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Thermal effects and management of lithium ion batteries for automotive applications

PhD Thesis

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I hereby declare that this thesis and the work presented is my own except where appropriately referenced and acknowledged.

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Abstract

In recent years the use of lithium ion batteries in hybrid and electric vehicles has increased enormously. Due to the high cost of lithium ion batteries, maximising their performance and reducing the rate of degradation is vitally important to vehicle manufacturers. There are many ways in which this can be done, however this thesis focuses on the thermal behaviour of lithium ion batteries and how thermal management can affect performance and levels of degradation.

The importance of good experimental design is discussed, with a specific focus on thermal boundary conditions. In addition, some experimental examples are shown highlighting the impact that thermal boundary conditions can have when testing batteries.

The thermal properties of cells were measured, and an approach based on Searle's bar technique and using cells of different sizes was used in order to measure the thermal conductivity of different components and interfaces in a cell. This approach was successful in measuring the thermal conductivity through the layers of a cell, and the results showed a 32% discrepancy with often-used literature values, showing how important the measurement of thermal conductivity is when designing battery thermal management systems or parameterising coupled electrochemical-thermal models.

The effect of temperature gradients on the performance of batteries was investigated, showing that a cell under a temperature gradient exhibits poorer performance compared to a cell at a temperature equivalent to the mean of the gradient. This result was

reproduced using a simple data-driven model, which showed significant inhomogeneous behaviour of the different layers of the cell.

Finally, the effects of cell surface cooling and cell tab cooling were investigated, reproducing two typical cooling systems that are used in real-world battery packs. For new cells using slow-rate standardized testing, very little difference in capacity was seen. However at higher rates, surface cooling led to a loss of useable capacity of 9.2% compared to 1.2% for cell tab cooling. After cycling the cells for 1,000 times, surface cooling resulted in a rate of loss of useable capacity under load three times higher than cell tab cooling. Understanding how thermal management systems interact with the operation of batteries is therefore critical in extending their performance. For automotive applications where 80% capacity is considered end-of-life, using tab cooling rather than surface cooling would therefore be equivalent to extending the lifetime of a pack by 3 times, or reducing the lifetime cost by 66%.

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I.A. Hunt, Y. Zhao, Y. Patel, J. Offer, **Surface Cooling Causes Accelerated Degradation Compared to Tab Cooling for Lithium-Ion Pouch Cells**, J. Electrochem. Soc. 163 (2016) A1846–A1852. doi:10.1149/2.0361609jes.

Conference presentations

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1 Introduction

1.1 Motivation

Due to their high energy and power densities, Lithium-ion batteries are a very important component of electric vehicles, and their use has increased dramatically in recent years as the uptake of hybrid and electric vehicles has increased [1–3]. One of the major challenges of using lithium ion batteries in hybrid and electric vehicles is thermal management [4], which is important in order to manage degradation at an acceptable rate whilst maximising the performance of the batteries and reducing the risk of thermal runaway [5–7].

It is generally well understood that increasing the operating temperature of a lithium ion battery will increase the rate of degradation [4,8–11]. However, there is limited understanding about the best way in which to thermally manage the cells in a battery pack, and the effects of temperature gradients both between cells in a pack and within a cell itself. Whilst this is a very complex problem, and it is likely that the solution will be different for different cells, pack topologies and use cases, the work embodied in this thesis represents a significant step forward in the understanding of thermal management in lithium ion battery packs.

1.2 Research

The work in this thesis is split into several sections, each of which addresses an area that is important in understanding thermal management in lithium ion battery packs.

1.2.1 Thermal properties of cells

Understanding the thermal properties of cells is very important when designing thermal management systems for lithium ion battery packs. It is known that the thermal properties of cells are anisotropic, however there has been little work in looking at the contributions of the different components of a cell to the thermal properties. This will be addressed by looking at:

- What are the thermal properties of cells?
- Is our current understanding of the thermal properties of cells sufficient?
- Is there a simple way to measure the thermal properties of cell?
- What are the thermal properties of the interface between the casing and the active material, and of the tabs to the active material?

1.2.2 Effects of temperature gradients

Following on from previous work conducted by Troxler et al., where the effect of temperature gradients on the performance of cells at electrochemical equilibrium was explored using EIS, this section will look at the performance of cells in dynamic conditions during charge and discharge [12]. This will be addressed by answering these questions:

- What is the effect on performance of a cell under a temperature gradient during charge and discharge?
- How is capacity affected by a temperature gradient?
- How does the performance of the lithium-ion battery change when under a temperature gradient?

1.2.3 Cooling techniques

It is possible to thermally manage lithium-ion batteries in a number of different ways, for example the GM Volt employs cooling plates that thermally manage the large planar surfaces of the cells, however AVL and Williams use a different approach where the cell tabs or terminals are cooled. This section will compare how surface cooling or tab cooling affects the performance and degradation of lithium-ion batteries. This will be done by answering these questions:

- How does surface and tab cooling affect the performance (energy, useable capacity), of lithium-ion cells.
- How does surface and tab cooling affect the degradation of lithium-ion cells
- Are there any techniques that can be used to begin to understand how the cell is performing in different use cases.

2 Literature review

2.1 History of batteries.

The invention of the battery is commonly ascribed to Volta, who wrote to the Royal Society in 1800 describing his experiments [13]. His battery, dubbed by him as an ‘artificial electric organ’, was a simple pile of silver and zinc disks separated with cloth soaked in brine. Although Volta’s battery was of little practical use, his designs were quickly improved upon, enabling batteries to power a range of industrial applications, perhaps the most notable being telegraph networks. The first rechargeable cell was designed by Planté in 1859, which utilised lead electrodes with a sulphuric acid electrolyte [14]. This design is very similar to modern lead acid batteries that are in use today.

Lithium batteries were first explored by Whittingham et al. in the 1970s. They used lithium metal and titanium sulfide as electrodes. This was not commercially viable, mainly due to cost and safety issues with using a solid lithium electrode, and therefore development was shelved.

In 1977, Samar Basu demonstrated the intercalation of lithium into graphitic carbon, where lithium is inserted between the graphene layers [15,16]. This work was continued by Yazami et al., who demonstrated reversible electrochemical intercalation of lithium into graphite for the first time [17].

At the same time, Mizushima et al., along with John Goodenough were working on lithium cobalt oxide, LiCoO_2 , as a lithium insertion compound for use as a cathode material.

In 1985, Yoshino et al. combined these two developments, and constructed a cell with a graphitic carbon anode and a LiCoO_2 cathode [18]. This was a major breakthrough, mainly due to the lack of a dangerous lithium metal electrode. Using chemistry very similar to this, in 1991, Sony were the first company to commercialise rechargeable lithium-ion batteries [19].

Cells with chemistries very similar to that demonstrated by Yoshino are still used today, however there have been many developments and advances in order to improve performance, safety, lifetime, and cost. Compared to some transition metals, cobalt is scarce and expensive, and LiCoO_2 is not as stable as some other materials, and therefore work continued to find other promising cathode materials. Nickel oxide was one of these, and a mix of nickel and cobalt oxides proved to combine positive attributes of both compounds.

Additionally, other compounds for use as cathodes in lithium-ion batteries have been developed. Some of these include manganese spinel in 1983 [20], and the use of olivine structures, such as lithium-iron-phosphate, LiFePO_4 in 1996 [21].

2.2 What is a lithium ion battery?

Very simply, a lithium ion battery consists of two electrodes, a separator and electrolyte, along with current collectors connected to the electrodes. Most lithium-ion batteries have a graphite anode, and a transition metal oxide cathode. When fully charged, the lithium is intercalated in the graphite anode. During discharge, lithium ions de-intercalate from the anode, diffuse into the electrolyte and across the separator, and intercalate into

the metal oxide cathode. At the same time, an electron travels around an electrical circuit, does some work, and meets the lithium ions back at the cathode.

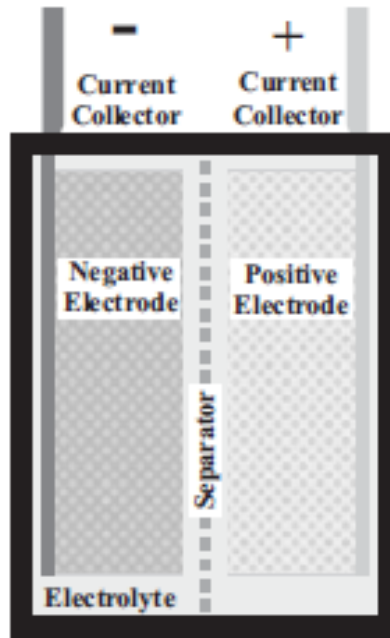


Figure 1 - Simple diagram of a lithium-ion battery (taken from [22])

2.2.1 Form factors

In order to ensure that a lithium-ion battery can operate consistently, efficiently and safely, many more components are required than those shown in Figure 1. The electrodes and current collectors must be insulated from the external casing, safety-related components such as PTC (positive temperature coefficient) devices are included to shut down the battery at high temperatures by increasing the resistance, and pressure release valves are included in the case of cylindrical and prismatic cells in order to prevent catastrophic rupturing of the case due to a build-up of pressure inside the casing of the battery. Schematics of a cylindrical, a pouch, and a prismatic cell are shown in Figure 2 to Figure 4

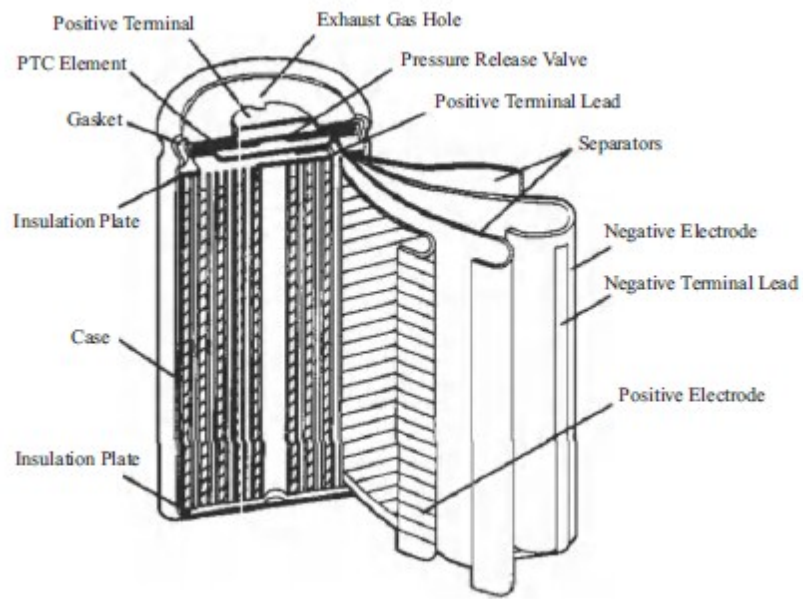


Figure 2 - Schematic of a cylindrical cell [22]

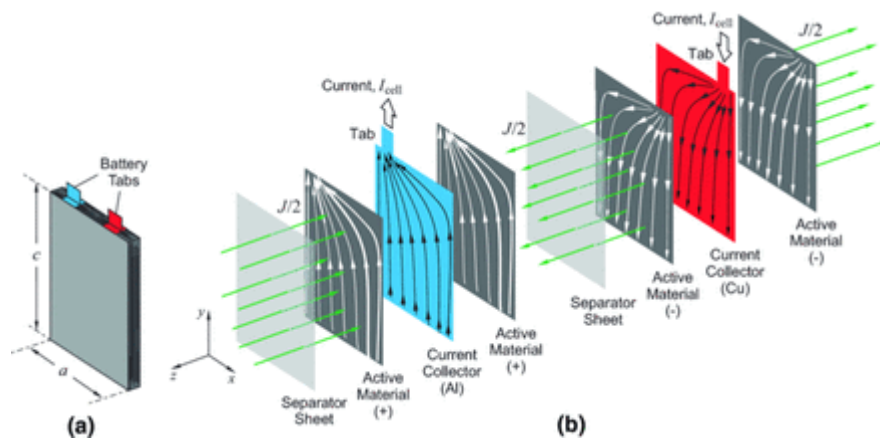


Figure 3 - Schematic of a pouch cell [23]

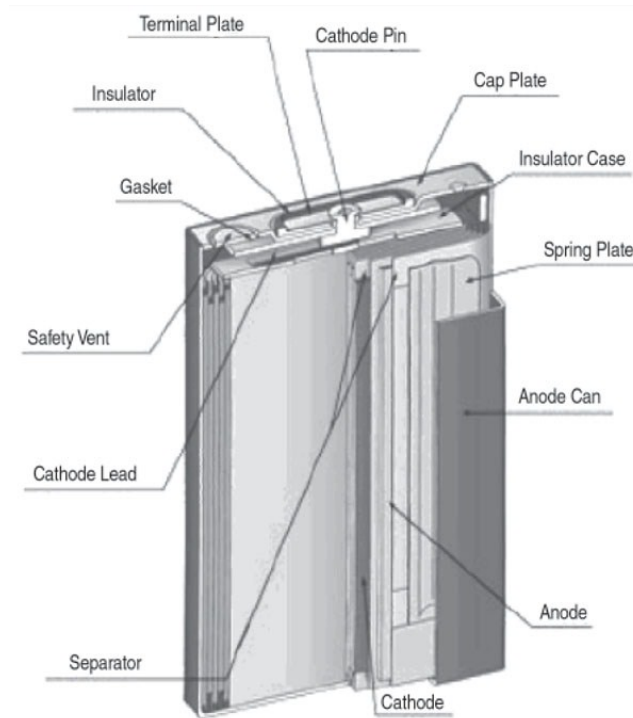


Figure 4 - Schematic of a prismatic cell [24]

The different types of cells shown in Figure 2 to Figure 4 are called the form factor, of which cylindrical, pouch, and prismatic are the most common, along with coin cells for smaller applications. Each form factor has positive and negative attributes, and may suit some applications better than others. For some applications such as lithium ion batteries for mobile phones, there is a general consensus between manufacturers that pouch and prismatic cells are the most suitable form factor, mainly due to the impracticalities of packaging a cylindrical cell into such a small, flat device. However, for larger applications such as electric and hybrid-electric vehicles, different manufacturers use different form-factors for very similar applications. For example, Tesla use a large number of relatively small cylindrical cells in their vehicles, whereas Nissan use much larger pouch cells in the Nissan leaf [25,26].

Whilst the basic electrochemical operation of different form factor cells is the same, they provide different characteristics, especially when formed into battery packs. For example, cylindrical cells are much cheaper to manufacture than pouch cells due to the lower part count; they employ a single sheet of electrode material, which is rolled up and inserted into the can, whereas pouch cells generally have individual electrodes for each layer. However, by their very nature cylinders can only occupy 90.7% of the available space, therefore reducing the volumetric energy density of a battery pack.

Another advantage of cylindrical cells is their relatively small size, making thermal management easier due to the reduced distance that heat must flow to any external cooling system. The dimensions of prismatic cells and pouch cells can vary significantly; some are thin with large planar areas, whereas others are much thicker.

Due to their small size, an electric vehicle that uses cylindrical cells must contain many hundreds of cells; the Tesla Model S has over 7000. This means that the likelihood of a cell failure is greatly increased, however the severity of a single cell failure is reduced, meaning it is possible for the vehicle to continue to operate even if a single cell has failed. If larger pouch or prismatic cells are used, a single cell failure is enough to render the battery pack unusable, and the severity of any resultant fire from a cell failure will be much larger.

2.3 Lithium ion battery chemistries

In addition to different form factors, there are a number of different chemistries that can be used inside lithium ion batteries. Most lithium ion batteries employ a carbon anode, and therefore convention is to describe cells using their cathodes. In addition to carbon,

it is possible to use different materials at the anode, examples of which are lithium metal, lithium titanate, or silicon.

2.3.1 Anodes

Lithium metal anodes are potentially an ideal choice of lithium ion battery anode due to its high specific capacity (3860 mAh/g), and low electrochemical potential [27]. However, there are many problems with using a lithium metal anode in a battery, namely dendrite growth and low coulombic efficiency, which lead to safety issues and high rates of degradation [28].

Silicon is another promising anode material, with a theoretical specific energy of 3590 mAh/g at room temperature [29]. However, during lithiation and delithiation, silicon undergoes volume changes of up to 370%, and 3D imaging of silicon particles undergoing lithiation and delithiation reveals severe particle cracking [30]. This particle cracking results in a loss of capacity and increases in resistance, and is discussed further in Section 2.7. In order to overcome these problems, it is possible to use a small amount of silicon in a graphite electrode, increasing the specific capacity without increasing the rate of degradation to unacceptable limits [31].

Lithium titanate is another promising anode material [32]. Whilst the high insertion potential vs Li, between 1.2 V and 2 V, leads to a lower overall voltage for a cell, this is above the stability window for most organic electrolytes, and therefore these batteries do not exhibit SEI growth (see Section 2.7.1), leading to excellent cycle life and coulombic efficiency [33]. Small volume changes on cycling also leads to low degradation (discussed further in Section 2.7), and other advantages include excellent high and low temperature charge and discharge characteristics and good thermal stability of the electrodes [3]. The

main disadvantage of lithium titanate anodes, along with the high lithium insertion potential is the relatively low capacity, 170 mAh/g compared with 370 mAh/g for conventional graphite, and high cost.

Whilst these alternative anode materials offer some large advantages compared to graphite and may be suitable for some specialist applications, by far the most commonly used anode material is carbon, in particular graphite, however other forms of carbon such as hydrocarbons and single layered hard carbons can be used [3,34]. Graphitic carbon has a theoretical specific capacity of 372 mAh/g and a lithium insertion potential of 0.05 V vs Li [3,17,35].

2.3.2 Cathodes

As mentioned previously, due to most lithium-ion batteries' use of graphite as an anode material, they are usually named after the composition of the cathode materials used. Common cathode materials are lithium manganese oxides (LiMn_2O_4) with a spinel structure, lithium cobalt oxides (LiCoO_2) with a layered structure, and olivine structures such as lithium iron phosphate (LiFePO_4). Table 1 gives an overview of the characteristics of different cathodes materials [36].

Property	LiCoO_2	LiNiO_2	LiMn_2O_4	LiFePO_4
Practical capacity (Ah/kg)	150	170	120	155
Energy density (Wh/kg)	180	170	100	130
Nominal voltage (V)	3.7	3.5	4	3.3
Cycling capability (Cycles)	>500	>500	>500	>2000

Table 1 - Overview of characteristics of different battery cathodes [36]

The material most used as a cathode in lithium-ion batteries is LiCoO_2 , which has a distorted rock-salt structure ($\alpha\text{-NaFeO}_2$) [37]. However, due to the relative scarcity of

cobalt and poor stability of cobalt oxide, alternative materials or mixes of transition metal oxides such as manganese, nickel and aluminium are often used and mixed together to form compounds such as $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, also known as nickel cobalt manganese or NCM, and $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, NCA [37,38].

Spinel structures, such as LiMn_2O_4 , have 3D networks of paths for lithium intercalation and deintercalation. LiMn_2O_4 has a lower capacity than LiCoO_2 , however it has good rate capability and is less susceptible to thermal runaway than some other battery chemistries. Manganese is also much more abundant and therefore cheaper than cobalt [37].

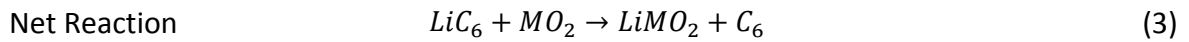
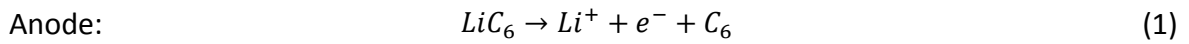
Lithium iron phosphate, or LiFePO_4 or LFP, has an olivine structure and is a relatively modern battery material. It has a modest specific capacity, however produces a very flat voltage curve, the bulk material is low cost and it is considered safe due to the strong P-O covalent bond which inhibits oxygen release [3]. LFP has low transport properties, and therefore in its bulk form it is difficult to utilise the full theoretical capacity and it has a high resistance, however reducing the particle size and coating the particles with carbon allows LFP to demonstrate very good high rate cycling capability [39]. Other olivines, such as LiMnPO_4 and LiCoPO_4 , are also being developed for use in certain applications [3].

2.4 How a lithium battery works

Cells are electrochemical devices that enable the energy released in chemical reactions to be turned directly into electricity. In general, a battery consists of two electrodes, a separator and electrolyte, along with current collectors connected to the electrodes.

In a Li-ion cell, the anode is made from a lithiated carbon intercalation material and the cathode is made from a lithiated transition metal intercalation compound ($LiMO_2$ in Equations (2) and (3)) [36].

During discharge, Lithium ions flow from the anode to the cathode through the electrolyte, and electrons flow through an external load to complete the circuit. The opposite is true during charging. A distinction of electrochemical reactions is that oxidation and reduction occur in different locations; therefore the complete reaction can be broken in two half-cells with corresponding reactions at each electrode [40]. These are shown for a Lithium-Ion cell during discharge in Equations (1) to (3) [36]:



A battery is a closed system, and therefore the current that leaves one electrode must enter the other one. Where the electrode and electrolyte meet, the charge-carrying species changes from an electron to an ion via a charge-transfer reaction [40].

2.4.1 Thermodynamics

When a cell is fully charged, all of the useable lithium atoms are intercalated into the carbon anode. The measured voltage of the cell comes from the thermodynamic potential difference between the anode and the cathode. As the cell discharges, the thermodynamic potential difference changes due to the amount of lithium that is intercalated in the anode and the cathode, and therefore the measured voltage of the

cell changes. Equation (1) to Equation (3) describe how the energy change for each reaction is determined by the change in Gibbs free energy for the reaction at each electrode, which is shown in Equation (4).

$$\Delta G = \left(\sum_i s_i \mu_i \right)_{right} - \left(\sum_i s_i \mu_i \right)_{left} \quad (4)$$

In Equation (4), G is Gibbs free energy, μ is the electrochemical potential of species i and s_i is the stoichiometric coefficient of species i . In simple terms, ΔG can be thought of as the free energy of the products minus the free energy of the reactants.

In an electrochemical device, the equilibrium or open-circuit potential is the potential at which no net current flows, denoted as U , and can be related to the Gibbs free energy by

$$\Delta G = -nFU \quad (5)$$

At equilibrium, reactions are still happening in the forwards and backwards directions, however the rate of these reactions are equal. The potential of an electrode at equilibrium is a measure of the electrochemical potential, μ_i of electrons, which is related to the molarity m_i , and activity coefficient, γ_i , by

$$\mu_i = \mu_i^0 + RT \ln m_i \gamma_i \quad (6)$$

When Equations (5) and (6) are combined and all activity coefficients are assumed to be unity, the Nernst equation is formed as showing in Equation (7)

$$U = U^\theta - \frac{RT}{nF} \ln \left(\prod_i m_i^{s_i} \right)_{right} + \frac{RT}{nF} \ln \left(\prod_i m_i^{s_i} \right)_{left} \quad (7)$$

Equation (7) shows that temperature has an effect on the open circuit potential of a cell. It is often expressed using only one term – in this case the potential of one electrode is measured against some form of reference electrode.

2.4.2 Lithium battery operation

When a cell is discharged, the lithium atoms in the anode are split into a lithium ion and an electron at the interface between the electrode and the electrolyte. The lithium ion moves into the electrolyte, and because the separator forms an electrically insulating layer between the two electrodes preventing electrons from flowing, the electrons move through an external circuit to the cathode, re-joins a lithium ion at the interface between the electrolyte and the electrode and the resulting lithium atom intercalates into the cathode. The separator and electrolyte are able to conduct lithium ions, and therefore the concentration gradient that is formed from the production of lithium ions at the anode and the consumption of lithium ions at the cathode results in a flow of lithium ions from anode to cathode.

During charging the reverse of this process occurs; an external voltage is applied to the cell, leading to the formation of lithium ions at the cathode and consumption of lithium ions at the anode.

It is very important to understand the relationship between current density and the deviation of potential from equilibrium conditions. This is described by the current-overpotential equation

$$i = i_0 \left[\frac{C_O}{C_O^*} e^{-\alpha f \eta} - \frac{C_R}{C_R^*} e^{(1-\alpha) f \eta} \right] \quad (8)$$

In Equation (8), the first term relates to the cathodic contribution to current and the second term relates to the anodic contribution.

C/C^* is the ratio between the concentration of a species at the electrode interface and the bulk concentration.

α is the transfer coefficient and relates to the change in the free energy barrier for a reaction as the potential changes. The transfer coefficient can vary between 0 and 1, however for most systems lies between 0.3 and 0.7, often it is approximated to 0.5 if measurement or prediction is not possible.

f is F/RT .

η is called the overpotential, and is the deviation of the potential from the formal potential, or measured potential. The formal potential is the potential that is actually measured, and contains corrections to the potential predicted by Equation (7). This error

is caused by the assumption that the activity coefficients are unity, and by ignoring some chemical effects.

i_0 is the exchange current. As mentioned above, at equilibrium current is flowing in the forwards and backwards directions at equal rates. The exchange current can be thought of as the current flowing in either direction. i_0 is used as allows the current to be described in terms of overpotential rather than formal potential. It is directly proportional to k^0 , which is the standard homogenous rate constant. As with many rate constants, k has an inversely proportional relationship with temperature, and therefore can be written as

$$k = Ae^{-\frac{E_A}{RT}} \quad (9)$$

where E_A is an activation energy.

Equation (8) can be simplified to ignore mass transfer effects if the current is kept small, usually taken as below 10% of the limiting current. The limiting current is the current at which the electrode reaction is limited by the mass-transfer conditions. This allows the assumption that the concentration at the electrode interface is the same as the bulk concentration, leading to the Butler-Volmer equation:

$$i = i_0 \left[\exp\left(\frac{\alpha F}{RT} \eta\right) - \exp\left(\frac{(1 - \alpha)F}{RT} \eta\right) \right] \quad (10)$$

For small overpotentials, the Butler-Volmer can be linearised using the approximation

$e^x = 1 + x$, leading to

$$i = -i_0 \frac{F}{RT} \eta \quad (11)$$

Equation (11) shows that the current has a linear relationship to overpotential, but only in a narrow band near to the equilibrium potential. When rearranged, this takes the form

$$\frac{\eta}{i} = R_{ct} = \frac{RT}{Fi_0} \quad (12)$$

R_{ct} has units of resistance, and is called the charge-transfer resistance. As discussed above, i_0 is directly proportional to k^0 , which has an Arrhenius relationship with temperature.

2.4.3 Porous electrodes

As with any chemical reaction, one way to increase the rate of reaction is to increase the surface area. This concept is employed in lithium ion batteries by the use of porous electrodes. Rather than being a single sheet, the electrodes in lithium ion cells are constructed of small particles, usually held together by some sort of conductive binder material to provide the necessary electrical connectivity [41].

The porous nature of the electrode can be easily seen from SEM images, such as those in Figure 5 which shown an image of an anode from a lithium ion cell. The electrolyte permeates through the electrode, providing a very large contact area between the electrolyte and the electrode. Additionally, the use of small particles means that the distance that lithium must diffuse through the solid electrode particles is kept to a minimum.

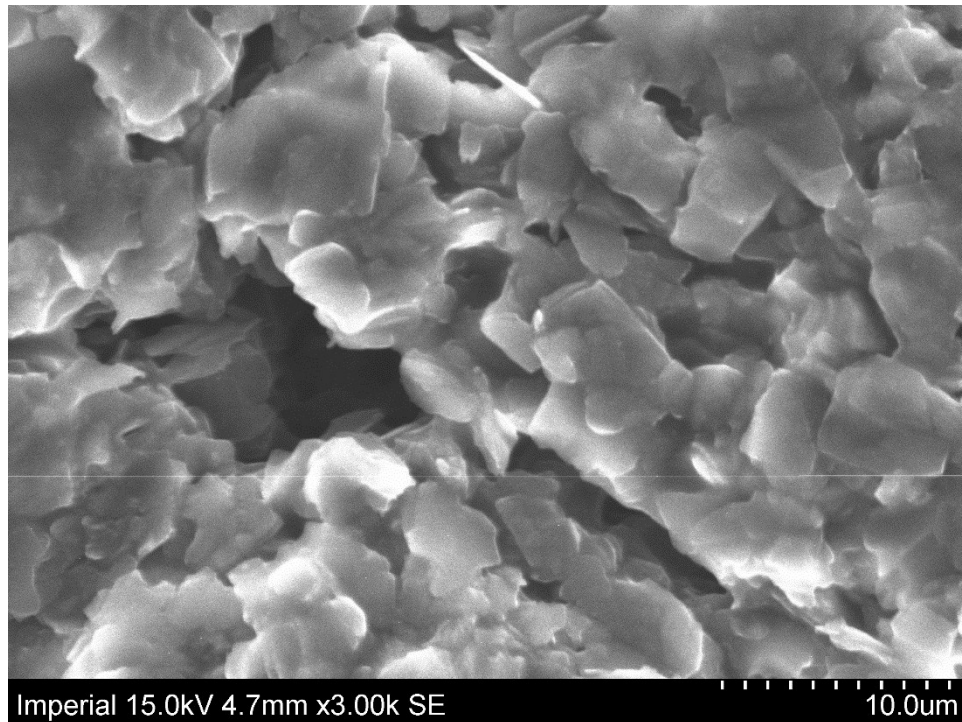


Figure 5 - SEM image of lithium-ion battery anode showing porous nature of the electrode

The design of the porosity of lithium ion batteries is vital to their operation. If the electrodes are too porous the cell will have low energy density (both volumetric and gravimetric), however if the electrode is not porous enough the cell will not work effectively, especially if the cell is to be used in a high-rate application. In addition, some degradation mechanisms are related to the total surface area of the particles that comprise the electrode (such as SEI layer growth; more information in Section 2.7.1). If the surface area is increased too much, these degradation mechanisms lead to an unacceptable rate of degradation [42].

2.5 Why are batteries important?

In comparison to older battery chemistries, lithium-ion batteries have much improved energy density in terms of both mass and volume. This has allowed great advances in different technologies; two of the most notable being consumer electronics and devices and electrified vehicles. Lithium ion batteries have allowed smartphones to become

increasingly more powerful and able to perform a wider range of tasks [43], and the range of some electric vehicles has increased to levels where the transition from electric vehicles being a small niche in the passenger vehicle market to a significant proportion of the cars on the road is occurring. The Tesla Model S has a range of 250 miles, whereas older electric vehicles such as the GM-1, which used a huge 600kg lead-acid battery pack could only travel 55-95miles before needing to be recharged [44].

Whilst the market for lithium ion batteries for consumer electronics is relatively mature, with estimates from statista predicting that the growth in this market will increase from \$9.6b in 2012 to \$14.7b in 2020, the outlook for lithium ion batteries in automotive applications is expected to grow substantially in this time; from \$2.2b in 2012 to \$10.2b in 2020 [45].

2.6 Battery challenges

2.6.1 Energy Density

Lithium-ion batteries have provided huge improvements when compared to older chemistries, however there are still many issues that have yet to be solved. Whilst they provide superior energy density, the mass and volume of batteries can and still need to be improved. This is evident when looking at electric vehicles – for example the mass of the Nissan Leaf’s battery pack is 300 kg, making up 20% of the total mass of the car [46]. In addition to this, batteries that are designed for high power applications such as hybrid vehicles, where a battery might be charged and discharged in a matter of seconds or a few minutes, exhibit significantly lower energy density than the theoretical maximum due to the necessary design changes to ensure that a battery can discharge quickly. Figure 6

shows a diagram showing the practical energy and power densities of different battery chemistries [47].

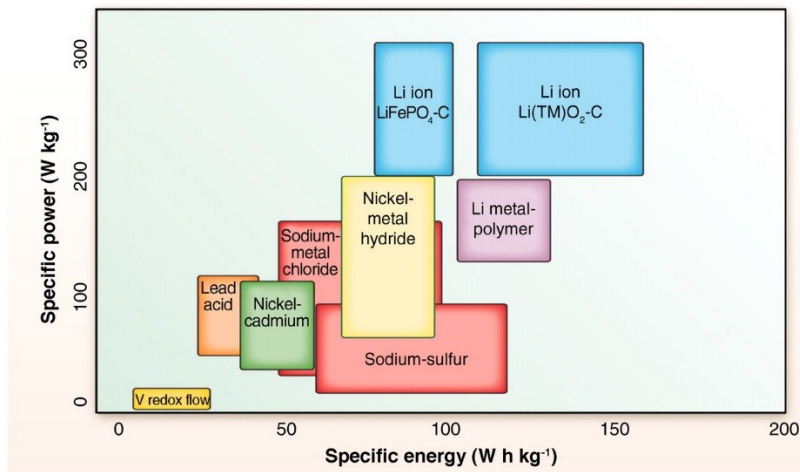


Figure 6 - Graph showing energy and power densities of different battery chemistries [47]

2.6.2 Cost

Another problem is cost; although the cost of cells is falling, and is currently estimated to be at around \$200-250/kWh for BEV battery packs, the cost of cells is still prohibitively expensive, representing a huge proportion of the cost of manufacturing an electric vehicle [48]. It is estimated that the cost of lithium-ion batteries is falling by about 8% a year, and will continue to fall especially as manufacturing volumes increase, however if battery- and hybrid-electric vehicles are going to become mainstream technology, these costs must fall further [49].

2.6.3 Safety

Another problem that the use of lithium-ion batteries brings is safety, of which the most obvious problem is thermal runaway. If the temperature of lithium-ion battery increases to around 140-150°C, it is possible that the electrolyte, anode and cathode can undergo an exothermic reaction [50]. If this reaction produces enough heat, the fire will propagate through a cell very rapidly, and potentially to other cells in a battery pack. There have

been several high-profile examples of thermal runaway in both consumer electronics and electric vehicles. In 2006, Sony recalled nearly 10 million laptop batteries after reports of overheating [51], whereas there have been numerous reports of Nissan Leafs, GM Volts, and Tesla Model Ss all having thermal runaway incidents, either due to a crash or during charging [52–54].

There can be several causes of thermal runaway in lithium-ion battery packs, but in general part of a pack or a cell must be heated to a level whereby an exothermic reaction will take place. This heat can come from a variety of sources including; externally, such as from a fire; internally, due to the internal resistance of cells and current flow; or internal short circuits, caused by manufacturing defects, dendrite growth, or external damage [50]. More detail on these effects is given in Section 2.7.

Differential scanning calorimetry (DSC) or accelerated rate calorimetry (ASC), can be used to study the performance of lithium-ion batteries at elevated temperatures. Both techniques increase the temperature of a sample and simultaneously measure the heat flux, and can therefore be used to measure the rate of internal heat generation in a cell. A number of studies have used these techniques to study the thermal stability of lithium-ion batteries up to and including thermal runaway [55–59]. In addition to this, there have been attempts to model the effect of elevated temperature on certain components within cells [7]. There have also been attempts to further explore the mechanisms and effects of thermal runaway. Finegan et al [60], imaged 18650 cells using high speed synchrotron tomography during thermal runaway, showing the location of the propagation of thermal runaway when an external heat source is applied, and Spinner et

al [61] designed a thermal chamber in order to explore the effect of thermal runaway on adjacent cells.

When using lithium-ion cells, especially in large applications such as in electric vehicles, care must be taken when designing a battery pack in order to mitigate against thermal runaway. Packs are monitored very carefully in order to capture any erroneously high temperatures before thermal runaway is instigated, and many manufacturers incorporate additional safety devices in their packs such as large amounts of containment and intumescent materials that are designed to suppress battery fires.

In addition to this, many cells have in-built safety devices. Most 18650 cells now include a PTC, or positive temperature coefficient device [62], where the resistance increases dramatically above a certain temperature and therefore prevents most of the heat-generating current flow through a cell. Other internal safety devices include current-interrupt devices to prevent high currents, and shut-down separators that severely inhibit the performance of a cell once the temperature has reached a certain limit. Whilst increasing the safety of cells, these devices can cause problems themselves; shut-down separators have lower performance than conventional separators, and it has been shown that the small resistance the PTCs add to a cell, a negative attribute in itself, can increase the temperature gradient in 18650 cells [63,64].

2.6.4 Degradation

Degradation is another problem concerning lithium-ion batteries. There are two forms of degradation; the first being calendar aging, where cells degrade during storage; the second is cycle life, where cells degrade during use [65,66]. Degradation has two major effects on the batteries, these are reduced capacity, and increased resistance [67].

Increased resistance reduces batteries' usability at high rates, and is therefore often known as power fade. Degradation reduces the lifetime of batteries, and also leads to increased costs as larger batteries must be installed to ensure that they will still be suitable for their application when the capacity has fallen and the resistance increased. Batteries that have reached the end of their lives must also be replaced, usually at significant cost.

There are many degradation mechanisms that can affect the performance and lifetime of lithium-ion batteries. Additionally, many of these mechanisms are interdependent and occur simultaneously, which makes studying them and isolating their effects very difficult.

2.7 Degradation mechanisms

2.7.1 Anodes

As discussed in Section 2.3.1, graphitic carbon is one of the most common materials used in the anodes of lithium-ion batteries, and a large amount of literature is available exploring the degradation of these materials [9,68–71]. Although graphite is the main constituent part of these anodes, they are also comprised of binder to hold the electrodes together and of conductive additives to increase the conductivity of the electrodes and allow current to flow unimpeded during operation.

Different degradation mechanisms cause different effects and in different areas of the electrode, namely at the electrode/electrolyte interface, of the active material and of the composite electrode. Most literature attributes the leading degradation mechanism of the anode to the electrode/electrolyte interface [72,73].

Lithium-ion anodes operate at voltages outside the electrochemical stability window of the electrolyte. Due to this, as the cell is charged for the first time electrolyte decomposition occurs. This produces electrolyte decomposition products, some of which are released as gas and others react with lithium. This results in permanent loss of lithium ions, and the build-up of a layer on the electrode surface. During intercalation and deintercalation, lithium ions must travel through this solid layer between the electrode and the electrolyte, and therefore the layer acts as a solid electrolyte interphase, or SEI layer [74]. The SEI layer is electrically insulating and mostly impermeable to the electrolyte, and therefore acts to decelerate the rate of electrolyte decomposition.

A stable SEI layer is vitally important in order to reduce the rate of degradation. By adding different compounds to the electrolyte during cell manufacture, the properties of the SEI layer can be altered to ensure that it is stable during the lifetime of the cells, and to reduce the resistance to lithium ion transport [75–77].

However, the SEI layer does not act to completely protect the anode, and therefore some electrolyte decomposition and lithium consumption continues throughout the life of the cell. This leads to a thicker SEI layer, which in turn both increases the resistance of the cell but also slows down the rate of degradation [78]. Other aspects that increase the rate of SEI formation are holding the cell at high SOC and high temperatures.

During the lifetime of a cell, due to the thickening of the SEI layer, the capacity of cells drop due to the consumption of active lithium, and the cells also undergo power fade due to the increased resistance caused by the thicker SEI [67].

Temperature is very important to SEI layer growth. There are a number of different ways of modelling SEI layer growth, however most relate the rate of lithium-ion diffusion through the SEI to growth of the SEI itself. This means that the rate of SEI layer growth slows as it gets larger, which is evident from the experiments conducted by Smith et al [79]. In this work, it was also found that time and temperature were the dominant factors for SEI layer growth, with the number of cycles not being such an important factor.

SEI layer growth can be modelled similarly to the formation of metal oxides on the surface of a metallic object using a parabolic growth law, shown in Equation (13).

$$\frac{dx}{dt} = \frac{1}{2} k^{\frac{1}{2}} t^{-\frac{1}{2}} \quad (13)$$

where k is a proportionality constant.

It has also been shown that SEI layer growth is extremely dependant on temperature. Cordoba-Arenas et al [80] produced a simple model looking at the capacity fade and power fade of lithium ion batteries used in plug-in hybrid electric vehicles, and used Equation (14) to model SEI layer growth.

$$f_c = a_c e^{-\frac{E_{ac}}{R_g T}} \quad (14)$$

where f_c is the rate of SEI later growth, E_{ac} is the activation energy, and R_g is the universal gas constant.

This exponential relationship between SEI layer growth, a very important degradation mechanism in lithium ion batteries, and temperature show the vital important of thermal management in lithium ion battery packs.

In addition to the strong relationship between SEI layer growth and temperature, it has also been shown that the SEI layer can begin to break down at elevated temperatures [81]. This both exposes the surface of the anode, leading to an increased rate of SEI layer growth, and therefore increasing capacity fade further, and also means that the SEI dissolution might cause insoluble particles in the electrolyte. These particles might travel to and block pores in the separator, decreasing the ease of lithium ion transport and therefore increasing the resistance of the cell [81].

Another problem caused at the interface of the electrode and the electrolyte is lithium plating and dendrite growth [82]. This is caused by the intercalation potential of lithium into graphite being very close to the potential of lithium metal, and therefore, especially at low temperatures and fast charging rates, it is possible that lithium metal is deposited on the surface of the anode in preference to intercalation [83,84].

Lithium that has plated onto the surface of the electrode can react with the electrolyte to form stable secondary products. This causes both the loss of active lithium and consumption of the electrolyte, both of which reduce the performance of the cell.

Lithium plating and dendrite growth is also a safety concern, whereby dendrites can grow so big as to puncture the separator and cause internal short circuits [85]. Additional factors that can lead to lithium plating are excess cathode material, geometric problems such as where the cathode overlaps the anode and therefore when lithium deintercalates from the cathode there is no equivalent anode for it to intercalate into, and local polarisation effects.

During intercalation and deintercalation, the volume of graphite can change by up to about 10% [69]. Whilst this is relatively minor and should only have a small effect on the

structure of the material, it is possible that mechanical stress can cause damage. Of more importance here is the effect that particle expansion can have on the SEI. During expansion if the SEI layer is not flexible, the change in particle size can lead to the SEI cracking, revealing new surfaces for fresh SEI to form, and therefore adding to active lithium consumption or capacity fade [68].

Additionally, graphite exfoliation, where the outer layer of graphite can become detached from the electrode particle, intercalation of solvent molecules leading to particle cracking, reduction of the electrolyte inside the graphite can all lead to high rates of degradation [86].

Another degradation mechanism, this time concerning the composite electrolyte, is contact loss. As the anode changes volume, it is possible that contact is lost between graphite particle, binder and the current collector. This leads to increased resistance as the pathways for electrical conduction are reduced, or in the worst case “dead zones” in the electrode, reducing the capacity of the cell.

2.7.2 Cathodes

The degradation mechanisms that are active and prevalent at the cathode in a lithium ion battery vary depending on the material used to manufacture the cathode. For example, pure LiNiO_2 cathodes exhibit structural disordering, where a nickel ion occupies a lithium ion site, reducing the capacity of the cathode and increasing the resistance due to the increased barrier to diffusion. Adding cobalt oxide up to concentrations of about 20% by mole stabilises the electrode and decreases the structural disordering. Additionally, doping with aluminium or manganese can also have the same effect [87].

Other degradation mechanisms are present for all cathode materials; as for anodes, insertion and de-insertion of lithium ions into transition metal oxides results in changes to volume of the materials. This in turn leads to mechanical stresses in the electrode particles, especially during fast charge and discharge rates where large gradients in lithium concentration build up [88,89]. This mechanical stress can lead to the breakup of cathode particles, or the separation of the particles from the electrically conductive binder [88]. In addition to this, over time the repeated cycling, and therefore intercalation and de-intercalation can lead to stress fractures in the cathode particles [90,91].

Whilst it is widely considered that the increase of interfacial resistance at the anode is the main contributor to degradation, this effect is also present at the cathode [66,92–95]. Factors that contribute to the increase in the interfacial resistance at the cathode are believed to be high temperature storage and operation and the storage of cells at high voltages. Additionally, surface films caused by electrolyte oxidation and lithium salt decomposition have also been reported. The oxygen in the metal oxides that cathodes are composed of is the source for these oxidation reactions, forming a layer of rock-salt structure on the edges of the cathode particles. This layer has low lithium ion conductivity, leading to an increase in surface impedance [96,97].

Another material specific degradation mechanism is manganese dissolution into the electrolyte. Once manganese has dissolved into the electrolyte, it can either re-deposit onto the surface of the cathode, or alternatively travel to the anode and form a surface film [98]. Both of these surface films lead to an increase in the resistance of the cell, and

therefore contribute to the degradation of the cell [99]. Additionally, the loss of active material from the cathode decreases the capacity of the cell [9].

There are two aggravating factors in manganese dissolution; manganese disproportionation at low potentials and acid dissolution at high potentials. At low cathode potentials, manganese undergoes disproportionation, forming divalent manganese ions that are soluble in the electrolyte [100]. Avoiding deep discharges can prevent this effect from occurring. At high potentials, electrolytes become less stable and can undergo decomposition leading to the formation of small amounts of HF. This HF can then cause chemical de-lithiation, dissolving manganese into the electrolyte and producing lithium fluoride as a by-product [9].

2.7.3 Other degradation

In addition to degradation specific to the anode and cathode materials, there are a number of other degradation mechanisms that can contribute to the ageing of lithium ion batteries. These include electrolyte decomposition, electrolyte drying and salt deposition, degradation to the current collectors, gas evolution, and separator deterioration.

It is possible for the electrolyte in lithium ion cells to undergo decomposition. Aggravating factors in electrolyte decomposition include overcharging and undercharging [101]. In addition to this, storage and cycling at high temperatures can increase the rate of electrolyte decomposition [102,103]. Many electrolytes in use in lithium ion batteries also decompose when exposed to even trace amounts of water [104]. Electrolyte decomposition generally leads to gas evolution, which can be a big problem in lithium ion batteries; causing increased pressure in cylindrical cells, which can eventually trigger the

pressure relief valve to blow rendering the cell redundant, or cause significant physical deformation in soft-case pouch style cells [105].

Another consequence of electrolyte decomposition is electrolyte drying, where there is not enough electrolyte to efficiently carry lithium ions between the electrodes. Another contributing factor to this is long-term storage; it is possible that over long periods of time the electrolyte escapes from the packaging (either can or pouch) of the cell [106]. It has also been speculated that electrolyte drying can occur at the edge of pouch style cells, leading to increased rates of degradation in these areas [107].

It has also been shown that the binder that is used to hold the particles of graphite together and ensure a good electrical connection to the current collector can react with the anode particles, especially when the anode is charged [58,108,109].

Another area that is susceptible to degradation are the current collectors [110]. Corrosion of the current collectors can lead to an increase in resistance due to the inclusion of the current collector materials in surface films on the electrodes, in addition it is possible in extreme cases that dendrites of current collector material can form, leading to potential short-circuits and safety concerns [111]. As with many degradation mechanisms, avoiding extremes of state of charge, and the inclusion of electrolyte additives can reduce the rate of current collector corrosion [112,113].

2.7.4 Degradation summary

Figure 7 shows a summary of the different degradation mechanisms that can occur in lithium ion batteries.

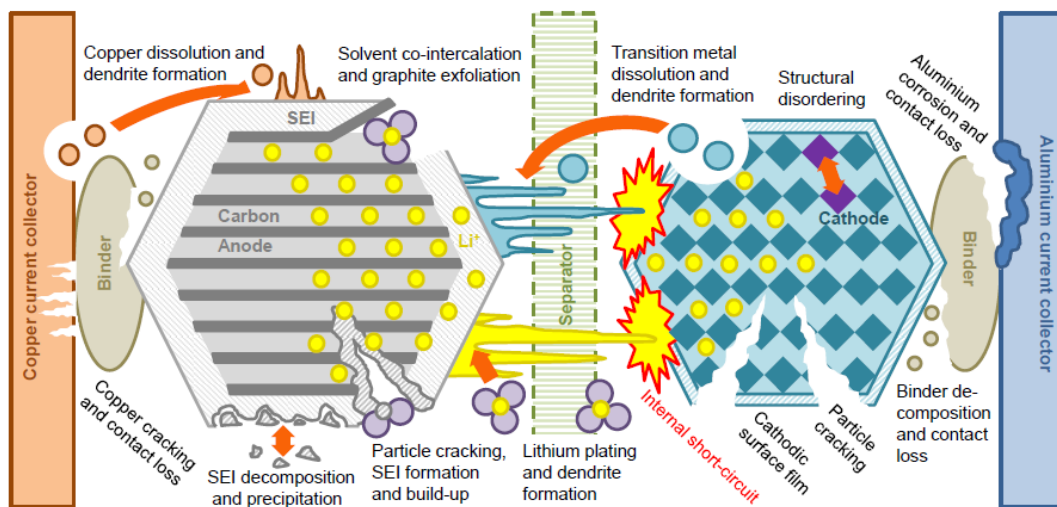


Figure 7 - Summary of different degradation mechanisms in lithium ion batteries. Taken from[114].

Whilst the specific degradation mechanisms that occur have been discussed here, in real-world applications degradation is mainly discussed in terms of capacity fade and power fade.

Capacity fade is the reduction in the capacity of the cell, and can be caused by the loss of cycleable lithium, or the loss of active material in the electrodes. Loss of lithium is generally caused by irreversible side-reactions such as SEI layer growth, where lithium is consumed in the formation of stable lithium-containing surface layers. Active material loss can be caused in a number of ways, but generally is the result of particles in the electrodes becoming electrically isolated from the current collectors, and therefore can no longer be electrochemically active.

Power fade is the increase in the resistance of the cell, caused by things such as surface layer or SEI formation. When the resistance of a cell is raised, in high power applications where the battery is being discharged quickly the resistance causes a large voltage drop across the battery, meaning that there is a limit to the amount of power that a cell can provide. This also limits the useable capacity of a cell, as lower voltage limits are reached

sooner. It is possible that there can still be a relatively large amount of capacity left in a cell, however for some applications it is not possible to use this capacity due to the high resistance of the cell.

In addition to this, the loss of active lithium and changes to the useable capacity of the individual electrodes can lead to a phenomenon called stoichiometric drift [115]. This can lead to problems in battery management as it can lead to the effective and safe voltage window of a cell to change, meaning that cells can be inadvertently over-charged or over-discharged if this effect is not taken into account.

Depending on the application, the end of life of a cell can be defined in different ways.

Often, once the capacity of a cell has dropped below a certain percentage of the original capacity it is considered to have reached the end of its life and must be replaced.

However, in some high-power applications, the resistance of the cell is much more important than the remaining capacity.

Degradation of lithium-ion cells is complex, and although some detail of different mechanisms has been given above, in reality many degradation mechanisms are linked, with some mechanisms increasing the rate at which other mechanisms are progressing. An example of this is manganese dissolution; its primary effect is the loss of active material from the cathode, however the dissolved manganese ions dramatically increase both the rate at which the SEI layer grows on the anode and the morphology of the SEI layer with possible negative consequences, therefore increasing the rate of degradation (both loss of lithium and increasing resistance) further. Because of this it is very difficult to separate and study individual degradation mechanisms, and therefore capacity fade

and power fade are often used to describe the degradation of cells, even if the fundamental mechanisms that caused them are different.

2.8 Heat transfer

2.8.1 Fourier's Law

Fourier's law states that the rate of heat transfer through a material is proportional to both the temperature gradient through the material and to the area, at right angles to the gradient [116]. Mathematically it can be expressed as equation (15)

$$q = -k\nabla T \quad (15)$$

Where q is the heat flux, k is a constant called thermal conductivity, with units of W/mK, and ∇T is the temperature gradient in three dimensions. Many heat transfer processes can be simplified to a one-dimensional problem, and therefore Fourier's law becomes

$$q = -k \frac{dT}{dx} \quad (16)$$

2.8.2 Heat equation

The change in internal energy of a body is proportional to the change in temperature of that body. If zero energy is chosen at a temperature of absolute zero, this can be expressed as equation (17).

$$Q = C_p \rho T \quad (17)$$

Where C_p is the specific heat capacity of a material in J/K and ρ is the density in kg/m³.

If Fourier's law is applied to both faces of a slab of material, and the relationship in equation (17) is used, the heat diffusion equation can be derived:

$$\frac{\partial T}{\partial t} = \frac{k}{C_p \rho} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \frac{1}{C_p \rho} q \quad (18)$$

Equation (18) is given for the case of internal heat generation – given here as q.

2.8.3 Newton's law of cooling

Newton's law of cooling states that *"the heat loss of a body is directly proportional to the temperature different between the body and its surroundings"*. Mathematically is can be expressed by equation (19)

$$\frac{dQ}{dt} = hA\Delta T \quad (19)$$

Where h is the heat transfer coefficient in W/m²K, and is usually taken as an average over the surface of a body. Due to this, the heat transfer coefficient varies with the geometry of an object, and with the type, speed and direction of airflow around it. It can also be a function of the temperature difference between the body and the surroundings, especially when this is large.

2.8.4 Biot number

The Biot number is a dimensionless number that relates the heat transfer coefficient, h, the thermal conductivity, k, and the geometry of an object, and is shown in equation (20)

$$Bi = \frac{hL}{k} \quad (20)$$

The Biot number shows the relationship between the rate of heat flow through a body to the rate of heat flow to the surroundings, and can be used to understand whether it is possible to treat a body as a lumped mass (i.e. the temperature is the same), or whether significant temperature gradients will build up within the body. If the Biot number is small (often taken as less than 0.01), the conduction process within the body is much faster than the convection process to the surroundings, and therefore a lumped capacity solution can be used.

2.8.5 Thermal resistance

A useful way to understand heat transfer problems is by using an electrical resistance analogy. Here, heat flux, Q is analogous to current flow, the temperature difference is analogous to the potential difference (or voltage), and the material properties and dimensions can be combined to calculate the “thermal resistance”. This is shown in equation (21)

$$Q = \frac{T_2 - T_1}{R} \quad (21)$$

Where:

$$R = \frac{L}{kA} \quad (22)$$

A is the area of the body, and L is the perpendicular length that the heat must flow through.

This is a very useful analogy, and can be used to understand heat transfer of composite materials, composed of different layers with different thermal properties, such as those seen in Figure 8

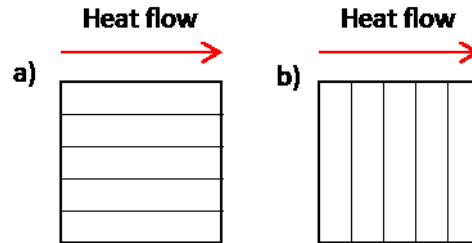


Figure 8 - a) Heat flow along layers, and b) Heat flow through different layers

In Figure 8a), the heat is flowing along different layers, and therefore the total thermal resistance of the material can be calculated as if they are electrical resistors connected in parallel (equation (23))

$$R_{tot} = \frac{1}{\frac{1}{R_1} + \frac{1}{R_2} \dots + \frac{1}{R_n}} \quad (23)$$

In Figure 8b), the heat is flowing through the different layers, and therefore the total thermal resistance of the material can be calculated as if they are electrical resistors in series (equation (24))

$$R_{tot} = R_1 + R_2 \dots + R_n \quad (24)$$

This is useful when calculating the heat transfer properties of lithium ion batteries, as they are composite materials comprising of many different layers of different materials,

and using this method the total thermal resistances in the different directions within a cell can be found.

Thermal resistance, R , has units of K/W , which can be used to illustrate how thermal gradients build up in materials. Equation (21) can be rearranged to understand how large a thermal gradient will be if the heat flux and thermal resistance is known. This is very useful, especially when it is not possible to calculate the Biot number.

2.9 Heat generation

There are two main processes of heat generation in lithium ion batteries, and the heat generation rate can be calculated using equation (25)

$$Q = |I(E_{oc} - V)| - IT \frac{dE_{oc}}{dT} \quad (25)$$

Where Q is the heat generation rate, I is current, E_{oc} is the open circuit voltage, V is the cell voltage, and T is the temperature [117].

The first term in equation (25) relates to heating caused by the internal resistance of the cell, whereas the second term is a result of reversible entropy changes as the cell charges and discharges.

There are a number of things that contribute to the internal resistance of a lithium ion battery, with the main ones being Ohmic resistance, charge transfer resistance and mass transport resistance [117,118]. Ohmic resistance is caused by the resistance in the current collectors, interface between the current collectors and the electrode, and the ionic resistance of the electrolyte. Mass transport resistance is caused by the resistance

to solid-state diffusion within the electrode particles, and charge transfer resistance is governed by the Butler-Volmer equation and is discussed further in section 2.4.

The second term in equation (25) is related to entropy [117]. From the second law of thermodynamics, the change in entropy under a reversible process at constant temperature and pressure is related to the Gibbs free energy and the temperature. This leads to equation (26)

$$Q_{entropy} = T\Delta S\left(\frac{I}{nF}\right) = \frac{\partial \Delta G}{\partial T_{cell}} = nFT\left(\frac{\partial E_{oc}}{\partial T}\right) \quad (26)$$

The entropic heat generated according to equation (26) can be either positive or negative, and for lithium ion batteries this equates to an exothermic reaction during discharge, and an endothermic reaction during charge [118,119].

3 Experimental Techniques

There are many different ways that batteries can be tested, however for most of these tests there is a limit on the number of parameters that can be controlled or measured.

The simplest parameters to measure are current, voltage and temperature, and a lot of information can be obtained simply by using these parameters. It is well known how dependent the performance of lithium-ion cells are on temperature, and therefore it is very important to control and measure the temperature precisely when conducting experiments.

3.1 Charging and Discharging

Arguably the simplest way of testing a battery is to charge and discharge at constant rates, whilst recording the voltage and measuring the capacity. If a cell is discharged at a very slow rate, typically at C/10, C/20 or slower, the resulting voltage curve can be approximated as the OCV curve. This is useful, as the effects of diffusion are negated by the slow discharge rate. The capacity at a slow rate gives an indication of the true capacity of a cell – i.e. how many lithium ions are available to move between the anode and the cathode on discharge whilst the cell remains within some predetermined voltage limits.

In addition to charging and discharging at very slow rates, higher rate discharges can give further insight into the behaviour of a lithium battery. Of the many physical processes that occur in a cell during charge and discharge, diffusion in the electrode particles and electrolyte are some of the most important. At higher rates, diffusion becomes the limiting factor in the performance of a cell, causing the “usable capacity” to decrease.

Slow diffusion means that some lithium cannot diffuse through the particles and the electrolyte quickly enough, and therefore cannot be used during charging and discharging, resulting in the decrease in usable capacity of a cell [120,121].

Charge and discharge tests provide two interesting items of information – the capacity and the voltage curves. The voltage curves change depending on discharge rate and temperature. As all cells have an internal resistance, the voltage curves tend to be lower during faster discharges as the voltage drop across the cell due to this internal resistance is higher. This can be seen in Figure 9, where the discharge curves at 1 A and 8 A are shown for a 5 Ah kokam cell using the setup described in Section 5.3.

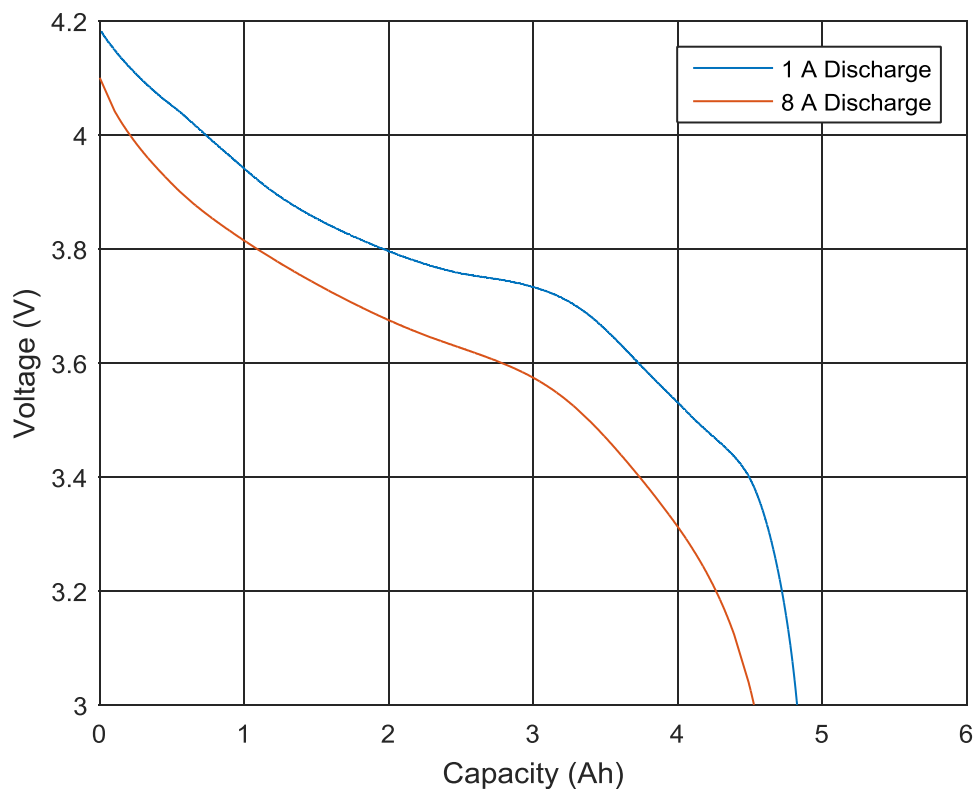


Figure 9 - Voltage vs capacity curves at different rates of discharge

It can be seen in Figure 9 that the voltage curve of the faster 8 A discharge is lower than that of the slower 1 A discharge, and also that the 1 A discharge provides a larger capacity before the cut-off is reached.

Temperature also has a large impact on the discharge curves of lithium ion batteries. Again, the internal resistance plays a large part in this; the resistance of cells is much higher at low temperatures and therefore the voltage drop is higher, leading to lower voltage curves during discharge. An example of this can be seen in Figure 10, where 5 Ah Kokam cells were discharged at 8 A at different temperatures using the setup described in Section 5.3.

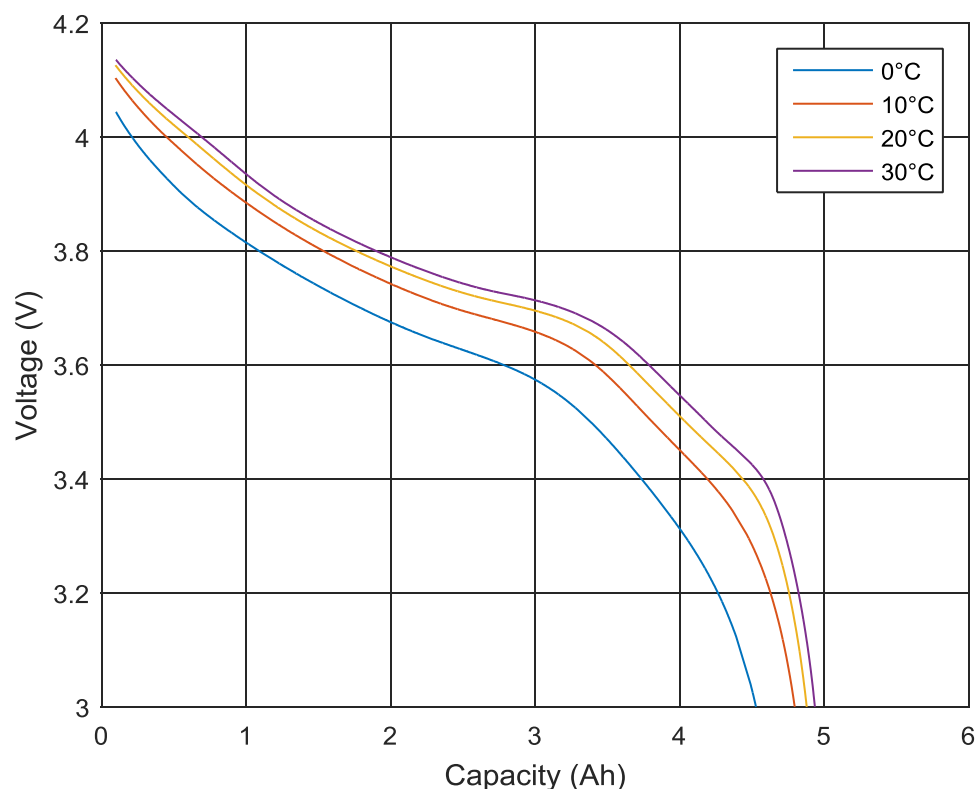


Figure 10 - Capacity vs voltage curves for cells at different temperatures

It can be seen in Figure 10 that not only is the voltage curve much lower at lower temperatures, but the capacity provided by the cell before the voltage cut-off is reached

is also much lower. This is partly due to the large voltage drop and partly due to the lower rates of diffusion as discussed earlier in this section.

3.2 Incremental Capacity Analysis

Whilst differences in the voltage curves can be seen, a lot of the changes and interest are contained in the flat plateaued section of the curve, and when these changes are subtle they can be difficult to see, quantify and understand. If the differential of the voltage curve is taken with respect to capacity, more information can be gleaned from the resulting curves [122,123]

Additionally, the reciprocal of this curve is often taken, turning the flat parts of these curves into peaks. These peaks correspond to phase equilibria, and how these change in magnitude, position (in terms of voltage) and shape, can lead to insights into the cells characteristics and how they might be changing over time or under different conditions [124].

3.3 Electrochemical Impedance Spectroscopy

3.3.1 Introduction

Electrochemical Impedance Spectroscopy, or EIS, is a technique used to characterise many different electrochemical systems, and can be used to measure the resistive, capacitive and inductive behaviour of complex systems [125].

3.3.2 Ohm's law

Ohm's law states that for an ideal conductor, the potential difference across it is proportional to the current flowing through it. The constant of proportionality is called the resistance, and therefore Ohm's law can be described using Equation (27):

Ohm's law:

$$V = IR$$

(27)

Whilst this holds true for a circuit that contains only an ideal resistor, many systems are much more complicated and therefore the concept of impedance is introduced.

Electrochemical impedance is measured by applying an alternating current to a system at different frequencies and measuring the voltage response. In a complex system, the voltage response will have both an amplitude and a phase difference, which will vary at different frequencies, this is illustrated in Figure 11.

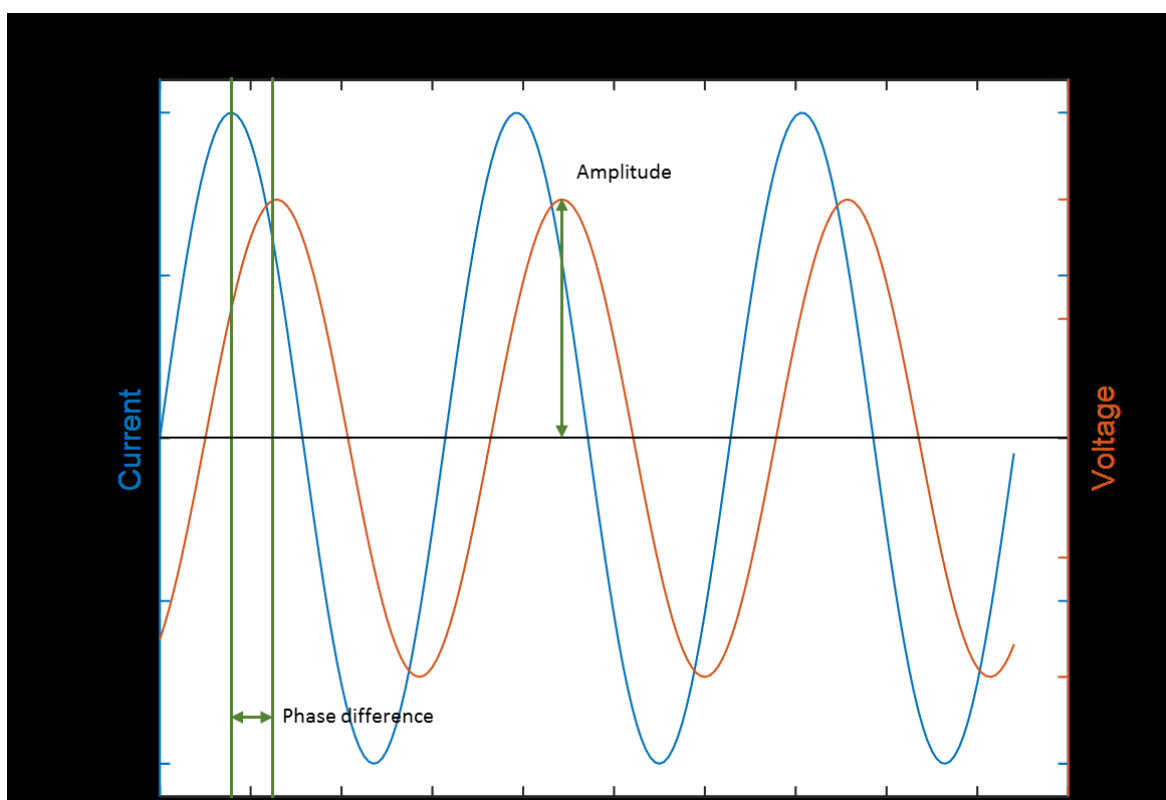


Figure 11 - Illustration of amplitude and phase shift

These amplitudes and phase differences can be used to calculate the complex impedance response.

An alternative method is to apply an alternating voltage to the cell and measuring the current response. When an alternating current is applied, this is called galvanostatic

impedance spectroscopy, and when an alternating voltage is applied it is called potentiostatic impedance spectroscopy.

3.3.3 Typical response

Figure 12 and Figure 13 show a typical nyquist plot and a typical bode plot that would be produced by performing EIS on a lithium ion battery. It should be noted that in Figure 12, the vertical axis shows negative imaginary impedance, and therefore the EIS plot shows a mirror image reflected in the horizontal plane to that which might be expected.

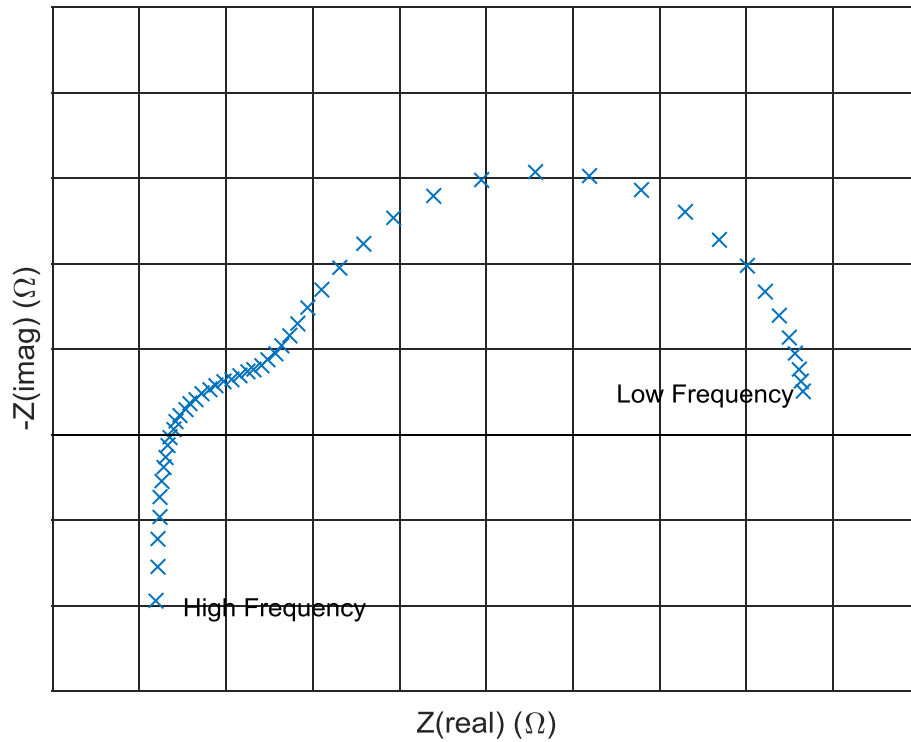


Figure 12 - Typical nyquist plot from conducting EIS on a lithium-ion battery

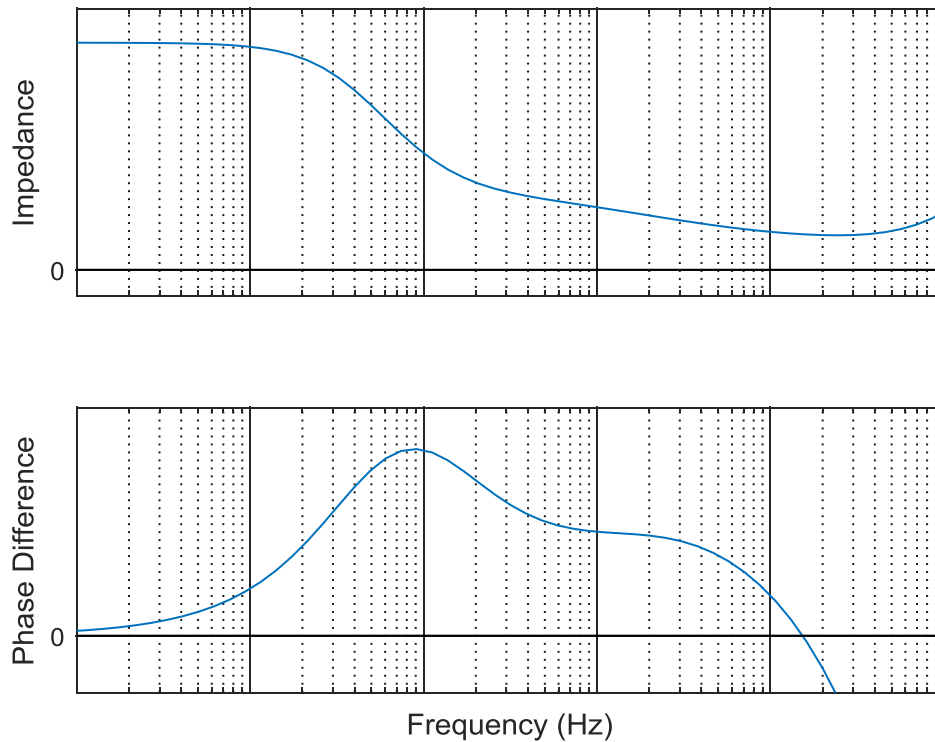


Figure 13 - Typical bode plot from conducting EIS on a lithium ion battery

The high frequency parts of Figure 12 and Figure 13 represent inductive behaviour, and the lower frequency areas represent a mixture of capacitive and resistive behaviour.

3.3.4 Equivalent circuit modelling

The complex impedance response can be fitted to networks of ideal circuit elements, in a process called equivalent circuit modelling. Many different equivalent circuits can be used to fit impedance data, and a typical equivalent circuit model can be seen in Figure 14.

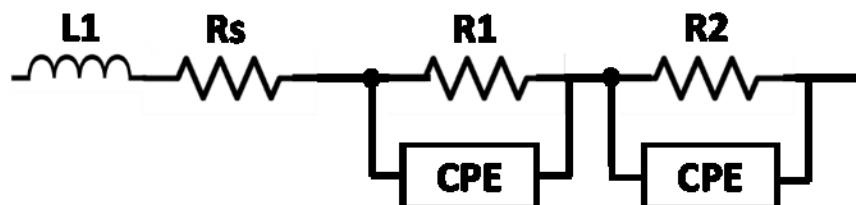


Figure 14 - Equivalent circuit model used to fit the EIS data

This equivalent circuit is made up of several elements, each of which are prominent at different frequencies, which are described in more detail in Table 2, with their contributions to a typical nyquist plot shown in Figure 15.

Element(s)	Corresponding area
L1	Very high frequency behaviour
R _s	Series resistance
R1 & CPE1	First, higher frequency semi-circle
R2 & CPE2	Second, lower frequency semi-circle

Table 2 - Description of different circuit elements

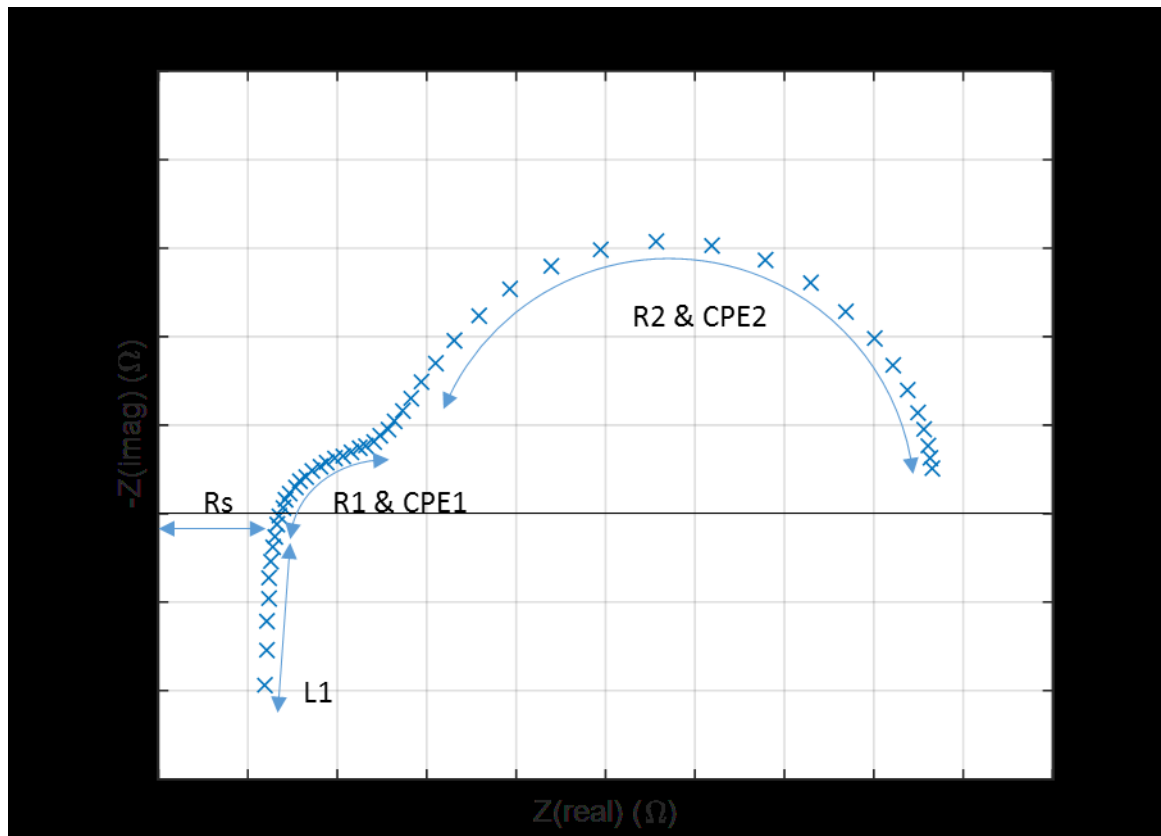


Figure 15 - Illustration of contribution of different circuit elements

The inductor, L1, is mostly active at very high frequencies, and is attributed to the current collectors, connection leads to the batteries and the porous nature of the jelly roll. The high frequency intercept, where a spectrum intersects with the imaginary- (y-) axis, is the

total Ohmic resistance of the cell, and can be attributed to the electrolyte resistance, any contact resistances, such as between the active material and the current collectors, and electronic contacts such as between the current collectors and the cell tabs [126–128].

In addition to this, there are two pairs of a resistor and a constant phase element (CPE) in parallel. These represent the two depressed semi-circles that can be seen in Figure 15.

The first of these CPE-resistor pairs is related to the first depressed semi-circle, and can be ascribed to the SEI layer of the electrodes at interface between the film and the electrode, while the second CPE-resistor pair relates to the second depressed semi-circle, and can be ascribed to the charge transfer at the electrode-electrolyte interface [126,129,130].

A CPE, or constant phase element is a non-ideal capacitor, which has some resistance effect alongside its capacitance. On a nyquist plot, a resistor in parallel with an ideal capacitor would produce a perfect semi-circle, whereas a CPE can be used to model the depressed, or flattened shape that is often captured when conducting EIS on lithium-ion batteries. The impedance of a CPE is shown in Equation (28), where $0 \leq n \leq 1$.

$$\text{CPE impedance} \quad Z_{CPE} = \frac{1}{Q_0(\omega i)^n} \quad (28)$$

In the special cases where $n=1$, the CPE will describe a perfect capacitor, and when $n=0$, the CPE will describe a perfect resistor [125,131,132].

For the purposes of this thesis, whenever EIS data are fitted to an equivalent circuit, the circuit used will be the one shown in Figure 14 unless stated otherwise.

3.4 Degradation Tests

In general, there are two types of degradation tests; calendar ageing and cycle life.

Calendar aging is simply concerned with how a battery degrades when sitting on a shelf, and cycle life looks at how many cycles a battery can provide. Both of these processes are strongly dependent on temperature, with more information available in Section 2.6.4.

Calendar aging tests are relatively simple to conduct. Cells are held at different temperatures, usually using an oven (for more information see Section 3.5), and periodically the cells are tested to understand how their capacities and resistances have changed.

3.5 Temperature Control

There are various ways in which temperature can be controlled, although the simplest way is usually to use an oven/incubator, most of which usually have a fan, and the temperature of the cell is controlled via convective heating and cooling. Whilst this is a simple and relatively effective technique, the control of the temperature is not particularly consistent. Convection heat transfer is dependent on the convective heat transfer coefficient, which can vary with the surface material, the flow rate, and the flow regime (laminar, turbulent) surrounding the object in question. The heat flux and the surface temperature also varies depending on the temperature difference between the cell casing and the fluid, leading to an inconsistent thermal boundaries. This makes comparing similar tests, for example at different discharge rates, difficult. Additionally, modelling these types of thermal boundary conditions is difficult and computationally intensive than simple dirichlet boundary conditions.

Another concern with incubators/ovens is their control – they often employ an on-off control system whereby the heating/cooling is turned on and off when the temperature reaches a certain amount above or below the set point. This can lead to temperatures fluctuating by a couple of degrees, which is enough to affect the results of some tests so significantly that the results become meaningless. Also, there are concerns that the different areas of the units will have different temperature profiles – similar to a conventional oven used in a kitchen; unless the air is thoroughly mixed up inside, the top of the oven will be hotter than the bottom.

It is widely known that liquids have much more effective heat transfer properties than gases, mainly due to their increased densities and heat capacities, therefore if high rates of heat transfer are needed then convective heat transfer involving liquids can be used, usually in the form of a dielectric oil bath [133]. However, similarly to incubators and ovens, this method is reliant on convective heat transfer and is therefore limited by the downsides discussed earlier.

If more accurate control is needed, it is possible to use direct cooling plates that can control the temperatures of the surfaces of the cell more precisely. Using this style of set-up, the surfaces of a cell can be controlled far more precisely, giving potentially more accurate experiments [12]. Here, dirichlet boundary conditions are employed onto the cell, and therefore the modelling of these experiments becomes simpler and computationally less intense.

It is worth noting that no matter how good a temperature control system is, it is not possible to control the temperature of a whole cell. As soon as current flows, heat is generated inside a cell and therefore the centre of a cell will be hotter than the

controlled edges. This makes the comparison of different experiments very difficult, as although a cell may be tested at a certain temperature, for the majority of the test, the temperature inside the cell may be significantly greater than this. In much lithium-ion battery literature this effect is ignored, and the assumption that the cell is at a homogenous temperature equal to its surroundings is taken.

For example, Bloom et al. [134,135] conducted experiments on a variety of 18650 cells at different temperatures, however gave no explanation of how the cells were held at these temperatures. Ramadass et al. [136,137] conducted experiments on Sony LiCoO₂ 18650 cells at room temperature and at elevated temperatures, using an environmental chamber to control the high temperature tests, however give no mention to any internal temperature increase that might occur during the test. Waldmann et al. [8] also used an environmental chamber to control the temperature of cells during degradation tests, but again there was no discussion on how the temperature of the cells may vary during the tests. Lohman et al. [138] conducted experiments utilising EIS to characterise aging, however only give a cursory mention to a thermal chamber used to control the temperature of the cells, again ascribing no comment to any increase in internal temperatures during testing. Belt et al. [11] also use an environmental chamber but do not discuss internal heat generation. Finally, Niehoff et al. [139], Belt et al. [140], both mention the use of thermal chambers but provide no more information.

Additionally, many investigations into degradation do not give details of any thermal management during degradation testing. Dubarry & Liaw [141], conducted experiments on 18650 LFP cells yet gave no explanation of thermal management during their tests. Liaw et al [142], conducted degradation experiments on cells at different temperatures

and SOC's in order to form an Arrhenius relationship, however they do not describe how temperature was controlled during their experiments.

3.5.1 Inhomogeneity

Due to the construction of cells and internal heat generation during charging and discharging at anything but the slowest rates, most cells under test will have a degree of temperature inhomogeneity. Whilst sometimes this is kept to a minimum, especially for small cells under relatively low rates of operation, at higher rates and for larger form factor cells significant temperature gradients can form within a cell. Often these gradients are ignored, however there have been some studies exploring inhomogeneity in lithium ion batteries.

An area that inhomogeneity has been explored in some detail is within a whole-pack scenario, looking at the effects of thermal conditions and cell-to-cell differences in order to predict the performance of a pack [143–148].

Gogoana et al. [149], conducted a study looking at the importance of matching the series resistance of cells in parallel strings. They found that a 20% difference in internal resistance of cells in parallel can lead to a reduction of 40% in the lifetime of those cells when cycled. They found that differences in internal resistance leads to high current passing through each cell in turn, during charging and discharging, which in turn leads to much higher levels of degradation.

Paul et al. [145], looked at both the effects of thermal boundary conditions and manufacturing tolerances on the performance of battery systems. They found that

differences in capacity and resistance can lead to performance limitations in a pack, reaffirming that the “worst” cell in a pack is the limiting factor.

Chen et al. [147], conducted a thorough thermal analysis of a lithium ion battery, focusing on modelling the heat distribution within a cell under operation. They found that under some cooling conditions, there is significant variation in the temperature of cells.

Additionally, they found that there is a greater degree of homogeneity in the X-Y plane compared to the Z plane due to the greater thermal conductivity along the layers of a cell when compared to through the layers. Damblanc et al. [148], also conducted a similar study, focusing on how temperature affects the performance of lithium batteries.

3.6 Temperature measurement

There are a number of ways of measuring temperature during battery testing. The most basic form of this is assuming that a cell is at the same temperature as its surroundings.

Whilst under load, this is unlikely to be the case due to internal heat generation, however some studies make this assumption without ever mentioning if the temperature of the cells has been measured. Alternatively, there are contact methods of measuring temperature such as thermocouples or thermistors, or alternatively there are non-contact methods such as thermal imaging.

3.6.1 Contact methods

Thermocouples and thermistors offer a cheap and relatively easy method to measure the temperature at a single point on the surface of a cell. Thermocouples rely on the Seebeck effect; where if two ends of a metal are at different temperatures then current will flow along it. If two dissimilar metals are joined together at one end to form a junction, if this

junction is at a different temperature to the other end, a small EMF is produced which can be related to the temperature difference between the hot and cold junctions.

Normally, a thermocouple consists of two thin gauge wires that are welded together at one end, and the voltage produced is measured by a dedicated thermocouple reader. An example of a thermocouple can be seen in Figure 16.

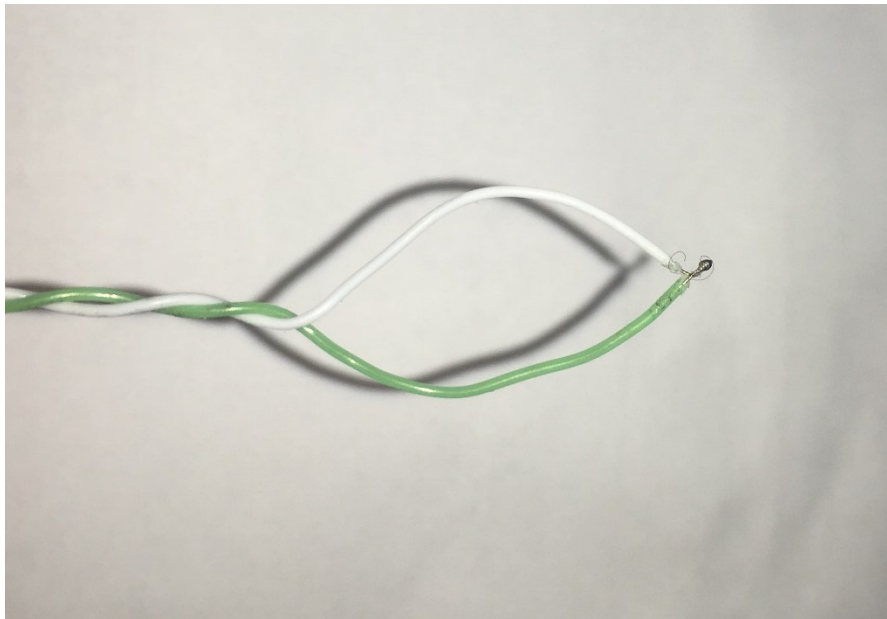


Figure 16 - Example of a K-type thermocouple

Thermocouples can be attached to a cell in a variety of different ways. A simple method is to stick them down with some sort of tape, often polyamide or kapton. Whilst this is a quick, non-damaging and relatively effective method, it can lead to variable contact between the thermocouple and the test piece, and this contact can deteriorate over time, leading to inaccurate measurements especially during highly transient conditions. This method can be combined with a small amount of thermally conductive paste in order to improve the contact between the tip of the thermocouple and the test piece, or alternatively a thermally conductive epoxy can be used to attach a thermocouple to the

test piece. This method is reliable and will not deteriorate over time, however it leads to a permanent connection – it is very difficult to remove the epoxy once it has set.

Thermistors operate under a similar principle to thermocouples, however rather than producing a voltage their resistance changes at different temperatures. There are two types of thermistor; positive temperature coefficient (PTC), where the resistance increases with temperature; and negative temperature coefficient (NTC), where the resistance decreases with increased temperature.

3.7 Experimental Example

3.7.1 Introduction

This section will show some examples of how the experimental techniques discussed in Section 3 can be applied, and will explain some of the difficulties that testing batteries in a controlled, repeatable way can impose. In addition, examples of some techniques such as thermal imaging will be shown, showing how in some situations using more advanced techniques such as these can be vital in understanding the behaviour of lithium batteries in different scenarios.

3.7.2 Temperature control of large form factor cells

3.7.2.1 Introduction

As part of a student-led project to design an electric Formula Student car, some large form-factor cells were tested in order to understand if they were suitable for the car in terms of their capacity and thermal behaviour. Formula Student is a motorsport series run for students where teams from universities around the world design and build formula-style racing cars for competition. Different types of cars compete together in a

single category, pitching conventional gasoline powered cars against electric, hybrid and hydrogen-powered vehicles.

The cells are 20 Ah NCM cells manufactured by EIG [150]. 82 cells are connected in series in the car in an 82S1P configuration.

3.7.2.2 Experimental

It was proposed that the battery pack would run without any active thermal management system, and due to the nature of the pack casing and enclosure, the loss of heat from the pack would be minimal, therefore a test rig using insulating glass foam was manufactured in order to mimic the conditions that a cell would experience in a car as closely as possible. The cell terminals were bolted onto aluminium bus-bars, and the temperature was measured in several locations on the cell using thermocouples connected to PicoLoggers.

The discharging was done using a Kikusui loadbank controlled by Wavy, which is a piece of proprietary software used to control Kikusui loadbanks. A picture of the setup can be seen in Figure 17, and a schematic of the location of the thermocouples can be seen in Figure 18.

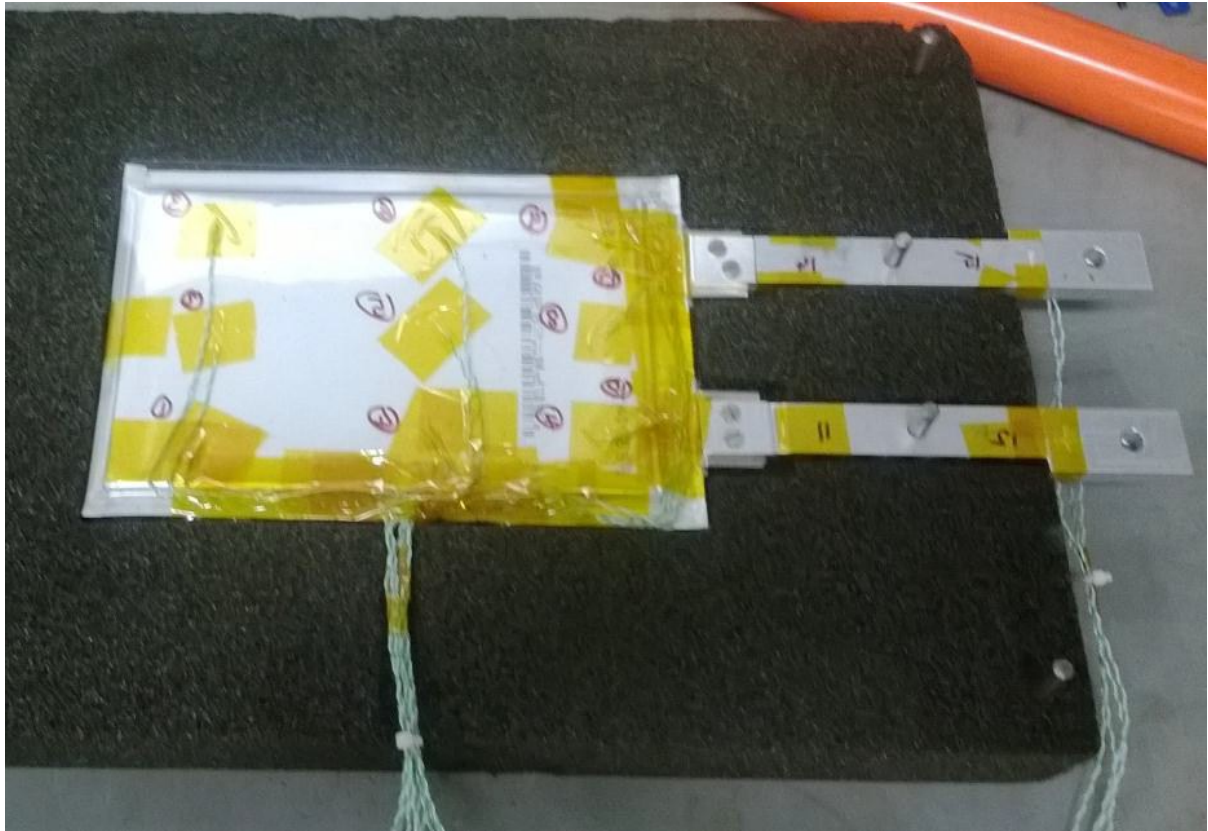


Figure 17 - Image of the cell in the insulating glass foam with bus bars and thermocouples (top foam slab removed)

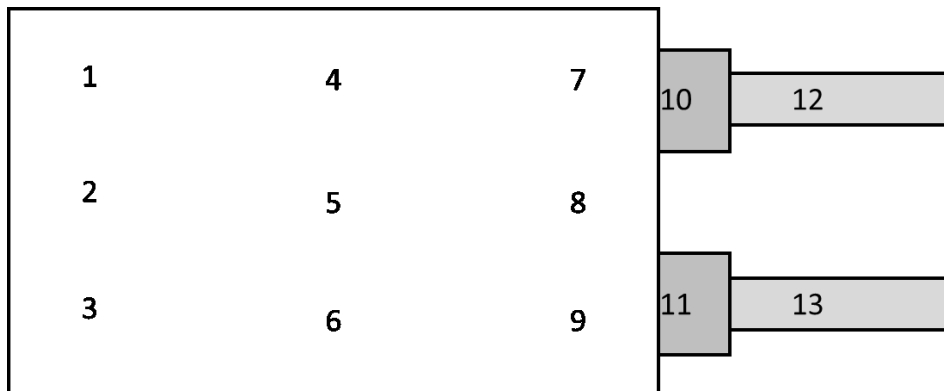


Figure 18 - Schematic of the location of the thermocouples

The endurance event at formula student takes between 20 and 30 minutes to complete, and therefore two discharges at 2C and 3C were conducted in order to gauge the performance of the cells over a similar time frame to the competition. Voltage traces against capacity for these tests can be seen in Figure 19, and the temperature measurements at the different cell locations can be seen in Figure 20.

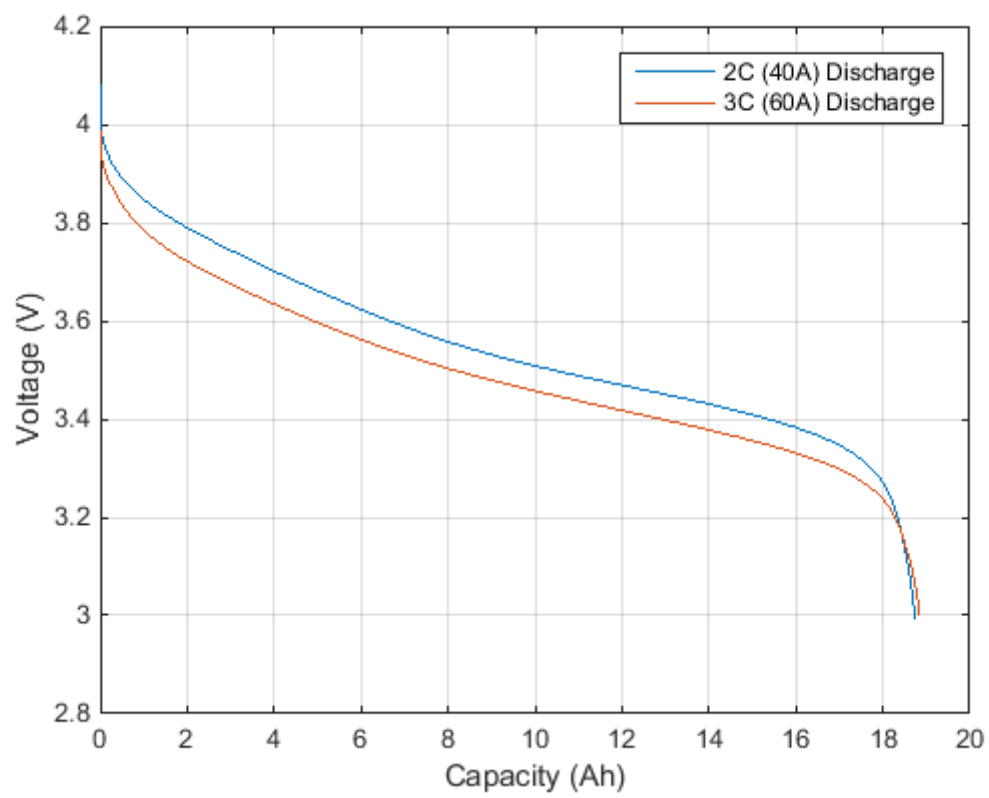


Figure 19 - Voltage curves against capacity for 2C and 3C discharges

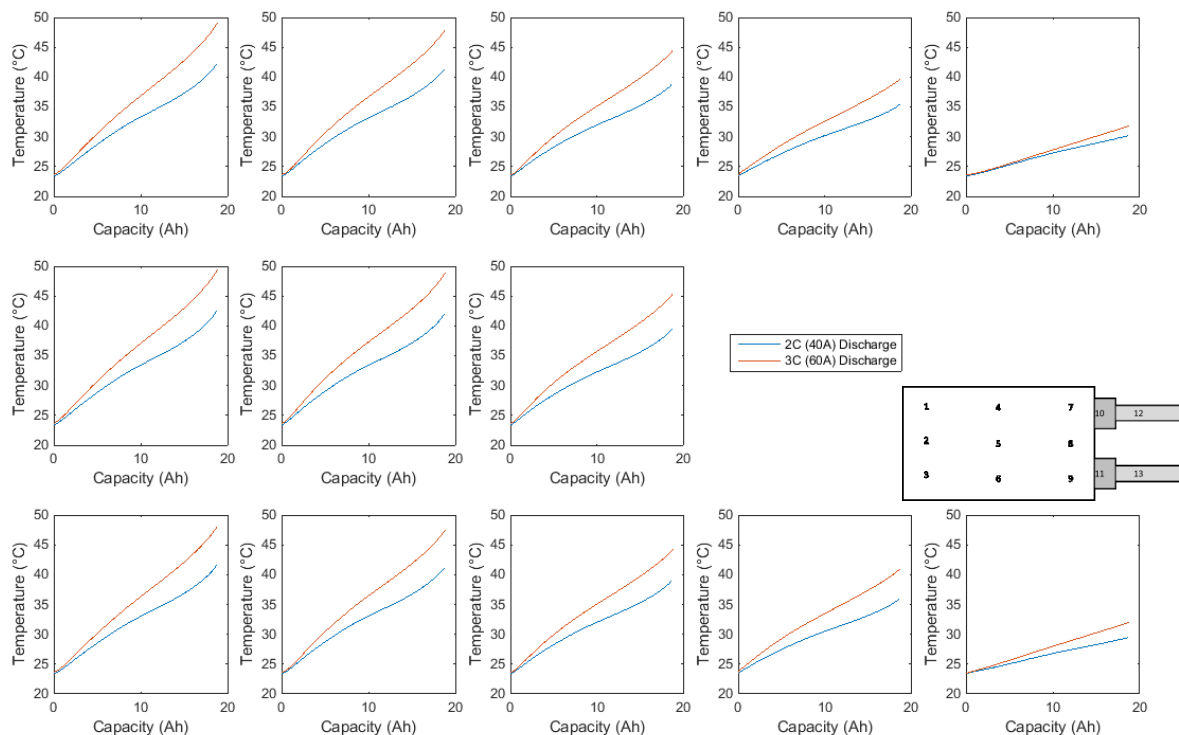


Figure 20 - Temperatures at different cell locations for 2C and 3C discharges

Figure 19 shows that the voltage curve for the 3C test is lower throughout most of the discharge when compared with the 2C test. This is to be expected, as the higher current flowing in the 3C test will lead to a greater voltage drop and therefore a lower overall voltage. However, an unexpected result from these tests was that the capacity of the cell before the 3.0 V cutoff was reached was slightly higher during the 3C discharge than the 2C discharge.

In order to explain the results, the temperatures in Figure 20 must be examined, and used in conjunction with an understanding of what is happening in the cell at the end of discharge. The temperature of the cell at the end of the 3C discharge is significantly higher than at the end of the 2C discharge; this is to be expected as a higher current is flowing leading to a higher rate of heat generation. However, the higher temperature of

the 3C cell will also lead to a reduction in the resistance, specifically the charge transfer resistance and the diffusion resistance. This is evident from the gradients of the temperature plots in Figure 20; the gradient is much higher for the 2C cell at the end of discharge, indicating that despite the higher current flow, the 2C cell is producing more heat per Ah of capacity discharged than the 3C cell.

At the end of discharge, the usable capacity of the cells is limited by diffusion of lithium through the electrode particles and the electrolyte. Diffusion is strongly dependent on temperature, and therefore if diffusion is happening at a faster rate, more of the lithium in the electrodes can be used leading to a higher useable capacity from the higher rate cell. In addition to this, the resistance of the 3C cell will be lower, reducing the voltage drop seen on this cell.

This result is significant, as it is commonly assumed that increasing the rate of discharge will reduce the useable capacity of a cell. This would be the case for an isothermal cell, and many experiments attempt to mimic and assume isothermal conditions by aggressively thermally managing the cells however the centre of the cells will always be at a different temperature to the edges of the cells.

3.7.2.3 Real world duty cycle

Formula student provides a relatively unique scenario where the balance between performance and degradation is far more towards performance than in many other applications. This is because the car will only race once or twice during competition, and before the competition during testing it is possible to de-rate the powertrain performance in order to protect the battery.

Due to the findings shown in Section 3.7.2.2, the idea that the usable capacity of the cells could be increased for the event by heating the battery pack before the event started was investigated further in order to improve the performance of the vehicle.

In order to investigate whether this would work, a drive cycle similar to that used in the competition was used in order to try to mimic the event as closely as possible. Using data from a previous formula student competition, a drive cycle for a single lap was found, with the speed data converted into power based on estimates for mass, aerodynamics and efficiencies. The speed and total power of this drive cycle can be seen in Figure 21.

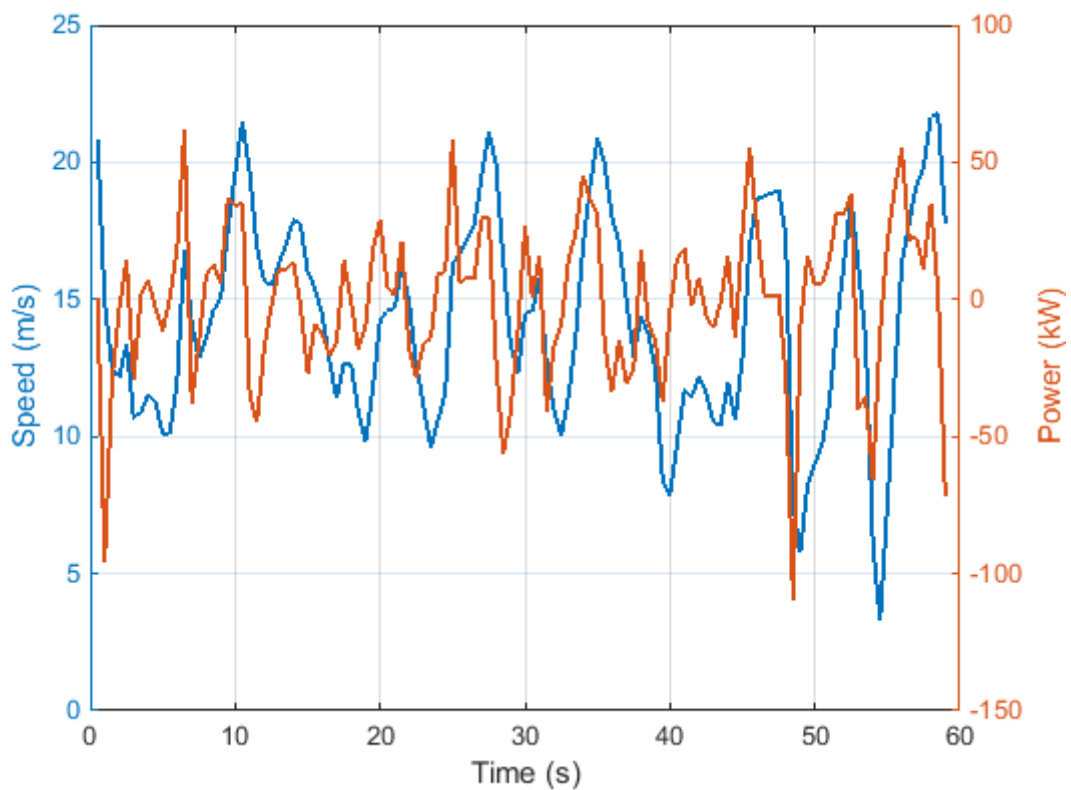


Figure 21 - Speed and power traces for a typical Formula Student lap

For single cell testing, each cell will only be providing 1/82 of the total power of the car.

Additionally the motor controller on the car cannot perform regenerative braking, and therefore during periods of deceleration the power required from the batteries is 0. From

this, a representative load cycle for a single cell around one lap can be formed, and this can be seen in Figure 22.

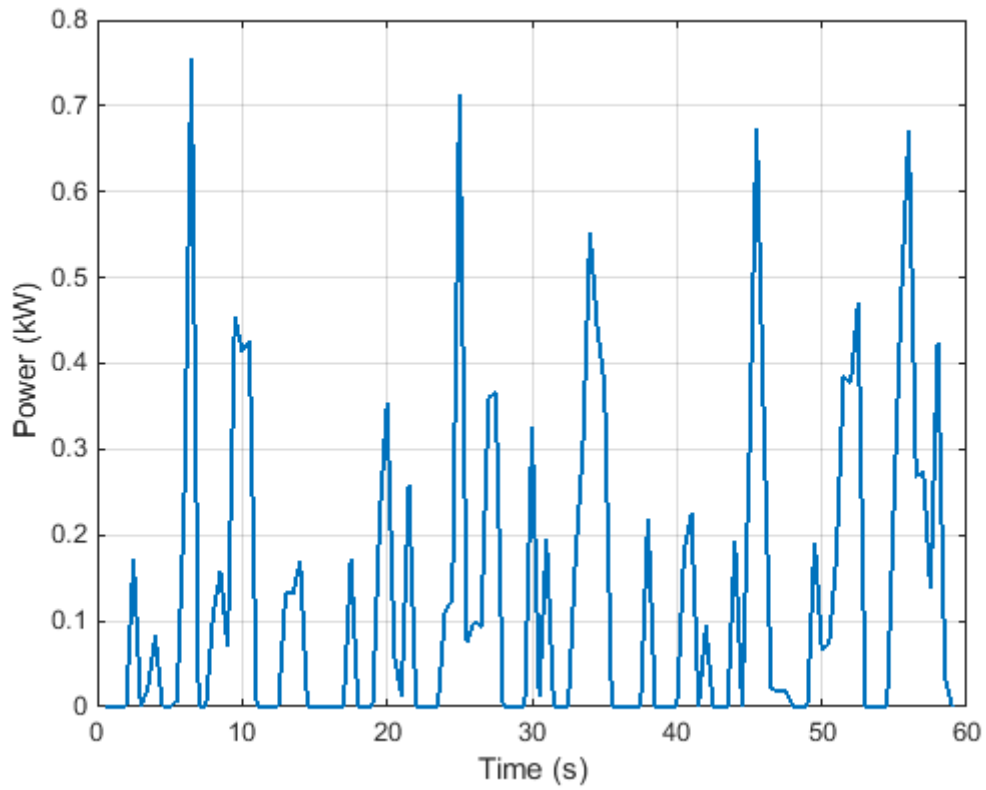


Figure 22 - Duty cycle for a single cell around a typical formula student lap

During the competition, there is an enforced 3 minute break in the middle of the endurance run for a change of driver; therefore a full drive cycle was constructed taking this into account, which can be seen in Figure 23.

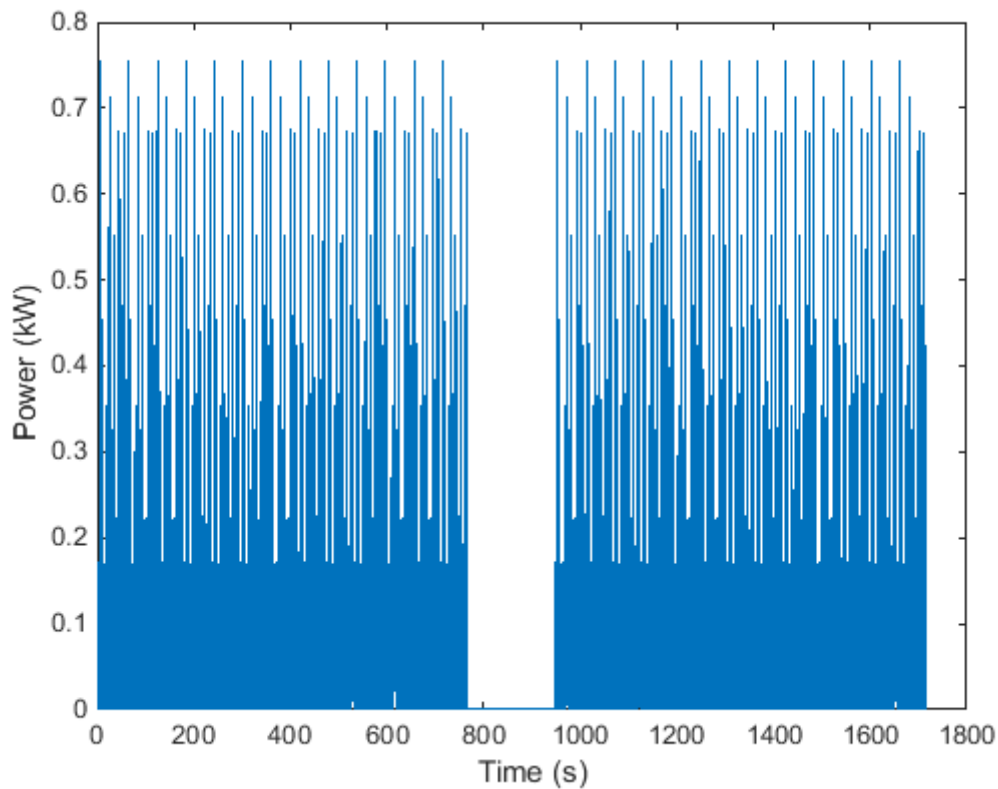


Figure 23 – Complete typical formula student drive cycle

The cell was tested using this testing cycle at different starting temperatures. The starting temperatures were 22°C, 30°C, 40°C and 50°C. These temperatures were reached by placing the cell setup in an oven for 24 hours before the beginning of the test to ensure that the temperature was homogenous throughout.

3.7.2.4 Results

Figure 24 shows the temperature profiles at different positions on the cell and the busbars (refer to Figure 18) during discharge of the cell for different starting temperatures.

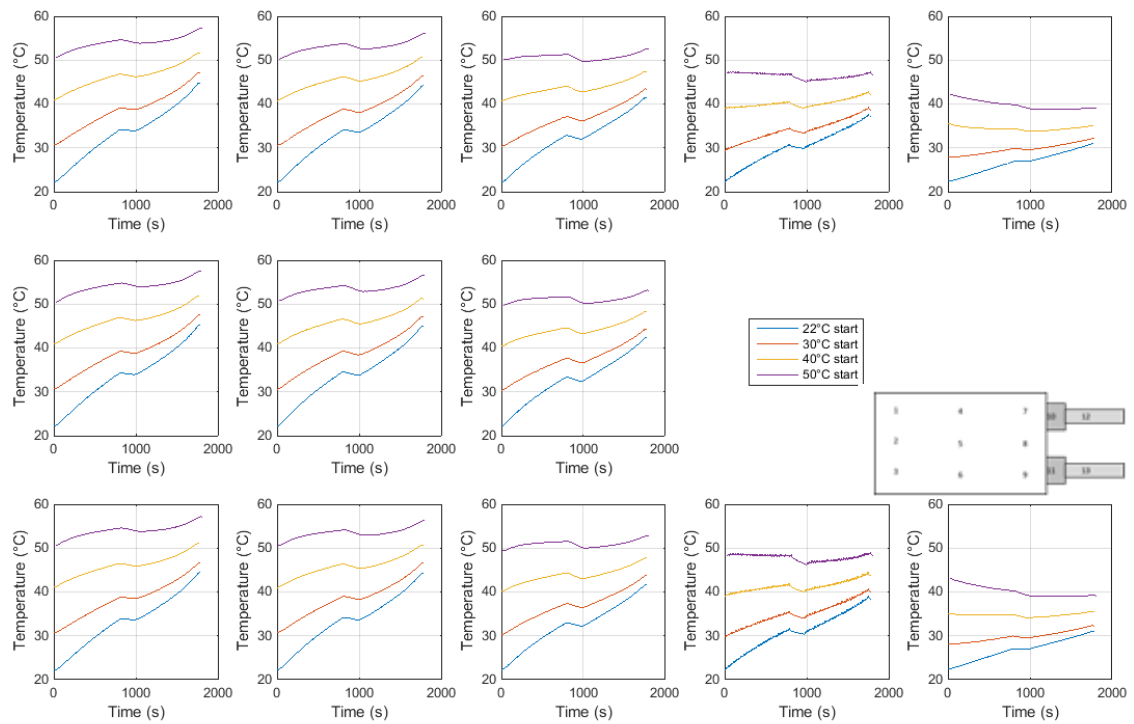


Figure 24 - Temperature profile during discharge for different starting temperatures and at different positions

Figure 24 shows that the temperature rise for the tests starting at lower temperatures were significantly higher than for those starting at higher temperatures. In order to highlight this, the temperature difference for the central measurement (number 5 in Figure 18) was calculated and displayed in Figure 25.

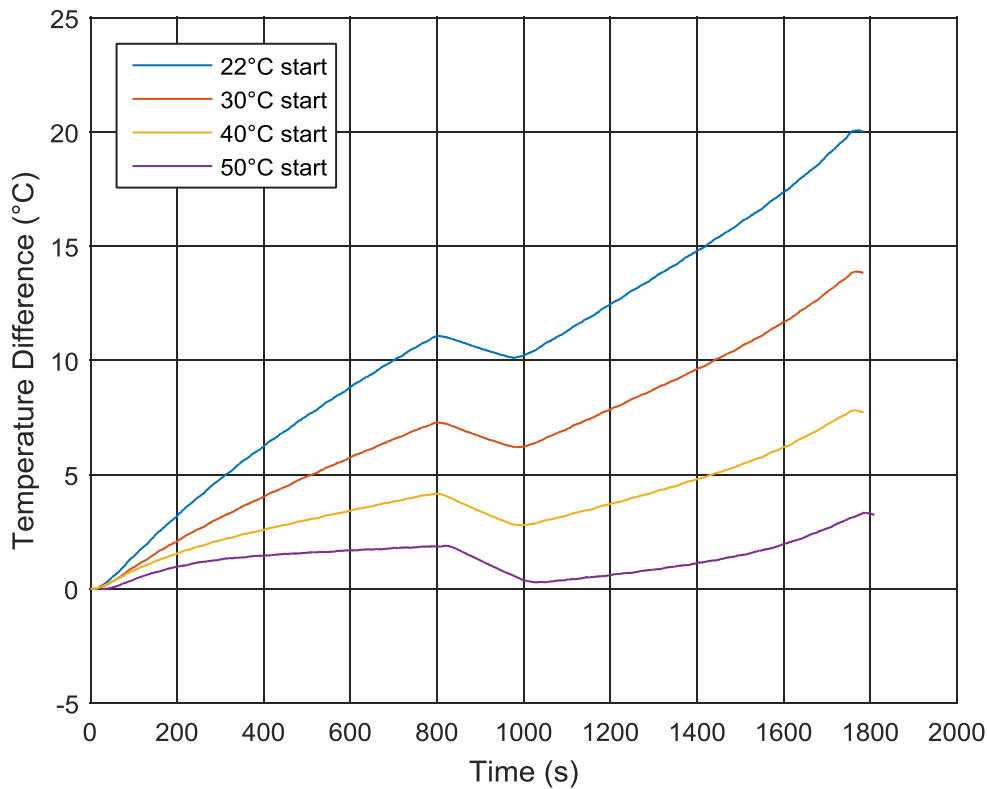


Figure 25 - Temperature difference at the centre of the cell for different starting temperatures

Figure 25 shows that for the tests that start at higher temperatures, there is a large reduction in the heat generated in the cell, showing that the cell is delivering power much more efficiently at lower temperatures. In order to quantify this, the cell was discharged at 2C after the tests had completed and the energy remaining in the cell before the 3V cut-off was measured and shown in Table 3.

Starting temperature	22°C	30°C	40°C	50°C
Capacity remaining (Ah)	0.68	0.82	1.44	1.71
Capacity remaining (%)	3.4	4.1	7.2	8.6

Table 3 - Capacity remaining after tests at different starting temperatures

The result shown in Table 3 shows that there can be a significant increase in the useable capacity of a cell if the starting temperature is raised, especially when a profile based on power consumption rather than specific capacity is used. This is interesting in high-

performance applications where degradation and safety are less of a concern, such as the battery packs used in Formula 1 and Formula E cars.

3.7.2.5 Discussion and conclusion

Whilst the increase in performance at higher starting temperatures is not particularly surprising and has been shown in many other studies, these results also highlight the difficulties in testing lithium batteries. Figure 20 and Figure 24 show that even though at the beginning of discharge the temperature across the surface of the cell is homogenous, by the end of the discharge the temperatures vary significantly; over 6°C in the case of 3C constant current discharge for the temperature measurements over the surface of the cell. When this is the case, the temperature of the cell can no longer be considered homogenous, and therefore the effect of the temperature gradient must be taken into account, which rarely happens in academic literature.

These tests were performed under pseudo-adiabatic conditions, however even if a cell is insulated perfectly it is impossible to insulate the wires or busbars that must be connected to the cell terminals in order to test the cell. This leads to a cooling effect, and is why during these tests the temperature is lower at the end of the cell where the terminals are and higher at the end of the cell away from the terminals. Due to the highly temperature dependent behaviour of lithium batteries, it is important that the thermal management of cells during testing is well designed in order to negate the effect of temperature gradients as far as possible.

Under constant current discharge conditions it was shown that for an insulated cell under pseudo-adiabatic conditions, it is possible that under higher current rates the useable capacity of cells can be higher than during lower current rates due to the increased

temperature of the cell undergoing a higher rate of discharge. This result contradicts most conventional thinking on lithium ion batteries, and proves to show the importance of thermal management when designing tests to understand the performance and behaviour of lithium ion batteries.

4 Thermal Properties of Cells

4.1 Introduction

Understanding the thermal properties of cells is important for many reasons when working on lithium-ion batteries. In order to design a good thermal management system, it is important to understand both the heat capacity of cells and how heat will flow through the cells. Even a small miscalculation in the thermal properties could lead to the temperature of the cells being significantly different to what is expected, leading to poor performance and increased levels of degradation.

Additionally, when modelling cells it is important to couple electrochemical models to thermal models. The electrochemical performance of cells is highly dependent on temperature, and therefore a poorly parameterised thermal model can lead to large discrepancies between modelling results and real-world testing data.

4.2 Research Questions

- Is there a simple method to measure the thermal properties of cells?
- How can the thermal properties of the different components of cells be measured, namely the active material and the casing?

4.3 Literature

4.3.1 Measurement techniques

A number of studies report the measurement of the thermal properties of cells. Maleki et al. [151] conducted a comprehensive study to measure the heat capacity, thermal diffusivity and thermal conductivity of Sony 18650 cylindrical cells using a xenon flash technique and by applying a constant heat flux to certain surfaces. A number of other

studies have used the same technique to measure the thermal properties of lithium-ion cells [152–154]. Barsoukov et al. [155], Forgez et al. [156], Schmidt et al. [157] and Fleckenstein et al. [158], all used a technique dubbed electrothermal impedance spectroscopy to measure the thermal properties of 18650 cells. Chen et al. [147] conducted a detailed study looking at the structure and thermal properties of prismatic cells, and Awarke et al. [159] explored the thermal behaviour of a module of cells in real-world operating conditions. Vertiz et al. [160] measured the thermal conductivity in the z direction (through the layers) using a guarded hot plate procedure. Drake et al. [161] measured the thermal conductivity and heat capacity of cylindrical cells using a method employing heating individual surfaces of a cell and then matching the results to a model. Koo et al. [154], Drake et al. [162] and Gholami et al. [163] used a transient plane source technique to measure the thermal properties of lithium-ion batteries and their components.

Many studies, most of them related to thermal modelling, simply take literature values for the thermal properties of the components of cells and combine these to produce a lumped thermal model of a cell, often taking data from old papers and paying little attention to how the make-up of the cells under examination differs to the cited literature. This trend was reported in a review paper by Bandhauer et al. [4]. Whilst this will provide a rough estimate of the thermal properties, it has been shown in previous studies that cells of similar chemistries and construction fabricated by different manufacturers can have significantly different thermal properties [131]. This underlines the importance of determining the thermal properties of cells being studied in order to accurately understand and predict their behaviour.

4.3.2 Thermal impedance spectroscopy

A method that has been widely used is thermal impedance spectroscopy, first developed by Barsoukov et al. [155], and then explored in greater detail by Forgez et al. [156], Schmidt et al. [157] and Fleckenstein et al. [158]. The approach initially developed by Barsoukov involved wrapping an external heating coil around a variety of 18650 cells and applying alternating currents of different frequencies to the coil in order to heat the cell. A thermal equivalent circuit model composed of electrical components was then devised, and the thermal impedance spectra fitted to this model in order to extract parameters for thermal resistances and capacitances. This technique shows promise, however is only applicable to cylindrical cells. In addition, the authors attribute a relatively high thermal conductivity perpendicular to the electrode to the high thermal conductivity in the circumferential direction leading to increased rates of heat conduction to outside of the cell. If this effect is real, the effective thermal conductivity in the radial direction will vary due to the differing circumferences of the coils.

Forgez et al. [156] and Schmidt et al. [157] developed the thermal impedance spectroscopy technique further by applying a sinusoidal current to the cell to introduce internal heat generation. However, in both of these studies homogenous heat generation is assumed throughout the cell. The cells in both studies are cooled via convection, and therefore temperature gradients will be present in the cell. Due to the highly dependent behaviour of cell impedance with temperature, the resistance of different areas of the cell will be significantly different leading to unequal current flow, and therefore unequal heat generation. This effect was not considered by either of these studies, and will have

major implications on the accuracy of the results, which should therefore be treated with some scepticism.

4.3.3 Xenon (or laser) flash technique

Another technique that has been used in numerous studies to determine the thermal properties of lithium ion batteries is the xenon flash technique. The approach has been used by Maleki et al. in numerous studies to measure the thermal diffusivity of lithium-ion cells [151–153]. Xenon flash is a recognised technique used to measure the thermal diffusivity of materials. One surface of a sample is subjected to a short pulse of radiation from a xenon lamp, and the time taken for the temperature to rise on the opposite surface can be used in conjunction with the sample thickness to measure the thermal diffusivity by solving the unsteady one-dimensional heat conduction equation.

4.3.4 Transient plane source

Transient plane source is a technique whereby two circular samples are placed around a sensor. The sensor consists of a spiral etched from a metal foil. A current pulse is then passed through the spiral, providing heat to a sample. Care must be taken to ensure that the sample can be treated as a semi-infinite solid, negating the influence of the boundaries of the sample. By using the relationship between temperature and resistance in metals the spiral can also be used as a temperature sensor, allowing the thermal properties of the samples to be calculated from the temperature response [164]. Koo et al. [154] used this technique to measure the thermal conductivity of lithium-ion electrodes employing carbon nanotubes to increase the thermal conductivity of the cells. Drake et al. [162] used this method to measure the heat capacity of the cells under study, although no details on the experimental procedure used to do this were given.

4.3.5 Effect of casing material

Very few studies tried to understand how the casing material, and its thermal interaction with the active material of cells affects the thermal characteristics of full cells. Barsoukov et al. [131] explored this for a number of 18650 cells and found widely different results for cells fabricated by different manufacturers, attributing these differences to the construction of the cell and the thermal contact between the jelly roll and the cell casing. Whilst the thermal properties of the active materials are important, it is equally important to understand how heat flows throughout the whole of the cell, and that includes the cell casing and the interface between the cell and the casing. Chen et al. [147] conducted a study where the contact layer between the active material and the cell casing was increased, and found that it did not lead to a significant increase in the thermal resistance of the cell, however the additional electrolyte used in this contact layer increased the heat capacity of the cell, therefore changing its thermal properties. In this study, increasing the contact layer thickness actually reduced the measured temperatures under natural convection conditions, whereas the temperature increased if the cell was subjected to forced convection. This study did not try to measure the thermal properties of the contact layer; it simply compared how the temperature of cells was affected under discharge if the thickness was changed. Zhang et al, [165] extracted a parameter relating to the heat transfer between the core and the casing. The reliability of this result must be questioned – calculations were done however when these did not match up to their experimental results, an empirical method was used in order to obtain this parameter.

It is difficult to measure the effect of the casing and the interface between the casing and the active material in a cell, as it is not possible to measure the temperature and the heat flux at that interface without inserting extra components into the cell. Inserting thermocouples or heat flux sensors into this area of the cell will affect the thermal properties, and therefore is not a technique that can be relied upon.

4.3.6 Specific heat capacity

There have been many studies looking into measuring the specific heat capacity of cells, and the effect of state of charge on heat capacity [160,165–168]. Most of these studies use a calorimeter to measure the heat capacity, which is a well-established method for measuring the heat capacity of any sample. In addition, it has been shown that other methods can be used to measure the heat capacity, some examples being Zhang et al [169], who used a transient plane source method to measure the heat capacity, and Murashko et al [166], who use heat flux measurements. Measuring heat capacity has been explored widely, not just in lithium-ion battery literature but in many other applications, and therefore this will not be explored further in this thesis.

4.3.7 Summary

Whilst there is a lot of literature related to thermal modelling of lithium ion batteries, many papers take a simplistic approach and simply use literature values in order to develop a thermal model. These literature values are often taken from old papers, since when battery technology has changed significantly, and therefore there must be some doubt as to whether these values are accurate for modern batteries. Further to this, very little work has been done looking at how the different components of cells interact with

each other, for example looking at the thermal barrier that the casing of a cell provides between the active material and the immediate environment of the cell.

4.4 Experimental

In this study, cells of differing thicknesses were procured from Kokam Inc. The cells are of the same form factor, however have different numbers of layers of active material, therefore leading to different capacities. By studying the thermal properties of the differently sized cells, it was proposed that it would be possible to discern the thermal properties of the individual components and their interactions with each other.

The cells and their properties given by the manufacturer can be seen in Table 4.

Serial Number	Capacity (Ah)	No. of cell layers	Thickness (mm)	Length (mm)	Width (mm)	Mass (g)
SLPB8043140H5	3.2	64	8.2	143	43.5	93
SLPB8643140H5	3.6	72	8.8	143	43.5	100
SLPB9543140H5	4.0	80	9.7	143	43.5	114
SLPB10843140H5	4.5	90	11.0	143	43.5	125
SLPB11543140H5	5.0	100	11.7	143	43.5	132

Table 4 - Properties of Kokam cells given by the manufacturer [170]

4.4.1 Cell disassembly

The first thing that was done in order to understand the thermal properties was to disassemble the cells to see how they were constructed. A fresh cell was discharged to 2V and then taken apart in a fume cupboard using a non-conducting ceramic scalpel. Images of a cell during disassembly can be seen in Figure 26 to Figure 30.

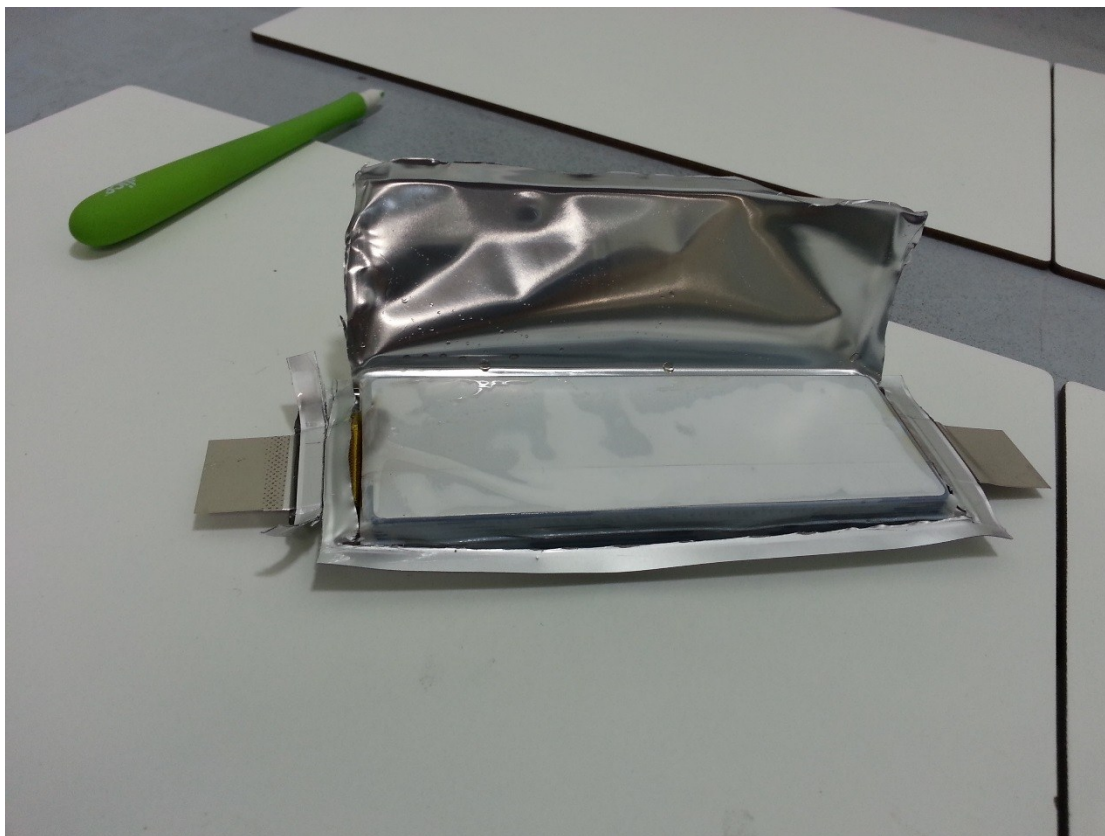


Figure 26 - Kokam cell with pouch material slit open



Figure 27 – Cell with pouch material removed

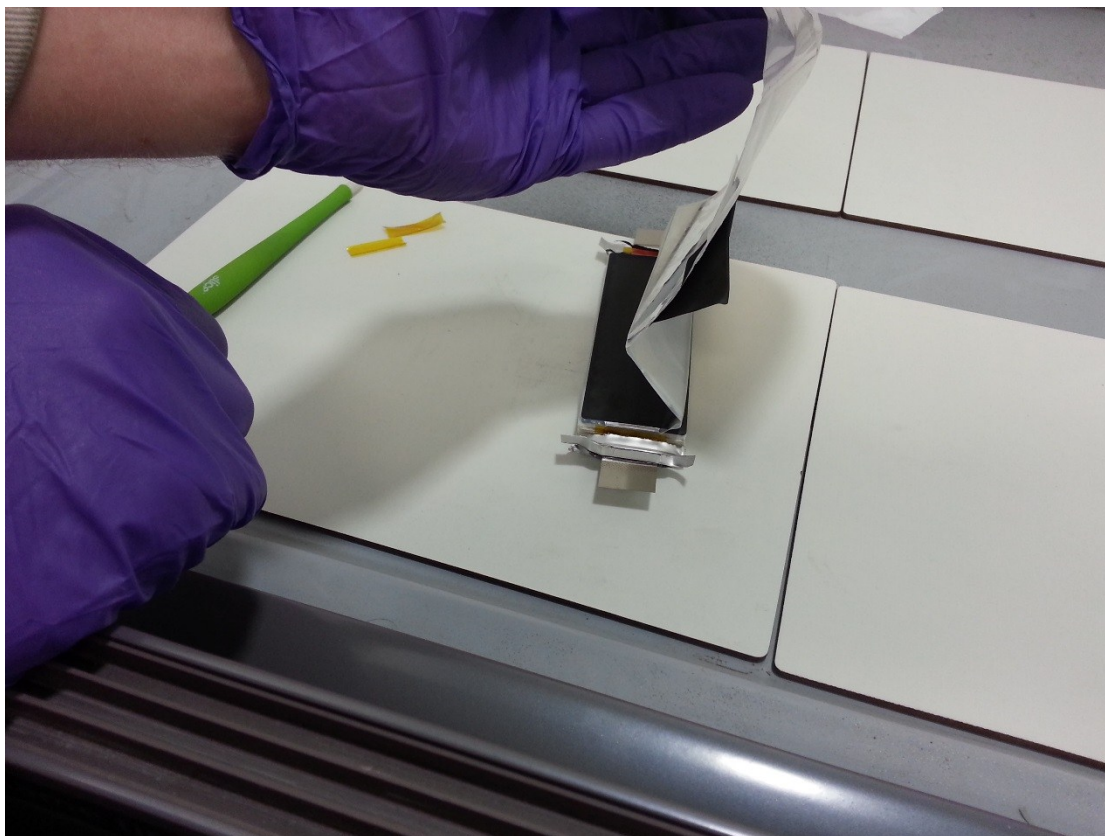


Figure 28 - Layers expanded, showing the concertinaed construction of the cell

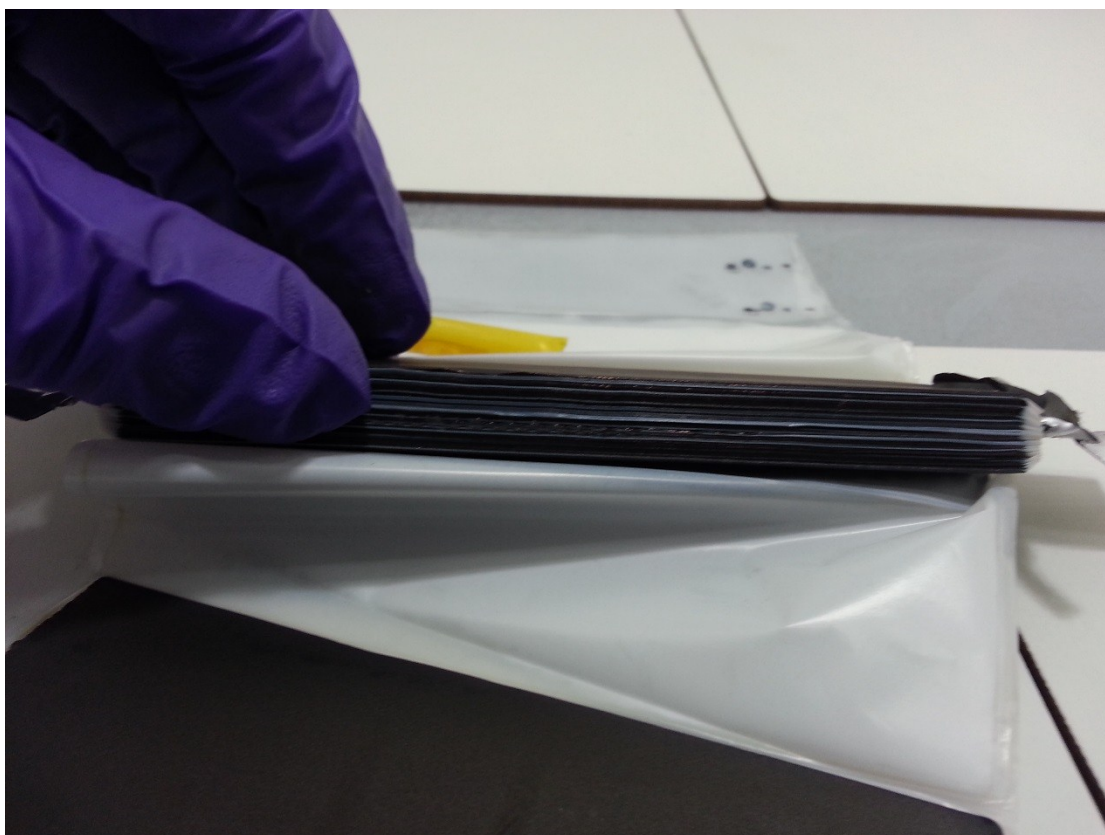


Figure 29 - Cell from the side, showing the stacking of the layers



Figure 30 - All layers of the cell

Figure 26 to Figure 30 show that the cells are constructed from alternating layers of anodes and cathodes, separated by a continuous concertinaed separator membrane. The current collectors are coated on both sides by electrode material, apart from the first and last collectors, which are coated only on the side facing inwards. The current collector for the anode is copper, and the current collector for the cathode is aluminium. Extra separator is wrapped around the stack of individual layers, adding three additional layers of separator to the stack.

The thickness of each layer was measured using a calibrated Mitutoyo 293-832 outside micrometer. These are shown in Table 5.

Component	Thickness [μm]
Copper foil	21
Aluminium foil	21
Separator	24
Anode	38
Cathode	29
Casing	160

Table 5 - Thickness of each layer

4.4.2 Thickness and mass

When the cells are delivered, they arrive with a variety of stickers on the surfaces, which both increase the thicknesses of the cells and will act as a thermal barrier. During all testing these stickers were removed, and therefore the thicknesses and masses of the cells were measured in order to ensure accuracy. Three cells were measured in order to reduce the influence of manufacturing differences. The thicknesses were measured using a pair of calibrated electronic calipers (Mitutoyo 293–832) in three places on the cell, and then a mean of these values were taken. The masses were measured using a set of Acculab L-series scales. The parameters varied slightly to those given by the manufacturer, and these can be seen in Table 6 and Table 5.

Capacity (Ah)	Cell 1			Cell 2			Cell 3			Mean Thickness (mm)
	T1	T2	T1	T1	T2	T1	T1	T2	T1	
3.2	7.49	7.49	7.48	7.47	7.49	7.49	7.50	7.48	7.48	7.49
3.6	8.35	8.37	8.36	8.37	8.37	8.35	8.35	8.37	8.35	8.36
4.0	9.23	9.23	9.23	9.24	9.24	9.22	9.22	9.23	9.23	9.23
4.5	10.31	10.31	10.33	10.32	10.33	10.33	10.31	10.32	10.32	10.32
5.0	11.41	11.39	11.41	11.40	11.41	11.39	11.41	11.39	11.40	11.40

Table 6 - Thickness measurements of different Kokam cells

Capacity (Ah)	Cell 1	Cell 2	Cell 2	Mean Mass (g)
	Mass	Mass	Mass	
3.2	86.53	86.36	86.52	86.47
3.6	98.40	98.36	98.36	98.37
4.0	106.65	106.51	106.67	106.61
4.5	120.77	120.88	120.74	120.80
5.0	132.67	132.66	132.71	132.68

Table 7 - Masses of different Kokam cells

Figure 31 shows the measured with of the cells plotted against the capacity along with a line of best fit calculated using the *polyfit* function in Matlab, which employs a least squares regression technique to calculate the coefficients of the line. The coefficient of determination, or R^2 value for this fit is 0.9995.

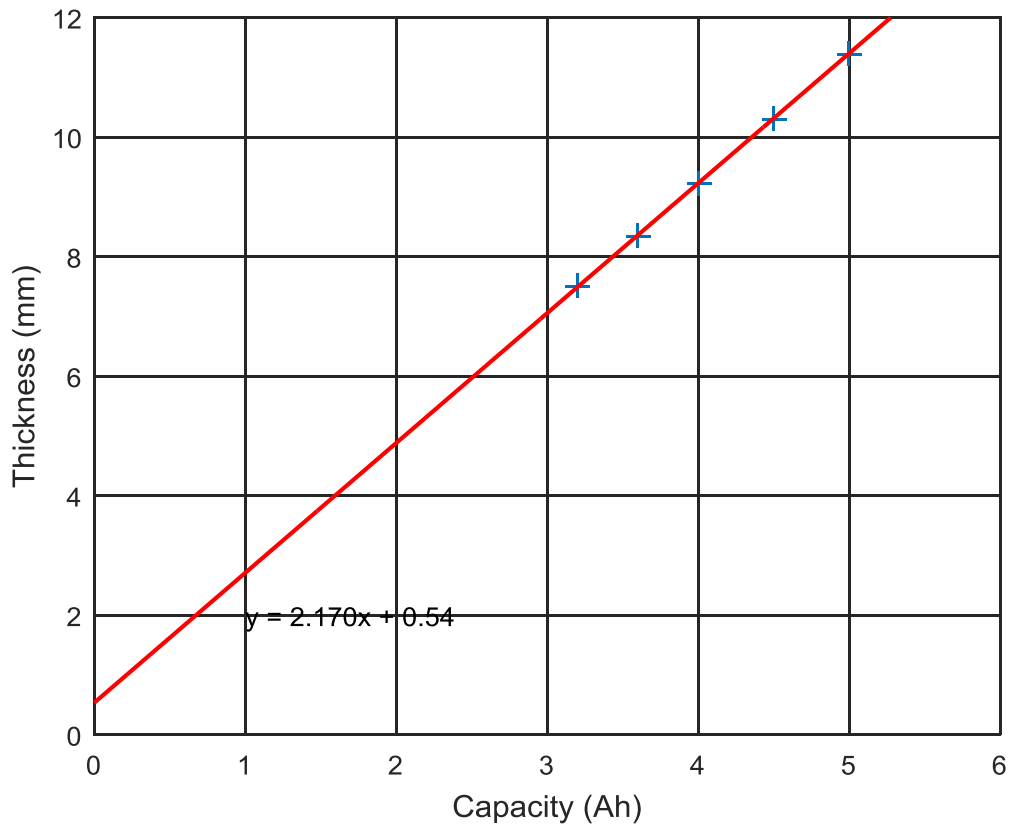


Figure 31 - Measured thickness of Kokam cells plotted against capacity

Figure 31 shows that there is a linear relationship between the thickness of the cells and the capacity, showing that the cells of different thickness have consistent construction, however this line of best fit does not intersect the origin. At $x=0$, which would represent a theoretical cell with a capacity of 0 Ah, the value of the thickness is 0.54 mm, indicating that the non-active material areas of the cell contribute 0.54 mm to the thickness.

Table 5, shows the thicknesses of the components of the cells. Each cell has two layers of pouch material, three layers of separator and one cathodic current collector in addition to the active material stack. The thickness of these component total 0.413 mm, which is slightly less than the 0.54 mm calculated from the least squares regression line shown in Figure 31.

It is well known that during operation, especially during the first few cycles, a small amount of gas is produced from side-reactions that occur. It is proposed, although cannot be proved, that it is this gas that contributes to the additional thickness that cannot be attributed to the measured components of the cell.

A similar process was carried out looking at the mass of the different cells, and the results are displayed in Figure 32. Again, a line of best fit was calculated using the same method as previously, this time giving a coefficient of determination, R^2 , of 0.9979.

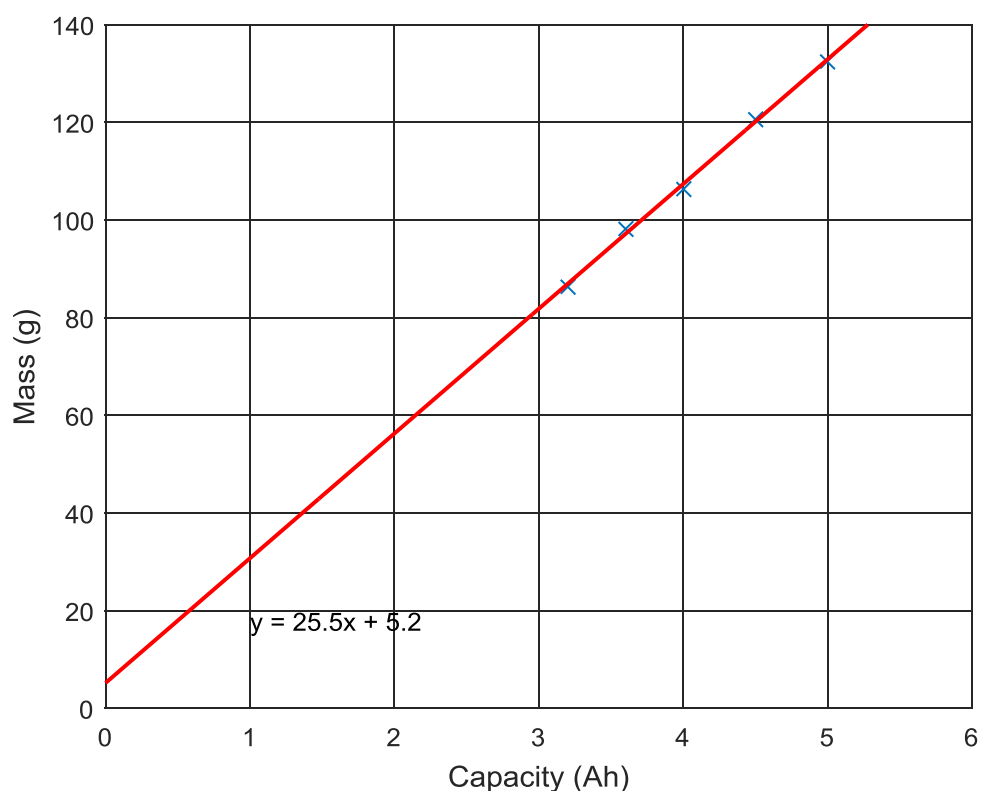


Figure 32 - Measured masses of Kokam cells plotted against capacity

Figure 32 shows a similar linear relationship to that seen for the thicknesses, which again adds to the evidence that the cells have a consistent construction. The line of best fit does not go through the origin, rather passes through $x=0$ Ah at 5.2 g, indicating that there is 5.2 g of excess mass for each cell that does not comprise any active material. The remaining components and their masses are shown in Table 3.

Component	Mass (g)
Positive tab	1.09
Negative tab	2.14
Pouch material	3.16
Excess separator	0.15
1 cathodic current collector	0.29
Total	6.83

Table 8 - Masses of additional components other than the active material of a cell

The measured mass in Table 3, 6.8 g, does not correspond completely to the 5.2 g calculated in Figure 32. The discrepancy, whilst small, is difficult to explain, but could be attributed to the amount of electrolyte used when filling the cell; in general cells are filled

with a small amount of excess electrolyte, and it is likely that larger cells need less excess electrolyte proportionally to their capacity than smaller cells.

4.4.3 Cell Construction

The disassembly of the cells, shown in Figure 26 to Figure 30 show that the cells have a complex construction and it is not possible to treat them as a homogenous mass, however it is possible to break the cell into a number of different components.

The stack of layers that constitutes the active material is the first component that can be treated as a homogenous mass. Although the layers are stacked between a concerted separator, and therefore the separator will act to increase the thermal conductivity from one layer to another, the separator is very thin and has a low thermal conductivity, therefore making this effect negligible.

The current collectors are electrically and therefore thermally connected at the ends of the cell where they protrude from the stack of active material and connect to the cell tabs. This connection provides a thermal “short circuit” at the end of each layer, and will therefore alter the overall thermal conductivity of the cell.

The cell casing or pouch material encases the active material. The pouch material is constructed from two sheets that are heat sealed along the edges of the cell. Where the cell tabs protrude from the cell, there is a layer of polymer between the cell tabs and the cell casing that acts as electrical insulation to ensure that the pouch material does not short circuit the cell.

4.4.4 Methodology

In order to measure the thermal conductivity of the cells, an approach based on Searle's bar technique was proposed.

Searle's bar method employs a principle that if two reservoirs at different temperatures are thermally connected by a good conductor of heat, after a period of time a steady state condition will be reached where the temperature profile along the conductor is not changing and linear. A schematic of this idea can be seen in Figure 33.

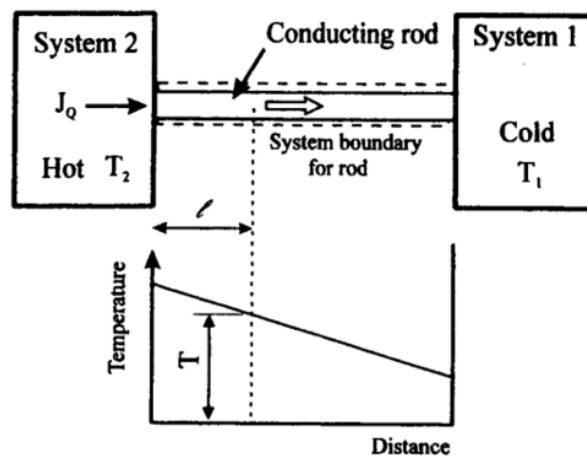


Figure 33 - Diagram showing basis of Searle's bar technique, adapted from [171]

Two test rigs were designed to measure the thermal conductivities of the cells. One test rig measures the thermal conductivity of the cell between the cell tabs, and the other measures the thermal conductivity between the two large faces of the cell. Schematics of the test rigs can be seen in Figure 34 and Figure 35.

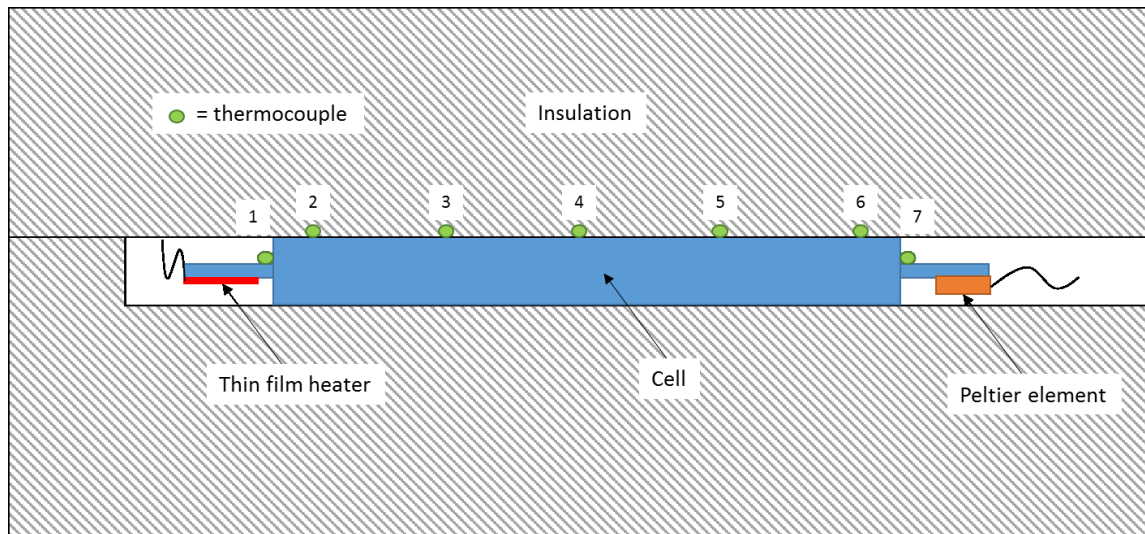


Figure 34 - Schematic of test rig to measure thermal conductivity along the length of the cells

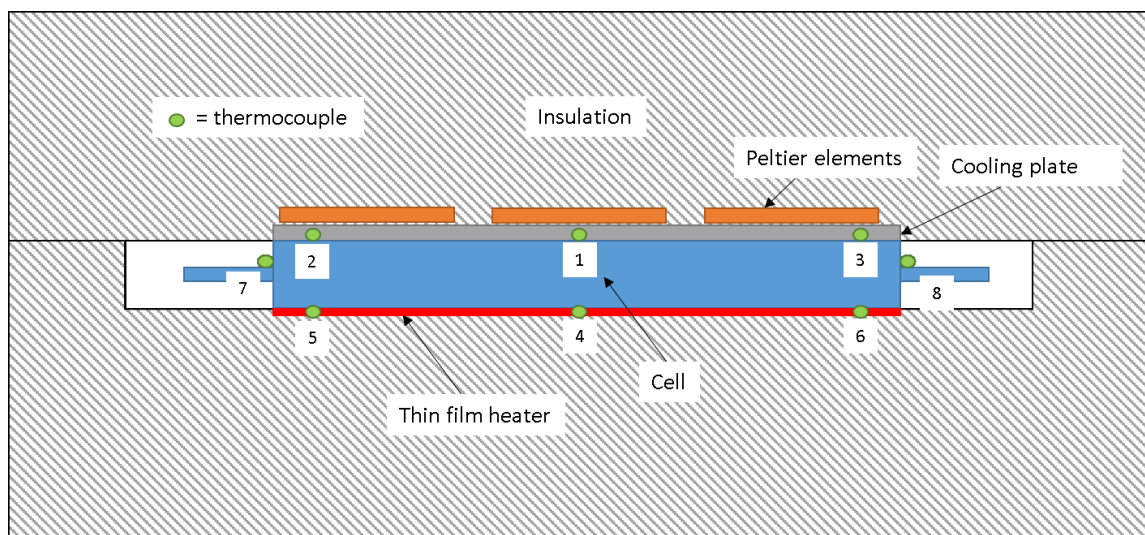


Figure 35 - Schematic of test rig to measure thermal conductivity through the thickness of the cells

Each peltier element was connected to a power supply, which in turn is controlled by a custom built Labview (NI) script, which employs PID control to maintain the temperature at a certain value. The thin film heaters were connected to a calibrated power supply, which supplied a controlled amount of power to each heater. The insulation was 100 mm thick expanded polyurethane foam with a thermal conductivity of 0.025 W/mK [172].

One side of the cell is heated using a thin film heater, and the other side of the cell is cooled down using peltier elements. The temperature at both ends is controlled, and the heat flux required to produce this temperature difference is measured.

A “thermal resistance” can be calculated by dividing the temperature difference by the power required to produce that temperature difference, and once the thermal resistances of all the components of the cell have been calculated, the thermal conductivity can be calculated using Equation (29).

$$\dot{Q}_{cell} = -kA \frac{\Delta T_{cell}}{L} \quad (29)$$

The thermal conductivity was measured at an ambient temperature of 20°C. In order to increase the accuracy of the results, multiple measurements were taken by varying the temperature difference applied to the cell. The temperature differences applied to the cell were 5, 10, 15 and 20°C. These results were then plotted, allowing an extrapolation to a zero temperature difference in order to negate the effect of any heat loss that might occur during testing. Whilst thermal conductivities vary with the rate of heat flux and temperature, the variation here is small and therefore it can be assumed that these are constant.

An example of the trace of temperatures taken for tests along the length of the cell can be seen in Figure 44. It can be seen that the measurements were left for long enough to ensure that steady state was reached. To smooth the noise in the thermocouple and power readings, once the temperature and power measurements had reached steady state, an average of the next 100 measurements were taken and this value used to calculate the thermal conductivity.

4.5 Test rig calibration

The test rigs were calibrated on a number of materials with known thermal properties in order to validate the method used and the accuracy of the test rigs. A number of samples of different materials were machined to a thickness of 5mm and 10mm and of the same dimensions as the active material part of the cells (115 mm x 45 mm). For the measurement along the length of the 'cell', a 50 mm excess was left at either end to place the heater and the peltier cooler. A diagram of the set-up for measurements along the length of a cell is shown in Figure 36.

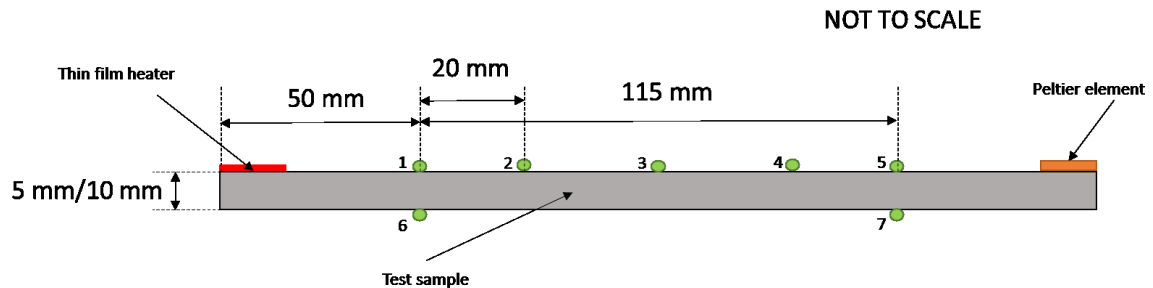


Figure 36 - Thermal properties test rig calibration test piece

The values of the thermocouples labelled 6 and 7 were compared with the thermocouples labelled 1 and 5 respectively in order to check that a 1D heat flow had developed at the point where the measurement was taken.

The materials to be tested, along with their thermal conductivities taken from literature are shown in Table 9.

Material	Grade	Thermal Conductivity (W/mK)
Stainless Steel	304	16.2 [173]
Nylon	6,6	0.28 [174]
Bronze	PB1	47.0 [175]

Table 9 - Calibration samples and their corresponding thermal conductivities

Due to its low thermal conductivity, Nylon is not suitable for testing in the lengthwise direction, and therefore was only tested in the rig for measuring conductivity through the cell, shown in Figure 35.

4.5.1 Calibration results

4.5.1.1 Through the thickness of the cell

Figure 37 shows the an example of the power required to produce a temperature difference in the case of 5mm Nylon through the thickness of the 'cell'.

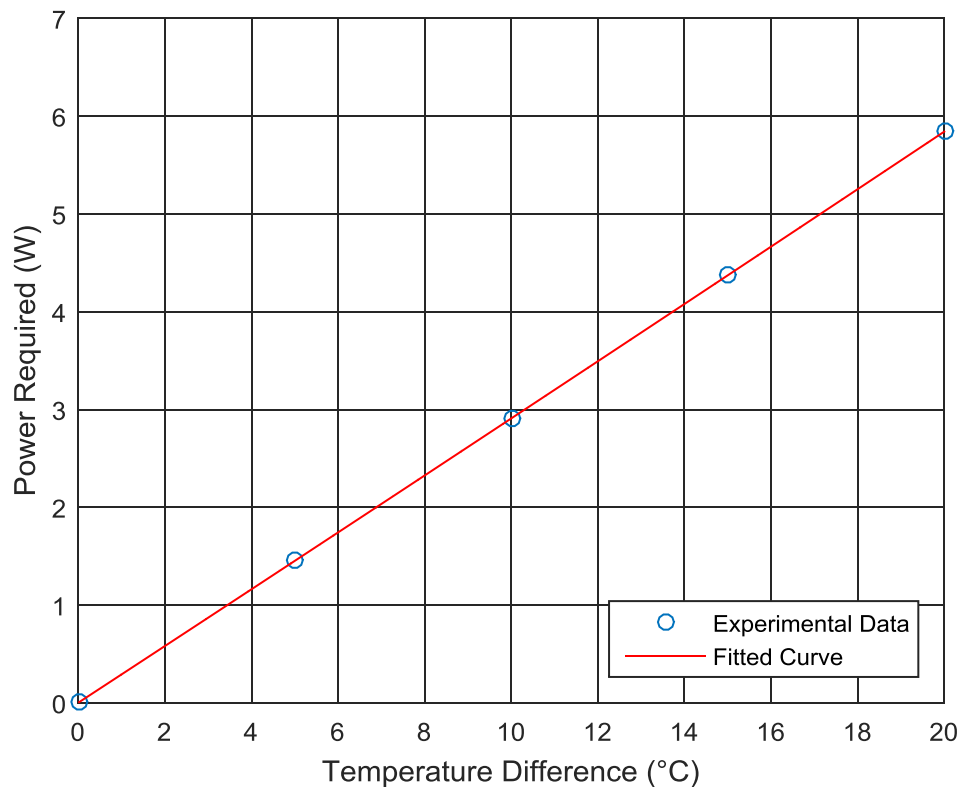


Figure 37 - Example of temperature difference and power for 5 mm Nylon through the thickness of the 'cell'

The data in Figure 37 shows a good linear fit with an r^2 value of 0.99999 when fitted using MATLAB's 'fit' function. This implies that there is minimal heat loss in the test rig, and therefore the results can be relied upon.

The thermal conductances and the corresponding thermal conductivities, along with the percentage error when compared to the literature values for the different test samples can be seen in Table 10.

Material	Thickness (mm)	Thermal Conductance (W/K)	Calculated Conductivity (W/mK)	Error (%)
Nylon	5	0.294	0.284	1.45
	10	0.146	0.282	0.76
Steel	5	17.12	16.54	2.11
	10	8.51	16.44	1.51
Bronze	5	49.50	47.83	1.76
	10	24.70	47.73	1.55

Table 10 - Thermal conductivities and error from quoted value for tests through the thickness of the 'cell'

The results show that the rig is capable of measuring the thermal conductivity of materials to an accuracy within 2.1%.

4.5.1.2 Along the length of the cell

Figure 38 shows an example of the power required to produce a temperature difference in the case of 5mm steel.

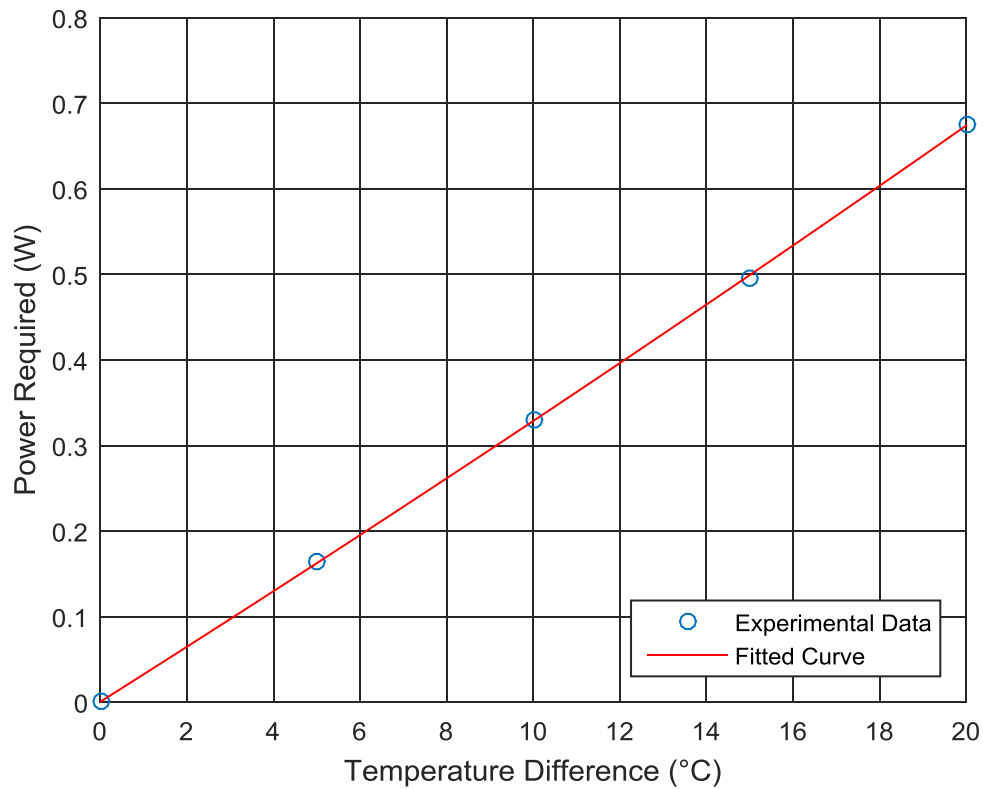


Figure 38 - Example of temperature difference and power for 5mm thick steel along the length of the 'cell'

Whilst the data shown in Figure 38 is close to linear, a better fit is achieved if the data are fitted to a quadratic equation. This can be explained by a small amount of heat loss occurring, leading to a slight increase in the power required to produce the temperature difference. In the case of 5mm steel, a linear fit using MATLAB's 'fit' function leads to an r^2 value of 0.9997, whereas a quadratic fit leads to an r^2 value of 0.99996. In order to negate the effect of the heat loss, the gradient at $x=0$, equating to a temperature gradient of 0, and therefore where there is no heat loss was taken. This leads to a thermal resistance, which can then be used to calculate the thermal conductivity using Equation (29).

The thermal conductances and the corresponding thermal conductivities, along with the percentage error when compared to the literature values for the different test samples can be seen in Table 11.

Material	Thickness (mm)	Thermal Conductance (W/K)	Calculated Conductivity (W/mK)	Error (%)
Steel	5	0.0325	16.59	2.38
	10	0.0645	16.48	1.75
Bronze	5	0.0935	47.79	1.68
	10	0.1860	47.53	1.13

Table 11 - Thermal conductivities and error from quoted value for tests along the length of the 'cell'

The results in Table 11 show that the rig is capable of measuring the thermal conductivity of materials to an accuracy within 2.4%.

4.6 Results

4.6.1 Through the thickness of the cell

When using the rig shown in Figure 35 to measure the thermal conductivity through the layers, the pouch material acts to short circuit the heat around the active material, therefore making it difficult to measure the thermal conductivity of the active material. In order to negate this, a cell of each size was disassembled in such a way as to leave the pouch material intact, apart from at the ends where the cell tabs are. A piece of insulating expanded polyurethane from of the same thickness as the active material stack was then inserted into the pouch material, and this assembly was tested using the rig shown in Figure 35. This allowed the thermal resistance of the pouch material to be measured.

The thermal resistance of intact cells of all sizes were also tested, and the combination of these results used to measure the thermal resistance of the active material. An example of the power required to produce a number of temperature differences for the full cell and the pouch material of a 5 Ah cell is shown in Figure 39.

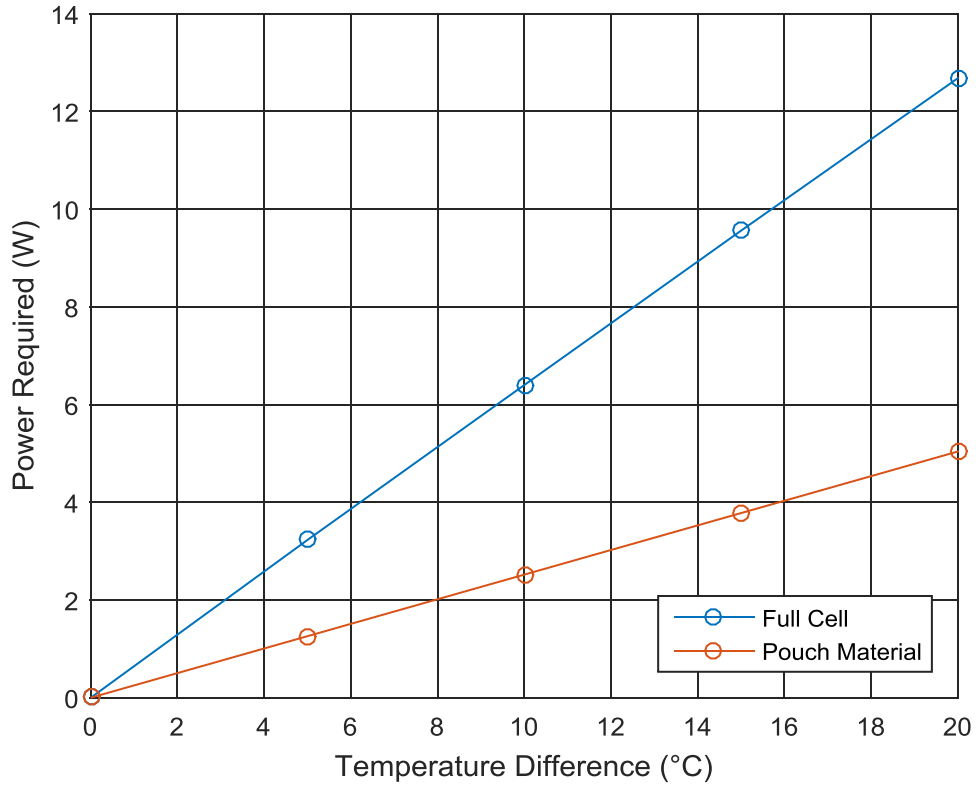


Figure 39 - Power required to produce temperature difference for full cell and for pouch material of 5Ah cell

Similar data to that shown in Figure 39 was collected for all sizes of cell. The thermal resistance of the different components was then calculated by taking the gradient of the line. The thermal resistance of the cell minus the pouch material was then calculated using the parallel resistor analogy shown in Equation (30).

$$R_{remainder} = \frac{1}{\frac{1}{R_{full\ cell}} + \frac{1}{R_{pouch}}} \quad (30)$$

The results from this analysis is shown in Table 12.

Capacity (Ah)	Thickness (mm)	Resistances (K/W)		
		Full Cell	Pouch Material	Remainder
3.2	7.49	1.04	2.53	1.76
3.6	8.36	1.15	2.85	1.93
4.0	9.23	1.27	3.15	2.12
4.5	10.32	1.40	3.37	2.40
5.0	11.40	1.59	3.97	2.64

Table 12 - Measured and calculated thermal resistances through the cells

The results from the remainder of the cell can then be plotted against cell capacity, which is shown in Figure 40.

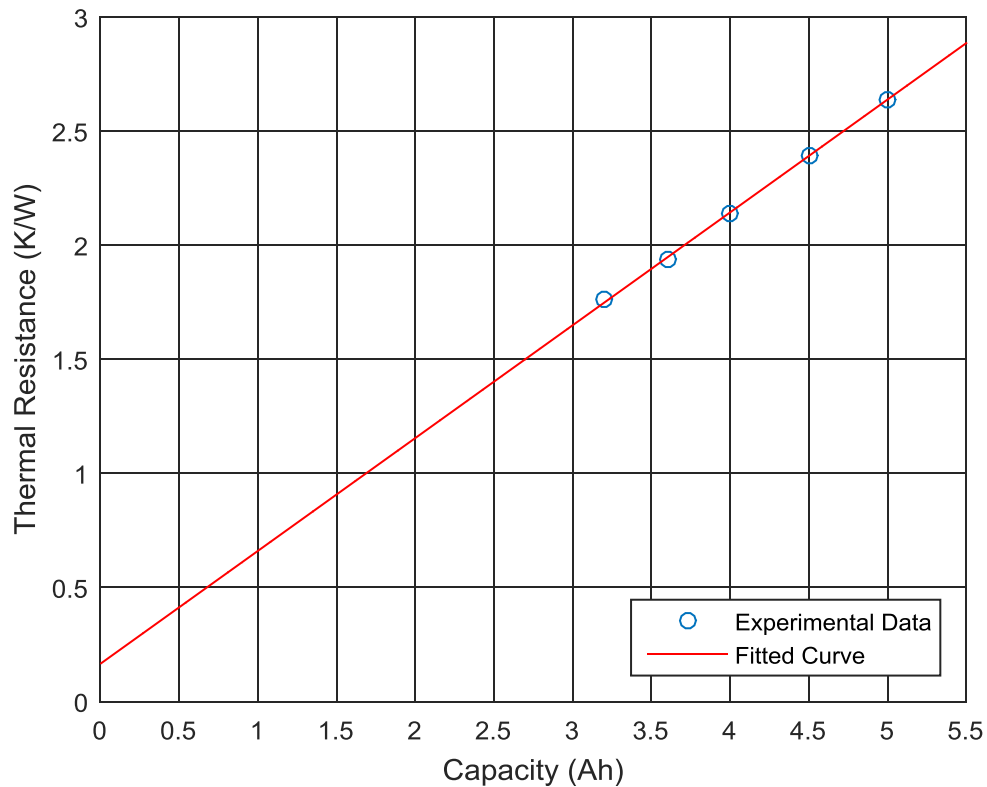


Figure 40 - Data and fit for the thermal resistances of the remainder of the cell

The results in Figure 40 show that there is a linear trend in the thermal resistance of the remainder of the cell. The line of best fit was calculated using the in-built 'fit' function in MATLAB. The gradient of the line is 0.495 K/W/Ah, and the intercept is 0.159 K/W. This means that for a cell with 'zero' capacity, the thermal resistance would have a value of 0.159 K/W. This value relates to the thermal resistance through the pouch material (but not down the sides), and the thermal resistances between the pouch material and the

stack of active material layers. This is a significant value, and equivalent to 9.0% of the thermal resistance of the active material stack for a 3.2 Ah cell, and 6.0% for a 5 Ah cell.

4.6.2 Along the length of the cell

Using the test rig shown in Figure 34, the cells of different sizes were tested at a number of temperature differences and the heat flux required to produce those temperature differences were measured. Figure 41 shows an example of the test data gathered for a 5Ah cell.

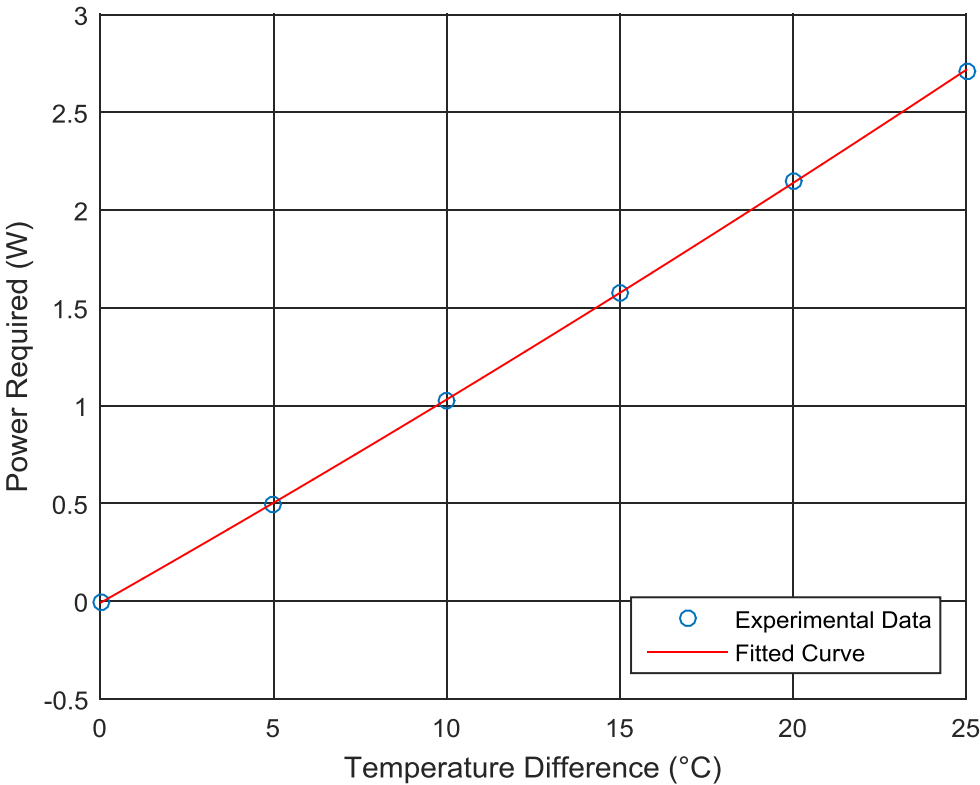


Figure 41 - Power required to produce temperature difference along the length of a 5Ah cell

The results for the different sized cells can be seen in Table 13.

Capacity (Ah)	Thickness (mm)	Thermal Resistance (K/W)
3.2	7.49	14.886
3.6	8.36	13.343
4.0	9.23	12.127
4.5	10.32	10.875
5.0	11.40	9.940

Table 13 - Measured thermal resistances along the length of the cells

The data from Table 13 is also displayed in graphical form in Figure 42.

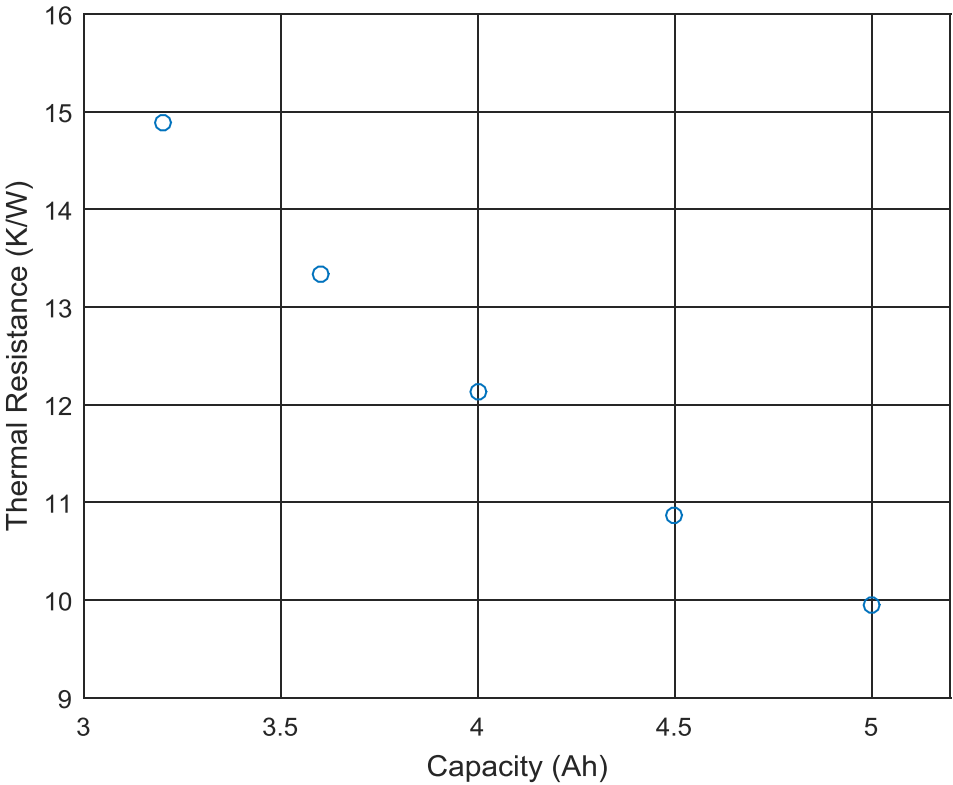


Figure 42 - Measured thermal resistances along the length of the cells

Due to the thermal resistance increasing as the cell capacity decreases, an alternative way to display the data are to look at the reciprocal of the resistance, or the conductance.

This is shown, along with a linear fit, in Figure 43.

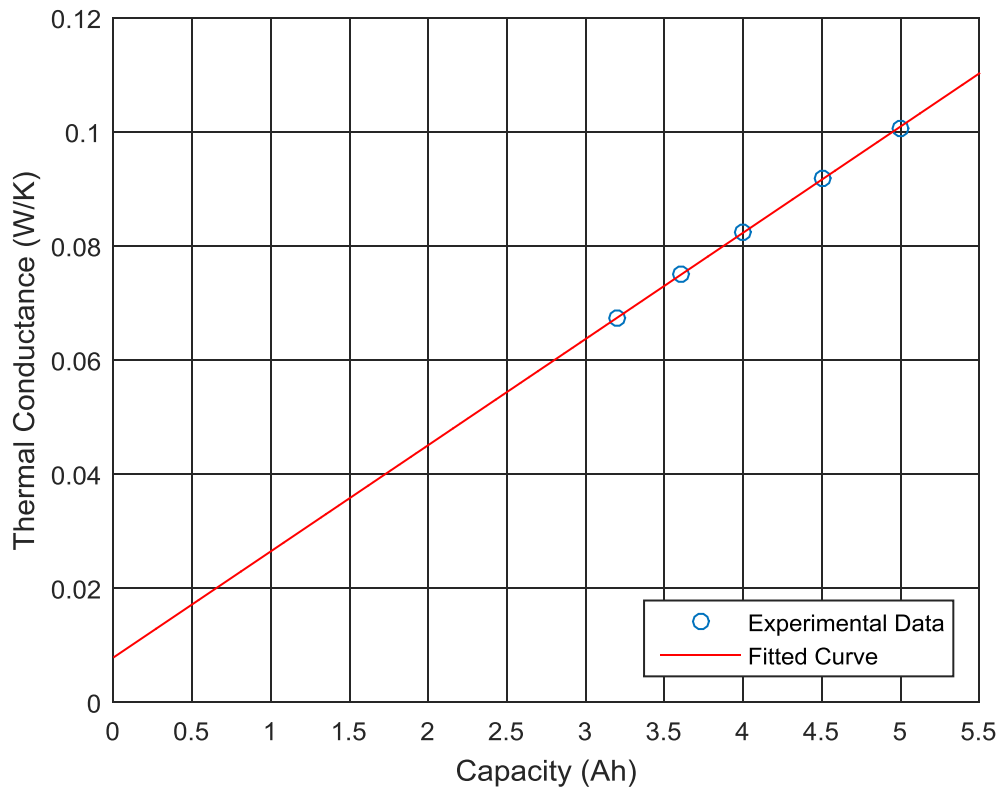


Figure 43 - Measured and fitted thermal conductances along the length of the cells

The results shown in Figure 43 show a good linear fit with an r^2 value of 0.9996, and a y-intercept of 0.00784 W/K, which corresponds to the thermal conductance of a cell with no layers. This is equivalent to an empty pouch with no active material. The gradient of the line is 0.0186 W/K/Ah, which corresponds to the thermal conductance of the combination of the active material and the connection of the cell tabs to the current collectors.

This result includes the thermal effect of the connection between the tabs and the current collectors. In order to understand this contribution, and therefore calculate the thermal conductivity of the active material of the cell, the values of the thermocouples placed along the length of the cell, numbered 2-6 in Figure 34 were examined. An example of a temperature trace for all of the relevant thermocouples can be seen in Figure 44, which is for a 5 Ah cell.

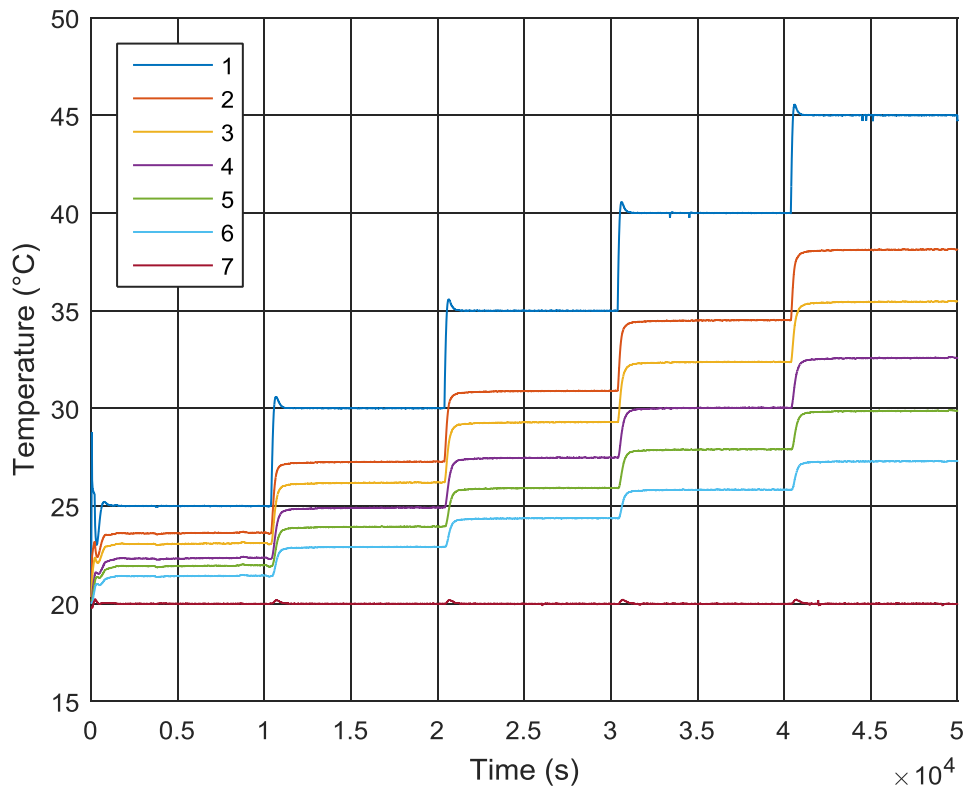


Figure 44 - Example of temperature traces during thermal conductivity measurement along the length of the cell

If the assumption is made that the temperature is homogenous through the thickness of the cell, it would be possible to calculate the thermal conductivity of the active material part of the cell from this data, however there is not enough information to ensure that this assumption is correct, and therefore calculating the thermal resistance of the different components through the cell is not possible from this data.

However, what can be found from this data are that the cell tabs and the connection between the cell tabs and the current collectors inside the cell contributes to a significant thermal resistance through the length of the cell. This can be seen from the differences between temperature measurements 1 & 2, and temperature measurements 6 & 7 in Figure 44. In addition to this, it can also be seen that the thermal resistance of the different cell tabs is slightly different, as the temperature difference between

temperature measurements 1 & 2 is smaller than the temperature difference between temperature measurements 6 & 7.

In order to truly understand the contributions of thermal conductivities of the different components of the cell, more tests must be done to investigate the thermal interface between the cell tabs and the current collectors. This would require the ability to ultrasonically weld some blank current collectors to a cell tab, which was not possible with the resources available.

4.7 Full cell properties

By combining the results of measuring the thickness of the cells and measuring the thermal conductivity, it is possible to understand the thermal properties of the different components of the cells and compare them to literature values often used in academic literature. In the case of the thermal conductivity through the layers, the thermal conductivity for the stack of layers of active material, not including the cell casing or the layer between the cell casing and the active material is 0.682 W/mK. This is calculated using the knowledge of how the thickness varies with capacity, how the thermal resistance varies with capacity, and the area of the active material layers. This is shown in Equation (31) to Equation (33).

$$Thickness = C_{Thickness} \times capacity + 0.54 \quad (31)$$

$$Thermal\ resistance = C_{conductivity} \times capacity + 0.159 \quad (32)$$

$$Thermal\ conductivity = \frac{C_{Thickness}}{C_{conductivity} \times Area} \quad (33)$$

where $C_{Thickness}$ is the gradient of the thickness vs capacity plot and $C_{conductivity}$ is the gradient of the thermal resistance vs capacity plot.

If the values for thermal conductivity of the different components in the cell are taken from Maleki et al [151], the thermal conductivity through the layers of the cell is 0.902 W/mK. This represents a 32.3% difference to the thermal conductivity calculated using the experimental setup. This difference is very large, and could lead to problems with the design of thermal management systems for battery packs in real-world applications, or the parameterisation of coupled electrochemical and thermal models.

4.8 Conclusion

A simple method was proposed to measure the thermal conductivity of different components of a cell. A method based on Searle's bar technique was devised and used to measure the thermal conductivity of cells in different directions. By testing cells of the same construction and form factor but with different numbers of layers it was possible to isolate the thermal conductivities of different components of a cell in the z-direction (through the layers of the cell), and calculate a value for thermal conductivity for the cell pouch, the active material and the interaction between the cell pouch and the active material. The measured value for thermal conductivity of the active material was 32.3% different when compared to often quoted literature values, showing how important it is to accurately measure thermal products when designing battery cooling systems or parameterising thermally coupled battery models.

It was not possible to measure the thermal conductivity of the different components of a cell along its length due to the uncertainty over the thermal resistance of the interface between the cell tabs and the foil current collectors, however if the resources were available it would be possible to measure these thermal resistances, subtract these from the full cell results and then calculate the thermal conductivity of the different components along the length of a cell.

5 The effect of temperature gradients during the performance of lithium ion batteries

5.1 Introduction

During operation, especially if a thermal management system is in operation, temperature gradients will form in lithium-ion cells, with the edges at a cooler temperature than the core of the cells. Many studies, both theoretical and experimental, have shown that the formation of temperature gradients is unavoidable, however the effect of these temperature gradients has not been examined in detail [63,176,177].

Robinson et al. [63] used a combination of x-ray tomography, thermal imaging and EIS to show how temperature gradients naturally form in 18650 cells due to the asymmetrical nature of the cells and the presence of a positive temperature coefficient safety device and a safety valve that add a small resistance, and therefore a heat source at one of the terminals. Their work showed a temperature difference of nearly 10°C along the length of the cell when subjected to a discharge rate of 2C.

Fleckenstein et al. [176] showed that cells at different temperatures have different impedances, and when they are connected in parallel they will provide different currents during charge and discharge, leading to unequal SOC. They extrapolated this result using a thermally-coupled equivalent circuit network model to show that a cell under a temperature gradient will behave in a similar way; if areas of a single cell are thought of as individual cells in parallel with each other, these different areas will provide different amounts of current during charge and discharge with the hotter areas providing more current. Due to this, the hotter areas of the cell have a larger amount of heat generation,

and therefore the temperature gradients produced are higher than if homogenous behaviour is assumed in all areas of the cell.

Troxler et al. [12] followed on from this work to analyse a cell under imposed temperature gradients. Their work showed that a temperature gradient has an effect on the static, complex impedance response of a cell when tested using EIS, such that the cell behaves as if it is hotter than its mean temperature. They included a simple parallel cell model employing the well-known Arrhenius relationship of temperature and resistance to accurately predict the charge-transfer resistance of a cell under a variety of imposed temperature gradients. Whilst this work demonstrates that temperature gradients must be accounted for; it is not possible to simply take the effective mean temperature of the cell, it does not address how a temperature gradient affects the performance of a cell whilst under load.

Klein et al. [178] described the performance of cells held under temperature gradients, using the edges of the cell as the heat conduction surfaces. Whilst their work provides an insight into the performance of cells under load whilst being held under a temperature gradient, noisy drive cycles were used to collect the data, and therefore the data collected from the study were limited to understanding only the ohmic and bulk resistances of the cells, and then using these to estimate the power capability of the cells.

Wu et al. [144] explored how unequal current paths and interconnect resistances leads to unequal current flow and heat generation on a pack scale. They show that unequal interconnect resistances and current paths can lead to significant differences in the current provided by cells connected in parallel in large scale battery packs. This work focused on understanding how the design of a battery pack, especially in respect to how

current flows through a packs, is important to ensure that batteries connected in parallel behave homogeneously.

Some designs of cells, especially pouch cells with separate anodes and cathodes between a concertinaed separator such as the deconstructed cell seen in Figure 26 to Figure 30, can be thought of as a battery pack with many cells in parallel. This section will focus on the behaviour and performance of these types of cells when their temperature is inhomogeneous, as will be the case in normal operation when a thermal management system is applied to the cells in order to prevent them from overheating.

5.2 Research Questions

This chapter will attempt to answer the following research questions.

- Does the conclusion by Troxler et al. [12], that a cell under a temperature gradient behaves as a hotter cell remain correct when a cell is under load?
- How are other performance parameters, such as useable capacity and power delivery, affected by temperature gradients?
- How does the operation of the lithium-ion battery change when under a temperature gradient?

5.3 Experimental

The test rig used by Troxler et al. was modified in order to connect a Biologic HCP-1005 high current potentiostat to the cell. The remainder of the test rig and control system remained as described in [12]. A schematic of the test setup can be seen in Figure 45.

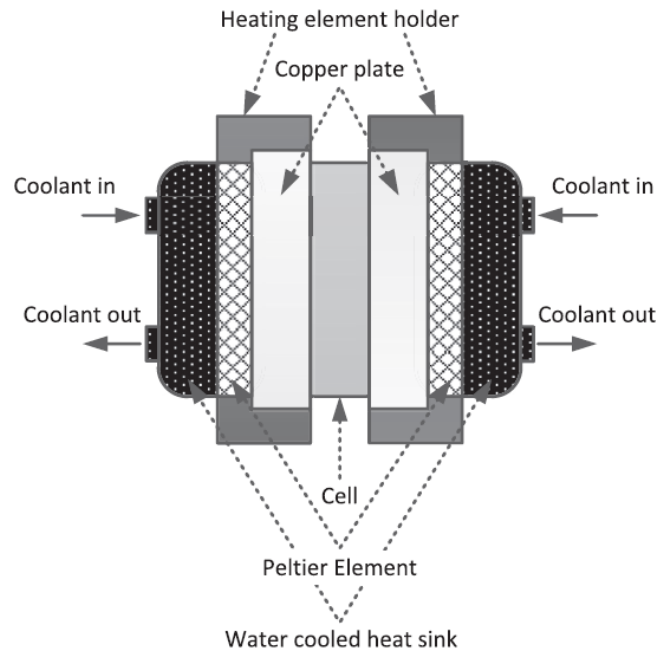


Figure 45 - Schematic of temperature gradient test rig. Taken from Troxler et al [12].

A fresh 5 Ah Kokam pouch cell (model number SLPB11543140H5), with a graphite anode and an NMC cathode was tested at different temperature gradients and currents. The cells were tested around an average of 20°C, with the temperatures profiles that were applied to the cell shown in Table 14. The cells were tested at 4 different rates; 1 A, 2 A, 4 A and 8 A.

T1 (°C)	T2 (°C)
-10	50
0	40
10	30
20	20

Table 14 - showing temperatures of each side of the cell during testing

During discharge, EIS measurements were taken at every 10% SOC interval defined by the nominal capacity of the cell, or after every 0.5 Ah of discharge. EIS was taken between 1 kHz and 1 Hz whilst the discharge continued using 200 mA amplitude sine waves. As the EIS measurements were taken whilst the discharge continued, it was important to minimise the time taken to conduct the EIS sweep to ensure that each measurement was

taken as close to a single SOC as possible. The parameters were optimised so that the EIS spectra took 35s, meaning that even at the fastest discharge rate of 8A, this only accounted for a 0.48% change in SOC from the beginning to the end of the EIS measurement.

5.4 Results and discussion

5.4.1 Electrochemical Impedance Spectroscopy

As discussed in section 5.3, EIS measurements were taken at 10% SOC intervals during the tests. An example of some spectra can be seen in Figure 46, which shows data taken at a 1 A discharge rate, 40% SOC, and at different temperature gradients.

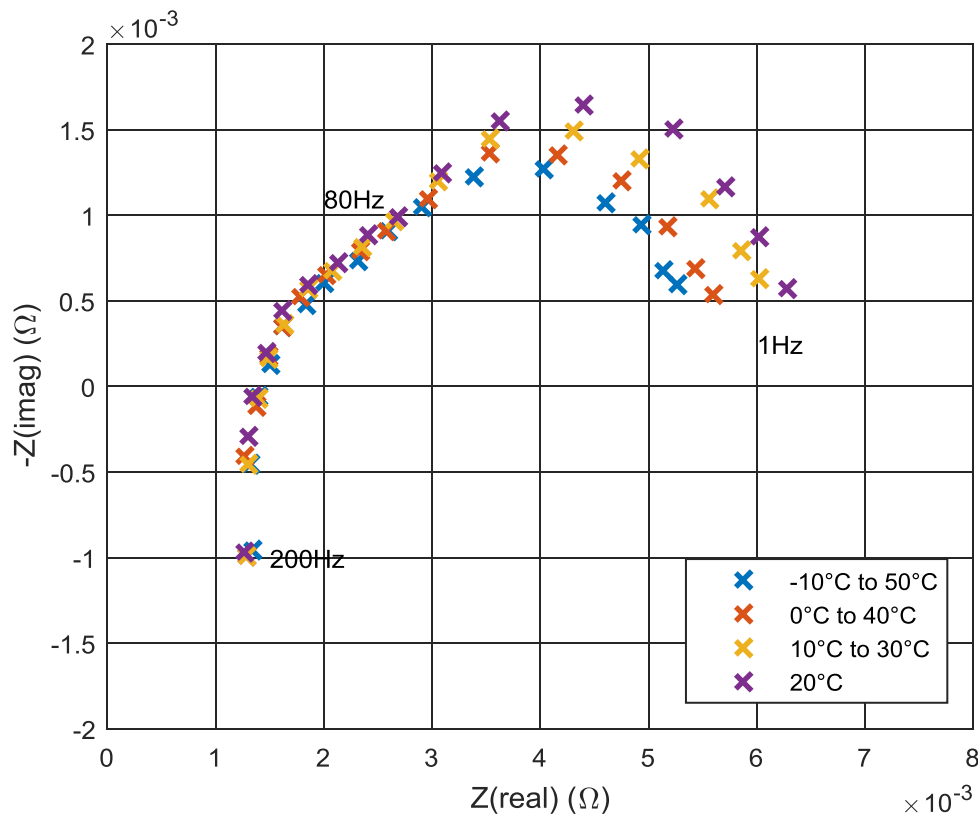


Figure 46 - EIS spectra taken at 1A, 40% SOC and at different temperature gradients but the same average temperature

As can be seen in Figure 46, the area of the spectrum that is affected the most by temperature gradients is the lower-frequency depressed semi-circle relating to R_2 and CPE_2 . This depressed semi-circle relates to the charge-transfer resistance (refer to Section 3.3.4), and in the plot shown in Figure 46, it is clear that as the temperature gradient increases, the size of this semi-circle decreases, indicating that the charge-transfer resistance decreases as a larger temperature gradient is imposed upon the cell.

In order to quantify the results, and to assess how the charge transfer is affected at different currents and SOC, each EIS spectra was fitted to the equivalent circuit shown in Figure 14 using Zview software (Scriber and Associates Inc.), which employed a Levenberge-Marquardt complex non-linear least-squares fitting algorithm.

Plots of R_3 at different temperature gradients and for different currents can be seen in Figure 47 to Figure 50. The EIS measurements taken at 10% SOC were very noisy and it proved impossible to obtain a reliable fit using Zview, and therefore have been omitted. It is thought that the results at 10% SOC were unreliable due to the voltage of the cell changing rapidly at the end of discharge.

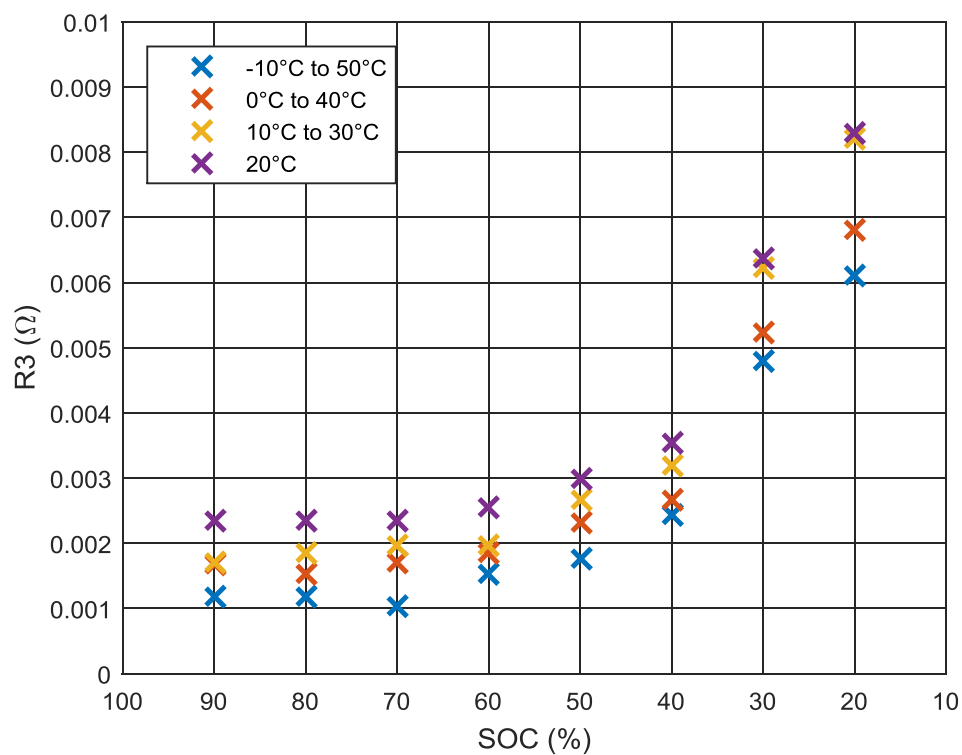


Figure 47 - EIS results for cell tested under different temperature gradients at 1 A

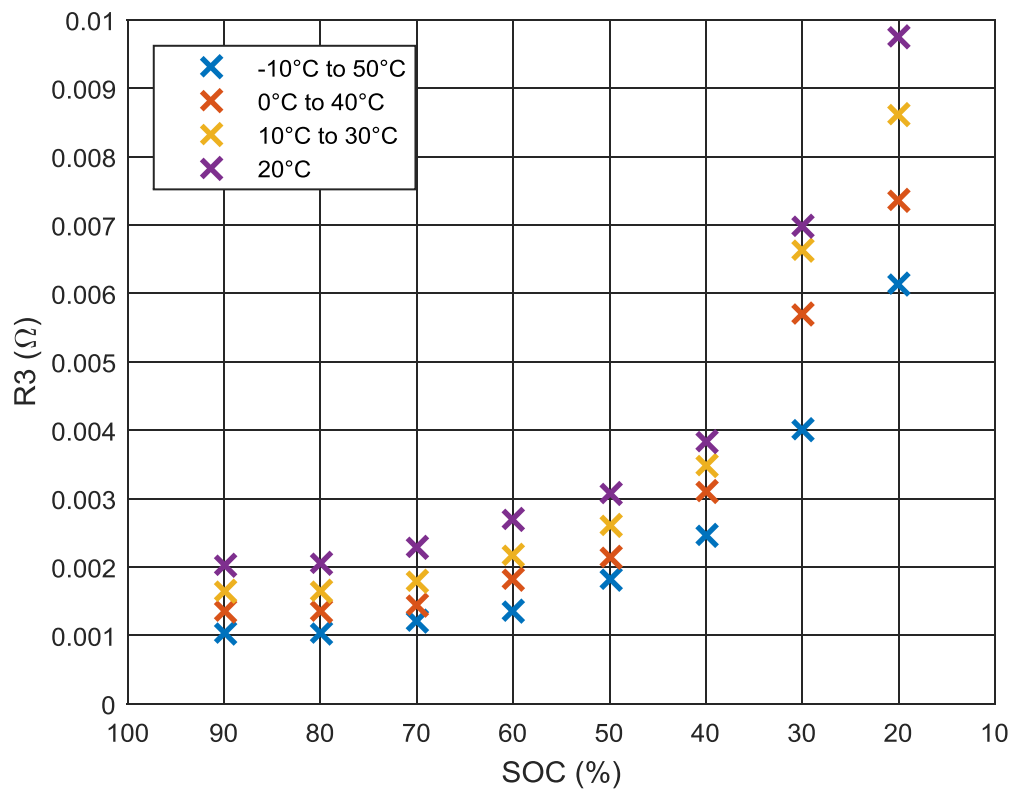


Figure 48 - EIS results for cell tested under different temperature gradients at 2 A

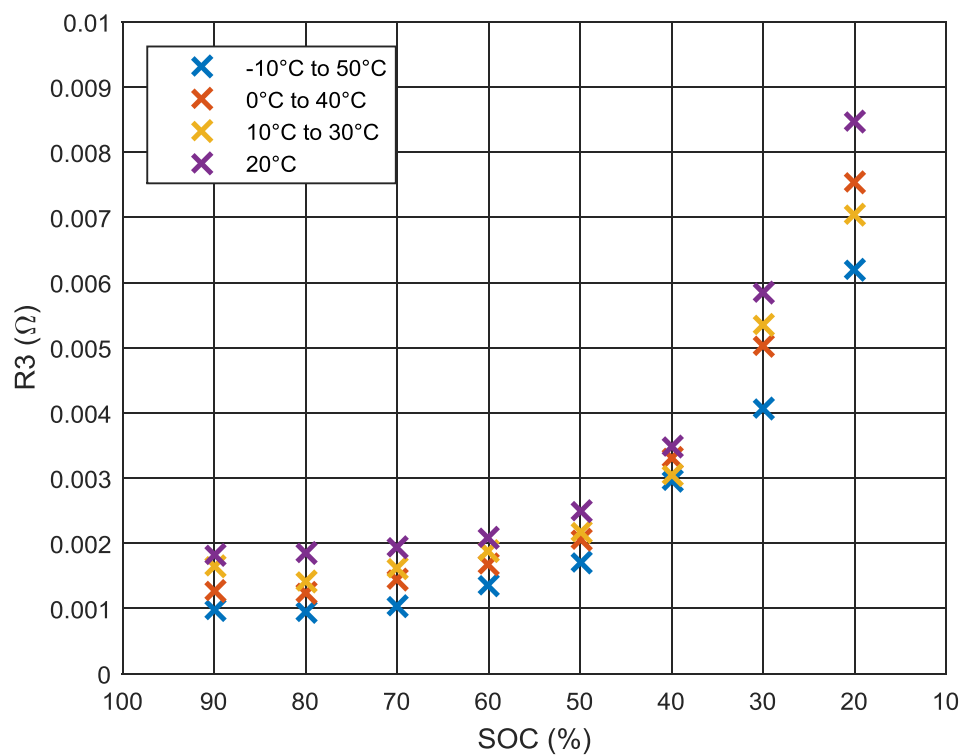


Figure 49 - EIS results for cell tested under different temperature gradients at 4 A

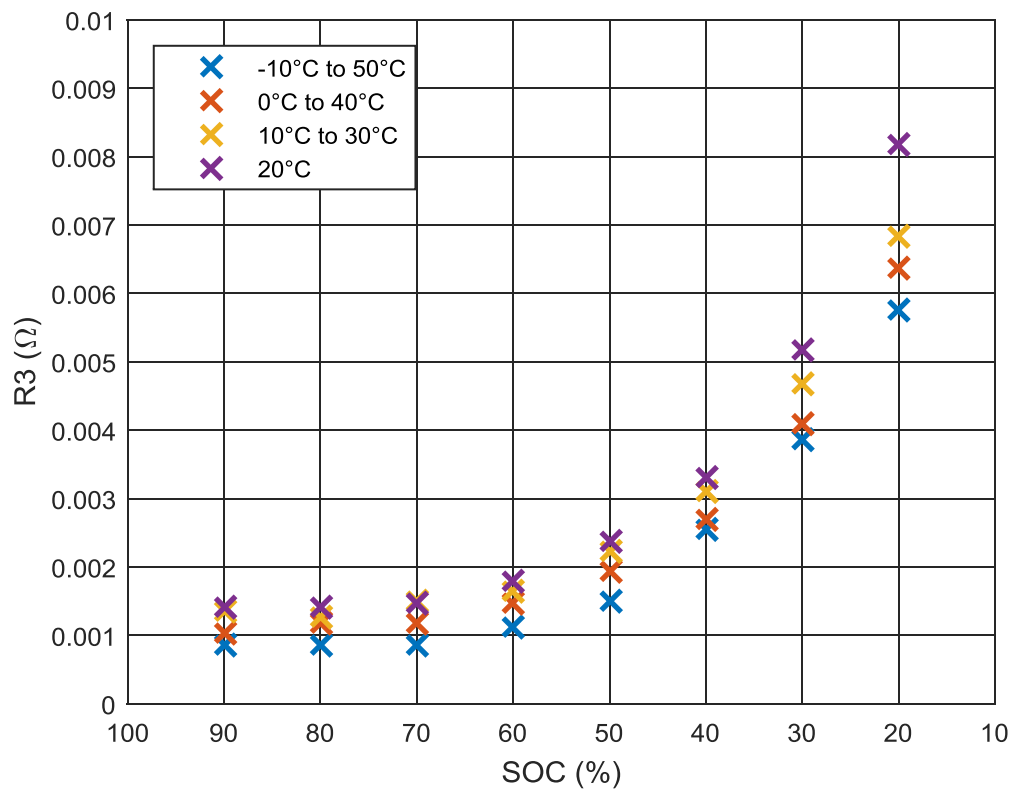


Figure 50 - EIS results for cell tested under different temperature gradients at 8 A

Figure 47 to Figure 50 show that the charge transfer resistance (R_3 in Figure 14) is relatively constant between 90% and about 70% of the nominal SOC, and at the measurement taken at 60% SOC the charge-transfer resistance begins to increase. As the cell continues to discharge, the charge transfer continues to increase until it is close to an order of magnitude higher at 20% SOC compared to 90% SOC. The increase in charge-transfer resistance with decreasing SOC is a commonly reported phenomenon [126,179,180].

It is clear from looking at the trends in Figure 47 to Figure 50 that the assertion that charge-transfer resistance falls as temperature gradients increase is true when a cell is under load, for different currents and for all SOC. Therefore, in terms of charge transfer resistance, a cell behaves as a cell that is hotter than its mean temperature when a temperature gradient is imposed.

Troxler et al. produced a simple model, taking the charge transfer resistance measured during isothermal tests, to predict how the charge-transfer resistance would change with temperature gradients. This methodology was repeated here for cells under load, and therefore the cell was tested isothermally between -10°C and 50°C using the same procedure as the tests under temperature gradients. This data were then fitted to the same equivalent circuit model (Figure 14), and the values of R_3 can be seen in Figure 51 to Figure 54, where the values of R_3 have been plotted on a logarithmic scale.

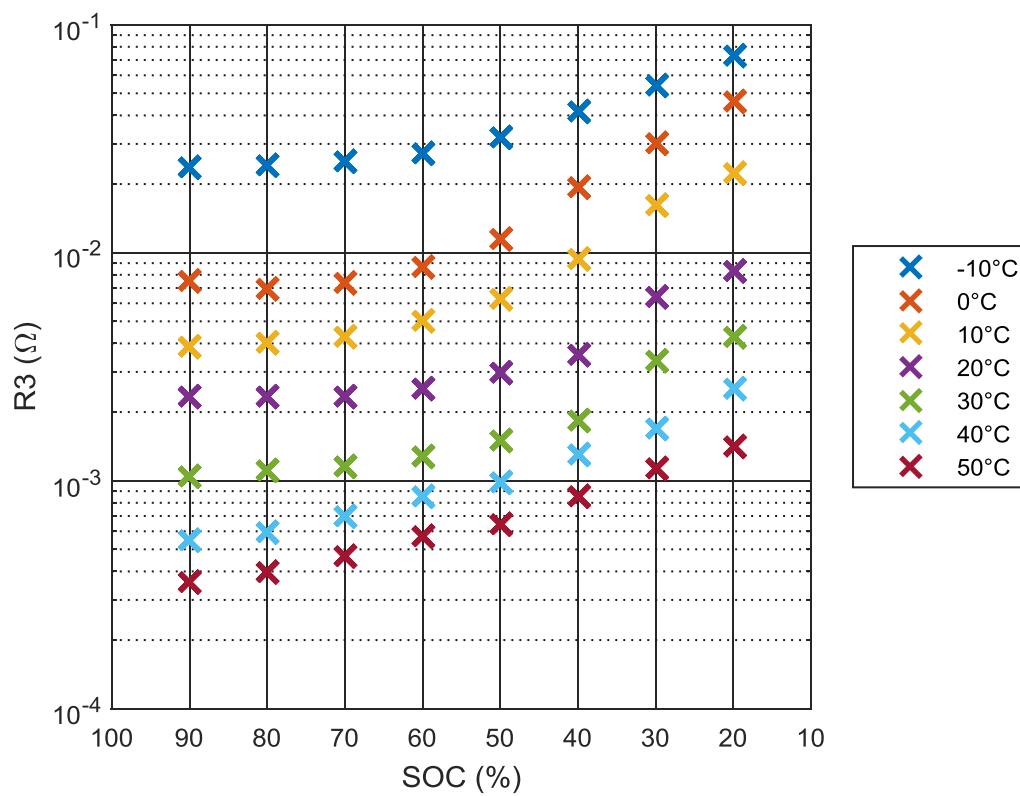


Figure 51 - R_3 tested at 1 A and at different temperatures

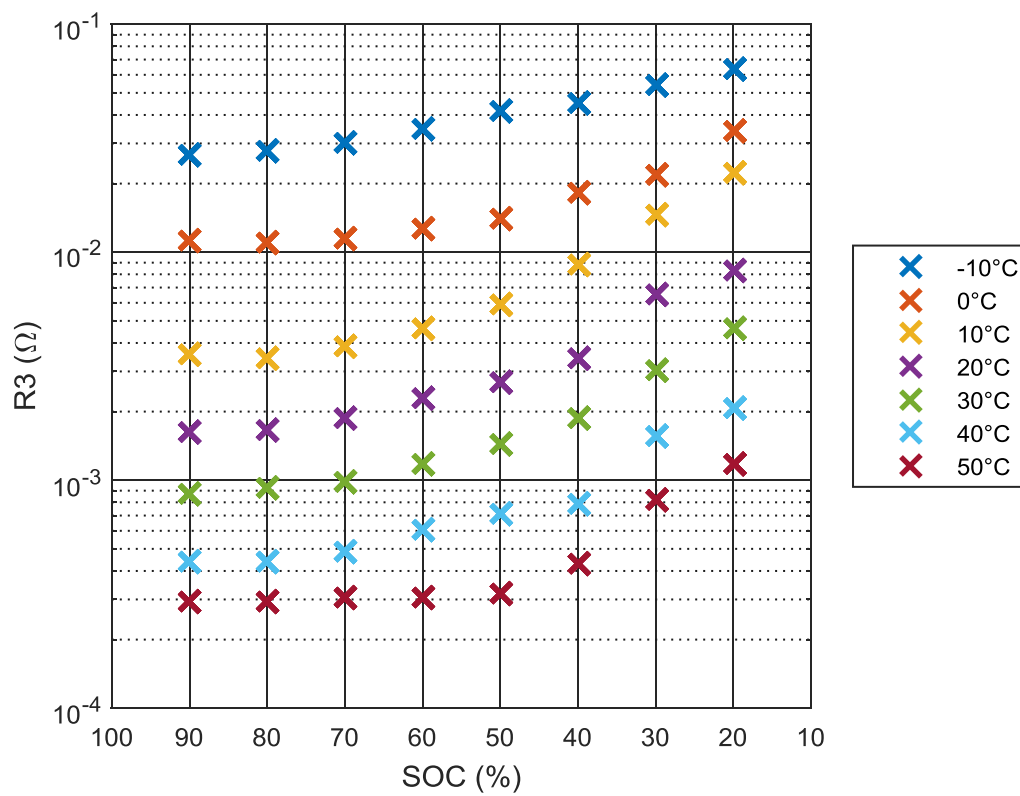


Figure 52 - R_3 tested at 2 A and at different temperatures

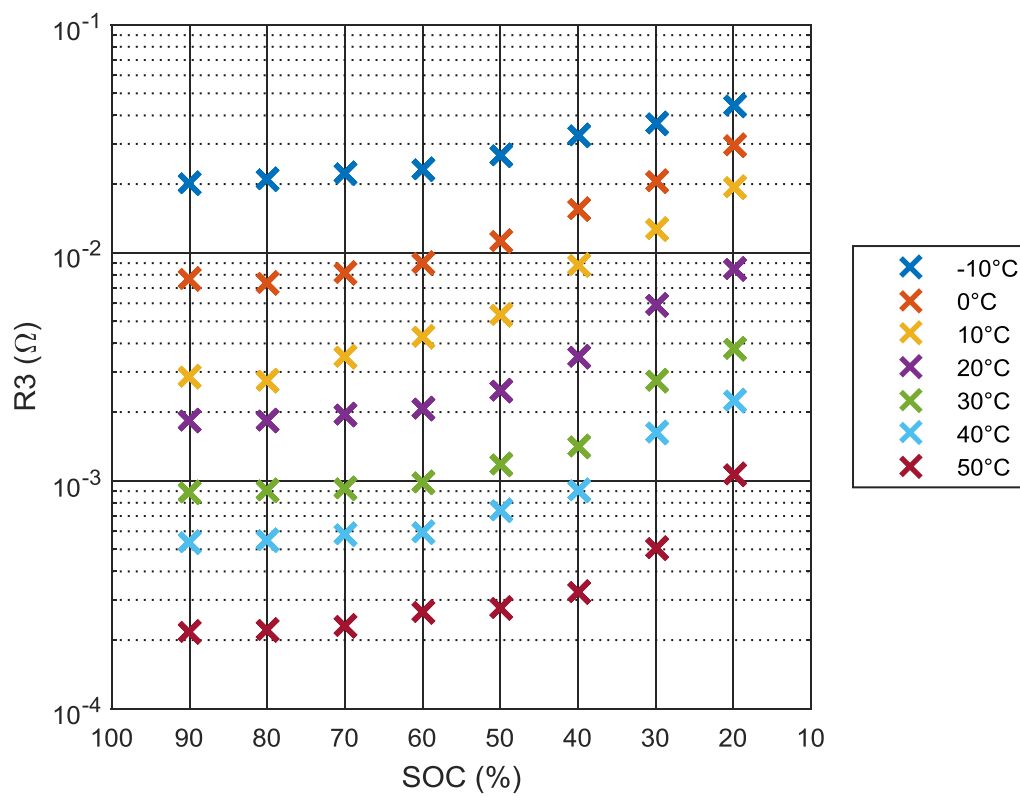


Figure 53 - R_3 tested at 4 A and at different temperatures

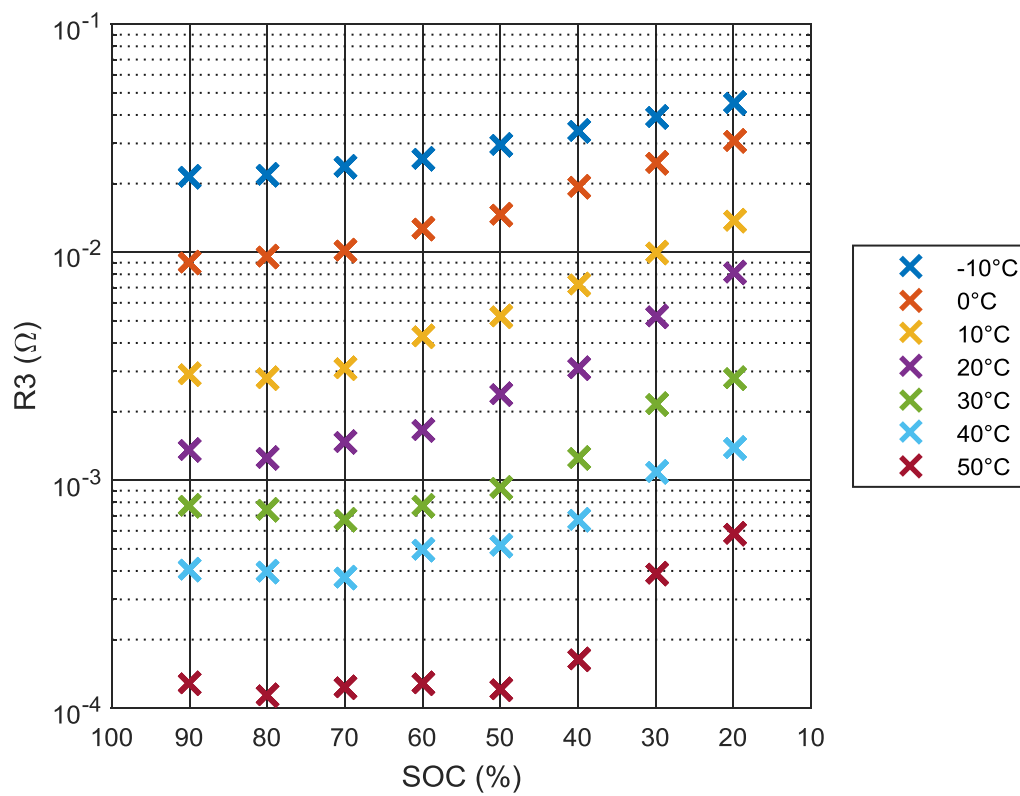


Figure 54 - R_3 tested at 8 A and at different temperatures

Figure 51 to Figure 54 show that the charge transfer resistance increases dramatically as temperature decreases, and is also lower at higher currents, which has been reported extensively in previous literature [181].

The cell is of the same type as shown in Figure 27 to Figure 30, with 100 individual anode-cathode pairs. A simple 1D model was used and parameterised using the data gathered in Section 4. It was assumed that each anode-cathode pair was thin enough that it could be treated as an isothermal cell, and that there was a linear temperature gradient between the layers of the cell. 100 resistors were modelled in parallel, and their values were taken using linear interpolation of the data shown in Figure 51 to Figure 54.

The results of this model are shown in Figure 55 to Figure 58.

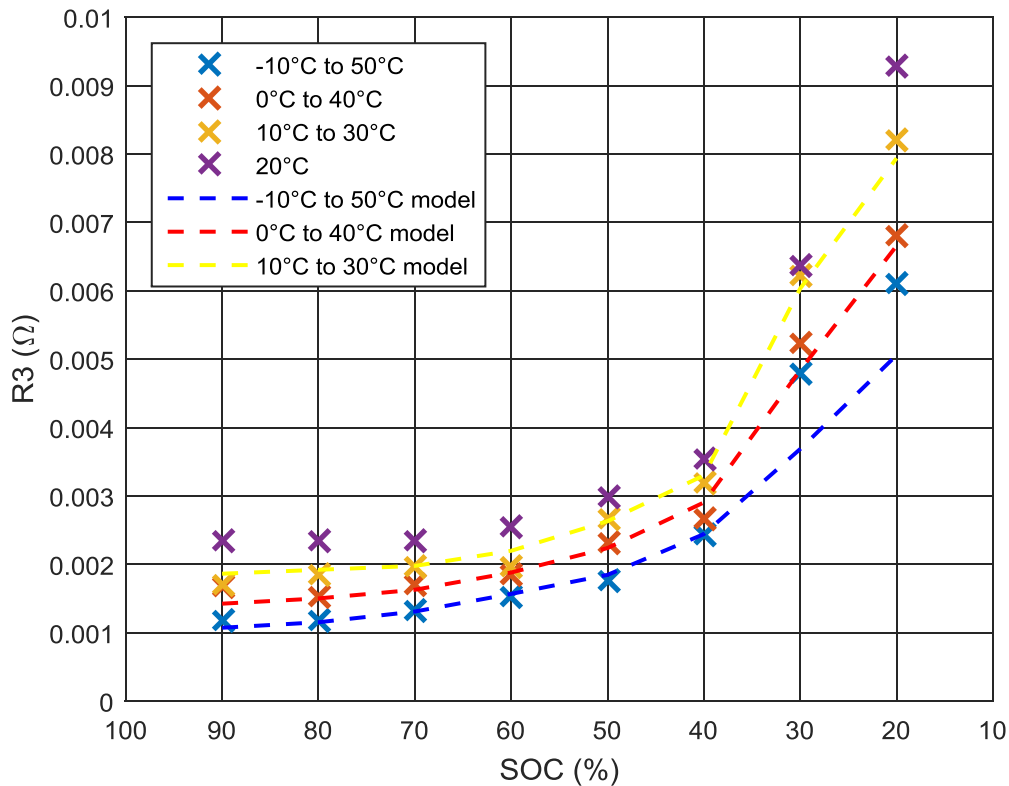


Figure 55 - Comparison of model and test data for cell tested under different temperature gradients at 1 A

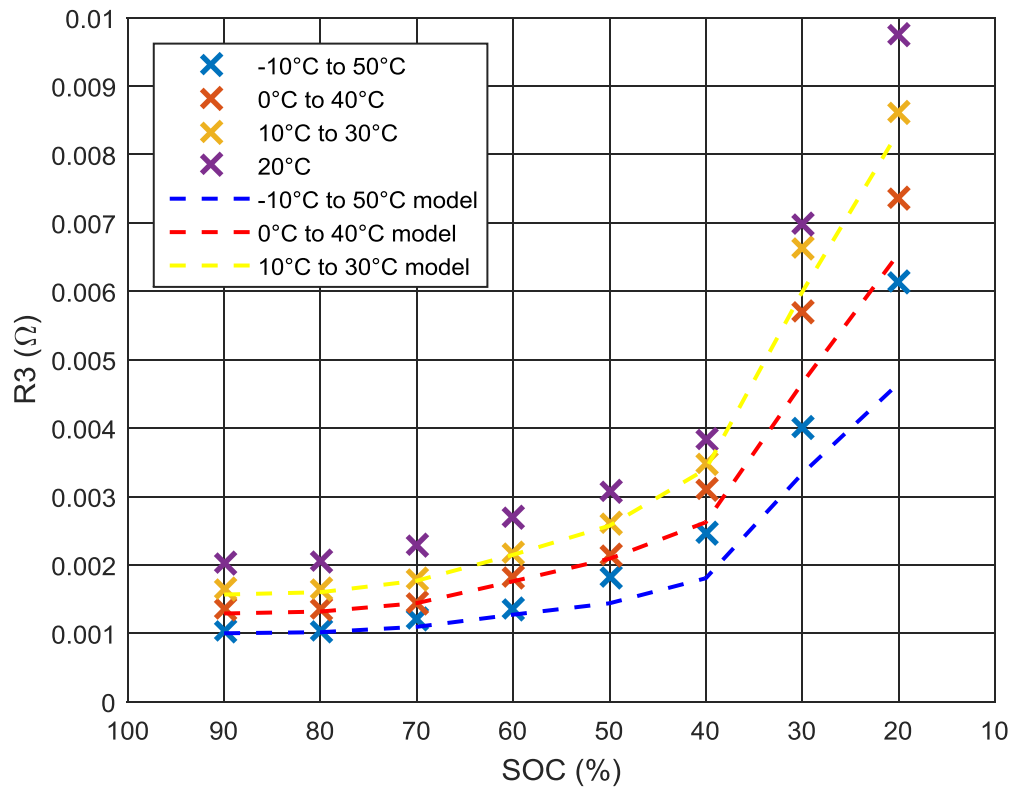


Figure 56 - Comparison of model and test data for cell tested under different temperature gradients at 2 A

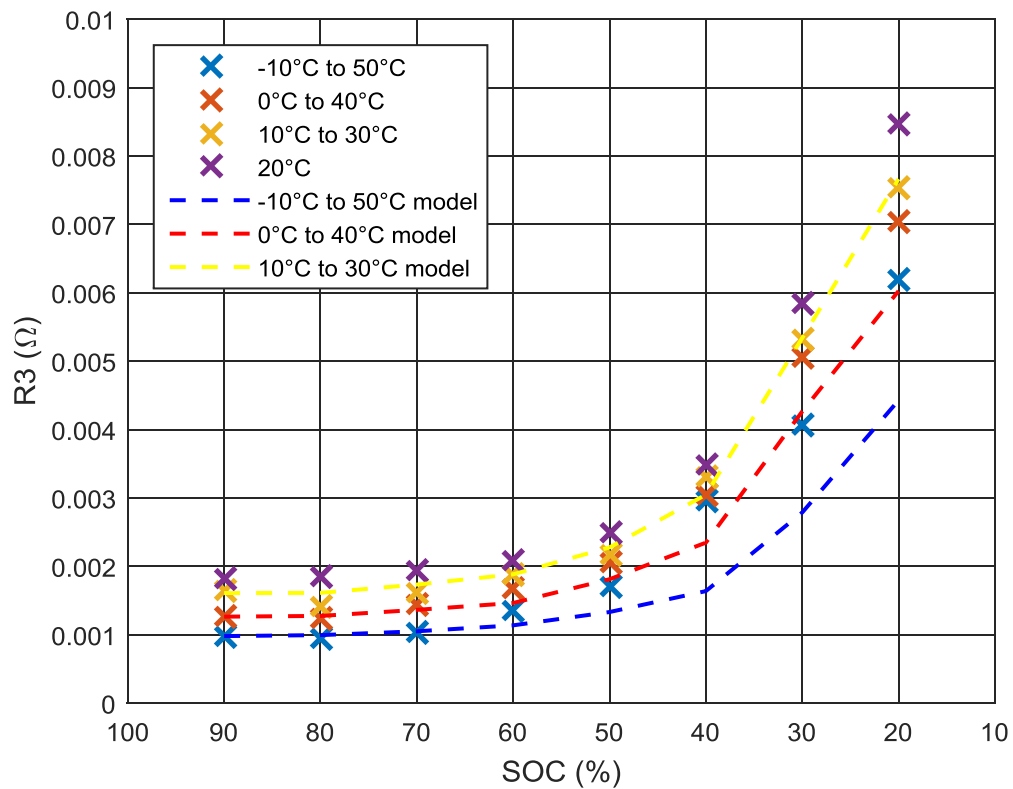


Figure 57 - Comparison of model and test data for cell tested under different temperature gradients at 4 A

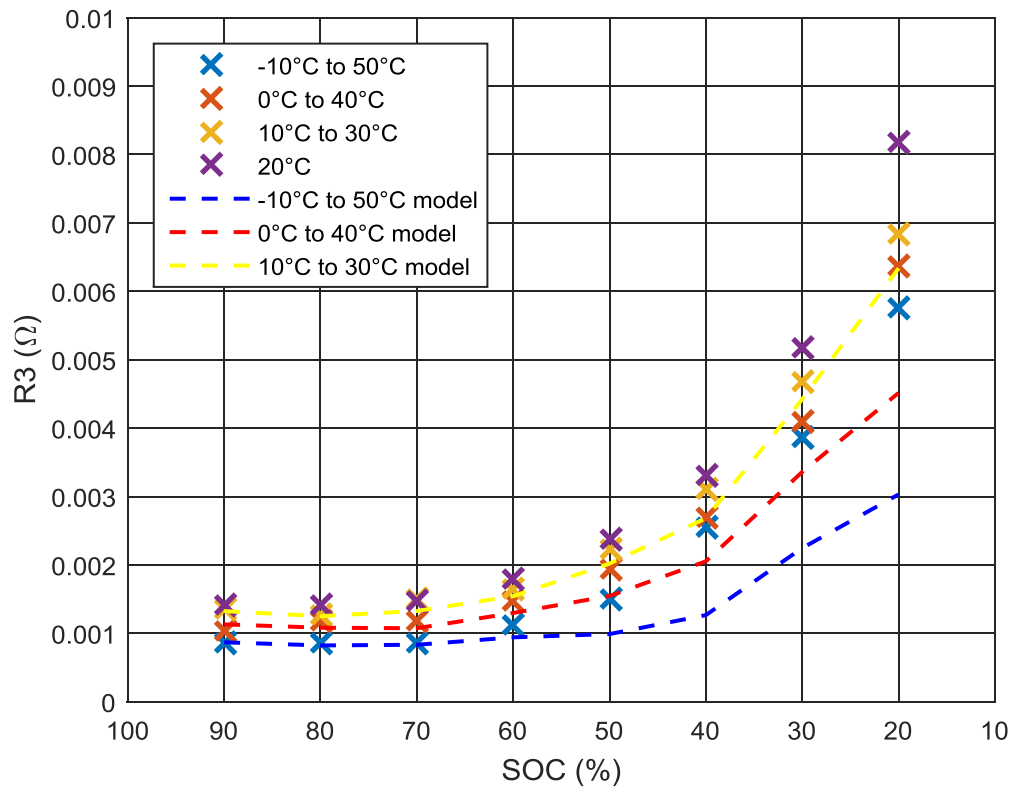


Figure 58 - Comparison of model and test data for cell tested under different temperature gradients at 8 A

The results shown in Figure 55 to Figure 58 show that at the beginning of discharge the model can accurately predict the charge transfer resistance of the cell under temperature gradients, however for the 1A case, at around 30% SOC the model starts to significantly underestimate the charge transfer resistance, especially for the tests under higher temperature gradients (-10°C to 50°C and 0°C to 40°C). For higher rates of discharge, this underestimation begins earlier in the discharge cycle, which can be seen in Figure 58, where the model begins to underestimate the charge transfer resistance at 50% SOC. In this case, by the time 20% SOC is reached, the model is incorrect by nearly a factor of 2 for the cell tested between -10°C and 50°C.

This is a significant result, and shows that towards the end of discharge, the charge transfer resistance increases significantly for cells under a temperature gradient. In a real-world application, this will reduce the efficiency of the battery pack, increase the amount of heat generated and mean that the lower cut-off voltage will be reached earlier. All of these are negative consequences, and will significantly reduce the performance of a battery pack.

It is clear from these results that under load it is not possible to simply look at the charge transfer resistance and predict how a cell will behave under discharge when a temperature gradient is applied, and that a more complex model is required in order to predict the behaviour of a cell. It is well known that the useable capacity of lithium-ion batteries changes with temperature, and therefore the useable capacity during discharge of the cells under temperature gradients was examined.

5.4.2 Capacity

Table 15 shows the capacity of the cell under discharge when measured between 4.2 V and 2.7 V.

Temperature	Discharge Current			
	1 A	2 A	4 A	8 A
-10°C to 50°C	5.062	5.012	4.911	4.797
0°C to 40°C	5.110	5.043	4.934	4.806
10°C to 30°C	5.124	5.087	4.981	4.835
20°C	5.153	5.116	5.016	4.902

Table 15 - Capacity of cell tested under different temperature gradients and at different rates

As can be seen in Table 15, the capacity is lower at higher discharge rates, reducing from 5.153 Ah at 1 A to 4.902 Ah at 8 A when discharged at 20°C. A similar trend is seen for all

of the tests at different temperature gradients. Additionally, the capacity decreases as a larger temperature gradient is applied to the cell.

Whilst the capacity of the cell under different conditions provides an insight into how the cell is behaving, it is important to consider the whole of the discharge, the voltage curves for which can be seen in Figure 59 to Figure 62.

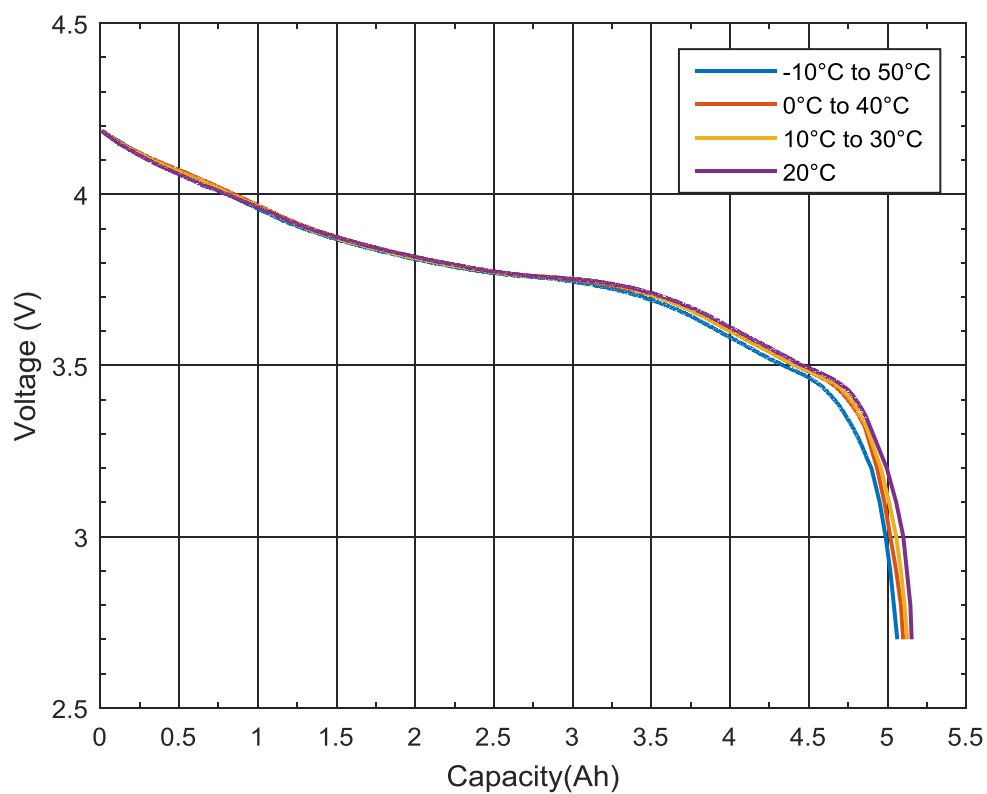


Figure 59 - Discharge curves for cell tested under different temperature gradients at 1 A

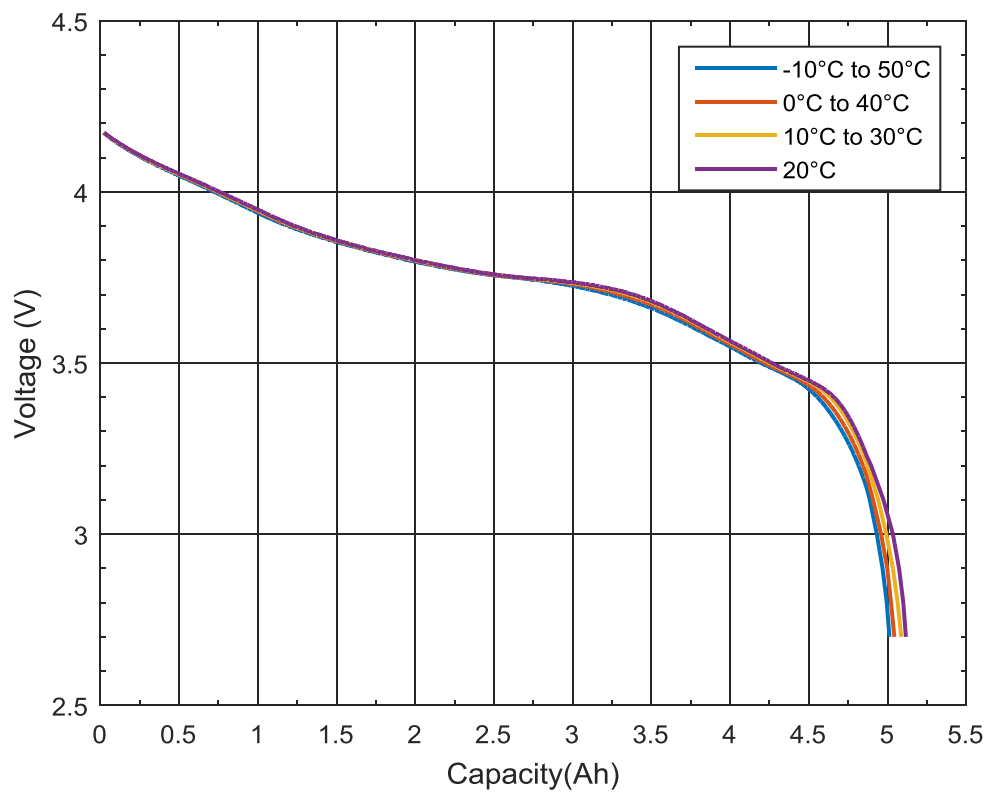


Figure 60 - Discharge curves for cell tested under different temperature gradients at 2 A

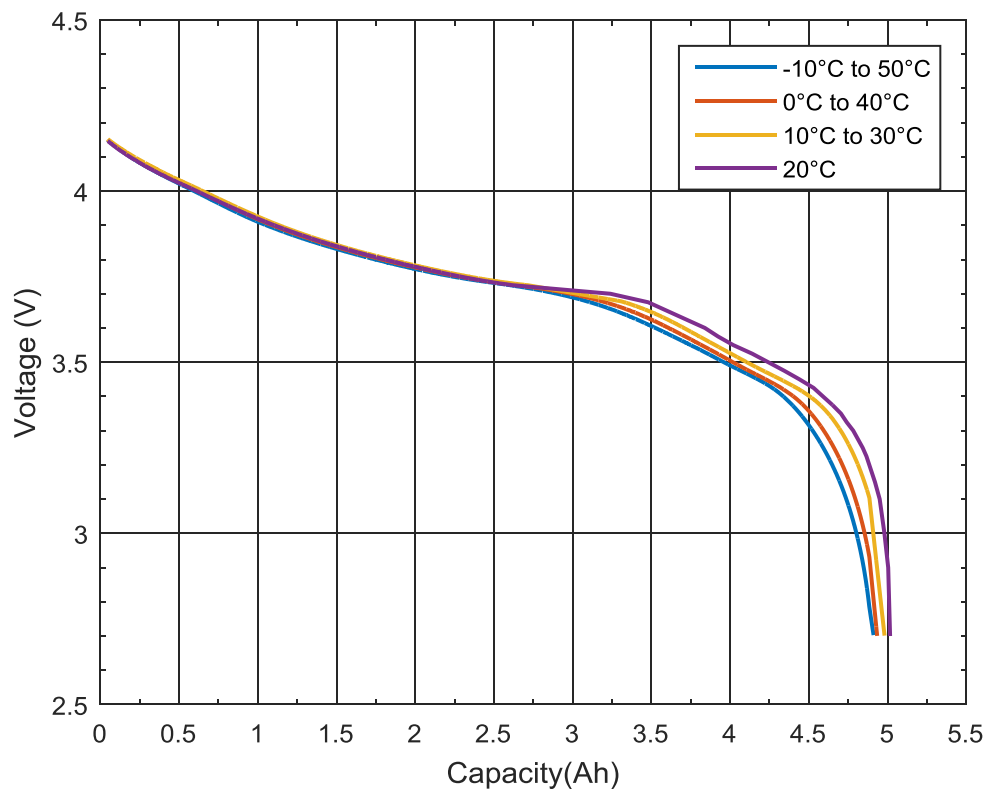


Figure 61 - Discharge curves for cell tested under different temperature gradients at 4 A

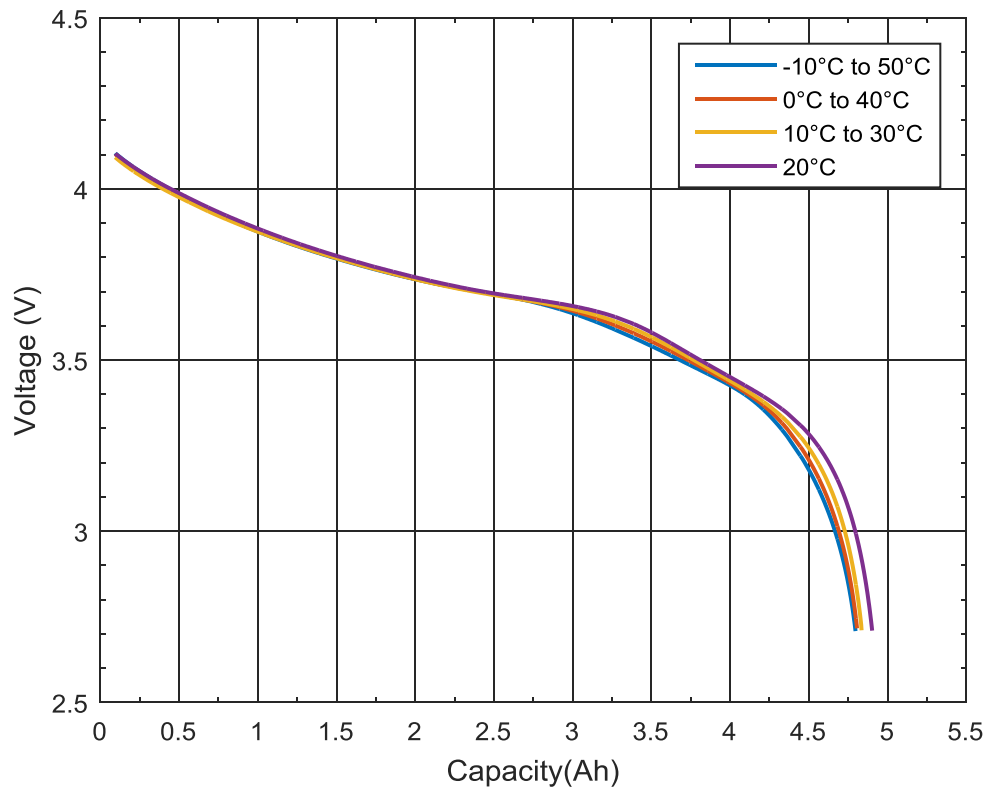


Figure 62 - Discharge curves for cell tested under different temperature gradients at 8 A

At the beginning of discharge, the difference between the voltage curves is minimal, meaning that the temperature gradients do not have much of an effect at this point. For all discharge rates, the curves can be seen to noticeably diverge at around 3 Ah, equivalent to 40% SOC.

The discharge curves at higher temperature gradients are lower than for the isothermal tests, meaning that the resistances of cells under temperature gradients is higher. Higher resistances are normally associated with cells at lower temperatures, therefore leading to the conclusion that a cell under a temperature gradient behaves as a cell colder than its mean. This directly contradicts one of the conclusions made in Section 5.4.1.

In addition, because the voltage curves of cells under temperature gradients are lower than for the isothermal cell, in these cases the cell will be providing less power.

Alternatively, if a constant power demand was required the cell would have to provide more current in order to meet that demand. In order to quantify this, Figure 63 shows the total energy provided by the cell during discharge under different conditions.

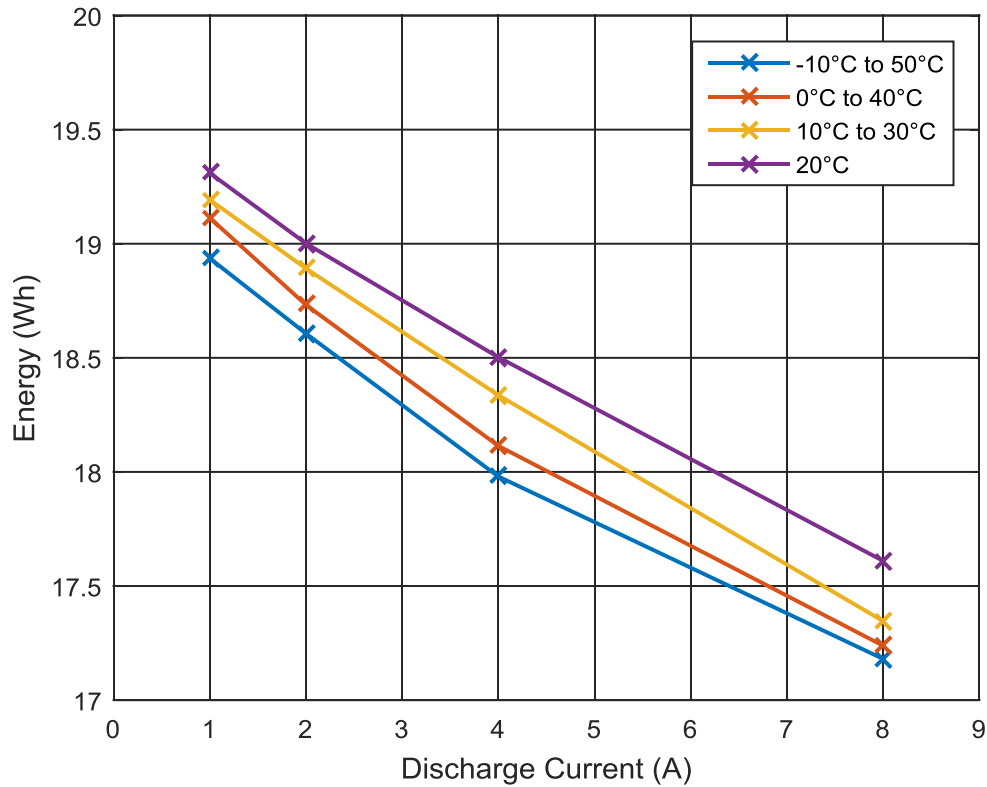


Figure 63 - Energy provided by the cell during discharge between 4.2 V and 2.7 V

Figure 63 shows that as the temperature gradient increases, the total amount of energy provided by a cell before a voltage cut-off is reached decreases. As expected, the amount of energy provided is also lower at higher currents. Interestingly, the percentage drop in energy provided at higher rates is relatively unchanged as the discharge rate changes.

5.4.3 Incremental Capacity Analysis

Whilst the voltage curves under discharge provide a useful insight into the behaviour of the cell, it can be difficult to distinguish some of the features, especially in the flatter

plateau regions of the curves, and therefore incremental capacity analysis, or ICA, can be used to shed more light on these areas. ICA is discussed in more detail in Section 3.2.

Figure 64 to Figure 67 show ICA performed on the voltage curves from the cell tested under different temperature gradients and at different loads. Unfortunately due to a data corruption error, the curve at 20°C and 4 A is not shown.

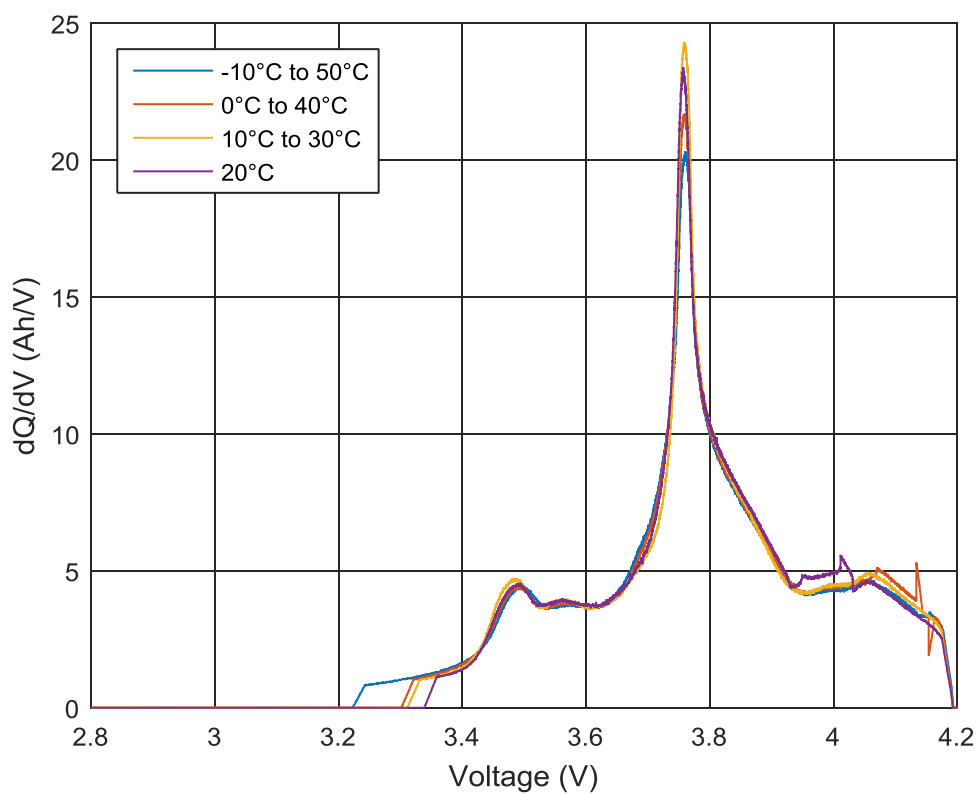


Figure 64- ICA for cell tested under different temperature gradients at 1 A

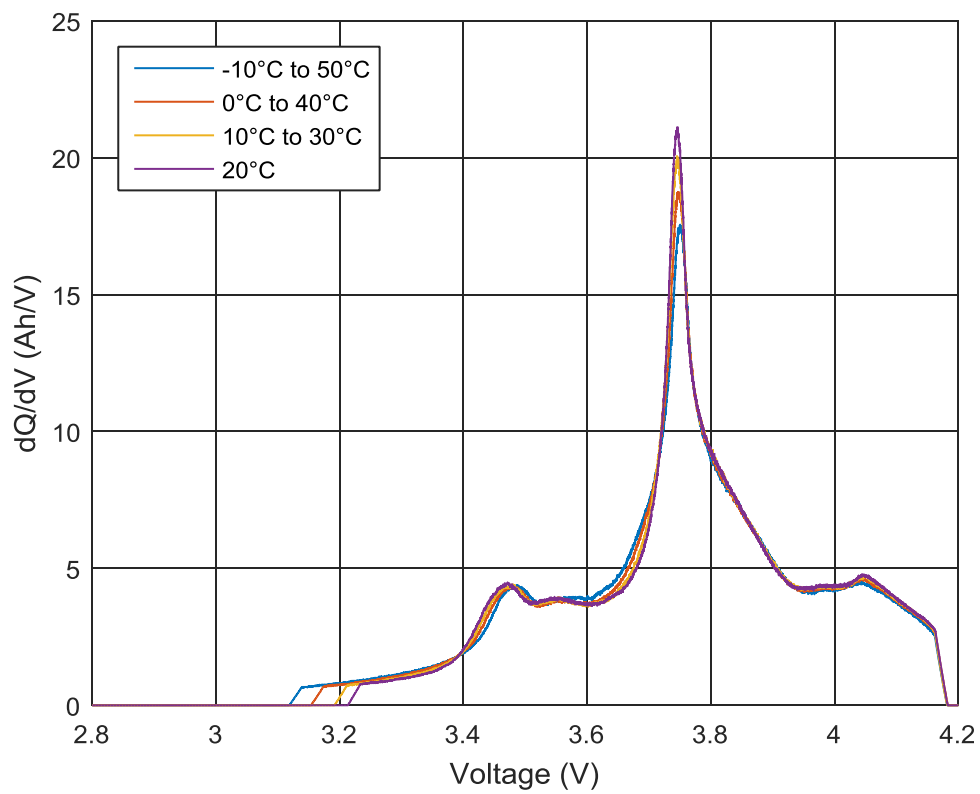


Figure 65 - ICA for cell tested under different temperature gradients at 2 A

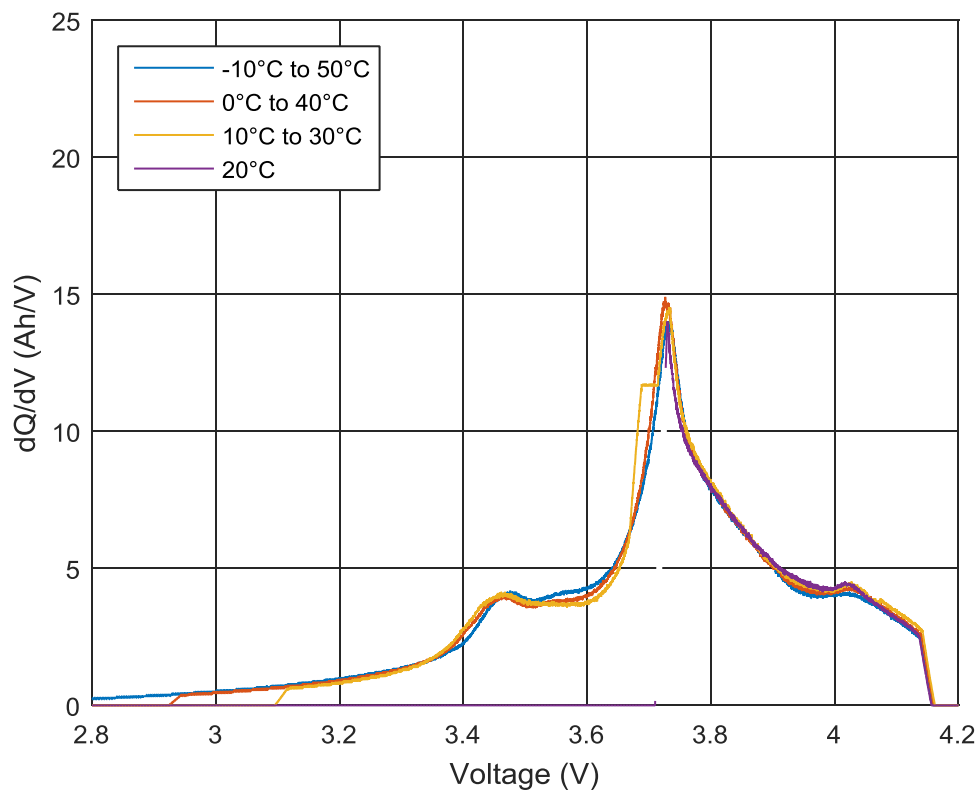


Figure 66 - ICA for cell tested under different temperature gradients at 4 A

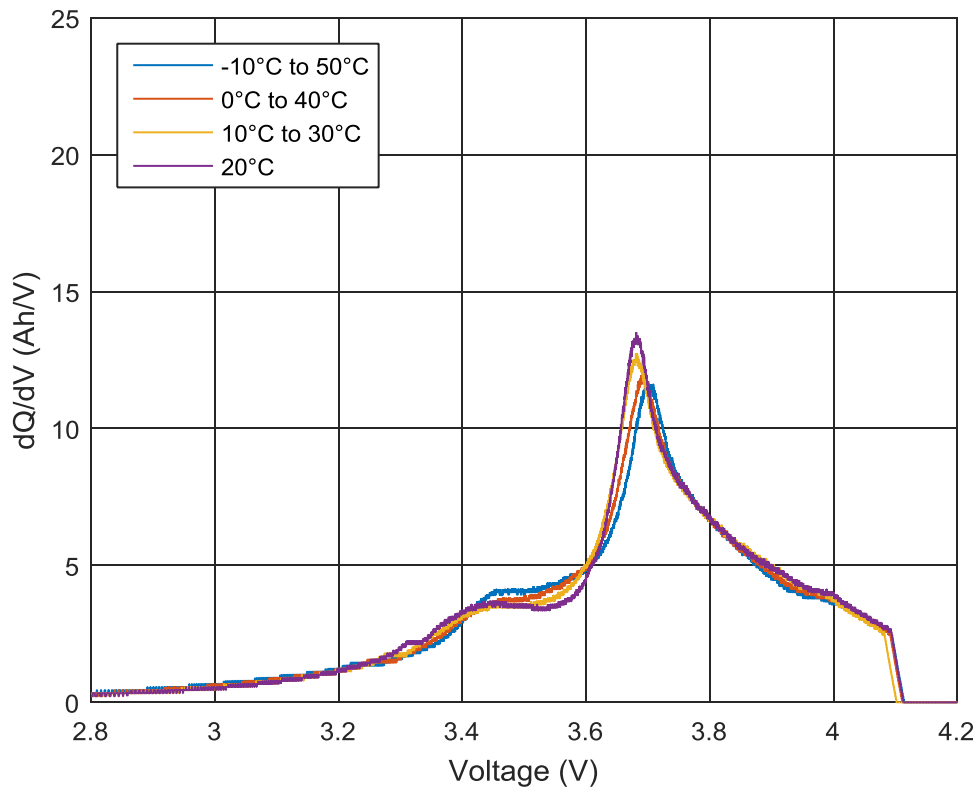


Figure 67 - ICA for cell tested under different temperature gradients at 8 A

At 1 A (Figure 64), there is very little difference between the curves, however as the current increases the differences between the cells at different temperature gradients increases. When cells are under larger temperature gradients, the peak at around 3.7 V is less intense and also wider than the cell at a homogeneous temperature. The peaks on an ICA curve indicate that a phase equilibrium is taking place, and therefore a flattening and widening of this curve over a greater voltage range indicates that the phase transition for different areas of the cell are taking place at different voltages during discharge.

The flattening and widening of this peak under larger temperature gradients and at higher currents can be explained by looking at how the resistances and voltages change for cells at different temperatures under discharge. The voltage of each layer must be equal as they are in parallel, however due to the fact that colder layers have higher

resistance, less current flows through these layers. This means that more current flows through the warmer layers of the cell, which then become depleted more quickly, leading to a drop in their open circuit voltage. Due to this voltage drop, the colder parts of the cell must discharge more. Because the different areas of the cell discharge at different rates and at different times, they go through their phase equilibria at different times, meaning that the peaks on the ICA curves are wider and lower. This process is explained in the flow chart seen in Figure 68.

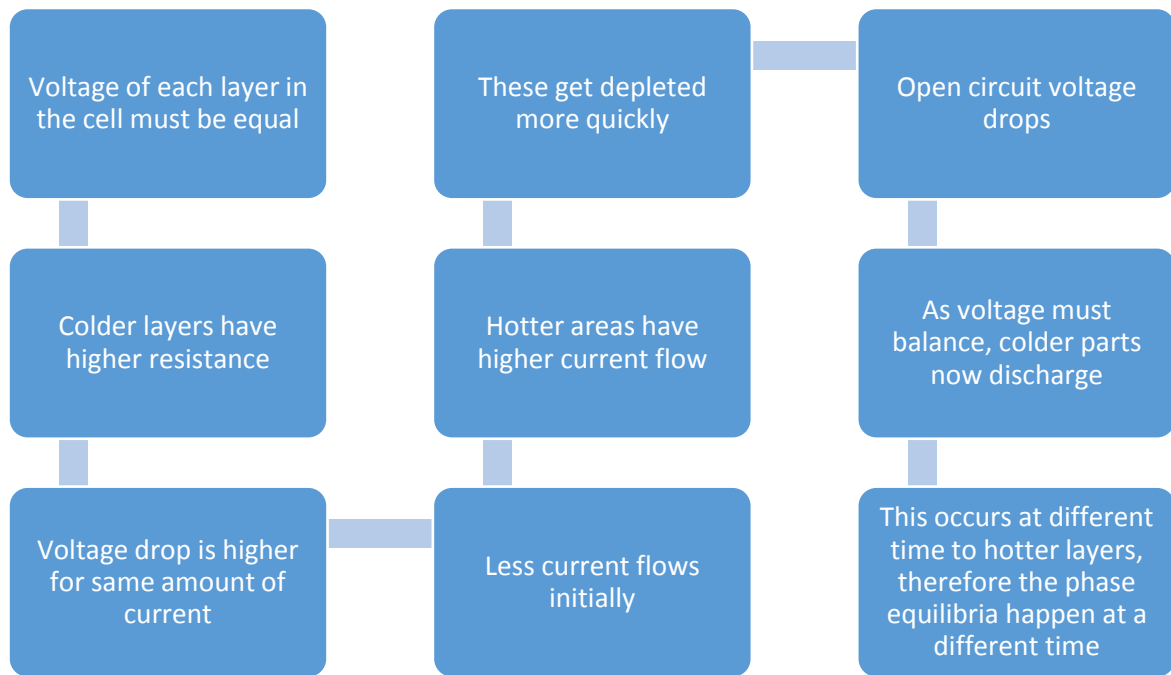


Figure 68 - Flow chart detailing processes occurring during discharge under a temperature gradient

The inhomogeneity in current flow can also be used to explain why cells under temperature gradients have voltage curves that are lower than for isothermal cells, and why their capacities are lower. As the cell becomes depleted, more current is flowing through the colder areas of the cell. Because these areas are cooler and the current flow

is relatively higher, lithium cannot diffuse to the surface of the electrode particles at a fast enough rate and therefore the lower voltage cut-off is reached earlier, reducing the useable capacity of the cell.

Additionally, the inhomogeneous current flow can be used to explain why the simple model could not predict the charge transfer resistance in Section 5.4.1. Once the cell had been depleted, the hotter layers of the cell were at a lower SOC and therefore their charge transfer resistance was higher, and the charge transfer resistance of the colder areas of the cell is naturally higher due to the colder temperatures. These two factors combine to increase the overall charge transfer resistance of the cell.

5.5 Updated model

5.5.1 Method

In order to accurately predict the performance of a cell under a temperature gradient, the unequal current flow in areas of the cells that are at different temperatures must be understood and modelled.

In order to do this, a simple model based on the data collected was made. The resistance of the cell can be estimated by looking at the voltage curve of the cell at different discharge rates. For each temperature, discharge curves were obtained for 1 A, 2 A, 4 A and 8 A. If it is assumed that the values of the voltage curves obtained are comprised of an open circuit voltage and a voltage drop relating to the current flowing and the resistance of the cell, the open circuit voltage and the resistance can be found using Equation (34). This was done by extrapolating the curves obtained at different currents to 0 A using MATLAB's 'fit' function.

$$V_{measured} = OCV - IR \quad (34)$$

It is well known that the current of a cell can have an effect on the internal resistance. The charge-transfer resistance of a cell falls as the discharge current increases, and resistances relating to diffusion increase as current flows, especially towards the end of discharge [126,181]. This modelling approach takes no account of how the current affects resistance, however using a linear fit provided a mean coefficient of determination of 0.9992, showing that at the range of currents used the voltage drop is quite linear with current, implying that the resistance is not changing greatly. Due to the low capacity of the cell when held at -10°C and 0°C, the data collected at -10°C was ignored, and the remaining data are only valid up to 4.6 Ah, which was the capacity of the cell when held at 0°C. This means that it will not be possible to complete a full discharge to 0% SOC using the model.

The calculated resistances at different temperatures can be seen in Figure 69.

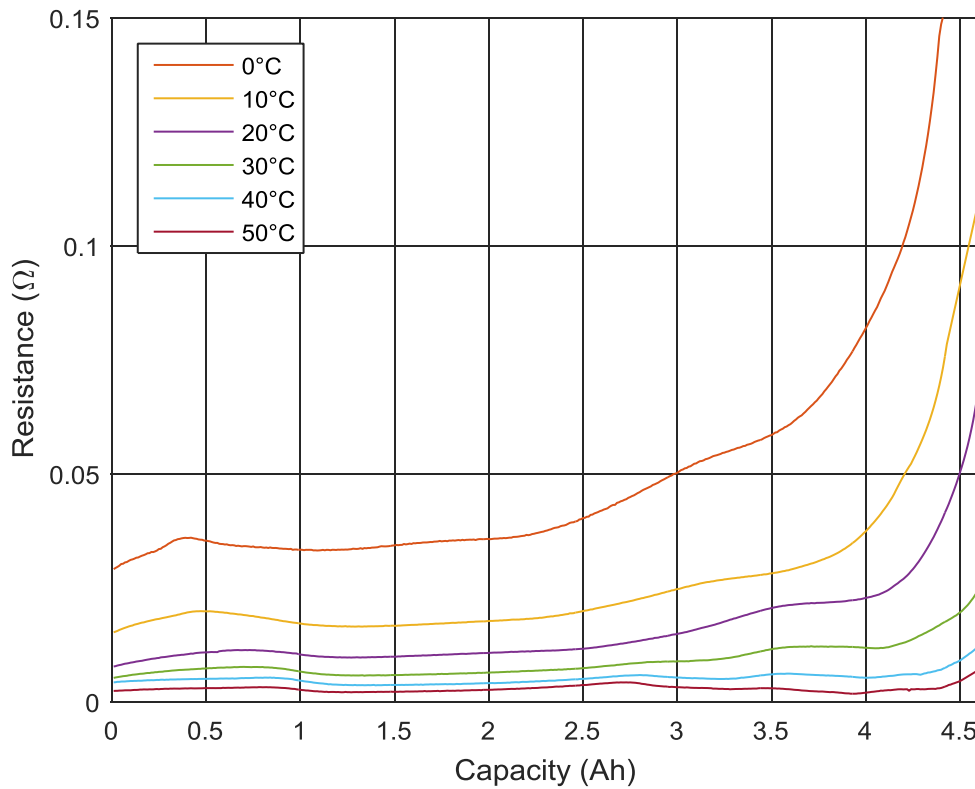


Figure 69 - Calculated resistances at different temperatures and SOC's

Whilst the method to calculate the resistance of the cells at different SOC's and temperatures is simplistic, the results show similar trends to other work where more in-depth studies have been used to calculate these values, giving confidence that the method used is appropriate and the results are a fair reflection on the behaviour of the cell [182–184]

The resistance and OCV values were then used to parameterise a simple parallel cell model, mimicking the discharge tests shown in Section 5.4 where the surfaces of the cell were held at different temperatures. Two temperature distributions were looked at; 10°C to 30°C, and 0°C to 40°C.

The model works on the basis that each cell must be at the same voltage when under load, which will be a combination of the OCV of the individual cells and the voltage drop across that cell due to the current flow and the internal resistance. This can be explained using Equation (34), where V_{measured} must be the same for each cell. Due to differences in the resistance and therefore current flow through each cell, the OCV must be different for each cell, meaning that the SOC of each cell will be different during the discharge.

If V_{measured} is known to be the same for each cell, using Kirchoff's current law, and knowledge of the OCV and resistance of each cell, it is possible to produce a set of simultaneous equations that can be solved to predict how much current will be provided by each cell during the discharge. For each time-step, the SOC of each cell is updated, and the OCV and resistance of each cell is calculated depending on the SOC and the temperature.

Due to the simplistic modelling approach, the results from this model will not be particularly quantitatively accurate, however they will illustrate in a qualitative way how the individual layers of a cell will behave when the cell is held under temperature gradients. In order to keep the model simple and the results easy to analyse and understand, 5 cells were connected in parallel. A schematic of the model can be seen in Figure 70. In order to show the biggest effect of inhomogeneous behaviour, only the 8 A case was modelled.

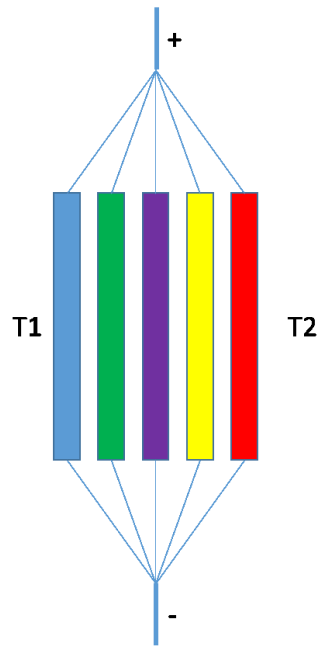


Figure 70 - Schematic of the model used to explore the effects of temperature gradients on the performance of cells under load

5.5.2 Results

In order to validate the results, the discharge curves obtained using the model were compared to the curves obtained using the experimental test rig in Section 5.4.2.

These discharge curves can be seen in Figure 71 and Figure 72, where it can be seen that the model produces a good fit to the experimental data.

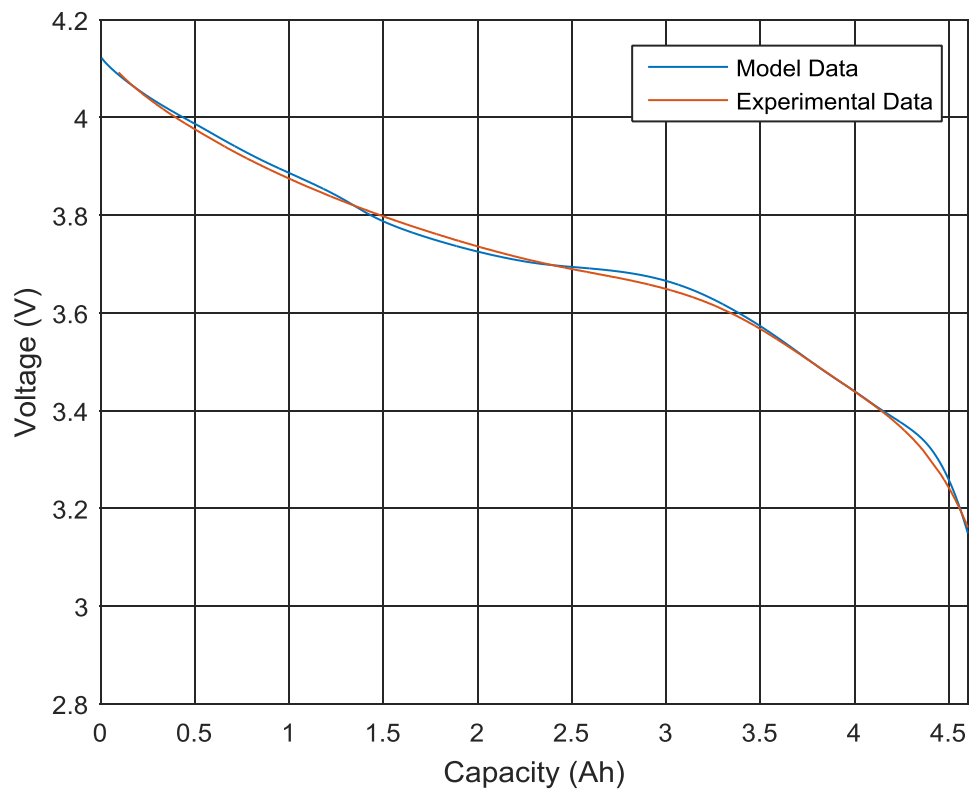


Figure 71 - Modelled and experimental discharge curves for 10°C to 30°C temperature distribution

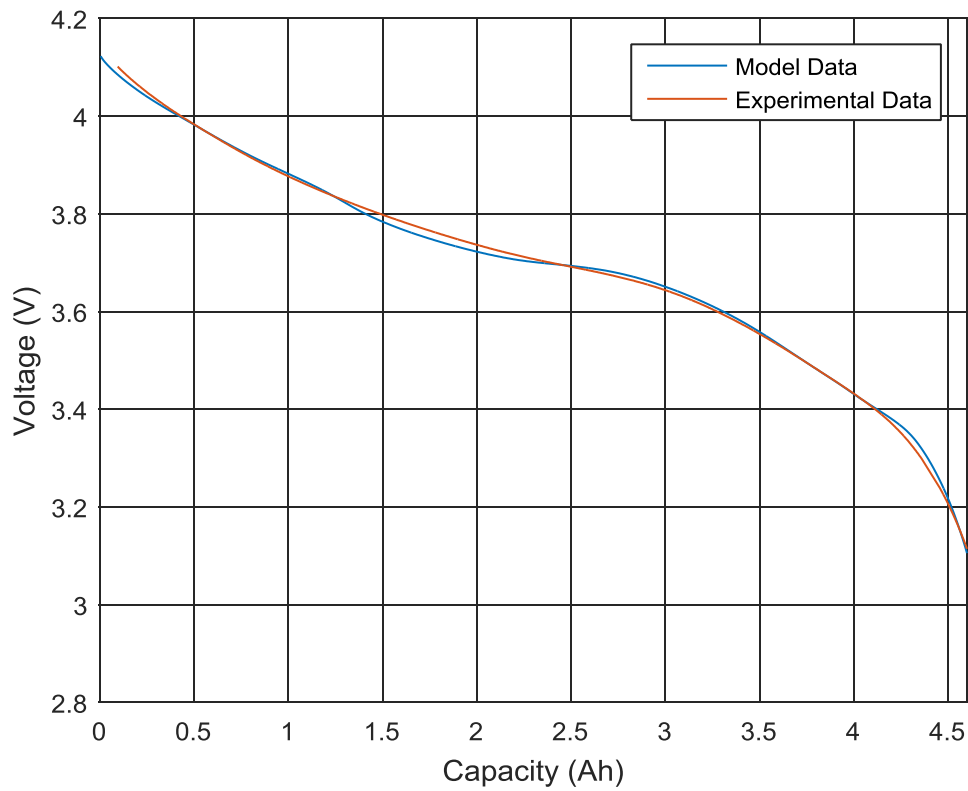


Figure 72 - Modelled and experimental discharge curves for 0°C to 40°C temperature distribution

In order to understand the inhomogeneous nature of discharges when a cell is under load, the SOC at different point of the discharge for the 5 cells connected in parallel were plotted. These can be seen in Figure 73 and Figure 74, where the lines get lighter as the discharge progresses, and each line is at 0.5 Ah steps (equivalent to 10% SOC).

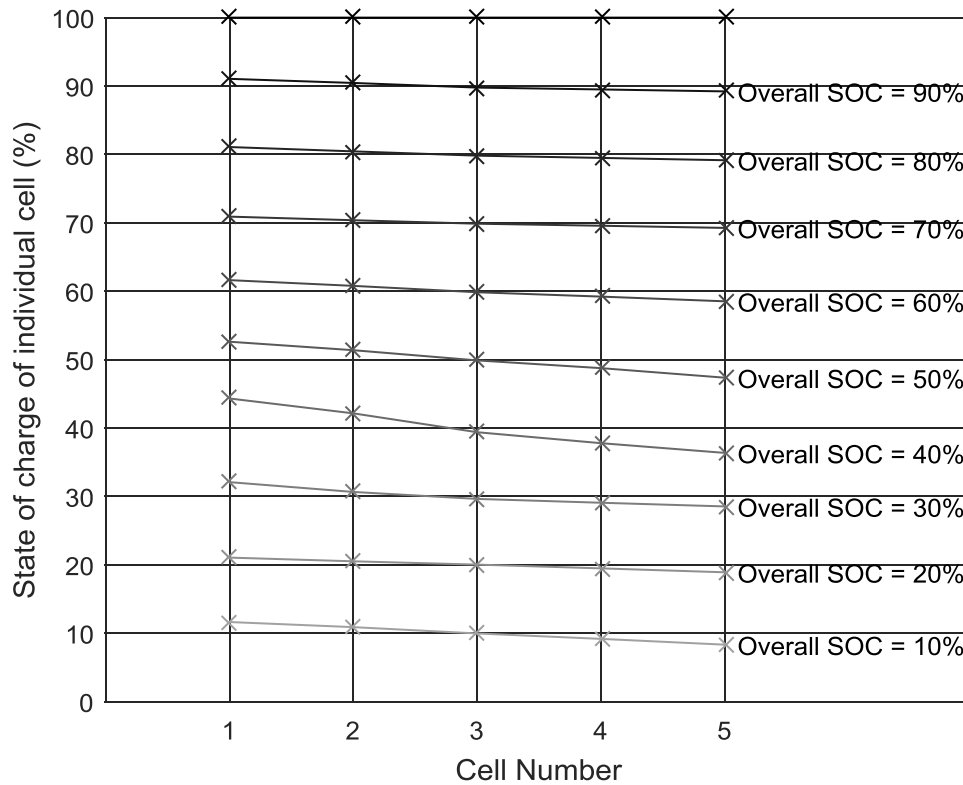


Figure 73 - SOC of each cell in parallel for 10°C to 30°C temperature distribution. The lines get lighter as the discharge progresses, and are at 0.5 Ah steps.

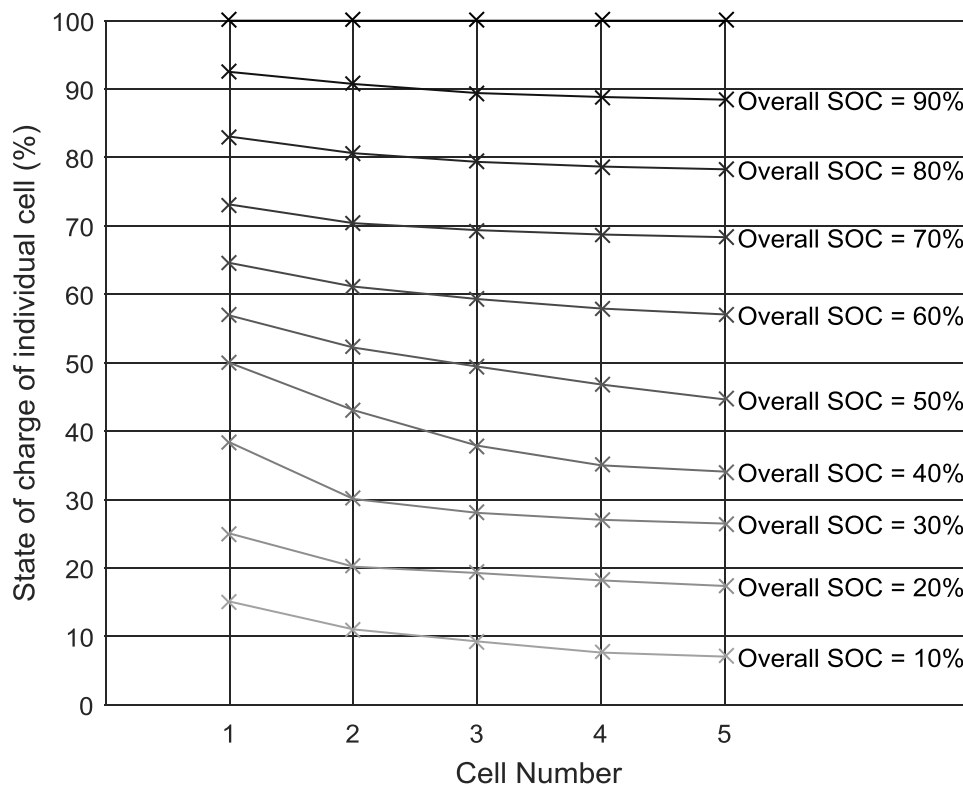


Figure 74 - SOC of each cell in parallel for 0°C to 40°C temperature distribution. The lines get lighter as the discharge progresses, and are at 0.5 Ah steps.

It can be seen in Figure 73 and Figure 74 that initially, all cells begin at 100% SOC, and even after 10% of the discharge there is a noticeable difference in the SOC of the cells at different temperature. As expected, this difference is greater in the case of a temperature distribution of 0°C to 40°C, due to the bigger temperature gradient and therefore larger differences in resistance.

Interestingly, the biggest difference in the SOC of the cells occurs at around 40% SOC, or 3 Ah of discharge. For the cell with a 0°C to 40°C temperature distribution, the difference in SOC for the cell at 0°C compared to the cell at 40°C was 16%. After this point the SOC difference between the different cells narrows.

This effect can be explained by the flat plateau in the voltage curve between about 1.5 Ah and 3 Ah capacity. Due to the low gradient of the voltage curve, the voltage does not change very much as the cell discharges, meaning that hotter cells with lower resistance will provide more of the current, and this will not be compensated for by a large drop in OCV. After about 3 Ah into the discharge, the voltage curves becomes steeper, meaning that less current will flow from the areas at lower SOC as they will have significantly lower OCVs. Additionally, the resistance of the cell shown in Figure 69 is relatively common until approximately 3Ah of discharge, at which point it rises, meaning that as the SOC of the hotter parts of the cell drop, the resistance doesn't rise significantly until the cell reaches about 40% SOC, leading to the hotter cells continuing to provide more current until this point.

In order to explore this effect further, the current provided by the different cells was plotted over the course of the discharge. These plots can be seen in Figure 75 and Figure 76.

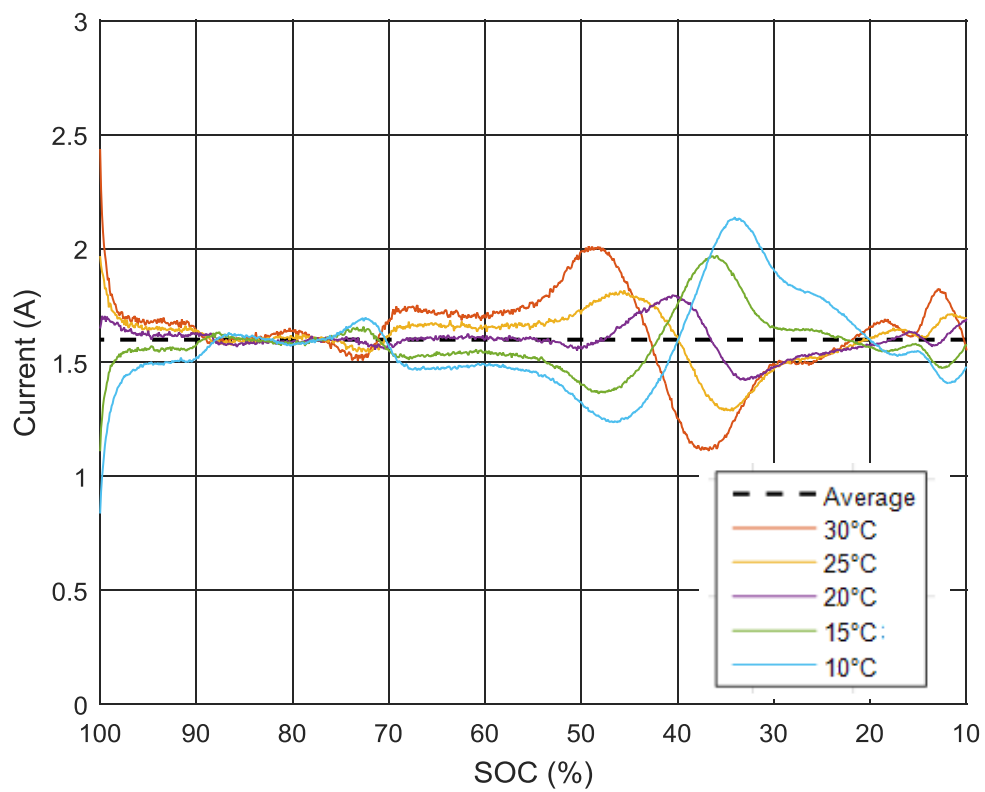


Figure 75 - Current provided by each cell for 10°C to 30°C temperature distribution

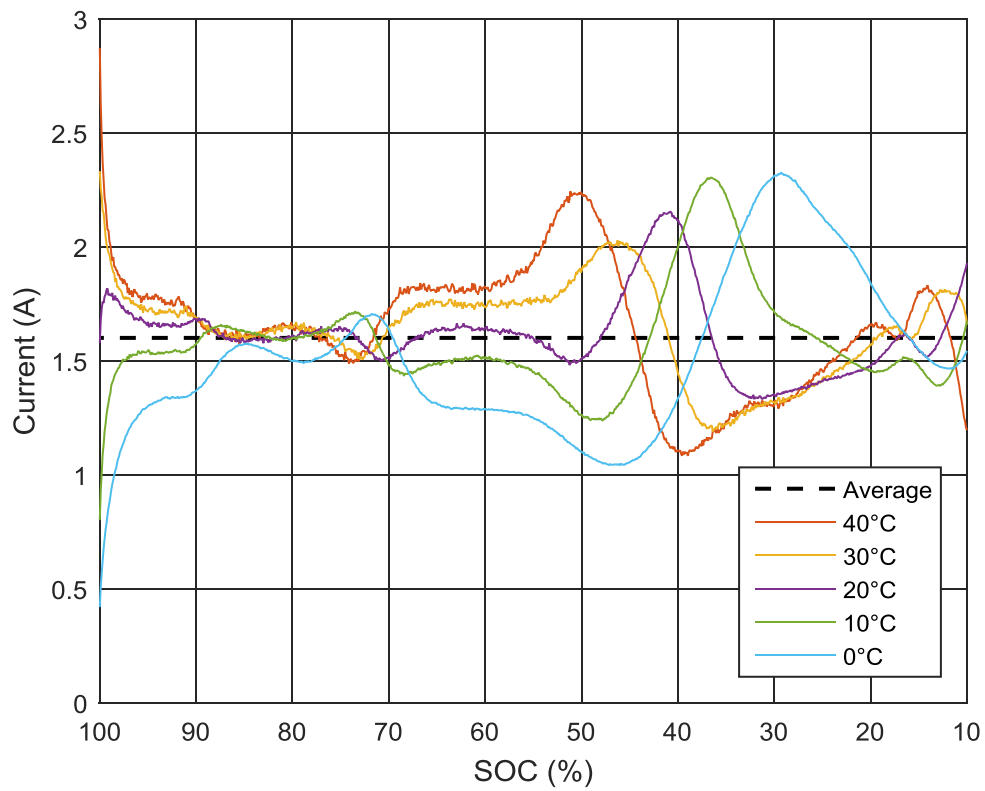


Figure 76 - Current provided by each cell for 0°C to 40°C temperature distribution

Both Figure 75 and Figure 76 show there is significant inhomogeneous behaviour between the cells at different temperatures. Initially, most of the current is provided by the hotter areas of the cell, until the cell reaches about 90% SOC. After this, all areas of the cell provide a similar amount of current, which continues until about 70% SOC, where the hotter areas of the cell begins to provide more current than the cold areas of the cell. This region coincides with a flatter area of the discharge curve.

Between 45% and 40% SOC, this trend is reversed, leading to the hotter areas of the cell providing less current, and the colder areas of the cell providing more current. This does not happen simultaneously; the middle parts of the cell pick up the current load first before becoming depleted, at which point the even colder areas of the cell pick up the majority of the current load. This means that the coldest area of the cell has a current spike at about 30% SOC. Additionally, the cell with the largest temperature distribution, 0°C to 40°C, exhibits more inhomogeneous behaviour than the cell with a shallower temperature gradient.

For both temperature gradients examined, the coldest area of the cell has the highest peak current; 2.14 A for the 10°C to 30°C case, and 2.38 A for the 0°C to 40°C case. For an 8A discharge, each 1/5th of the cell should provide an average of 1.6 A, so these values represent an increase of 34% and 49% respectively. These local peaks and minima in current will lead to a reduction in performance of the cell. Towards the end of discharge, when different areas of the cell have different SOC's, the voltage cut-off will be reached earlier as the hotter areas of the cell become completely depleted and unable to provide any current, leading to most of the current flowing from the colder areas of the cell, which have significantly higher resistance and therefore producing a larger voltage drop.

The temperature distributions used for this study are quite extreme, and might only be seen in real-world applications where the cell begins cold and is subsequently warmed during use. In order to understand how a more realistic temperature distribution will affect a cell, the model was re-run using a temperature distribution of 18°C to 22°C, just a 4°C temperature rise. The current of each part of the cell can be seen in Figure 77.

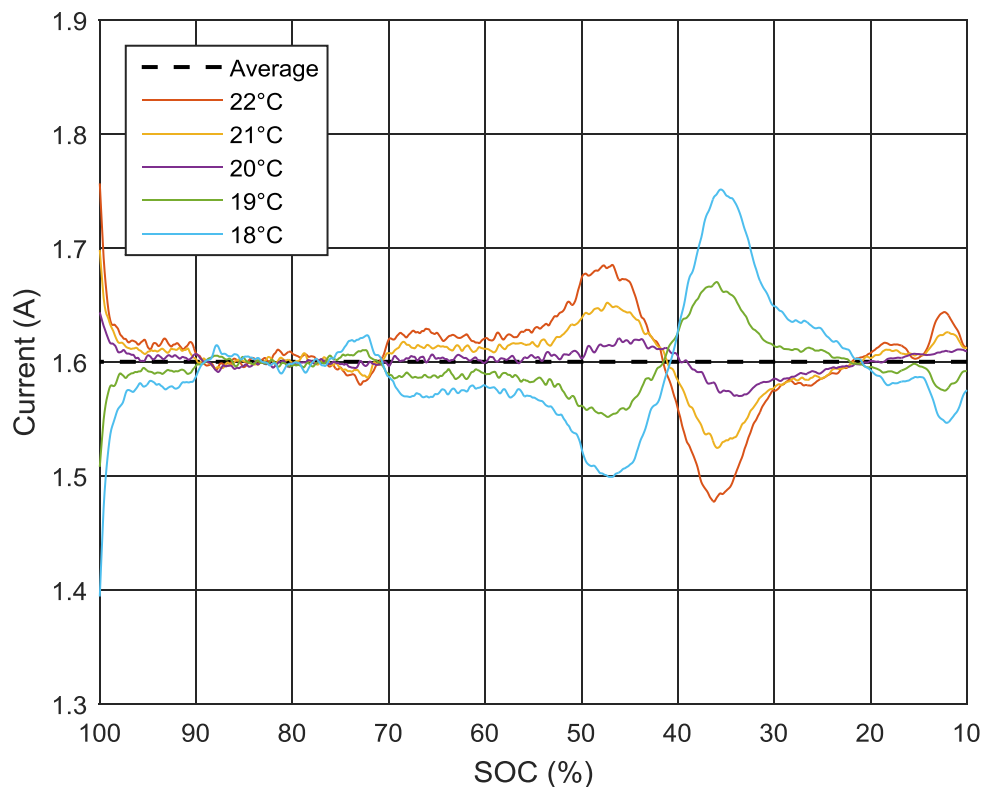


Figure 77 - Current provided by each cell for 18°C to 22°C temperature distribution

Figure 77 shows that even under a small temperature gradient of just 4°C, this is enough to cause a peak in current flow of over 10% of the average current flow.

5.6 Conclusion

Continuing the work conducted by Troxler et al. [12], this work has provided a greater insight into the behaviour of cells whilst under temperature gradients by expanding the work to include dynamic (charge/discharge) behaviour on top of static behaviour.

Similarly to the previous study which was performed in a static condition, when under load the charge transfer resistance of a cell under a temperature gradient is lower than for a cell at a constant temperature equivalent to the average temperature of the cell under a temperature gradient. In effect, when looking at the charge transfer resistance, a cell under a temperature gradient behaves as if it is a “hotter” cell.

Generally, hotter cells exhibit better performance than colder cells, and therefore this result suggest that a cell under a temperature gradient will have better charge/discharge performance than a cell at a constant temperature, however this is not the case. Cells under temperature gradient show lower usable capacity under load, and the voltage curves for cells under temperature gradients are lower than for cells at homogenous temperatures, showing that the effective resistance of the cell is actually higher when a temperature gradient is applied when compared to a cell at a homogenous temperature equivalent to the mean of the temperature gradient.

By using incremental capacity analysis (ICA), it is possible to begin to understand how a cell under a temperature gradient behaves. The peaks on ICA curves are wider and lower for cells under temperature gradients, meaning that the phase equilibria that these represent are occurring at different times for different areas of the cell.

By using a simple data-driven model, it was possible to estimate the performance of a cell at different states of charge and temperature. Whilst the modelling approach was simplistic, the results produced showed similar trends to other in-depth studies looking at the performance of cells at different temperatures and SOC [182–184]. The model corroborated the hypothesis that initially the warmer parts of the cell conduct more current until they become depleted and their voltage drops and resistance rises, at which

point the current must flow from the colder parts of the cell. This is explained in the flow-diagram shown in Figure 68. Any inhomogeneity in current flow stress the cell more, and means that at any point the voltage drop due to internal resistance is higher, reducing the efficiency of a cell and leading to a lower amount of useable capacity and energy that a cell can provide.

Finally, it has been shown that even small variations in temperature can lead to significant inhomogeneities in current flow between different parts of a cell, making this a very important consideration when the design of a thermal management system for a battery pack is considered.

6 Effect of different cooling techniques on performance and degradation[185]

6.1 Introduction

The previous sections in this report have explored the thermal properties of cells, and how temperature gradients affect the performance of cells. An unavoidable consequence of thermal management systems is the build-up of temperature gradients in individual cells, which will affect the performance and degradation of a pack as a whole.

Many studies have shown that increased temperature leads to an increase in the rate of degradation [4,8–11], therefore the effectiveness of a thermal management system is vital in order to maximise the lifetime performance of the pack. The design of a good thermal management system for a battery pack should consider both the overall temperature of the pack and both intra-cell and internal temperature gradients. Poor design of thermal management systems could be a major contributing factor in increasing degradation rates to unacceptable levels [186].

There are many different techniques that can be used to thermally manage batteries in hybrid and electric vehicles. It is possible to use either air or liquid as the cooling medium, and both of these can be used in either a direct (with cooling medium in contact with the cell) or indirect way. In addition to this, different areas of the cell can be cooled, namely the surfaces of the cell or the cell tabs [187,188]. In general, systems employing air as the cooling medium are considered to be simpler and cheaper to implement, although the performance is limited especially in applications where there is a high heat generation rate or if the batteries are being operated in a high ambient temperature environment. In

general, the thermal properties of liquids enable them to remove heat at a greater rate than air when being used as a cooling medium, and therefore are used in applications where large amounts of heat needs to be removed from the batteries, such as in high-power applications.

In addition to standard cooling techniques, there has been some research looking at more esoteric methods of thermal management. These include taking advantage of the latent heat of vaporisation through the use of heat pipes, or using evaporative heat transfer fluids in direct contact with the cells [189–193]. Additionally, solid to liquid phase change materials have been investigated, some employing a slurry of small particles of emulsified paraffin, and some employing carbon sheets impregnated with a phase change material [194–196].

Degradation of lithium-ion batteries is very complicated, with various interdependent mechanisms contributing to both capacity loss (capacity fade) and increased resistance (power fade). Degradation can occur during storage (calendar ageing) and during operation (cycle life), both of which have a strong dependence on temperature [65,66].

Degradation mechanisms include loss of cyclable lithium, as well as the physical breakdown of the anode and cathode materials, and changes at the interfaces of the electrodes and electrolyte [9].

Several studies have used a semi-empirical approach to find an Arrhenius relationship between temperature and degradation [8,142,197–200]. These studies generally treat the cell as a homogeneous system with a single average temperature. Whilst this methodology provides a simple framework for measuring and characterising degradation in lithium-ion batteries, it has been shown that significant temperature gradients can

build up during charging and discharging [156,201], which are ignored when taking this approach.

Battery pack manufacturers spend a large amount of time and resources designing battery packs and thermal management systems that try to maintain each cell in identical thermal and electrical boundary conditions, however the temperature gradients that can build up within the cells themselves can easily be ignored. Additionally, complex battery management systems (BMS) are employed; with increasingly complex models used to estimate the state of charge, state of function, and state of health of each cell in a pack. The BMS then uses this information to make interventions such as de-rating performance, balancing cells or controlling the thermal management system. However if these models treat the cells as lumped thermal masses, and do not take into account variations in temperature during operation, then their effectiveness will be compromised. Additionally, cells are often pre-screened before being assembled into packs in order to group 'similar' cells together to ensure homogenous behaviour from each cell in a pack. In a series string of cells, balancing the capacity is most important to maximise pack capacity. For cells in parallel balancing the impedance is most important to minimise current inhomogeneities between cells.

Section 5 showed how the performance of cells changes under the imposition of a thermal gradient. Additionally, there has been some work exploring the effects of temperature gradients on degradation that show that a temperature gradient increases the rate of degradation of lithium-ion batteries [202].

Previously, a small amount of work has been done looking at different cooling techniques for lithium-ion batteries [178]. This work concluded that temperature gradients limit the

performance of the cells, namely the instantaneous discharge power, especially at low mean temperatures. In contrast there have been many studies exploring the effect of temperature on the performance and degradation of lithium-ion batteries, however most of these studies use forced air convection in thermal chambers in order to control the temperature of the cells. These conditions are rarely indicative of the conditions that a cell will experience as part of a battery pack in a real world environment, and more often than not it is assumed that the temperature of the cell is homogenous and the same as the surrounding air.

This chapter reports for the first time the difference in performance and degradation of cells that are being cooled by different techniques. The techniques were chosen in order to mimic as closely as possible three different thermal boundary conditions that a cell might experience in a battery pack under normal operation, namely cell tab cooling, cell surface cooling and lab-style forced air convection.

6.2 Experimental

5 Ah Kokam pouch cells (model number SLPB11543140H5) were used in this experiment. The cell cooled by forced convection was placed into a Binder incubator set to 20°C with the fan speed set at 100%. The tab cooled and surface cooled cells were placed in custom designed rigs that used Peltier elements to control the temperature of the different surfaces, as shown schematically in Figure 78. Hereafter, the tab cooled cell will be referred to as Cell T, the surface cooled cell as Cell S and the convection cooled cell as Cell C.

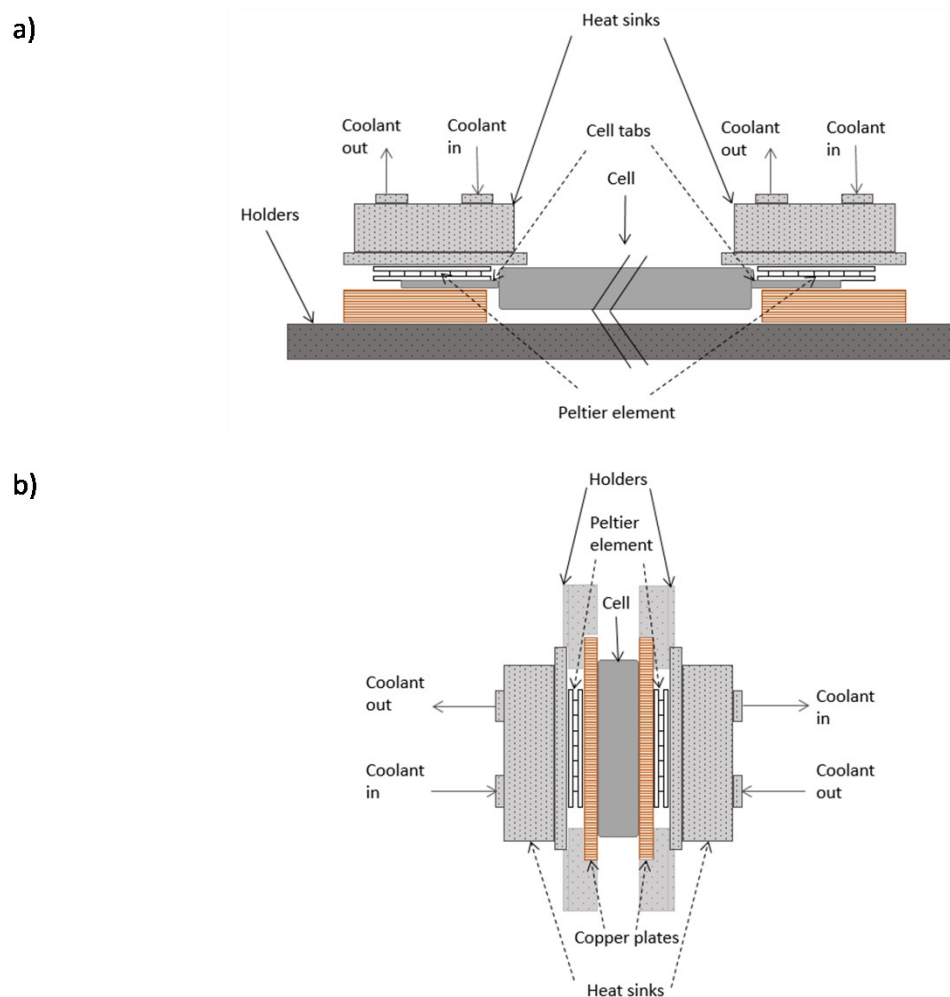


Figure 78 - Schematics of a) cell tab cooling and b) cell surface cooling

The Peltier elements were controlled using a proprietary LabView script utilising PID control, and powered by two Aim-TTi CPX200DP power supplies. Two battery cyclers were used, a Biologic BCS-815 and a Maccor 4000. Brand new cells from the same batch were used with both battery cyclers. The cells were cycled using the Biologic on run 1 and the Maccor for run 2.

The cells were characterised before cycling. On the Biologic, a 1C charge and discharge was performed, along with electrochemical impedance spectroscopy at 2.7 V and 4.2 V.

On the Maccor system, 1C charge and discharges were also conducted, along with a C/20 discharge.

The cells were then cycled using a 6C (30A) discharge, along with a 2C (10A) charge. The cells were cycled between 4.2 V and 2.7 V, without employing any constant voltage mode or any rest period between charge and discharge, to ensure that internal temperature gradients did not have time to dissipate. After every 50 cycles, the cells were re-characterised using the same method.

6.3 Results & Discussion

6.3.1 Temperature Control

For the surface cooled cell, the temperature was kept within +0.5 °C and -1.0 °C at the beginning of the degradation cycles. This level of accuracy gradually decreased as the cell degraded with a maximum variation of +0.7 °C and -1.2 °C measured at cycle 1000. For the tab cooled cell, the temperature was controlled within +0.2 °C and -0.6 °C at the beginning of cycling, and +0.3 °C and -1.0 °C at cycle 1000.

The maximum temperature of the tab cooled cell, measured in the middle of the surface of the cell, was 35.5 °C after cycle 1 and 37.8 °C after cycle 1000. For the surface cooled cell, the temperature of the tabs was measured giving a maximum of 23.0 °C after cycle 1 and 23.2 °C after cycle 1000, however due to the electrical connection made at the tabs and therefore additional cooling effect, it is not thought that the measurements for the surface cooled cell are a good indication of the internal temperature.

6.3.2 Comparison between battery cyclers

Figure 80 and Figure 81 show the measured capacities for the cells cycled during run 1 and run 2 at 1C and 6C. The results are very comparable, with little variation between the measured capacities at both rates and for all cells. This shows that the results are reliable, and not down to differences such as manufacturing defects within the cells being tested. During run 1, some characterisations were completed at intervals other than 50 cycles due to a number of operational errors and no C/20 discharge was measured. For this reason, the data and results from run 2 will be used from hereon in.

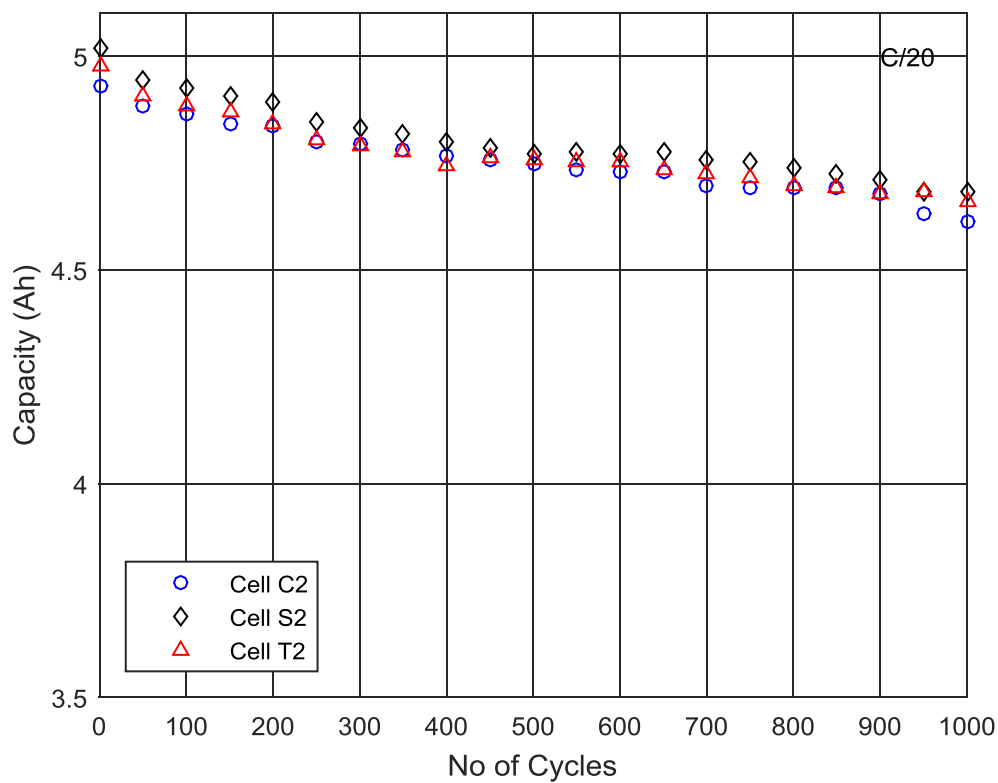


Figure 79 - Capacities of cells at discharge rate of C/20

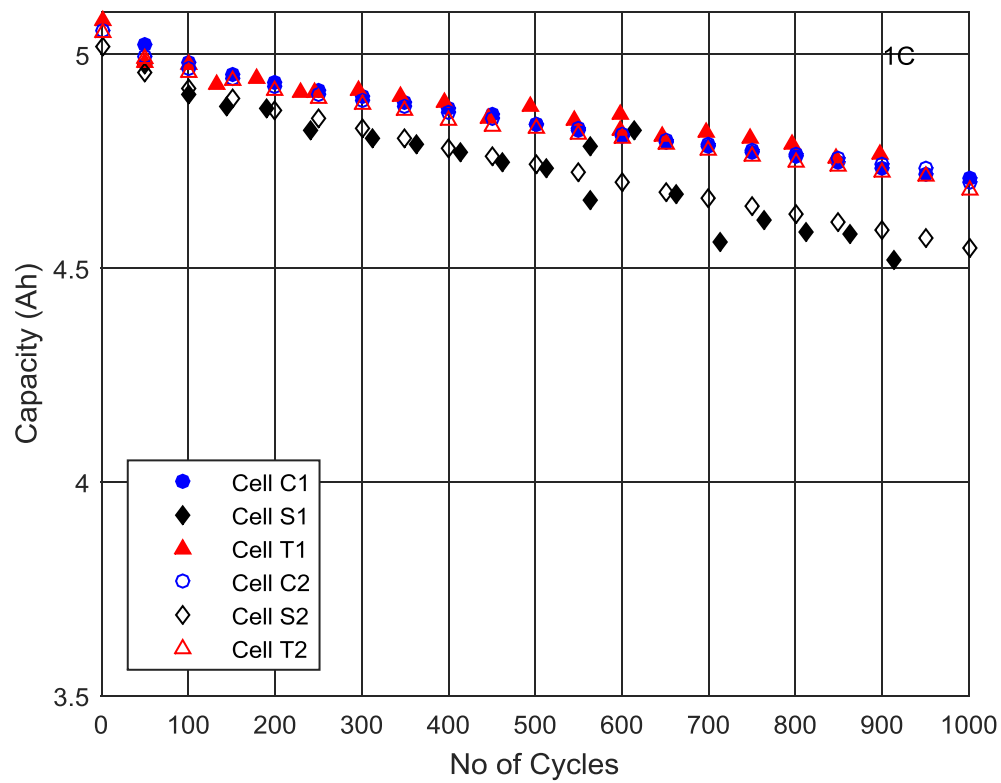


Figure 80 - Capacities of cells at discharge rate of 1C

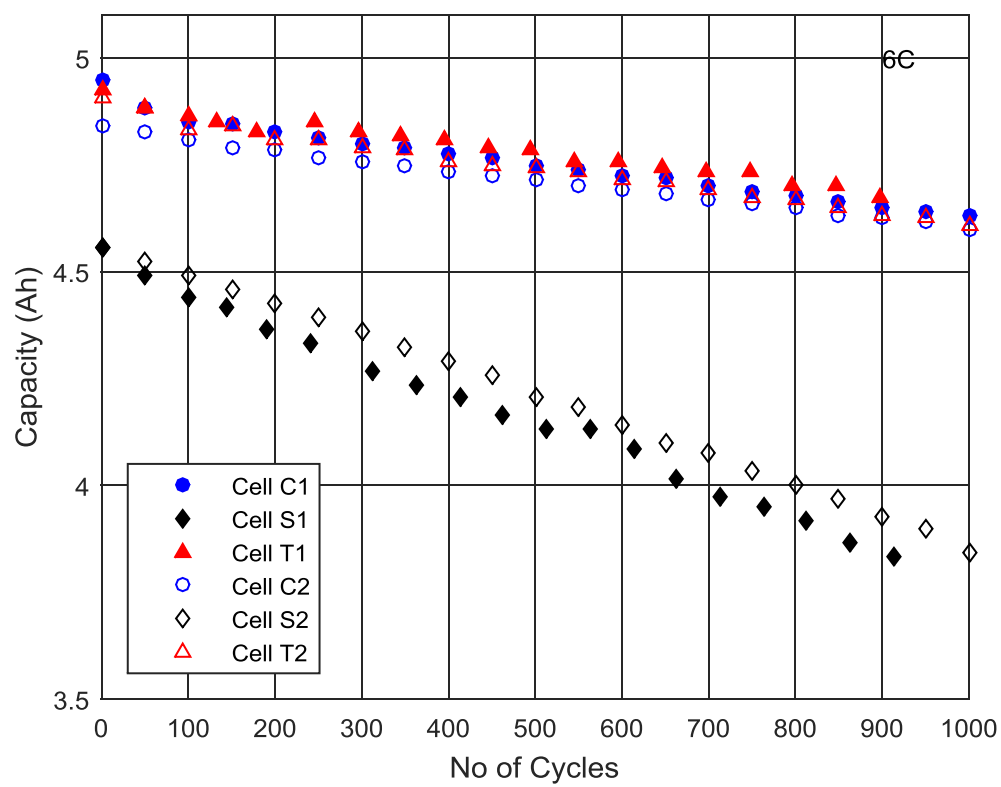


Figure 81 - Capacities of cells at discharge rate of 6C

6.3.3 Changes in capacity

Figure 79 shows the capacity at C/20 against number of cycles for the 3 cells tested by the Maccor and the Biologic. The initial capacities of the three cells were 5.02 Ah, 4.97 Ah and 4.93 Ah for Cell S, Cell T, and Cell C respectively. The loss in capacity when measured at this rate was relatively small throughout the course of the tests, and after 1000 cycles the capacities of the cells had dropped to 4.68 Ah, 4.66 Ah and 4.61 Ah. Table 1 summarises the capacities at the beginning and after 1000 cycles for the various test rates.

Cycle Number	Capacity at C/20 (Ah)		Capacity at 1C (Ah)		Capacity at 6 C (Ah)	
	0	1000	0	1000	0	1000
Cell S2	5.02	4.68	5.02	4.55	4.56	3.84
Cell T2	4.97	4.66	5.05	4.69	4.91	4.61
Cell C2	4.93	4.61	5.05	4.70	4.84	4.60

Table 16 - Capacities at different rates for the beginning and end of cycling

It can be seen that the loss of active lithium during the duration of the tests is small, with the drop in capacity between 4.0% and 6.7%.

Whilst very slow discharge tests give a good indication of the capacity fade, i.e. how much active material has been consumed by processes such as SEI formation, they do not give much information regarding how usable the cells are, i.e. power fade. In order to understand this, the capacities at faster discharge rates must be examined. Figure 80 and Figure 81 show the capacity of the cells when measured at 1C and 6C respectively.

At 1C, the initial capacity of all the cells is very similar to the C/20 tests. Additionally, for Cell T and Cell C, the capacities after 1000 cycles are similar between C/20 and 1C tests.

However Cell S shows different behaviour, with the capacity after 1000 cycles measuring 4.55 Ah, showing a significant decrease in capacity at the higher discharge rate.

At 6C, the initial capacity for all the fresh cells is reduced. This is a reflection of the voltage drop under load triggering the minimum voltage cut-off earlier than at lower C rates. In the case of Cell T and Cell C, the drop in usable capacity is relatively small, with the capacities at 4.91 Ah and 4.84 Ah respectively. In contrast, Cell S's usable capacity is considerably lower at 4.56 Ah. This trend is continued throughout the duration of the test, with the useable capacity of Cell T and Cell C dropping to 4.61 Ah and 4.60 Ah respectively, and usable capacity of Cell S dropping to 3.84 Ah.

Due to the nature of convection cooling, the temperature gradients generated in Cell C will be complex and in multiple directions, and therefore the results for this cell will not be discussed further.

6.3.4 Significance of results

As shown in Figure 81, at higher rates of discharge the usable capacity before cycling of Cell S is reduced significantly in comparison to Cell T. This usable capacity is then reduced further as the cell is cycled. In order to understand whether Cell S had degraded more than Cell T, or if the apparent degradation was caused by the same mechanism as the initial drop in usable capacity for a fresh cell, two further tests were carried out in which Cell S and Cell T were swapped over after 1000 cycles and tested in their opposite test rigs (i.e. Cell S was tested in the tab cooling rig and Cell T the surface cooling rig).

The discharge curves at 6C (30 A) can be seen in Figure 82. When swapped to the surface cooling rig, Cell T loses some of its usable capacity, and Cell S gains some when placed in

the tab cooling rig. When comparing the discharge curves of both cells during tab cooling, the voltage curve of Cell S is consistently lower than Cell T, and the final usable capacity is slightly lower at 4.54 Ah compared to 4.61 Ah for Cell T.

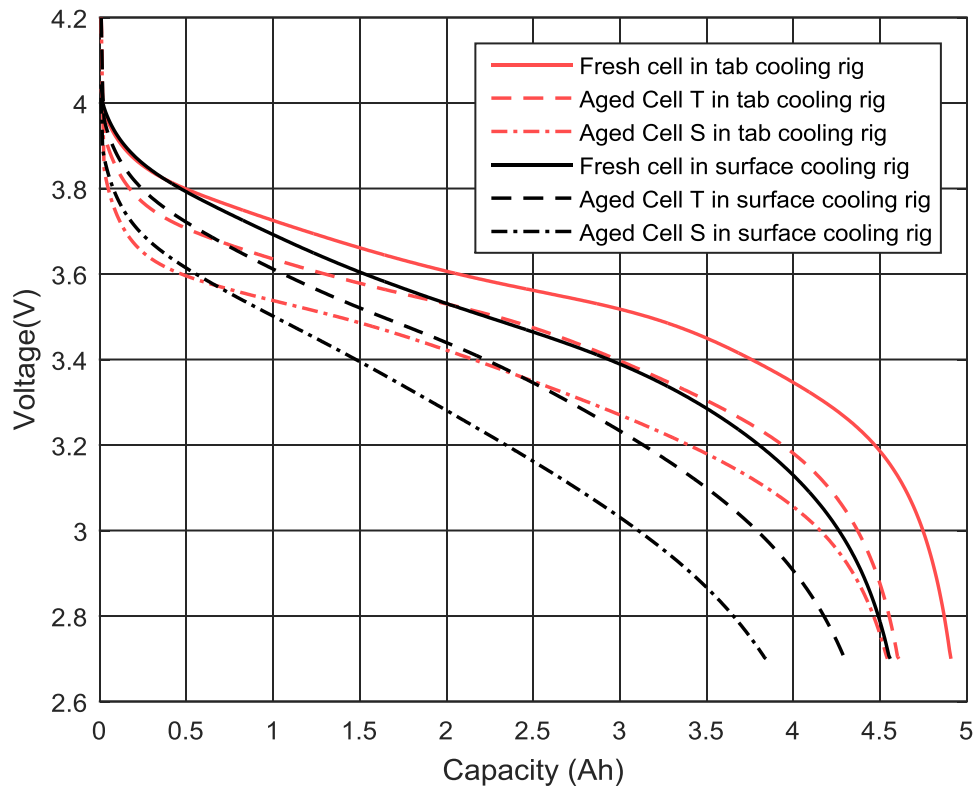


Figure 82 - Discharge curves of surface and tab cooled cells at 6C (30A) in both rigs

A similar trend is seen when comparing both the cells in the surface cooling rig. The voltage of Cell T is higher than that of Cell S, and the usable capacity of Cell T is significantly higher than that of the Cell S at 4.30 Ah compared to 3.84 Ah. Therefore, they are not in the same state, and have degraded differently. The difference is not just an effect of the cooling conditions.

One possible explanation for the lower useable capacity for Cell S at the beginning of life is that the mean temperature is lower than that of Cell T. However, it is accepted that higher temperatures lead to faster rates of degradation, and therefore this theory would

predict that cell T should degrade at a faster rate, and therefore this result cannot be predicted using average temperature alone.

In Figure 82 after 1000 cycles the voltage curves for Cell S are always below that of Cell T, both when both cells are in the surface cooling rig, and when both cells are in the tab cooling rig. This indicates that the cause of the drop in usable capacity under load is an increase in the impedance of the cell. In order to consider the effects of lower usable capacity and increased resistance, the amounts of energy that the cells provided during discharge were examined and these can be seen in Figure 83. When both cells were discharged in the tab cooling rig, the amount of energy Cell T provided was 15.9 Wh compared to 15.2 Wh for Cell S. When both cells were discharged in the surface cooling rig, the amount of energy that Cell T provided decreased to 14.5 Wh, compared to Cell S which provided 12.6 Wh. This shows that the two effects, the drop in useable capacity caused by the different temperature profiles during surface cooling, and the drop in useable capacity caused by the increased rate of degradation, can be de-coupled and quantified separately.

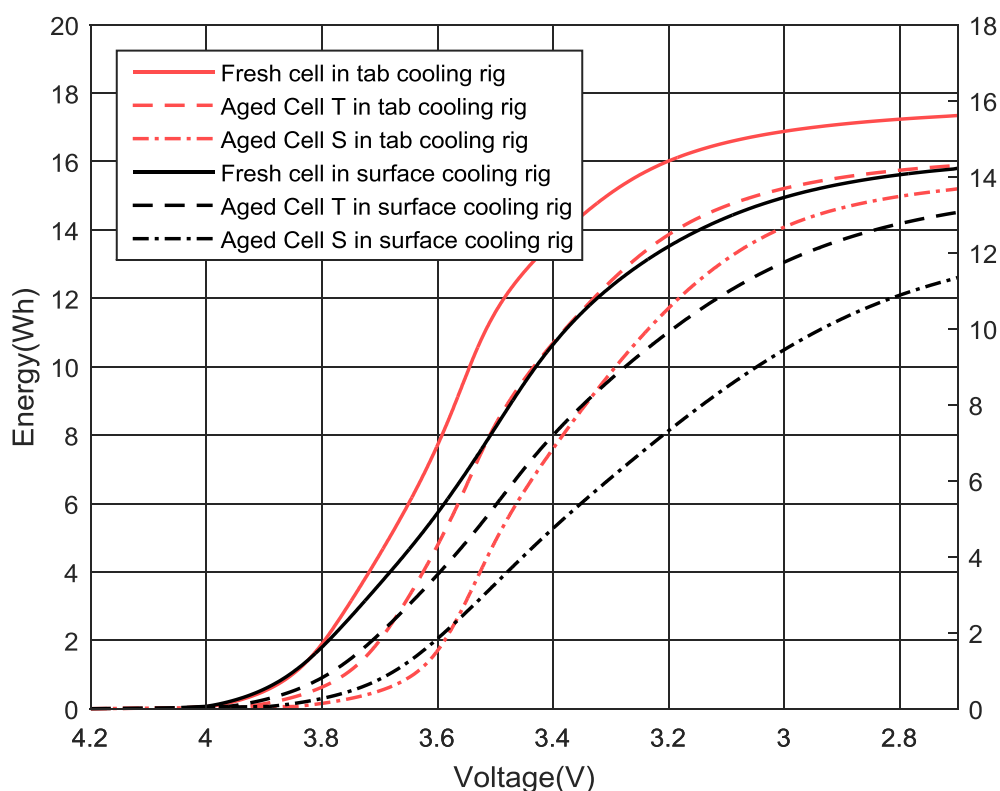


Figure 83 - Cumulative energy curves surface and tab cooled cells at 6C (30A) in both rigs

6.3.5 Electrochemical Impedance Spectroscopy

Further characterisation using Electrochemical Impedance Spectroscopy (EIS) was conducted every 50 cycles on the cells cycled using the Biologic. Impedance was measured using a 0.2A amplitude current at frequencies between 1 Hz and 2 kHz, with the cell at 4.2V and 20°C.

Figure 84 shows a selection of EIS spectra for both Cell S and Cell T and this shows that there is very little change in the high frequency part of the spectra, however the low frequency semi-circle increases with cycling for both cells, but with a significantly larger increase for Cell S.

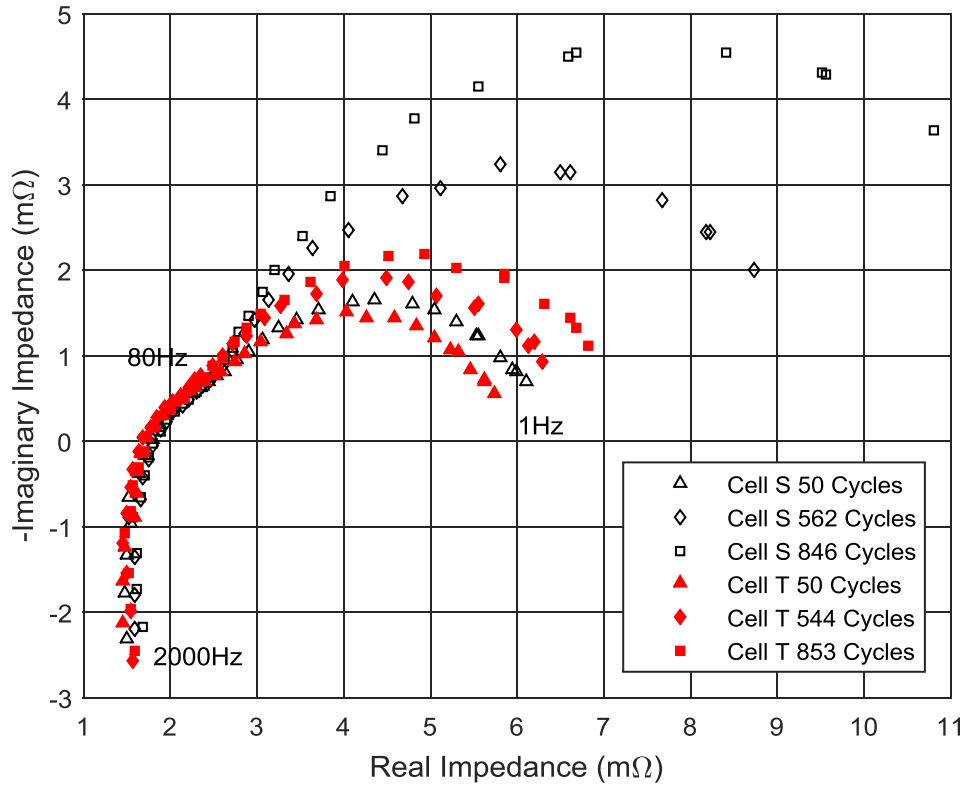


Figure 84 - Example EIS spectra from Cell T and Cell S

The spectra were then fitted to the equivalent circuit model shown in Figure 14 using Zview software (Scriber and Associates Inc.), and R_2 , which represents the size of the low-frequency semi-circle is shown in Figure 85. R_2 is commonly attributed to the polarisation or charge-transfer resistance of the rate limiting electrode [203]. For both cells, the increase in R_2 is relatively linear, however the increase is significantly faster for Cell S than Cell T, which reinforces the conclusion that the surface cooled cell degrades at a faster rate.

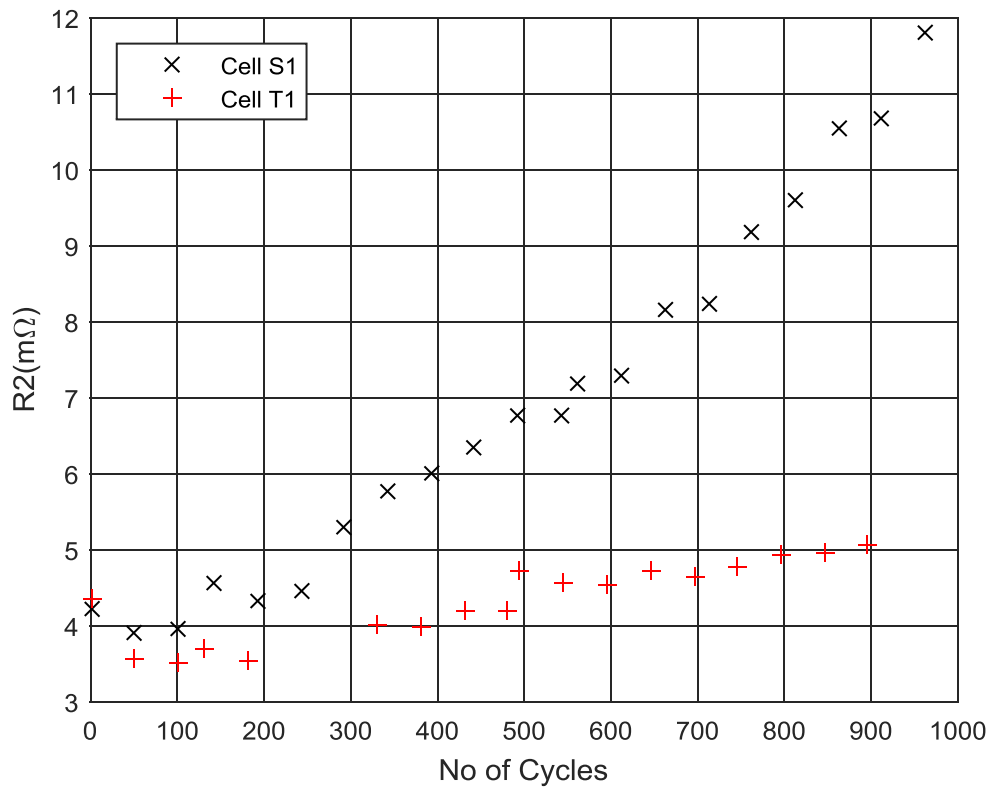


Figure 85 - Changes in parameter R2 plotted against number of cycles for Cell T and Cell S

6.3.6 Incremental Capacity Analysis (ICA)

Another technique that can be used to diagnose degradation is Incremental Capacity Analysis (ICA) [122,204]. Here, dQ/dV , approximated as $\Delta Q/\Delta V$, is plotted against voltage and can be seen in Figure 86 to Figure 88. The results were calculated from the C/20 discharges. The data were quite noisy, and therefore was smoothed using Matlab's 'smooth' function (The Mathworks, Inc.). Once the data had been smoothed, the residuals were calculated to check that the mean did not deviate from zero in order to ensure that no artefacts were introduced by the smoothing process. In Figure 86 to Figure 88, the lines get lighter as the number of cycles increases, and are taken every 50 cycles.

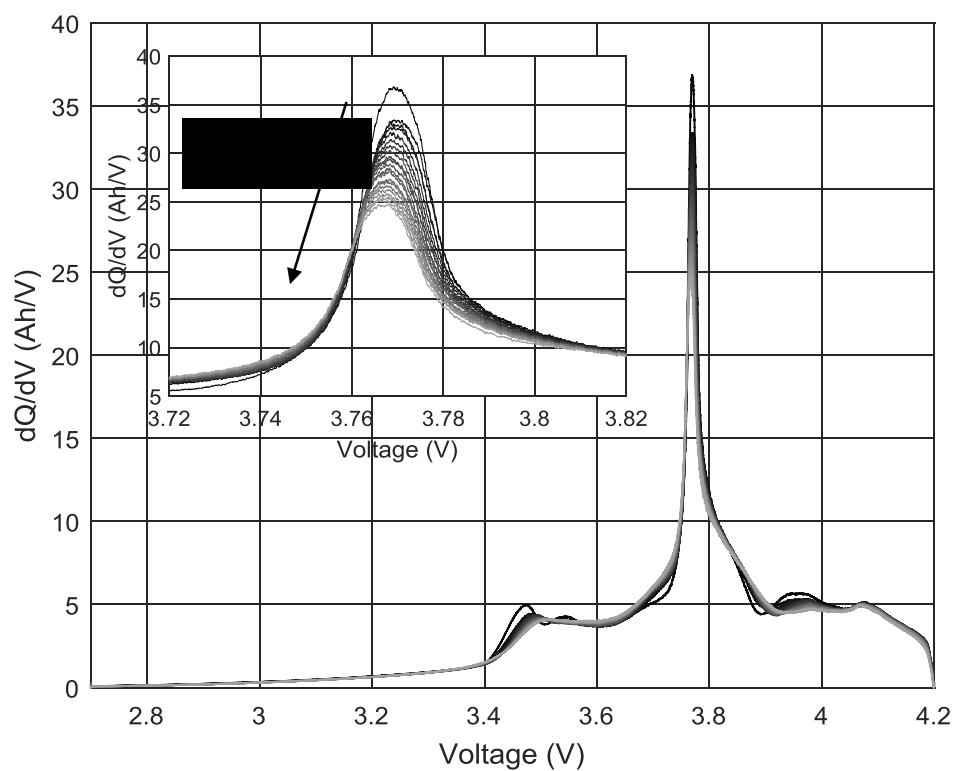


Figure 86 - Incremental capacity analysis for Cell T

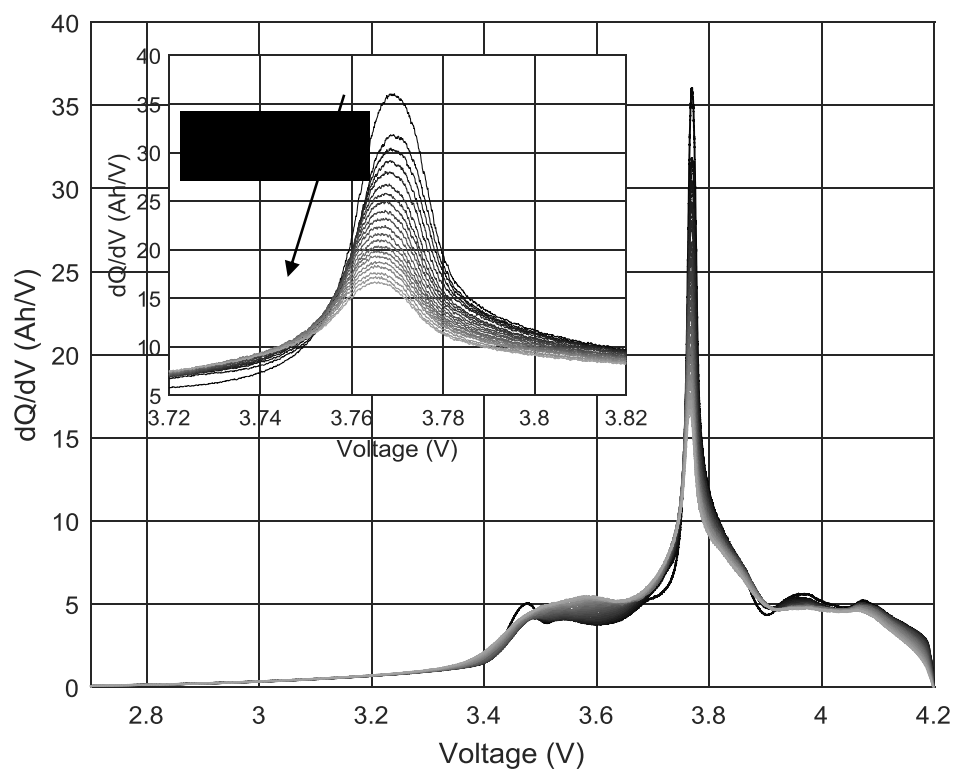


Figure 87 - Incremental capacity analysis for Cell S

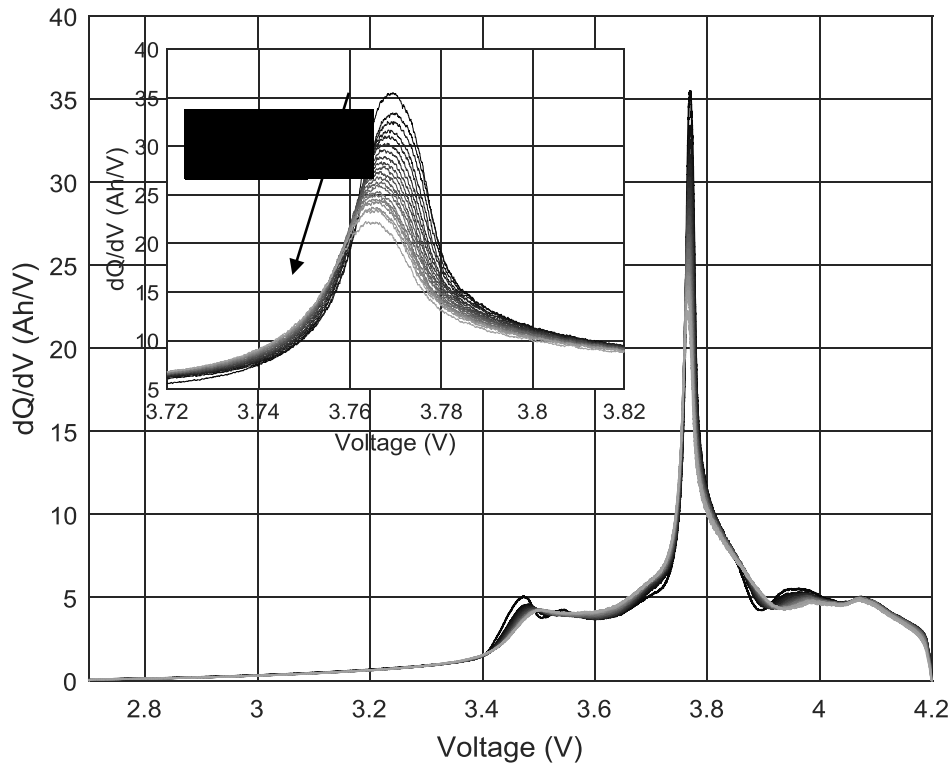


Figure 88 - Incremental capacity analysis for Cell C

All three sets of data have similar characteristics with a large peak at around 3.75 V and smaller peaks at around 3.5 V and 3.95 V. Figure 86 to Figure 88 also include a close-up of the top of the peak at 3.75 V for each cell. Large peaks on a dQ/dV plot indicate phase equilibria, and it can be seen quite clearly that the peak for the Cell S moves significantly more than the peaks for the Cell T and Cell C. For the fresh cells, the amplitudes of the peaks are quite similar at 36.62, 36.00 and 35.53 Ah/V for Cell T, Cell S and Cell C respectively. However, in the same order, the final magnitudes are 24.63, 16.61 and 22.22 Ah/V. This is a significant change, and indicates that Cell S has degraded differently to Cell T and Cell C.

6.3.7 Further Analysis

In order further analyse the results, it is important to understand how these cells are constructed and their thermal properties. These cells are the same as used in Section 4,

and photographs of their internal structure can be seen in that section in Figure 26 to Figure 30. These show that the cells are constructed from alternating layers of anodes and cathodes, separated by a continuous concertinaed separator membrane. The current collectors are coated on both sides by electrode material, apart from the first and last collectors, which are coated only on the side facing inwards. In total, there are 100 anodes and cathodes, on 50 copper (anodic) current collectors and 51 aluminium (cathodic) current collectors. The dimensions of these layers is given in Section 4.

In the case of surface cooling, the thermal resistance of the cell was calculated in in Section 4 and found to be $2.64\text{ }^{\circ}\text{C/W}$. In the case of tab cooling, the thermal resistance of this specific cooling case could not be calculated, however the overall resistance was found to be $9.94\text{ }^{\circ}\text{C/W}$. For this specific case, due to the control temperature measurement location being next to the active material and not on the cell tab itself, the thermal resistance will be significantly lower than this. A better understanding of the thermal resistance in this case would be to look at temperature measurements 2 & 6 in Figure 34 in Section 4, which gives a thermal resistance of $3.9\text{ }^{\circ}\text{C/W}$, which is relatively similar to the result found for the surface cooling case.

Due to the nature of the cooling in this case, where the temperature of different surfaces is held at a constant temperature, the heat transfer coefficient, h , will vary depending on the amount of heat generated, and therefore it is not possible to use the Biot number to understand the thermal gradients with these cells. However, if the resistance measurements from Section 5 show that these cells have a resistance of about $7\text{ m}\Omega$ at 20°C and 50% SOC, and this combined with a current of 30 A gives an approximate heat generation of 6.3 W . Using the thermal resistance values above with this heat generation

gives a temperature difference of 16.6°C for surface cooling and 24.6°C for tab cooling. It has been shown previously that the resistance of cells, and therefore the heat generation, varies greatly with current and SOC, and therefore these numbers should be used for illustrative purposes only, however they do show that the temperature gradients within these cells will be significant.

In order to explain these results, the structure of the cell was looked at in more detail. Rather than treating the cell as a single cell, it can be thought of as 100 small cells in parallel with each other. In the surface cooling case, each of these small parallel cells will be at a different temperature depending on how close they are to the edge of the cell. Therefore each layer should have a relatively uniform temperature, but with significant differences in temperature between layers. A schematic of this can be seen in Figure 89.

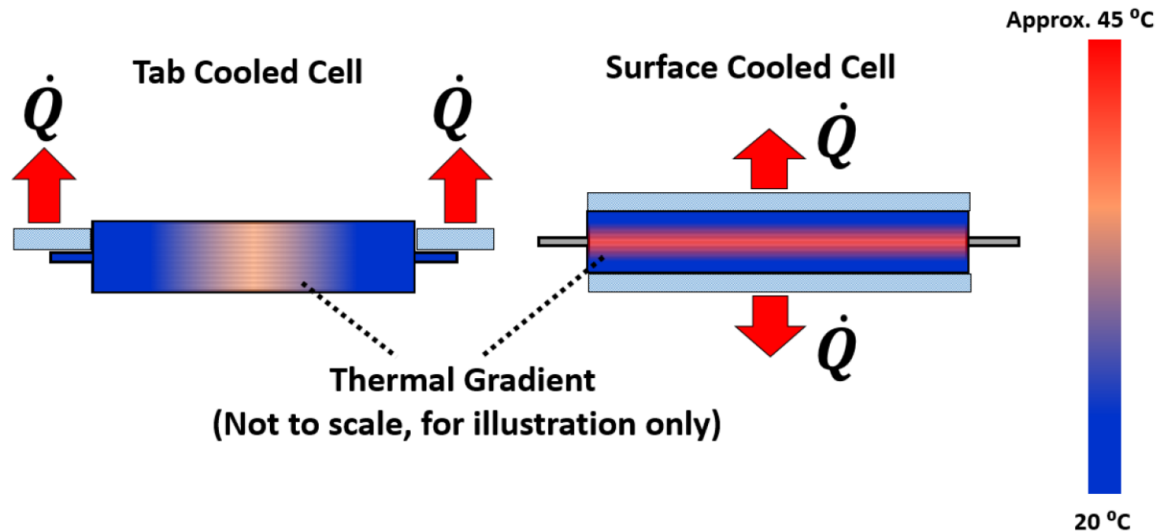


Figure 89 - Schematic of temperature gradients in cells subjected to different thermal boundary conditions

During the discharge, the hotter (more central) areas of Cell S will have a lower resistance and therefore provide more current. Heat generation is a function of the current squared, and therefore these areas of the cell will heat up even more, reducing the resistance further and contributing at times to a positive feedback mechanism. Additionally, the

heat is generated at the centre of the cell; the furthest point from the thermal management system. It has been shown previously that uneven temperatures can lead to inhomogeneous current flow in a parallel string of cells in a battery pack [144]. The construction of these cells is analogous to a parallel string of cells, leading to inhomogeneous current flow between the layers.

This effect can be used to explain why the fresh, uncycled, surface cooled cell exhibits a lower usable capacity at high rates than the tab or convection cooled cells. At the beginning of discharge the central layers of the cell will warm up faster and their impedance will drop and they will be discharged faster, such that by the end of discharge the majority of the current will flow from the outer layers of the cell. These areas are close to the cooling plates, and therefore will be much closer to 20 °C than the centre of the cell. The colder temperature inhibits solid-state diffusion and increases the polarisation resistance, which when coupled to the higher relative current flowing through these areas of the cell, results in the voltage cut-off of 2.7 V being reached much sooner, reducing the usable capacity of the cell.

It has also been shown that degradation is highly dependent on current [5]. If the cell is thought of as 100 small cells under a temperature gradient, uneven current will flow and therefore each “small cell” will see periods of higher current flow compared to the average, leading to a localised increased rate of degradation. The increased rate of degradation under temperature gradients has been shown previously [202].

The same processes will not occur in the case of cell tab cooling, where assuming purely 1-D heat transfer, all the electrode pairs will have the same temperature profile as each other, even though there will be a temperature gradient along the length of the layers.

Therefore although this temperature gradient will cause current inhomogeneities during discharge there is no positive feedback between the layers as they all behave and degrade relatively uniformly.

To confirm that at higher rates, the different layers of the surface cooled cell are at different states of charge, the ICA was examined for the fresh cells in the surface cooling and tab cooling rigs before cycling. Therefore the cells are identical except for the thermal boundary conditions during the discharge. Peaks in the ICA curves indicate phase equilibria, and as can be seen in Figure 90 the largest peak is the same for both cells at C/20 but is significantly wider and less intense for the surface cooled cell at higher rates. This indicates that these phase equilibria are happening at different points on the discharge curve for different layers of the surface cooled cell, and therefore take longer and are less intense, indicated by the flattening and widening of the peaks on the graph.

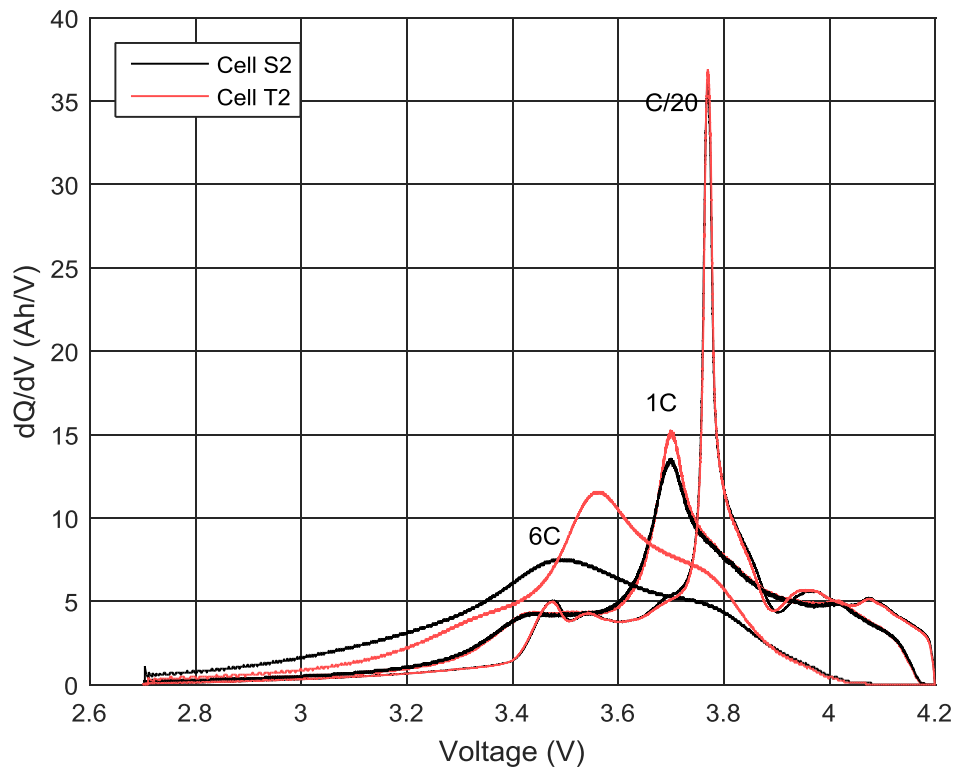


Figure 90 - dQ/dV plots for Cell S and Cell T before cycling at different rates

6.4 Conclusion

The effect of three different thermal management strategies, cell tab cooling, and cell surface cooling, and forced air convection, on the performance and degradation of lithium-ion batteries was investigated for the first time. 5Ah NCM cathode pouch cells were tested for 1,000 cycles with a 6C discharge and 2C charge between 4.2 V and 2.7 V voltage limits whilst being held at the same target temperature of 20 °C. Characterisation cycles were performed every 50 cycles to measure capacity fade, power fade and impedance.

All three strategies led to similar reductions of nominal capacity of around 7% measured at C/20. However, at higher rates, discharging the cell in around 10 minutes, surface cooling led to a loss of useable capacity of 9.2% compared to 1.2% for cell tab cooling. After cycling the cells for a 1,000 times, surface cooling resulted in a loss of usable capacity three times higher than cell tab cooling.

This is caused by two effects. Firstly, due to the way the cells are designed, surface cooling causes each parallel internal layer to be at a different temperature and therefore behave differently during discharge, whereas tab cooling causes each parallel layer to behave the same. For surface cooling this leads to non-uniform impedance and therefore non-uniform currents between layers, reducing usable capacity. Secondly, the non-uniform temperatures and currents then cause non-uniform ageing, such that although the same amount of active lithium has been lost in both cases, for surface cooled cells this degradation is distributed unevenly, which causes higher overall cell impedance, i.e. power fade, resulting in voltage cut-offs under load being reached earlier.

Many current battery applications using pouch cells employ surface cooling, taking advantage of the large surface areas of these cells, however this work suggests that this could lead to a significant loss of performance and increased rates of loss of useable capacity under load. Therefore this study shows the vital importance of understanding how cells perform under different thermal conditions before beginning the design of a battery pack and thermal management system.

In a recent MIT technology review, [44] the difficulties of introducing new technologies, such as new electrodes, were discussed including how this can lead to unforeseen problems that may only come to light after years of testing. In contrast, many of the biggest advances in battery technology have come via small incremental changes, often in the way a cell or pack is engineered rather than new cell technologies. Cooling cells via the tabs rather than the surfaces is an example of an improvement to battery pack engineering.

For automotive applications where 80% capacity is considered end-of-life, using tab cooling rather than surface cooling would therefore be equivalent to extending the lifetime of a pack by 3 times, or reducing the lifetime cost by 66%. Nykvist et. al. [48], found that costs of battery packs declined by around 14% annually between 2007 and 2014. Whilst this reduction was due to a variety of sources, it was found that the main reason was due to input material cost. By significantly reducing the level of degradation, using methods such as those shown in this paper, the costs of battery technology can be reduced further in order to make battery- and hybrid-electric vehicles cost competitive with conventional internal combustion powered vehicles. It is important to note that

alongside cell development, battery pack engineering will need to play an important role in making this a reality.

The impact of this work will be most important in high-rate applications such as in the automotive industry. Thermal management systems employing cell tab cooling should be looked at in much more detail, and possible changes to cell construction in terms of dimensions, cell tab location and the number of layers used in a cell should be explored in more detail, either to improve the performance of cell tab cooling thermal management systems, or to reduce the negative consequences of using surface cooling.

7 Conclusion

The aim of this work was to further understand how batteries behave in different thermal conditions. A number of examples were given showing the difficulties that can arise when testing lithium ion batteries under difficult thermal conditions, and the techniques that can be used to mitigate these difficulties. In addition to this, an example of testing a battery under pseudo-adiabatic conditions was given, showing increased useable capacity under a faster discharge rate, highlighting the importance of good experimental design and thermal boundary layer control when testing batteries in a laboratory.

The thermal properties of cells were investigated, and a novel approach using cells of different sizes was used in order to measure the thermal properties of cells, especially looking at the contribution of the cell casing and its effect on the overall thermal conductivity of a cell. The measured thermal conductivity through the layers of the active material in a cell in this study was significantly different to the thermal conductivity that was calculated using the most commonly used literature values, showing the importance of measuring the thermal conductivity of different cells when looking at the design of thermal management systems, and for the parameterisation of thermal models of lithium ion batteries. The method proposed was simple and could be applied to many types of cells, with the rig calibrated to an acceptable level using materials of known thermal properties.

It was not possible to isolate the thermal conductivity of different components through the length of a cell due to the difficulty in understanding the thermal interface between

the cell tabs and the current collectors, however a method was proposed to understand this effectively if the resources were available.

The effect of temperature gradients on the performance of lithium ion batteries was investigated, and it was shown that temperature gradients can have a large effect on the characteristics of a cell when under load. In contrast to previous work, it was shown that under a temperature gradient, although the charge transfer resistance is lower than for a cell at a homogenous temperature, the overall resistance of a cell under a temperature gradient is higher, leading to the voltage curve under discharge being lower, and the cell performing less efficiently.

Using a simple data-driven model, the performance of cells under temperature gradient was reproduced, and these results showed that the current provided from different areas of a cell under a temperature gradient is very inhomogeneous. At different points during discharging a cell, some areas have to work much harder than others, with the hotter areas of the cell providing most of the current towards the beginning of discharge and the colder areas of the cell providing most of the current towards the end of discharge. This inhomogeneity leads to the cut-off voltage being reached sooner, reducing the useable capacity of the cell. Even under small temperature gradients of just 4°C throughout the cell, at different points during the discharge some areas of a cell see a current of over 10% of the average. This shows how important temperature gradients are when looking at the performance of cells, and when modelling lithium ion batteries.

Finally, the effect of different cooling techniques on the performance and degradation of lithium ion batteries was investigated. It was found that cooling the cells via the tabs rather than cooling the cells via the surface was a much more effective method, leading

to much higher useable capacity and a much lower rate of degradation. It was shown whilst surface cooling led to significantly lower capacity when the cell was discharged at a high rate, it also led to a rate of degradation that was higher, meaning that after 1000 cycles, the performance of the cell could not be recovered by swapping the cell to a tab cooling regime.

The aim of this thesis was to highlight the importance of good thermal management on the performance and degradation of batteries. Whilst it is well known that batteries require cooling to reduce degradation, and increasing the temperature improves the instantaneous performance, this thesis has shown the thermal management is more complicated than simply cooling cells down to a certain temperature during their use.

7.1 Further work

Whilst this thesis explores the importance of thermal management of lithium ion batteries, there are a number of areas where more work needs to be done in order to fully understand the effects of thermal management on performance, and use this knowledge to inform better battery pack and thermal management design.

Whilst a simple method was developed to measure the thermal conductivity of cells, it was not possible to measure fully the thermal properties in one direction along the cells, and this should be looked at in more detail using the method proposed above. In addition to this, the technique could be developed so that it can be used on different form factors of cells, such as larger format pouch cells and cylindrical cells.

The effect of thermal gradients on the performance of cells was measured and then subsequently modelling under forced thermal gradients, with the results of the modelling

matching well to experimental data under forced thermal gradients. This work can be expanded to understand the effect of thermal gradients on charge performance, and to understand how thermal gradients might affect battery performance when subjected to noisy load cycles.

The effect of different cooling techniques was explored, showing that cooling the tabs of pouch cells leads to better performance and lower rates of degradation. The next step in this work is to model these effects and use the results to fully understand the drivers behind the reduction in performance and increased levels of degradation. Surface cooling of cells is used in many automotive applications, and whilst this work showed that tab cooling has the potential to be much more effective, a good model showing the mechanisms of why this is the case would make the argument for tab cooling much stronger.

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9 Appendix A [205]

9.1 Introduction

Lithium batteries suffer from a number of safety concerns which limits their use in some applications. Nail penetration tests are used by the battery industry to compare the safety of different batteries during an incursion by a metallic object through a battery that physically violates the containment and locally damages the internal structure. For most lithium chemistries, such as mixed metal oxide or lithium iron phosphate cathodes, these tests result in rapid and dangerous failure. Lithium sulfur is an important next generation ultra-high energy density battery chemistry which can also be inherently safer. This section shows the results of nail penetration on lithium sulfur cells, showing how they heat up by less than 10°C during a 10 minute penetration and then cool down rapidly after removal of the nail. Thermal imaging was used to show the temperature distribution over the surface of the cell, giving a much more accurate picture of how the cell heats up during nail penetration than would be possible with discrete temperature measurement techniques, such as thermocouples or thermistors.

9.2 Experimental

16Ah pouch cells were provided by OXIS Energy (Abingdon, UK), and had dimensions of 180x75x8mm. These cells were produced for Lincad Ltd. (Ash Vale, UK) and the Defence Science and Technology Laboratory (Dstl) as part of a research programme to produce safe, lightweight batteries for military use. The cells were fabricated in a dry room maintaining a dew point of -50°C. The electrolyte used was a proprietary ether based variant containing less than 30 ppm of water. The cathode consisted of a sulfur-carbon composite slurry coated onto both sides of an aluminium foil current collector, the

composite was a minimum of 70% Sulfur. 50 μm Lithium foil (Rockwood Lithium) served as anode and current collector and a 12 μm polypropylene separator (Toray) was used to prevent electrical contact between electrodes.

A thermal imaging camera (FLIR A655sc) was used to monitor the surface temperature of the cell around the nail penetration site, and the cell was painted black using Krylon paint. Multiple T-type thermocouples were also positioned on the opposite side of the cell in order to validate the thermal imaging data, as shown in Figure 94. The data from the thermocouples was logged using a Grant Squirrel Data logger (model 2F16).

A 2.5mm diameter steel nail was used to fully penetrate the cell. Six tests were conducted, three at open circuit on fresh cells, two at open circuit on cells that had been cycled until they had been degraded to 80% of their initial capacity, and one fresh cell that was being discharged at 1.6A (C/10). For the open circuit tests, the voltage was measured using a squirrel data logger. The test under load was carried out using a Metrohm Autolab Potentiostat/Galvanostat (Autolab PGSTAT30) with a 10A Booster (Autolab BSTR10A) connected. The potentiostat was controlled using the software Nova.

Prior to each test, the cells were charged to between 2.42V and 2.47V, which relates to over 95% SOC. For each test the nail was removed after between 9 and 11 minutes, and data was continually logged before, during and after penetration.

9.3 Results and discussion

Figure 91 shows the voltage traces of the tests. During penetration the open circuit tests show a voltage drop of between 0.020V and 0.026V, and the test under load shows a drop of 0.015V. With the nail inserted the voltage of all of the cells drops at a steady rate

and all cells see a rise in voltage when the nail is removed, indicating that the cells are discharging through the nail. After removal, the voltage of the cells at open circuit rise and then level off, indicating that the severity of short-circuit is reduced with the removal of the nail. The voltage of the cell under load rises a little and then continues to fall due to the ongoing discharge.

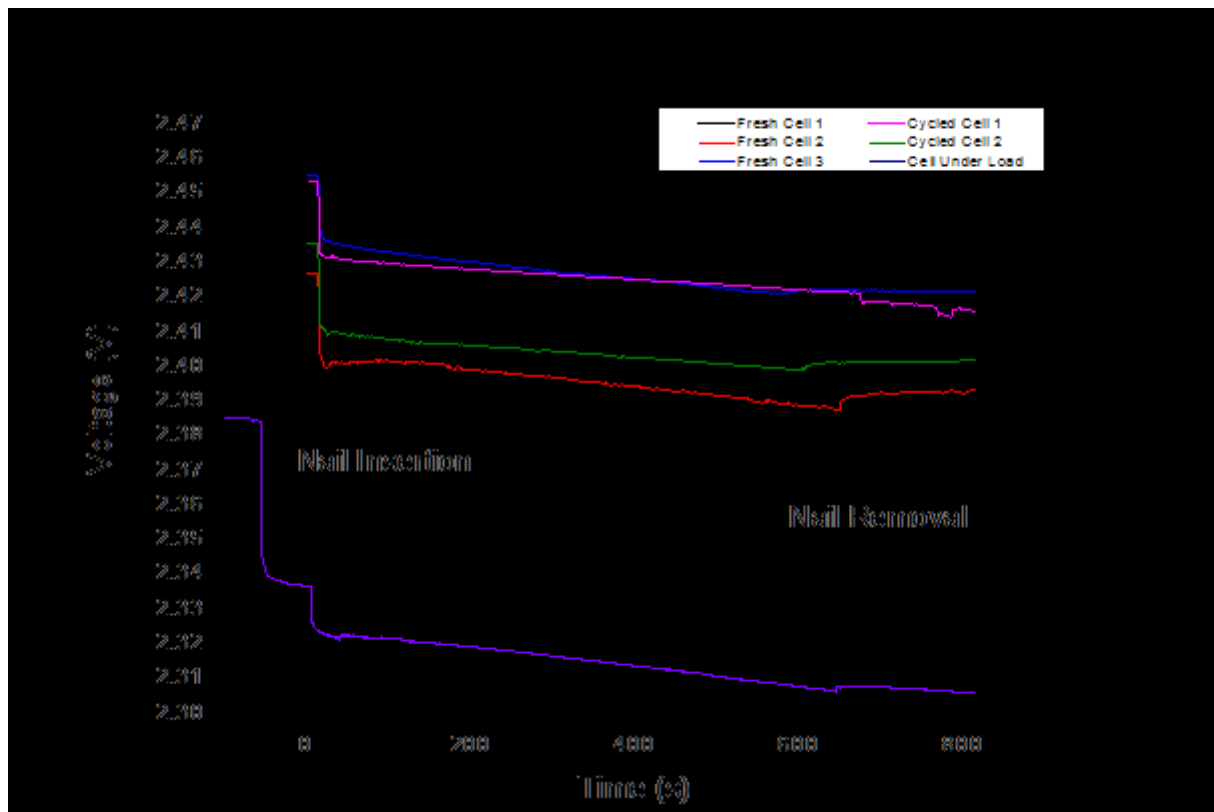


Figure 91 - Graph of voltage vs time for the nail penetration tests

During and after nail penetration, no smoke, flames or charring were observed, and there was very little electrolyte evacuation from the penetration hole. The painted surface of the cells can be seen in Figure 92.

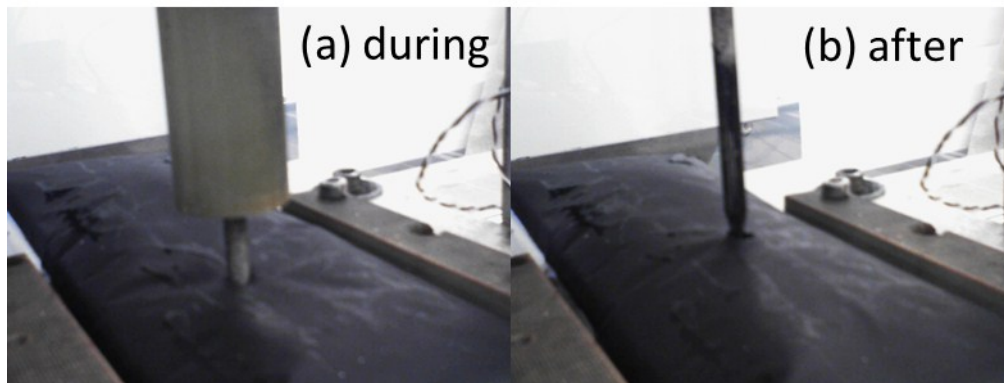


Figure 92 – Images of the cell (a) during and (b) after the penetration test

During all tests there was a modest rise in temperature. Figure 93 shows the maximum temperature of the different tests, measure at location 2 as shown in Figure 94. The maximum temperature rise for the different cells was between 4°C and 10°C. This compares to rises of 80°C and 140°C for intercalation lithium chemistries seen in previous tests under similar conditions [206,207].

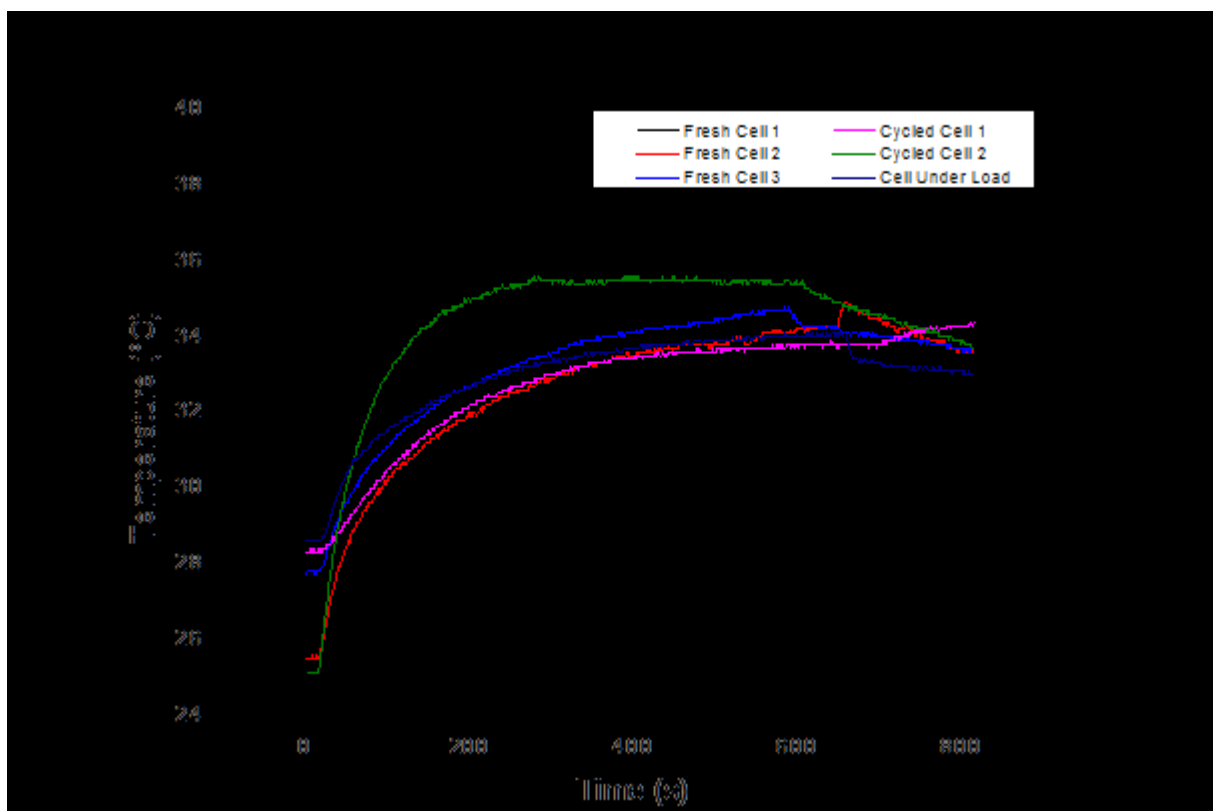


Figure 93 - Maximum temperature vs time during nail penetration tests

Figure 94 shows the thermocouple data from the test under load, and this matches well with the data from the thermal imaging camera, which can be seen in Figure 95. The drop in temperature seen by thermocouple 2 is thought to be due to the thermocouple becoming dislodged upon the removal of the nail.

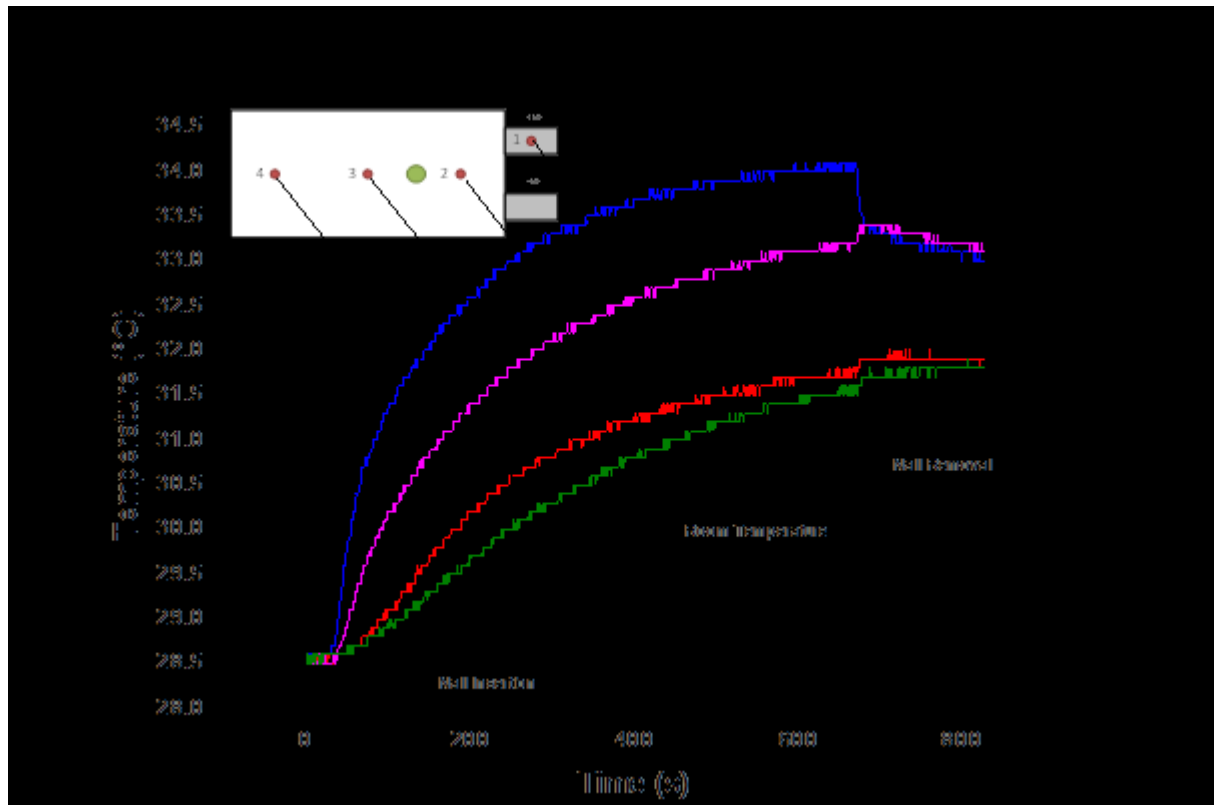


Figure 94 - Thermocouple data for the nail penetration test under load

Figure 95 shows snapshots from the thermal imaging camera, along with temperature data along the line drawn in the images. One minute after insertion of the nail, an increase in temperature at the site of penetration up to a maximum of 33.5°C can be seen. This heat then spreads throughout the cell as the test progresses. After removal, the surface of the nail shows up brightly on the thermal imaging camera. Although the emissivity of the nail is not known and therefore this cannot be used as an accurate

measurement of temperature, it is likely that the nail, and therefore the surrounding area of the cell, is hotter than the pouch material.

Once the nail was removed, the cell began to cool down. At this point, a current of 1.6A was still flowing from the cell, and continued to flow for approximately 3 minutes until the load was switched off.



Figure 95 - Progression of temperature over the duration of the test

In comparison with nail penetration tests on intercalation lithium cells, lithium sulfur cells show very small temperature rises, no catastrophic failure and the cells are able to continue to provide current during penetration and for a short period after the nail has been removed. Whilst it has been shown that the cell can continue to operate after a nail penetration event, due to the puncture of the pouch material electrolyte leakage would render the cell inoperable after a short period of time. When the nail is initially inserted, the terminal voltage drops and the temperature around the penetration site rises quickly due to a large, localised current flow. As the test progresses, the temperature levels off indicating that heat generation does not increase, and that this heat is dissipated through the cell in a way that avoids dangerously high temperatures, which can lead to thermal runaway.

The mechanism by which rapid discharge and catastrophic failure are avoided in lithium sulfur cells is unclear, however due to the high discharge rate at the site of penetration, non-conductive reaction products such as Li_2S may be formed, which insulate the short circuit and allow the cell to behave normally.

9.3.1.1 Conclusion

Lithium sulfur cells have been shown to be safe when subjected to nail penetration tests and able to continue to provide current during and for a short period after penetration. After penetration, the temperature can be seen to rise by approximately 5-10°C, and no flames, smoke or charring were evident.

The use of thermal imaging for this study was vital. If thermocouples or transistors had been used instead of a thermal camera, it would not have been possible to measure enough points on the surface of the cell to build up an accurate picture of the

temperature distribution over time. In addition, due to the nature of the nail penetration, it would not have been possible to place a thermocouple very close to the nail penetration site, and therefore valuable information about the temperature would have been impossible to measure.