradation will be tracked by remaining available capacity against the total energy throughput of the cells, this metric is deemed to be the most application relevant as it defines how much work the cell can do. The energy throughput value reached at 80% remaining available capacity will be used as

the key metric for defining the degradation performance in this study, including the predictions made in the previous section. Figure 42 displays all the available capacity for all the cells in this study, separated by rate and cell. This separation helps focus on the differences in degradation caused by the cooling. There are two key takeaways from this plot, the first is that for SS, the representative automotive test, the degradation is cooling agnostic. This is expected due to the minimal difference of the cooling on the energy output and temperature at beginning of life. This is likely the reason both cooling systems are popular in industry; if there was a clearly better cooling system, all automotive OEMs that use cylindrical cells, would likely adopt it.

The second key takeaway is that for the Samsung cell, both the SS and FS rates experience a knee point failure before or at 80% capacity fade, whereas the SF and FF rates experience a continual ‘linear’ death within the cycle life studied. The common factor in each of these two groups is the discharge: the slow discharge appears to be causing knee point failure and/or the fast discharge is preventing it. The BoL analysis in Figure 41 shows that between the slow and fast discharges there is around a 10% difference in utilisation of the lower SOC. Coupling this with the knowledge that this cell uses a silicon blended anode, it is hypothesised that the knee point failure is related to degradation of the silicon in the anode. This could be via mechanisms such as loss of active material in the negative electrode due to the expansion of the silicon particles, which can lead to a lithium plating related knee point.¹⁷⁵ Alternatively, depletion of FEC in the electrolyte can be facilitated by the volume change of the silicon particles,¹⁸³ which can cause an electrolyte dry out related knee points.¹⁷⁵

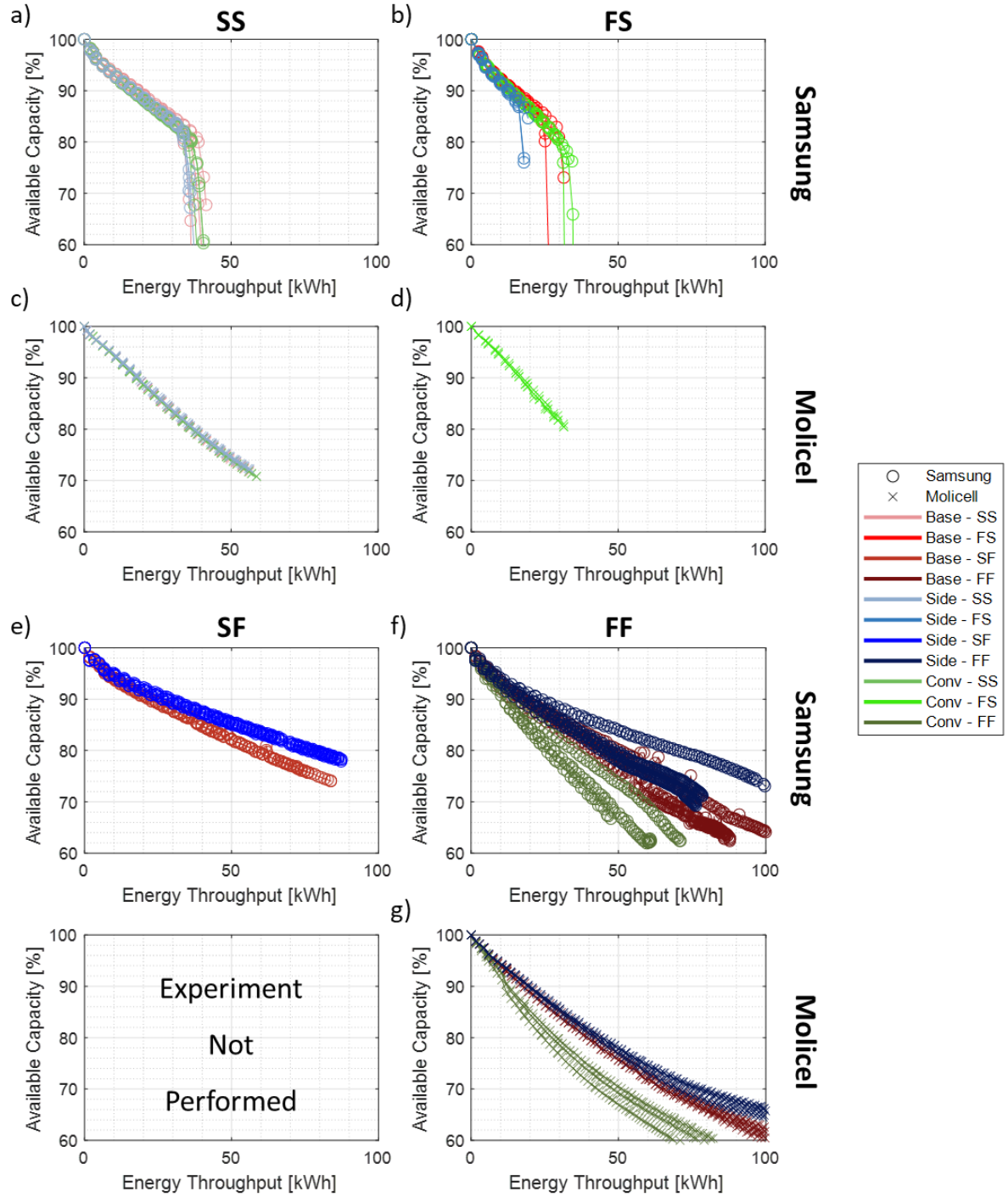


Figure 42: Available capacity against total energy throughput (Wh), separated into subplots by rate and cell. The available capacity is assessed from an RPT taken at regular intervals in the cycling. The 3 cooling mechanisms are displayed using different colours.

Figure 42 shows that for all rates other than the SS rate, the cooling appears to impact the lifetime of the cell. For the FS rate the cooling impacts when the knee point occurs, and for the SF and FF rates, the degradation rate of the cells is impacted, as measured by capacity fade assessed from the RPT.

80% SOH (Automotive) Cut-off

To better analyse the differences in degradation between the different rates, cooling and cells, the energy throughput to reach 80% available capacity is compared in Figure 43. 80% SOH is a typical cut-off used in automotive applications to classify the battery pack in need of replacement. The ohmic resistance of the cells as they reached this cut-off has also been displayed on the right axis of the figure, via the yellow markers, a plot of resistance against energy throughput can be found in Appendix C.1.

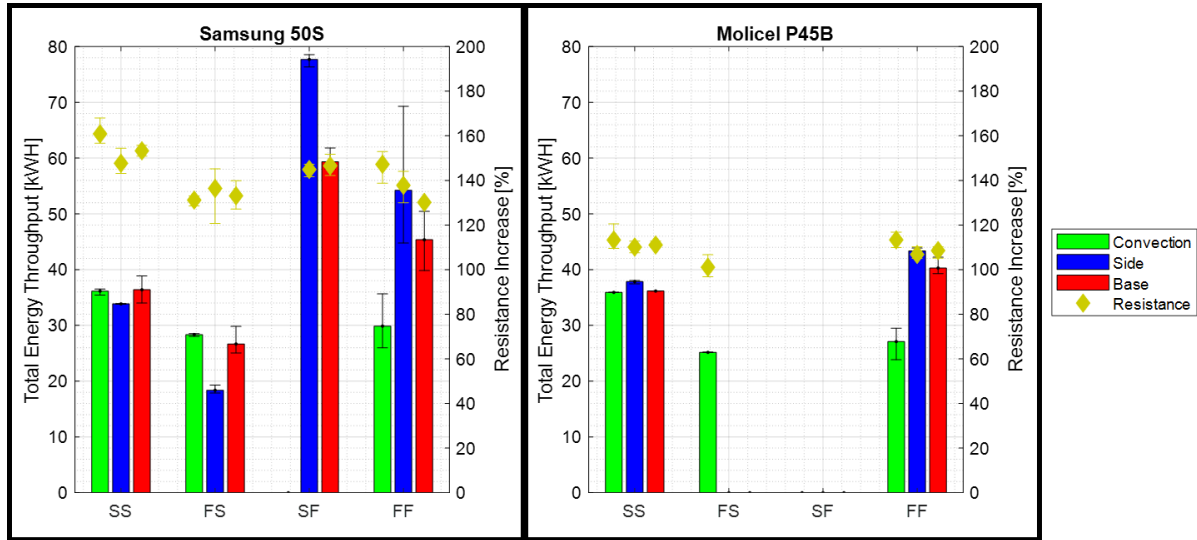


Figure 43: Energy throughput to reach 80% SOH (based on available capacity), for all cell, rate, and cooling combinations. The yellow markers also display the resistance increase when 80% SOH was reached (right axis). Error bars display the variance amongst the three repeats. The results of the Samsung 50S are presented on the left plot, with the Molicel P45B presented on the right.

Results vs. Predictions

Below the results are compared to the original predictions made at BoL, in-depth analysis of the results is presented in the sections that follow.

- **Cooling**
 - *Prediction:* Convection > Base > Side
 - *Results:* Convection > Base > Side
 - *Exception:* FS – Side > Base > Convection
- **Rate**
 - *Prediction:* FF > FS > SF > SS
 - *Results:* FS > SS > FF > SF
 - *Exception:* Convection – FS > FF > SS > SF
- **Cell**
 - *Prediction:* Samsung > Molicel
 - *Results:* Samsung = Molicel
 - *Exception:* FF – Molicel > Samsung

SS Rate

Starting with analysis of the SS rate, it is clear that all the cooling setups and both cells performed very similarly. The Samsung cells were well within the range of cell-to-cell variation, as shown by the error bars, with only a 10% difference between side cooling and the other two cooling setup (base and convection cooling, which performed almost identically). They all achieved around 35 kWh of energy throughput which is around 1000 full equivalent cycles. The resistance of the Samsung cells had increased by around 150-160% of the BoL value when they reached 80% SOH, whereas the Molicel only increased by around 110%.

FS Rate

Analysis of the FS rate shows that fast charging can significantly reduce the life of these cells; the differences caused by cooling are more significant than for the SS rate in both cells. The rapid degradation of the base and side cooled cells appeared to have a correlation with temperature, to further confirmation of this trend the F-S rate convection cooled cells were added upon the completion of these tests. For convection cooling the reduction in life is around 20%, whereas for base cooling the reduction is 30% for the Samsung cell. For side cooling the life reduction for the Samsung cell is almost 50%. This trend goes against the trend in measured BoL surface temperatures, meaning that the lower temperatures of side cooling likely worsened the degradation mechanism dominating this fast charge. One degradation mechanism that is known to be problematic when fast charging and is worsened by colder temperatures is lithium plating. Lithium plating is common when charging at high rates, cold temperatures and to high SOC. Most of these have already been mitigated, as the temperatures are not sub-ambient,¹⁴² and the charge stops before the end of the SOC range. Even the high rate is somewhat mitigated by the constant power protocol, where the current automatically reduces as the cell reaches higher SOC's due to the increasing potential. Even the impact of temperature-dependent resistance difference is mitigated by the constant power charge protocol, as the higher resistance of the relatively colder electrodes results in a higher overpotential which reduces the overall current flow into the cell. Thus, none of the typical conditions for lithium plating are present, but this does not mean that it cannot occur, lithium plating has been observed at room temperature¹⁸⁴ and above,¹⁸⁵ at high charge rates. However, it is possible that lithium plating is not the degradation mechanism causing this, or another degradation mechanism is making lithium plating more likely to occur.

One key point to note from Figure 42 is that the cells appear to follow a very similar path regardless of the cooling setup, up until the knee point is initiated. This may mean that lithium

plating is not the dominant degradation mechanism for the majority of the cells decline prior to the knee point, but it eventually becomes the defining degradation mechanism due to other mechanisms, such as loss of active material in the anode, reduced anode porosity, SEI growth or electrolyte dry out. Then the operating temperature of the cell becomes the key factor for when this possible lithium plating knee point becomes critical. The resistance increase for the FS rate is around 20% lower than for the SS rate, hinting at resistance not being the driving factor for the occurrence of the knee point. Together with the fact that no knee point occurred for the SF or FF rates, then it is plausible that either particle cracking or consumption of FEC in the electrolyte resulted in a significant loss of active material or pore clogging. This would increase the local current density in the remaining usable areas of the electrode and facilitate the compounding lithium plating that caused the death of these cells.

If the degradation differences are caused by the differences in overall temperatures, then this does not definitively mean that side cooling is worse for degradation compared to base cooling. With intelligent thermal control (that would not cool the cells as aggressively) and common fast charging protocols (such as pre-heating) it is possible that an optimised side cooled pack could outperform an optimised base cooled pack.

One counter hypothesis is that this result is caused not by the surface cell temperature, but rather by the potential internal thermal gradient¹⁸⁶ and subsequent inhomogeneous degradation.¹⁸⁷ This hypothesis is difficult to validate without knowledge of the real internal gradients. It is possible that the better perceived cooling of the side cooling results in higher internal gradients. Furthermore, it is understood that high internal thermal gradients can lead to lithium plating through uneven and highly localised current densities and overcharging.¹⁸⁸ It is not possible to know for certain, but disassembly may show evidence of these gradients if they exist, this can be seen in Section 5.4.3 End of Life Analysis. If this is the case, then side cooling could be worse than base cooling for fast charging the Samsung cells, which aligns with the data for the FS rate, but not with that of the FF rate.

SF Rate

Analysing the SF rate, it is clear that the fast discharge has significantly increased the life performance of the cell compared to the SS rate. Additionally, there is a significant difference between side cooling and base cooling, with the side cooling achieving almost 80 kWh of throughput, which is almost 2200 full equivalent cycles and over double the throughput of the SS rate. Under base cooling the cells are still able to achieve almost 60 kWh of throughput,

which is still around 1700 full equivalent cycles, and 70% higher the SS rate. Unlike the FS rate, side cooling is better for this rate combination than base cooling. The better performance of side cooling compared to base cooling can be explained by a conventional understanding of how temperature affects degradation, where hotter cells degraded faster. The key point of interest is that going from a slow discharge to a fast one increased life performance by a large margin. Conventional understanding suggests that higher currents lead to worse degradation, increasing the stress on all cell components, in particular on electrodes. It is useful to remember that the slow discharge has a E/3 average, and the fast discharge has a 2 E average with 5.5 E peaks. The impact of the higher currents and temperatures in SF must be less dominant than another mechanism. The only other variable that changes between the SS and SF rates is the SOC window (caused by the rate difference). It is shown in Section 5.4.1 Beginning of Life Analysis that the SF rate uses around 10% less of the lower portion of the SOC window, which possibly is extending the life of the cells. It is widely reported that for cells that contain silicon in the anode, the lower portion of the voltage window is where the silicon is most utilised.¹⁸⁹ While silicon increases the cell's energy density, it can exhibit short cycle life, due to its extreme expansion and contraction during lithiation and de-lithiation.¹⁹⁰ It is probable that avoiding cycling within the lower 10% of the SOC window resulted in drastic decrease in the silicon utilisation in the cell, thus preventing silicon-based degradation mechanisms that may have been occurring in the SS and FS rates.^{129,191}

FF Rate

The first thing to note about FF rate is that the variation across the three cell repeats is significantly higher than for any of the other rate combinations. This makes comparing the effect of cooling more difficult, as the difference in energy throughput is within the spread of the repeats. Overall, it seems that the effects of the fast charge and the fast discharge offset one another, leaving the life performance of the cells under this rate similar to that of the SS rate. Analysing Figure 43 it seems that the life performance in this rate is correlated to the BoL surface temperature, similar to the SF rate. However, looking back at Figure 42, it can be seen that the significant spread in the behaviour of these cells means that, while convection does seem to perform worse than base and side cooling, the latter two may, in fact, have performed similarly. This is particularly the case if the side cooled cell that exhibits the highest energy throughput is considered an anomaly. Looking at the Molicel results at this rate combination, it appears that they follow the same trends with cooling as the Samsung, but overall perform worse than the Samsung, achieving lower energy throughput. This contrasts the SS results

where both cells performed almost identically, suggesting that the Molicel, is less capable of handling the high rates or temperatures of the FF combination, compared to the Samsung cell.

Key points

The key takeaways from these results are as follows:

- For the automotive reference cycle SS, both Samsung and Molicel have equivalent life and the cooling has little impact on the cell life performance.
- Fast charge has a significant negative impact on life performance. It is hypothesised that this is due to lithium plating, but this cannot be confirmed with the data presented, as other than the high current rate, the high temperature and reduced maximum SOC would not typically facilitate lithium plating.
- Fast discharge significantly improves cycle life, probably due to reducing the utilisation of low SOC states.
- Cooling makes a significant impact on life when the cell is subjected to high electrical load.
- Internal cell structure does appear to impact which cooling system is best for life performance.
 - For the Samsung cell, with single negative tab and adhesive between the jellyroll and can, side cooling appears to be the better cooling system for fast discharge. The choice is opposite for fast charge and slow discharge however this could be due to over cooling the cell.
 - For the Molicel, with 3 negative tabs, both side and base cooling systems seem equivalent, and beneficial compared to convection cooling for faster rates.

5.4.3 End of Life Analysis

This section covers post-mortem analysis performed on the cells that have completed cycling, with the aim to investigate some of the potential reasons for the degradation trends seen in the previous section. The cells are removed from cycling as soon as one of the following three criteria is met:

1. The cell goes “open circuit”, where the cell still has voltage, but the cycler is unable to pass current.
2. The usable energy of the cell drops below 1Wh.
3. The cell begins ‘infinitely’ charging. *

*At the end of life some cells go into a CV hold where the current stops decaying to the current cut-off. While in this state, the cell is observed to start producing significant heat, while the current profile becomes noisy and unstable. This could be due to the cell short circuiting through internal lithium dendrites, or some form of self-discharge mechanism transferring lithium back to the cathode. This state was observed to continue for days. When this behaviour is observed, the cell is removed from cycling.

This analysis will be performed solely on the Samsung cell, as it has almost a full matrix of completed tests, allowing for full rate and cooling comparisons.

Gas Production

It is noted that many of the cells that reach the end criteria and complete testing no longer have a flat base. This is seen through extensive irregular oscillation caused by imbalance as they are placed on a flat surface. It is hypothesised that this is due to gas production in the cell pressurising and straining the cell can. This is further supported by the fact that some of the cells read 0 V indicating that their CID was triggered by internal overpressure. This is confirmed during disassembly of the cells, analysis of which is shown in the following section. To qualitatively assess the relative amount of gas production, the lengths of the cells are measured, using digital callipers (0.01 mm resolution, ± 0.01 mm accuracy), following the assumption that the displacement of the can is proportional to the internal pressure. The results of these measurements are presented in Figure 44.

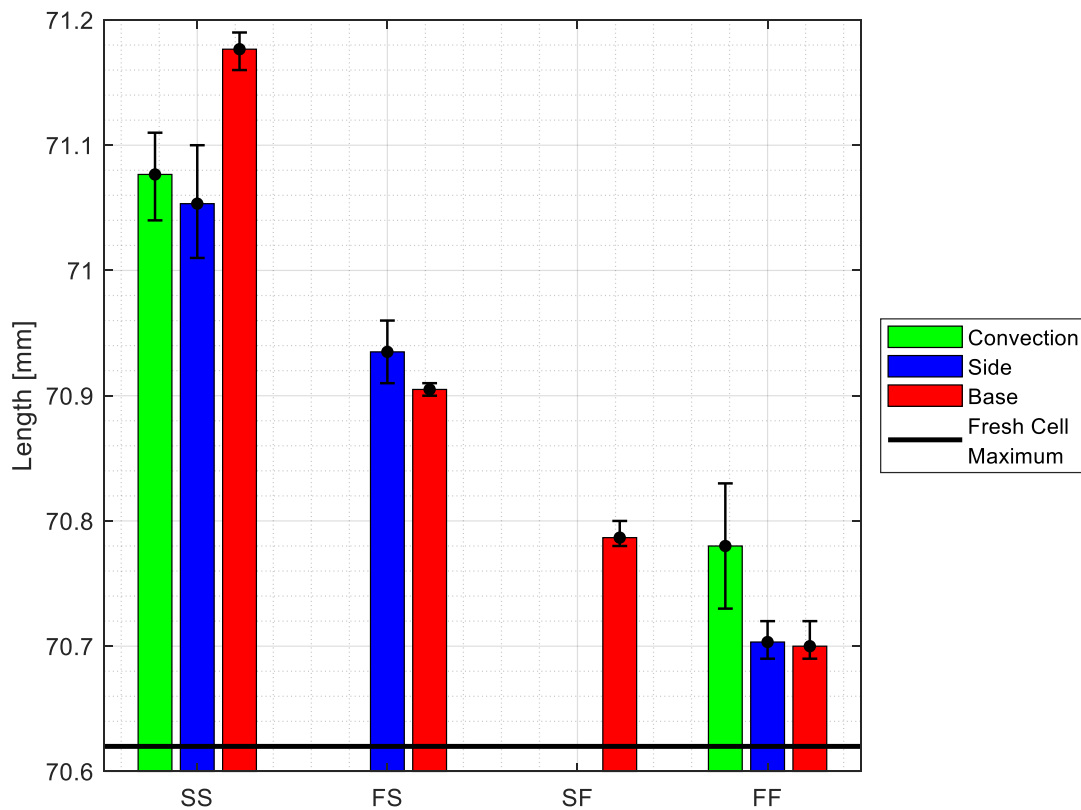


Figure 44: Cell length measurements for each cell, rate, and cooling combination for the Samsung cells. Cell length is hypothesised to be correlated to the internal gas production. The maximum length of a fresh cell (as per the specification sheet) is displayed via the solid black line at the bottom of the plot.

Figure 44 presents a clear trend between the cycling rate and the cell length, with the variance between cells being less than the differences between the rate combinations. There is one set of cells missing from this analysis, the side cooled cells on the SF rate - this is because they are yet to reach any of the three previously stated end of cycling criteria. The trend appears to correspond to the trend with the time duration of a single cycle at BoL, with the SS rate being the longest, then FS, SF, due to the slow discharge being slower than the slow charge, then lastly the FF rate, being the fastest cycle. This does not correspond to the ordering of cells in terms of real time to death, as in real time the FS rates died the fastest, then FF, SS and lastly SF. The trend found in Figure 44 is backed up by the occurrence of cells with 0 V (hence CID triggered): almost all the SS cells had 0 V after cycling, with some of the FS cells reading 0 V, and none of the SF or FF cells reading 0 V. Another trend to take note of is that the two rate combinations that resulted in knee points have the most apparent increased internal pressure; this might suggest that the mechanism leading to the knee point caused a significant increase in gas production.¹⁹² Most commonly, gas production is caused by electrolyte consumption and

SEI formation. Time-based frequency analysis of the voltage data on the cycles is given in the next section, Figure 45 shows that the SF and FF rates result in the cells spending significant portion of their cycling time, around 20%, in the charge CV hold, whereas SS and FS spend only around 5% of their life in the CV hold. This rules out high full-cell voltage mechanisms as a possible cause of the gas production trend seen in Figure 44.¹⁹³ The SS and FS rates result in the cells spending more time in low potentials than the other two rates; this agrees with the BoL analysis on the SOC window, which suggests that the SS and FS rates reach lower SOC. This gives a couple of potential mechanisms to explain the gas production trend. One likely mechanism is the high utilisation of the silicon in the anode resulting in particle cracking, leading to new SEI formation, and electrolyte consumption.¹⁹⁴ Another potential mechanism is H₂ production from the reduction of water at the anode, which occurs at high anode potentials vs Li.¹⁹⁵

Voltage Distribution Analysis

To support the analysis in the previous section, a histogram of voltage is given in Figure 45 presenting the fraction of time spent at each voltage over the course of the entire life of the cells. This is shown for the base cooled Samsung cells at all four rate combinations. It includes the degradation cycle as well as rest, RPTs and intermediate steps between RPTs. This plot is created by plotting the occurrence of voltage datapoints in the full dataset, adjusted for differences in logging rate, but not for the double recording of the 0s point when a step begins. The effect of the double counting is most significant for the drive cycle discharge where the step times are short, where the double recorded steps make up 2.5% of the datapoints only. The error caused by these extra points is deemed to be largely insignificant to the analysis of these plots.

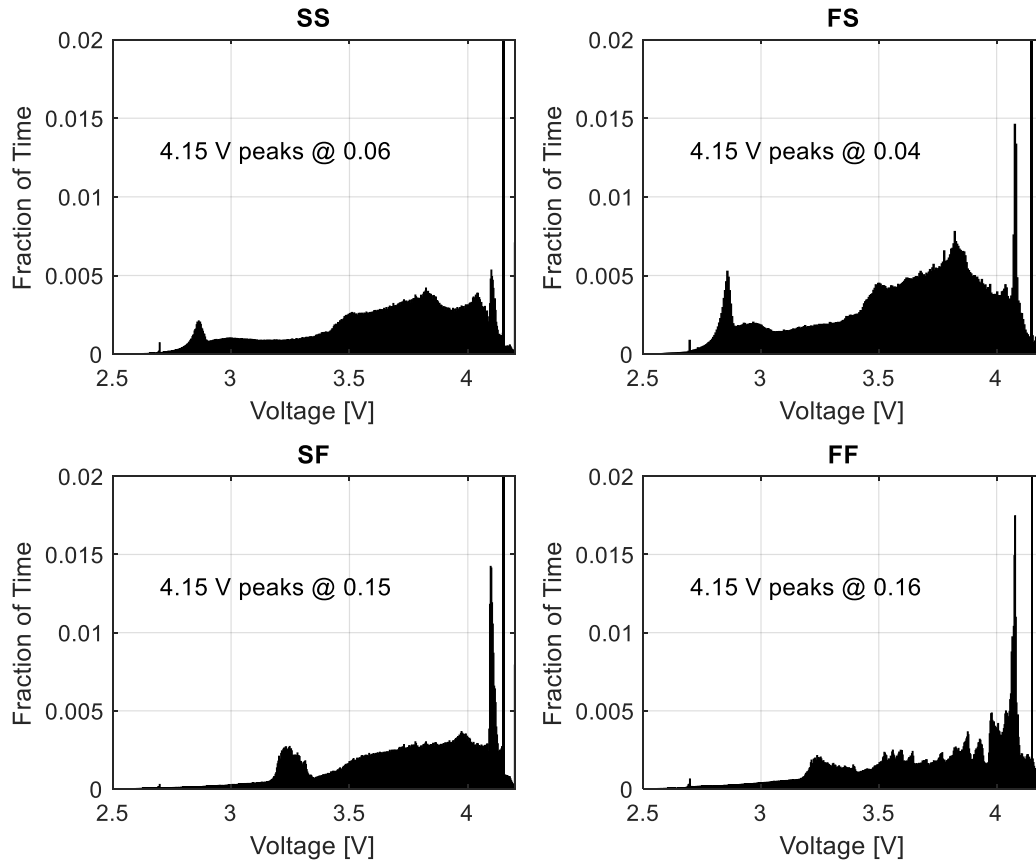


Figure 45: Histogram of voltage across the full life for one Samsung base cooled cells on each of the four rate combinations. The peaks at 4.15 V, caused by the charge CV hold, have been cropped from the top of the subplots, to allow for better clarity. The 4.15 V bin values are stated on the corresponding subplots.

There are 3 notable peaks visible in the histograms: one at the lower voltage, caused by the 15 min rest after the discharge, one at 4.15 V with height cut off by the limits of the y-axis, caused by the CV hold in the degradation charge cycle, and one just before the 4.15 V peak, caused by the 15 min rest after the charge. The biggest differentiator that can be seen in these plots is the presence of a fast discharge, in the SF and FF histograms shown in the bottom two plots. Compared to the SS and FS rates, both show significantly reduced time fractions spent in the lower voltage range of the cell, as well as significantly increased time fractions spent in the CV hold of the charge. Interestingly, the FS rate cells spends more of its life in the lower voltage range compared to the SS rate, potentially explaining its rapid death, such as caused by low voltage (possibly silicon) based degradation mechanisms.

Differential Voltage Analysis & Cell Disassembly

To further the investigation of the cause of death of the cells, a selection of the cells has been disassembled for visual inspection of the jellyroll and electrodes. The cells are disassembled inside an argon environment in a glovebox, where the positive cap is cut away from the cell

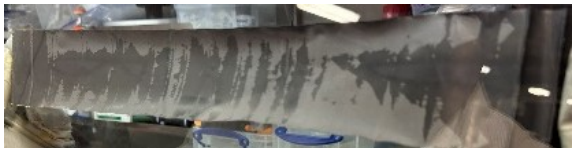
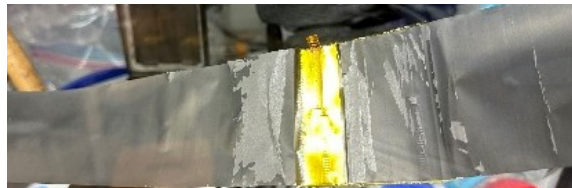
using a pipe cutter and the can peeled away from the jelly roll with pliers. The cell is then carefully unrolled, and the separators carefully peeled off the electrodes. None of the features analysed in this section are present in a fresh cell. For this selection of cells, differential analysis is performed on the C/10 charge curves from the RPT, with the aim of assessing if differential analysis can provide further information on the differences in degradation paths taken by the different cells. The charge data is chosen over the discharge to avoid the artifact that would be created by the 10 s pause in the discharge curve.

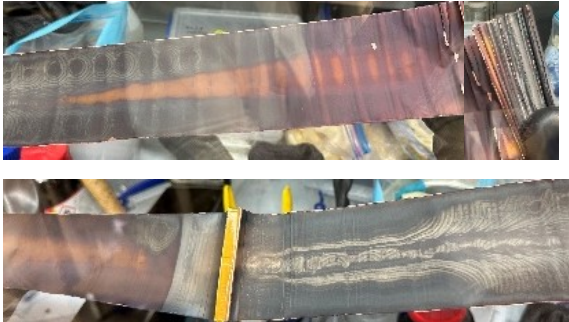
Cooling Comparison

Cell Disassembly

To compare the degradation differences between the three cooling systems, one cell from each of the FF rate runs is disassembled. Only one cell is disassembled so that the remaining two cells are available for other techniques to be assessed in future work, it is expected that all three repeats would present similar visual features of degradation. The FF rate is chosen as it is performed on all three cooling systems and displays significant differences in thermal and electrical performance between the cooling systems, as seen in Figure 42 and Figure 43.

Table 13: Cooling Comparison - Disassembly images and notes for one FF rate cell from all three cooling systems (convection, side and base cooling)

Convection	Side	Base
Cathode		
Inner Face:  Outer Face: 	Inner Face:  Outer Face:  	Inner Face:   Outer Face: 
Notes		
Significant flaking and detachment of inner face of cathode from tab to inside end of roll.	Minimal damage to both faces around the tab, the rest of the electrode is visibly free of damage.	Moderate damage to both faces around the tab, as well as at the inside end of the roll on the inner face.

No visible damage to inner face from tab to outer end of roll, nor to entire outer face.		The rest of the electrode is visibly free of damage.
Anode		
Inner Face:  Outer Face: 	Inner Face:  Outer Face: 	Inner Face:  Outer Face: 

		
Notes		
Note: Anode is partly lithiated. • Visible lithium plating on both inner and outer faces from the tab to the inside end of the roll, with increased intensity at the positive end of the cell, in the direction away from the tab. • Plated sections are attached to separator, tearing it (as seen on the left-hand side of the first outer face image). • Moderate portion of the outer face, near the inside end of the roll, detached from current collector.	Note: Anode is lithiated. • Significant plating on both faces around the tab, mostly in the direction towards the inside end of the roll. Starts mainly at the centre of the electrode height, then spreads to full height in the direction of the inside end of the roll. • Plating on the inner face at the inside end of the roll. • Lithiation of both faces, from the tab to outer end of the roll, with increased intensity in the centre of the electrode height.	Note: Anode is lithiated. • Plating on inner face around the tab, mostly on the side towards the inside end of the roll. Starts spreading across the height of the electrode, concentrating at the edges of the electrode height as it moves towards the inside end of the roll. • Significant detachment of the electrode from the current collector on the outer face from the tab to inside end of the roll.

Analysing the disassembled cells, shown in Table 13, there is a clear difference between the degradation caused by the three cooling systems. Degradation to the cathode structure and/or binder results in portions of the electrode separating from the current collector. The intensity of the visible degradation appears to be correlated with cells for which the surface temperature was high during cycling, with the convection cell displaying the most significant degraded area, and the side cooled displaying the least visible degradation. The visible degradation appears to be focused around electrode areas that are expected to have experienced higher current density and temperature, such as areas around the tab⁸³ and towards the inner coils of the jellyroll. High temperatures are known to promote transition metal and binder dissolution reactions which can help break down the structure of the cathode and separate it from the current collector, respectively. One potential difference in the cell state driven by the cooling scenario besides temperature is the time spent in different SOC windows. The significantly larger SOC window spanned by the cells cycling under convection may also be a driving factor in this cathode degradation. Achieving higher states of de-lithiation as well as spanning larger SOC windows is known to stress and crack the NCA cathode.¹⁷¹

The comparison of the anode degradation is challenging due to the base and side cooled cells being almost fully charged at the time of disassembly, whereas the convection cell is not. However, it does offer useful insight into the differences in lithiation gradients and plating between the side and base cooled cells. The convection cell displays a moderate amount of plating on both faces near the internal tab. While lithium plating is typically caused by high currents at high SOC's at low temperatures, it is still possible to trigger plating at these temperatures,¹⁸⁴ due to the high current and possibility for highly localised current densities¹⁸⁸ and possible localised overcharging.¹⁹⁶ There is more plating at the top of the electrode, near the positive end; this could be due to thermal gradients in the cell affecting local resistance and subsequently affecting the localised current density and/or SOC. When attempting to remove the separator, it was found to tear when in proximity to the plated lithium. This suggests the plated lithium has pierced the separator, potentially causing some short circuiting and LLI. Coupled with the severe cathode structural deterioration, this may explain why the convection cells did not last as long as the side and base cooled ones. Both the side and base cooled cells display significantly more plated lithium compared to the convection cell. However, as the electrode is significantly more lithiated, it is possible that some of this is reversible lithium plating, whereas on the convection cell, all of the visible plating is likely irreversible. Due to

the potential mix of reversible and irreversible plating, it is not possible to fairly compare the difference in quantity of plated lithium between the convection cooled cell and the cells under the other two cooling methods. However, a qualitative comparison can be done, focussed on the visible lithiation and plating patterns. The side cooled cell appears to have a higher lithiation and plating concentration in the centre of the electrode height. In contrast, the plating in the base cooled cell appears to be less concentrated in the centre, occurring at the top and bottom of the electrode height. Surprisingly there is no evidence of any impact caused by the surface axial thermal gradient that is measured at BoL. This may suggest that such gradient does not reflect that of the thermal profile of the jellyroll, thus highlighting the dangers of assuming jellyroll thermal gradients from surface measurements on a base cooled cell. Furthermore, while it is apparent there are differences in the spatial profiles of the anode degradation, for the cell as a whole, the degradation difference between these two cooling systems is minimal, as can be seen in Figure 42.

One aspect that is clearly different between the cells is the significant detachment of the anode in the base cooled cell, which occurred as the jellyroll was unravelled, with no force applied to remove the separator. While this could suggest severe delamination of the anode from the current collector, the electrode that remained on the separator was lithiated following the same patterns seen in the rest of the electrode. This means that this electrode was likely still active prior to the disassembly of the cell. This could still suggest a severe breakdown of the binder, with the mere pressure of the roll keeping the electrode in electrical contact with current collector. It is unclear why this only occurred in the base cooled cell. Further cells should be taken apart to ascertain whether this is a feature of chance caused by disassembly, or a critical outcome of the specific degradation of the cell.

Differential Voltage Analysis

While disassembly shows clear differences in the aspect of the cell internal components between the cooling systems, differential analysis does not reflect these differences beyond doubt. Figure 47 displays the differential voltage curves of all the FF rate combination tests, covering all three cooling systems, at 80% available capacity. This has been chosen as a comparison point rather than the final EoL RPT because the cells did not all achieve the same SOH before they completed testing, making it difficult to draw conclusions by comparing the EoL differential curves. The 80% SOH point provides a fair comparison point of the different degradation paths, as it is here that the cells would have typically stopped cycling. The data displayed in Figure 47 results from the RPT closest to 80% available capacity.

The analysis of the differential curves is based on work demonstrated by Keil et al. (2017), where they analysed a similar graphite-NCA 18650 cylindrical cell.¹⁹⁷ The differential voltage curve of the Samsung 50S used in this study is presented in Figure 46. The curve is largely similar to the one presented by Keil et al. (2017), with some differences; the extra features at 0.5 Ah and 2.5 Ah. But critically to this analysis, the two key peaks that were used in their analysis are clearly visible in Figure 46, labelled as peaks A and C. Keil et al. associated the peak labelled A with the graphite anode phase transition from the medium to low voltage plateau. Its distance from the beginning of the charge, indicates the storage capability of the anode. The peak labelled C is associated with the NCA cathode, its distance from the end of the charge indicates the storage capability of the cathode. Finally, differences in the distance between peak A and C indicate changes in the electrode balancing between the anode and cathode.^{170,197}

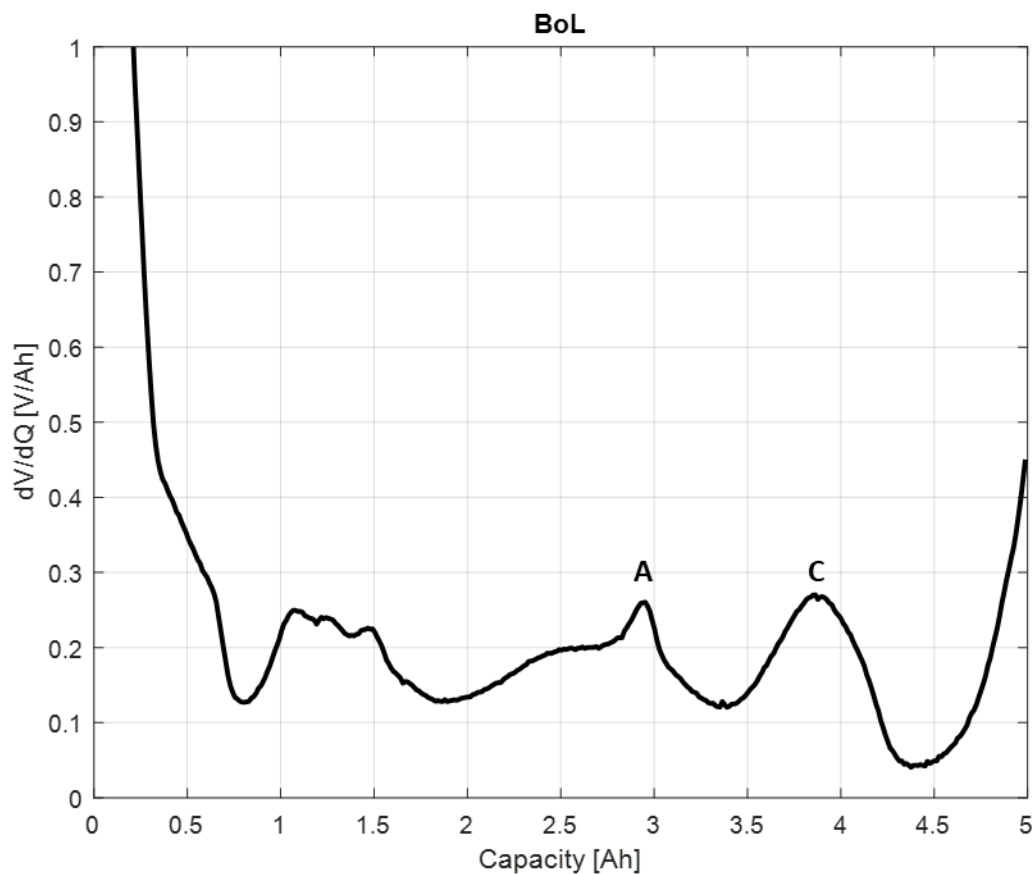


Figure 46: Differential voltage plot for Samsung 50S at beginning of life. Peaks identified as A and C are caused primarily by the anode and cathode, respectively.

The peak at 0.5 Ah can be associated to the silicon in the anode, this has been demonstrated by Wildfeuer et al. (2022), who identified a similar peak.¹⁹⁸ However, even though it appears that

this feature is caused by silicon in the anode, it is difficult to assess what the evolution of this peak means physically for the state of silicon in the anode, as there is little literature that explores this. Part of this could be due to specific issues that arise from silicon particle degradation. Research has shown that the significant volume change of silicon particles can lead to variability in the contact pressure between particles,¹⁸³ and the resistance of the SEI around particles, as cracks in the SEI open and close.¹⁹⁹ Both of these effects can impact when silicon particles lithiate and de-lithiate, affecting where its features appear on the differential voltage plot. Thus, while the evolution of this silicon feature at 0.5 Ah can be discussed, it will not be possible to make any conclusions on the state of silicon as a result.

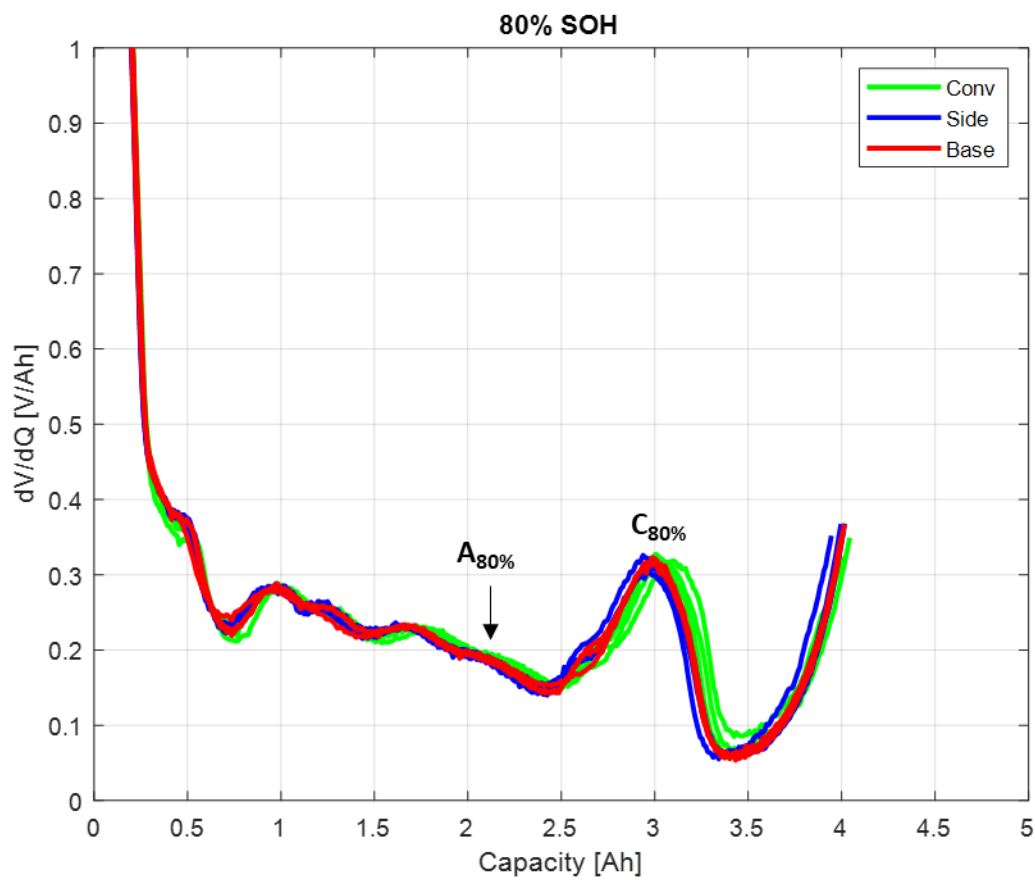


Figure 47: Differential voltage curves at 80% available capacity for the FF rate combination under convection, side and base cooling. All repeats have been displayed. Peak A (anode) and C (cathode) have been highlighted for degradation analysis.

Analysing Figure 47, there is minimal difference between the 3 cooling systems, with the cells from the base and side cooling tests having almost identical curves. Importantly, the cell-to-cell variation under a single condition is of the same magnitude as the difference made by cooling in the features of the differential voltage. For example, the most obvious difference is the shift of peak C. The convection cells display a range in the location of peak C that starts in

a position similar to the base and side cooled cells and ends in a position around 0.2Ah closer to the end of charge. This shift could indicate the higher observed cathode degradation seen by the convection cell that has been disassembled. Looking back at Figure 43, these cells displayed significantly different amounts of energy throughput before reaching the 80% point. This means that, while the cells follow roughly identical degradation paths, the rate at which they are degrading with energy throughput varies.

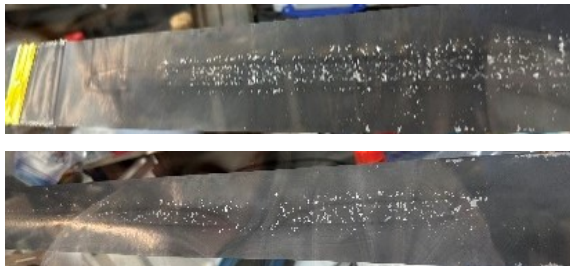
Peak A is hardly identifiable in the degraded curves, its position has been identified by tracking its shifts via the RPTs between BoL and 80%, not shown. It can be seen that peak A shifts by around 1 Ah, indicating a severe reduction in the anode capacity. Peak C, while it clearly occurs at a lower capacity, it maintains its approximate distance from the end of the trace, to around 1 Ah. The distance between peak A and C remains roughly the same, meaning that the electrode balancing is largely unaffected. Coupling the information provided from the disassembly with these differential voltage curves, it can be concluded that the majority of the degradation for these cells is due to the reduction of the storage capability of the anode, with the earlier death of the convection cells likely caused by slightly more degradation to the cathode. To briefly examine the 0.5 Ah silicon feature, its location on both axes appears unchanged from BoL, however the length of the feature is smaller in both x and y, this could suggest that the silicon in the anode has degraded but is ultimately inconclusive.

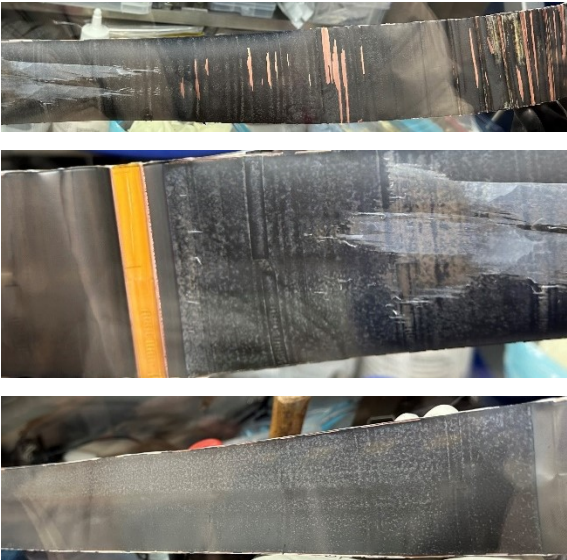
Rate Comparison

Cell Disassembly

To investigate the differences in degradation caused by the charge and discharge rate combinations, one cell from each of the remaining base cooled tests (FF disassembly is shown in the previous section) is disassembled. Base cooling is chosen for this analysis, as data is available for all the available rate combinations, and all the cells have reached one of the end of cycling conditions.

Table 14: Rate Comparison - Disassembly images and notes for one SS, FS and SF rate cells from the base cooling tests

SS	FS	SF
Cathode		
Inner Face:  Outer Face: 	Inner Face:  Outer Face: 	Inner Face:  Outer Face: 
Notes		
Visually the cathode is in very good condition.	Visually the cathode is in very good condition.	Portions of the centre region of the inner face are stuck to the separator and detach from the current collector during disassembly.

Anode		
Inner Face:  Outer Face: 	Inner Face:  Outer Face: 	Inner Face:  Outer Face: 

		
Notes		
• Significant lithium plating across the inner face, with a higher concentration between the tab and inner end of the roll. • Slight concentration at the top of the electrode on both faces from the tab to outer end of the electrode • Separator stuck to electrode areas with plated lithium. • Outer face has significant detachment of the electrode from the inner end of the roll to after the tab.	• Similar levels of plating to SS, with high concentrations on both faces between the tab and inner end of the roll. • Similarly to SS, from tab to outer end of roll, plating is concentrated towards the top of the electrode. • Separator stuck to plated lithium. • No detachment of electrode.	• Corresponding locations of the anode to where the cathode is attached to the separator are attached to the separator. • Significant detachment of the inner face, with only a central portion between the tab and outer end of the roll remaining attached to the current collector. • Different to previously seen detachment – electrode is not brittle and flaking, surface of the copper still contains traces of the electrode material. • No visible signs of plating.

Analysing the disassembled images in Table 14, there are clear differences between the different rate combinations. Comparing the cathode degradation, both SS and FS rates present almost no visible degradation of the cathode, while the SF rate displays a significantly different degradation pattern compared to the FF rate cell shown in Table 13. The FF rate displayed the electrode easily detaching and flaking from the current collector around the tab and innermost portion of the roll, whereas the cathode of the SF rate cell is still well attached to the current collector. Small regions on the SF cathode, dotted throughout the centre of the inner face, are more attached to the separator than to the current collector, resulting in these regions of the cathode being forced apart from the current collector as the separator is pulled off. In total contrast, the outer face of this cell's cathode is visually pristine, it's possible this difference is due to the difference in tensional/compressive forces between the inner and outer face of the electrode. Ultimately, both SF and FF rates display some form of cathode degradation where SS and FS display none. One potential reason for this could be an increased rate of transition metal dissolution and/or particle cracking caused by spending more time at high voltages and SOC_s,²⁰⁰ this is supported by the Voltage Distribution Analysis presented earlier in this section.

Analysing the anodes, it can be seen that both SS and FS rate cells show signs of significant lithium plating on both anode faces. Similar to the FF cell, the concentration of lithium plating is higher from the tab to the inner end of the roll. However, unlike the FF cell, both the SS and FS cells show signs of an axial gradient with more plating visible at the top of the electrode. The top of the electrode is expected to be the hotter region of the cell due to the base cooling, suggesting that the plating is occurring due to high localised currents and/or local overcharging caused by the reduced resistance and overpotential of these hotter regions of the electrode. Both the SS and FF rate display significant detachment of the outer face of the anode layer. As mechanisms can be suggested that can affect only these two rates and not the others, this observation gives more weight to the hypothesis that this detachment is a feature of chance during the disassembly. Thus, the mechanism leading to this detachment is likely occurring to all cells in the study. The exception to this is the anode from the SF cell, which is unlike any of the others. Firstly, the inner face completely detached from the current collector, but unlike the other anodes, it detached during the removal of the separator, with moderate adhesion still remaining to the current collector. This is the reason behind the different appearance of the bare copper: traces of the anode are still bound to it. Secondly, the detachment of the anode's outer face corresponds to the exact locations of where the cathode inner face is attached to the separator. Thirdly, the general appearance of the remaining anode is different from the other

cells, unlike that of a BoL cell; it appears shiny and smoot. This could be particle morphology changes and smoothing, potentially caused by the increased time spent cycling, possibly under pressure.

Differential Voltage Analysis

Differential voltage analysis of all the base cooled tests is presented in Figure 48. The first thing to note is the significant spread of the three FS repeats, specifically at peak C; this is likely due to these cells being past the “knee point” as they crossed 80% SOH. The rapid degradation that these cells experience during this period leads to significant evolution of the differential voltage, this results in large changes of the SOH between each RPT, making it harder to match one exactly at 80% SOH. Keeping this in mind, it appears that the FS curves largely match the curves of the FF cells. Similarly, the SF and SS cells have matching curves, that follow a slightly different profile to the FS and FF cells. This shows the cells degradation path is largely dominated by the difference in charge. The most obvious difference between these two groupings is seen at peak C, where the two fast charge cycling scenarios appear to have less cathode degradation compared to the two slow charge rates. This does not mean that the fast charge reduces cathode degradation, but instead that it increases anode degradation; this can be seen by the similar magnitude shift seen at peak A. This trade off occurs because the plot displays all cells at the same level of total degradation, so a relative increase in one type of degradation means a relative reduction to the others. One thing to note is that the lack of common features between the SS and FS curves means that this differential voltage plot does not offer any predictive insight into why these two rates displayed “knee point” failure and the two fast discharge rates did not.

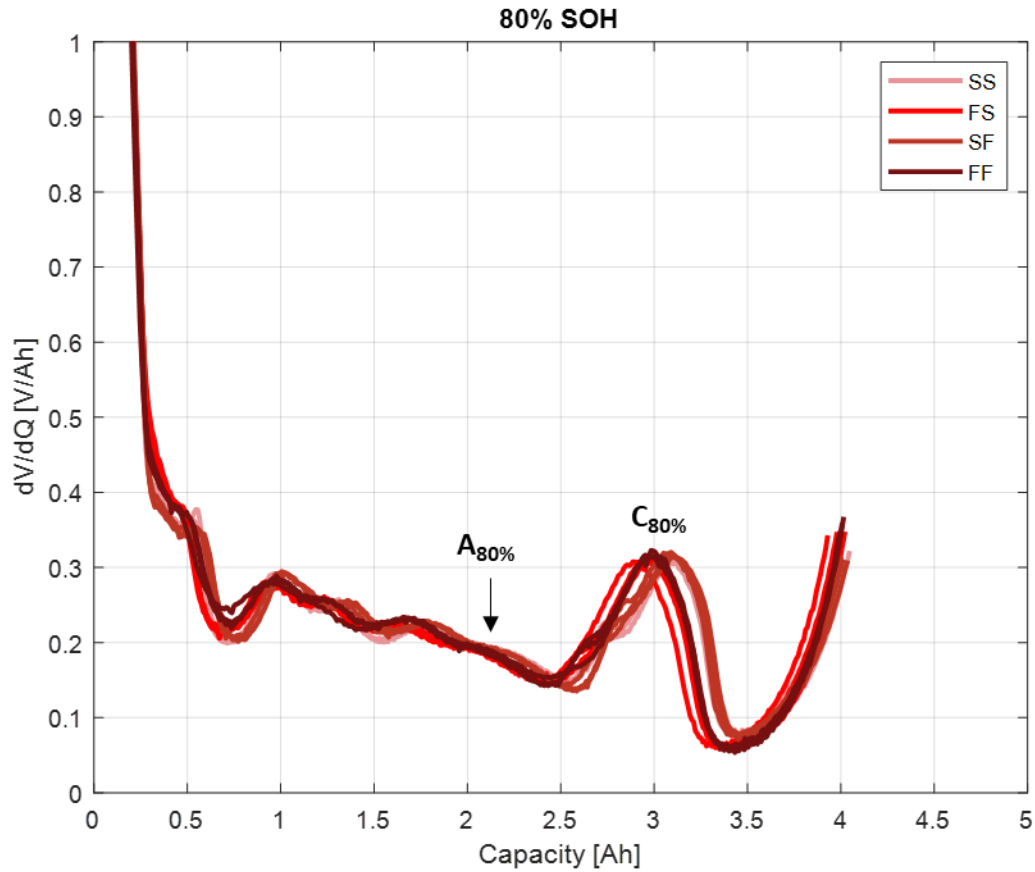


Figure 48: Differential voltage curves at 80% available capacity for the base cooled cells under all four rate combinations. All repeats have been displayed. Peak A (anode) and C (cathode) have been highlighted for degradation analysis.

Key Points

The key takeaways from this EoL analysis are as follows:

- The visible deterioration of the electrodes is possibly aggravated by the dismantling procedure; however, the weakened structure and weak adhesion of the electrodes are still reflective of their deteriorated state.
- The cells are primarily degrading via degradation of the anode, which is hastened by fast charging and utilising low SOC's (silicon).
- The “knee point” failure of SS and FS is possibly linked to high levels of gas production and lithium plating in the cells, which may be triggered by deterioration of the silicon in the anode.
- The cooling has a clear impact on the internal temperature of the cells, leading to different levels of overall deterioration of the electrode structures, as well as inhomogeneous degradation across the electrodes.

5.5 Conclusions

The work in this chapter aims to investigate the impact of base and side cooling on 21700 cylindrical cells and the subsequent impact on their life performance. Two high performance 21700 cylindrical cells are chosen based on their chemistry similarities and internal structure differences: the Samsung INR21700 50S and the Molicel INR21700 P45B. A matrix of degradation tests has been performed on the cells to assess whether high power charge and discharge rates impact which cooling system is optimal. Additionally, convection cooling has been used as a reference to the other two cooling systems.

Beginning of life (BoL) analysis highlighted side cooling being the optimal cooling system for both cells, achieving the lowest surface temperatures and surface temperature gradient, with base cooling leading to significantly higher surface temperature measurements and surface thermal gradients. Convection cooling led to the hottest surface temperatures overall. The reference (automotive) rate of slow charge slow discharge showed minimal difference between the 3 cooling systems. The BoL analysis also highlighted the importance of not only assessing the capacity throughput of a cycle but the energy throughput, with a significant difference between the two, depending on the charge or discharge.

For assessing the life performance, a cut-off of 80% SOH, based on remaining available capacity assessed at C/10, is used for comparison. Under the reference slow charge slow discharge cycle, the cooling made little difference to the cycle life of the cells. Fast charging is shown to be very detrimental to life, accelerating the anode degradation and the occurrence of a “knee point”. Lithium plating is identified as the cause of the knee point, with its occurrence likely increased by deterioration of the anode structure. The cooler surface temperatures of side cooling were correlated to lower cycle life compared to base cooling, under the fast charge slow discharge cycle. However, this result can be avoided with intelligent thermal control, using process such as pre-heating and increased coolant temperatures specifically for fast charging. Surprisingly, fast discharge was shown to significantly improve life performance, which was identified to be due to preventing utilisation of low SOC, thus likely reducing silicon (anode) degradation. Here the cooler temperatures of side cooling significantly improve life performance compared to base cooling, which is seen for both fast and slow charge combinations with fast discharge. Via disassembly and differential voltage analysis, part of this improvement is shown to be due to reduced cathode degradation. It can be suggested that the faster death of fast charge slow discharge compared to fast charge fast discharge is coupled to

silicon degradation. Thus, the absence of silicon in the cell anode may remove the coupling to lower temperature induced lithium plating, resulting in side cooling being best for all rate combinations.

Chapter 6: Conclusions

The aims of this thesis were to determine the best methods of selecting the best cylindrical cell and cooling system for an application. The work presented in this thesis helped further understanding on how best to test cells for the selection of the most optimum cell. The literature review identified that most cell selection must be done using the limited information available on cell datasheets, which specify the cell's electrical performance under standardised conditions, and rarely offer any insight into thermal performance. The work in this thesis, assessed a potential thermal metric for cell datasheets, as well as the viability of standardised testing for beginning of life (BoL) and end of life (EoL) performance.

6.1 Cell Cooling Coefficient

The cell cooling coefficient (CCC) was identified as a potential thermal metric for lithium-ion cell datasheets. The CCC is a thermal metric designed for lithium-ion cells, defining their heat rejection capability through a specified surface. The CCC is defined by the heat flow through the cooled surface divided by the thermal difference across the cell required to transmit this heat. The CCC had been demonstrated on pouch and prismatic cells but was yet to be applied to cylindrical cells. Before starting the experimental measurements, the method used to calculate the CCC from experimental data was improved, using the existing data. Rather than calculating an individual value of CCC for each value of heat generation, a line is fit through a plot of heat generation vs. thermal difference, the gradient of which is the CCC. By calculating a single CCC that fits all the experimental data, it is shown, on existing data, to help overcome experimental errors, making CCC calculations more consistent.

Following this updated calculation, an experimental rig was developed and used to successfully measure the CCC for base cooled cylindrical cells with tab welded electrical connections at both ends. This CCC was measured for a LG M50T 21700 cell and a Samsung 30Q 18650 cell. The CCCs were measured over a range of heat generation, SOC, and cooling temperatures, to demonstrate the invariability of the CCC. The two cells are compared using the CCC and other metrics. The CCC of the 18650 cell is 16% lower than the 21700. However, when comparing the CCC divided by the area of cooling, the 18650 rejects 13% more total heat per unit of area, making it more efficient at rejecting heat given its geometry. This difference is driven by the geometry of the cells, highlighting the fact that 18650s have a better surface area to length ratio compared to 21700s, making them better at base cooling. The analysis also highlights the

importance of coupling the CCC with information about the cell's heat generation. The 21700 cell was 20% more resistive compared to the 18650 cell, based on a rough approximation using the overpotential during the CCC pulsing. This would mean that if both cells were assembled into packs of equivalent capacity, the 21700 pack would generate significantly more heat for the same pack power, compared to the 18650 pack. While the comparison was not fair, due to differences in energy density between the cells, the analysis highlights the importance of coupling the CCC with a heat generation metric.

A second CCC rig was developed to measure the CCC for base cooled cylindrical cells with wire bonded electrical connections on the top of the cell. This is a more accurate electrical connection method for base cooled cylindrical cell packs. Unfortunately, the measurements attempted using this rig were inconsistent, with CCC values that varied by up to 75% due to slight setup changes. To assess the potential causes of this variation to the CCC, a model was required, so that each variable can be adjusted independently to assess its impact on the measured CCC.

The first model was developed with the aim of understanding the CCC at fundamental level, such that it is possible to gain analytical solutions to the CCC. To achieve this, a one-dimensional model of the steady state heat transfer equation with an internal heat source is solved. Solving the equation with ideal boundaries, the model revealed that for a body with uniform conductivity and heat generation, the CCC is equal to double the thermal conductance of the body. This means that CCC is only dependent on the properties of the body itself. Non-uniform heat generation and conductivity complicate the solution to the CCC, which is a problem for lithium-ion cells, as they are highly anisotropic. Nevertheless, analysis of simplified linear profiles revealed that the CCC of a body can be improved if the region of highest heat generation is nearest the cooling, and the region of lowest conductivity is nearest to the cooling.

Solving the model for real boundaries showed that in-line losses can have a significant impact on the measurable value of the CCC. No equation was found that could help compensate for real losses in CCC experiments, however it is shown that reducing the thermal resistance of the cooling path can help reduce the influence of losses on the measurement of the CCC. A simple 3D MATLAB model was also developed to assess the impact of perpendicular losses on the measurement of the CCC. It revealed that although perpendicular losses are much less impactful to the measurement value of the CCC, compared to in-line losses, they still do impact

the measurement, this means that it is important to ensure perpendicular losses are low in experimental rigs when making CCC measurements.

The identification of the impacts of heat generation and losses on the CCC measurement, mean that the CCC measured in a CCC rig will likely not be exactly the same as the CCC when the cell is operating in real conditions, under real loads. This means that the CCC cannot be used to predict the exact behaviour of the cell in application. This is reflective of most lithium-ion performance metrics, even the capacity of a cell is dependent on the specific loads and conditions of an application yet is crucial to cell datasheets. Similarly, the CCC still provides a useful standardised comparison point for the thermal performance of lithium-ion cells, and if it were to be adopted to cell datasheets, would provide a useful piece of thermal information that is currently absent. A key aspect of achieving this is the careful design of experimental rigs to create a low thermal resistance boundary for the cooled surface of interest and well insulated boundary conditions for all other surfaces.

6.2 Cell Benchmarking

Having established that the CCC requires strict standardised boundary conditions to make comparable measurements, and that cell datasheets also provide information based on standardised tests, neither of which are reflective of real applications. This section of work aimed to assess the validity of making cell comparisons based on standardised tests.

Six commercially relevant 21700 cylindrical cells are tested under a range of conditions, covering different electrical loads, and two cooling conditions. Base cooling and natural convection are used as the two boundary conditions for this study. The electrical tests range from constant current loads to power driven drive cycles. In order to compare how the conditions affect cell performance, from the perspective of choosing a cell, a percentile-based ranking system is developed for the thermal and electrical performance. The results show that the rankings between the cells can vary by up to 20% between the two cooling systems, and by a staggering 98% between constant current and an equivalent rate drive cycle. Thus, successfully proving that choosing a cell based on performance under one set of conditions may result in the wrong choice for use in another set of conditions. Fundamentally, these performance changes stem from how each cell responds to the changes in cooling and load type, this can come from differences in internal structure which can favour some types of cooling over others, or differences in the resistance response which may favour the shorter time periods of a drive cycle over constant current loads. These results highlight significant concerns

with using datasheets to choose cells, for accurate cell comparisons, bespoke testing must be performed using conditions as close to the desired application as possible.

Although performance was shown to not translate across different cooling systems and load types, results from a series of drive cycles hint at the potential for the translation of performance. A series of 15 synthetic drive cycles was performed, where the baseline and peak power was incrementally increased between each. The results from this displayed a linear relationship between the power and resulting output energy and temperature. This allowed for equations to be fit to predict performance between any of the tested drive cycles. These equations are used to demonstrate their use in predicting performance when varying the pack size for a given pack load. Ultimately, the translatability of these tests is only across varying power, not the different cooling systems, or load time periods, making it much simpler to track changes in performance, maintaining the validity of the previous conclusions of bespoke testing being required for true cell comparisons for application.

6.3 Degradation Under Cooling

As this work has established that test conditions can impact the BoL performance of cells for making cell comparisons, this section of work aimed to assess the impact of test conditions on long term life. The main aim of this work was to compare the two most popular cylindrical pack cooling systems, base and side cooling, to see which one is best for the degradation performance of cells, under automotive-relevant loads.

This study used two 21700 cylindrical cells with significant structural differences, and tested them against an array of tests, covering an automotive reference cycle, and combinations of faster rate charge and discharge. The experimental rigs were developed to replicate potential application, using wire bonded electrical connections, automotive grade adhesives, and cooling plates. To act as standardised reference a third cooling system was tested, that used convection cooling and spring-loaded test rigs.

BoL analysis of the rate combinations and cooling revealed that side cooling was superior for both cells, achieving significantly lower temperatures and cell level gradients. Base cooling displayed significant surface level axial gradient, that could be highly detrimental to life if reflective of internal electrode temperatures. Convection cooling performed the worst of all three cooling systems, resulting in the hottest temperatures. Thus, it was hypothesised that convection cooling would be the most degrading and side cooling the least. This analysis also revealed unintentional differences to the cyclable state of charge (SOC) window of the cell,

caused by the coupling between the voltage limits and the high-power rates. Established understanding that high currents lead to increased degradation led to the hypothesis that the combination of fast charge and discharge (FF) would be the most degrading, with the automotive reference (SS) being the least degrading. Between the two mixed rate tests it is hypothesised that fast charge with a reference (slow) discharge (FS), would be more degrading than a slow charge with a fast discharge (SF). It also highlighted a significant disparity between the output discharge energy and capacity, caused by the overpotentials, emphasizing the importance of comparing performance in terms of both capacity and energy.

The end of life (EoL) of the cells were defined by their available capacity (assessed at C/10) dropping below 80% of the BoL available capacity, comparing the total energy throughput to reach this point. These results indicate that for the automotive reference test the cooling system makes little impact on degradation as the temperature increases are almost negligible. The results largely confirm the predictions of degradation performance with cooling, where side cooling is shown to be the best cooling system when fast discharging, but not when fast charging with the reference discharge. The results also show that predictions of the rate combinations were incorrect, with FS being the most degrading, SF being the least degrading, and SS and FF being equally degrading. Further analysis via disassembly and differential voltage indicate that fast discharging prevented significant deterioration of the cell's anode, likely due to preventing utilisation of low SOC's, reducing silicon degradation in the cells. The deterioration of the anode seen in slow discharging, eventually leads to a lithium plating "knee" point failure, regardless of whether it is combined with a fast or slow charge. The fast charge causes this lithium plating to occur quicker, leading to a more sudden death at a higher state of health. This failure mechanism might explain why side cooling was not beneficial for fast charging, if lithium plating is the mechanism causing the "knee" point, then it could have been slowed by the hotter temperatures of base and convection cooling. This means that with intelligent thermal management and fast charging protocols, side cooling may remain the best cooling system for application. One key outcome is that the convection tests did not perform similarly to the other cooling systems, under high-rate loads. This confirms that cells need to be compared using application-relevant conditions, when comparing lifetime performance.

6.4 Future Work

6.4.1 Cell Cooling Coefficient

The CCC was not taken forward after Chapter 2, due to complexity of the rig design needed to accurately measure the cell's heat rejection. An area of future work would be to assess if there are ways to make heat generation assessments in-situ, for application-relevant single cell test rigs, or in full battery packs. Under normal conditions, this may not be possible without a fully parameterised and validated model. However, the high frequency pulsing profile used in the CCC should largely generate ohmic heat. This may be measurable through assessing the voltage profile and overpotentials caused by the CCC pulsing. This testing would need to be carefully carried out in CCC rigs on a variety of cells and conditions to ensure that the calculated heat generation matches the measured heat generation. Only then can it be assessed in-situ for more relevant rigs or packs. If this heat flow measurement problem can be solved, the CCC becomes significantly more useful, not for datasheet cell selection, but for the assessment of cells and cooling systems under application-relevant conditions.

6.4.2 Cell Benchmarking

The work on the benchmarking of cells can be carried forward, testing more types of cells under more application-based conditions, to assess whether the conditions are equally impactful for other form factors and chemistries of lithium-ion cells. Additionally, the test procedures can be developed further to gain more performance metrics and data, for example to expand the resistance tests to obtain a range of cell resistance that covers lower frequency resistances known to build up over time. This added information can allow for better comparisons between cells, comparing their full range of resistances, not only the instantaneous ones, as there is no way to gauge these resistances without making these additional experiments. Another example of a worthwhile addition is testing drive cycles that include regenerative braking pulses, in order to assess the impact of the regen presence and magnitude. Assessing the fast-charging performance of cells is also worthwhile. Other potential variations include the comparison of more cooling systems, and different electrical connections.

6.4.3 Degradation Under Cooling

The analysis of the degradation of the cells from this study can be taken further, using techniques such as degradation mode analysis, SEM, or models to validate the hypothesised degradation mechanisms and their coupling affecting these cells under these conditions. These techniques could help identify the mechanisms that led to the gas production and lithium

plating, with the hopes of understanding how these degradation mechanisms can be prevented. Also, to further the understanding of the role silicon played in the degradation of these cells, a complementary study is needed to identify the composition of the electrodes in the tested cells, and examine how the morphology and structure of the silicon changed in relation to the graphite as the cells aged, and explore the impact this has on the blended differential voltage curves extracted from the full cells. This work could have the potential to make a significant leap in understanding surrounding the fitting of differential voltage and subsequent degradation mode analysis in blended electrodes.

Further degradation tests can be performed to strengthen some of the hypotheses. Additional fast charge slow discharge tests, with increased lower voltage cut-offs, should be performed to assess if silicon utilisation is indeed the root cause of the “knee point” failure. Furthermore, state of the art fast charging algorithms and intelligent thermal management could be applied to assess if such approaches would result in side cooling promoting longer cycle life compared to base cooling.

Finally, an investigation into the “infinite” charging that occurred at the end of life for some of the cells should be investigated. This phenomenon is not mentioned in detail in the analysis of this work, as no satisfactory explanatory hypothesis was found. This phenomenon was only seen on some of the cells that went through “knee point” failure; this suggests that “infinite” charging could be caused by short circuiting via lithium plating dendrites. However, in some instances, the CV hold was held for several days, passing almost six times the nominal capacity of the cell. A physics-based model may be able to assess if a short circuit of this nature is possible and under which conditions it could be held for such a long period of time. Alternatively, other mechanisms could be assessed for their ability to explain this phenomenon, such as redox reactions, or some form of lithium shuttle.

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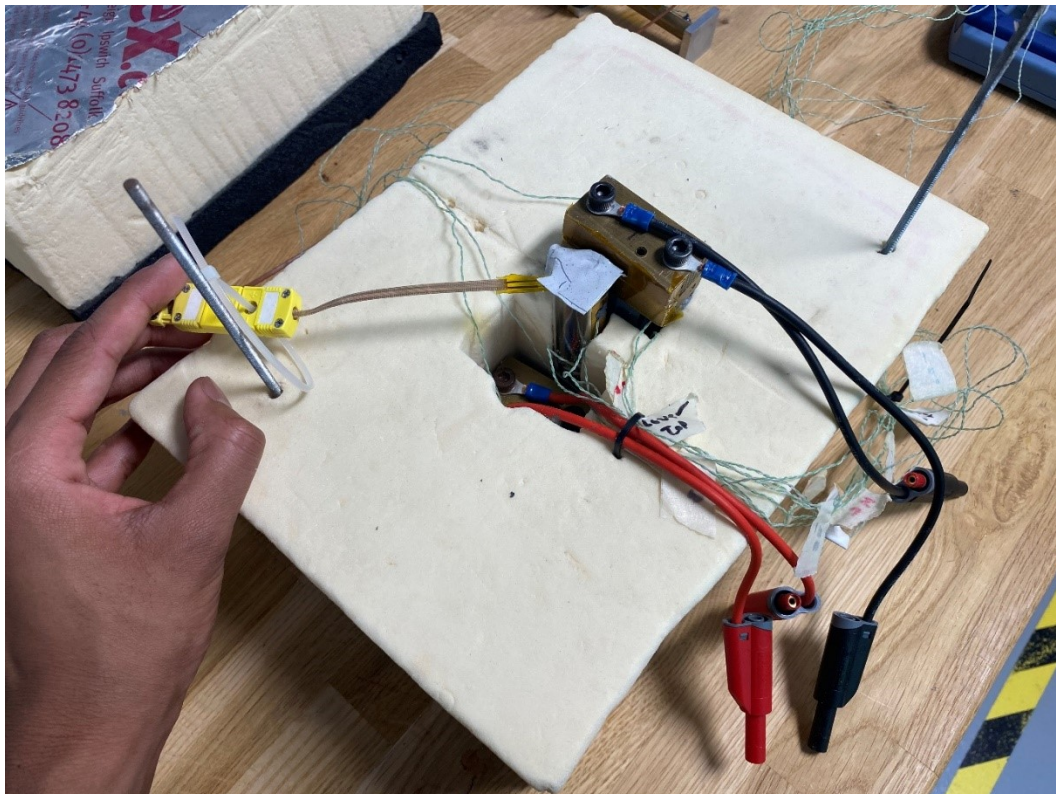
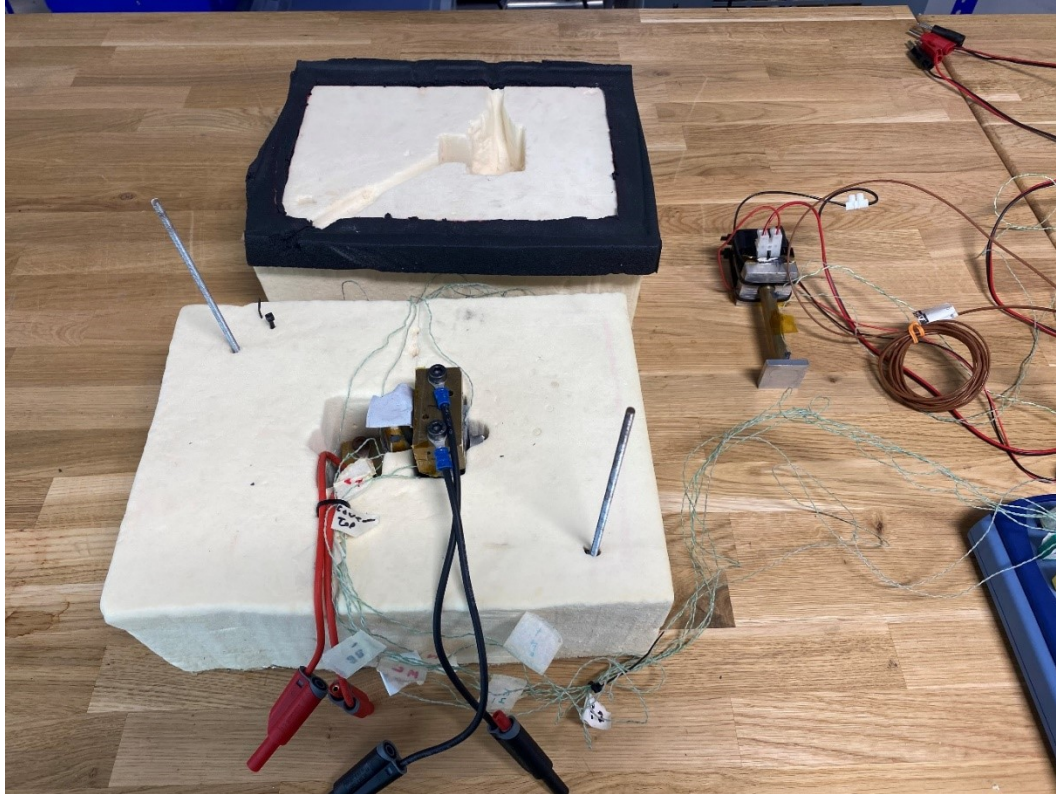
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Appendix A

A.1 Experimental Rig Images - Base Cooled Tab Welded CCC



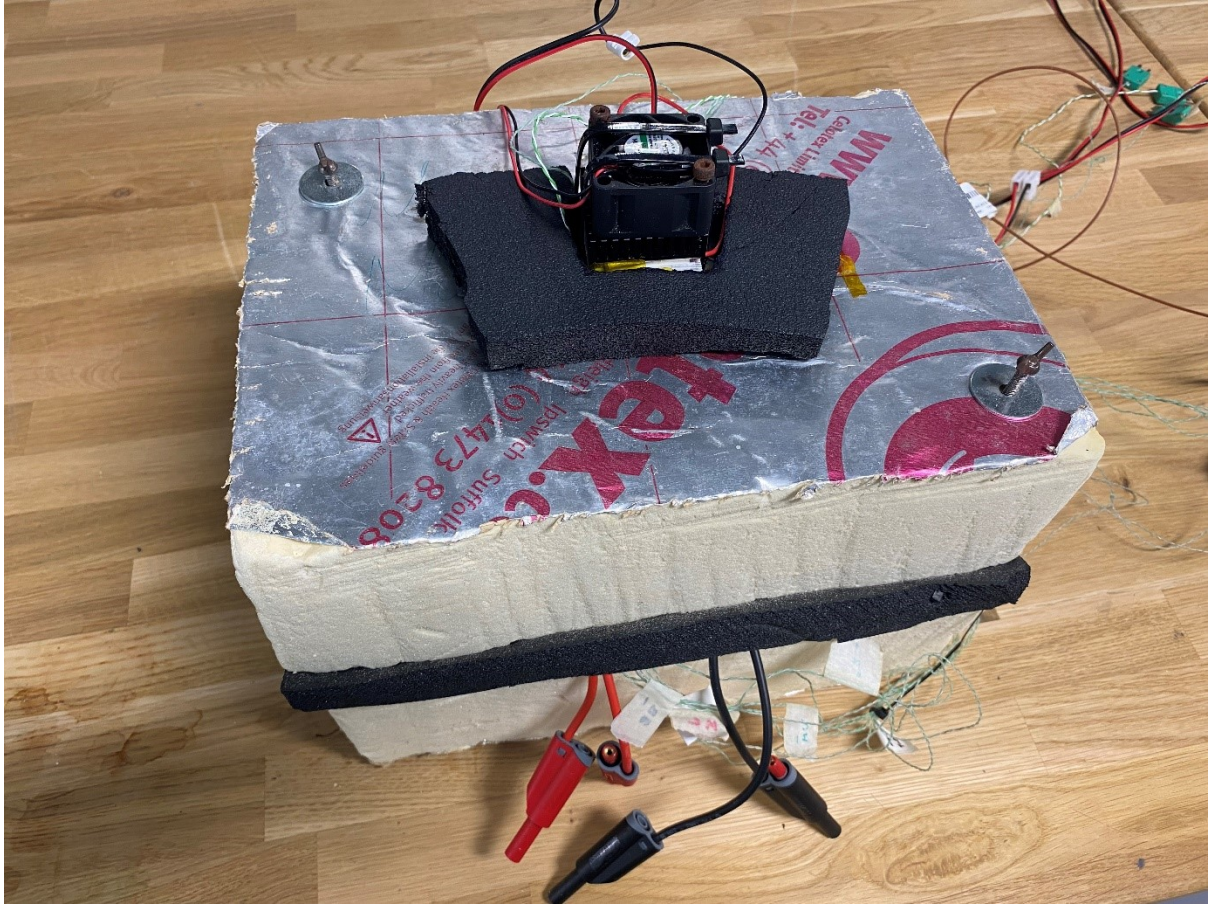


Figure 49: Photos of experimental test rig. Test setup (cell, brass blocks, cables, cooling fin) is encased in hard insulating foam, channels carved into foam allow the cables to exit the centre of the block. Black soft insulating foam allows for a compressible seal between the two halves of hard insulating foam. The cooling fin is inserted in through the top once the two halves are sealed and surrounded in soft insulating foam (as shown). The weight is then placed above the fin to ensure contact (not shown). Photos depict demonstrative setup; some aspects may be different in a real setup. Recreated from Ref. 177

A.2 3D MATLAB Model Equations for Assessment of Perpendicular Losses

The following equations are used to define the curves shown in Figure 21, using the outputs from the in-built 3D heat transfer solver based on the given inputs of heat, conductivity, geometry, and boundary conditions. The CCC ideal (Eq. 24) is calculated while the boundaries on faces 1 and 2 are still adiabatic, with CCC measured (Eq. 25) calculated with the variations to the thermal boundaries. The y values for Figure 21 are given by Eq. 26, and the x values are given by Eq. 27, each calculated for a given value of heat transfer coefficient applied to either face 2 or 3, depending on if in-line or perpendicular losses are being explored, respectively. All the $\dot{Q}$ values are given by the total heat flux through the stated surface, at steady state. The T values are given by the average temperature on the stated face, at steady state.

$$CCC_{Ideal} = \frac{\dot{Q}_{Total}}{\Delta T_{Axial}} = \frac{\dot{Q}_{Face\ 1}}{T_{Face\ 2} - T_{Face\ 1}} \quad Eq. 24$$

$$CCC_{Measured} = \frac{\dot{Q}_{Face\ 1}}{T_{Face\ 2} - T_{Face\ 1}} \neq \frac{\dot{Q}_{Total}}{\Delta T_{Axial}} \quad Eq. 25$$

$$CCC_{Impact} = \left| 1 - \frac{CCC_{Measured}}{CCC_{Ideal}} \right| \times 100 \quad Eq. 26$$

$$Loss\ \% = \left| \frac{\dot{Q}_{Loss}}{\dot{Q}_{Total}} \right| \times 100 = \left| \frac{\dot{Q}_{Face\ 2\ or\ 3}}{\dot{Q}_{Face\ 1} + \dot{Q}_{Face\ 2} + \dot{Q}_{Face\ 3}} \right| \times 100 \quad Eq. 27$$

A.3 Solution of Temperature with Variable Heat Generation Profile

Presented below are Eq. 15 and Eq. 16 from the main manuscript.

$$\frac{dT}{dx}(x) = -\frac{1}{k} \int_0^x \dot{q}(x) dx + \frac{1}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L}$$

$$T(x) = -\frac{1}{k} \int_0^x \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{x}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L} x + T_1$$

To solve $T(x)$ Fourier's Law is applied to both boundaries to achieve solutions to T_l and T_2 .

Applying Fourier's Law at $x = 0$

$$\dot{Q}_{ins} = \frac{T_A - T_1}{R_i} = -kA \frac{dT}{dx}(0)$$

$$\frac{dT}{dx}(0) = \frac{1}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L}$$

$$\text{Use } R_{cell} \rightarrow R_c = \frac{L}{kA}$$

$$\frac{T_1 - T_A}{R_i} = \frac{A}{L} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{R_c}$$

$$(T_1 - T_A)R_c = R_c R_i \frac{A}{L} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + (T_2 - T_1)R_i$$

$$\text{Use } \omega = \frac{A}{L} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx$$

$$T_1(R_c + R_i) = R_c R_i \omega + R_i T_2 + R_c T_A$$

$$T_1 = \frac{R_c R_i \omega + R_i T_2 + R_c T_A}{R_c + R_i} \quad \text{Eq. 28}$$

Applying Fourier's Law at $x = L$

$$\dot{Q}_{fin} = \frac{T_2 - T_c}{R_f} = -kA \frac{dT}{dx}(L)$$

$$\frac{dT}{dx}(L) = -\frac{1}{k} \int_0^L \dot{q}(x) dx + \frac{1}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L}$$

$$\frac{T_2 - T_c}{R_f} = A \int_0^L \dot{q}(x) dx - \omega + \frac{T_1 - T_2}{R_c}$$

Use $\varphi = A \int_0^L \dot{q} dx$

$$T_2(R_c + R_f) = R_c R_f(\varphi - \omega) + R_f T_1 + R_c T_c$$

Substitute Eq. 28 for T_1

$$T_2(R_c + R_f) = R_c R_f(\varphi - \omega) + \frac{R_c R_f R_i \omega + R_c R_f T_A}{R_c + R_i} + \frac{R_f R_i T_2}{R_c + R_i} + R_c T_c$$

$$T_2 \left(R_c + R_f - \frac{R_f R_i}{R_c + R_i} \right) = R_c R_f(\varphi - \omega) + \frac{R_c R_f R_i \omega + R_c R_f T_A}{R_c + R_i} + R_c T_c$$

$$T_2 = \frac{R_c R_f(\varphi - \omega) + \frac{R_c R_f R_i \omega + R_c R_f T_A}{R_c + R_i} + R_c T_c}{R_c + R_f - \frac{R_f R_i}{R_c + R_i}} \quad \text{Eq. 29}$$

Eq. 29 and Eq. 28 can be used to gain the solution to Eq. 16.

A.4 Solve for CCC Impact vs. In-Line Loss Ratio

The derivation for the equation that defines the in-line loss curve, shown in Figure 21, under uniform $\dot{q}$ and k , starts with Eq. 15:

$$\frac{dT}{dx}(x) = -\frac{1}{k} \int_0^x \dot{q}(x) dx + \frac{1}{kL} \int_0^L \left[\int_0^x \dot{q}(x) dx \right] dx + \frac{T_2 - T_1}{L}$$

Fourier's Law at $x = L$

$$\dot{Q}_{fin} = -kA \frac{dT}{dx}(L)$$

$$\frac{dT}{dx}(L) = -\frac{\dot{q}L}{k} + \frac{\dot{q}L}{2k} + \frac{T_2 - T_1}{L}$$

$$\dot{Q}_{fin} = -kA \left(-\frac{\dot{q}L}{k} + \frac{\dot{q}L}{2k} + \frac{T_2 - T_1}{L} \right)$$

$$\dot{Q}_{fin} = \dot{q}AL - \frac{\dot{q}AL}{2} + \frac{T_1 - T_2}{R_c}$$

$$\dot{Q}_{fin} = \frac{\dot{q}AL}{2} + \frac{T_1 - T_2}{R_c}$$

$$\dot{Q}_{fin} = \frac{\dot{Q}_{tot}}{2} + \frac{T_1 - T_2}{R_c}$$

Multiply both sides by $\frac{2}{\dot{Q}_{fin}}$

$$2 = \frac{\dot{Q}_{tot}}{\dot{Q}_{fin}} + \frac{T_1 - T_2}{\dot{Q}_{fin} R_c}$$

Let $\dot{Q}_{tot} = \dot{Q}_{fin} + \dot{Q}_{ins}$, and Ideal CCC = $\frac{2}{R_c}$, and the Measured CCC = $\frac{\dot{Q}_{fin}}{T_1 - T_2}$

$$2 - \frac{\dot{Q}_{tot}}{\dot{Q}_{fin} - \dot{Q}_{ins}} = \frac{1}{CCC_{Measured}} CCC_{Ideal}$$

$$\frac{1 - 2 \frac{\dot{Q}_{ins}}{\dot{Q}_{tot}}}{1 - \frac{\dot{Q}_{ins}}{\dot{Q}_{tot}}} = \frac{CCC_{Ideal}}{CCC_{Measured}}$$

Appendix B

B.1 Example Temperature Plots

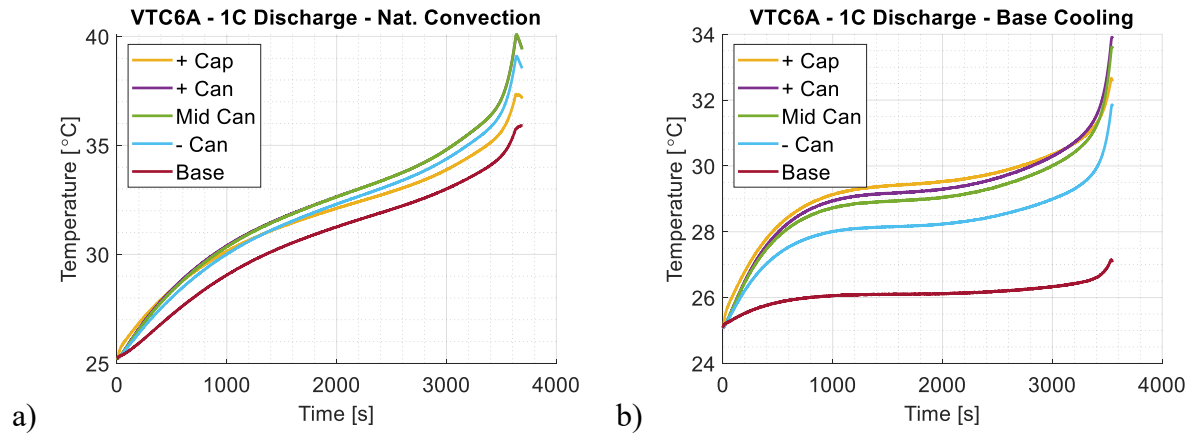


Figure 50: Temperature against time for the VTC6A for a 1C discharge at 25 °C for natural convection (a) and base cooling(b)

B.2 Parameters for WLTP conversion from velocity to power

Table 15: Tables of parameters taken for example Vehicle X

Pack Capacity	75 kWh
Nominal Cell Voltage	3.6 V
Lower Voltage Limit	3.0 V
Pack Configuration	96s46p
Super Charger Maximum Power, P_s	250 kW
Vehicle Maximum Power, P_v	258 kW
Powertrain Efficiency, μ	0.9
Cruise Speed, v	70 mph (31.3 m s ⁻¹) (112.6 km h ⁻¹)
Coefficient of Drag, C_d	0.23
Vehicle Mass, m	1,847 kg
Tire Pressure, p	2.9 bar
Frontal Area, A	2.22 m ²
Density of Air, ρ	1.2 kg m ⁻³
Gravitational Acceleration, g	9.81 m s ⁻²

B.3 Drive Cycle Fit Quality

Figure 51 displays the linear fits generated using Eq. 21 against the experimental results. The fitted equations display a good agreement with the experimental data. The worst fit appears to be for the M50T, where the fit seems to deviate about the points in the early DCs, this appears to be due to the fit for p not matching the data for these DCs (1-9). It is possible that the relationship of p is no longer linear for the M50T once it reaches the higher DCs (12-15), due to the extreme drop off in performance, thus the accuracy of p at the lower DCs has been sacrificed slightly. Even so, the root mean square of the fit is 0.9764, thus the fit is good enough for its predictive purpose.

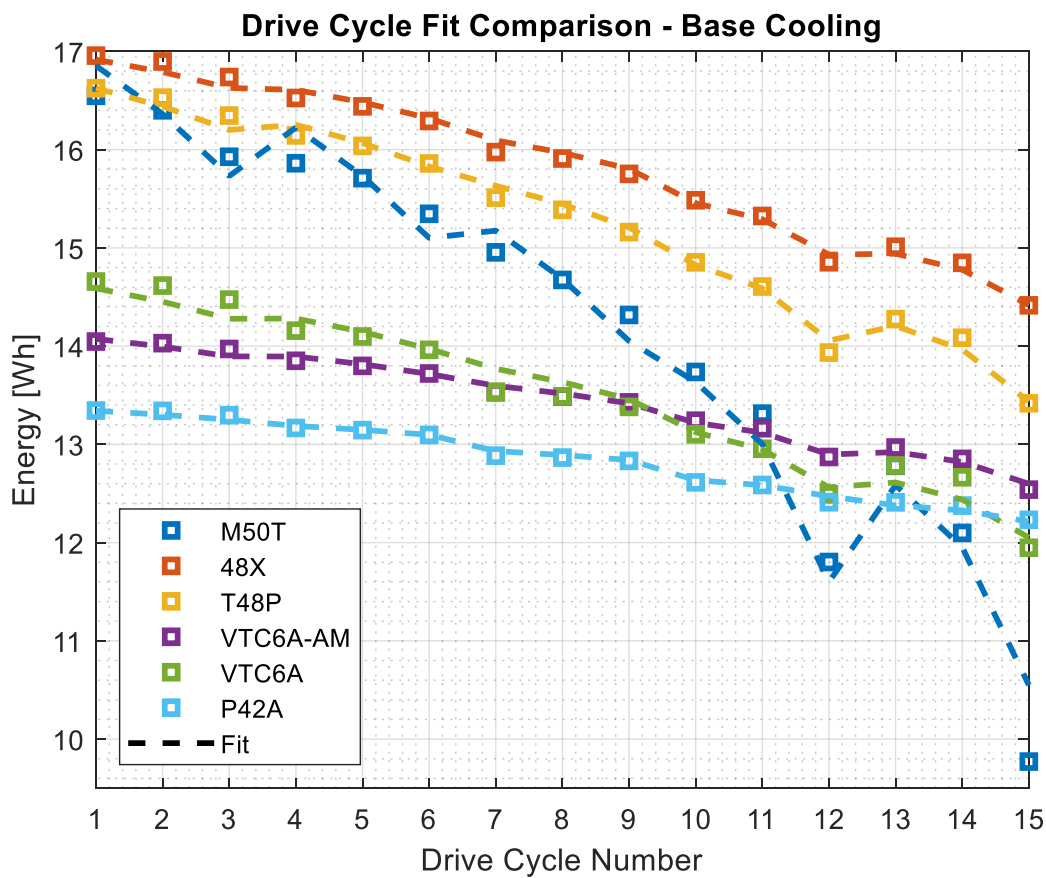


Figure 51: Experimental data of energy dissipated (discharge) for all 15 drive cycles, corresponding to Table 2, under base cooling with the linear fits of Eq. 21 shown via the dashed lines.

B.4 Table of Drive Cycle Fitted Parameters

Table 16: Fitted parameters for Eq. 21 for each cell and cooling combination across all 15 drive cycles.

Natural Convection	E_{DC1}	$b_E \times 10^{-1}$	$p_E \times 10^{-1}$	T_{DC1}	$b_T \times 10^{-1}$	$p_T \times 10^{-1}$
M50T	16.51	-0.93	-0.43	27.50	10.71	0.91
48X	16.60	-0.43	-0.22	26.54	8.02	0.97
T48P	16.50	-0.57	-0.27	27.35	10.65	1.76
VTC6A-AM	13.81	-0.30	-0.09	27.39	5.75	0.67
VTC6A	14.45	-0.40	-0.24	27.11	9.07	0.92
P42A	13.17	-0.26	-0.06	26.48	5.55	0.76
Base Cooling	E_{DC1}	$b_E \times 10^{-1}$	$p_E \times 10^{-1}$	T_{DC1}	$b_T \times 10^{-1}$	$p_T \times 10^{-1}$
M50T	16.85	-1.17	-0.78	25.32	8.38	0.38
48X	16.92	-0.57	-0.20	25.15	6.05	0.75
T48P	16.63	-0.69	-0.29	25.69	6.43	0.54
VTC6A-AM	14.07	-0.33	-0.12	26.04	4.49	0.50
VTC6A	14.59	-0.57	-0.21	25.38	6.33	0.85
P42A	13.34	-0.28	-0.06	25.59	4.50	0.69

B.5 Motorsport Example Performance Prediction Plots

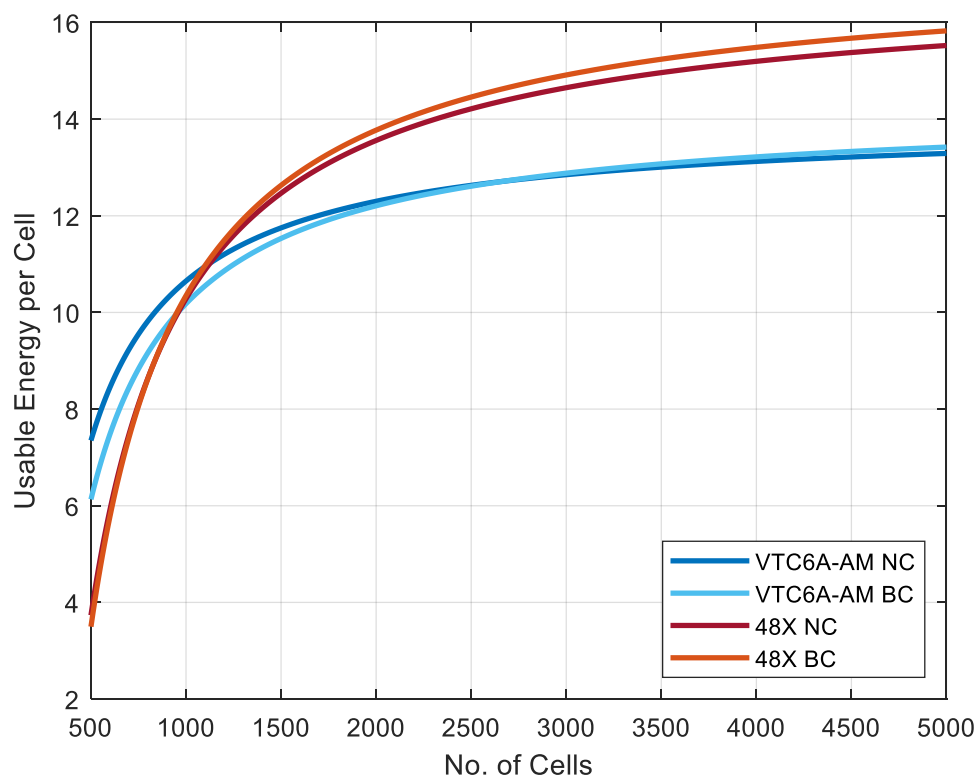


Figure 52: Predicted usable cell energy against the number of cells used in the pack. Displays 4 pack types, covering both cells, VTC6A-AM and 48X, for both Nat. Conv. And base cooling.

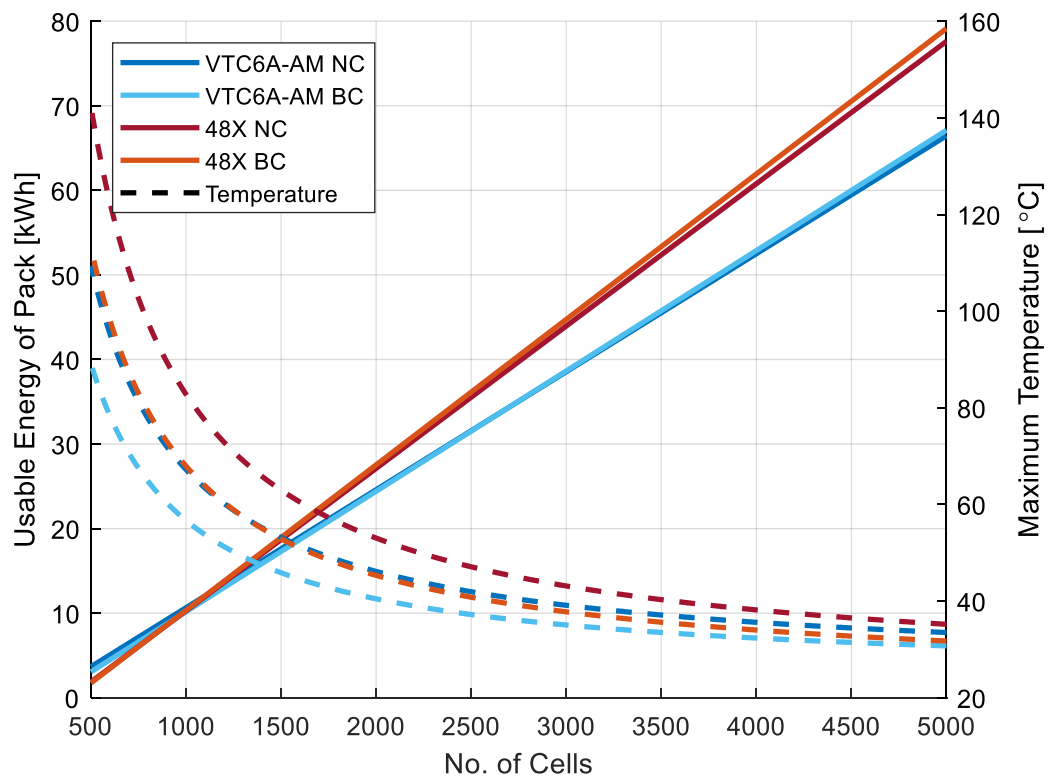


Figure 53: Predicted usable pack energy and maximum temperature against the number of cells used in the pack. Displays 4 pack types, covering both cells, VTC6A-AM and 48X, for both Nat. Conv. And base cooling.

Appendix C

C.1 Resistance Plot

Figure 54 presents the increase in cell ohmic resistance against the energy throughput over the life of the cells. The data is separated by rate and cell, and the resistance is presented normalised against the starting resistance (taken during the 10 sec rest from the short RPT). The plots are cut-off at 300% normalised resistance, to enhance visibility, because the cells that went through “knee point” failure rose to resistance values of well over 1000%. The biggest point to note is that, for each equivalent rate, the Molicel has less increase in relative resistance compared to the Samsung.

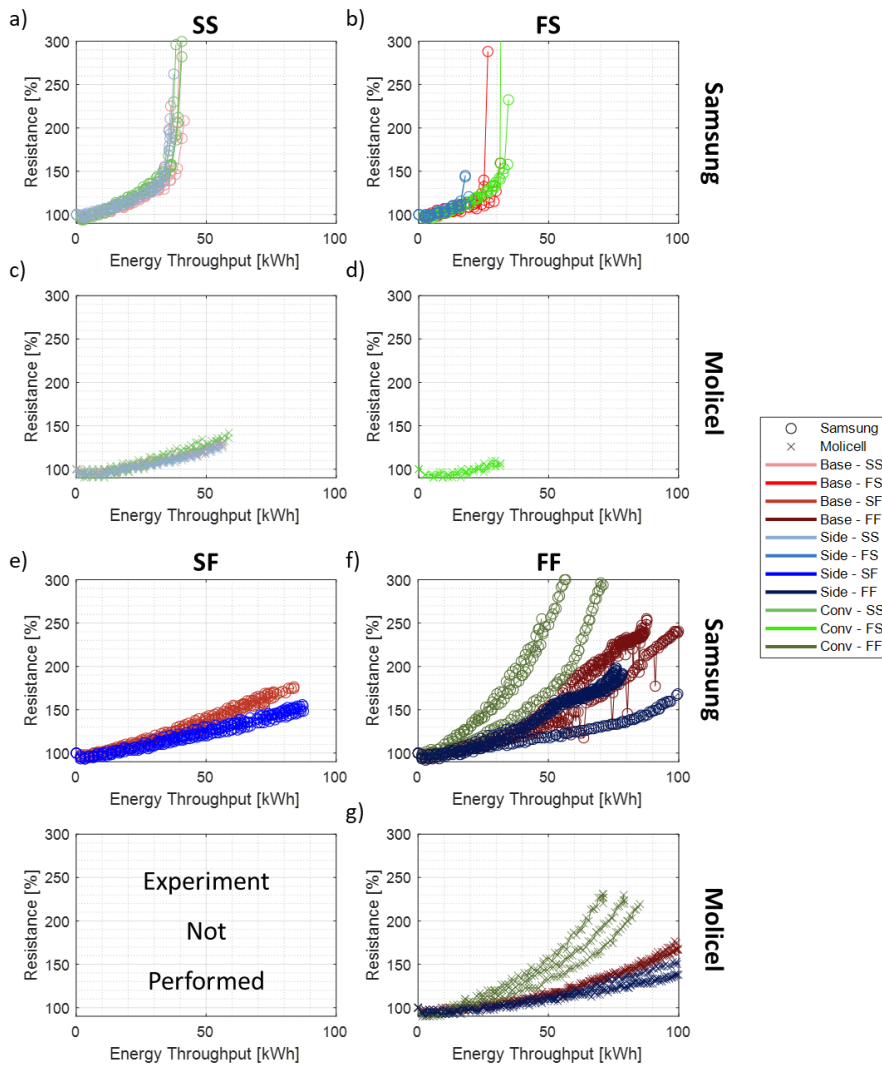


Figure 54: Normalised ohmic resistance against total energy throughput (Wh), separated into subplots by rate and cell. The 3 cooling mechanisms are displayed using different colours.