

Imperial College London
Department of Mechanical Engineering

THE EFFECTS OF COMPRESSION ON LITHIUM- ION BATTERIES

PhD Thesis

Alexander Alan Holland

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Supervisors

Dr Gregory Offer

Mechanical Engineering

Professor Ricardo Martinez-Botas

Mechanical Engineering

Dr Yatish Patel

Mechanical Engineering

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

Alexander A Holland

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In Dedication to My Parents.

Abstract

This thesis experimentally investigates the effects of compression on pouch cells. Cells made from stacked electrode layers, were compressed between 0 MPa – 0.43 MPa (@ 40°C, 50% SOC) and cycled 2000 times. It was found that pressure had no effect on the rate of degradation. Compression improved the volumetric energy density by 10% at 0.43 MPa down to a 5% improvement at 0.02 MPa. The response of lithium-ion batteries to compression throughout its lifetime can be categorised into four stages:

- I. **Initial compression to the battery:** - Pressure is applied from 0 MPa to a target pressure.
- II. **Viscoelastic relaxation, with no change in SOC or temperature:** - Passive relaxation of the cell, i.e. pressure/strain relaxes.
- III. **Further relaxation of the battery as a result from electrochemical cycling:** - During electrochemical cycling, the pressure/strain of the cell reduces for any given SOC.
- IV. **The operational stage of the battery:** - upon completion of Stage III, increases in strain/pressure occur as the battery ages.

Stage IV is the most important when the battery is in operation. Stages I – III take place during set-up. The assumption that the pressures/strains at the beginning of Stage IV are similar to those applied in Stage I are incorrect. To define the mechanical state of a compressed cell, the conditions at the end of Stage III should be used and the SOC and temperature declared (30% SOC and 20°C are proposed as a standard).

Compression at different rates showed that the response of a battery was highly variable, with no correlation between the measured strains at the end of Stage II and the rate at which the compression was applied in Stage I. Thickness changes due to thermal expansion and during charge/discharge were found to be of the same magnitude. Hence, future compression experiments require accurate thermal management.

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List of Symbols

Symbol (Latin)	Meaning	Units
C_i^*	Bulk concentration of species i	mol cm^{-3}
$C_i(0, t)$	Concentration of species i at the electrode surface at time t	mol cm^{-3}
E	Potential of an electrode vs a reference	V
$E^{o'}$	Formal potential of an electrode	V
E_{OCV}	Open circuit potential between two electrodes	V
$E_{cathode}$	Cathode potential vs a reference	V
E_{anode}	Anode potential vs a reference	V
F	Faradays Constant, charge of one mole electrons	C
	Force	N
f	Short hand form for: F/RT	V^{-1}
i	Current	A
i_0	Exchange current	A
i_{net}	Current across an interface (such as an electrode surface)	A
iR	Ohmic voltage across a resistor	V
j	$\sqrt{-1}$	-
P	Pressure	Pa
Q	Charge passed	Ah
$q - q_0$	Charge passed from a reference point	Ah
R	Ohmic resistance	Ω
R_{ct}	Charge transfer resistance	Ω
T	Temperature	$^{\circ}\text{C}$
V	Voltage	V
$Z(\omega)$	Impedance (as a function of angular frequency ω)	Ω
Z'_{Re}	Real component of the complex impedance	Ω
Z''_{Im}	Imaginary component of the complex impedance	Ω

Symbol (Greek)	Meaning	Units
α	Transfer Coefficient	-
ε	Strain	-
η	Over Potential	V
$\hat{\sigma}_{resid}$	Standard deviation of the residuals (squared for the variance)	-
$\Psi_{0.}$	Double Layer Potential (Figure 3)	V

List of Abbreviations

Abbreviation (In body of text)	Meaning
AC	Alternating Current
Al	Aluminium (Element/Material)
APC	Automotive Propulsion Centre - UK
atpt 2	Second Attempt
CC	Constant Current
Char	Characterise or Characterisation
Co	Cobalt (Element)
C-rate	Current normalised against the battery capacity (Current [Amps] / Capacity [Ah])
CSTR	Constrained
CTRL	Control
Cu	Copper (Element/Material)
CV	Constant Voltage (Hold)
DIA	Diameter
DOD	Depth Of Discharge
DTV	Differential Thermal Voltammetry
Dur	During
DVA	Differential Voltage Analysis
EIS	Electrochemical Impedance Spectroscopy
EOL	End Of Life
FSR	Full Scale Range
GEIS	Galvanostatic Electrochemical Impedance Spectroscopy
GITT	Galvanostatic Intermittent Titration Technique
ICA	Incremental Capacity Analysis
IHP	Inner-Helmholtz Plane
K-type	K-type Thermocouple
LCO	Lithium Cobalt Oxide
Li	Lithium (Element/Ion)
LiC ₆	Lithiated Graphite (Electrode Material)
Li-ion	Lithium-ion
LiMnCo	Lithium Manganese Cobalt (Electrode Material)
LiPF ₆ (PF ₆ ⁻)	Lithium hexafluorophosphate (hexafluorophosphate – anion)
LMO	Lithium Manganese Oxide (Electrode Material)
LTO	Lithium Titanite (Electrode Material)
LVDT	Linear Variable Differential Transformer
LVL	Lower Voltage Limit

Abbreviation (In body of text)	Meaning
Mn	Manganese (Element)
NCO	Nickel Cobalt Oxide (Electrode Material)
Ni	Nickel (Element)
NMC	Nickel Manganese Cobalt (Electrode Material)
Obround	Shape - consisting of two semicircles connected by parallel lines tangent to their endpoints
OCV (OCP)	Open Circuit Voltage (Open Circuit Potential)
OHP	Outer-Helmholtz-Plane
PEIS	Potentiostatic Electrochemical Impedance Spectroscopy
PID	Proportional-Integral-Derivative (control)
Post E-char	Post (after) Electrochemical Characterisation
PP	Polypropylene (Material)
Pre E-char.	Preceding (before) Electrochemical Characterisation
R ²	Coefficient of determination
SEI	Solid Electrolyte Interphase
S-G	Savitzky–Golay (smoothing filter)
S-Golay	Savitzky–Golay (smoothing filter)
Si	Silicon (Element)
Sn	Tin (Element)
SOC	State of Charge
UVL	Under Voltage Limit
VDC	Voltage of a Direct Current source
VED	Volumetric Energy Density
XRD	X-ray diffraction

Abbreviation (In figures)	Meaning
5% FSR	5% of the Full Scale Range of a sensor
atpt 2	Second Attempt
Cap. Loss	Capacity Loss
chg	Charge
CSTR	Constrained
CTRL	Control
Cyc (no.)	Cycle, Cycles, Cycle number
Diff Span	Window span when performing numerical differentiation
dis	Discharge
DOD	Depth Of Discharge
LiC ₆	Lithiated Graphite (Electrode Material)

Abbreviation (In figures)	Meaning
LR test	Loading Rate Test
MA	Moving Average (Smoothing Filter)
Meas	Measure, Measured
Mid	Middle
NE	Negative Electrode (Figure 11)
Norm.	Normalised
PC	Polycarbonate (Material)
PE	Positive Electrode (Figure 11: Figure showing the half -cell voltages and how they combine into the full cell voltage.)
PE foam	Polyethylene Foam (Material)
Post Char	Post (after) Characterisation
Post Cmpr	Post (after) [Initial] Compression
Pre Char	Preceding (before) Characterisation
Resid	Residual, Residuals
Rez	Residual, Residuals
SG	Savitzky–Golay (smoothing filter)
S-Golay	Savitzky–Golay (smoothing filter)
Smth Span	Window span of the Smoothing Filter
SOC ref	Reference SOC

1. Introduction

Lithium-ion (Li-ion) battery technologies have seen a recent and huge increase in use in mainstream automotive applications - Battery Electric Vehicles (BEVs), Plug in Hybrid Electric Vehicles (PHEV) and Hybrid Electric Vehicles (HEVs). Notable examples are: Nissan Leaf (2011), BMW i3 (2013) and Tesla model S (2013). Thirty different BEV models and over 100 PHEV/HEV models have been released between 2011 and 2017 (1). These applications are pushing Li-ion battery technology to new boundaries. The expectation from the consumer is for greater range, higher performance and high safety standards with the very low levels of pollution required by legislation. Also very important is low performance degradation of the battery, to extend the life cycle of their vehicle.

One of the key technologies that the automotive industry can use to tackle these engineering challenges is to develop the immature technology of pouch batteries.

Cylindrical and prismatic batteries are much longer established. The Li-ion pouch battery offers packaging efficiency advantages over the other formats. This serves the interests of the automotive industry by providing the potential for lower mass and lower cost battery packs.

The thin, laminated aluminium foil pouch packaging reduces the mechanical integrity and safety of the individual pouch batteries. These features therefore must be incorporated into the battery pack design. One of the most important requirements is mechanically securing the delicate pouch batteries into the battery pack/battery module. The most intuitive method for achieving this is to clamp the flat, rectangular batteries together. In so doing, this compresses the electrochemically active components inside the batteries.

This work experimentally investigates the effects of compression on Li-ion batteries to inform how best to compress the batteries and how the magnitude of this compression affects their electrochemical performance.

The research performed in this work is in the following sections

Short term compression experiments

Several short-term experiments were performed to understand the initial mechanical response of Li-ion batteries to compression and how the compression changes the electrochemical performance over a single charge/discharge cycle. The key questions were:

- Does the loading rate affect the mechanical state of the battery and how long does it take to reach a steady mechanical state?
- How does the battery impedance change with compression, and with relaxation after the initial compression?
- How does the operating temperature affect the mechanical changes that occur during electrochemical cycling of batteries?

Long term compression experiment

A long-term compression experiment was performed on eight batteries with a stacked electrode configuration. This built on the work of Cannarella and Arnold (2), where obround jelly-roll pouch batteries were tested. The objective was to see the differences between the two configurations. This experiment performed a wide range of electrochemical and mechanical tests, to track the electrochemical and mechanical changes as the batteries age.

Compression experimental methods

Running in parallel with the above research is a discussion of the methods employed to perform compression experiments on Li-ion batteries. This is primarily focused about how to define the compression magnitude that has been applied to the battery.

2. Literature Review

The literature research and background theory of the research within this body of work is broken into three sections. The first is in Chapter 2, which gives a more general introduction to Li-ion batteries covering:

- The physical construction of the batteries
- Background electrochemical theory of Li-ion batteries
- Degradation and safety
- Mechanical phenomena in the batteries

This body of work is experimentally focused, so Chapter 3 introduces the different experimental methods performed when testing Li-ion batteries, covering:

- Electrochemical testing methods
- Mechanical testing methods

Finally, the third section is the focused review of the literature related to the specific experiments performed in this work. This section is presented in the introduction to the specific experiments.

Sections 2.3.2, 2.4.1, 2.4.2, 2.4.5 and 2.4.6 are modified excerpts from a report published for the Advanced Propulsion Centre UK: Li-ion Mechanical Stimulation, feasibility study report (3). The report was written in collaboration with: Mr Ian Campbell, Dr Nasrin Shahed Khan, Dr. Yatish Patel, Dr. Gregory Offer. The excerpts were originally written/generated by the author of this thesis. The above co-authors will have had input into formatting and wording of these excerpts.

2.1 Battery Internal Structure

Li-ion batteries have a complex internal composite structure that fulfils different roles, enabling the electrochemical device to store energy. The following section introduces the:

- Components
- Purpose of each component
- Typical materials used for each component
- Internal configurations
- Battery performance metrics
 - Power vs Energy batteries
- Battery form-factors
- Battery pack configurations

The section concludes with a discussion of the battery structure in the context of the research in this body of work.

2.1.1. Battery components

Li-ion batteries are comprised of a laminar structure of electrodes, encased within a container with two external electrical contacts. A simplified schematic of a battery is shown in Figure 1.

The battery components can be split into three categories:

- Active components
- Passive components
- External components

Throughout this work, the terms ‘anode’ and ‘cathode’ will be used as a label for the negative and positive electrodes of Li-ion batteries respectively. This terminology is a convention within the Li-ion battery community, rather than to use ‘anode’ and ‘cathode’ to describe at which electrode the oxidation/reduction reactions are occurring.

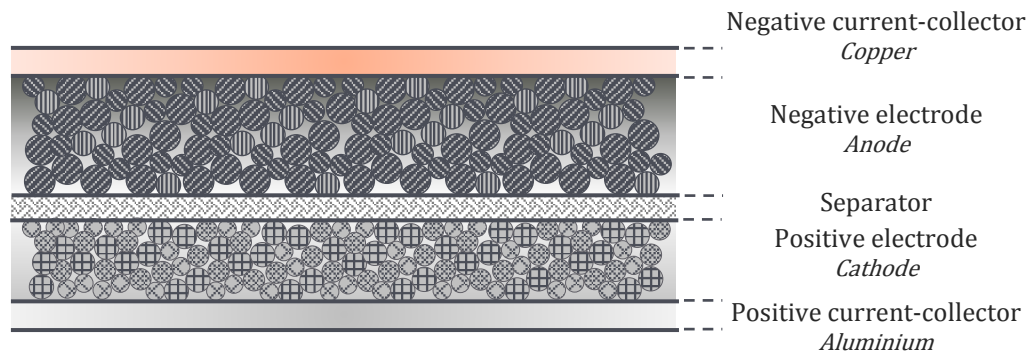


Figure 1: Schematic of the layered structure of a lithium-ion battery.

The three active components are the two electrodes, the anode (negative) and the cathode (positive) and the electrolyte (liquid that is located in the pores of the electrodes and separator). These components enable the battery to store electrochemical energy.

The passive components are the ‘infrastructure’ inside the battery that are required to enable the active material to store energy. These include the two current collectors that provide both structural support for the active material and a current path for the electrons. Also, the separator, which is typically a porous polymer sheet, that is electrically insulating but when wetted with electrolyte is ionically conductive. It isolates the two electrodes without restricting the transfer of ions from one electrode to the other.

The external components are the electrical contacts, the container and other features, such as pressure relief valves and cores. The electrical contacts provide the conductive path between the external electrical circuit and current collectors, through the battery casing. There are always at least two contacts, a positive (connected to the cathode) and a negative (connected to the anode). The battery casing fulfils three main purposes:

- Physically keeping the battery components together.
- Preventing anything from outside getting into the battery.
- Preventing the electrolyte from leaking and evaporating out of the battery.

2.1.2. Battery component materials

The different components inside the battery are made of different materials. Some of the materials used are different in different battery types, but many are universal. The active materials vary the most between different battery types. Batteries with different active materials are described as having different chemistries.

Anode materials

When describing a battery chemistry, usually only the cathode material is given. This is because Li-ion batteries typically use graphitic carbon as the anode material. The anode is comprised of small particles of graphite, bonded together with a conductive binder and deposited on the negative current collector.

Three other anode materials used are Lithium Titanate Oxide (LTO), lithium-metal and Silicon-doped-graphite. LTO anode batteries offer excellent cycle life compared to graphitic carbon, at the expense of reduced energy density and specific energy (4).

Lithium metal is an attractive anode material because it offers very high energy density and specific energy. Commercially, lithium metal anodes are not used in Li-ion batteries for reasons of safety. In the scientific community, lithium metal anodes are very common as lithium metal is used as the reference electrode when analysing other electrode materials.

Silicon doped graphite anodes have recently been introduced as an anode material, with the silicon doping increasing the energy density of the anode compared to pure graphite (5).

Cathode materials

The cathode material defines the type of Li-ion battery. These materials are typically a metallic oxide with a layered or tunnelled structure. Typical cathode materials include:

- Lithium Cobalt Oxide – LCO (used in the first commercial Li-ion battery in 1991 by Sony)
- Nickel Manganese Cobalt – NMC (used with different ratios of the three elements; recently in the automotive industry there is a trend towards nickel rich NMC - both to increase the operating voltage and to reduce the amount of the expensive cobalt)
- Nickel Cobalt Aluminium Oxide – NCA (chemistry used in the Tesla cars)
- Lithium Manganese Oxide – LMO

As with the graphite anode, the cathode is comprised of small particles held together with a conductive binder and deposited on the positive current collector (4).

Electrolyte

The electrolyte in Li-ion batteries are typically liquid electrolytes, with solutions of a lithium salt in an organic solvent. The most common salt is LiPF_6 . (4). The ‘additives’, which help produce a stable passivating layer on the anode (SEI layer), are a very important part of the electrolyte. The additives used are a key component of the Li-ion battery and are kept as industrial secrets by the battery manufacturers.

Current Collectors

The materials used for the current collectors are always the same for all Li-ion batteries regardless of chemistry. The positive current collector (cathode) is aluminium and the negative current collector (anode) is copper. The material choice is governed by the electrochemical stability of the material in the electrolyte (6).

Separator

The battery separator is most commonly comprised of a single or multi-layer micro-porous polyolefin sheet(s) (7). The multi-layer separators are comprised of a polyethylene core, sandwiched between two layers of polypropylene.

External Components

The external component materials are determined by the battery form factor and are discussed in Section 2.1.5.

2.1.3. Internal electrode configuration

To achieve a reaction area that is large enough for practical reaction rates, batteries contain many electrode layers. There are three configurations by which the multi-layered electrode structure inside Li-ion batteries is achieved, shown in Figure 2 (a)(b)(e):

- The 'obround jelly-roll' configuration is used in both prismatic and pouch batteries.
- The 'stacked electrode' configuration is used in both prismatic and pouch batteries.
- The 'cylindrically wound jelly-roll' is exclusive to cylindrical batteries.

2.1.4. Li-ion battery performance metrics

At the battery level, there are six key performance measures, five of which are quantifiable and one that is not:

- 1) Gravimetric energy density: The amount of energy the battery can store for a given mass (Wh kg^{-1}).
- 2) Volumetric energy density: The amount of energy the battery can store for a given volume (Wh m^{-3}).
- 3) Gravimetric power density: The maximum amount of power the battery can provide for a given mass (W kg^{-1}).
- 4) Volumetric power density: The maximum amount of power the battery can provide for a given volume (W m^{-3}).
- 5) Cycle life: the number of charge/discharge cycles that can be performed before the battery has reached its end of life (EOL). Typically, this is when the usable capacity has dropped below 80% of the rated capacity.
- 6) Safety and handling: Non-quantifiable factor, that is important for integration and use in battery systems.

Some of these metrics are linked and improving one will improve another, but this is not always the case. Generally, to improve one performance metric another will be negatively impacted. There are three stages at which the battery is optimised for an application:

- 1) Battery chemistry
- 2) Electrode area and thickness
- 3) Battery form factor

The intricacies of choosing a battery chemistry for a desired performance is beyond the scope of this work. The second and third design stages are of interest as they have a significant impact on the mechanical behaviour of the battery.

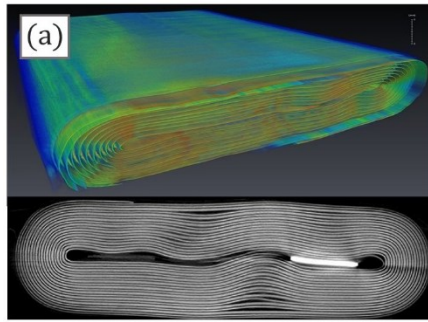
The electrode area and thickness design choice are at the root of the terms: ‘power-battery’, ‘energy-battery’. For a battery with a given chemistry and a fixed volume, the power density and the energy density are directly linked. Increasing one decreases the other.

To improve energy density, the amount of active material must be increased relative to the inactive material. In practical terms, one must increase electrode material thickness and reduce the number of electrode layers.

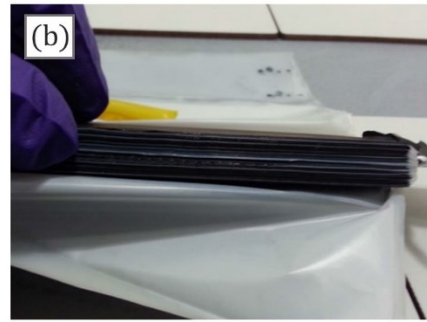
To improve the power capability of a battery, both the electrode area must be increased, and the electrode thickness reduced. This means an increase in the number of electrode layers and a reduction in the amount of active material.

In general, a power battery will have a larger number of thinner electrode layers – in contrast, an energy battery will contain a smaller number of thicker electrode layers.

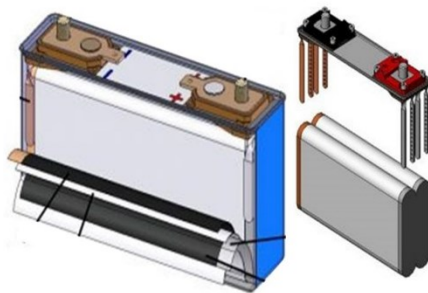
Obround jelly-roll
electrode configuration



Stacked
electrode configuration



Prismatic battery



(c)

Pouch battery

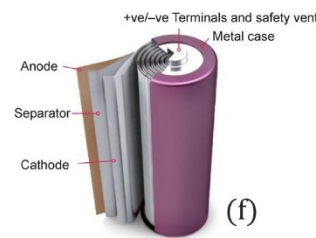


(d)

Cylindrically wound jelly-roll - Cylindrical battery

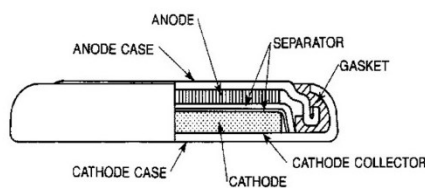


(e)



(f)

Coin cell



(g)



(h)

Figure 2: Images showing the three different electrode configurations and the four different form-factors used in Li-ion batteries. (a) X-ray tomography of an Obround jelly-roll electrode winding (111). (b) Edge view of a stacked electrode with Z-folded separator (82). (c) Schematic of prismatic battery, showing two obround jelly-rolls in a single battery casing (113). (d) Examples of pouch batteries of different sizes (e) End view of cylindrically wound electrode (118). (f) Schematic of a cylindrical battery (112). (g) Schematic of Li-ion coin cells (114). (h) Example of primary coin cells. Images (a)(b) reproduced with permission of the Authors, under open access licence. (c) Usage approved by copyright holder. (e) Reproduced with permission from Fire Protection Research Foundation Report, Lithium-Ion Batteries Hazard and Use Assessment: Final Report, Copyright© 2011, Fire Protection Research Foundation, Quincy, MA. All rights reserved. (f) reproduced with permission of Johnson Matthey, under Acceptable Use Policy.

2.1.5. Battery form factors

The shape and materials used for the external components define the battery form factor.

There are four common battery form factors, shown in Figure 2 (c)(d)(f)(g).

Aluminium is typically used as the casing material for both cylindrical and prismatic batteries.

In cylindrical batteries, the battery-can doubles as the negative electrical contact, with a small cap covering one end as the positive electrical contact. The two electrical contacts in prismatic batteries are isolated from the can and are often threaded so that mechanical fasteners may be used to make external electrical connections. Cylindrical and prismatic batteries often contain a pressure relief valve. In the event of battery failure this serves two purposes: to prevent an explosive level of pressure from building up inside the container and to direct the venting gases exiting the container. In contrast, the material used for pouch batteries is polymer laminated aluminium foil. The positive and negative tabs for pouch batteries are made from aluminium and nickel-plated copper respectively.

Cylindrical batteries are typically smaller than the other two form factors, the most common size being 18650 (18 mm diameter and 65.0 mm long). Pouch batteries generally have a maximum electrode stack thickness of slightly more than 10 mm. In general, higher capacities are achieved in pouch batteries by increasing the area of the battery, rather than the thickness. Currently the largest pouch batteries have an area similar in size to that of an A4 sheet. Prismatic batteries achieve higher capacities by increasing the thickness of the battery, whilst maintaining the area at a size of an A5 sheet. Prismatic batteries often contain more than one obround jelly-roll connected in parallel within the battery casing as shown in Figure 2 (c).

To maximise the ratio of active material to passive material in the battery, there is a drive towards larger batteries. Pouch batteries improve this ratio further by significantly reducing the amount of material in the external components. This is at the expense of the robustness of each individual battery. Pouch batteries are much less physically robust than prismatic and cylindrical batteries.

Finally, the fourth form factor is the coin cell. This form factor is most commonly seen as a primary battery for small electronics. Coin cells are used in the scientific community for testing new electrode materials and generating half-cell data.

2.1.6. Battery packs

In most applications either the voltage or the capacity of a single battery is not suitable. Hence, batteries are connected in series or parallel or both to achieve the voltage and capacity requirements. If the application requires a terminal voltage greater than 60 VDC, the battery pack is then comprised of multiple modules connected in series, with each module having a terminal voltage less than 60 VDC.

To avoid confusion Table 1 outlines the different terms used in this body of work to describe the different configurations of batteries. Many of these terms are used interchangeably within the battery community.

Table 1: Battery configuration terminology

Term	Configuration
Cell	A single electrode pair across a single chamber of active electrolyte.
Battery	Multiple cells connected in parallel only, inside a single container. The terminal voltage is determined by the chemistry.
Module	Multiple batteries connected in any combination of series and parallel, that has maximum terminal voltage of 60 VDC (Class A energy storage system), only used with constituent parts of battery packs.
Battery pack	Multiple modules connected in any combination of series and parallel make a battery pack. Has no maximum terminal voltage and a minimum terminal voltage of 60 VDC.
Low Voltage (LV) Battery	A LV battery combination that has a maximum terminal voltage of less than or equal to 60 VDC. Comprised of batteries connected in any combination of series and parallel. Differs from 'module', as it is not used to describe a constituent part of a battery pack.

2.2 Lithium-ion Battery Theory

The previous section introduced the Li-ion battery from an engineering perspective, outlining the components, materials and assembly. This section looks at the electrochemical theory that describes how Li-ion batteries store electrochemical energy. The topics introduced here are:

- Electrode reactions
- Electric double Layer
- Potential – current relationship

2.2.1. Electrode reactions

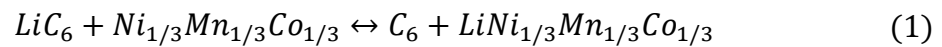
Li-ion batteries are electrochemical devices comprised of two electrodes (bonded to metallic current collectors), polymer separator and liquid electrolyte. These electrochemical devices enable useful electrical work to be performed by splitting a chemical reaction across two conducting phases:

- Electronic conductor (current collectors and external electrical circuit)
- Ionic conductor (electrolyte).

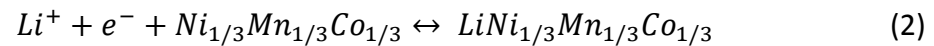
Cathodes in lithium-ion cells are made from lithiated transition-metal intercalation compounds. Most anodes are made from graphitic-carbon intercalation materials, such as LiC_6 . The example used below has an NMC cathode and graphitic-carbon anode. The NMC cathode has the chemical formula $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}$. Other chemical ratios of Ni, Mn and Co are also used. (4)

Equation (1) shows the complete electrochemical cell reaction that occurs during charge/discharge which can be broken down into two half-cell reactions, Equations (2) and (3). These Faradaic half-cell reactions occur at both electrode-electrolyte interfaces.

Net reaction:



Cathode:



Anode:



Charged State / *Discharged State*

2.2.2. Electric double-layer

The following section is a summary from electrochemistry text books (8–11).

This section looks at the electrode- electrolyte interface and the Double Layer model used to describe it. Inserting a conductive solid into an aqueous solution results in the interaction between the ions in solution and the conductive solid. This gives rise to surface charges. Consider an electrolyte solution with a salt commonly used in Li-ion batteries, such as LiPF_6 (4). With graphitic carbon, at the solid-solution interface there is a greater tendency for the Li^+ ions to be closer to the solid than the $[\text{PF}_6]^-$ anions. This tendency of the Li^+ ions is balanced in the graphitic carbon by a build-up of a negative surface charge. This structure of a double layer describes the composition of the solid and the solution in the immediate vicinity of the solid. The double-layer theory then developed through three significant stages, each named after the scientist who introduced them.

Stage 1, Helmholtz double-layer:

Here the charge difference across the solid-solution interface is balanced by a compact layer of ions located against the solid surface, schematically shown in Figure 3 (a). The term ‘double-layer’ comes from the two layers of charge, one on either side of the phase interface.

Stage 2, Gouy-Chapman double-layer:

This model of the double-layer is shown in Figure 3 (b). Here the charge is balanced via a diffuse layer of ions in solution, with greatest concentration of ions close to the interface, which gradually decreases further from the interface. This model was an improvement on the Helmholtz model, making the differential capacitance a function of potential and concentration. It has the drawback that the ions are considered points that can approach the interface infinitely closely.

Stage 3, Stern modification of the double-layer:

Stern combined the Helmholtz and Gouy-Chapman double-layers. To overcome the drawback of the Gouy-Chapman model a *plane of closest approach* was introduced as a starting point for the diffuse layer. This is offset from the interface, usually by the radius of an ion. Inside this offset the concept of the Stern-Layer was introduced, where ions and solvent molecules specifically adsorb on to the solid surface. This is shown schematically in Figure 3 (c), where the various layers are regions described below.

- *Stern layer*, the layer closest to the solid where the ions and solvent molecules are specifically adsorbed.
- *Inner-Helmholtz-plane* (IHP), the distance between the electrical centres of the adsorbed ions and the solid surface.
- *Outer-Helmholtz-plane* (OHP), the closest distance from the centre of the solvated ions to the solid surface.
- *Diffuse layer*. The diffuse-layer extends from the OHP to the bulk solution. The ions in the diffuse layer are said to be non-specifically adsorbed and are sufficiently far away from the solid to only interact with it via long range electrostatic forces.

Double-layer Potential Profile

The double-layer is very thin, and although the thickness does vary with the ionic concentration, the thickness is always of the order of nanometres. Despite the layer being incredibly thin, there is a significant change in potential between the solid and the bulk electrolyte. The potential profile across the double-layer region is shown in Figure 3 (c) by the line denoted by ψ_0 .

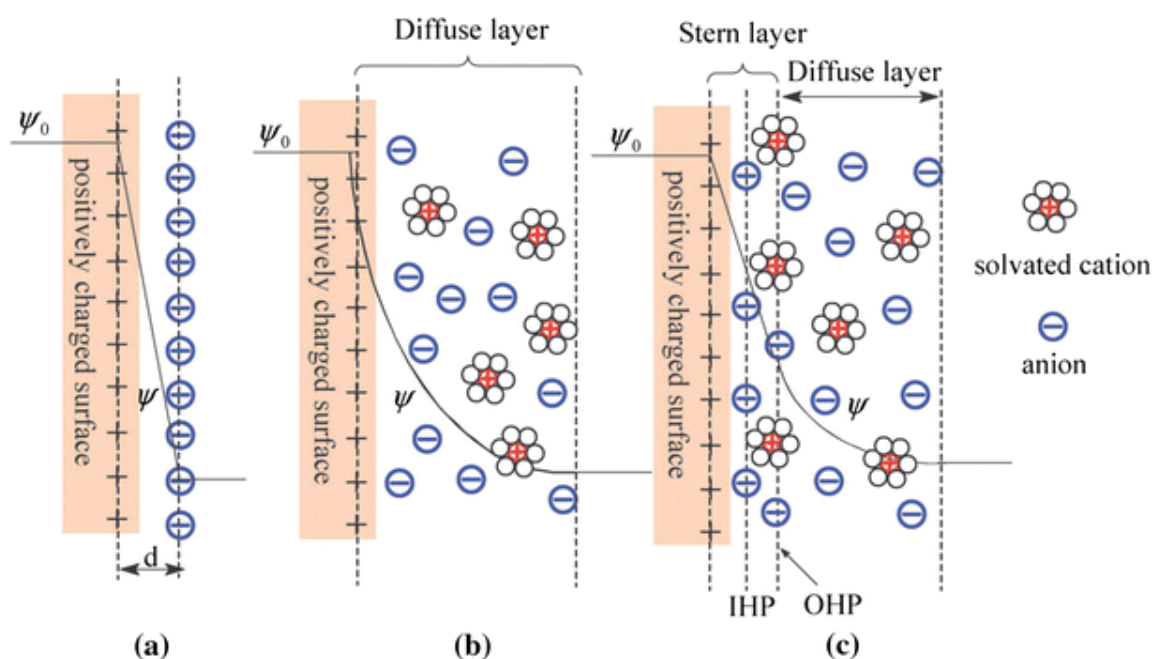


Figure 3: The three models of the electrical double layer: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) (115). Image reproduced with permission from the Royal Society of Chemistry.

Double-layer capacitance and external potentials

The electrical double-layer is analogous to a parallel plate capacitor. Some charge is stored in the double-layer, indeed this is the mechanism by which super-capacitors store charge. This charge stored in the double-layer is referred to as the double-layer capacitance. Parallel plate capacitor theory shows that the capacitance is proportional to the inverse of the distance between the plates. As mentioned above, the overall thickness of the double layer is of the order of nanometres, hence the capacity of the double-layer is very large.

To simplify this discussion, consider a cell where no Faradaic processes occur at the electrode-electrolyte interfaces (i.e. no intercalation occurs, as in a super capacitor). The application of an external potential results in an excess of electrons at one electrode surface and a deficit at the other. This charge excess/deficit is balanced in the electrolyte by changes in the electric double/diffuse layer. These changes manifest as storage of charge and change in the potential profile across the double-layer. The magnitude of the potential difference between the electrode and the bulk electrolyte increases.

Intercalation and the double-layer

In a Li-ion battery, there is an additional degree of complexity in that the lithium intercalates into and out of the electrodes. During intercalation a Li-ion pairs with an electron, forming a lithium atom which is embedded into the electrode lattice structure. Deintercalation is the reverse of this, resulting in a Li-ion being released into the electrolyte solution and the excess electron into the electrode/current collector. Intercalation of the anions in the electrolyte (eg. $[\text{PF}_6]^-$) does not occur due to their size.

Intercalation allows charge to be stored in the form of lithium atoms intercalated in the anode as opposed to the cathode. The amount of charge that can be stored in this manner is much higher than in the double-layer, resulting in the much higher energy densities of Li-ion batteries in comparison to super capacitors (in which no intercalation occurs).

2.2.3. Potential – current relationship theory

The following section is a summary from electrochemistry text books (8–11).

The electrochemical theory governing the behaviour of lithium-ion batteries can be broken down into three stages. Each of the stages is characterised by a reaction rate limiting process.

Thermodynamics at Equilibrium

The first stage is the cell at equilibrium with no current flowing. In this state the electrode potential can be related to the chemical concentrations using thermodynamics. The governing equation is the Nernst equation, shown in Equation (4).

$$E = E^{o'} + \frac{RT}{nF} \ln \frac{(C_i^*)_{left}}{(C_i^*)_{right}} \quad (4)$$

Where:

E = The EMF of the reaction

$E^{o'}$ = The formal potential of the electrode

C_i^* = Bulk concentration of species i

The Open Circuit Voltage (OCV) of the complete battery can be calculated from the subtraction of the anode potential from the cathode potential, as shown in Equation (5).

$$E_{OCV} = E_{cathode} - E_{anode} \quad (5)$$

Kinetics at low currents

The second stage is controlled by reaction kinetics and is valid between equilibrium and currents unaffected by mass transfer effects. The current at which mass transfer becomes the rate limiting condition is called the 'limiting current'. There are three forms of the same equation that describe the kinetics at the electrode-electrolyte interface. These equations relate the current across the interface (i_{net}) to the overpotential ($\eta = E - E_{eq}$). The

overpotential is the difference between the potential the electrode surface would be at if it were at equilibrium and the potential it is at, due to the charge transfer. The most general form the kinetics equation takes is Equation (6), called the 'Current-overpotential Equation'.

$$i_{net} = i_0 \left[\frac{C_O(0,t)}{C_O^*} \exp^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} \exp^{(1-\alpha) f \eta} \right] \quad (6)$$

Where:

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

O and R = Subscripts denoting the species being oxidised and reduced respectively

i_0 = Exchange current

α = Transfer coefficient

f = Short hand for F/RT

η = Over potential

For currents below 10% of the limiting current, the concentrations at the interface can be assumed to be those in the bulk solution. Thus, Equation (6) can be simplified to the 'Butler-Volmer Equation', Equation (7).

$$i_{net} = i_0 \left[\exp\left(\frac{\alpha F}{RT} \eta\right) - \exp\left(\frac{(1-\alpha) F}{RT} \eta\right) \right] \quad (7)$$

At very small currents, the overpotential becomes very small. Under these conditions the $\exp^x$ terms can be approximated as $1 + x$. Thus, the Butler-Volmer equation can be linearized to Equation (8) (rearranged into ohmic form $[V/i = R]$). R_{ct} is the Charge-transfer-resistance.

$$i = -i_0 \frac{F}{RT} \eta \rightarrow \frac{\eta}{i_{net}} = R_{ct} = \frac{RT}{F i_0} \quad (8)$$

Mass Transfer and Diffusion

The following section is a summary from electrochemistry text books (8–11)

At currents greater than the limiting current, the rate limiting process is the mass transfer of the reactants to (and products away from) the electrode-electrolyte interface. This is because the rate of diffusion is significantly slower than the rate of reaction. The mass transfer includes the diffusion of the lithium atoms within the electrodes and the migration and diffusion of the lithium-ions in the electrolyte. The mass transfer of ions in the electrolyte is faster than the diffusion of the lithium atoms within the electrode. Thus, the electrode diffusion is the most rate limiting process in the battery. Detailed mathematical understanding of the mass transfer within Li-ion batteries is beyond the scope of this body of work and is not presented here.

2.3 Degradation and Safety

Li-ion batteries degrade with use and time. This degradation is referred to as capacity fade and power fade. Capacity fade is used to define the end of life criteria for Li-ion batteries, where the usable capacity degrades to less than 80% of the nominal capacity of the battery. Power fade is less quantifiable and refers to the degradation of the rate capability of the battery and can be considered as an increase in the battery impedance. This section will give a general overview of the various degradation mechanisms. This is followed by a more in-depth look at mechanical degradation. The section concludes with an overview of the safety concerns for Li-ion batteries.

2.3.1. Degradation mechanisms

The mechanisms by which batteries degrade is covered in detail in the work by Birkel et al. (12). Figure 4, taken from that work, visually displays the different degradation mechanisms (a), and their different causes (b).

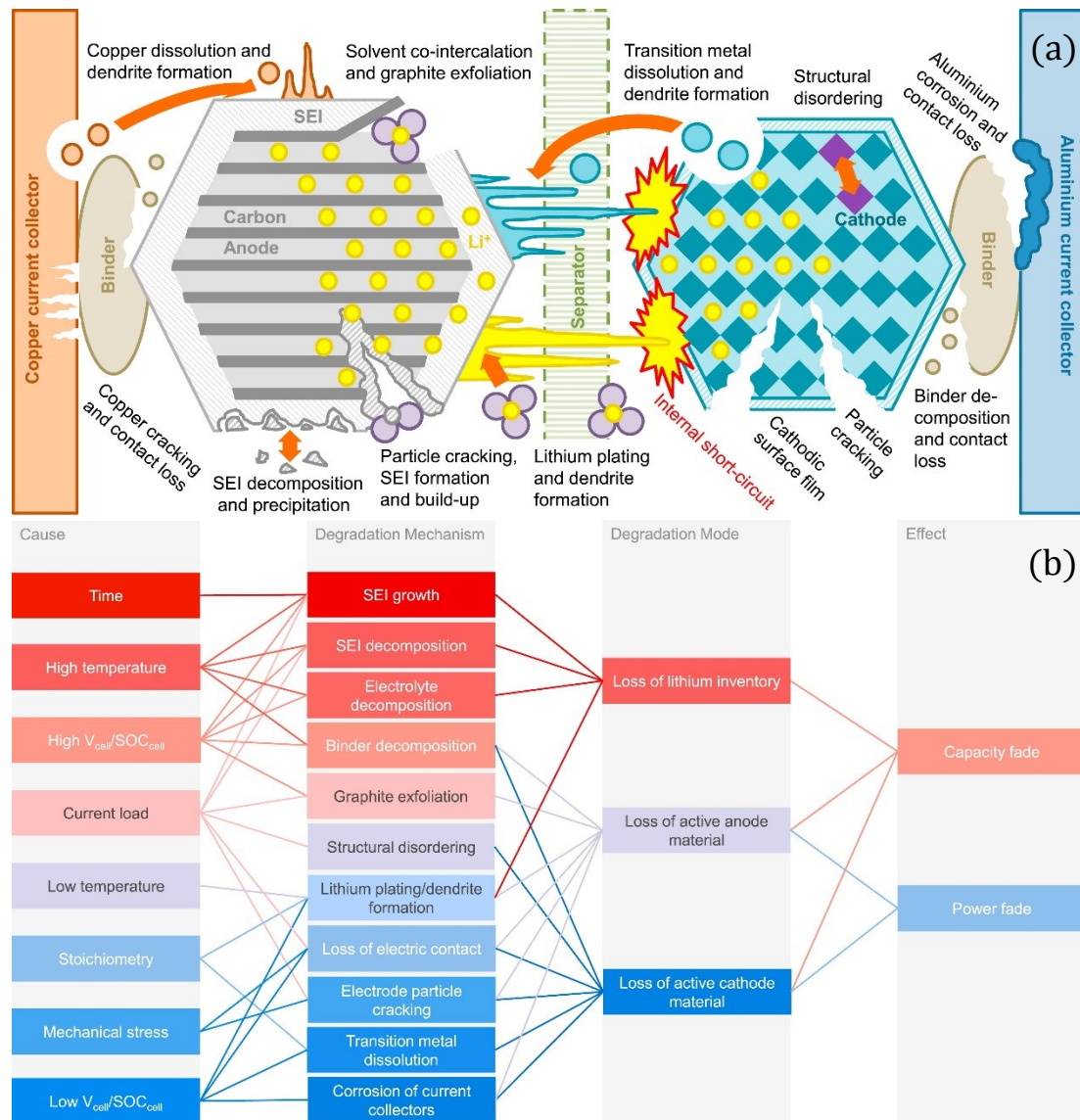


Figure 4: (a) Schematic showing Li-ion battery degradation mechanisms for all battery components. (b) Cause and effect of degradation in Li-ion batteries, displaying the degradation mechanisms and modes. (12). Images reproduced with permission from the Authors, under an open access licence.

Figure 4 (b) shows the degradation modes (12):

- Loss of lithium inventory. Li-ion batteries are a closed system in that only a finite amount of lithium atoms/ions that can partake in the electrochemical reactions. During the lifetime of the battery, lithium is consumed irreversibly, so it is no longer available for cycling. The primary mechanisms by which lithium is consumed are:
 - Parasitic side reactions (e.g. SEI formation).
 - Decomposition reactions (e.g. Lithium plating).
 - Intercalation into electrically isolated electrode particles.
- Loss of active material, both anode and cathode. Regions of the active electrode material can no longer intercalate/de-intercalate lithium due to:
 - Particle cracking.
 - Loss of electrical contact.
 - Blocking of active sites by resistive layers.
 - Structural disordering of the lattice structure.

Solid Electrolyte Interphase (SEI) layer growth is one of the primary degradation mechanisms and occurs at the graphitic anode electrode-electrolyte interface (13). This degradation mechanism is a double-edged sword, as the SEI layer is required for the Li-ion battery to operate but its growth in thickness both consumes lithium and increases the battery internal resistance.

The graphitic-carbon anode operates outside of the electrochemical stability range of the electrolyte. When in contact with the anode material, the electrolyte decomposes, which consumes lithium, generates a layer on the electrode surface and produces gas. The layer, referred to as the SEI, decreases the rate of electrolyte decomposition, because it is both electrically insulating and impermeable to the electrolyte. This effectively makes the anode more stable in the electrolyte. The downside to the SEI layer is that the lithium ions must travel through it to react at the electrode surface. A thicker SEI is harder to travel through, resulting in an increase in the resistance of the battery. Thus, the formation of a thin and

stable SEI is a very important part of producing a battery that has both good performance and reduced degradation (13–15).

During battery manufacture, the formation of the SEI layer has two associated processes:

- Formation cycles: the first few charge-discharge cycles with virgin electrodes. During these cycles the SEI layer is formed. Additives are included in the electrolyte to alter the properties of the SEI, to ensure that it is stable.
- Degassing: the formation of the SEI generates significant volumes of gas, which are removed from the battery during this process.

The SEI layer is not perfectly impermeable to the electrolyte and the SEI layer grows throughout the lifetime of the battery, consuming lithium and increasing its internal resistance. The primary mechanisms by which this occurs are (12):

- Slow diffusion of electrolyte species through the SEI. Once in contact with the anode reactions occur, forming new SEI.
- SEI decomposition. Cracking and/or breakdown of the existing SEI exposes fresh electrode surface to the electrolyte.
- Exposure of fresh electrode surface to electrolyte. Particle cracking, for example, can cause exposure of fresh electrode surface, where new SEI can form.

2.3.2. Mechanical battery degradation

Battery degradation can be a result of either mechanical or chemical breakdown of the electrode and is influenced by its composition. This was shown as early as the 1980s by Fritts, who demonstrated that fatigue mechanisms in nickel electrodes lead to work hardening and failure, thus reducing battery cycle life (16,17). However, historically there has been little interest in the mechanical characteristics of battery electrode materials. They have primarily been characterised in terms of their chemical compatibility, current carrying capability, and surface area. Mechanical degradation results from intercalation induced stresses and strains and is manifested as physical delamination/breaking of conductive paths and/or accelerating electrochemical degradation (2,18–23). The physical degradation mechanisms manifest as:

- Binder decomposition.
- Fracture and delamination of active electrode particles from rest of electrode.
- Delamination of electrode from current collector.
- Buckling of electrode-current collector assembly, resulting in loss of contact between electrodes, resulting from in-plane stresses.

The electrochemical degradation of the SEI layer is heavily influenced by the intercalation induced stresses. Generally, anodes are composed of carbon (20,24). Electrolytes react with the lithiated carbon electrode forming a solid electrolyte interface (SEI) layer. This forms naturally upon the first charge, when the carbon is first lithiated.

Graphitic carbon undergoes a volume change during lithiation and de-lithiation. Hence, the SEI layer is not mechanically stable and cycling of a cell can cause fatigue cracking of the SEI (25,26). This exposes fresh lithiated carbon which, reacts quickly with the electrolyte, consuming lithium irreversibly and leading to capacity fade (27,28). This mechanism is shown in the schematic in Figure 5. During repetitive cycling the SEI can continuously break and

reform over time, causing accelerated degradation (29–32), particularly at high temperatures and during rapid charging/discharging (33).

It is worth noting that the cathodes and anodes are composed of different materials and they

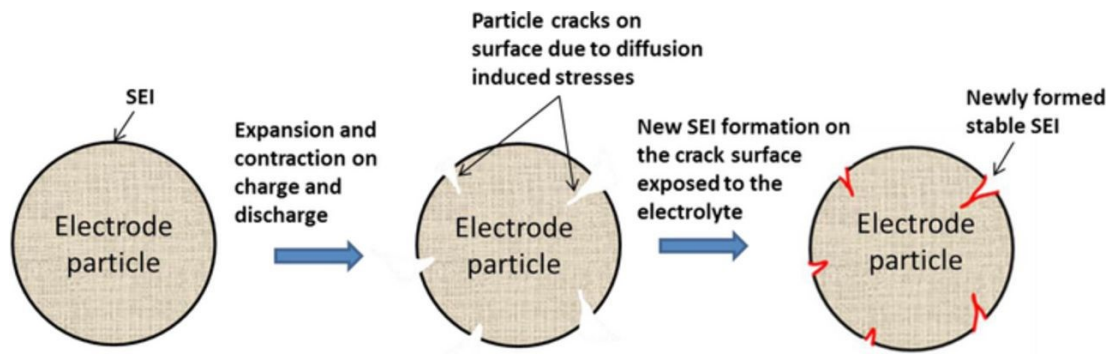


Figure 5: Schematic demonstrating anode particle fracture, resulting in exposed surface for new SEI to form, irreversibly consuming lithium (18). Image reproduced with permission from the Authors, under open access licence.

degrade through different processes. A SEI layer can also form on the cathode, which is generally harder to detect (34–37). Typically, cathodes undergo less morphologic change and hence less degradation (30,38,39).

2.3.3. Lithium-ion battery safety

The purpose of Li-ion batteries is to store as much energy as possible in as small a volume/mass as possible and then use that energy in a controlled manner to perform useful work. The major safety concern is what happens when that energy is released in an uncontrolled manner. The most notable and catastrophic manner by which Li-ion batteries uncontrollably release their stored energy is through thermal runaway. At high temperatures (~150 °C) the electrode and electrolyte undergo an exothermic reaction (21). This exothermic reaction generates more heat, accelerating the reaction further and ultimately resulting in catastrophic battery failure and fire.

Safe operation of Li-ion batteries includes measures to prevent the initiation of thermal runaway. The two most common conditions in which thermal runaway initiates are (21):

- Internal short circuits. Whereby the current flow across the short circuit generates enough heat to initiate thermal runaway. Common causes of internal short circuits are:
 - Manufacturing defects
 - Dendrite growth
 - External damage
- External and internal heating. The battery is heated to a temperature high enough to trigger thermal runaway. Common causes include:
 - External heat source.
 - Internal heat generation.

2.4 Mechanical Phenomena in Li-ion Batteries

When designing a battery pack, the ideal mechanical situation would be that the individual batteries can be assumed to be a solid brick that requires securing in place (with possibly some form of thermal management). Although this simplification can be applied to both cylindrical and prismatic batteries to some degree, it is not applicable to pouch batteries. This is due to the lack of structure of the pouch material, so any mechanical forces applied to the battery are applied directly to all the internal components of the battery.

As shown in Section 2.1, the internal structure of Li-ion batteries is a complex laminar structure with several different components, each with very different mechanical properties. An additional level of complexity is present because the mechanical properties of the active materials change with cycling. The following section introduces the literature on the material properties of the different components, which is followed by an overview of how and why the active materials change during cycling.

2.4.1. Mechanical properties of the separator

This section reviews the research assessing the mechanical properties of the separator. Where possible, the links between mechanical properties and electrochemical properties are highlighted. Peabody et al. (40) outline an argument stating that during electrochemical cycling the intercalation and de-intercalation of lithium ions to and from the electrodes results in the expansion and contraction of these materials. When the electrode stack is constrained (such as inside a cylindrical or prismatic cell or clamped in place inside a battery pack), other constituent parts of the battery must contract or expand to accommodate any change in the electrodes. They subsequently suggested that because the polymer separator has a greater compliance than the other materials in the electrode stack, the separator will absorb the majority of any electrode expansion. The values given in Table 5 show the separators have a Young's modulus an order of magnitude smaller than the electrodes. Based on this line of thought, Peabody et al. estimated that in a constrained electrode stack (with no initial stack pressure) the separator strain could increase by 25%-50% during charging (40).

Research to assess how this affects the separator both mechanically and electrochemically has been performed (40–45). It has been shown that the porous separator undergoes viscoelastic creep leading to pore closure, which in turn leads to increased internal resistance and capacity fade. These effects were shown to have an effect at compressive stresses as low as 1 MPa. The Arnold group have produced two models to describe these effects. The first model (45) relates the increase in impedance to separator strain. The developed model was parameterized using EIS analysis of the wetted separator only. The second (43) models the mechanical response of a single layer PP (polypropylene) separator to compressive loading. This model incorporates the viscoelastic properties of the wetted separator by combining

what is termed ‘poroelastic’ behaviour, caused by the flow of the fluid into the pores, and the viscoelastic behaviour of the separator’s polymer skeleton.

2.4.2. Mechanical properties of the electrodes

The literature that models cells during short-circuit indentation (46,47), shows that under compression, the electrode material initially shows non-linear stiffening, followed by a linear region of stiffening. This is illustrated in the experimental data given in Figure 6. In this work by Elham Sahraei et al. (46) the battery chemistry and separator material are not specified. The non-linear region is attributed to the compacting of the porous electrode materials. When looking at the effects of compression on electrochemical performance, the applied stresses in this thesis are likely to be within the initial non-linear region.

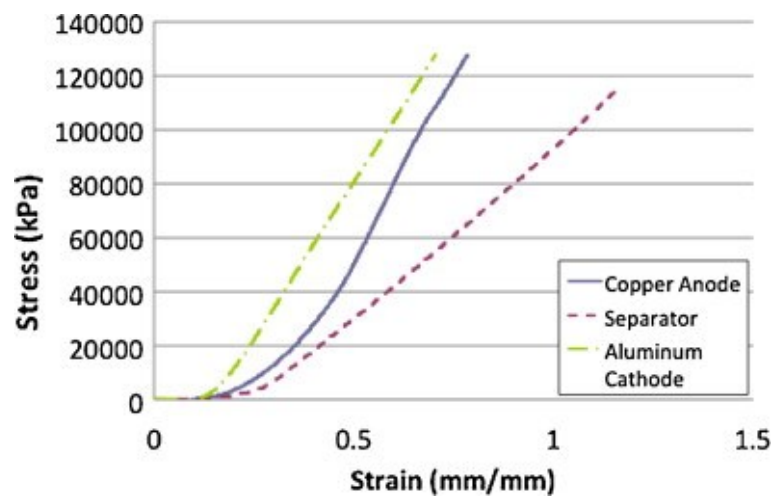


Figure 6: Engineering stress strain for the load-displacement curve of cathode, separator, and anode under compression. (46) image reproduced with permission from Elsevier.

2.4.3. Mechanical properties of the current collectors

The two current collectors are considered passive materials and the compression magnitudes in this thesis are within the elastic limits of the materials. Hence, with respect to compression normal to the electrode plane, the current collectors will be ignored with respect to the effects of compression on the battery. Conversely, for in-plane stresses the current collectors cannot be ignored as they constrain the in-plane electrode expansion.

2.4.4. Li-ion battery breathing

Breathing is a descriptive term for how the thickness of the battery changes with cycling. As the battery is charged the battery expands and during discharge it contracts. The term ‘breathing’ is technically misleading, as it implies an input/removal of matter into/out of the closed-system battery. However, it does provide an intuitive understanding of how the battery thickness changes with the state of charge (SOC). The battery:

- Expands during charging (energy input)
- Contracts during discharge (energy output)

As will be discussed below these phenomena are caused by the intercalation driven strain in both electrodes.

Intercalation driven electrode strain

Typical secondary lithium battery (i.e. non-graphitic) electrodes have one of two working principles. The more common involves reversibly intercalating and de-intercalating the lithium into a host crystal lattice. The second works on the principal of alloying/de-alloying the lithium with a metallic electrode (Li, Si, Sn and Al anodes) (4,48).

The electrode particles are the part of the battery where the lithium atoms intercalate/de-intercalate during electrochemical cycling. The stresses that occur due to the intercalation can be split into (48):

- Internal stresses, present in the active material due to intercalation, resulting in phase changes and lithiation gradients.
- External stresses, induced by the changing particles interacting with each other and the rest of the electrode.

The key driver of the internal stresses in the active material are the phase changes. These are changes in the crystal lattice structure resulting from the variable number of lithium atoms present (48).

2.4.5. Graphite intercalation strain

Graphite anodes undergo significantly larger volumetric changes during lithiation, compared to most common cathodes with which they are paired (48). This is the major cause of the net expansion of the battery during charging.

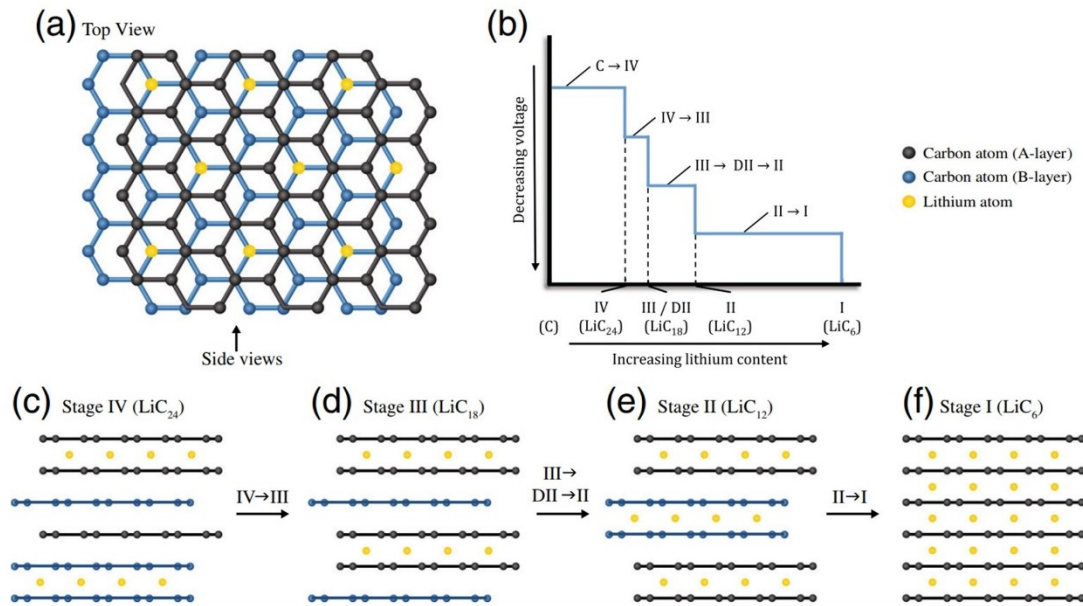


Figure 7: Structure of graphite-lithium intercalation compounds (G-LICs). (a) Top view showing the in-plane spatial arrangement of lithium atoms in a fully intercalated (not dilute) stage, with one lithium atom per six carbon atoms. (b) The theoretical voltage of a graphite electrode as a function of lithium content. The voltage is constant during phase transitions and drops sharply once a stage is complete. (c)–(f) Side views showing the arrangement of layers of lithium atoms between graphite layers for stage IV, stage III, stage II, and stage I G-LICs. The roman numerals refer to the number of graphite layers associated with a single layer of intercalated lithium. (116). Image reproduced with permission from the Society for Experimental Mechanics.

Graphite is known to have five phases through lithiation. These are variously labelled in the following figures as follows: Graphite, Stage-IV (LiC₂₄), Stage-III (LiC₁₈), Dilute-Stage-DII (LiC₁₈), Stage-II (LiC₁₂), Stage-I (LiC₆) (49–51). Figure 7 demonstrates the position of the lithium in the graphite lattice at each stage. As can be seen, the stage number corresponds to the number of graphene layers present between each layer of intercalated lithium. Dilute-Stage-DII and Stage-III have the same ratio of lithium atoms to carbon but a different layer spacing. This is due to the amount of lithium inserted in the Dilute-stage-DII not being

maximised. Additionally, Dahn (51) demonstrated that at very low levels of lithiation (Li_xC_6 | $x < 0.04$) a randomly distributed Dilute-Stage-I occurs, prior to the formation of Stage-IV. The different phases can be seen in the voltage vs lithiation curve shown in Figure 8. Plateaus represent a single phase, while the steep voltage changes represent the transition from one phase to another.

The volumetric change in the graphite has been assessed at both the lattice unit cell level and

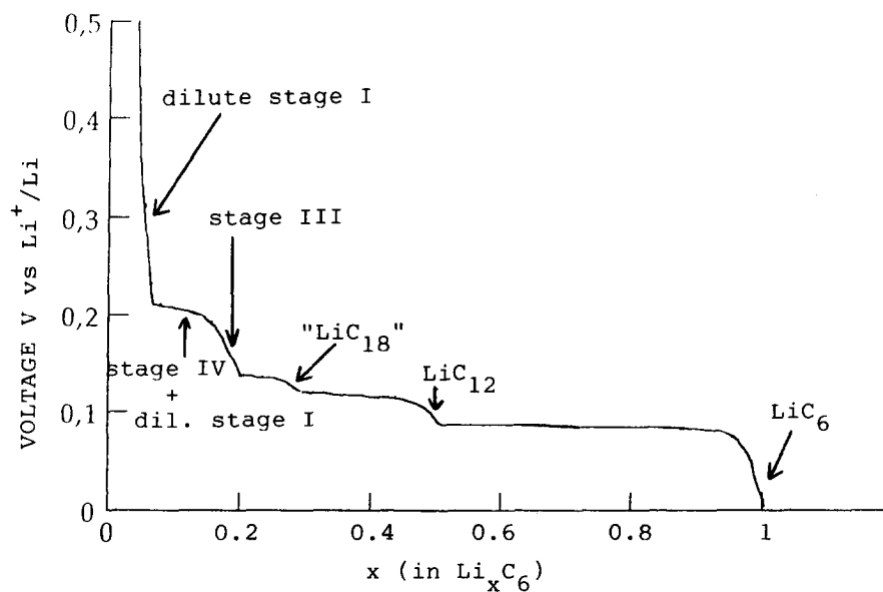


Figure 8: Graphite voltage (vs Li) against degree of lithiation. Arrows indication the location of the different phases (50). Image reproduced with permission from Elsevier.

electrode level. Qi et al. (49) showed a general two stage volumetric change with an expansion of ~5% between graphite (Li_0C_6) to Dilute-Stage-DII (LiC_{18}), Stage-III (LiC_{18}) and Stage-II (LiC_{12}). Subsequently, there is a further ~5% increase in volume, to a total of 10% volume increase to the fully lithiated graphite or Stage-I (LiC_6). It also demonstrates that the volumetric change is non-isotropic within the lattice: with the distance between the graphene layers increasing by 7.4% but within the basal plane by only 1.2%. These findings concur with the work performed by Hahn et al. (52), where the thickness (height) change in a graphite electrode was directly measured using an electrochemical dilatometer. The resulting plot of

electrode height change vs degree of lithiation is shown in Figure 9. It shows a high rate of volumetric expansion until Stage-III, dilute Stage-DII and Stage-II start to form. Subsequently a plateau exists until the formation of Stage-I begins, at which point the rate of expansion increases again.

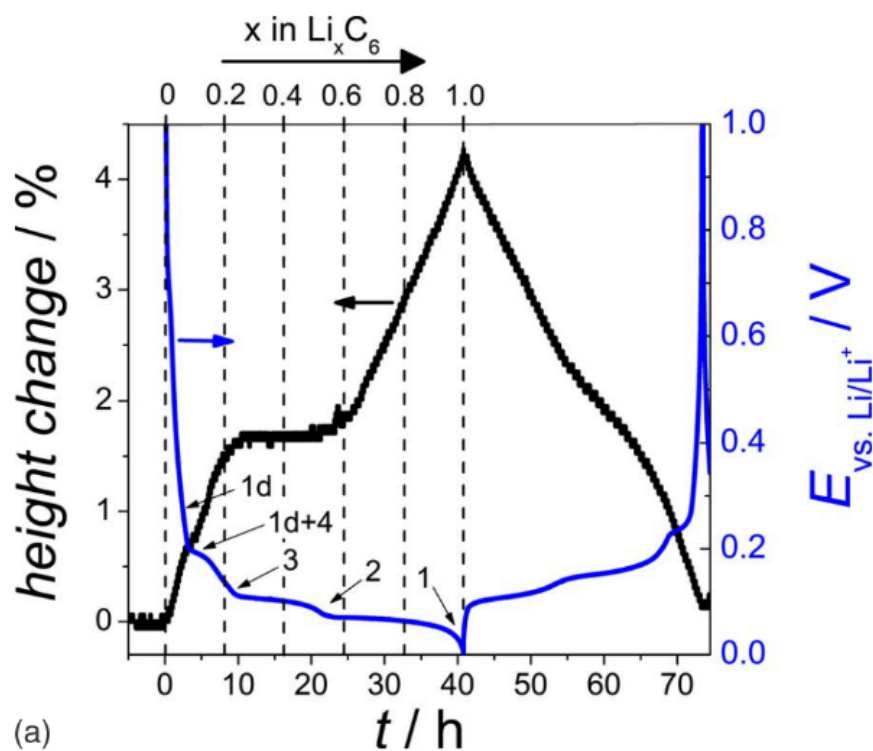


Figure 9: Potential profile (blue/narrow) and corresponding dilatation (black/thick) of 101 μm thick graphite electrode (52). Numbered arrows denote stages formed according to (50). Image reproduced with permission from ECS

2.4.6. NMC intercalation strain

NMC is an attractive cathode material because of the high operating voltage (4.7 V vs Li) and its high energy density (48). Koyama et al. (53) performed coin cell experiments on NMC cathode vs Li metal anode materials to determine the electrode lattice parameter changes and phases. They determined that NMC has three phases (excluding fully delithiated) between 2.5 V and 5.0 V (vs. Li): centred about the voltages 4.67 V, 4.01 V, 3.76 V. This is shown graphically in Figure 10 (a) (b) with the E vs (dx/dE) plot and the discharge curve. The regions of constant voltage gradient represent where the various phases exist, and the non-linear regions represent where the transitions between phases occur. This is most apparent when $y > 2/3$, when Stage III is nearly exclusively being formed and hence a lot of charge is passed for a small change in voltage. Figure 10 (c) displays the Lattice-unit-cell volume vs degree of lithiation, calculated by Yabuuchi et al. from X-ray diffraction (XRD) patterns. This shows that the units cell volume is relatively stable for $y > 1/3$ or $E < \sim 4.3\text{V}$ (vs Li). Below this threshold the lattice unit cell volume reduces linearly with the reduction of lithium concentration.

In contrast to the above scanning method, Nagayama et al. performed dilatometer (54) measurements directly to an electrode pair, to find the NMC volumetric change. The NMC cathode is paired with a lithium-titanate (LTO) electrode, which is shown to have no volumetric change and maintains 1.55 V vs. Li during lithiation/de-lithiation. Figure 10 shows the NMC voltage vs. LTO and the change in NMC electrode volume, as well as the rate of change of volume. These results agree with the unit cell volume results showing a stable electrode volume until voltages (vs. Li) of greater than $\sim 4.3\text{ V}$ (1.55V [LTO vs Li] and $\sim 2.55\text{ V}$ [NMC vs LTO]).

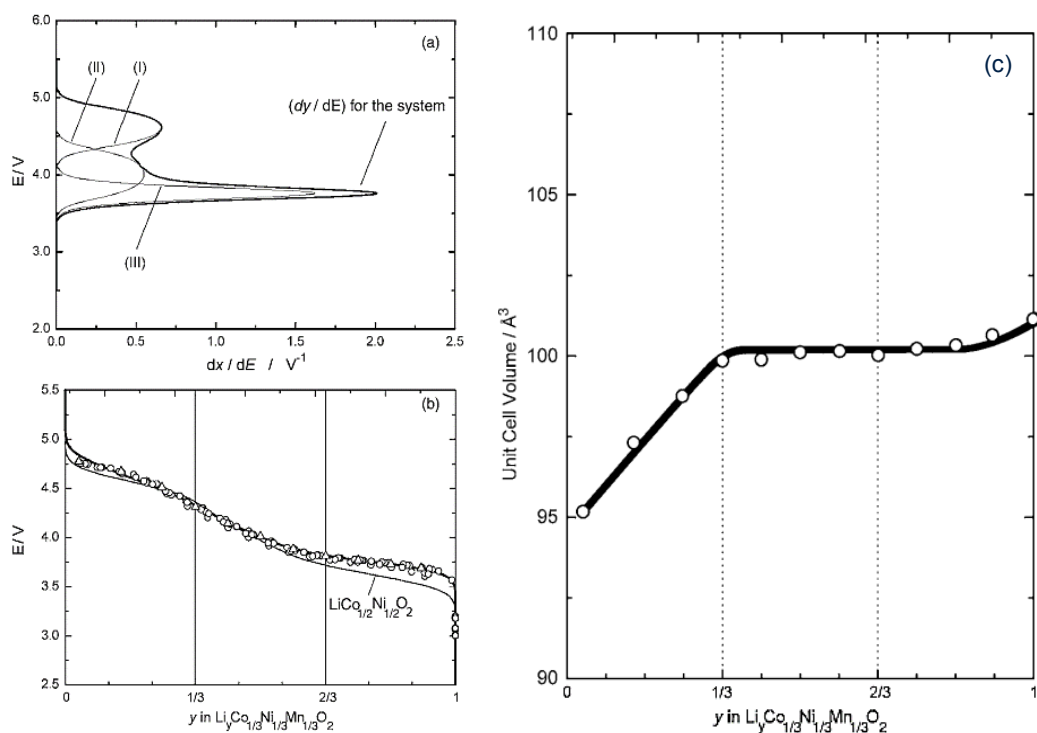


Figure 10: NMC voltage vs. LTO and the change in NMC electrode volume. (a) E vs (dx/dE) for the three NMC solid-state redox potentials with the dy/dE curve overlaid. (b) Comparison between integral of dy/dE curve from (a) [solid line] and observed reversible potentials [open circles]. (c) NMC lattice unit cell volume against degree of lithiation, calculated from XRD patterns (53). Image reproduced with permission from ECS.

2.5 Research Groups

Mechanical research into Li-ion batteries is a relatively small research community with a few key research groups generating a large proportion of the work, with other groups contributing only one or two papers. Note that this is referring to mechanical testing of commercial Li-ion batteries during operation rather than materials studies of mechanical phenomena in the electrodes or mechanical abuse studies. A comprehensive study of the mechanical phenomena at the electrode is given by Mukhopadhyay and Sheldon (48).

The two primary contributors are the Arnold Group (at Princeton University) and the group at Michigan University.

2.5.1. Arnold group

The Arnold group, with the primary investigator Cannarella have looked at various aspects of compression of Li-ion batteries. Their initial works in this area and their primary research area assess the mechanical affects in the polymer separators. This concluded that mechanical deformation in the separator can cause pore closure and restrict ionic-transport, increasing the battery impedance (40,42,43,45). This initial work was followed by investigating how the electrolyte solvent affects the separator mechanical properties(44). Their most recent works on separators look at the consequence of localised defects inducing pore closure which subsequently causes localised plating (41,55).

Another line of investigation focuses on using the mechanical changes in the battery as a metric for tracking state of health of batteries (56–58). In these works, the changes in the mechanical state of the battery both strain and stress can be used to track ageing in Li-ion batteries.

The remaining two works test the effects of compression on Li-ion batteries. The first of the two papers is discussed in detail in Chapter 5. Here the batteries were constrained at different compression magnitudes and pressure change and capacity fade were monitored over time. It was concluded that there is an optimal compression magnitude for maximising cycle life (2). The follow-on work from this studied how the effects of cycling in different regions of the SOC window affected the capacity fade and stress evolution (59).

2.5.2. University of Michigan

Oh et al. produced two important papers looking at the effects of temperature and charge/discharge rate dependence on the expansion of Li-ion batteries (60,61). These demonstrate the importance of temperature and internal heat generation when looking at mechanical effects in batteries. The magnitude of thermal expansion (within Li-ion battery operating temperatures) is of the same order as the lithiation driven volume changes during cycling.

On a similar theme to some of the Arnold group's work Samad et al. use the force changes from a constrained battery as a capacity fade metric (62) demonstrating that the rate of change of force during discharge showed features analogous to other differential techniques such as ICA.

Lai et al. investigated how the laminar structure of the battery responds to in-plane and out-of-plane compression. The paper concluded the stress-strain relationship of the out-of-plane compression was characterised by the buckling of the layers. The in-plane stress-strain relationship suggested the battery could be modelled as an anisotropic foam (63).

2.5.3. Other contributions

Beyond the Arnold group and the Michigan University group, other work has been performed looking at the mechanical changes in batteries. Two papers by Barai from Warwick University investigated the effect of external compression on batteries (64,65). These focused on the changes in battery impedance due to the applied compression. They are of note for the non-standard methods by which the compression was applied and measured. One used pneumatic bladders to apply a uniform pressure to the battery surface and the second used a pressure mat to map the pressure across the battery surface.

Mussa et al. performed a compression experiment on single layer pouch cell (66). This work concluded that an optimum compression magnitude could be applied to a battery for extending battery life and that higher stack pressures limit kinetic and mass transfer effects thus increasing the battery impedance.

Fabian et al. from the Fraunhofer Institute for Silicate Research produced a limited ageing experiment comparing the effect of compressing the battery within a compliant constraint against a rigid constraint (67). This initial report (250 cycles of a longer degradation experiment) concludes the rigidly constrained battery ages faster due to the pressure peaks that occur at high states of charge.

Sauerteig et al. from Bosch mechanically parameterised a electrochemical-mechanical model (68). The results from the model are used to conclude that at high pressures can influence the intercalation into the electrodes potentially increasing the probability of lithium plating.

2.5.4. Conclusions – literature on mechanical effects

Looking at the body of literature addressing the mechanical effects in Li-ion batteries during operation there are several general conclusions and consensuses present:

- Compressing a Li-ion battery causes an increase in impedance. The increase is attributed to a restriction in ion-diffusion principally due to pore closure of the separator.
- During ageing experiments of a compressed battery there is an initial relaxation due to viscoelastic creep. Subsequently the pressure/thickness increases as the battery ages.
- In constrained batteries, the electrode expansion due to lithiation is principally absorbed by the compliant separator.
- There is an optimal ‘initial compression magnitude’ for maximising battery cycle life but the value is different between different experiments, by orders of magnitude.
- The mechanical changes in the battery during cycling can be used to infer information about the internal mechanisms within the battery - both during a single cycle and with ageing. There is little work independently applying the methods of analysis of data obtained from experiments of this sort.

3. Experimental Techniques

This chapter introduces the different techniques and methods employed for testing Li-ion batteries. The first section discusses the electrochemical methods employed. The limitations on the inferences that can be drawn from the measurements are given. The electrochemical methods section is concluded with a discussion of the thermal boundary conditions applied during battery testing, emphasising their importance. The second part of the chapter introduces the different approaches to mechanical testing of batteries. The experimental methods and techniques relevant to this body of work are then examined in more detail.

3.1 Electrochemical Testing

When electrochemically testing commercial Li-ion batteries there are three experimental factors that can be measured:

- Terminal voltage
- Charge passed/Current
- Temperature

For most battery testing, either the voltage or current is the controlled variable, and the other measurement is the response variable. Temperature is also a measured variable; however, it is usually held at a constant value (fixed control factor). This chapter introduces the different methods by which inputs and responses of these three factors can be manipulated to provide data that can then be used to infer conclusions about batteries. The battery testing methods introduced here are the following:

- Constant current charge/discharge
- Electrochemical Impedance Spectroscopy (EIS)
- Differential Techniques (ICA, DVA, DTV)

Battery thermal control has a great influence on the results of all these methods. This section concludes with a discussion of the thermal control of battery experiments.

3.1.1. Discharging and charging

Constant current (CC) testing is a well-accepted method used by battery scientists. It is also referred to as Galvanostatic testing. The method provides the baseline battery performance metrics of Capacity and Capacity fade.

When performing CC experiments the current applied to batteries is normally quoted as a C-rate, rather than in Amps. The C-rate is the battery capacity (units Ah) divided by the CC current applied.

To understand the usefulness of constant current tests and the battery - capacity metrics that are generated from them, the full context of the tests should be understood. Commercial Li-ion batteries are provided with two voltage limits, upper (UVL) and lower (LVL). For an NMC-graphite battery these values are 4.2 V and 2.7 V respectively. These limits are the terminal voltages between which the battery should be operated. When performing CC tests, these voltage limits are used as the start and end criteria for a full discharge or charge. The terminal voltage is the difference in the electrode potentials. Each electrode potential is a function of the degree of lithiation at the electrode surface, as discussed in Section 2.2.

Figure 11 shows that the voltage cut off limits are not at the theoretical maximum amount of lithium that can be intercalated into the two electrodes. The voltage limits are set by the undesirable processes that occur if operating outside of them. At voltages below the LVL, copper dissolution occurs at the negative current collector, which results in delamination of the anode and deposition of copper on the anode, cathode and separator surfaces. Operating at voltages above the UVL can overcharge the anode and cause lithium-plating, that can lead to dendrite growth and short circuits.

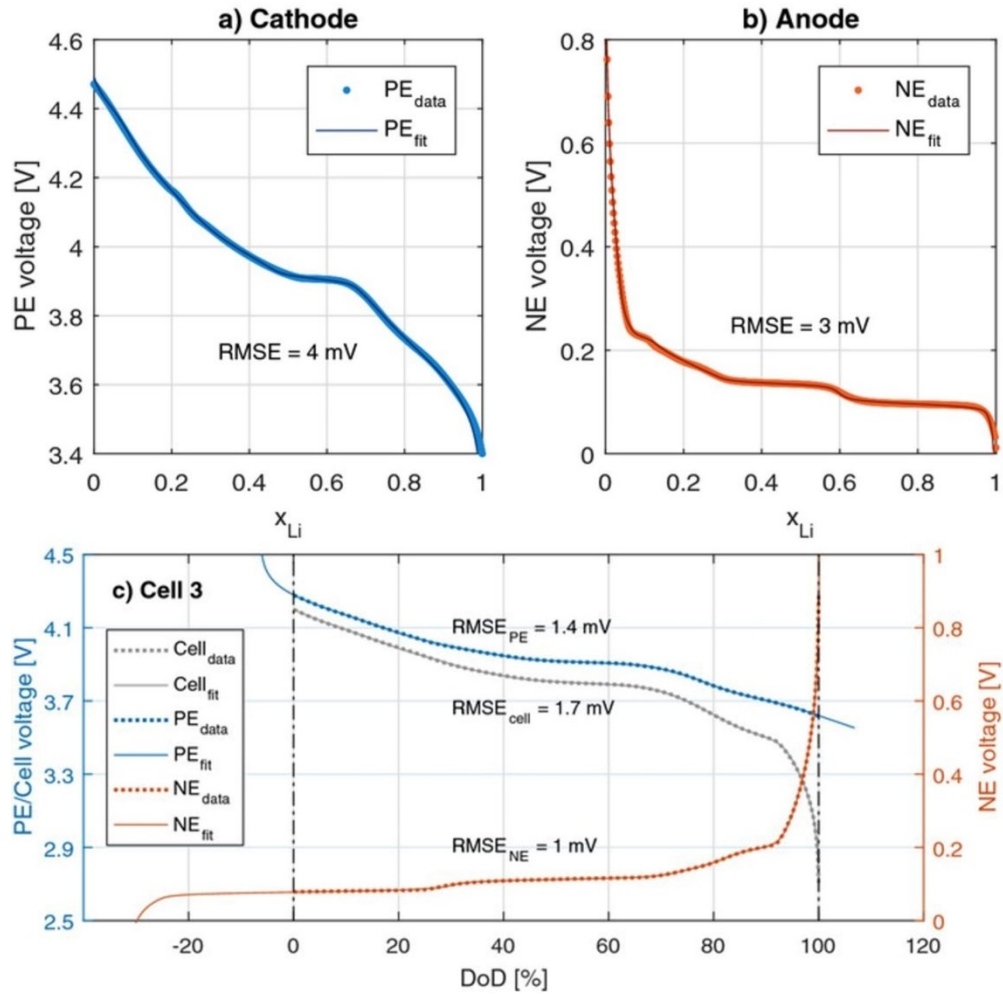


Figure 11: Figure showing the half-cell voltages and how they combine into the full cell voltage. All voltages referenced against lithium except for the full cell voltage in (c). (a) Positive electrode voltage vs degree of lithiation. (b) As for (a), but the negative electrode. (c) Half-cell and full cell voltages plotted against the Depth of Discharge (DOD) of the full cell. Both the positive electrode and full cell voltage scale are shown on the left y-axis in (c). All three plots taken from (117). Image reproduced with permission from the Authors, under open access licence.

This means that the limits of the CC process are not a direct measurement of the amount of charge passed during the CC process. If the terminal voltage measured was purely a function of the degree of lithiation of the two electrodes, this would not be a problem. This is not the case, the battery terminal voltage is a function of a wide range of variables. Two of the principal variables are the current magnitude and the battery temperature.

This means that the capacity of the battery is heavily influenced by the testing conditions. This is shown graphically in Figure 12, which shows the discharge curves for the same battery being discharged at three different currents. The capacity of the battery is reduced by 1.3%

at 1C and 2.5% at 3C, normalised against the capacity from a 0.1C discharge. A 30C discharge of the same battery would see an approximate drop in capacity of 12% (69). Understanding and controlling all the variables that can affect the capacity measurement is an important part of battery-testing experimental design.

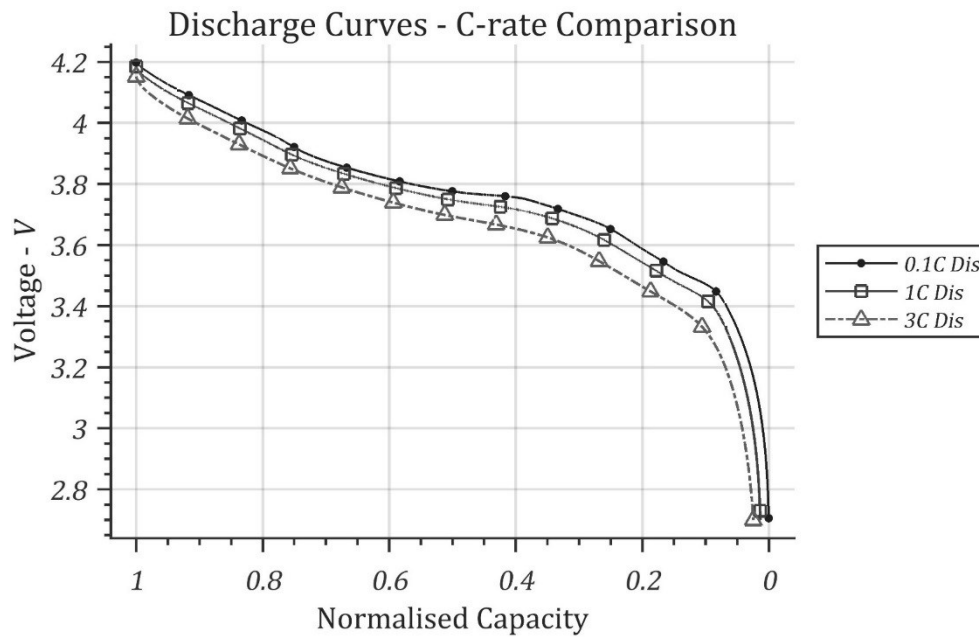


Figure 12: Example showing the difference in the battery voltage during discharge because of increased current.

The maximum capacity obtainable from a battery, at a fixed temperature, is that found from the Open Circuit Voltage (OCV) curve. At all points along the OCV curve, the battery is at equilibrium. Obtaining the OCV curve is a very time-consuming experimental process, so CC tests at low currents are used as an approximation of the OCV curve (70).

Slow rate CC tests provide information on true capacity of the battery, but they miss other important aspects of battery behaviour. As the current increases, the limiting factor on battery performance becomes lithium diffusion into the electrodes. Thus, CC tests at higher currents also produce valuable information.

Constant Voltage Hold

Constant voltage (CV) holds are used to set the battery terminal voltage to the OCV quickly. Once the desired terminal voltage is reached under CC conditions, the CV hold is started. The desired OCV is maintained by reducing the current accordingly. This continues until the current magnitude drops below a pre-set value, 0.01C is a good rule of thumb. This results in a negligible change in terminal voltage, once the current is removed and the battery equilibrates. This procedure is very important when performing capacity CC tests, defining a consistent starting point between different tests.

Stoichiometric drift

The battery voltage is a function of the degree of lithiation of both the anode and the cathode. 'Stoichiometric drift' is a descriptive term for changes in the degree of lithiation of both electrodes, as a function of charge passed, as the battery ages and degrades. Stoichiometric drift can be visually viewed as the squashing and shifting of the PE_{data} , NE_{data} and $Cell_{data}$ curves in Figure 11 (c) along the x-axis. These changes in the curve shape result from the loss of active material of both electrodes. This results in different degrees of lithiation (and so different half-cell voltages and full cell voltage) for the same amount of charge passed because there is a reduction in the total amount of electrode material.

3.1.2. Electrochemical Impedance Spectroscopy (EIS)

The following section is a summary from the text books (10,71,72).

Electrochemical Impedance Spectroscopy (EIS) is an established experimental method taken from electrochemistry. EIS is used to analyse not only the Resistive, but also the Capacitive and Inductive behaviour of the battery. The EIS test is performed by applying a small alternating signal to the battery. For example, a battery that is originally held at OCV, has a

small sinusoidal AC current applied at a given frequency to the terminals and the resulting voltage response is measured. One of the advantages of this technique is that the response to the AC signal is indefinitely steady, hence high precision measurements can be made by averaging over many cycles. The above process describes a single EIS measurement at a single frequency. An EIS test takes the form of a frequency sweep (EIS-sweep). This sweep consists of multiple EIS measurements that are performed over a range of frequencies.

EIS has inherent limitations:

1. Time consuming, especially with low frequency measurements.
2. Requires a clear understanding of the state of the battery when performing an EIS test.
3. This testing method is only a snapshot of the battery, at one SOC.

Point 3 makes an important distinction between EIS and CC results. One CC result gives information on the entire SOC window. To get a similar breadth of information with EIS, multiple EIS-sweeps at different points in the SOC window are required. This is because the battery impedance is dependent on the SOC.

EIS Testing Theory

EIS and the associated Equivalent Circuit Modelling can be considered as a more complex version of the simplified depiction of the 'real' battery. This assumes the battery internal resistance is a single ideal ohmic resistor of fixed value. The internal resistance of Li-ion battery systems is time dependent, so the concept of impedance must be used.

EIS measures the battery impedance by applying a small sinusoidal alternating signal to the battery and measuring the response. There are two types of EIS, each characterized by the alternating signal that is applied:

- Galvanostatic (GEIS) - alternating current.
- Potentiostatic (PEIS) - alternating potential perturbation.

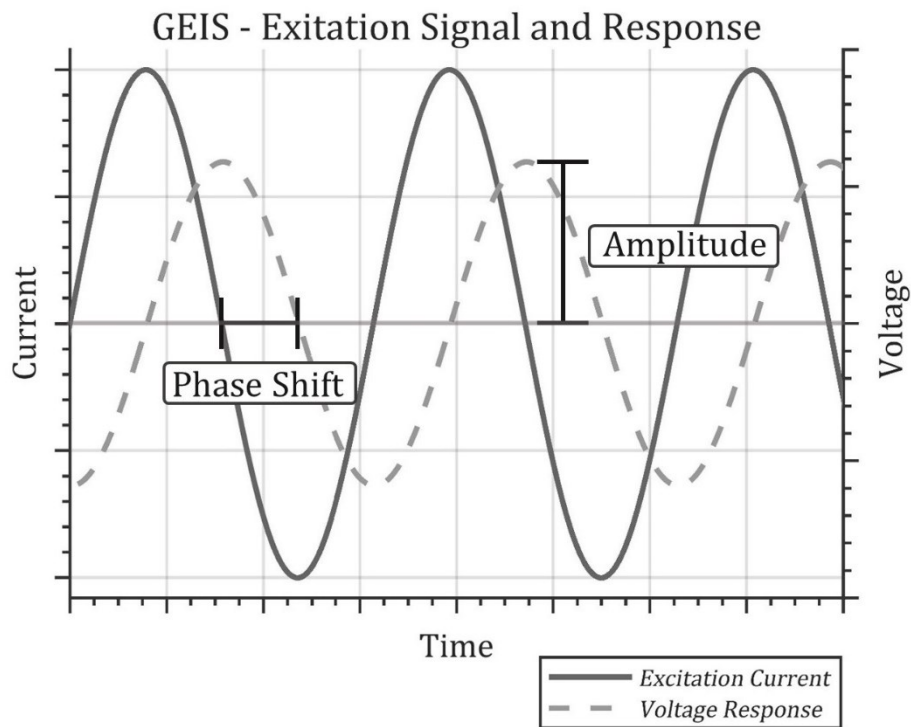


Figure 13: Schematic of the Amplitude gain and phase shift in the battery voltage in response to an AC excitation signal during GEIS.

Figure 13 shows a graphical representation of the sinusoidal AC excitation current and the corresponding voltage response. The frequency remains the same between the input current and the output voltage and the key measurements taken are the amplitude gain and the phase shift. The use of sinusoidal excitation enables the relationship between the current and voltage of the battery to be written in complex notation.

Equation (9) expands Ohm's Law to include complex impedance, with both a real and imaginary part.

$$V = i Z(\omega) = i * [Z_{Re} - jZ_{Im}] \quad (9)$$

Where:

ω = Angular frequency of the excitation frequency at that measurement point

Z_{Re} = The real component of the complex impedance

Z_{Im} = The imaginary component of the complex impedance

Results from an EIS sweep are plotted on a Nyquist plot with the real impedance along the x-axis and the inverse of the imaginary component of the impedance plotted on the y-axis. An example of this is shown in Figure 14.

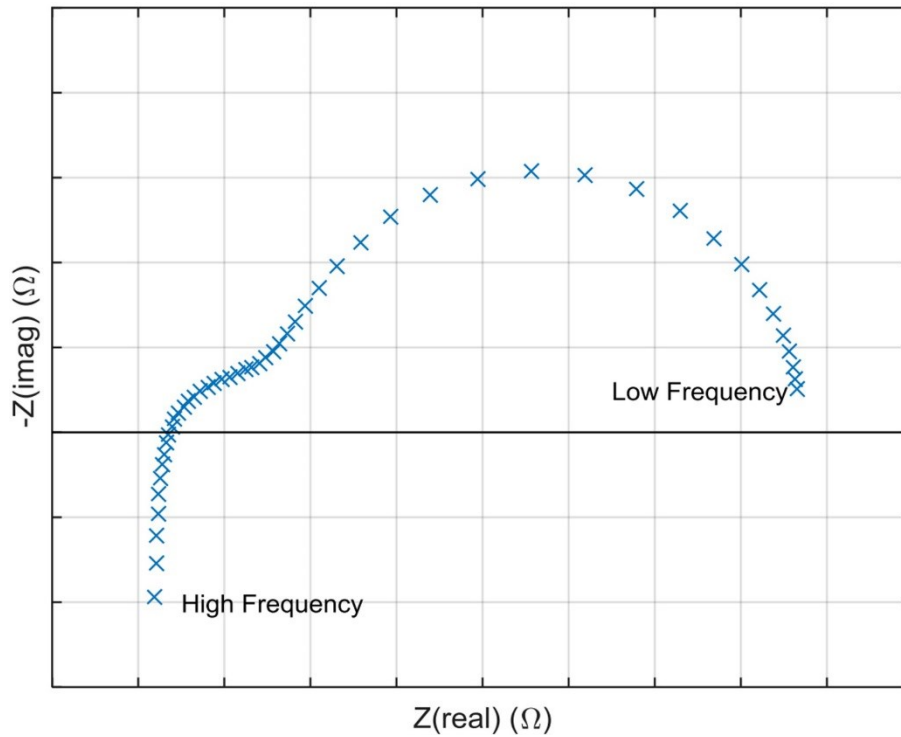


Figure 14: Example of a typical Nyquist plot showing EIS data from a Li-ion battery. Figure taken from (82). Image reproduced with permission from the author, under open access licence.

3.1.3. Differential analysis methods

Differential Analysis Methods are data analysis methods primarily applied to CC data sets. Differential methods such as Incremental Capacity Analysis (ICA) look at the rate of change of terminal voltage with respect to charge passed (dQ/dV). These differential methods greatly expand the inferences to be drawn from a CC test. There are three differential methods used, which all use the same principle. The following list describes each method and the key information that can be gleaned from them.

Incremental Capacity Analysis (ICA) and Differential Voltage Analysis (DVA)

These two methods are the reciprocal of each other. ICA is the rate of charged passed for a given voltage change (dQ/dV). DVA is the rate of change of voltage with respect to charge passed (dV/dQ). Examples of both are given in Figure 15 (a) and (b). Both these plots demonstrate how the differential curve changes as the batteries ages. All lines are from 0.1C charges performed every 200 cycles over a total of 2000 cycles. The grey-scale from dark to light signifies the change as the battery ages.

ICA highlights voltage plateaus in the discharge curves. Conversely the peaks in the DVA curves highlight the regions where the terminal voltage changes rapidly. Papers in the literature have linked the different peaks in these curves to phase transitions in the two electrodes and then used this to track stoichiometric drift and degradation (70,73–79).

Differential Thermal Voltammetry (DTV)

This differential method analyses how the battery temperature changes throughout a constant current discharge. A higher discharge current than that used in ICA/DVA methods, is required to induce a significant temperature rise. The surface temperature measurement

can be taken with a thermocouple. The rate of change of temperature with respect to voltage (dT/dV) provides similar results to ICA, but with the addition of an entropic term (80,81).

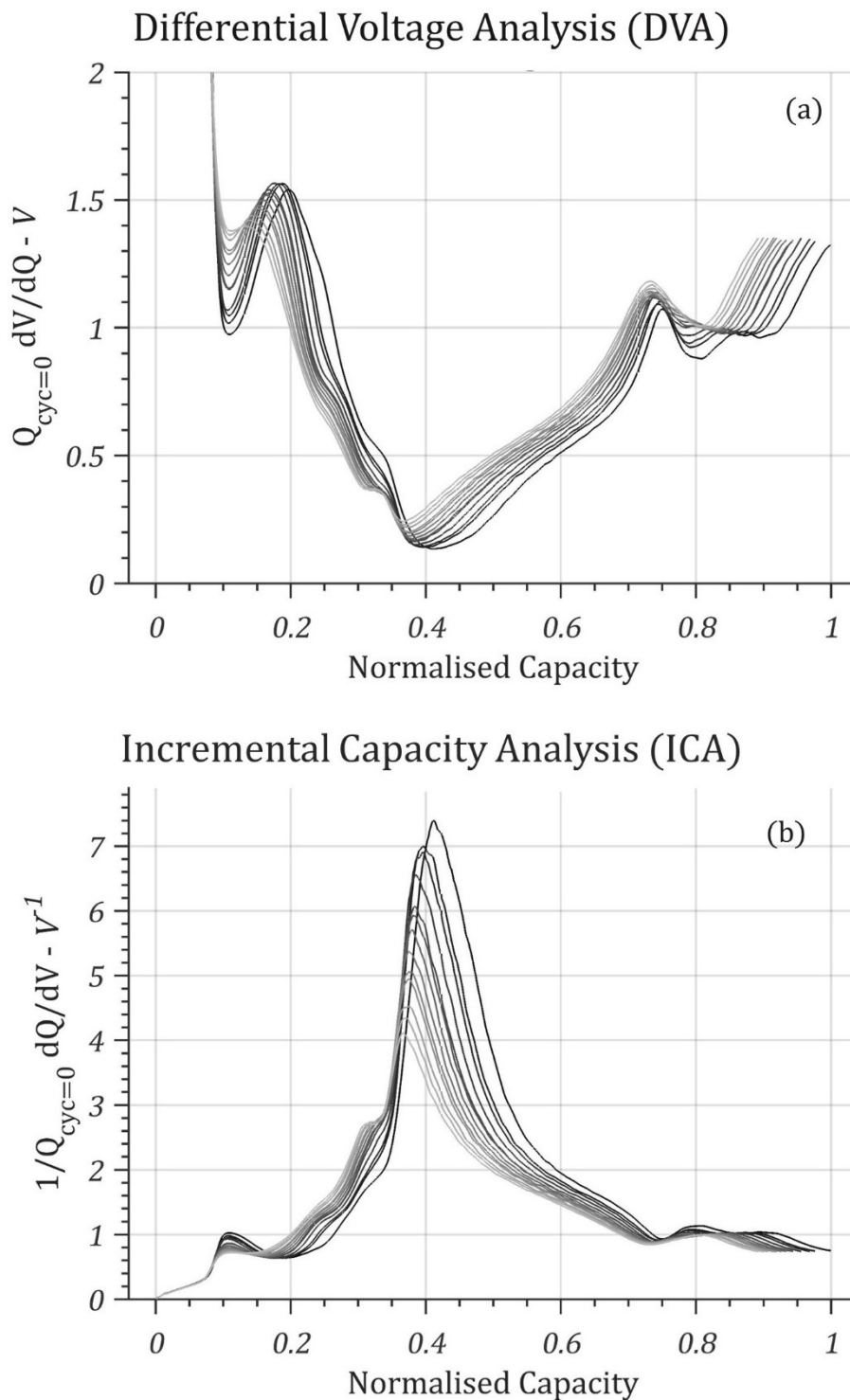


Figure 15: (a) Differential voltage analysis curves for a Li-ion battery as it is aged. (b) Incremental capacity analysis curves for a Li-ion battery as it is aged. Both DVA and ICA curves generated from 0.1C charges of a battery every 200 cycles for 2000 cycles. Curve colour transitions from dark to light as the battery ages.

3.1.4. Temperature effects

The three measurement variables for Li-ion battery testing are terminal voltage, charge passed and temperature. The rate of charge passed, current is the control variable for the techniques listed above, with the voltage being the measured variable.

Battery temperature is very important, as it significantly influences the current-voltage relationship of the battery. It also accelerates various degradation mechanisms, see Sections 2.2 and 2.3. The thermal conditions of the battery must be understood throughout experiments. Ideally, temperature would be a controlled variable, maintained at a constant value. In Li-ion battery testing, temperature is both a controlled and measured variable. Generally, the battery temperature is set to a target temperature, but internal losses within the battery cause internal heat generation. Thus, the thermal management of the batteries during testing is a very important part of experimental design to generate reproducible and comparable results (82).

The thermal management of batteries is performed in several ways, by applying different thermal boundary conditions to different battery surfaces.

Insulation in Adiabatic and Isothermal conditions

Often in battery testing the internal losses are the variable of interest. The temperature rise in the absence of any heat transfer from the battery may be measured. During these experiments, insulated thermal boundary conditions are required, adiabatic conditions.

Alternatively, in very slow rate experiments, where internal heat generation is negligible, insulated thermal boundaries can prevent heat transfer from the environment to the battery. Insulation from environmental temperature changes is important in isothermal experiments.

Bench-top testing of batteries

The simplest form of battery thermal management is with the battery resting on a laboratory work surface at ambient room temperature. This is a poor method of thermal management because:

- Fluctuating ambient temperature, night to day and seasonal variations.
- Different boundary conditions to different surfaces. Top surface exposed to convective heat transfer, bottom surface insulated by work surface.
- Little to no control of air currents over battery surfaces. Uncontrolled rate of heat-transfer due to variable forced air convection.

Thermal chamber

The testing rig is contained inside a chamber where the ambient temperature is controlled. This is an improvement over a benchtop method, as it reduces fluctuations in the ambient temperature and enables a wider range of temperatures to be applied.

Conductive heat transfer

The use of conduction thermal management (rather than simple convection) increases the rate of heat transfer from the battery. This enables greater thermal control of the battery temperature. Conductive heat transfer refers to the heat transfer from the battery surfaces. Subsequent transfer of the thermal energy to the surroundings can be performed in many ways. Examples include:

- Water cooling loop with radiators.
- Forced convection over finned heat sinks.
- Thermal inertia of large thermal mass, with subsequent passive convection to the surroundings.

Conductive heat transfer methods increase the rate of heat transfer per unit area. They also enable different thermal conditions to be applied to different regions of the battery.

Temperature measurement

The most basic method of temperature measurement is to assume the battery is at the same temperature as the surroundings. Due to internal heat generation this assumption will only hold when performing very low current tests.

A far more accurate battery temperature measurement method is to monitor the battery surface temperature. This is usually performed using either thermocouples or thermistors. Thermal imaging cameras can also be used to measure the battery surface temperature.

3.2 Mechanical Testing

There are three levels of mechanical testing of Li-ion batteries:

- Single electrode pair/component testing.
- Mechanical abuse.
- Mechanical testing of batteries in use.

Single electrode pair testing is the mechanical equivalent of coin cell testing. This simplification of the battery enables the isolation of specific mechanical phenomena and provides information to inform hypothesis on full battery testing. Testing is generally performed using a dilatometer (52,53,66,83–85).

Mechanical abuse testing of batteries is a large field, covering safety concerns about the general use of Li-ion batteries. It is focused on the mechanical abuse tolerances of batteries and their catastrophic failure. This large field is beyond the scope of this work and not discussed further.

Mechanical testing of batteries in use

Mechanical testing of Li-ion batteries in use investigates different mechanical boundary conditions that affect the battery during normal operation. Such work can be further divided into two aspects: Vibrations and Compression/Expansion. Vibration testing is beyond the scope of this work and not discussed further. Compression/Expansion research investigates the mechanical state of batteries during both cycling and ageing. This is the primary focus of this body of work. The methods that have been employed to monitor the mechanical state of batteries are discussed below.

3.2.1. Compression/expansion testing techniques

Mechanical testing of commercial batteries monitors the mechanical changes in the battery using two methods that measure either:

- Thickness changes in the battery
- Pressure changes in the battery due to mechanical constraint.

In the literature, the thickness change measurements are exclusively made using linear variable displacement transducers (LVDTs), predominantly on unconstrained batteries (2,42,44–46,57,62,65).

There is more methodological variety in assessing the pressure changes in a constrained battery. The most common method employed is using load cells to measure the force and then converting that force to a pressure (2,42,44–46,57,62,65). This is performed with a stand-alone load cell, or in a tensile testing machine. An alternative has been employed by Barai et al. (64), where pneumatic bladders were used to apply compression to the battery surface and the air pressure in the bladder was used as the pressure measurement. Barai et al. (65), in a different work, also measured the pressure distribution across a large form factor battery, using a Tekscan pressure sensor.

Degradation experiments primarily focused on the effect of pressure on the lifetime battery performance, have employed different constraints and loading procedures. Cannarella et al. (2,57) applied different initial compression to four batteries and measured the subsequent pressure changes throughout the 2000 cycle experiment. Mussa et al. performed an experiment using the testing method and loading procedure on single layer pouch batteries (66).

In other work performed by Fabian et al. (67), the focus was to compare the difference between different constraint configurations. One battery was rigidly constrained, and the pressure measured. Another battery was compressed under a compliant constraint and battery thickness measured. This experiment followed the same loading procedure as in (2) where an initial compression was applied at the beginning of the experiment and no further external changes were applied.

Barai et al. performed a similar experiment on rigidly constrained batteries (measuring pressure) but with a different loading procedure. The compressed batteries were cycled for a total of 1200 cycles. To maintain the target pressures throughout the duration of the experiment, the pressure was re-set to the target pressures every 150 cycles (65).

These different approaches can be considered as passive and active compressive boundary conditions. During the active experiments, the compression conditions externally applied to the battery change throughout the experiment. In passive experiments, no external changes are performed after the initial compression has been applied. Note that the pressure or thickness will change under passive conditions. This is due to changes in the battery and/or due to the use of compliant components in the testing set-up, such as springs. Applying passive conditions are much simpler to apply and represent conditions that simulate real

applications. Using the active condition in Barai et al. (65) is not justified, beyond wanting to return the pressures to the 'target pressures'. There is no explanation what the active condition represents, or why it should be desirable.

3.2.2. Effects of compression on different battery chemistries

This body of work is focused on batteries with an NMC cathode paired with a graphitic anode. Other battery chemistries could be affected by compression differently. The following brief discussion splits the different cell chemistries into three categories and theoretically discusses how compression might affect them. The primary differentiator between the three categories is the anode material being employed in the battery.

- 'Standard' cathode chemistries paired with graphitic anode.
 - NMC, LCO, LMO etc.
- 'Standard' cathode chemistries paired with silicon doped (< 10%) graphitic anode. (86)
- Lithium Titanate (LTO) anode batteries.

The first category includes the NMC battery chemistry being tested and it is considered that this category of battery chemistries will be affected by compression in a similar manner. All the different batteries have the same internal structure and components, except the active material in the cathode. The different cathode materials exhibit similar levels of intercalation driven strain to that of NMC that are much smaller than that of the graphite anode (48). Hence the graphite anode dominates the battery thickness change during cycling for all the batteries.

The second category encompasses the same cathode chemistries as the first but paired with a silicon doped graphite anode. This battery chemistry typically exhibits a faster rate of capacity fade compared to pure graphite batteries. This is attributed to the large volumetric expansion of the Si particles when alloying with the lithium during charging. This expansion causes amorphization and pulverisation of the Si particles resulting in the following (86,87):

- Particle cracking leading to additional SEI formation (consumption of Li).
- Pulverised Si becoming electrically isolated (loss of active material).
- Greater irreversible thickness change with ageing due isolation of the alloyed Si.
- Pulverised Si particles disperse in the anode pores blocking ion access (increased battery impedance).

Silicone doped anodes also show significantly greater thickness changes than that of graphite only, up to 1.5 times the proportional thickness change (87).

No studies have been found reporting the effects of compression on the cycle life of silicon doped anode batteries. It is hypothesised that the effects of compression will be different to that of graphite only batteries. The primary differences being:

- Improved electrical contact to pulverised Si particles reducing the loss of active material.
- Increased volume change during cycling and ageing inducing greater separator strain.

The third group has LTO anodes that exhibit no lithiation driven strain. These show significantly smaller thickness changes than other Li-ion battery chemistries. As with the silicon doped anode batteries there are no studies looking at the effects of compression of LTO batteries. It is hypothesised that the lack of anode expansion/contraction with cycling will result in the effects of compression being different to that of graphite only batteries. The primary difference being the reduced cyclic strain of the separator with electrochemical cycling of the battery.

4. Short-Term Mechanical Experiments and Data Analysis for Differential Techniques

This chapter is comprised of 5 sections. The first section discusses an evaluation methodology of the data processing required by differential analysis techniques. The remaining four sections introduce short term experiments investigating the effects of compression on Li-ion batteries.

4.1 Data Processing for Differential Techniques

As introduced in Section 3.1.3, within the battery-testing community there is a range of techniques for analysing experimental datasets by differentiating one variable by another.

The two most common techniques are:

- Incremental capacity analysis (ICA), evaluates dQ/dV
- Differential Voltage (DV), evaluates dV/dQ

Other methods including mechanical variables are:

- Differential Thermal Voltammetry (DTV), evaluates dT/dV (80,81)
- Strain derivatives, evaluates $d\varepsilon/dQ$ & $d^2\varepsilon/dQ^2$ (typically strain with respect to charge passed) (57,58,60)
- Force derivatives, evaluates dF/dQ (62)

Where:

- V = Voltage - Volts
- Q = Charge passed - Coulombs or Ah
- T = Temperature - °C
- ε = Strain
- F = Force - Newtons

These analytical methods produce graphs which show different features, such as peaks or troughs. Processes or phenomena are then attributed to them. Subsequently, changes in these features are used to understand what changes have occurred inside the battery.

Ideally, all measurements made would have sufficient accuracy so that numerical differentiation can be performed on the raw experimental data. This would produce what can be considered a “useful” differential curve; namely a smooth continuous curve with minimal noise, where clear features can be identified. Li et al. have produced a paper that discusses the quality of the differential curves. (88)

Direct numerical differentiation is possible with very high precision coulometry testing machines. However, for testing using standard battery cyclers some form of smoothing of the raw experimental data is required to produce a differential curve without excessive noise.

Examples of methods employed to perform smoothing include:

- Moving Average filtering
- Piecewise curve fitting, most notably Savatzky-Golay filters (S-G).
- Modelling techniques (89–91)
- No description of (or if) smoothing that has been performed (70,92)

The most commonly applied techniques are the moving average and piecewise curve fitting, and these are the methods that will be discussed here.

There are three principal smoothing parameters that can be varied to control the degree of smoothing:

- Smoothing window
- Number of times the smoothing is performed
- Degree of polynomial curve being fitted

From personal experience, discussions with colleagues and in the literature (88), smoothing is an imprecise process. The smoothing of data is more of an art than a science, with the goal of achieving a “Goldilocks region” - where the resulting differential curve is sufficiently clear to draw conclusions but avoiding introducing smoothing artefacts. Examples of smoothing artefacts are:

- Reducing peak heights
- Introducing new peaks and troughs
- Removing small peaks completely

The current practice in the literature is to only state the smoothing method used. There is usually no discussion of the validity of the resulting curves and any artefacts that could have

been introduced by the smoothing performed. The first of two exceptions to this are Samad et al. (62) who briefly discuss the influence of the width of the smoothing window on the S-G filter and then justify the window chosen. The second is Merla et al. (80) who in the smoothing of data for DTV analysis sets a Pass/Fail criterion of: *“median of the absolute deviations of recorded dataset about the smoothed line is below <0.3%”*. This has the advantage of simplicity in performance and gives a quotable confidence metric.

This section introduces a methodology for testing the validity of the smoothing, and thus the confidence that can be placed in the resulting differential curves. The purpose of developing the methodology is:

- To standardize the technique for checking the smoothing process.
- To be easily quotable.
- To provide a quantifiable metric.

Figure 16 is a schematic of the process of performing differential analysis and where this method is applied, acting as a feedback loop.

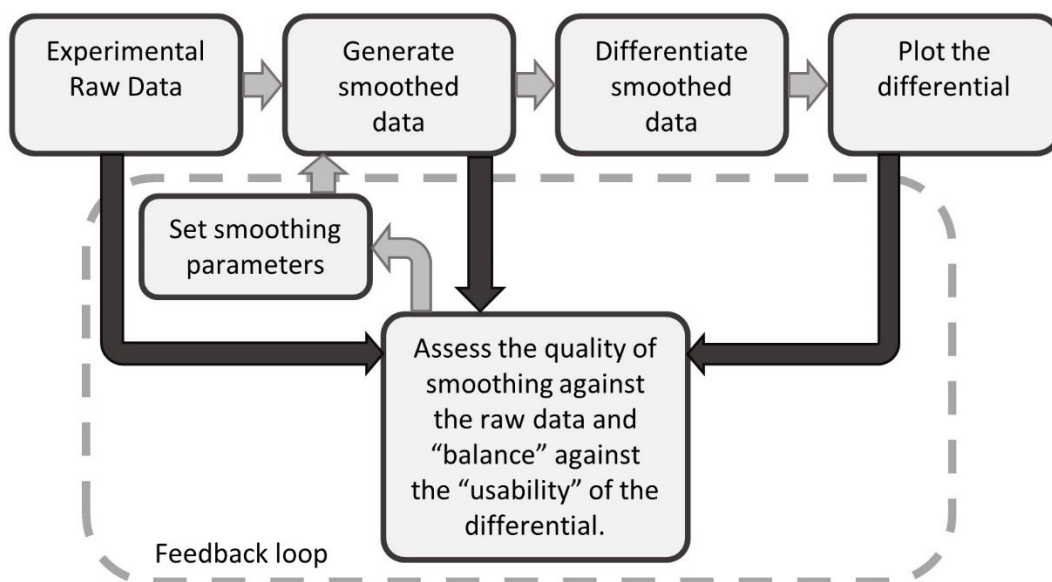


Figure 16: Flow diagram for generating differential plots from experimental data. Highlighted is where the proposed feedback loop fits into the process and what information is used in the feedback analysis.

4.1.1. Underlying assumptions of the smoothing process

Fundamental assumptions are implicit when using smoothed experimental data. All experimental measurements have some form of uncertainty that is referred to as error. Experimental error can be split into two categories; Systematic error and Random error. In the context of this discussion systematic errors could take the form of:

- significant temperature fluctuations of the battery during the experiment.
- iR drops in the voltage sensing circuitry.
- Poor isolation between the mains supply and the voltage measurement causing a 50 Hz fluctuation in the data.

Minimising these systematic errors must be addressed at the experimental design stage, as post processing of the data can only account for them in a limited fashion.

The Random errors are intrinsic to the process of taking the measurements. Small random fluctuations are insignificant when looking at the data in its raw form, like a discharge curve. When attempting to numerically differentiate the data, these random fluctuations manifest as significant noise, hence, smoothing is required.

The underlying assumptions that have been made in performing all differential analysis in this body of work are:

1. The real/true phenomena being measured and analysed are a continuous function.
2. The deviation in the physical measurements is only due to random errors
3. The deviations are normally distributed about the true value.
4. Smoothing of the data is an attempt to reproduce the true continuous function and eliminate the random error component of the measurement.

With these assumptions the residuals between the raw data and the smoothed should represent the random error in the measurement and any non-random features should

highlight any smoothing artefacts and systematic errors. Hence these methods focus on regression and residual analysis to assess the validity of the smoothing performed.

4.1.2. Residual analysis

The regression and residual techniques are split into two sections, numerical and graphical. (93,94) The numerical methods have the appeal of being a quantifiable assessment of the quality of the smoothed data. The numerical measures include:

- Coefficient of determination (R squared)
- Residual variability

These compare the different contributors to the variance in the data set.

Coefficient of determination (R^2)

If the residuals are negligible compared to the variability in the data set, R^2 will be close to 1.

If the residuals are significant, then R^2 will be close to 0. Hence, to have confidence in the validity of the smoothed data, R^2 must be sufficiently large.

Residual variability

This assesses the variance of the residuals between the raw data and the smoothed data, with the standard deviation being the square root of variance. This combined with the mean of the residuals can be used to question the quality of the smoothed data in the following ways:

- Is the mean of the residuals close to zero? A value significantly greater or less than zero suggests a shift in the curve resulting from the smoothing process.
- Are the residuals close to the mean? Assuming a normally distributed set of residuals, 95.4% should lie within $\pm 2\hat{\sigma}_{\text{resid}}$ of the mean. Thus, the value of 2 standard deviations of the residuals can be used as a comparative metric for how large the residuals of smoothing are.

Division of the residual values by the measurement error can further improve the usefulness of the above two metrics by standardisation. This links the residuals' mean and the residuals' range back to the equipment, thus making smoothed data from different equipment types comparable.

Graphical methods with residuals

Residual plots can be used to observe patterns in the data. (93,94) This enables trends, outliers and residual variance to be observed. As with differential plots themselves, interpretation of the residual plots is somewhat subjective.

The first plot to graphically investigate the residuals involves the predicted values and the raw residuals. The initial plot should show the residuals randomly scattered about the x-axis. It highlights any systematic patterns in the residuals, such as increase in residual variance. Then plotting the square of the residuals aids in detecting systematic variation in the residuals. The residuals should be plotted against the predicted (or smoothed) value and not the observed value. This is because the observed values and residuals are generally correlated by a linear trend.

As is the case for the numerical values, the magnitude of the raw residuals can be related back to the measurement equipment by dividing the residuals by the measurement error (the error associated with the testing equipment used to gather the raw data).

Normal Probability Plot

A Normal Probability Plot is a graphical method for showing if the residuals are approximately normally distributed. To do this the residuals are ordered by magnitude (smallest negative to largest positive) and plotted on the y-axis of a special graph paper known as the “normal probability paper”. If normally distributed, all the points should lie on roughly in a straight line and departures from this indicates departures from normality (93).

4.1.3. Smoothing from numerical differentiation

It should be noted that a form of smoothing may be implemented whilst performing the numerical differentiation. In the same way that piecewise curve fitting can be implemented to smooth the data, the gradient of the fitted curve can be used as a measure of the gradient at that point. Although not discussed in depth here, it is ill-advised to attempt smoothing during the differentiation process. It would be very difficult to refer back to the original data and pick up any artificially introduced artefacts.

Unless otherwise stated, the differentiation was performed by taking the gradient of a 1st order, least-squares fit polynomial with a centred window of 10 data points. All data sets in the body of work where differential methods are applied are from 0.1C discharges with a sample frequency of 1 Hz. Thus, the 10-point span is less than 0.3 % of the total span of the data set. The author is therefore confident that the numerical differentiation has not introduced any smoothing artefacts.

4.1.4. Implementation of residual analysis

This section introduces a method of presenting the regression and residual analysis. It subsequently discusses the usefulness of each of the methods. The data used in this section is an example and is the 0.1C discharge data set from the Isothermal Breathing experiment, Fresh battery at 25 °C. See Section 4.6 for detail on how this data was gathered. This dataset was smoothed using two techniques:

- Moving average filter
- 3rd order S-Golay filter

For these two smoothing methods there are two control variables:

- Number of times the smoothing is performed
- Smoothing window span

A high and low value for both control variables was chosen and smoothing with all four combinations of these variables was performed. Table 2 shows the high and low control variables used.

Table 2: Smoothing control variable values

	Loops	Span (% of the total number of data points)
Low	1	100 (0.3%)
High	10	675 (2.0%)

Figure 17 and Figure 18 show the analysis for the small window span and the low number of loops and Figure 19 and Figure 20 are the same for the large span with many smoothing iterations. The figures for the other two combinations of control variables can be seen in Appendix A.

In the top left of Figure 17 and Figure 19 is a table containing the outputs of the numerical techniques. The bracketed values for the Residual mean and Standard deviation are normalised against the measurement error (for this data-set 1.2 mV). The numerical techniques on their own cannot be used as an independent metric for the quality of the smoothing but rather are more useful as a warning flag that the smoothing is likely to be very poor. This is evidenced in the moving average data in Figure 17 where the moving average has shifted significantly from zero with a standard deviation of 11 times the size of the measurement error. The R^2 values are almost always 1 unless the smoothing employed is very aggressive.

Plot (a) in both Figure 17 and Figure 19 are the normal probability plots of the residuals. As with the tabulated values, this plot acts as a red flag for the smoothing having been too aggressive. Typically, between 0.05 and 0.95 on the y-axis, the residuals follow a straight line with two tails at the extremes. This is a common feature of this type of plot and does not prove that the residuals are not normally distributed. For the voltage data, changing the smoothing parameters tends to simply change the magnitude and the starting points of the two tails. For other lower quality data sets, this plot shows some additional features, discussed in Section 4.6.2.

	Mov_Avg	S-Golay
Meas' Error	1.20e-03	1.20e-03
Resid Mean	1.69e-05(0.01)	-8.47e-08(-0.00)
Resid SD	2.00e-04(0.2)	1.28e-04(0.1)
Rsquared	1	1
Smth Span	102(0.3%)	101(0.3%)
Smth Loops	1	1
SG Degree	-	3
Diff Span	10(0.03%)	10(0.03%)

Light: Mov. avg Dark: S-golay

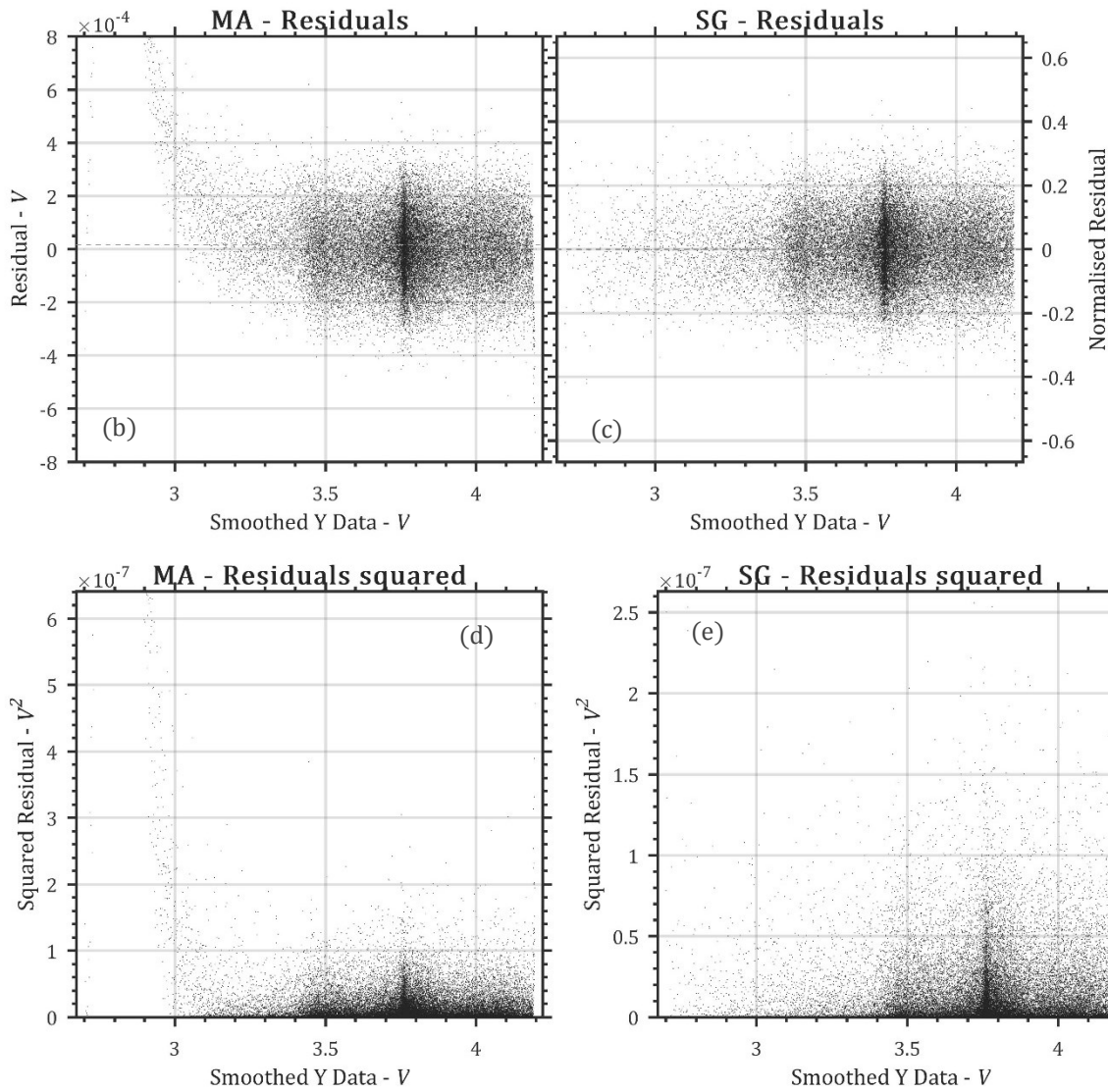
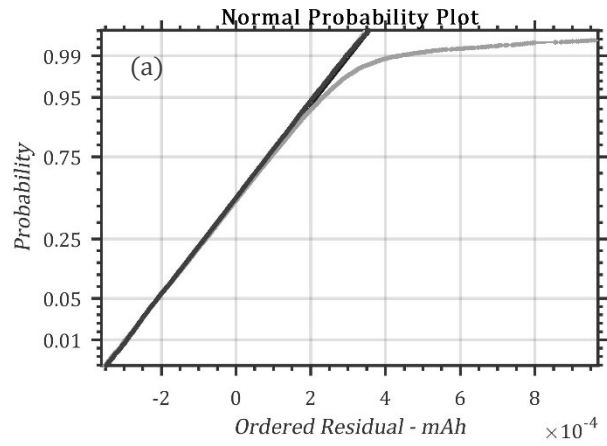


Figure 17: Residual Analysis – small span, few loops (page 1 of 2)

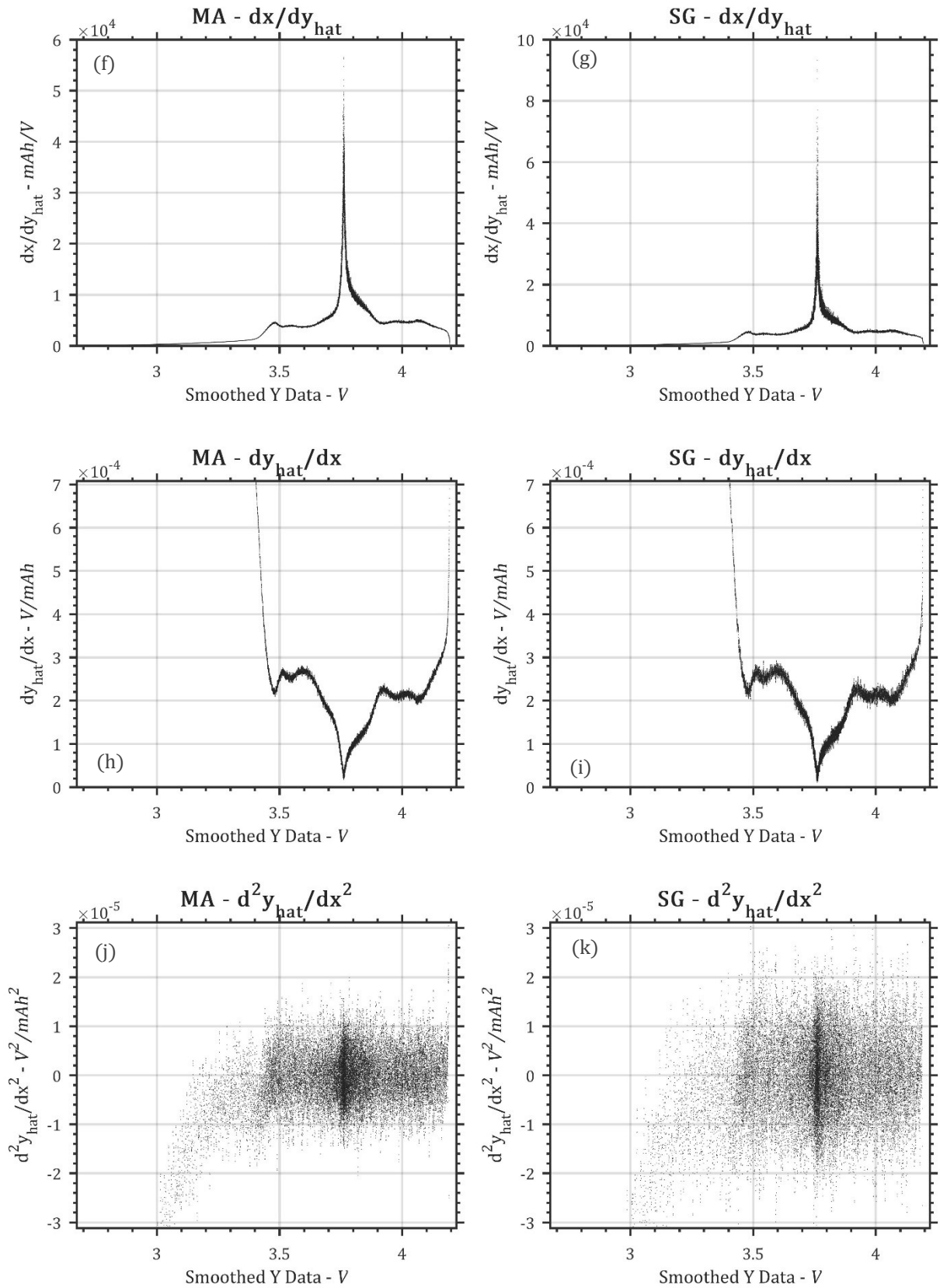


Figure 18: Residual analysis - small span, few loops (Page2 of 2)

	Mov_Avg	S-Golay
Meas' Error	1.20e-03	1.20e-03
Resid Mean	3.16e-03(2.63)	-6.89e-05(-0.06)
Resid SD	1.32e-02(11.0)	8.33e-04(0.7)
Rsquared	0.997	1
Smth Span	676(2%)	675(2%)
Smth Loops	10	10
SG Degree	-	3
Diff Span	10(0.03%)	10(0.03%)

Light: Mov. avg Dark: S-golay

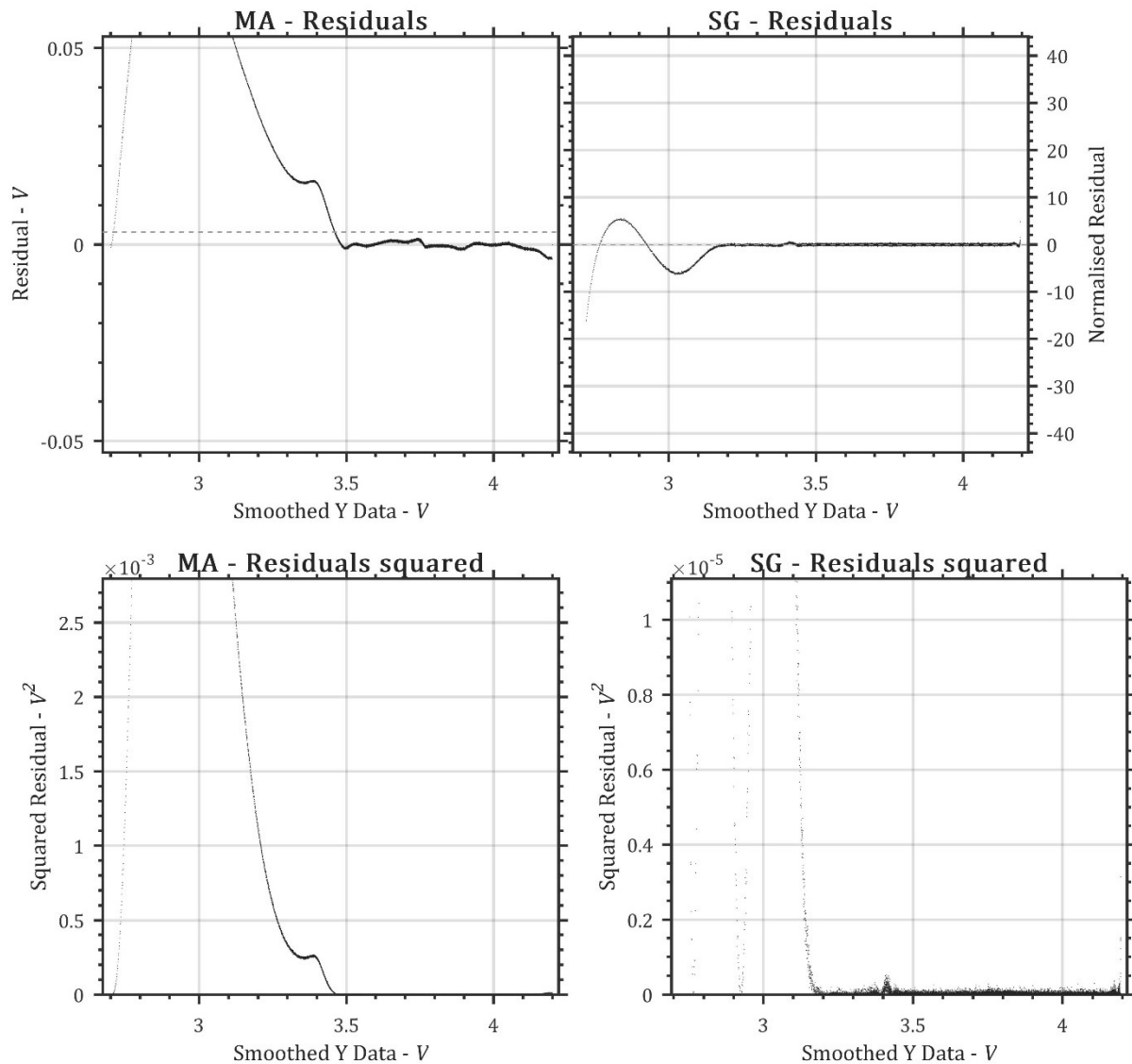
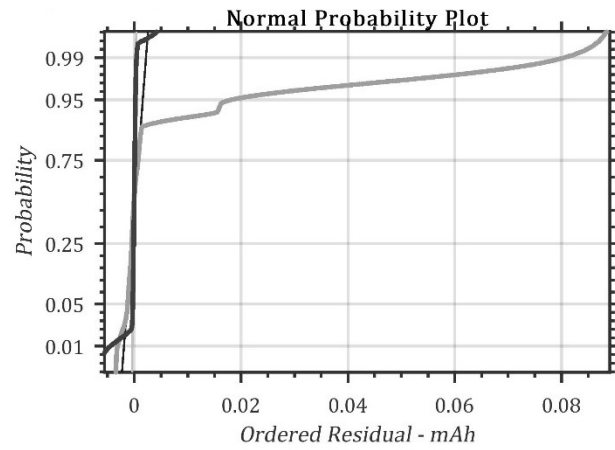


Figure 19: Residual Analysis – large span, many loops (page 1 of 2)

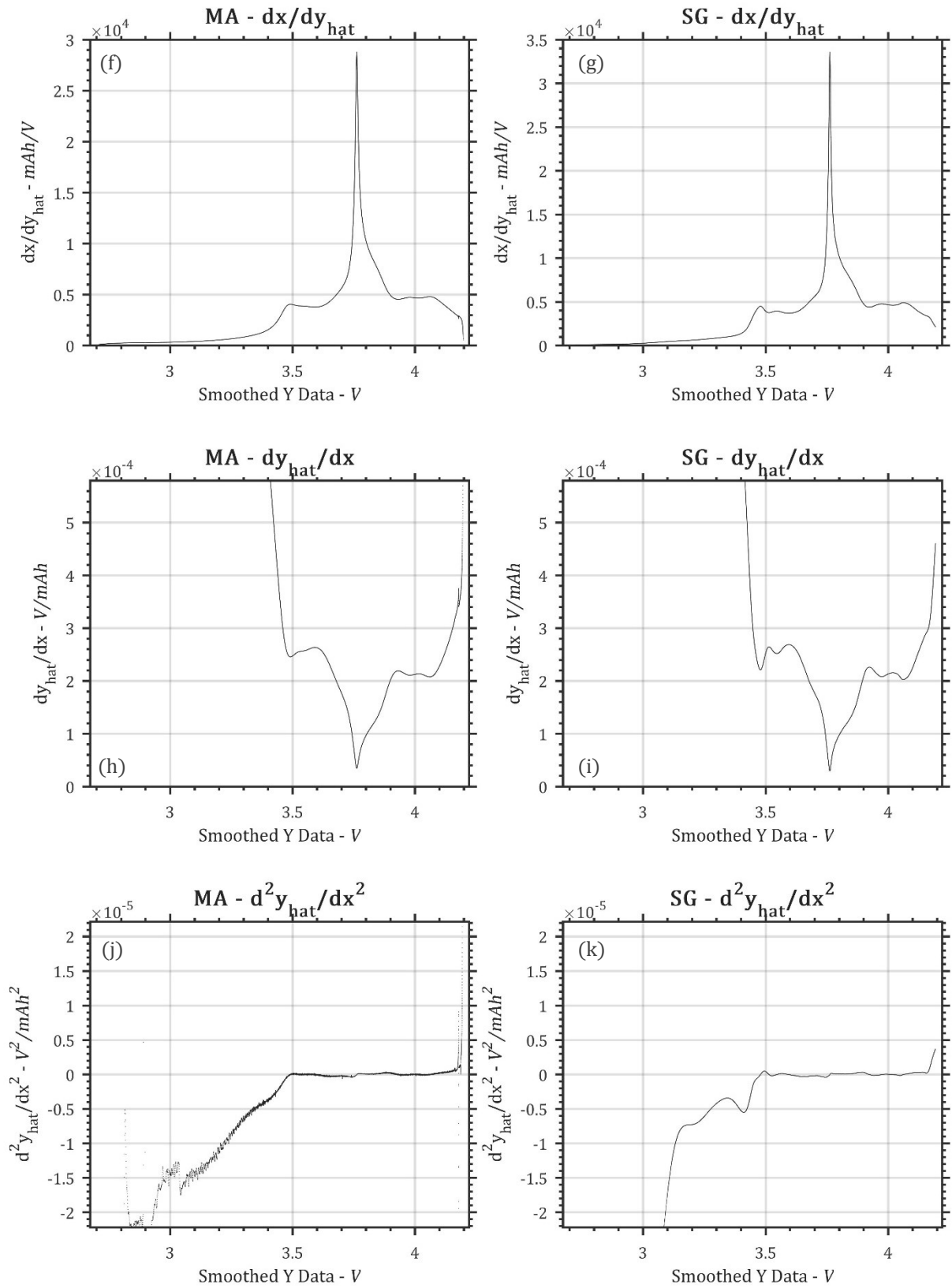


Figure 20: Residual Analysis – large span, many loops (page 2 of 2)

In Figure 17 and Figure 19, plots (b) and (c) show the raw residuals for both smoothing techniques on the same y-axis scale. The magnitude on the left y-axis has been normalised against the measurement error on the right axis. These are the most useful plots for assessing the quality of the smoothing. Features such as:

- Large deviations from zero, this manifests as vertical stripes across the x-axis where there are no data points. It shows that for that region the smoothed curve runs above or below the raw data.
- Concentrations of data points.
- Deviations at the two ends.
- General magnitude of the residuals.

In Figure 17 (c) the residuals can be seen to be small and in a consistent band across the entire data set. This is in contrast to the other three residual plots in Figure 17 and Figure 19 with the two moving average residuals showing a very large positive deviation at the lower voltages. This is a common feature of the moving average filter and is due to the high rate of change of voltage at that stage of the discharge. Although a similar deviation occurs in the S-Golay curves, this feature in the moving average filter has a larger magnitude at lower voltages and settles back to random distribution about the x axis at higher voltages. Thus, the S-Golay smoothing filter is used for all differential analysis in this body of work.

The residuals in Figure 19 (c) show that the smoothed data deviates above and below the raw data at low voltages. This is a common feature with these voltage vs capacity data sets and is due to the high rate of change of voltage in that region. This is due to it being near the edge of the data set measurements.

Both ends of the data set are prone to large non-random residuals. This results from the piecewise curve fitting being limited by there not being as many data points “forwards” or “backwards” of the data point at the edge. This makes the curve fitting biased to one side and so less precise. This is more of a concern as the size of the smoothing window increases.

In Figure 17 and Figure 19, plots (d) and (e) are the squared residuals. This plot is useful for highlighting small fluctuations in the raw residuals. An example is the small spikes in plot e of Figure 19 at 3.4 V and 4.2 V. The 3.4 V spike can be seen to be comprised of three smaller spikes, suggesting the smoothed curve fluctuated above and below the raw data.

In Figure 18 and Figure 20, plots (f) to (i) are the end goal for this entire process; the differential curve. These are the ICA in plots (f) and (g), DV in (h) and (i). In Figure 18 these plots are noisy, suggesting the data has been under-smoothed. The differential plots in Figure 20 demonstrate the importance of looking at the residuals from the smoothing process. In isolation both plots seem to be serviceable (except for the discrepancy at 4.15 V in the moving average curves) and potentially someone inexperienced could use either. When compared, some information has been lost in the moving average smoothing around 3.5 V and 4 V and the magnitude of the central peak of the dx/dy curve is being lowered. Looking back, plots (b) and (c) clearly show that the moving average differential should not be used; large amounts of information or features are either removed or introduced by the applied smoothing. The S-Golay differentials between 3.5V and 4.1 V are a good representation of the raw data.

Finally, the second order differential plots (j) and (k) do not provide any information on the smoothing of the data but does provide a good visual guide for detecting over-smoothing.

Smoothing data to produce 'useful' differential curves is somewhat of an art, where the Goldilocks region of just enough smoothing is the goal. Not enough smoothing and there is a lot of noise; too much and information might be lost, or artefacts added by the over-smoothing. Plotting the second differential gives a clear indication of the level of noise in the first differential. A second differential that looks like a spread of randomly scattered points, as in Figure 18, indicates insufficient smoothing. A smooth continuous curve suggests over-smoothing. Hence the object is to achieve a suitably smooth and continuous first differential, with noise in the second differential.

4.1.5. Residual analysis - conclusion

The goals from developing this data processing methodology were:

- To standardize the technique for checking the smoothing process.
- To be easily quotable.
- To provide a quantifiable metric.

Unfortunately, this has not been fully implemented using numerical methods (R^2 and residual variability). They are unable to capture all the nuances of the smoothing process, and act more as a red flag. Despite this, the graphical methods do give very useful feedback on the smoothing process. Where the nature of the raw data means a consistent or high-quality differential cannot be generated across the whole data set, the graphical methods show where sections or features can be ignored or analysed. They also provide multiple red flags of problems in the smoothing.

Producing differential curves is an iterative process, with many decisions and judgments to be made, as shown in the wealth of information in Figure 17 –Figure 20.

4.2 Battery Selection

In the context of researching the effects of compression on Li-ion batteries, the battery structure is a very important consideration. The key considerations in deciding the batteries to be tested were:

- Battery form factor
- Electrode configuration
- Power or energy of battery
- Battery chemistry

The battery form factor chosen to be tested was pouch batteries. This is because the thin foil pouch material has a negligible stiffness. It is therefore assumed that all the compressive force applied to the battery is wholly transmitted through the electrode stack.

The electrode configuration chosen was stacked electrode. This was because compression applied to this configuration can be assumed to be uniform across the entire electrode area. The same assumption cannot be made for an obround jelly-roll, where significant stress concentrations will occur at the folds in the electrodes.

Ideally, an energy battery would have been tested. The thicker electrodes and greater ratio of active to passive material would have exaggerated the mechanical effects that occur in the battery, as discussed in Section 2.1.4. The battery chosen was a power battery, because it is a main battery type tested within this research group. Further, an established body of testing knowledge exists within this research group of this battery model.

The most important factor in choosing the battery chemistry was that it had a graphitic carbon anode. This is the most common anode material used and has a significant impact on the electrochemical-mechanical battery properties, discussed in more detail in Section 2.4. The power battery tested, has this graphitic anode, paired with an NMC cathode. The battery model and specifications are given in Table 3 and an image in Figure 21.

Table 3: Li-ion battery used in all experiments, specifications (69).

Property	Value
Manufacturer	Kokam Co. Ltd
Model	SLPB11543140H5
Rated Capacity	5.0 Ah
Thickness (nominal @ 3.7 V)	11.6 mm
Electrode Area	4600 mm ² (40.5 mm x 113.6 mm)
Voltage Limits	UVL: 4.2 V LVL: 2.7 V
Maximum Discharge Rate	150 A [30C] (continuous)
Maximum Charge Rate	10 A [2C] (continuous)

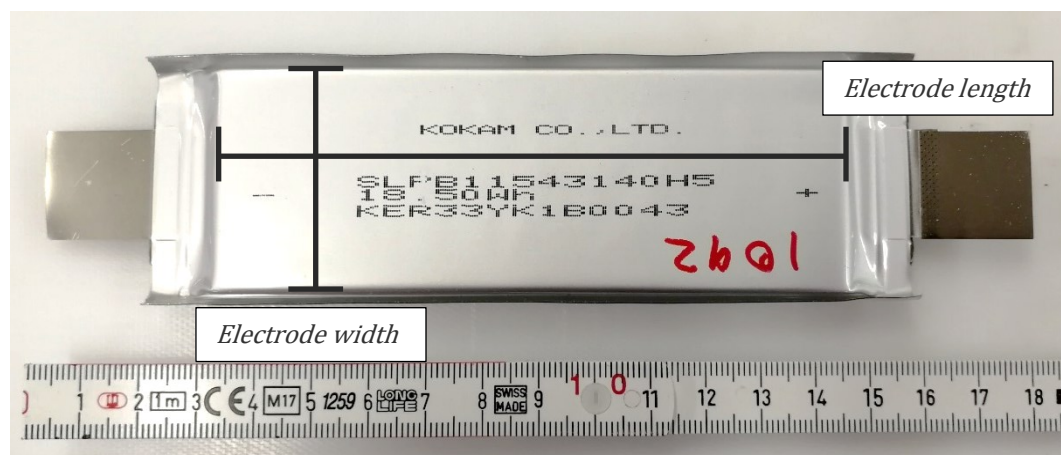


Figure 21: Kokam SLPB11543140H5 NMC battery. 180 mm approximate length including tabs. Length and width dimensions of the electrode area used to calculate the pressure applied to the battery, from force measurements.

Throughout this work the electrode area (used to convert force to pressure) was assessed by externally measuring the length and width of the electrode stack of fresh batteries. The annotation in Figure 21 shows the length and width of this area in relation to the physical battery. The layer quantities and thicknesses of the electrode stack of the Kokam battery are given in Table 4.

Table 4: Kokam Battery [SLPB11543140H5] layer quantities and thicknesses (82,95).

Component	Number of layers	Thickness / μm	Total Thickness / mm	Proportion of total thickness
Casing	2	160	0.32	2.8%
Copper Foil	50	21	1.05	9.0%
Aluminium Foil	51	21	1.07	9.2%
Separator	103	24	2.47	21.3%
Anode (graphite)	100	38	3.80	32.7%
Cathode (NMC)	100	29	2.90	25.0%
Complete stack	406	-	11.61	-

The Youngs modulus (E) and Thermal expansion coefficient (α_t) for the cell internal components are given in Table 5. All values are taken from the literature with the Youngs modulus values for the anode and cathode being the effective values from (96). The Youngs modulus value for the cathode taken is for $\text{Li}_y\text{Mn}_2\text{O}_4$ rather than NMC in the Kokam battery tested, as an equivalent value for NMC could not be found in the literature. The battery casing/pouch material is assumed to have the same material properties as the aluminium foil.

Table 5: Material properties for different battery components.

Component	Youngs Modulus (E) / GPa (96)	Thermal Expansion Coefficient (α_t) / K⁻¹ (95)
Casing	70	$2.30 * 10^{-5}$
Copper Foil	117	$1.60 * 10^{-5}$
Aluminium Foil	70	$2.30 * 10^{-5}$
Separator	0.5	$2.50 * 10^{-3}$
Anode (graphite)	8.9	$5.50 * 10^{-5}$
Cathode (NMC)	5.9	$5.50 * 10^{-5}$

4.3 Initial Loading Rates

Before looking at how compression affects the electrochemical performance of a battery, it is important to understand how the battery responds mechanically to compression. This is necessary from an experimental point of view, as the mechanical response is important in defining the boundary condition applied and ensuring consistency between different experiments and batteries.

This simple initial set of experiments was designed to answer the following questions:

- Does the rate at which a battery is compressed influence the mechanical state of the battery?
- How long does it take for a steady mechanical state to be established?

It was hypothesised that the highly laminar construction of a battery, including wetted electrodes and separator, does not exhibit linear elastic behaviour. A battery exhibits a viscoelastic response. In the literature, Cannarella et al. suggested that batteries respond viscoelastically to instantaneous compression (93).

4.3.1. Initial loading rates – methods

This experiment was designed using an Instron testing machine, which ramped the pressure applied to the battery at different rates and then applied a controlled constant pressure. These initial tests investigated the mechanical response of the battery. These tests were preceded by setting the battery SOC to 50% via a constant-current discharge to 3.76 V followed by a constant-voltage hold to $i < 0.01C$. These experiments were performed at ambient temperature with no thermal management.

The test set-up for the initial experiments is shown in Figure 22, note that this is a representation of the test set-up, without the additional safety containment required during the actual testing. The compressive load was applied as outlined in Table 6.

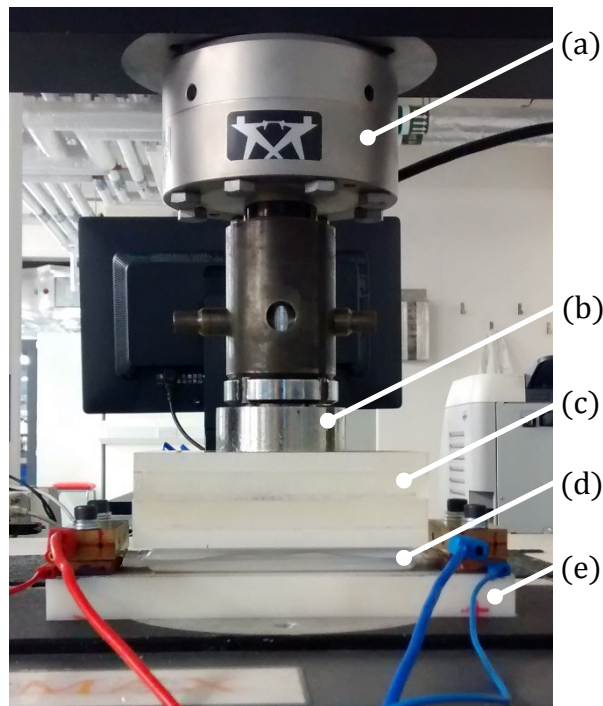


Figure 22: Loading rates experimental set-up. 5Ah NMC pouch battery mounted in an Instron testing machine. Highlighted set-up components: (a) 5kN load cell, (b) Compression platen, (c) Polycarbonate spacer, (d) 5Ah lithium-ion pouch battery, (e) Delrin/nylon battery mounting jig, including the brass connection terminals with a four-electrode configuration.

Compliance correction testing was performed on the experimental setups used in Sections 4.3, 4.4, 4.5 and 4.6. The results from the compliance tests were used to correct for strain of the compression stack (plastic blocks, platens, load cell, etc.) in the displacement data gathered. This was required because the machine crosshead displacement was used. All the strain measurements presented have been corrected for compliance in the test setup.

Table 6: Initial Loading Rates Procedure

Step	Description	Notes
1	Out of The Box (OTB) EIS.	
2	Compress to 10 N pre-load	Fixed displacement rate of 0.05 mm s^{-1}
3	Hold at 10 N pre-load	Hold at 10 N for 5 minutes.
4	Linearly increase the compressive pressure to 0.13 MPa at different rates. (a compressive force of 600 N applies a pressure of 0.13 MPa to the battery)	The rate of pressure increase is a control variable. The three different rates are: 217 Pa s^{-1} (1 N s^{-1}) 2.17 kPa s^{-1} (10 N s^{-1}) 21.7 kPa s^{-1} (100 N s^{-1})
5	Hold the pressure at 0.13 MPa for 24 hours.	Allows the battery to mechanically relax
6	Linearly reduce the compressive pressure on the battery at a rate of -217 Pa s^{-1} (-1 N s^{-1}) to 10N.	Removes the pressure on the battery and hold at 10N for 5 minutes.
7	Fully remove the load from the battery.	

Justification for different values used:

- **10 N 5-minute hold.** This part of the procedure is to give a displacement reference point for calculating the battery strain from the Instron data set. It is assumed the battery thickness will not have varied significantly from the thickness measured prior to the test.
- **0.13 MPa compressive pressure.** The magnitude of the pressure was chosen as it lies within the range that is generally accepted as the compression range applied to pouch batteries within battery packs. This is an anecdotal value with only one reference referring to a compression magnitude range of ~0.1 MPa (15 psi) as an estimate of the pressure inside an automotive battery pack (65). It is hypothesized by the author that this value has an origin in two results looking at cycle life vs compression: Cannarella and Arnold published work (2) and a report issued by battery manufacturer A123 (97). Both suggest a compression magnitude of about this level to be optimal for battery cycle life. A compressive force of 600 N applies a pressure of 0.13 MPa to the battery with the electrode area defined in Section 4.2.

4.3.2. Initial loading rates – results

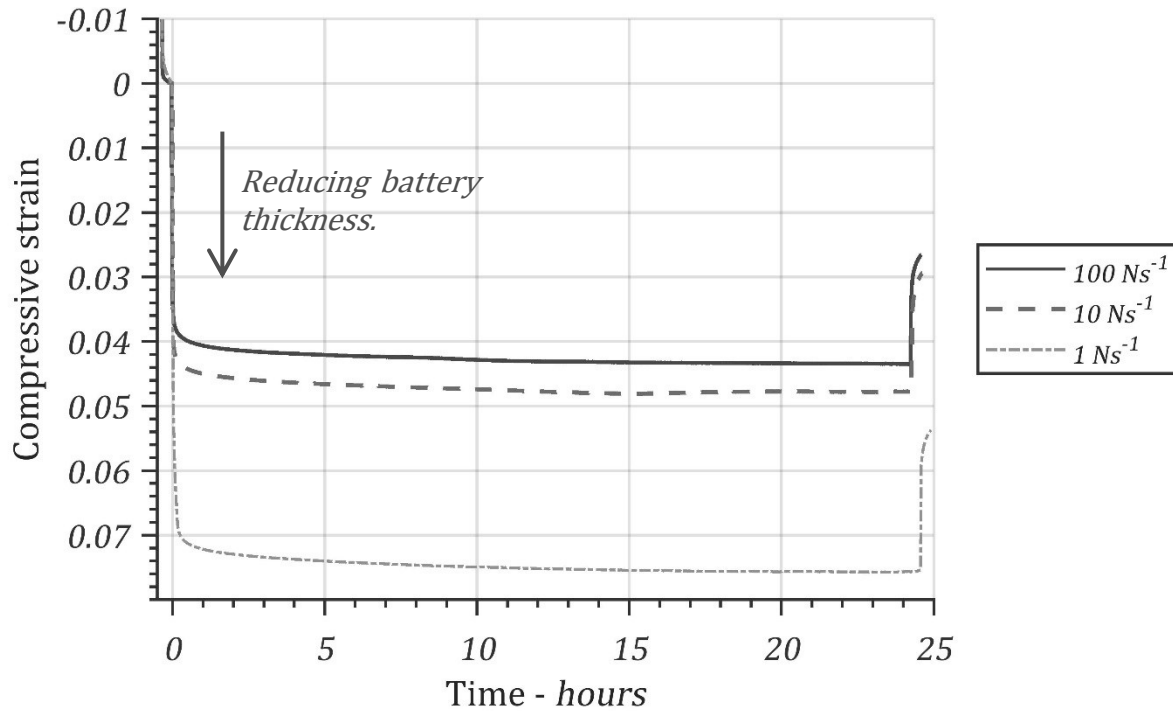


Figure 23: The compressive strain of three fresh 5 Ah Li-ion batteries at 0.13 MPa compression. Pressure was applied at three different rates, 100 Nsec⁻¹, 10 Nsec⁻¹ and 1 Nsec⁻¹ and held subsequently for 24 h.

The compressive strain resulting from the 0.13 MPa compression, applied at three different loading rates to three fresh batteries, is shown in Figure 23. Here the origin is at the end of the step 2 described in Table 6, after a 5-minute hold at 10 N (pre-load). The key points of interest from Figure 23 are:

- The negative strain prior to (t=0) results from the Instron crosshead moving down towards the battery and engaging the platen against the top surface of the battery. This does not correspond to any significant thickness change of the battery.
- There are significant differences in strain from the same compressive load in different batteries.
- The magnitude of the strain suggests that it is a function of the loading rate, with the largest strain corresponding to the slowest loading rate.

- The strain is high for the pressure applied, with a maximum of ~10% which corresponds to ~1.1 mm deflection for a 11.3 mm thick battery.
- It takes a long time for the strain to reach a steady state.
- The strain response is time dependent, confirming the literature, that batteries exhibit viscoelastic properties.
- Upon unloading the force returns to zero, but the strain does not indicating irreversible strain.

4.3.3. Initial loading rates – discussion and conclusion

These experiments were intended to answer the following questions:

- *Does the rate at which a battery is mechanically compressed influence the mechanical state of the battery?*
- *How long does it take for a steady mechanical state to be established?*

The results in Figure 23 show that the mechanical response of the battery is viscoelastic and also suggests the mechanical state of the battery is influenced by the rate of compression.

This will be shown not to be the case in section 4.5.2. It is also considered that the pre-load of 10 N was insufficient to ensure a consistent starting point between batteries. This influenced the subsequent comparison of the change in mechanical state between batteries. Experiments performed after this (Section 4.5), increase the magnitude of the pre-load to 100 N to provide a consistent starting mechanical state between batteries

Figure 24 shows the rate of creep with respect to time for the 100 N s⁻¹ test. The other two tests produced very similar curves. For clarity, only this data set is plotted. An exponential curve has been fitted to show that the strain rate decays with time. The deviations from the fitted values after 15 hours are due to measurement error influencing the very small values of creep rate.

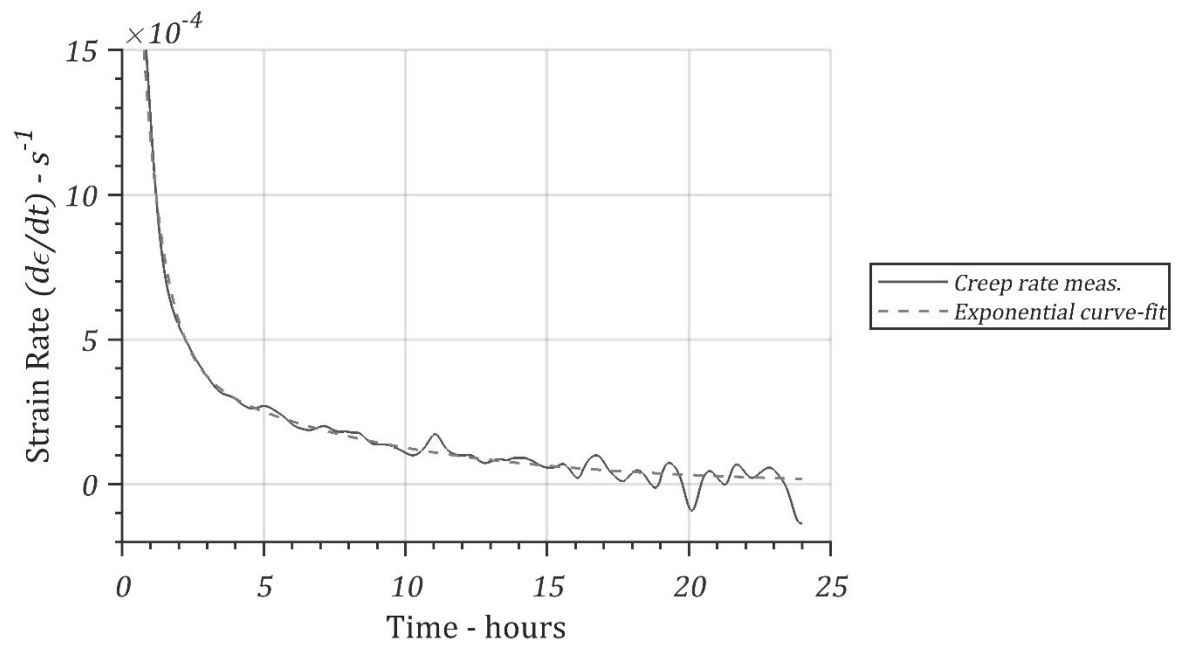


Figure 24: Creep rate for the 100 N s^{-1} loading rate test plotted against time. Fitted exponential curve shown with experimental data.

From the fitted curve and its extrapolation, the following times give the creep rates in Table

7.

Table 7: Creep rate decay over a four-day period

Time taken / hours	Creep Rate / s^{-1}
~6.5	$0.2 * 10^{-3}$
~12	$0.1 * 10^{-3}$
~17	$0.05 * 10^{-3}$
92	$2 * 10^{-9}$

For the purposes of testing, a 12-hour relaxation period was considered sufficient to achieve mechanical steady state. This has been chosen for three reasons:

- 12 hours is a convenient time duration in relation to the 24-hour day.
- Beyond 12 hours the magnitude of the battery relaxation is the same as the strain fluctuations, resulting in little advantage in allowing relaxation for longer.

The battery strain fluctuations are a result of the active feedback control that maintained a constant compressive pressure.

Upon unloading, the battery is thinner than at the beginning, indicated by the strain being non-zero after unloading. The thickness reduction is partly caused by the viscoelastic nature of the battery. The viscoelastic expansion of the battery after unloading does not account for the complete thickness reduction of the battery. The remainder of the thickness reduction is attributed to irreversible strain due to all the electrode stack layers being squashed together more closely. Further work could address this irreversible thickness reduction upon unloading and if it is maintained, even after cycling of the battery.

4.4 Impedance Changes with Compression

This set of tests addresses the following questions:

- Is there a difference in impedance at different levels of compression?
- If this difference occurs, can changes in the impedance be seen during the relaxation of the battery?
- Is there any change in the impedance once the pressure has been removed?

4.4.1. Impedance changes with compression – method

The following experiment was performed using the same experimental set-up described in Section 4.3.1. The compression combined with EIS sweeps was performed on a single battery and is outlined in Table 8.

Table 8: Impedance change with compression procedure

Step	Description	Notes
1	Hold at 10 N pre-load and perform a single Pre-load-EIS	Held at 10N for 20 minutes.
2	Linearly increase the compressive pressure to 0.13 MPa at 2.17 kPa s^{-1} (10 N s^{-1}).	Increased the pressure on the battery to the next level.
3	Hold the pressure at 0.13 MPa for 12 hours. Perform multiple EIS sweeps throughout the 12 hours. See Table 9 for the pattern of EIS sweeps during relaxation.	Allowed the battery to mechanically relax and monitored how the impedance changed.
4	Repeat steps 3 and 4 at three different pressures: • 0.26 MPa • 0.65 MPa • 1.30 MPa	
5	Linearly reduce the compressive pressure on the battery at a rate of -2.17 kPa s^{-1} (-10 N s^{-1}).	
6	Once battery is un-constrained, perform multiple EIS sweeps throughout a 24-hour period.	Allowed the battery to mechanically relax and monitored how the impedance changed.

Table 9 lists the intervals between the EIS sweeps during the mechanical relaxation.

Table 9: EIS Sweep Sampling intervals

Time between start of the EIS sweeps	Number of EIS sweeps	Part of the resting period
6 minutes	6	0:00 – 0:30
10 minutes	10	0:30 – 2:00
30 minutes	20 (44 for the 24-hour post compression relaxation)	2:00 – 12:00 (24:00)

The EIS sweeps were performed initially at a higher frequency to give greater resolution, whilst the rate of strain relaxation is at its greatest. The parameters for the EIS measurements are given in Table 10: EIS measurement parameters

Table 10: EIS measurement parameters

Parameter	Value
EIS type	Galvanostatic (GEIS)
Signal amplitude	0.2 A
Frequency range	0.01 – 2000 Hz
Points per Decade	6
Measures per frequency	4

4.4.2. Impedance change with compression – results

The battery strain resulting from the stepped load is shown in Figure 25. The origin of Figure 25 is set to the end of the 20-minute hold at 10 N (Pre-load). The key points of interest from Figure 25 are:

- After each step change in the pressure, there is viscoelastic relaxation in the battery.
Consistent with the results of the initial loading rate experiment.
- The steady state strain values for the different pressures show a highly non-linear relationship with significantly larger strains occurring at lower pressures. This is shown in Figure 26.

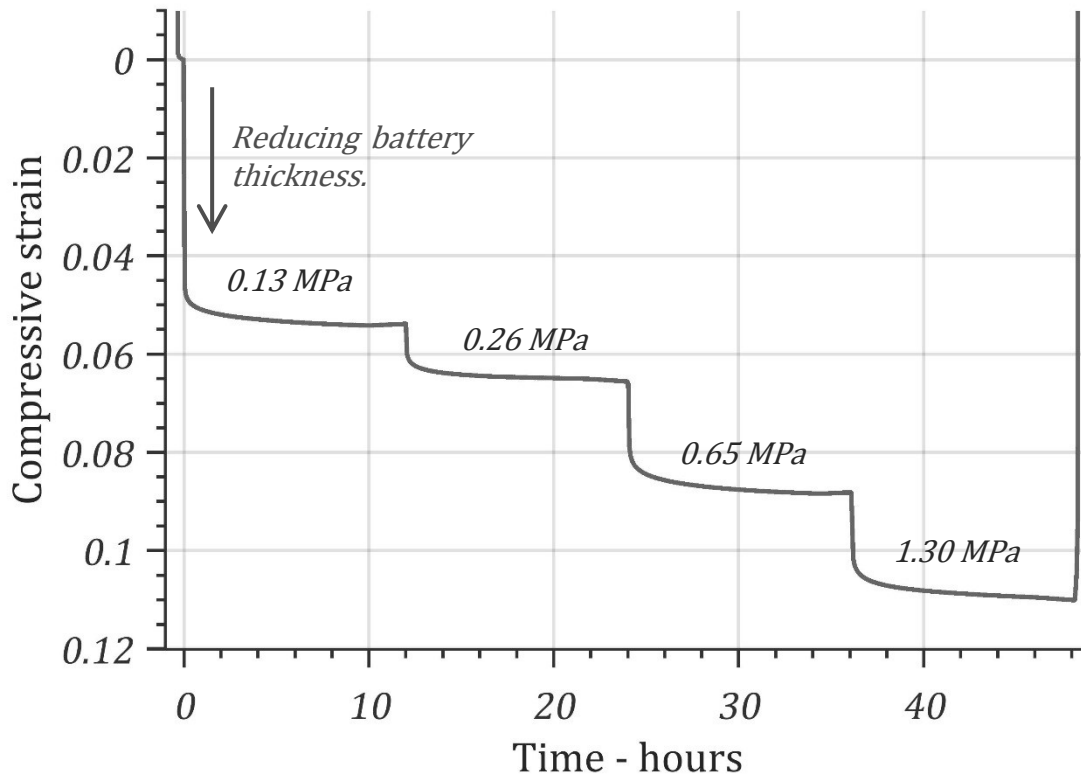


Figure 25: Strain response to stepped pressure, pressure steps are: 0.13 MPa, 0.26 MPa, 0.65 MPa, 1.30 MPa.

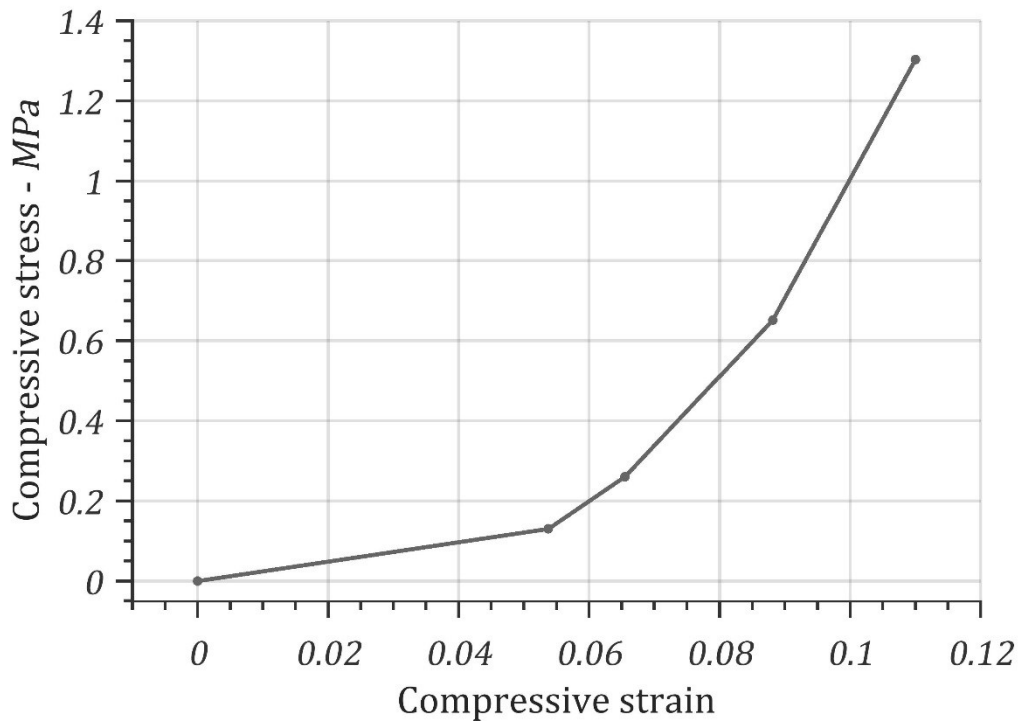


Figure 26: Stress plotted against the strain of the battery at the end of the 12-hour relaxation period at each stress magnitude.

This experiment had no form of thermal management, so the battery temperature was dominated by the room temperature. This resulted in the battery temperature changing throughout its duration. The battery tracked the room temperature that fluctuated during the day by up to 3°C in magnitude. The battery impedance and thus the EIS data gathered is very sensitive to temperature. The small temperature fluctuation dominated the impedance, masking any change that might have occurred during the 12-hour relaxation periods after each step change in the compression applied to the battery.

Figure 27 shows the impedance at the end of a 12-hour hold at one pressure state and the subsequent six EIS sweeps that were performed during the first 30 minutes of the next pressure step. Showing how the impedance changes as the pressure changes. Over this shorter time-period the battery temperature was approximately |0.5°C|. This temperature change is assumed small enough not to have significantly affected the battery impedance.

The EIS curves shown in Figure 27 matches the shape of the EIS curves generated by other members of the research group, testing the same battery model.

Figure 27 shows no significant change in impedance resulting from:

- The step change in compressive load applied to the battery.
- During the initial 30 minutes of strain relaxation once the new pressure has been applied

Figure 27 shows only the data for the step between 0.65 MPa and 1.3 MPa. The other five pressure transitions show similar results, which are not shown.

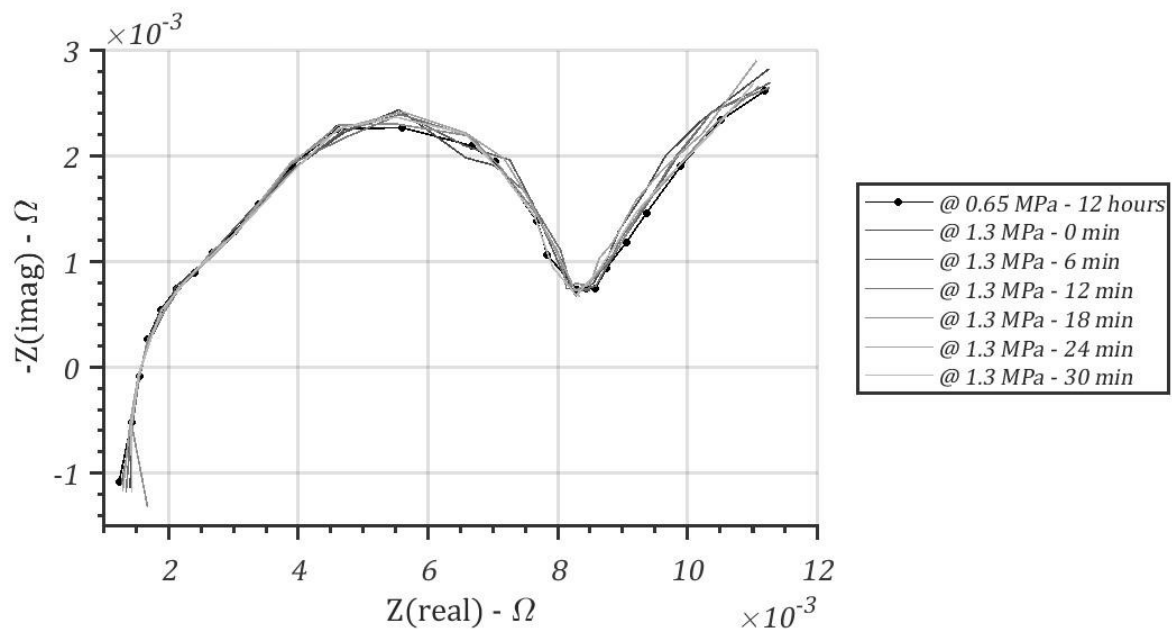


Figure 27: Battery impedance immediately before and after the step-in compression magnitude from 0.65 MPa to 1.30 MPa.

4.4.3. Impedance change with compression – conclusions

The conclusions to be drawn from the above tests are:

- Within the loading range of this experiment (0 to 1.3 MPa) the relationship between stress and strain is highly non-linear. This is consistent with the mechanical testing of a pouch battery compressed to pressures orders of magnitude larger (130 MPa) performed by Elham Sahraei et al. (46). For the battery tested (with a stacked electrode configuration) a linear stress-strain relationship started to occur at pressures greater than ~30 MPa.
- This experiment has highlighted a very important point to be considered in future mechanical testing of batteries. Small temperature fluctuations significantly impact the impedance results, masking any potential effects caused by the change in mechanical state. This suggests the mechanical effects (if there are any) are small relative to the effects of temperature. Good/consistent thermal management is required for meaningful results describing how compression affects batteries (on the scale of single electrochemical cycles).

4.5 Loading Rates with Electrochemical Characterisation

The experiment in Section 4.3 was repeated to include measurement of the electrochemical characteristics of the batteries.

One source of inconsistency in the strains measured was the 10 N preload that proved insufficient to provide a consistent starting reference point between different batteries. This could be for the following reasons:

- Li-ion batteries are not uniformly thick, so a high spot on a battery could skew the strain results with a small preload.
- Any misalignment in the compression stack could result in a relative high point, skewing the strain results.

To counter these two sources of error, the following changes to the test set-up and procedure were introduced.

- The magnitude of the preload was increased from 10 N to 100 N, to flatten any high spots.
- To account for any misalignment occurring in the compression stack, a self-aligning platen was introduced.

The electrochemical characterisation procedure is listed in Table 11. Note that each charge/discharge cycle was preceded by a constant voltage hold with an $|i| < 0.01C$ cut-off.

Table 11: Electrochemical characterisation procedure

Step No.	Process	Description
1	2C Charge to 100% SOC	Charge the battery from the default 50 % SOC
2	3C Discharge	High Rate CC discharge 100% DoD, No CV hold.
3	2C Charge	High Rate CC charge 0 - 100% SOC
4	1C Impedance Sweep, Discharge	See description in Section 4.5.1
5	1C Impedance Sweep, Charge	See description in Section 4.5.1
6	3C Discharge	Standard CC discharge 100% DoD.
7	2C Charge	Standard CC charge 0 – 100% SOC
8	3C Discharge	High Rate CC discharge 100% DoD
9	2C Charge	High Rate CC charge 0 - 100% SOC
10	2C Charge to 50 % SOC	Return battery to the default 50 % SOC (Including CV hold).

Justification for the values used in Table 11

- **1C charge/discharge:** Standard battery parametrization test.
- **3C discharge:** Higher C-rate CC discharge to see how battery performance at higher C-rates is affected. Limited to 3C by the current limit on the battery cycler used.
- **2C charge:** High C-rate CC charge to see how battery performance at higher C-rates is affected. Limited to 2C by the battery manufacturer's recommended charging limit.
- **Steps 2-3 and 8-9** are repeats of each other which was not intended. This was due to an error in the programming of the battery cycler that was only noticed after some of the tests had been completed. The process given in Table 11 was used for the remainder of the experiments to maintain a consistent testing procedure.

4.5.1. Impedance sweep procedure

This testing procedure generates a large amount of impedance data quickly. It combines testing elements from both EIS and GITT. High frequency impedance data is gathered using EIS (10 Hz and above) and short (10 sec) GITT pulses to gather the lower frequency information. This process pair is performed multiple times during a charge/discharge to give a spread of the information across the SOC range, hence the name 'sweep'. Both processes are performed during a 1C constant current charge/discharge.

Generating high quality EIS data sets suitable for equivalent circuit modelling is difficult and time consuming. The process requires long resting periods for the battery to reach clearly defined equilibrium conditions. This procedure performs the EIS under dynamic equilibrium conditions with the small AC signal being applied over the constant current (equivalent to 1C). The EIS is limited to higher frequencies to reduce the SOC spread over which the EIS data is gathered. The EIS data gathered by this method is not suitable for quantitative comparison of different batteries under different conditions. However, it does enable changes in impedance between different batteries to be compared. This method also enables impedance data at different points in the SOC window to be compared more easily, due to the speed at which data is gathered.

The voltage curve from an impedance sweep discharge is shown in Figure 28. The GITT pulses can be seen as periodic downwards spikes. The points at which the EIS sweeps were performed are highlighted.

Each high frequency EIS sweep is followed by a GITT of a 10 second 2C pulse. The resulting voltage response from the current pulse is used to infer low frequency impedance information about the battery. As with the EIS sweeps, this is not true GITT as the current pulse is not relative to the open-circuit voltage of the battery. Thus, the data can only be used as a comparative impedance tool.

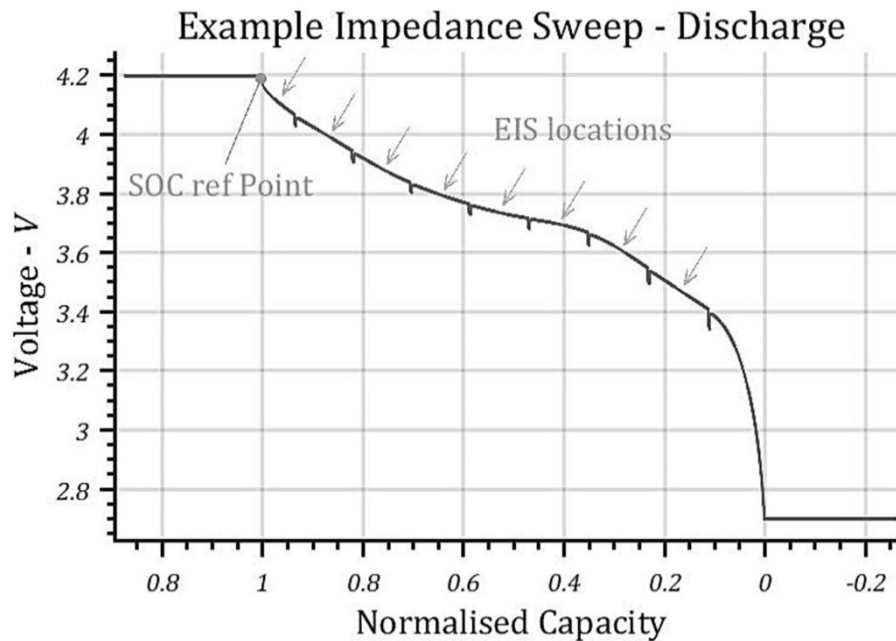


Figure 28: Example of the voltage curve generated during an Impedance sweep. The EIS locations are indicated by the arrows. The SOC ref point is indicated at 4.2V at the end of the preceding CV-hold. The small vertical drops in voltage indicate the 10 second 2C pulses.

Graphically displaying the data from each sweep becomes unwieldy once the number of tests being compared becomes larger than two or three. To process and examine the volume of impedance data gathered, a two-stage analysis process was used. The first stage was to look at the impedance at three points inside the SOC window, ~80%, ~50% and ~20%. If there were results of interest, then the remainder of the data was analysed.

From different tests, there are two key values required for comparison of impedance: the temperature during the test and the SOC. The temperature of the main body of the battery is very simply measured (details of the temperature measurements made for all experiments are noted in the relevant method section). The SOC is more complex and requires a consistent measurement process between tests. For the purposes of the impedance sweeps performed in this work, the following definition of SOC is used:

Discharge impedance sweep:

- The SOC reference point is the charge present in the battery at the end of a CV-hold at 4.2 V with a current decay of $|i| < 0.01C$.
- The SOC for all impedance measurements for that sweep (pulse and EIS) is the amount of charged passed between the reference point and the start of the measurement.

Charge impedance sweep:

- The SOC reference point is the charge present in the battery at the end of a CV-hold at 2.7 V with a current decay of $|i| < 0.01C$.
- The SOC for all impedance measurements for that sweep (pulse and EIS) is the amount of charge passed between the reference point and the start of the measurement.

Thus, every EIS curve and pulse is quoted with both a temperature and charge passed value, to ensure the data sets are comparable between tests.

4.5.2. Loading rates with characterisation – results

Figure 29 shows the strain response for four batteries compressed to 0.13 MPa, with the pressure initially applied at different rates. There were two sets of measurements at the 100 N s⁻¹ loading rate due to an error when performing the electrochemical characterisation once the compression was removed (atpt 2 follows the correct procedure). The origin of Figure 29 is set at the end of the 15-minute, 100 N preload.

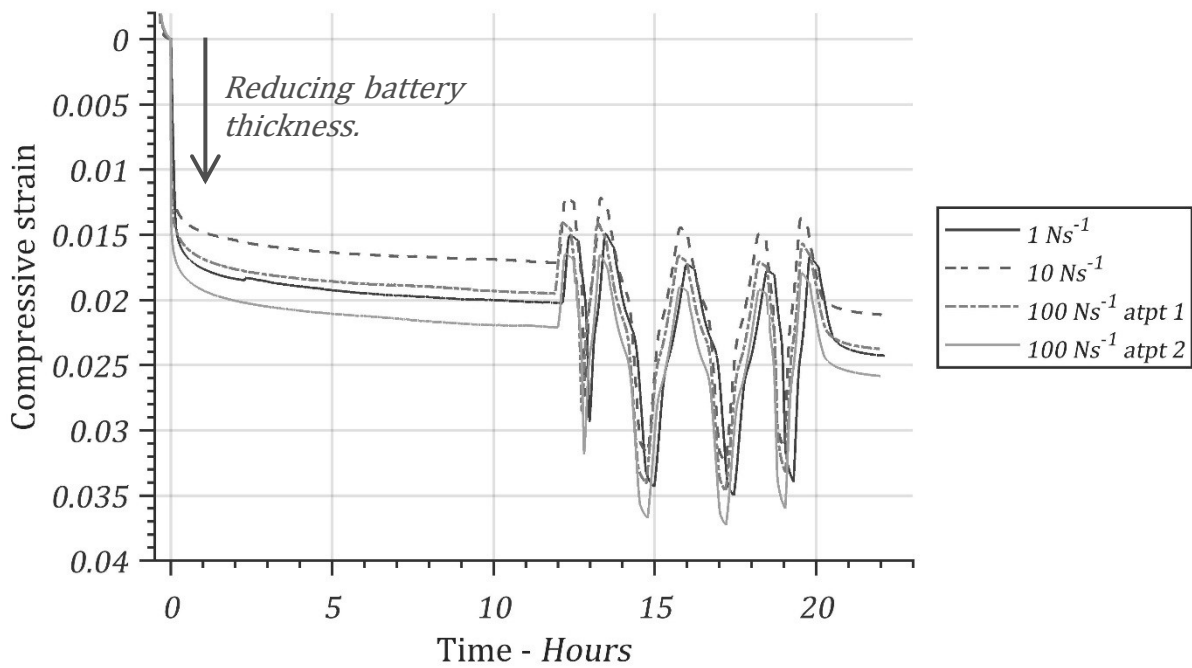


Figure 29: The compressive strain of four fresh 5 Ah Li-ion batteries at 0.13 MPa compression. Pressure was applied at three different rates, 100 Nsec⁻¹, 10 Nsec⁻¹ and 1Nsec⁻¹ and held subsequently for 24 h. At 12 hours the batteries were electrochemically characterised.

Key features of Figure 29:

- The initial loading-rate results (Figure 23) suggest a relationship between the loading rate and the strain magnitude for the same pressure. That is shown not to be the case at strains of the two 100 Nsec⁻¹ loadings. The magnitude of the difference between the two 100 Nsec⁻¹ tests is of the same magnitude as those between the 1 and 10 Nsec⁻¹. This suggests that the variability between batteries is of similar magnitude of any potential trend resulting from different loading rates. Hence, to thoroughly investigate the effects of loading rate on the mechanical state of the battery and provide statistically significant results, a larger sample size is required. This is beyond the means of this project, both in terms of resources and time.
- The initiation of the electrochemical cycling can clearly be seen with the battery expanding once the initial charge to 100 % SOC begins.
- All four batteries show the same strain profiles throughout the characterisation.
- The minima and maxima in the strain cycles resulting from the electrochemical cycles do not remain constant (i.e. the strain at 100% and 0% SOC is not constant). This is partially due to the preceding electrochemical process (60) and the further net creep of the battery.
- Further creep can be seen to have occurred after the electrochemical cycling is complete, once the battery was returned to 50% SOC.

Creep due to electrochemical cycling

To further investigate the additional creep that occurs during the electrochemical cycling of the batteries, the strain data from the Initial Loading Rates Experiments (Figure 23) were overlaid on the data from the Loading Rate Experiments (Figure 29). This is presented in Figure 30 for the 100 Ns^{-1} and gives a direct comparison between the projected strains for the battery with and without electrochemical cycling. In Figure 30 the origin has been moved. The origin of Figure 30 is the point at which the 0.13 MPa hold starts, rather than at the start of the loading rate ramp-up. This accounts for the difference in the preload settings between the two experiments.

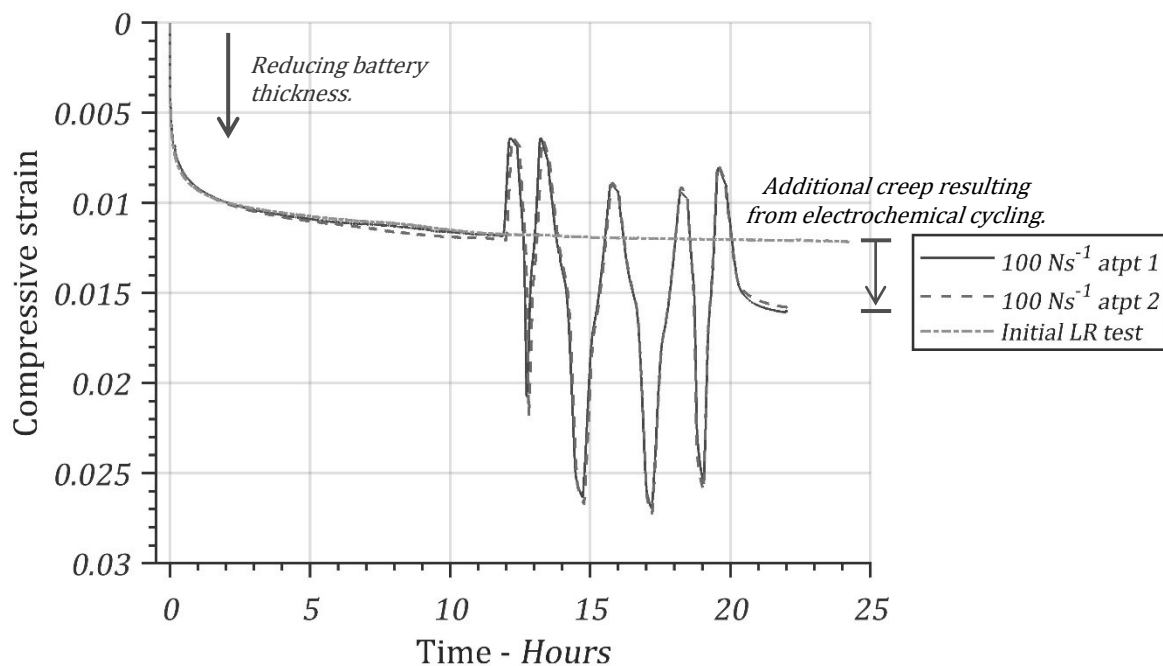


Figure 30: Strain plot comparing the strain relaxation of a lithium ion battery with and without electrochemical cycling.

The creep that occurs is the same for all three batteries in Figure 30. The different pre-loading regimes have not affected the creep, which is due to the speed at which the load was applied. The two pre-loading forces were 10 N and 100 N. When the pressure was applied at a rate of 100 N s^{-1} the loading ramp duration for the two loads were 5.9 seconds and 5 seconds, respectively. With the viscoelastic creep occurring over hours, both can be considered effectively instantaneous step changes. In contrast, the results for the other two loading rates (1 and 10 N s^{-1}) show a variation in the creep curves once the fixed pressure has been reached. This variation is due to the duration of the loading ramp being significantly different between the two pre-loading conditions.

The further creep resulting from the electrochemical cycling is a phenomenon that has been found in the literature (2). This phenomenon is discussed and investigated further in Chapter 6.

Electrochemical results

The electrochemical results showed no significant differences in any test. The charge/discharge capacities of both 1C and 3C showed insignificant differences for all tests. This included transitioning from being loaded to unloaded. The variation in capacity was always negative and of the order of -0.1% relative to the characterisation prior to compression.

Impedance Data

Due to the lack of thermal management of the batteries, the temperature variation masked any influence the mechanical state had on impedance and is not shown.

Strain changes during electrochemical characterisation

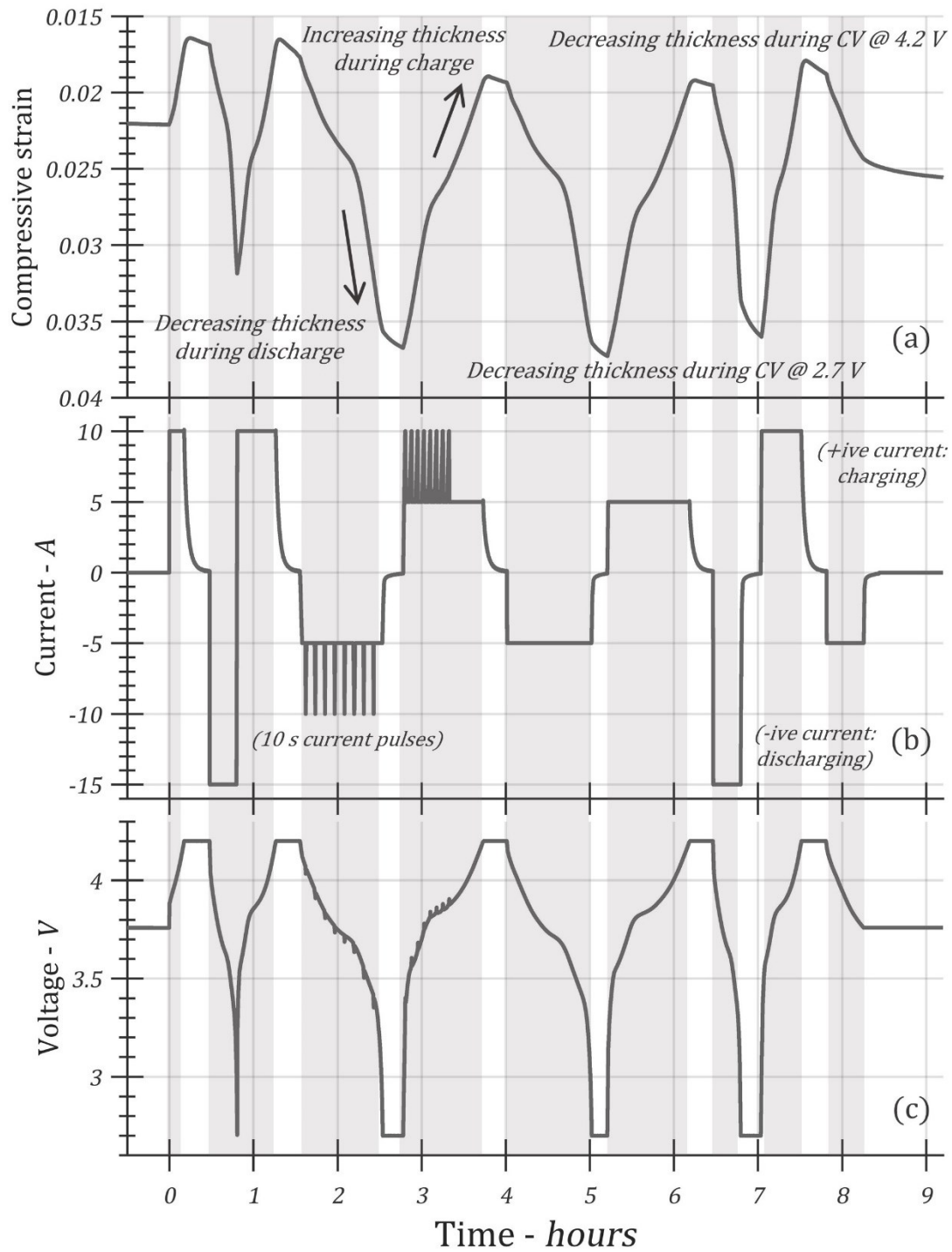


Figure 31: 100 Ns^{-1} attempt 2. The Compressive-strain (a), Current (b) and Voltage (c) during the electrochemical cycling. Vertical greyed-out regions signify where a constant current is applied. Else constant voltage or no current is applied to the battery. The 10 second pulses in (b) and the corresponding voltage blips in (c) result from the impedance sweep procedure applied to the battery as part of the electrochemical characterisation.

Figure 31 shows the compressive strain (a), current (b) and terminal voltage (c) from the 100 Ns^{-1} atpt 2 test. The changes in strain as the battery is electrochemically cycled are what is to be expected from the literature:

- Increase in compressive strain (reduction in battery thickness) as the battery is discharged.
- Decrease in compressive strain (increase in battery thickness) as the battery is charged.
- The shape of the strain curve in the CC regions, examined in more detail in Section 4.6.2.

The features of most interest in Figure 31 (a) is the change in strain during the CV holds. During all CV holds there is an increase in compressive strain (reduction in battery thickness). These features are a result of viscoelastic creep and thermal contraction becoming more dominant processes over intercalation driven strain from the small current during the CV holds. Oh et.al (60) saw similar creep in batteries after discharges (left at OCV after the CC phase, not a CV hold) in their work studying the C-rate dependency of the thickness change of the battery. The creep after the discharge was attributed to a combination of thermal expansion and viscoelastic creep (60). Figure 32 shows how the battery temperature changed during the characterisation, showing an increase in temperature during the CC phases (especially during the 15 A discharge and 10 A charge) and drops in temperature during the CV phases. Demonstrating the potential influence of thermal contraction on the compressive strain during the CV holds. Section 4.6 will demonstrate that thermal expansion cannot be considered insignificant when analysing changes in battery thickness during cycling.

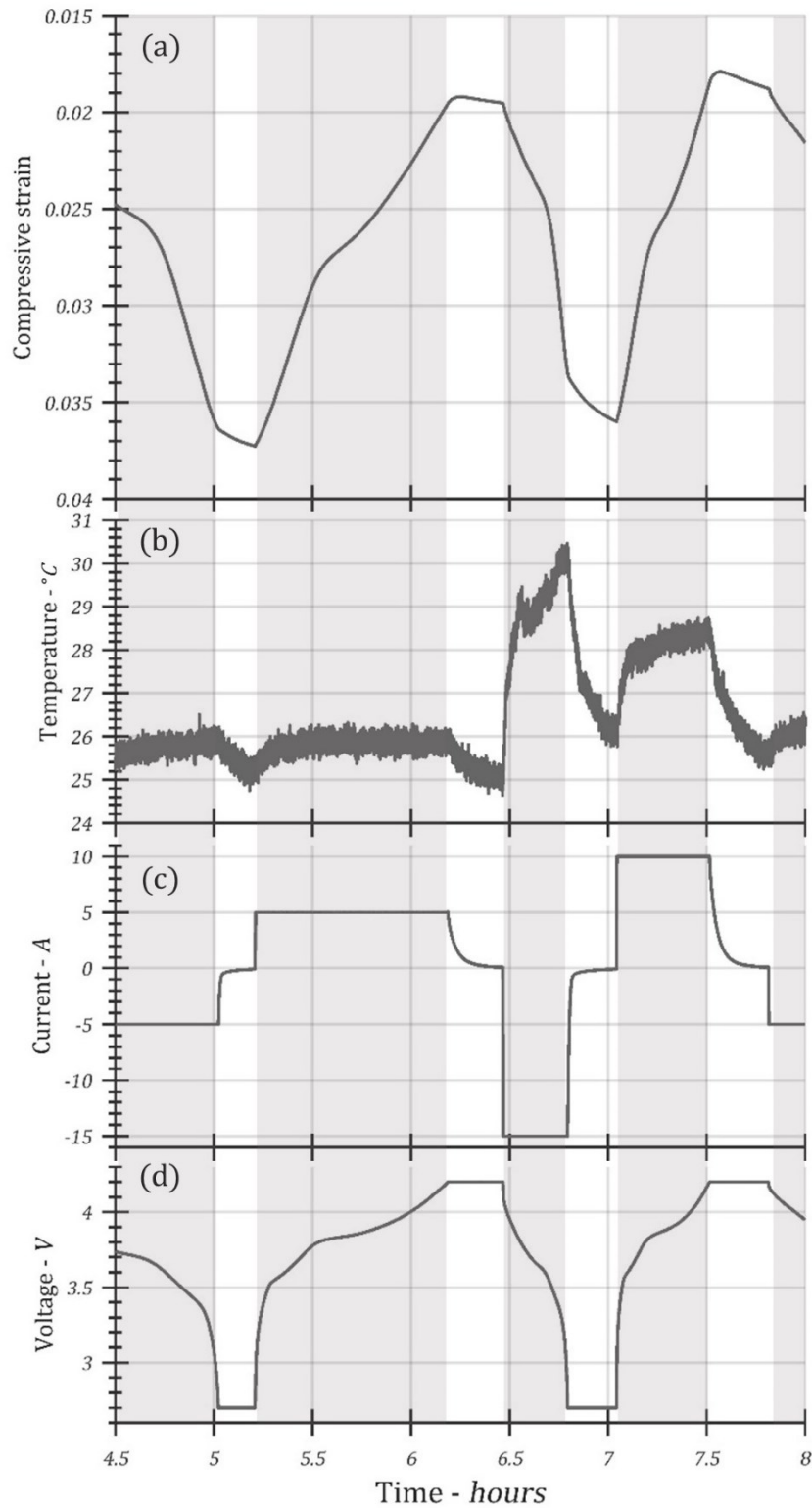


Figure 32: 100 Ns^{-1} attempt 2. The Compressive-strain (a), Temperature (b), Current (c) and Voltage (d) during cycling. Vertical greyed-out regions signify where a constant current (CC) is applied. Else constant voltage (CV) is being applied. Temperature plot (b) shows temperature rise during CC regions and temperature drop during the CV holds.

4.5.3. Loading rates with characterisation – conclusion

The loading rates experiments with electrochemical characterisation showed that for a given pressure there is no relationship between the battery strain and the rate at which the load was applied. It is acknowledged that this is a very small sample size and considering the complex composite structure of Li-ion batteries, there is likely to be a large variance in the results. Testing of a much larger sample size (>20) would be required to produce statistically significant results.

The creep in the batteries compressed at a rate of 100 Nsec^{-1} was the same from the start of the constant pressure period. Thus, all variation in the strain for a given pressure occurs during the loading process. During the electrochemical cycling the battery expands and contracts which induces additional creep.

The electrochemical data showed no significant difference between any of the batteries tested regardless of the loading procedure. The impedance data reiterated the conclusion from Section 4.4.3, that the thermal conditions must be very accurately controlled for any mechanical effects, if present, to not be overshadowed.

4.6 Isothermal Breathing Experiments

The mechanical expansion and contraction of Li-ion batteries is predominantly due to two mechanisms, intercalation driven strain and thermal expansion. The relative magnitude of the two components has been investigated by Oh and Epureanu (61) This work produced an experimentally verified expansion model, predicting thermal expansion at a variety of C-rates (1C, 2C, 5C). The model presented was for an obround jelly-roll, prismatic battery. In creating the model, they performed low C-rate discharges, where negligible temperature increases occurred. To characterise their model, they assumed that the intercalation-driven strain is independent of C-rate, and so only a function of SOC. Thus, the isothermal intercalation-driven strain was constant for all C-rates. Therefore, it could be subtracted from the total strain, to give the thermal strain. The subsequent validation of the model led the authors to believe that the assumption of C-rate independent intercalation strain is valid.

The work of Oh and Epureanu (61) highlights two other interesting phenomena:

- The lumped thermal expansion coefficient for a Li-ion battery varies with state of charge. It is highest at 0 % SOC and lowest at 50% SOC, with a difference of about 10% between the two extremes.
- The order of magnitude of the lumped thermal expansion coefficient of the battery is the same as that of the separator and is much larger than that of the other materials. It is thus suggested that the separator could have a significant role in the thermal expansion of the battery. However, the following large caveats are noted:
 - The electrode configuration could affect the measurements.
 - Polymers typically have a wide range of thermal expansion coefficients.

One aspect that has not been studied in detail is the effect of isothermal battery operation on the intercalation-driven strain. Therefore, the next section of work employed mechanical differential methods to study in detail how temperature affects the intercalation-driven strain. Low C-rate tests were performed to minimise the influence of thermal expansion. The differential methods were implemented following the data analysis methodology, introduced in Section 4.1

4.6.1. Isothermal breathing – methods

Mechanical set-up

Mechanical expansion was measured using the same tensile testing machine that was introduced in Section 4.3.1. The only difference was the greater stack height of plastic blocks above and below the battery, providing additional insulation around the battery. An image of the original set-up is shown in Figure 22. A self-aligning platen was included at the bottom of the compression stack.

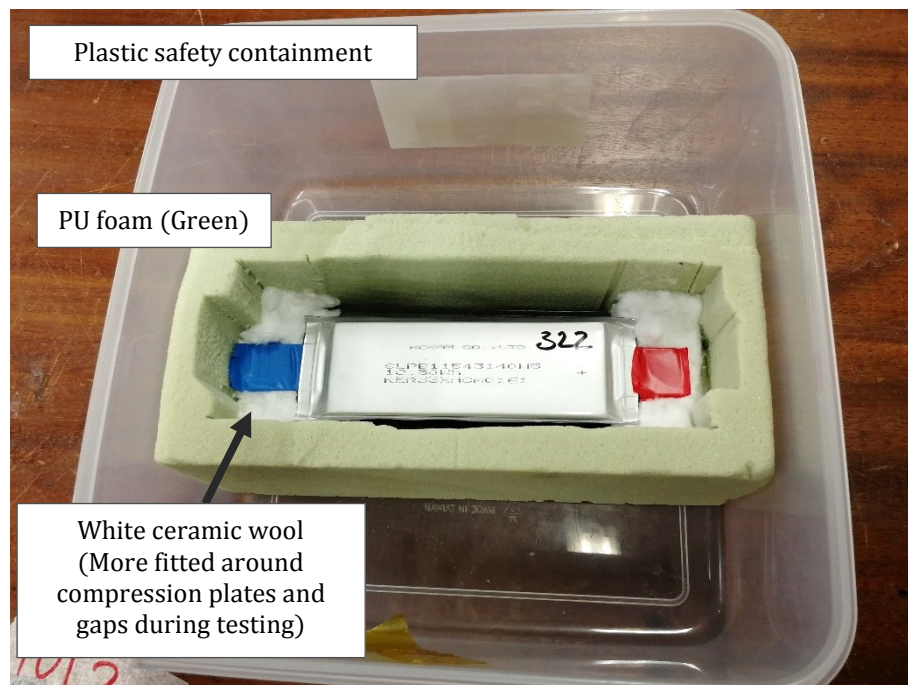


Figure 33: PU foam/Ceramic wool insulation set-up for the isothermal expansion experiments.

Thermal set-up:

To perform the isothermal tests the battery being tested needed insulating. This was achieved by using a combination of polyurethane foam and white ceramic wool insulation. Figure 33 shows the insulation set-up around a battery, all within the plastic secondary containment. After all sensor connections had been made and the top compression stack put in place, further ceramic wool was inserted into any gaps.

Sensor and thermal management set-up:

Thermal management was employed to achieve isothermal conditions throughout electrochemical cycling. This took the form of tab heating via thin film heating elements with PID control. A K-type thermocouple connected to the root of each battery tab was used to provide the feedback. The 20x20 mm² heaters were incorporated into the tab-sensor assembly, a schematic diagram of which is shown in Figure 34.

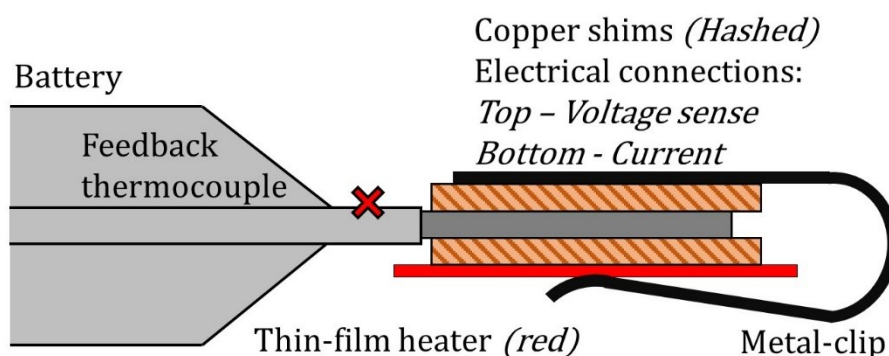


Figure 34: Schematic diagram of the tab assembly for isothermal breathing experiments. Assembly includes: two copper shims to independently make the voltage sensor and current connections to the battery cyclor, thin-film heater and the location of the feedback thermocouple. The assembly is held together using metallic clip.

To verify that the cycling was performed under isothermal conditions, the battery temperature was monitored in eight places (this includes the two feedback thermocouples). All thermocouples were attached by embedding the thermocouple tip in a small volume of thermally conductive epoxy resin and bonding to the battery surface, for the following reasons:

- Reliability of attachment with epoxy resin is much better than that of the traditional Kapton tape method. This is important as the test set-up is complex and at several stages the thermocouples might be knocked off.
- Thermocouples must be located on the sides of the battery where there is significantly less area to secure the thermocouples. This makes the Kapton tape method significantly less reliable. The top and bottom surfaces of the battery are unavailable for thermocouple attachment.
- The additional thermal inertia of the thermocouple tip and the epoxy resin should not impact the results as it is an isothermal test without any rapid changes in temperature.

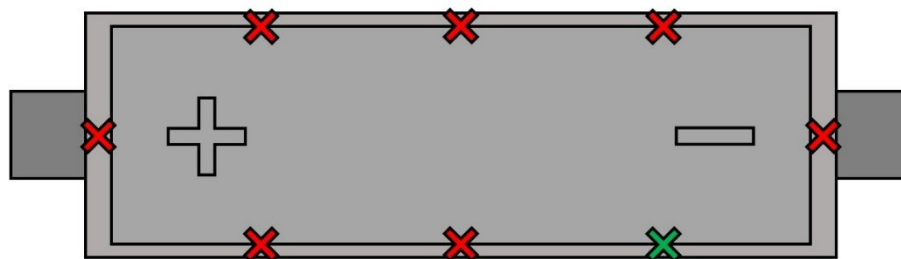


Figure 35: Thermocouple location schematic. The green cross (bottom right) shows location of temperature safety cut-off thermocouple connected to the battery cyclers.

The thermocouples were attached to the battery as shown in Figure 35:

Temperature measurements (excluding the safety cut-off thermocouple) were taken using a National Instruments NI-9213 temperature cartridge.

The electrical connections (at each tab) were made via two copper shims that were soldered to the battery cycler sensor cables. The shims were clamped against both sides of the tab, thus isolating the voltage sensing cable from any iR losses from the testing current. This connection method does not have as low a contact resistance as clamping with brass blocks and is a less repeatable connection method. These compromises were considered acceptable for the following reasons:

- With careful cleaning and assembly, the contact resistance would be sufficiently low.
- The voltage sensing wire is isolated from the current path; thus, the voltage measurements will not be affected by the additional contact resistance, as no current flows through that contact.
- Testing is at low charge/discharge currents ($0.1C = 0.5A$), so ohmic heating across contact resistances will be negligible.

Electrochemical cycling and data acquisition were performed using a Bio-logic BTS-815 battery testing machine.

Batteries tested:

The batteries tested were the 5 Ah Kokam power batteries with NMC cathode and a graphitic carbon anode (specification given in Table 4). The test was performed on both a fresh and an aged battery. The aged battery was aged following the third procedure outlined in Merla et al. paper, namely 1C cycling at 25°C for 450 cycles (80).

Testing Procedure

The procedure is broken down into the following stages.

1. Battery standard conditions.
2. Set battery temperature to 25°C.
3. Apply nominal compressive load to battery.
4. Electrochemical testing at 25°C.
5. Set battery temperature to 45°C.
6. Electrochemical testing at 45°C.

1) Battery standard conditions

To ensure equivalent initial mechanical conditions for the two batteries, both batteries were charged to the nominal 50% SOC voltage of 3.76 V. A constant current hold at 3.76 V was performed until $|i| < 0.01C$ at ambient conditions.

2) Set battery temperature to 25°C

Once the battery is fully mounted in the testing rig and ready for the compression to be applied, the thermal management system was switched on for ~15 minutes before the compression was applied.

3) Apply standard compressive load to battery

To provide consistent displacement measurements as discussed in Section 4.3.3, a standard compressive load was applied to the battery and maintained throughout the duration of the experiment. This load was 100 N, that is equivalent to a pressure of 21.7 kPa. Once the 100 N load was reached, the battery was allowed to mechanically relax for 12 hours prior to any electrochemical processes being performed.

4) Electrochemical testing at 25°C

After the 12 hours relaxation, the battery was charged at 1C to 100 %SOC (4.2 V with CV hold). Once this SOC was reached the battery was left to equilibrate for a further ~24 hours. Then the 0.1C 100 %DOD discharge was performed, followed immediately by a 1C charge back to 100 %SOC.

5) Set battery temperature to 45°C.

After return to the 100% SOC, the battery was rested for 8 or 12 hours for the fresh and aged batteries, respectively. This difference was due to difficulty gaining access to the laboratory on the following morning for the aged battery test. The battery temperature was subsequently raised to 45°C and allowed to rest for a further ~24 hours.

6) Electrochemical testing.

The 0.1C discharge was repeated at the higher temperature, followed immediately by a 1C charge back to 50 % SOC. After this the battery remained under compression and at 45°C until the following morning (4-6 hours), at which point it was removed from the testing rig.

4.6.2. Isothermal breathing –results

Isothermal conditions

The temperature distribution of the batteries throughout the four tests are shown in Table 12. These temperature values averaged over the duration of the discharges shows there was no temperature distribution along the length of the battery and that the battery temperature was constant throughout all the tests. Thus, the assumption of isothermal conditions during the discharges is valid. The targeted 45 °C for the battery was however not achieved, rather the main body of both of the batteries was maintained at a temperature of 41 °C. This was due to the location of the feedback temperature measurement of the thermal management system being placed at the tab root. Thus, the tabs were maintained at 45 °C, but not the main body of the battery. The control feedback temperature values given in Table 12 do not have and associated standard deviation because the variability in these data sets was negligible compared to the error in the measurements taken.

Table 12: Battery temperature distribution during isothermal discharges.

Test	Pos tab <i>ctrl. feedback</i>	Body <i>pos end</i>	Body <i>middle</i>	Body <i>neg end</i>	Neg tab <i>ctrl. feedback</i>
	<i>Mean temperature during discharge $\pm \sigma$ (°C)</i>				
Fresh 25°C	25.0	24.7 $\pm$ 0.1	24.6 $\pm$ 0.1	24.6 $\pm$ 0.1	25.0
Fresh 41°C	45.0	41.4 $\pm$ 0.2	41.5 $\pm$ 0.5	41.7 $\pm$ 0.1	45.0
Aged 25°C	25.0	24.5 $\pm$ 0.1	24.5 $\pm$ 0.1	24.6 $\pm$ 0.1	25.0
Aged 41°C	45.0	40.8 $\pm$ 0.2	41.1 $\pm$ 0.5	41.4 $\pm$ 0.1	45.0

Discharge Results

Figure 36 shows the strain relaxation that occurred during all four discharges, alongside the discharge curve. The points of interest from Figure 36 are:

- The aged battery has a reduced capacity, which is to be expected.

- The change in strain during the discharges has the same shape as in the literature (58). This profile can be split into three regions:
 - From 100-75% SOC a gradual decrease in strain accounting for ~20% of the total strain.
 - Subsequent strain plateau over 75-35% SOC accounting for ~14% of the total strain.
 - Finally, the rate at which the strain decreases becomes much larger for the remainder of the discharge, accounting for the remaining ~65% of the total strain.
- At 25 °C, zero strain occurs at about 50 % SOC. However, at 41 °C, the strain curves have shifted up by $\sim 10 \times 10^{-3}$. This is due to the thermal expansion that occurred during the temperature rise from 25 °C to 41 °C. In the 41 °C discharges, the two strain curves have a greater spacing between them. This is due to the magnitude of the thermal expansion of the aged battery being greater than the fresh battery. This is shown in Figure 37: the strain increases of fresh and aged batteries (at 100% SOC) during the temperature rise.

With the absolute strain shown in Figure 36, it is difficult to compare the different shapes of the strain curves. This difficulty is avoided using the normalised strain relaxation ($\varepsilon - \varepsilon_0$), where ε_0 is the strain at the beginning of the discharge (at 4.2V) which is examined later in this section.

The change in strain, of the two batteries that occurred during the temperature rise from 25 °C to 41 °C is shown in Figure 37. The feature of note in the figure is the magnitude of the increase in strain, resulting from the temperature increase.

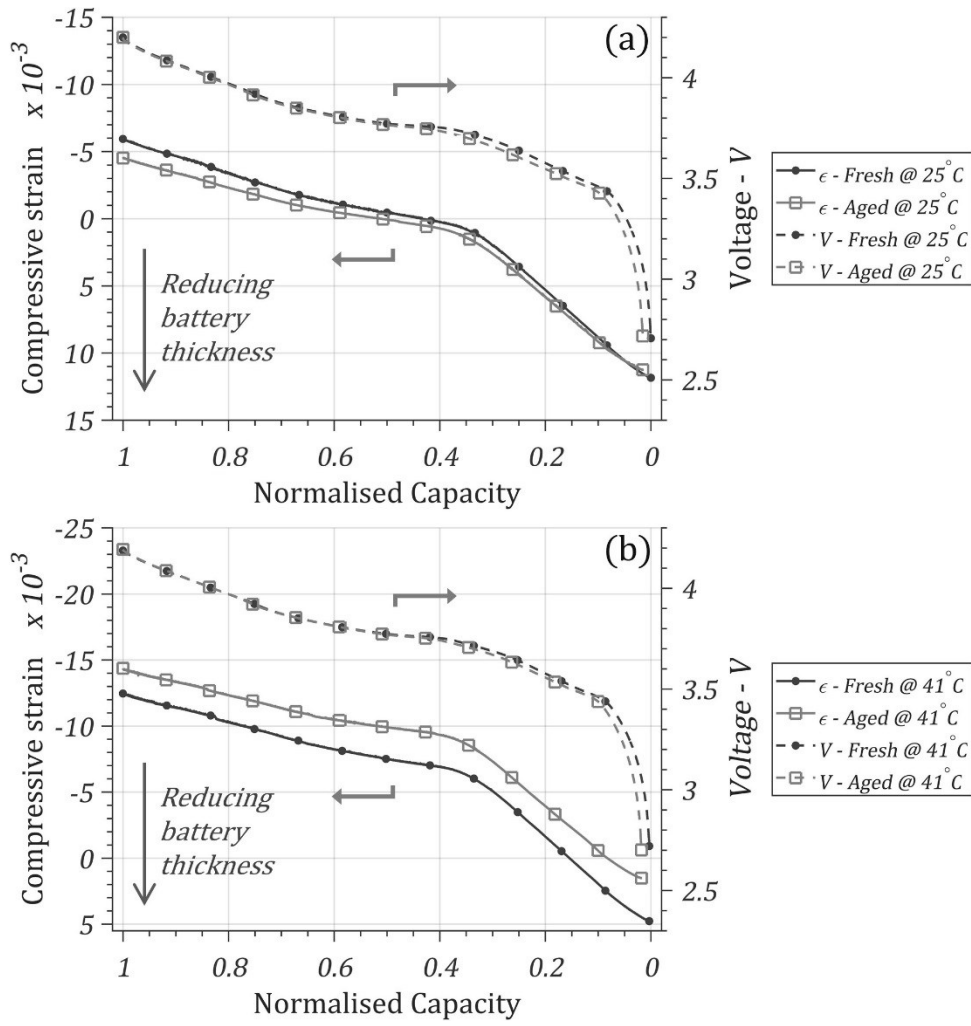


Figure 36: Voltage and Strain against capacity curves for a fresh and aged 5 Ah battery. (a) Isothermal 0.1C discharge at 25 °C. (b) Isothermal 0.1C discharge at 41 °C

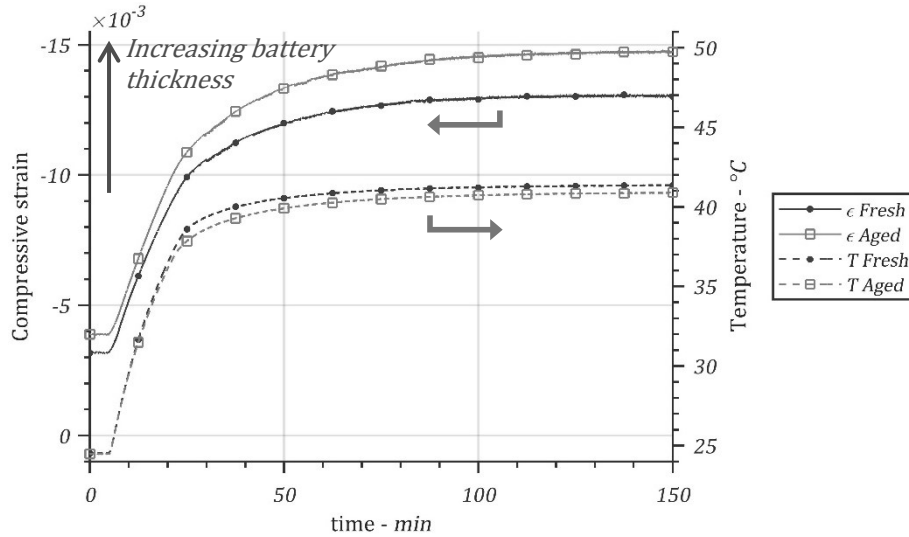


Figure 37: The strain increases of fresh and aged batteries during a 15 °C temperature rise. Both batteries at 100%SOC

To verify that the thermal expansion results are similar to that which would be expected an estimation from the electrode layers and the component thermal expansion coefficients was calculated. The estimation calculates the thickness change for each individual component in the electrode stack and sums them together. The thermal expansion coefficients, thicknesses and quantities are given in Table 4 and Table 5 and taken from (95,96).

The thickness change calculated is shown in Table 13. The original thickness used to calculate the strain value is the sum of the thicknesses of the electrode stack components from Table 4, and was 11.61 mm.

Table 13: Thermal expansion estimation from layer thicknesses and thermal expansion coefficients.

Battery	Thermal expansion (dT = 16°C) / μm	Strain due to thermal expansion.
Theoretical	105.6	0.009
Fresh	110	0.009
Aged	125	0.011

This estimated thickness change agrees well with the thickness changes experimentally measured.

Comparing Figure 36 to Figure 37 shows the relative magnitudes of the thermal strain and intercalation-driven strain. A temperature rise of $\sim 15^\circ\text{C}$ induces a strain approximately two thirds that of a full charge. It is concluded that isothermal conditions are required for precise mechanical differential analysis to avoid significant thermal expansion effects. All mechanical datasets to which differential techniques are applied in the body of this work were performed under isothermal conditions, unless otherwise stated.

Normalised strain

Figure 38 shows the normalised strain for all four discharges where ϵ_0 is the strain at the beginning of the discharge (at 4.2V).

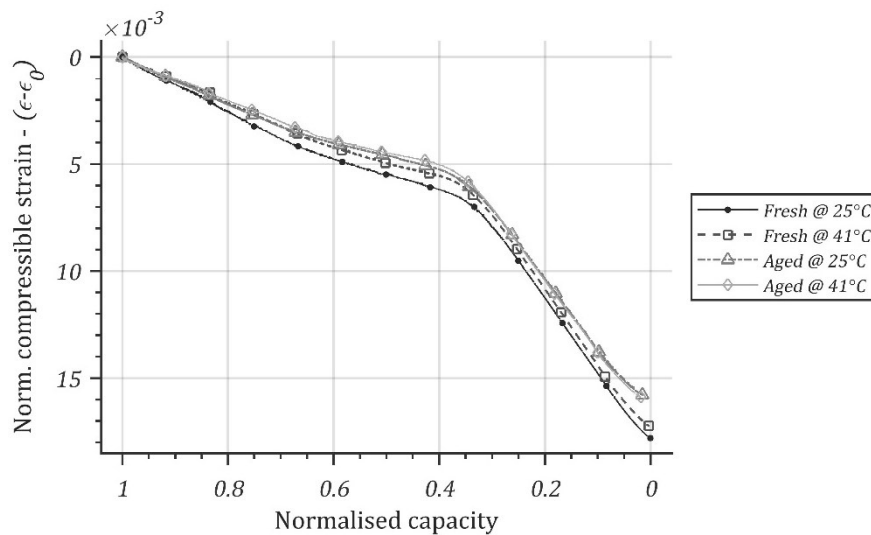


Figure 38: Normalised strain relaxation for a fresh and aged battery at 25 °C and 41 °C.

Key features of Figure 38:

- The magnitude of the change in strain for the fresh battery is larger than that of the aged battery.
- The difference between the strain curves at the two temperatures is much larger for the fresh battery than the aged battery. The aged battery shows little to no difference in the strain path resulting from the different temperature.
- The knee shape in the strain relaxation that occurs during the discharges shows the dominance of the graphite electrode in this process. The knee matches the

shape of the intercalation driven strain in graphite shown in the literature in Figure 9.

To investigate the difference in the total strain between the aged and fresh batteries, the reduction in strain is compared to that of the reduction in capacity. Using the 25 °C data as an illustration, the normalised capacity and strain magnitude are shown in Table 14. Table 14 shows that the reduction in strain for the aged battery compared to the fresh battery is not directly proportional to the drop in the capacity of the aged battery compared to the fresh battery. A ~1.5% drop in capacity at both temperatures results in a 11.5 % (at 25 °C) and 8 % (at 41 °C) reduction in the magnitude of the strain during the discharge.

Table 14: Normalised capacity and Strain relaxation magnitude values for the four discharges.

	Fresh @ 25 °C	Aged @ 25 °C	Fresh @ 41 °C	Aged @ 41 °C
Normalised Capacity	1	0.985	0.997	0.981
Normalised Strain	1	0.885	0.969	0.892

The reduction of the strain with ageing is attributed to losses in both active lithium and active material. The isothermal strain is solely due to intercalation-driven strain, and with the loss of active material there is simply less material to expand and contract. This reduces the total strain within the battery. Additionally, the loss of active lithium and material could also introduce stoichiometric drift, changing the degree of lithiation in the electrodes. Referring to the Figure 9 in Section 2.4.5, at both low and high levels of lithiation the volumetric change of the graphitic carbon increases, with a plateau in the middle. Thus, a shift in the degree of lithiation due to stoichiometric drift could cause a large change in the magnitude of expansion of the anode, whilst not necessarily showing a large change in capacity. Due to the relative magnitudes of the expansions of the two electrodes, the NMC cathode is not considered here.

Strain Derivatives

Schiffer et al. (58) identify three regions within the strain curve for a Li-battery discharge. They analyse the location of the transition between these regions using the first and second differentials of strain with respect to capacity. As discussed in detail in Section 4.1, producing the differential strain curves requires smoothing of the raw data. The application of residual analysis to the smoothed data gives an indication of the quality of the differential curve. Hence, this section will look at the differential curve generation for both strain and voltage, and comment on their quality and usefulness.

Strain derivatives curve generation.

An example of one of the four residual analysis sheets is shown in Figure 40, the other three can be seen in Appendix B. It is immediately obvious from plots (a) and (b) that the residuals are far from normally distributed and that there is some sort of systematic pattern in the residuals. In Section 4.1.1, the assumption was made that the noise removed by the smoothing process is random. Hence, the residuals resulting from the smoothing should also be random. The systematic pattern seen in Figure 40 (b) could be due to two causes:

- The smoothing itself.
- A small systematic noise present in the raw strain data.

Figure 39 looks in detail at the raw strain data and confirms that systematic noise is present. The cause of this noise is the control feedback being implemented to maintain the 100 N compression to the battery. To maintain the constant force, the crosshead of the testing machine is continuously being adjusted in very small increments by the control software. These very small changes are manifested as systematic noise in the strain data. This makes performing the smoothing and differentiation difficult, as there are now three potential causes of features in the curves:

- Phenomena of interest
- Features introduced by smoothing
- Features resulting from the feedback control

Because it is impossible to disassociate these three phenomena, the traditional peak analysis of the first and second differentials, as performed by Sheffer (58), cannot be made with any confidence.

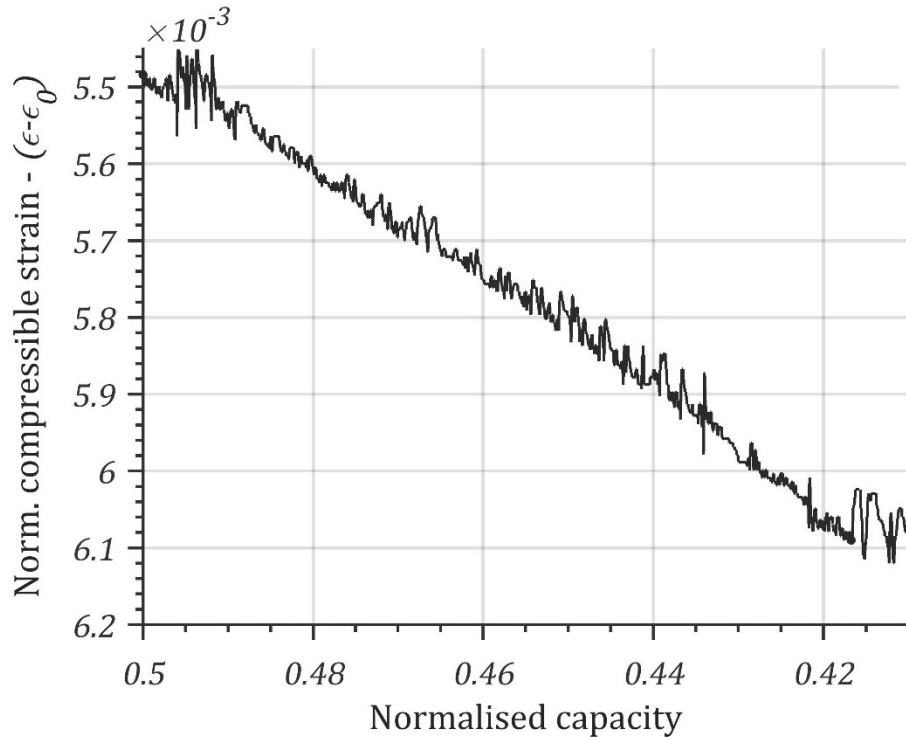


Figure 39: Zoomed in image showing the systematic error present in the normalised raw-strain data of the fresh battery at 25 °C.

Attempts were made to use the strain differential curves that were generated. It was concluded that they were of insufficient quality for confidence to be given to any conclusions that could be drawn from them. Hence, no further analysis is presented here.

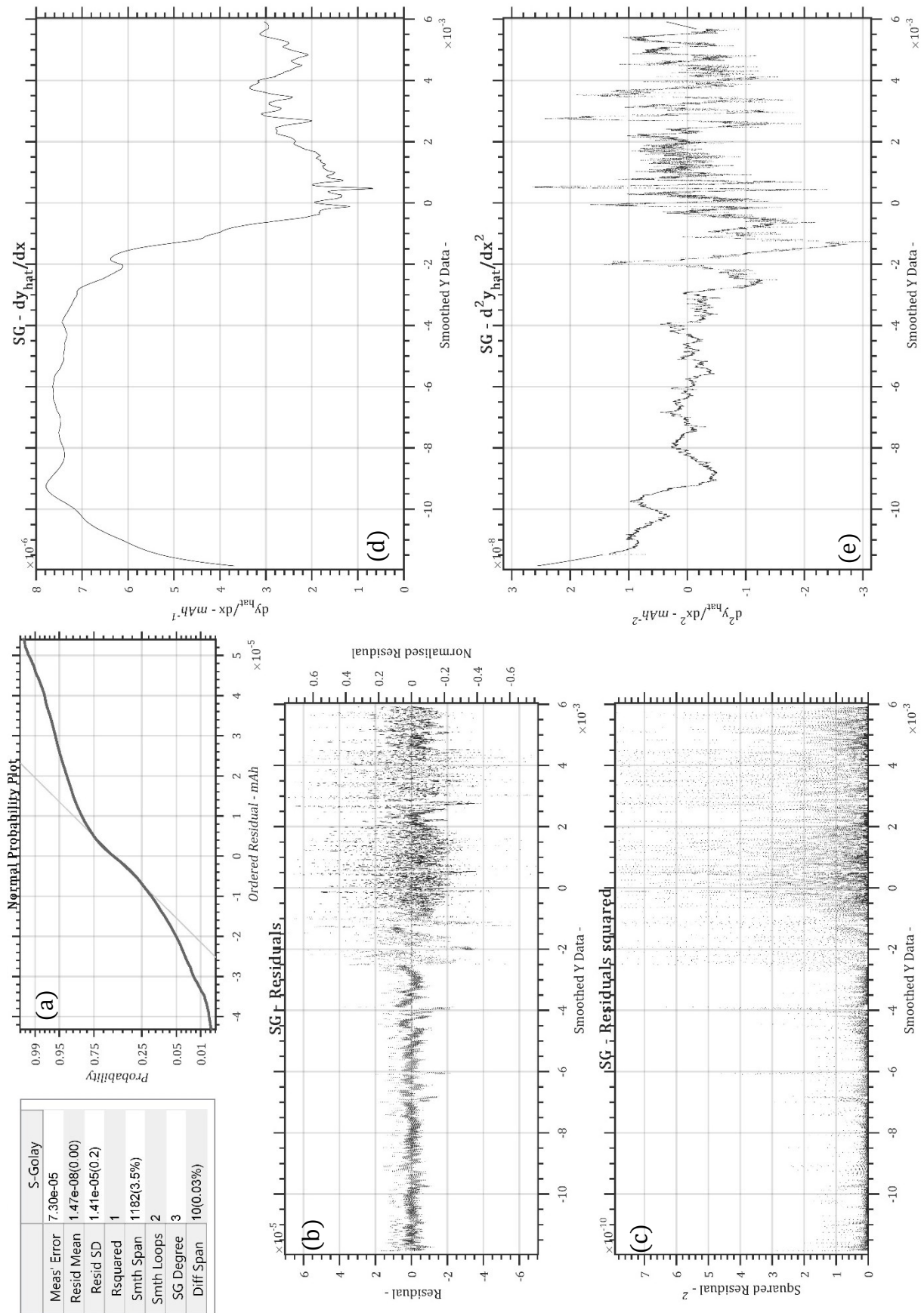


Figure 40: Residual Analysis plots for the smoothing and differential of the strain curve from 0.1C discharge of a fresh battery at 25 °C.

4.6.3. Isothermal breathing – conclusion

The isothermal breathing experiments showed that the magnitude of the strain due to the thermal expansion of a battery is of the same magnitude as strain changes due to electrochemically cycling the battery. The change in strain due to a 15 °C temperature rise is approximately two thirds of that of a full discharge. Thus, the battery temperature is a key variable when comparing the mechanical results of compression experiments.

The drop in discharge capacity due to ageing was unaffected by temperature. The reduction in strain due to ageing was greater at the lower temperature. The reduction in strain for the aged battery compared to fresh battery is not directly proportional to the drop in the capacity of the aged battery compared to fresh battery. A ~1.5% drop in capacity at both temperatures results in a 11.5 % (at 25 °C) and 8 % (at 41 °C) reduction in the magnitude of the strain during the discharge. It is hypothesised that this is due to small levels in stoichiometric drift. Small shifts in the anode potential manifest as large changes in the volume of the electrode.

The smoothing method outlined in Section 4.1 was applied to the strain curves from the discharges. This highlighted that a small systematic error caused by the constant force control feedback loop. Thus, the differential curves were of insufficient quality for traditional peak analysis to be applied and further analysis would not generate any substantiated conclusions.

4.7 Chapter 4 – Conclusion

The four experiments introduced in this chapter investigated the mechanical response of batteries to different boundary conditions and how the mechanical state affects the electrochemical performance. Sections 4.3 and 4.5 investigated the effect of the loading rate on the battery. After loading the batteries were held at a constant pressure of 0.13 MPa.

These experiments showed that:

- The mechanical response of the battery was highly viscoelastic, confirming the findings by Cannarella and Arnold (2).
- The viscoelastic creep of the battery exhibited exponential decay, where a relaxation period of 12 hour was considered sufficient for mechanical steady state to have occurred.
- The viscoelastic nature of the batteries made defining a consistent ‘mechanical starting point/reference point’ for testing difficult.
- No consistent relationship between the loading rate and the resulting steady state strain was found between batteries under the same constant pressure. This was due to the composite nature of the battery electrode stack resulting in significant variance in the data. An experiment with a large sample size would be required to generate statistically significant results.
- Once a steady state strain had been achieved, subsequent electrochemical cycling causes additional creep to occur.
- The electrochemical performance of the batteries showed no significant difference between the pre-compression, compressed and subsequent post-compression states. This showed that during short term experiments the effects of compression are either very small or non-existent, for the compression magnitude applied.

The experiments performed in Section 4.4 investigated how the battery impedance changes at different magnitudes of compression, within the range of 0 MPa – 1.3 MPa. These produced two conclusions:

- Good thermal management of the battery is required during mechanical testing of batteries for the electrochemical results to be compared. The effect of temperature on the battery performance is significantly larger than any mechanical effects.
- The impedance of the battery immediately before and after a step increase in compression of the battery does not change at all.

The final section in this chapter investigated the effect of ageing and temperature on the strain change of the battery during discharge. These experiments concluded:

- The strain resulting from thermal expansion for a 15 °C temperature rise is of the same order of magnitude as a discharge. Thus, if looking at the change in mechanical state of a battery with changing SOC, the temperature of the battery is an important control variable. If not held as a constant, the temperature variations must be accounted for in the results.
- There is a disproportionate difference in the reduction of capacity due to ageing compared to the reduction of the change in strain that occurs. It is hypothesised that this is due to small levels in stoichiometric drift. Small shifts in the anode potential manifest as large changes in the volume of the electrode.

At the beginning of this chapter the residual analysis methodology was introduced as a means of evaluating the quality of any smoothing performed when generating differential curves from experimental data. The analysis method is unable to provide a numeric quantification for the quality of smoothing as the numerical metrics generated are unable to capture the nuances of the smoothing process. The graphical methods provide very useful visual assessments of the quality of the smoothing. The user's judgment and experience are still key parts of the process of generating differential curves, but this methodology can speed up the process of tuning the smoothing parameters and so the improve the user's confidence in the differential curves generated.

5. Long-Term Compression Degradation - Electrochemical

Credit to Mr Ian Campbell for his contribution to the work presented in Chapters 5 and 6.

Including: Initial experimental design and scope definition, Force sensor specification and verification testing and programming of the force sensor data logging software.

The experiments presented in Chapter 4 are short term, of the scale of 1-10 electrochemical cycles. It was concluded that, within the pressure range tested, the effects of compression on a single electrochemical process are either negligible or so small compared to other variables, such as temperature, that they are extremely difficult to detect. This being the case, the next step was to perform degradation experiments, to test if any small differences, undetectable during an isolated process, manifest as measurable differences over the lifetime of the battery.

One key study gave the effects of compression over the lifetime of a battery (2). This work looked at both the electrochemical and the mechanical changes within batteries. The key points of the experimental set-up were:

- 500 mAh Pouch-batteries (LCO – graphitic carbon)
- Obround jelly-roll electrode configuration
- Initial compression applied at 0% SOC
- Fixed displacement constraint
- Force (pressure) experienced by the battery monitored by a load-cell.
- Four batteries tested at initial pressures (the term ‘initial’ is discussed in more detail Section 6.5)
 - Un-constrained
 - 0.05 MPa Low
 - 0.5 MPa Medium
 - 5 MPa High
- Cycled at room temperature, without precise thermal control.

Figure 41 (a) and (b) from this published work show how the 0.5C capacity and the pressure applied to the battery are related over time. The experiment was set-up with an initial compressive strain applied to the battery that corresponded to the initial pressure. After this point, the thickness constraint on the battery was unchanged. All pressure changes were due to reactions within the battery. With the thickness of the battery fixed, the pressure was used

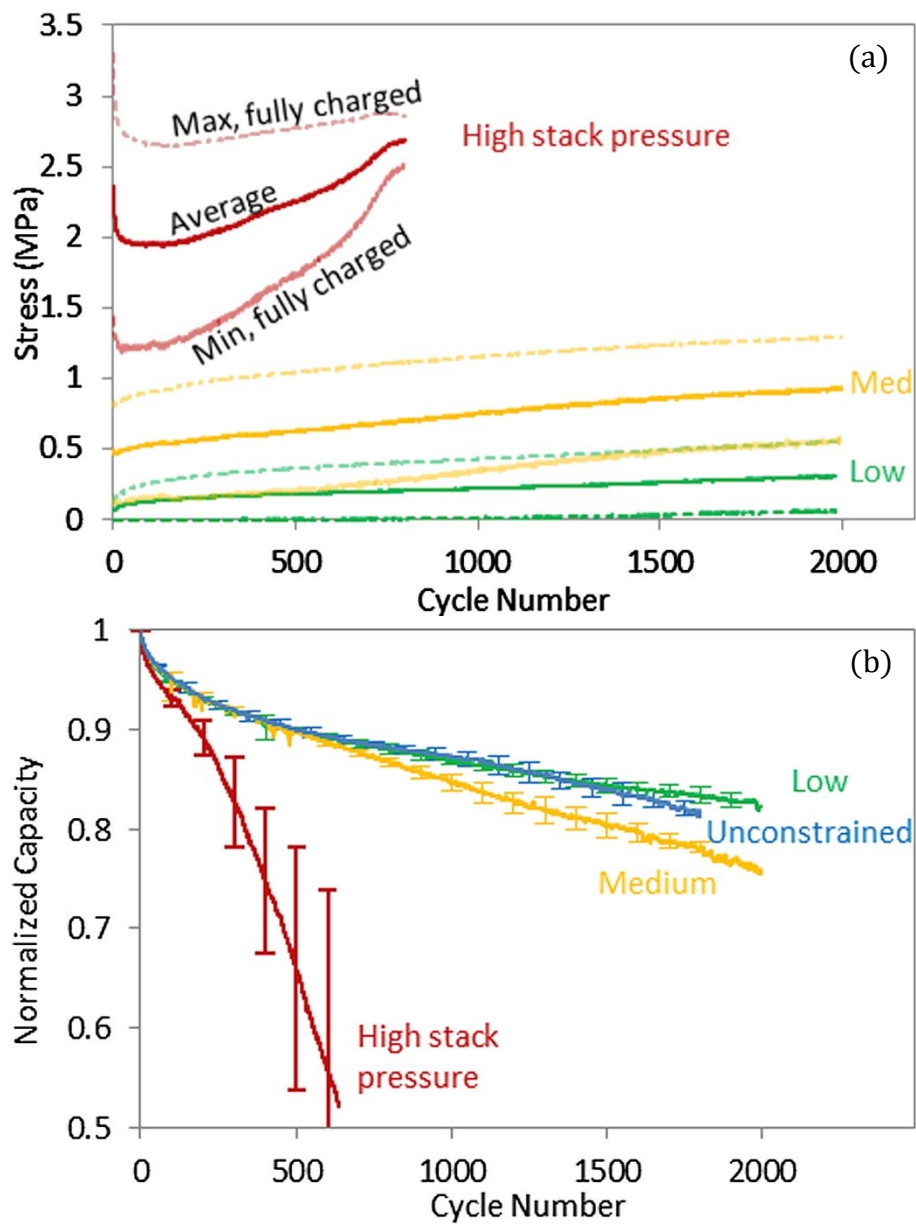


Figure 41: Pressure (a) and capacity (b) change in four batteries cycled under different compression magnitudes. 500 mAh, LCO vs Graphite, Obround jelly-roll batteries tested (2). Images reproduced with permission from Elsevier.

to measure the mechanical changes of the battery, rather than the strain. Thus, the breathing of the battery manifested itself as fluctuations in pressure.

Figure 41 (a) shows three pressure lines per compression magnitude. These represent the minimum, maximum and mean pressures experienced by the batteries, resulting from the electrochemical breathing of the batteries.

The conclusion for this earlier work is that the magnitude of the pressure applied during fixed displacement compression of Li-ion batteries significantly impacts the cycle life of Li-ion-batteries. Best capacity retention is achieved with a low level of compression. The following damaging mechanisms were identified through post-mortem analysis of the batteries tested:

- Loss of contact between the electrode layers, manifesting as a rippling effect of the layers.
- Periodic formation of surface films that align with the folds in the jelly-roll.
- Delamination of active material from the current collector, periodic and present at the electrode folds.
- Periodic reductions in separator porosity, aligning with the electrode folds.

Insufficient emphasis was placed upon the common feature of these four mechanisms; namely, the periodicity and the relation to the folds in the obround jelly-roll electrode configuration. This strongly suggests that the effects of compression are heavily influenced and exacerbated by the electrode configuration of the specific batteries tested. Thus, the conclusions cannot be applied to all Li-ion batteries, simply to obround jelly-roll batteries. The following discussion theorises why electrode configuration exacerbates the influence of compression on capacity fade of Li-ion batteries.

5.1 Theoretical Discussion of Electrode Configuration Under Compression.

The mechanical degradation of the aged cells in the work by Cannarella and Arnold (2), showed a very strong relationship to the obround jelly-roll electrode configuration in the batteries used. What follows is a discussion of the cause of this relationship and why testing batteries with a stacked electrode configuration would be significantly different.

In an obround jelly-roll, the electrode stack height is not uniform. Along the folds in the electrode, the stack will be slightly thicker. Thus, in the case where the battery is compressed between two rigid plates, the folded region is being clamped under a disproportionate pressure. This has the following impacts on the battery electrodes:

- The pressure applied to the electrode area of the entire jelly-roll is very non-uniform.
- The two edges of the electrode stack are now pinned in place.
- The folded regions are subjected to additional stresses, where the electrodes and current collectors are already under stress due to the fold

This is considered to be the underlying cause of the results seen in the work by Cannarella and Arnold. The pressures concentrated at the electrode folds introduce severe inhomogeneities. As the pressure is increased, so too is the inhomogeneity and localised damage, hence increasing the rate of degradation.

One conclusion made by Cannarella and Arnold is that a low level of stack compression improves the cycle life of the battery, due to preventing rippling in the electrode stack. This prevents loss of active area of the electrode. This is considered a particular feature of the obround jelly-roll electrode configuration. The obround jelly-roll form applies an in-plane constraint on all the electrode layers, restricting in-plane expansion and contraction to one direction. As discussed in Section 2.4.4, the intercalation electrode material expands and

contracts with cycling. Expansion is generally discussed in terms of change in thickness. However, the electrode expansion is not simply unidirectional. There is also some in-plane strain, which encourages rippling in electrodes. Low levels of compression reduce the rippling and thus maintain good electrode contact. The negative impact of the low pressure is predominantly transmitted through the folds and is small enough not to outweigh the benefits low pressure induces. It is concluded that a low level of compression is beneficial to the cycle life of obround jelly-roll batteries.

The question raised from this discussion is:

“What is the effect of constraining a Li-ion battery that does not have this specific electrode configuration, such as a stacked-electrode configuration pouch battery?”

This question is addressed in this and the following chapter.

5.2 Constraint Configuration

The experiment investigates the effect of mechanical constraint on stacked electrode configuration pouch batteries. Several factors influence the design of the experiment:

- Should a fixed displacement constraint be applied or constant pressure?
- Should the constraint be of some other type?
- How should that constraint be applied?
- What should be measured?

The decision was made to perform a fixed displacement constraint and the force/pressure measured throughout the experiment. This section discusses the constraint methods considered, and why the fixed displacement was chosen.

5.2.1. Compliant compression

The industry trend in battery pack design is to stack pouch batteries interspersed with a layer of compliant material, an example being a foam sheet (98). For this, each battery would have been tested with a layer of compliant material in the compression stack and compressed to different pressures. Although this is the most industry-relevant constraint method, the compliant material introduces significant uncertainty into any mechanical measurements. Thus, drawing of confident links between the mechanical and the electrochemical phenomena would be extremely difficult with compliant material in the stack. This constraint requires both the pressure and the strain on the batteries to be monitored, as both will change as the batteries breathe and age.

5.2.2. Constant pressure

Constant pressure is considered from a scientific point of view the most attractive approach. The applied pressure is the same for all the components in the electrode stack and remains constant throughout the duration of the experiment, regardless of the SOC or cycle number. As will be discussed, this is not the case for fixed displacement constraint. The problem with the constant pressure constraint is how to apply it. In Chapter 4, a constant pressure constraint was applied via a large and expensive tensile testing machine with a complex control system. The control system impacted the quality of the results. This method of implementation is too impractical for a long-term degradation test.

There are two passive methods for applying a constant pressure to the batteries:

- Place under a large mass
- Compressed springs

Placing the batteries under a large mass is impractical. The highest pressure tested, 0.65 MPa, corresponds to a force of 3 kN and an approximate mass of 300 kg (for the battery being tested, see Table 4 for the battery specifications).

Using springs offers a more practical and compact method for applying the required pressures and is a solution that has been used in the literature (67). But to accurately know what pressure is being applied to the batteries would require some form of force measurement. This results in the added complexity of measurement, both for the pressure and the strain of the batteries.

5.2.3. Fixed displacement

The fixed displacement constraint was chosen for this experiment, after balancing these requirements:

- Size
- Complexity of measurements to be taken
- Controllable variables
- Confidence in and usability of the mechanical data
- Applying consistent mechanical and thermal conditions

This method only requires the pressure applied to the battery to be measured. Passive testing jigs can be designed in a compact size that can be placed inside a thermal chamber. High levels of compression can easily be applied. The disadvantages of the fixed displacement constraint are:

- The battery breathing is a volumetric change in the electrodes. Fixed displacement of the complete electrode stack will result in the volumetric expansion being absorbed disproportionately by the more compliant components in the stack - namely the separator. Thus, the results could be skewed by this phenomenon, which would not be present in an industrial application, as discussed in Section 5.2.1.
- The pressure is measured using load cells which function by monitoring very small deflections in the sensor - strain gauges. Thus, to monitor the pressure changes of the battery during testing, the nominally 'fixed' displacement boundary condition is not perfectly fixed. Section 6.1.2 discusses this in detail and concludes that the displacement changes in the boundary conditions can be considered negligible.

5.3 Experimental design

The configuration chosen was a fixed displacement constraint. The five sections of the experimental design were:

- Mechanical design
- Thermal design
- Definition of compression magnitude
- Pressure range
- Electrochemical procedure

The batteries tested were the 5 Ah NMC-Graphitic carbon type, from the manufacturer Kokam. The same battery model was used in the short-term tests (Chapter 4, battery specifications given in Table 4). These are high power batteries with a stacked electrode configuration and tabs at either end of the battery.

5.3.1. Mechanical design

A rendering of the final mechanical design of the compression jigs can be seen in Figure 42.

The different components highlighted have the following functions:

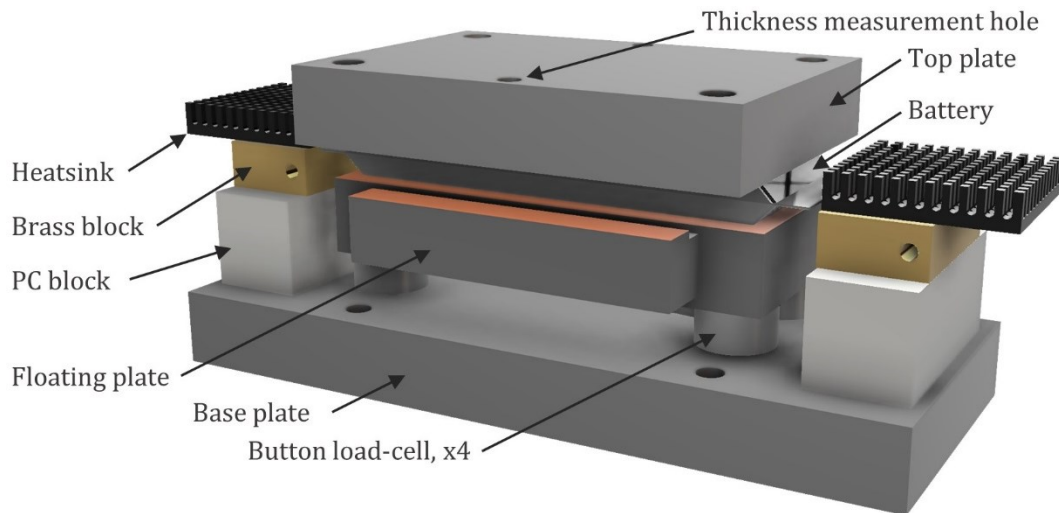


Figure 42: CAD rendering of battery compression rig used in long term compression experiment. Key components labelled. Four bolts (not shown) are placed through each corner of the Top plate and are threaded into the Base plate. This CAD rendering was generated in collaboration with Mr I. Campbell.

Top and Base plates

Four bolts pass through the 20 mm thick aluminium top plate and are threaded into the aluminium base plate. Tightening these four bolts applies the compression to the battery, floating plate and load-cell stack. Details of the bolts used in the different jigs are described in Section 6.1.2.

Battery, Floating Plate and Load-Cell Stack

The floating plate is a 20 mm thick aluminium plate and transmits the pressure from the battery to the load-cells. The detailed load-cell configuration is discussed in Section 6.1. Four regularly spaced button-type load-cells are used per testing jig, to ensure that a uniform pressure is applied to the battery. This also enables any non-uniform mechanical evolution of the batteries to be monitored.

Heat sink and Brass Block

The heat sink and brass block are the current and voltage measurement connection points to the battery cycler (brass block – current, aluminium heat sink - voltage). The battery tabs are clamped between the two. To provide strain relief for the delicate battery tabs, this assembly is mechanically secured to the base plate through the polycarbonate (PC) blocks.

5.3.2. Thermal design

One of the key conclusions from the short-term experiments presented in Chapter 4 is that the influence of compression on the electrochemical performance is either negligible or insignificant compared to the effects of temperature. Hence the thermal design of the degradation experiment is very important. Active thermal management akin to that used by Hunt et al. (99) was considered to add too much complexity to the experimental set-up.

The passive thermal management chosen was to maintain a fixed temperature of the battery, in a thermal chamber. This method relies on:

- The aluminium blocks pressed against the battery surfaces acting as heat sinks for the thermal energy generated by the battery and them having sufficient thermal inertia to avoid large temperature changes.
- Small fans mounted on the aluminium heat sinks attached to the battery tabs. They create a forced convection heat transfer from the battery to the surrounding air.

Temperature Measurement

The temperature of the batteries was measured using K-type thermocouples attached to the edge of the battery pouch. For the same reasons outlined in Section 4.6.1, the thermocouples were attached to the battery using thermally conductive epoxy resin. An example is shown in Figure 43. Figure 43 (a) is a schematic showing the location of the thermocouples on the batteries.

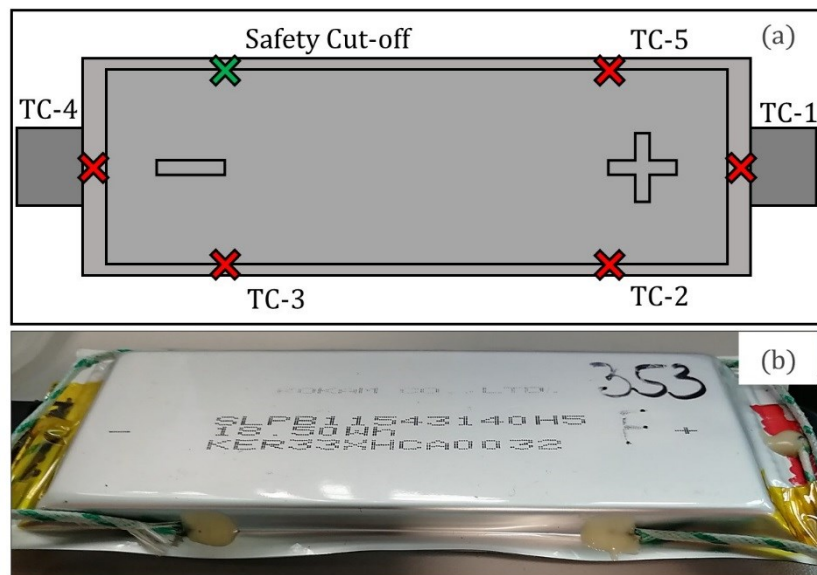


Figure 43: Figures showing the thermocouple location and bonding method. (a) Schematic showing the thermocouple locations on the batteries. (b) Image of the thermocouple tips bonded to the edge of the battery using thermally conductive epoxy.

Ambient Temperature

The ambient temperature maintained in the thermal chamber was 40 °C, to accelerate the rate of ageing of the batteries.

5.3.3. Definition of compression magnitude

The pressure magnitude applied to the different batteries at the beginning of the experiment defines the fixed strain applied to the batteries for the entirety of the experiment. Hence defining the initial pressure in a consistent manner is important. The mechanical results in Chapter 4 show that applying a specified boundary condition to a Li-ion battery is not easy

and some additional requirements need to be defined to make different experiments comparable. This is due to:

- a) The change in the mechanical state of the battery with SOC.
- b) The viscoelastic relaxation of the battery.

This concern partially comes from the work by Cannarella and Arnold (2), where the target pressures were not achieved, due to the method used for applying the initial load and the subsequent battery relaxation.

SOC when Initial Pressure is applied

When the initial pressure was applied to the battery, the SOC had been set at 50%. This was chosen because it was considered at the time to be the most likely SOC that the battery pack assembly would be performed at. For this experiment, 50% SOC state is indicated when the battery was charged to 3.76 V with a CV-hold to $|i| < 0.01C$ at 25 °C.

Accounting for the Viscoelastic Relaxation

To account for the viscoelastic relaxation, a process of recompression of the batteries was employed at 25°C. Figure 44 shows the flow diagram of the recompressing procedure employed.

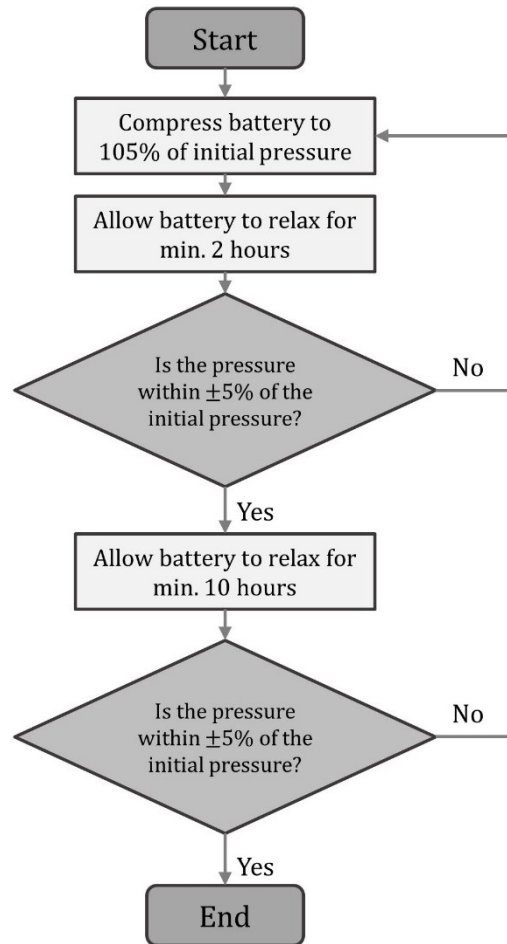


Figure 44: Flow diagram of the initial compression procedure, with repeated re-compressions to account for relaxation in the batteries.

Comments on initial compression

As stated above, the procedure in Figure 44 was intended to provide a consistent definition of mechanical state for comparing all the batteries and account for the relaxation. In Section 6.4 it will be shown that this was not the case and further relaxation of the batteries occurred after the procedure was completed. The further relaxation occurred because of electrochemical cycling and a change in temperature.

To that end, the 'True pressure' will be used to describe the pressure magnitude for the different batteries and not the 'Initial pressure'. The True pressure is the pressure applied to the battery after all relaxation has occurred, when electrochemical cycling returns the battery

to the same SOC and the pressure also returns to the original value. The True pressures quoted in Table 15 are for batteries at 50% SOC and at 40 °C.

5.3.4. Pressure range

The BCS-815 Bio-logic battery cyler used has eight channels (100), so eight batteries were tested at different initial/true pressures. The pressure magnitudes tested were:

Table 15: Initial pressures and true pressures applied to the eight batteries tested.

Initial Pressure	True Pressure	Abbreviation
Control (0 MPa)	Control (0 MPa)	CTRL
Constrained (0.022 MPa)	Constrained (0.019 MPa)	CSTR
0.043 MPa	0.040 MPa	-
0.065 MPa	0.057 MPa	-
0.13 MPa	0.097 MPa	-
0.20 MPa	0.134 MPa	-
0.26 MPa	0.182 MPa	-
0.65 MPa	0.434 MPa	-

The control battery, although unconstrained was placed in a compression jig to mimic the thermal boundary conditions of the other batteries tested.

The constrained battery was compressed by a pressure equivalent to 100 N, in a similar manner to the preload condition outlined in Section 4.5.

Equivalent Pressures Applied in Cannarella paper

The mechanical state of the batteries used to define the pressure applied is different to that used by Cannarella and Arnold (2). The equivalent true compression conditions used in this experiment were visually estimated for the Cannarella graphs and are shown in Table 16. This accounted for both the different SOC at which the compression was applied and the relaxation that occurred.

Table 16: Pressure applied to batteries in the work by Cannarella and Arnold (2). Initial pressure refers to the pressure quoted in the paper. The True pressure estimate is the pressure magnitude applied to the batteries using the same definition of the mechanical state in this work.

Label	Initial Pressure (@ 0% SOC)	True pressure estimate (@ 50% SOC)
Low	0.05 MPa	~ 0 MPa
Medium	0.5 MPa	~ 0.4 MPa
High	5.0 MPa	~ 2.0 MPa

These are approximate values, visually measured from a graph, estimating that 50 % SOC occurred halfway between the minima and maxima of the pressure fluctuations during the battery breathing.

Note the large difference between the two values quoted, especially for the high pressures. This clearly shows the importance of a standardized means of quoting the mechanical state of a compressed battery.

5.3.5. Electrochemical procedure

The flow diagram of the electrochemical processes performed in this degradation experiment is shown in Figure 45. The batteries are cycled 2000 times in 10 sections of 200 cycles each. Every 50 cycles, a characterisation procedure is performed. Every 200 cycles an additional isothermal 0.1C discharge and charge is made, denoted by [C/10] in Figure 45. The cycles were performed at C-rate of 2C for both discharge and charge, with no CV-holds and voltage cut-offs at 2.7 V and 4.2 V.

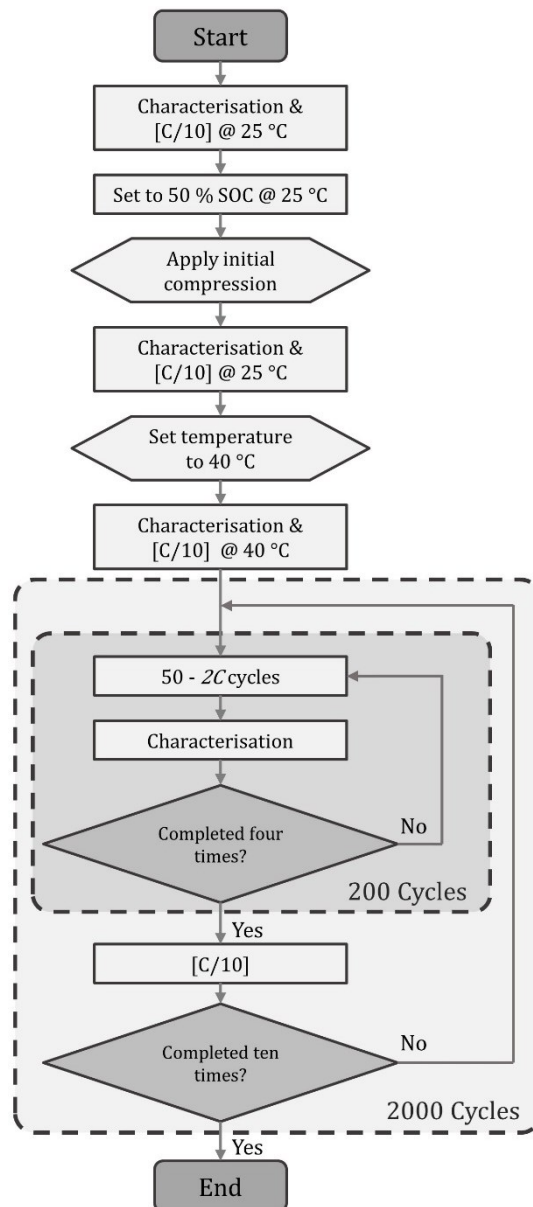


Figure 45: Flow Diagram showing the electrochemical procedure followed for the long-term compression experiment. Applied to all eight batteries. Hexagonal stages refer to either a change in a thermal or mechanical boundary condition.

The 200 cycle groups were not achieved throughout the entire experiment. From 0 to 600 cycles, a mixture of software bugs and user error resulted in multiple stops/starts in the testing procedure. After ~600 cycles a software update meant there were no more unanticipated stop/starts and the cycles were performed in groups of 200. The exception to this was between cycles 1201 and 1600 where a split of 100 and 300 cycles was performed to fit the restart around holidays.

Electrochemical Characterisation Procedure

The electrochemical processes performed during the characterisations are outlined in Table

17. All CV-holds have a cut off at $|i| < 0.01C$

Table 17: Constrained Degradation - Characterisation Procedure

Step	Process	Notes
1	Charge to 4.2 V with CV-hold	Standard starting point
2	1C discharge to 2.7 V with CV-hold	
3	1C charge to 4.2 V with CV-hold	
4	3C discharge to 2.7 V with CV-hold	High-rate discharge limited by the current capability of the cycler
5	2C charge to 4.2 V with CV-hold	Charge at fastest rate recommended on battery data-sheet.
6	Impedance discharge and charge 1C sweeps	Details in Section 4.5.1

Channel Staggering

The battery cycler used for this experiment was the BCS-815 with eight testing channels per module. The EIS capability of the module is multiplexed across the eight channels. Multiple channels attempting to access the EIS capability simultaneously resulted in catastrophic battery failure. To prevent this occurrence the testing of the batteries was staggered over a 24-hour period with a 3-hour offset between each. This 24-hour staggered period at the beginning and end of each 'lump' of testing significantly increased the duration at which the batteries were sitting inactive throughout the duration of testing. The impact of this and the resulting calendar ageing is discussed in Section 5.6.

5.4 Constrained Degradation – Results

Chapters 5 and 6 of this work present results from the same experiments, split into two sections:

- Electrochemical results are in Chapter 5
- Mechanical results are in Chapter 6

The electrochemical results are broken down into 4 sections:

- Capacity fade of the 0.1C, 1C and 3C data from the characterisation procedures.
- Calendar ageing rate estimation and Capacity fade of the 2C cycling.
- Change in the battery impedance.
- Change in the differential of the 0.1C cycles.

5.5 Capacity Fade – Introduction

This section discusses the charge and discharge capacities performed during the characterisation procedures, every 50 cycles. The 0.1 C data was gathered every 200 cycles. All discharges were performed between the voltage limits of 4.2 V and 2.7 V with a CV hold performed prior to the discharge at 4.2 V until $|i| < 0.01\text{ C}$. The same is true for the charges with the preceding CV performed at 2.7 V. All capacities have been normalised against the capacity measurement taken under compression, at 40°C and zero-cycles. This is one of three reference capacities (shown in Table 18) that could have been used, all under slightly different conditions:

Table 18: Three states at which the batteries were characterised prior to cycling.

	State 1	State 2	State 3
Temperature	25 °C	25 °C	40 °C
Under Compression?	No	Yes	Yes
Cycle number	0	0	0

The battery was characterised under these three states to monitor the changes when transitioning between them. It was decided to assess the transitions between the states in isolation. Thus, State 3 was chosen as the reference point for normalisation of the capacities.

5.5.1. Capacity fade – 0.1 C

The normalised capacity of all eight batteries from the 0.1C discharges and charges is shown in Figure 46 (a) and (b) respectively. All charging processes were isothermal and at 40 °C. All except three passed the isothermal test (outlined in Appendix C) with a target temperature of 40 °C $\pm$ 1.2°C. The three failures were visually inspected and found to have one of three temperature channels just outside the error boundary, but still within the error of a K-type thermocouple ($\pm$ 2.2 °C). Hence all are considered isothermal.

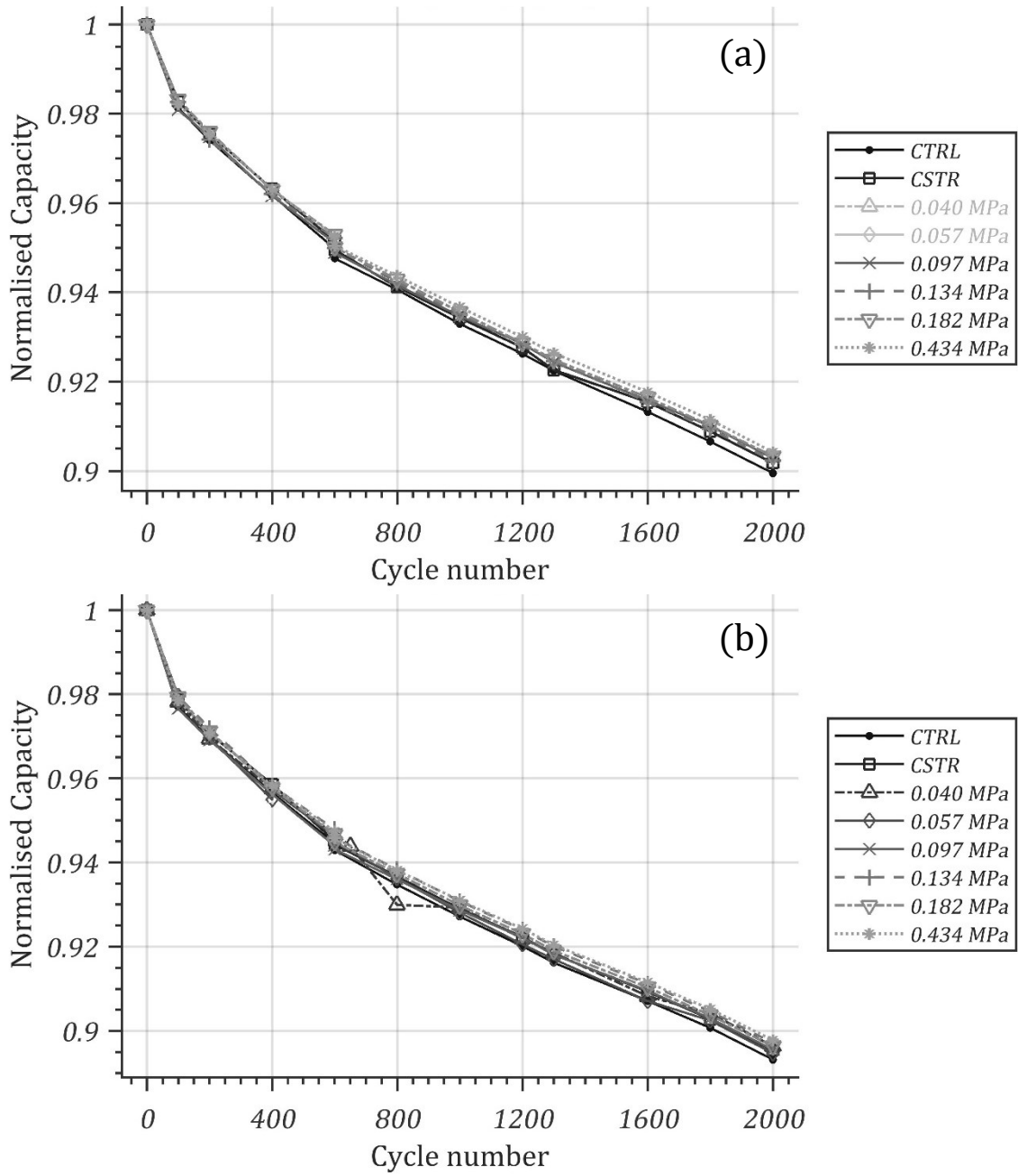


Figure 46: Normalised capacity from the 0.1C discharges (a) and charges (b) taken every 200 cycles. Eight batteries under fixed displacement constraint, at different pressures. Dark to light represents increased pressure. Plot (a) does not show the two erroneous data sets, greyed out in the legend (0.040 MPa and 0.057 MPa).

Key features of Figure 46:

- The discharge datasets for '0.040 MPa' and '0.057 MPa' in Figure 46 (a) were subject to experimental error and can be ignored. Justification for this is given below.
- There is no significant variation in the rate of capacity fade between the eight batteries. There is a subtle trend that could be drawn from looking from dark to light (increasing pressure) showing a slight increase in capacity retention. For this experiment with this small sample size this trend is not considered significant. The trend is not distinct enough to exclude other factors such as battery variability.
- Large capacity drops between 0 and 100 cycles. This is a typical feature of Li-ion battery testing with an initial higher rate of capacity fade, but this feature has been exaggerated in Figure 46 by calendar ageing. A combination of software bugs and user error required the stopping, restarting and re-aligning of the different batteries. This resulted in periods of inactivity and so significant calendar ageing occurred over the first 100 cycles.
- Slight step in the curves at 600 cycles. This is due to the presence of an additional data point at 600 cycles. A power blip caused the thermal chamber temperature controller to reset and the chamber temperature gradually increased from 40 °C to 55 °C for a period of two hours. This occurred after the 400-600 cycle 'lump' had finished but before the testing had resumed. To verify the batteries had not been affected by this an additional characterisation was performed, hence an additional data set. The results showed a slight drop in capacity of the same magnitude for all the batteries, resulting in the step. This drop is more a result of calendar ageing from the additional time, rather than the temperature variation and thus affected all the batteries similarly.
- The battery compressed to 0.040 MPa was cycled an extra 50 cycles at the end of the third group and was at 650 cycles rather than 600 during the temperature rise.

Experimental error in the 0.1C discharge data

The discharge datasets for '0.040 MPa' and '0.057 MPa' were subject to experimental error and are not shown in Figure 46 (a).

5.5.2. Capacity fade - 1C

Figure 47 (a) and (b) show the capacity fade for the 1C discharge and charge respectively.

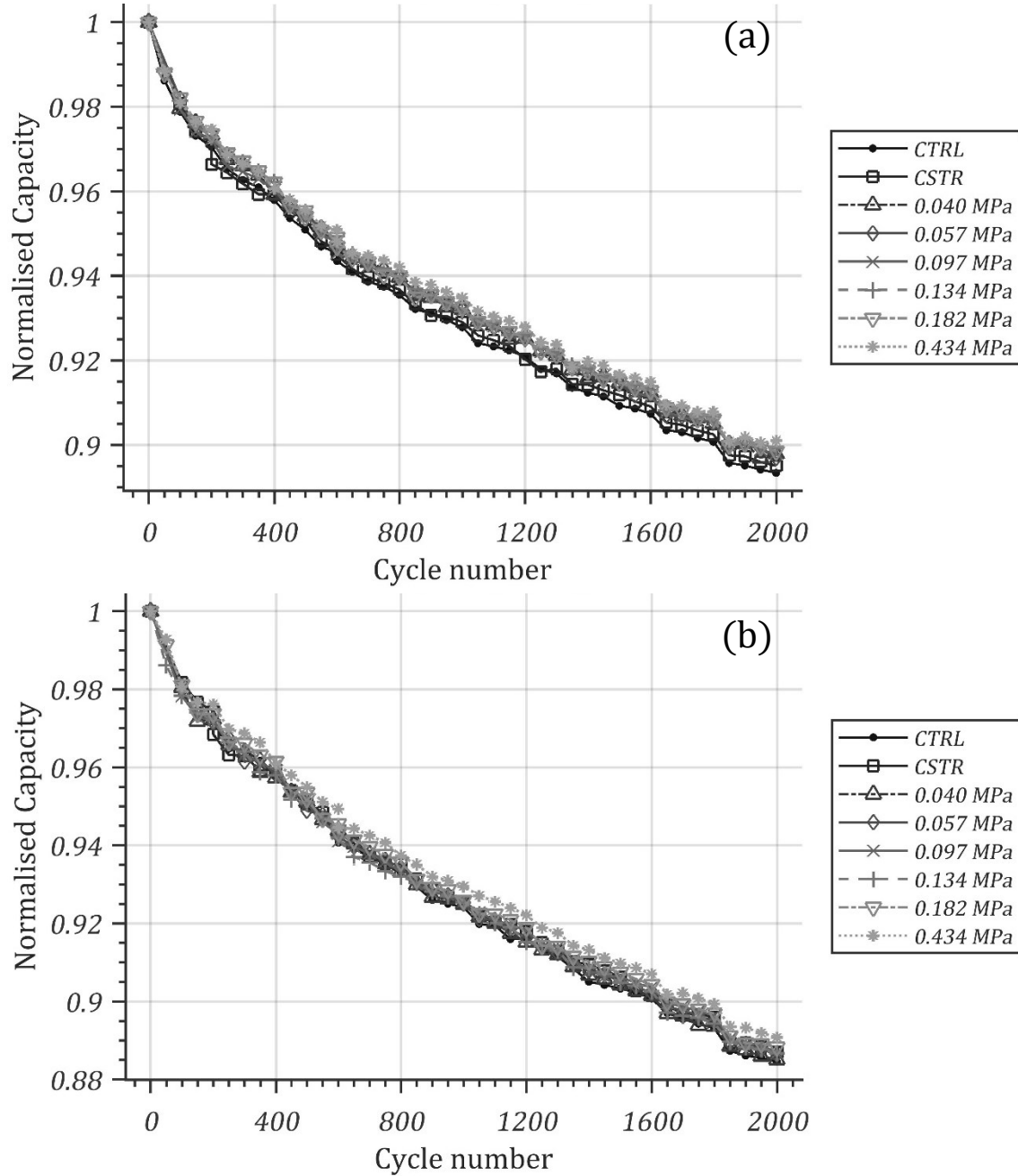


Figure 47: Normalised capacity from the 1C discharges (a) and charges (b) taken every 50 cycles. Eight batteries under fixed displacement constraint, at different pressures. Dark to light represents increased pressure.

Key features of Figure 47:

- Figure 47 (a) and (b) show the same overall result for the 1C capacity fade as for the 0.1C results shown in Figure 46. Namely that there is no significant change in capacity fade at the different pressures.
- The additional resolution from the 50-cycle sample rate shows distinctive stepped patterns in the capacity fade curves. The stepped pattern coincides with the 200 cycle groups (100 and 300 between cycles 1201 and 1600). A linear drop in capacity occurs between cycle 50 and the end of one group of cycles. Subsequently a larger drop occurs between cycle 0 and 50 of the next group. This disproportionate drop in capacity over the first 50 cycles of each group is due to the calendar ageing that occurs whilst the batteries are inactive between groups of cycles. The calendar ageing that occurred during the experiment is discussed in Section 5.6.

5.5.3. Capacity fade – 3C discharge and 2C charge

The capacity fade for the 3C discharges and the 2C charges are shown in Figure 48 (a) and (b) respectively.

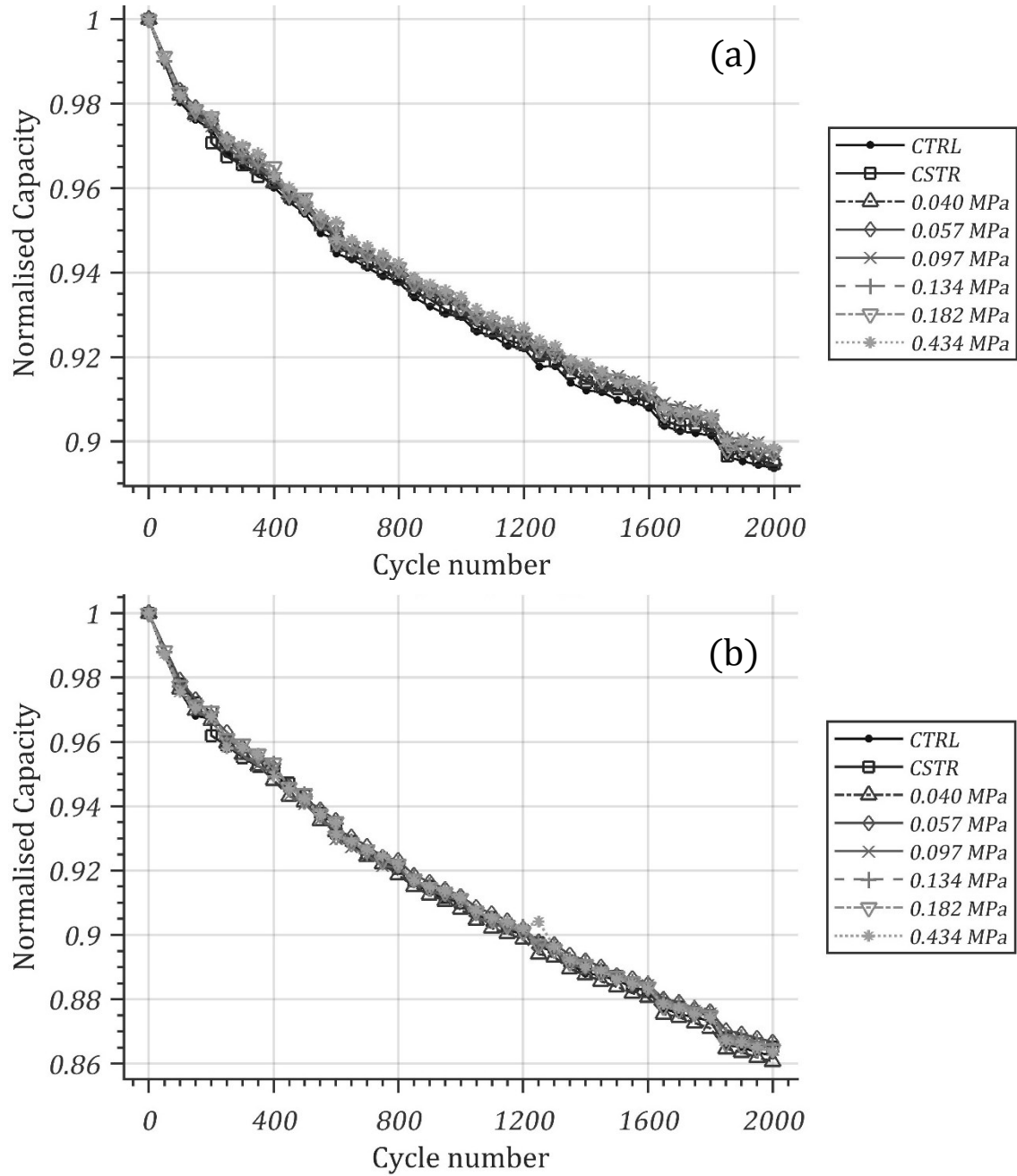


Figure 48: Normalised capacity from the 3C discharges (a) and 2C charges (b) taken every 50 cycles. Eight batteries under fixed displacement constraint, at different pressures. Dark to light represents increased pressure.

Key features of Figure 48:

- Figure 48 confirms the results from the 0.1C and 1C data, namely that there is no significant change in rate of capacity fade for different pressures.
- The Stepped profile due to calendar ageing is present, as in the 1C data.
- Comparing the rate of capacity fade between the 1C discharges (Figure 47 (a)) and the 3C discharges (Figure 48 (a)) shows very little difference, with both ending at just under 90% capacity at 2000 cycles. This is unexpected, as with ageing there is an increase in internal resistance and so it would be expected that the capacity fade for the higher C-rate to be larger. The battery is a power-cell rated to 30C peak discharge rate. Thus, it is considered that the battery is so rate capable that on discharge the difference in 1C and 3C is very small.

5.5.4. Capacity fade – discussion and conclusions

The capacity fade data from the characterisations performed throughout the experiment shows no significant difference between the eight different compression levels, ranging from unconstrained to 0.434 MPa. This is in direct contradiction to the results shown in the work by Cannarella and Arnold (2). In the Cannarella work the three batteries tested within the same range (with equivalent pressures of: Unconstrained, 0-0.05 MPa and 0.4 MPa) showed the best capacity retention at 0-0.05 MPa and worst at 0.4 MPa. The unconstrained battery was in between these two. This difference is attributed to the difference in the electrode configuration inside the battery - namely the obround jelly-roll tested by Cannarella and Arnold (2) and the stacked electrodes tested in this work. The influence of the electrode configuration on the results of Cannarella work is discussed in detail in Section 5.1. This result shows that the stacked electrode configuration is insensitive to compression within this pressure range. This is due to the pressure being applied uniformly across the area of the electrodes with no significant pressure inhomogeneities being created causing non-uniform ageing within the battery.

The sample size and the unknown variability of the batteries tested under these conditions has led to the conclusion that the very subtle trend, of improved capacity retention with higher pressure, present in the data is considered insignificant.

5.6 Calendar Ageing – Introduction

The capacity fade results in Section 5.5 show that calendar ageing contributed significantly to the degradation of all the batteries. This section estimates the proportion of the total capacity fade that can be attributed to calendar ageing.

Calendar ageing is the degradation that contributes to ageing of the battery and is independent of cycling. For batteries with graphitic carbon anodes, the predominant calendar ageing mechanism is SEI layer growth (12,101–103). The formation and growth of the SEI layer consumes cyclable lithium as well as increases the impedance of the battery. Pinson and Bazant (101) generated a model to predict the growth of the SEI layer. After the initial formation of the SEI layer during the formation cycles (performed during battery manufacture) the subsequent SEI layer develops from the slow diffusion of electrolyte solvent particles through the existing SEI layer. These molecules then react with the graphite and lithium at the SEI-graphite interphase. The rate at which these reactions occur is a function of the rate at which the solvent molecules diffuse through the SEI layer. This is both a function of temperature, that follows an Arrhenius relationship, and the thickness (t) of the SEI layer. The reaction rate is proportional to the square root of the thickness ($\sqrt{t}$) (101).

The model generated by Pinson and Bazant showed that the formation rate of the SEI layer was independent of cycling. This is confirmed by the work performed by Ball (104), that concluded that the degradation due to cycling and due to calendar ageing can be simply added together to get the cumulative capacity fade.

With this, an estimate of the proportion of the capacity fade caused by calendar ageing can be made, making the following assumptions:

- The SOC at which the batteries were inactive was consistent throughout the experiment. A good practice at the end of all procedures sets the battery to a voltage of 3.76 V with a CV hold.
- The time during which the batteries were characterised, the battery is assumed to be inactive. This assumption is the result of balancing two potential sources of error. The first error is that during the characterisations, the state of the battery is changing and so not inactive, slightly affecting the calendar ageing process. The second error is that the duration of the characterisation periods ($\sim 24\text{h}$) is a significant proportion of the inactive periods between groups of cycles ($\sim 48\text{h}$). The $\sim 30\%$ known error in the time duration is much larger than the error introduced by assuming the battery is inactive during the characterisation. Thus the above assumption was made.
- All eight batteries calendar age at the same rate. This assumes that the different compression magnitudes applied to the batteries do not affect the diffusion rate of solvent molecules across the SEI. The capacity fade results in Section 5.5 support this assumption, in that there is no evidence that any of the batteries aged differently from any others.

5.6.1. Calendar ageing contribution – estimation method

The magnitude of the calendar ageing cannot be calculated directly because the necessary capacity measurements were not taken. This is shown schematically in Figure 49 using the transition between cycles 801-1000 and 1001-1200 as an example.

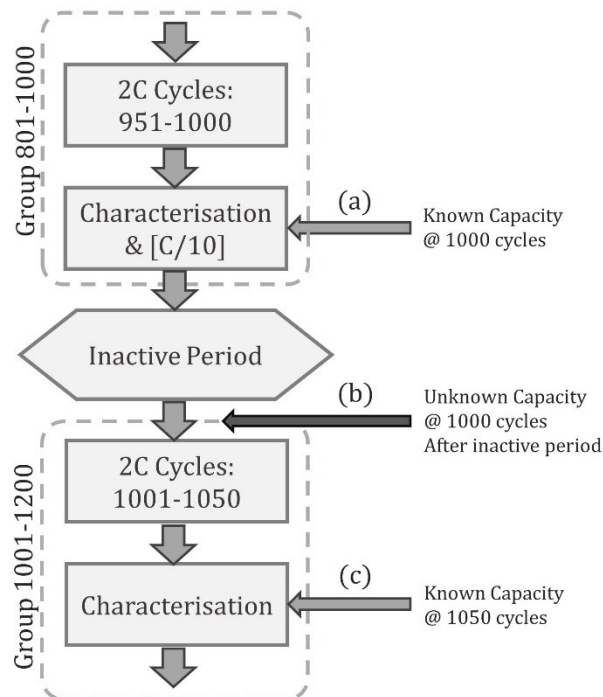


Figure 49: Flow diagram of the electrochemical procedure before and after an inactive period, between cycling groups. Arrows (a) and (c) show where characterisation of the battery occurs and where an accurate capacity measurement exists. Arrow (b) highlights the capacity value needed to calculate the capacity fade that occurred during the inactive period.

Instead of using the characterisation capacities shown in Figure 49, the capacities from the 2C cycling could have been used, as that data includes the difference in capacity between the last cycle before the inactive period and the first cycle after it. In the Figure 53 example, the capacity is known for both cycle 1000 and 1001. Unfortunately, there are significant features in the 2C cycle capacity datasets that meant that this could not be performed. This is discussed in Section 5.6.2.

To estimate the amount of capacity fade that occurred during all the inactive periods of the experiments, the unknown capacities need to be calculated. This was done by performing a line fit to the capacity vs cycle number for each of the cycling groups and using that fit to back calculate the unknown capacity. An example of one of the line fits and back calculations is shown in Figure 50.

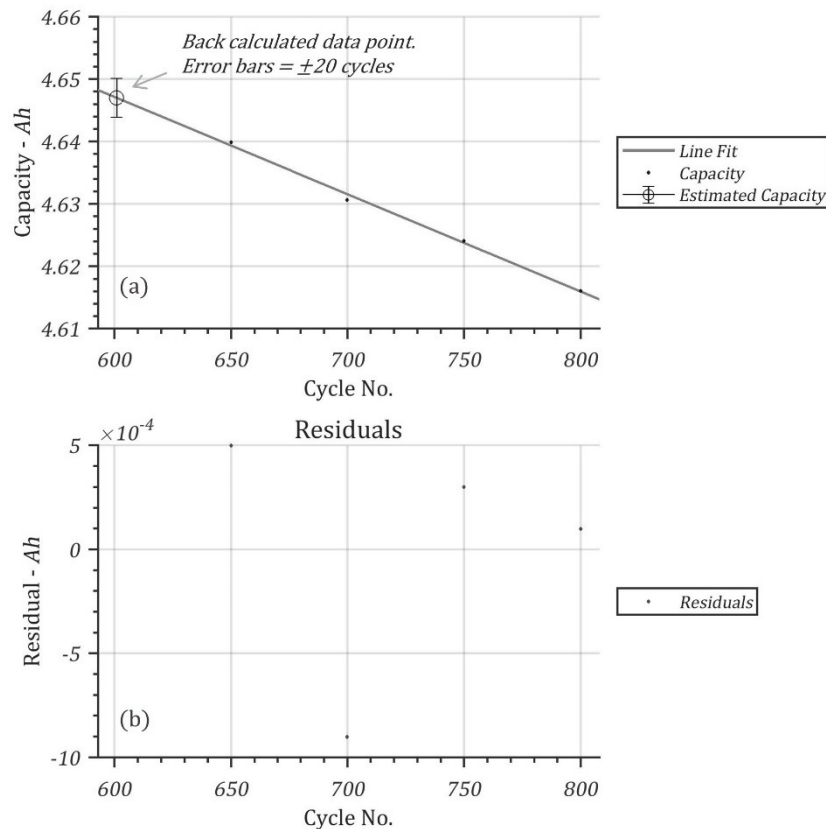


Figure 50: Example of a line fit performed on the 1C discharge capacities during a group of 200 Cycles. Plot (a) shows the data points and the fitted line. Plot (b) shows the fitting residuals. In the top left of plot (a) is the back calculated capacity from the line fit.

Note the errors bars shown in Figure 50 (a). These denote the capacity value calculated for ± 20 cycles about the target cycle number. 20 cycles were chosen as it is 1 % of the 2000 cycles of the entire experiment. These error bars are not intended to represent a known error, but rather act as a scale indicator in the following figures.

The fitting shown in Figure 50 was performed where possible. Due to the random nature of the stops and restarts in the first 600 cycles this could not be performed for all periods of inactivity, due to lack of data points. Most fits were performed using four data points as in Figure 50 but some were fitted to 2, 3 or 6 data points. At 600 cycles there is a direct measurement because of the extra characterisation that was performed. In Figure 51 (a-c) the number of data points used to perform the fitting is stated.

With the capacity after the inactive periods known, the capacity drop was calculated. Dividing this by the time duration gave the calendar ageing rates. These values are shown in Figure 51 for the control battery, generated from the 1C discharge data.

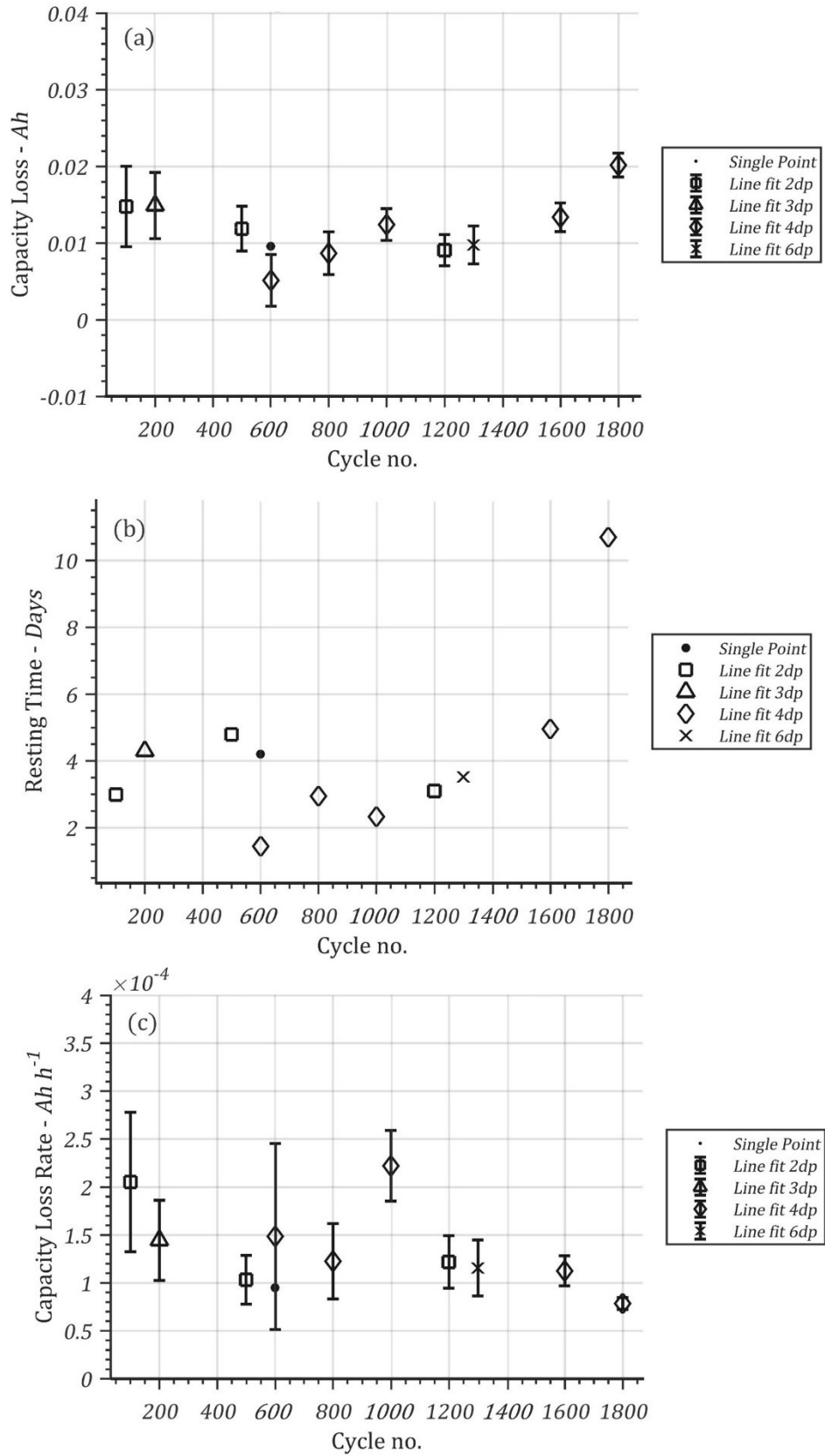


Figure 51: Example plots of the Capacity loss, Resting time and Capacity loss rate throughout the 2000 degradation cycles for the Ctrl battery. (a) The calculated capacity loss during the inactive periods between groups of cycles. Error bars represent the capacity if the calculation was performed at a cycle number ± 20 cycles. (b) The duration of the inactive period. (c) The capacity loss rate during the inactive periods, error bars carry forward from (a).

Figure 51 (c) shows the variability in the calculated calendar ageing rates is not insignificant, but also not so large that the values can be considered meaningless. This is acceptable, as the calculation method used will introduce inaccuracies and is intended to generate an estimate for the magnitude of the calendar ageing, not an exact value. Hence this data was considered of sufficient quality for further analysis. Comparing the 'loss rate plots' from all eight batteries, the capacity fade rates fell between 1 and $1.5 \times 10^{-4} \text{ Ah h}^{-1}$. The times in Figure 51 (b) include, where applicable, the duration of the characterisation procedure.

Assuming all batteries calendar age at the same rate, stated at the beginning of this section, a histogram of all the 'Calendar ageing rates' values calculated from all eight batteries was plotted. This data is shown in Figure 52, for the 1C discharges, with a Gaussian probability function fitted to the data. A total of 93 data points were generated by the method described above. Four of these were excluded from the histogram shown in Figure 52 as outliers. These were identified as outliers as they were either significantly larger or smaller than the other values. Upon inspection, these four points were linked together as two pairs. The first of each pair was generated from a line fit across two data points that had a positive gradient. The gradient could only be negative as the battery ages. The second point in the pair was calculated for the inactive period immediately after the first. Thus, one erroneous capacity value impacted on two ageing rate values.

Figure 52 shows that the calendar ageing rate values fit the Gaussian distribution well and the mean can be used as a reasonable estimate for the calendar ageing rate for the experiment. There is a slight right-hand skew to the data, which is to be expected. The rate of calendar ageing is not constant and is initially faster, slowing down as the thickness of the SEI layer grows (12,101,103).

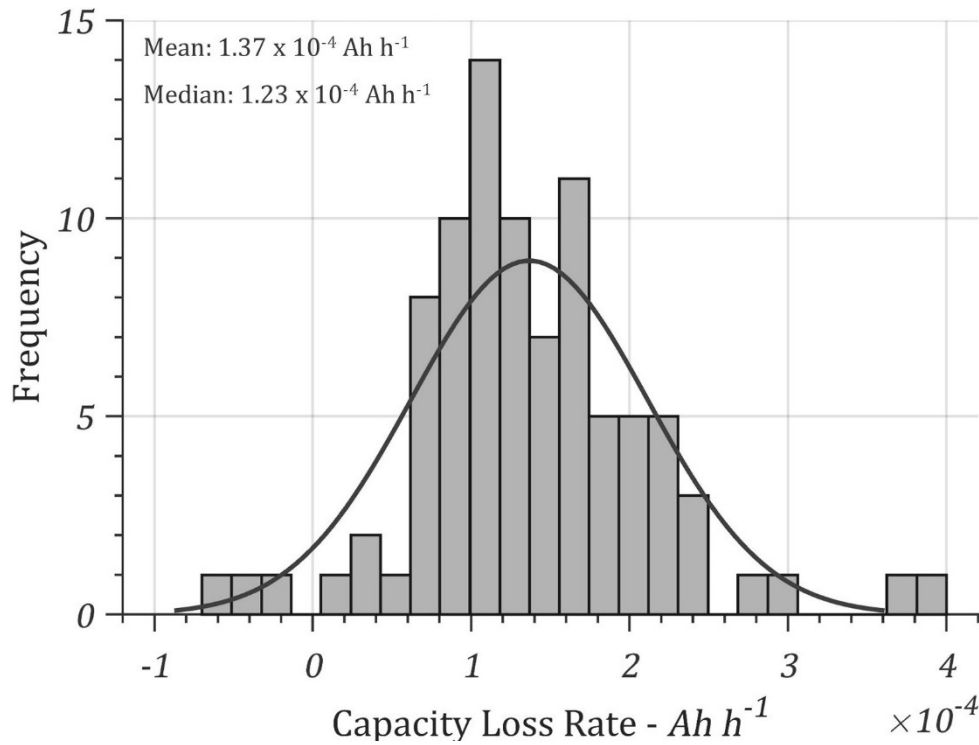


Figure 52: Histogram of the calendar ageing rates from all eight batteries and all inactive periods during the experiment.

Using the average calendar ageing rate shown in Figure 52, an estimate of the proportion of the capacity fade can be attributed to calendar ageing that occurred during the inactive periods. The total number of inactive hours was ~ 1530 hours (~ 63.5 days) throughout the duration of the test. This is approximately 1.5 times the duration shown in Figure 51 (b). This is because the times displayed in Figure 51 are only the times that the corresponding capacity change could be calculated.

This gives an estimated value of capacity lost due to calendar ageing of $\sim 0.2 \text{ Ah}$, which for the 1C discharges corresponds to about 40% of the total capacity fade ($\sim 0.5 \text{ Ah}$).

5.6.2. Capacity fade – 2C charge/discharge cycling

In Section 5.6.1, the 2C charge/discharge capacities were not used to estimate the calendar ageing despite having the capacity values before and after each period of inactivity. This section looks at the different features in the capacity fade curves for this data set and explains why it was not used. Figure 53 shows the capacity fade for the 2C discharges from the 2000 cycles. Figure 53 shows only the curve for the control battery. The plots for the other seven batteries are similar.

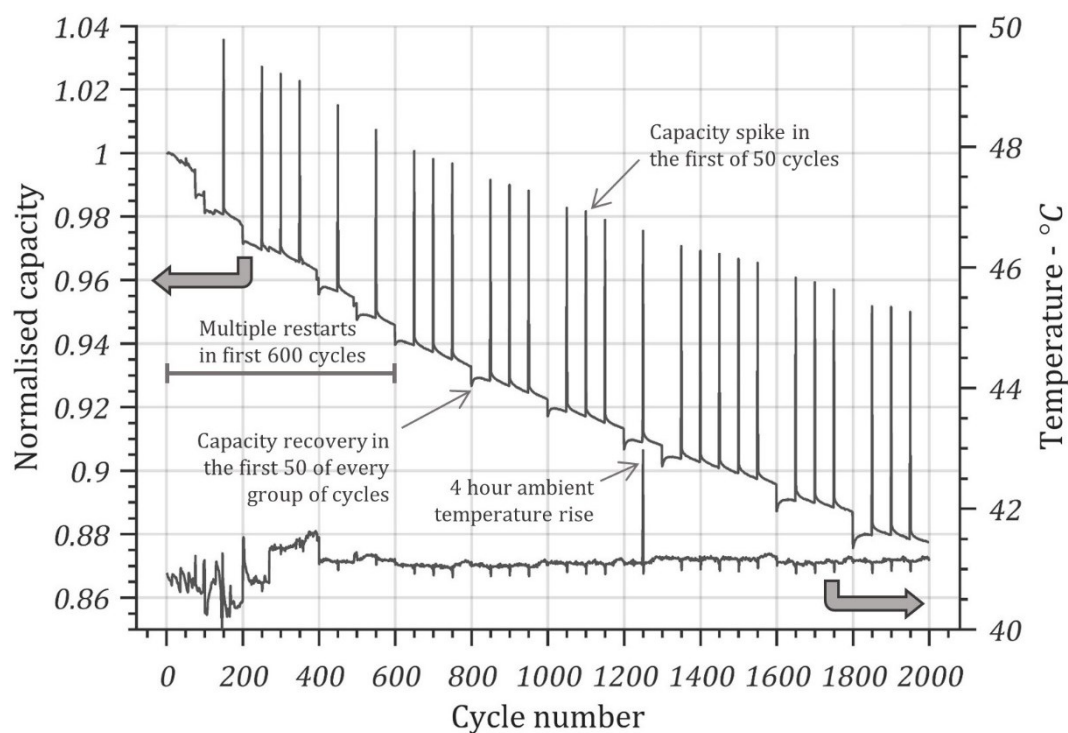


Figure 53: Normalised capacity (left axis) and mean temperature (right axis) for all 2C discharge cycles for the control battery. Key features such as capacity spikes and capacity recovery highlighted.

Figure 53 shows the mean temperature for each cycle along the bottom of the figure. The battery temperature fluctuated by ± 1 °C about the mean while discharging and charging. This shows the battery temperature was maintained within a band between 40 and 42 °C excluding the short temperature spike at ~1250 cycles. Here the ambient temperature in the thermal chamber rose to 45 °C for a short period before returning to 40 °C, for an unknown reason.

The spikes in capacity at the beginning of groups of 50 cycles are a result of the testing procedure. This first discharge is preceded by a CV hold at 4.2 V. The subsequent discharges follow immediately after a 2C charge with a cut off voltage of 4.2 V and no CV hold. After the initial large drop-off in discharge capacity, there is a slight capacity decay in the next 5-10 cycles before the capacity fade proceeds linearly. These features are highlighted in Figure 54 as points (c) and (b) respectively. Feature (a) is not a mathematical fit and is a representation of the linear capacity fade that each group of 50 cycles recovers/decays towards.

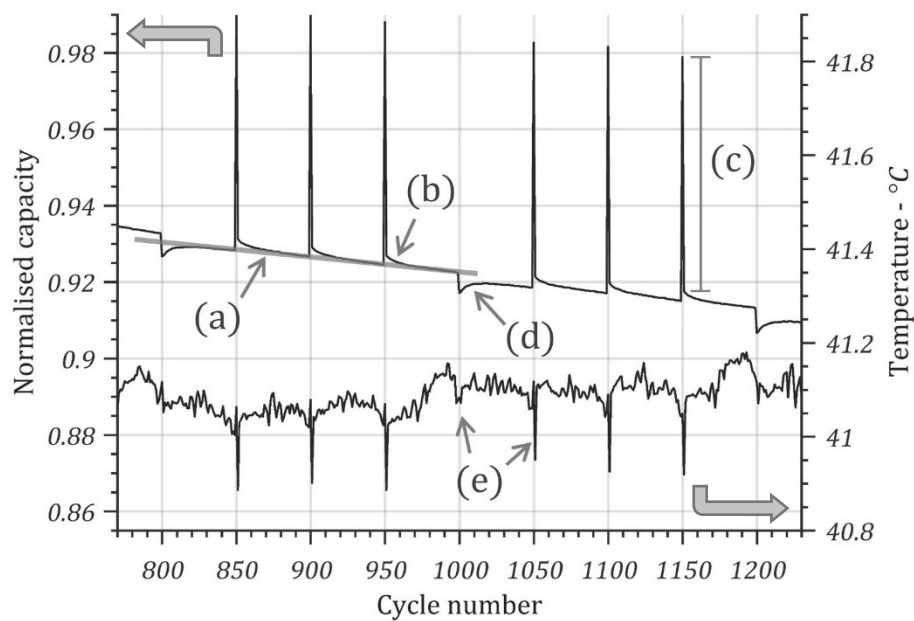


Figure 54: Normalised capacity (left axis) and mean temperature (right axis) for 2C discharge cycles 800 -1200 for the Control battery. Highlighted features described in body of the text.

Feature (d) shows the capacity recovery that occurs during the first 50 cycles of the group of 200. Unlike the other groups of 50, this group was not preceded by a CV hold at 4.2 V. Rather the battery was at 3.76 V (50% SOC) for a significant time period (> 2 days). Immediately prior to the start of the 2C cycles, the battery was charged at 2C to a voltage cut-off of 4.2 V. This is the cause of the first 50 in each group showing capacity recovery and the remaining three groups showing capacity decay. Feature (e) highlights that the temperature of the battery is

not significantly different during the beginning of the groups of 50 cycles, so these phenomena cannot be attributed to temperature effects.

The cause of these phenomena and the difference between them stems from the definition of the end of the cycles and the evolution of concentration gradients inside the electrodes. For the cycling, the limits are solely voltage cut-offs at 2.7 V and 4.2 V. The measured battery voltage is a function of the concentration of lithium at the electrode surfaces. The capacity recovery occurs as the concentration gradient inside the electrode changes during cycling. The change enables more lithium atoms to diffuse to the surface of the electrode and partake in the electrochemical process, prior to the surface concentrations reaching the point at which the voltage limit is triggered. The opposite effect occurs in the capacity decay, where the concentration gradient inside the electrode changes during cycling and effectively removes lithium from the electrochemical process.

After several charge/discharge cycles (~10), the battery reaches a state of dynamic equilibrium. The concentration gradient within the electrodes, at the ends of the charge/discharge, no longer changes between cycles.

Using the cycling capacities for estimating calendar ageing

The capacity recovery phenomena meant that the capacity change from immediately before and immediately after each period of inactivity could not be used to estimate the calendar ageing. This was because the batteries were in significantly different states, although the procedure was the same for both capacity measurements. Attempts were made to perform a line fit to the cycling data to estimate the capacity of the battery under dynamic equilibrium conditions. To generate a satisfactory fit equivalent to the line (a) in Figure 54, required manual exclusion of significant portions of the data sets (both from the capacity recovery and decay regions). At this point it was decided the fitting process had deteriorated to 'programmatically drawing a line of fit with a ruler'. Hence attempting to use the cycling data to estimate the calendar ageing was abandoned.

5.7 Impedance – Long-Term Compression

Throughout the long-term compression experiment, the battery impedance was measured using the impedance sweeps outlined in Section 4.5.1. This was performed during every characterisation, every 50 cycles. To analyse the data, three SOC points were examined. In the event of any noticeable trends, the remainder of the data was looked at. The three SOC points initially studied were at 20%, 50% and 80% SOC, termed Low, Mid and High, respectively. The High and Mid data sets were taken from the discharge impedance sweeps, the Low was taken from the charge impedance sweeps.

To confirm that the impedance data sets are comparable, temperature and capacity (SOC) tolerance bands were set to ensure the battery state was comparable. The following acceptability parameter ranges for temperature and SOC were applied, to reject any data sets that were not under comparable conditions:

Temperature acceptability limits

Any process which had a mean battery temperature outside of $40 \pm 1.5^{\circ}\text{C}$ was rejected.

SOC acceptability limits

Any process that had a charged passed value that deviated more than 1.5 standard deviations from the mean for all eight data sets (i.e. all batteries) was rejected.

For the different batteries, the change in four impedance values at the three different SOC were compared. The first of the four impedance values compared is the series resistance, taken from the x-axis intercept of the EIS curve. The remaining three impedances were taken from the 2C pulse data. The impedance was calculated using Equation (10), absolute values as applicable for charge and discharge.

$$Z_{pulse}(dt) = \frac{|dV|(dt)}{|di|} \quad (10)$$

Where:

$|dV|(dt)$ = Change in battery voltage from the start of the pulse, over time dt

$|di|$ = Difference in current magnitude between normal current and pulse current.

Figure 55 shows a schematic of a 2C pulse (10 A) over a 1C discharge (5 A). In the schematic are highlighted the values inputted into Equation (10) to calculate the Pulse impedance. The three time-differences used to calculate the pulse impedance at were 0.5, 1 and 5 seconds. The change of these four metrics as the batteries age are shown in Figure 56 - Figure 59 with plots (a) for the high SOC, (b) for mid SOC and (c) for low SOC.

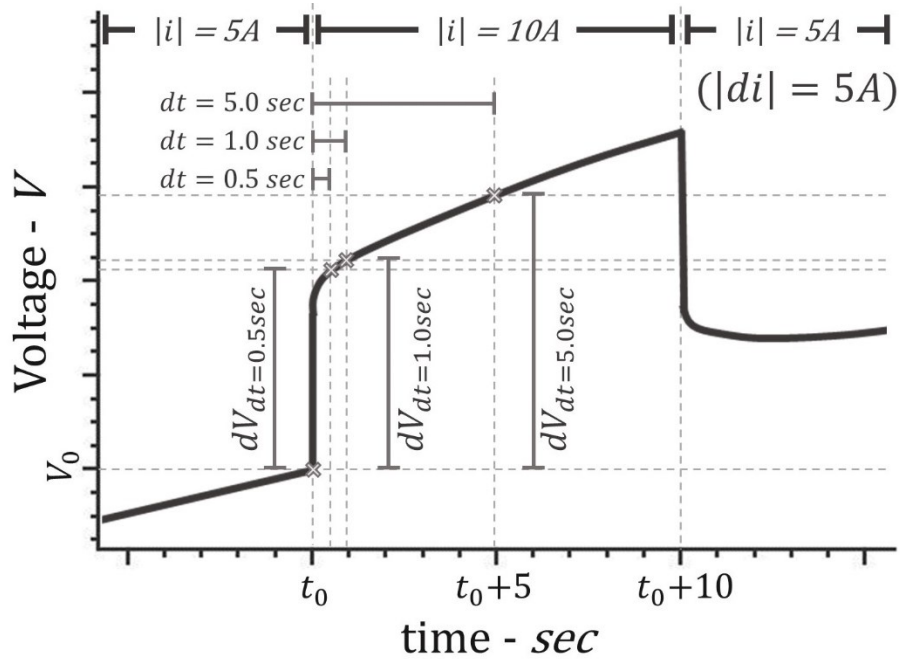


Figure 55: Schematic of a 2C pulse over a 1C charge. The three time-differences (relative to t_0) highlighted and the associate change in voltage.

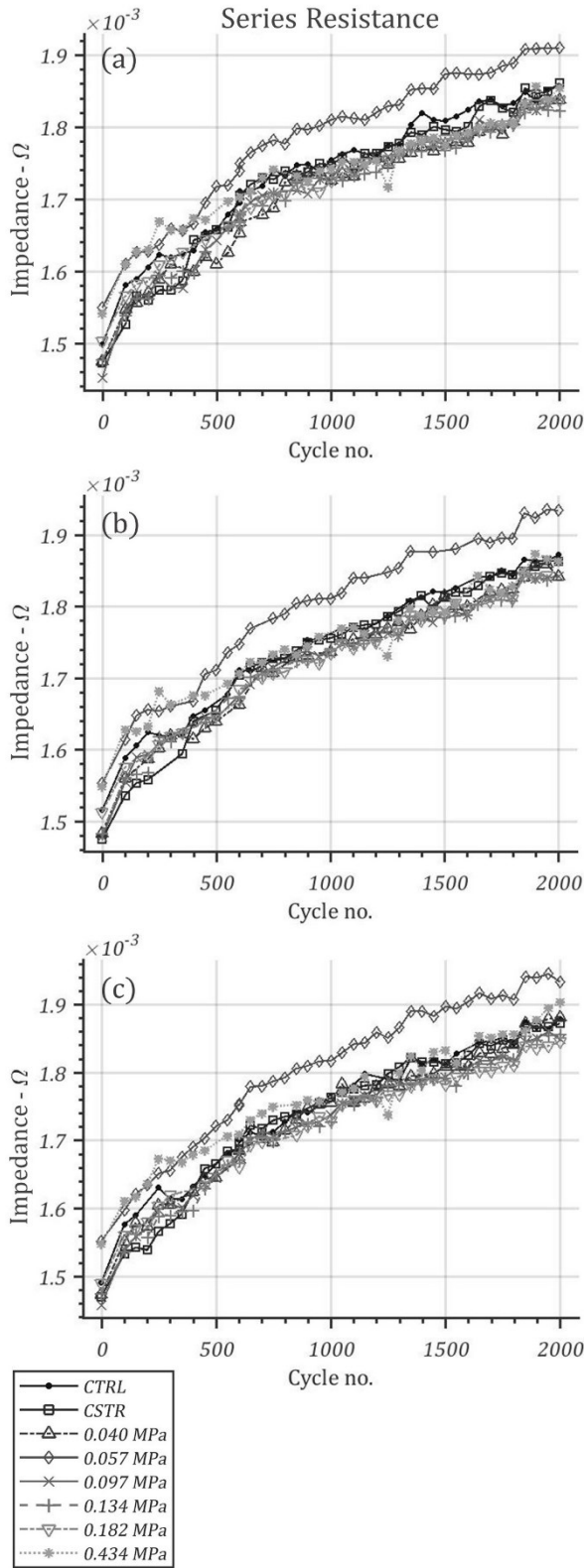


Figure 56: Series resistance change with cycling. (a) High SOC, 80%. (b) Mid SOC, 50%. (c) Low SOC, 20 %

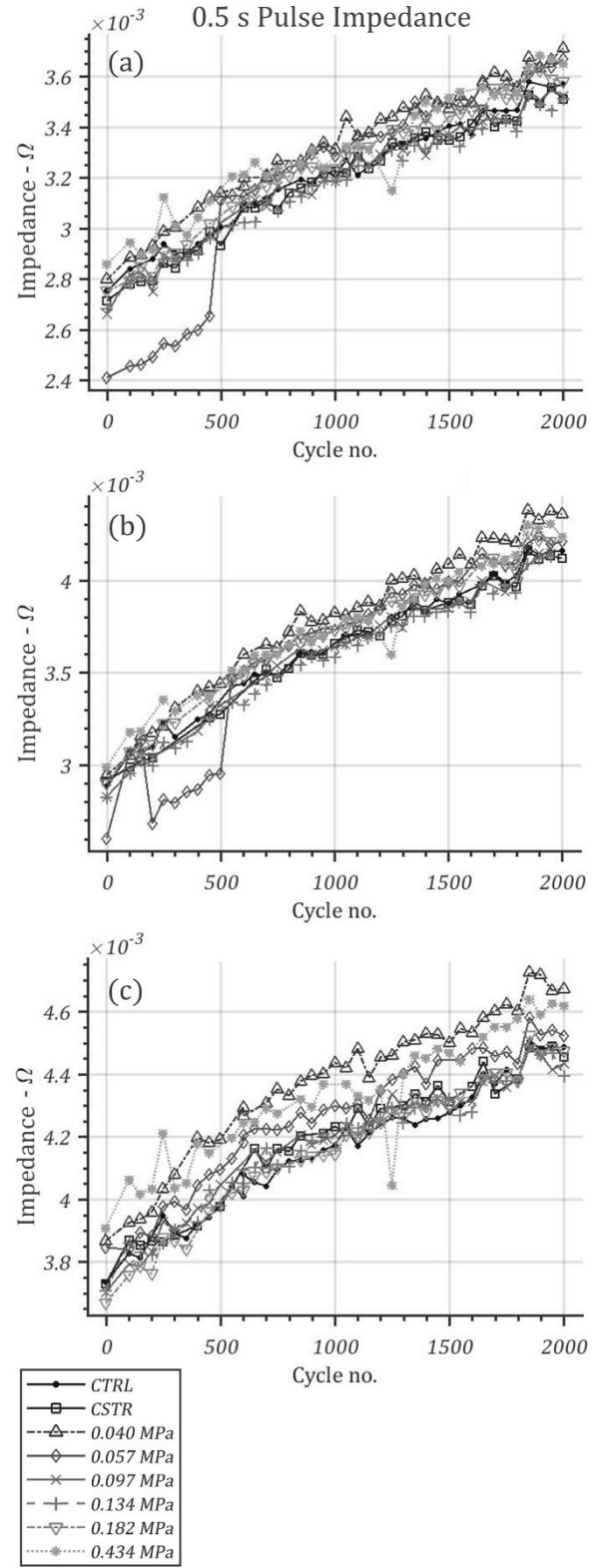


Figure 57: 0.5 Second pulse impedance change with cycling. (a) High SOC, 80%. (b) Mid SOC, 50%. (c) Low SOC, 20 %

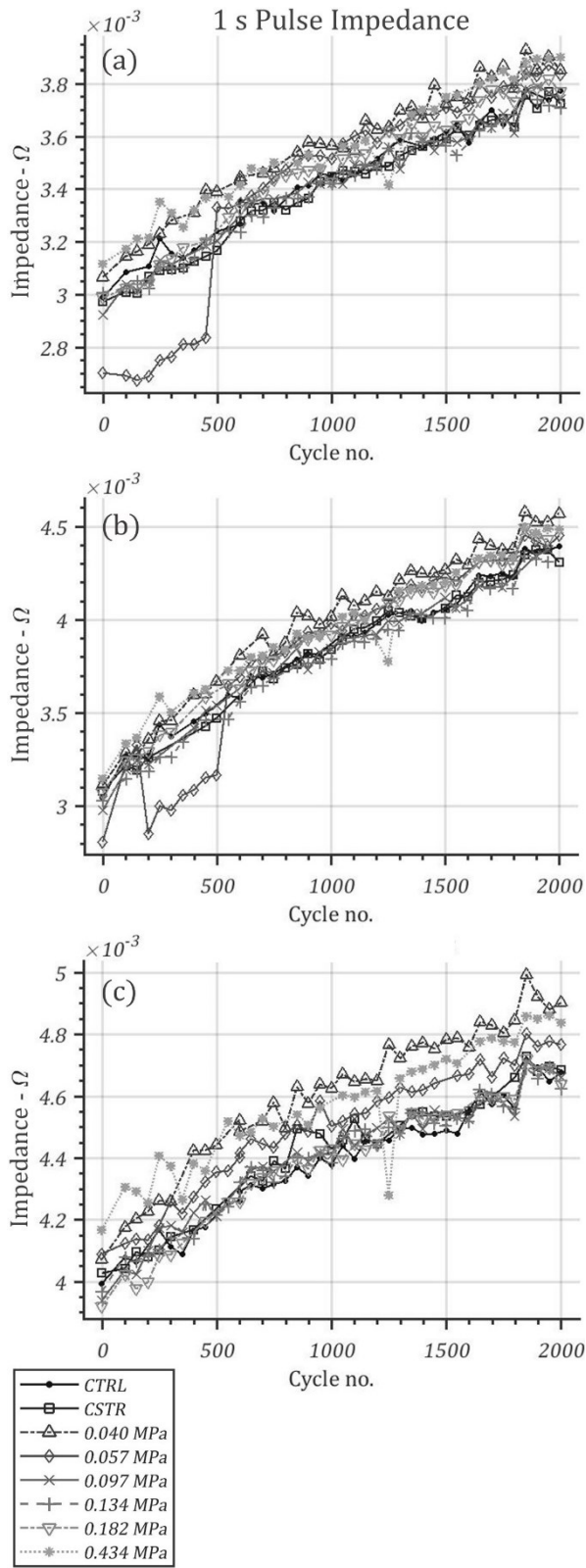


Figure 58: 1 Second pulse impedance change with cycling. (a) High SOC, 80%. (b) Mid SOC, 50%. (c) Low SOC, 20 %

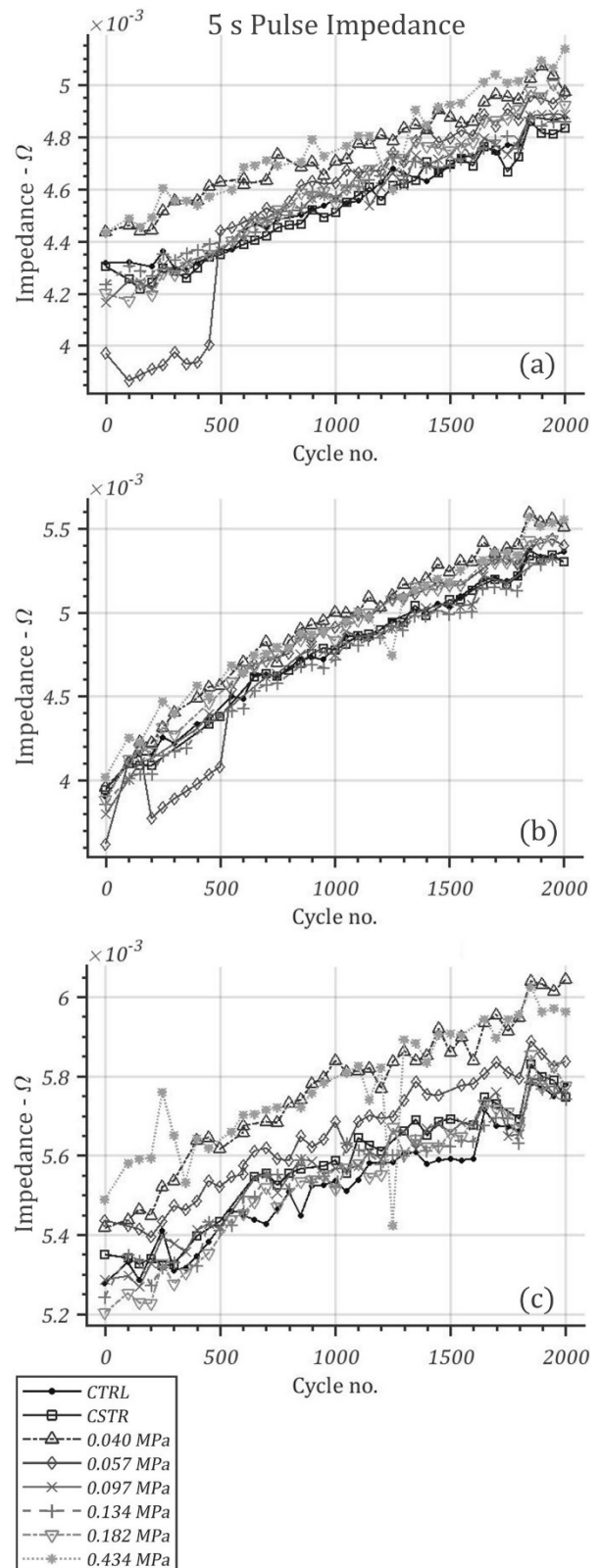


Figure 59: 5 Second pulse impedance change with cycling. (a) High SOC, 80%. (b) Mid SOC, 50%. (c) Low SOC, 20 %

Key features of Impedance in Figure 56 - Figure 59:

- For all four impedance measurement points, there is no significant trend relating the pressure to:
 - The impedance.
 - The rate at which the impedance increases.
- The series resistance for the battery compressed to 0.057 MPa follows the same increasing path as the other batteries but has a larger magnitude. This is considered to be specific to that battery, and not due to it being the greatest compression.
- Although less distinct than in the Capacity Fade Plots in Section 5.5, the impedance does show the same steps in profile. This confirms the importance of calendar ageing, that occurs between the groups of cycles.
- The battery compressed to 0.057 MPa shows lower pulse impedances for the High and Mid SOC, during the first 500 cycles. At cycle 550 the pulse impedances rise to become similar to the other batteries.

The lower pulse impedances for the 0.057 MPa battery are considered to be experimental error rather than a true difference in the impedance. The reasons for this are:

- The difference only appears in the discharge pulse data sets. The high SOC and mid SOC data sets were gathered on the same discharge using the same looped 'bio-logic testing technique'. The Series resistance and the Low SOC data sets were gathered separately and do not show the difference.
- The difference occurred during the first 600 cycles, at around this time the battery cycler software was updated (discussed in Section 5.3.5). Beyond this point the battery impedance follows the trend of all the others.
- An investigation into the pulse impedance at ~50% from the charge 'impedance sweep' showed no difference between the battery at 0.057 MPa and the rest of the batteries.

Impedance Conclusion

From studying the three points in the SOC window (20%, 50% and 80%), it is concluded that the impedances of the eight batteries are not significantly different. The change in the battery impedance with cycling does not vary with compression magnitude. This confirms the similar conclusion made from the capacity fade data. With there being no significant difference between the batteries, the remainder of the impedance data was not processed, and it is assumed to show similar results.

The changes in the battery impedance show the same stepped profile that was seen in the capacity fade data sets. This confirms that the periods of inactivity between cycling introduced significant calendar ageing, that manifested itself as increased battery impedance.

5.8 Incremental Capacity Analysis – Long-Term Compression

To perform ICA on the long-term compression experiment results, the 0.1C charge data sets were used. These were chosen because they were complete data sets and these processes were isothermal (discussed in Section 5.5.1). Two of the 0.1C discharge data sets displayed experimental error. This analysis was performed to confirm that although the ageing pathway for all of the batteries was the same, it was not affected by the different levels of compression.

The smoothing and differentiation method performed on the data is discussed in detail in Section 4.1, a brief overview is described here. Prior to differentiation, the raw data was smoothed using a 3rd order S-Golay filter. In total 104 data sets were smoothed across the eight batteries. Five data sets were selected at random and used for tuning the smoothing parameters of window-size and number of iterations. Residual analysis, described in Section 4.1, was used as feedback in tuning the smoothing parameters. Once the parameter tuning was complete, all data sets were smoothed using these parameters and then differentiated. The smoothing quality of the remainder of the data sets was assessed by inspection of the residuals. One in four data sets was randomly selected for checking. The numerical differentiation was performed by fitting a 1st order line to a small window and taking the gradient of the line as the differential. The smoothing and differential parameters used are shown in Table 19. The S-Golay procedure was implemented using the Smooth Function in MATLAB. The least squares line fitting was implemented using the Fit function in MATLAB. (105). All points evaluated were central in the window.

Table 19: Smoothing and differentiation parameters used to generate ICA curves

Parameter	Value
Smoothing Filter	Savitzky-Golay – 3 rd order
Smoothing Window Size	2.0% of the data length (~700 data points)
Smoothing Iterations	2
Differentiation Window Size	0.1% of the data length (~35 data points)

The changes in the ICA curves for all eight batteries can be seen in Figure 60 (a) – (h). These plots show no significant differences between the different batteries. This is further confirmation that the different levels of compression did not have a significant impact on the degradation of the batteries.

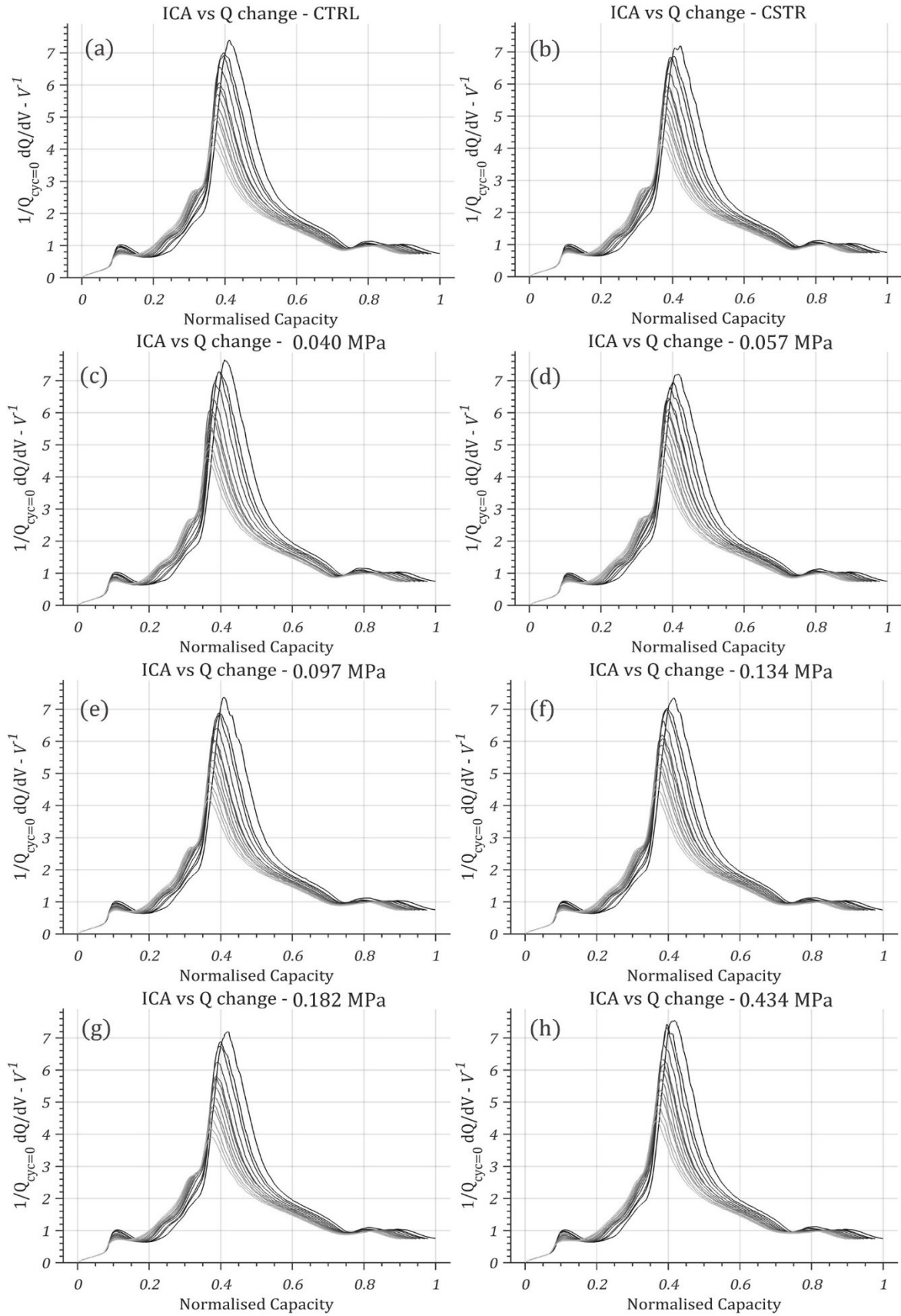


Figure 60: ICA curves for all eight batteries. Plots (a) – (h) for all eight pressure magnitudes: (a) Ctrl, (b) Constrained, (c) 0.040 MPa, (d) 0.057 MPa, (e) 0.097 MPa, (f) 0.134 MPa, (g) 0.182 MPa, (h) 0.434 MPa. Dark to light represents the battery ageing every 200 cycles over a total of 2000 cycles.

5.9 Electrochemical Conclusion – Long-Term Compression

The first key conclusion to the electrochemical results from the long-term compression experiment is:

For a stacked electrode battery, the pressure range of 0 to 0.43 MPa has no significant impact on the battery ageing.

This conclusion is consistently shown in:

- The capacity fade plots - at three different C-rates,
- The battery impedance - at three states of charge,
- The ICA curves - from 0.1C charges.

This conclusion is in direct contradiction to results in the literature (2). These differences can be attributed to differences in the electrode configuration of the batteries tested. The compression applied to the obround electrode batteries tested in the literature was concentrated in the folds in the electrodes. This induced inhomogeneities inside the battery and periodic, visible mechanical deterioration of the electrodes that significantly affected the ageing of the battery. The compression, when applied to a stacked electrode battery, is uniformly distributed across the electrode area and is always normal to it. The magnitude of the compression used here is insufficient to impact on the electrochemical performance of the battery. Nor does it cause mechanical deterioration of the electrodes.

This leads to the second key conclusion from this experiment:

The electrode configuration of the battery has a significant impact on the compression tolerance of the battery. A stacked electrode battery can be compressed to a larger magnitude without deterioration in performance, compared to an obround electrode battery.

The results from this experiment showed several features attributed to the experimental procedure employed. The most noticeable is calendar ageing, that occurred during inactive periods between groups of cycles. The batteries were cycled 2000 times in groups of 200 while maintained at 40 °C. Both the capacity fade and impedance data showed a stepped profile, that resulted from calendar ageing. This calendar ageing occurred in addition to the cycling ageing inherent to the experiment. The capacity drops over the inactive periods were estimated and then divided by their time. This gave the calendar ageing rates. The calendar ageing rates of all the batteries were found to be normally distributed. The mean value from the Gaussian distribution was used to estimate that approximately 40% of the total capacity fade that occurred in the batteries was due to the calendar ageing. Calendar ageing was experienced during the inactive periods.

After having rested at 50% SOC, the capacity for the 2C discharges generated from cycling the battery showed significant capacity recovery, that occurred in the first few cycles. This took 15 – 20 charge/discharge cycles to establish a dynamic equilibrium. It is theorised that this phenomenon results from the charge/discharge limits being set on a voltage cut-off, with no CV hold. Under these conditions, there are several cycles where the concentration gradient within the electrode changes from cycle to cycle. This changes the amount of lithium accessible from cycle to cycle, causing the capacity to increase. At some point, the concentration gradient reaches a dynamic equilibrium and stops changing from cycle to cycle. The capacity then changes linearly from this time onwards. The same phenomena occur when the 2C cycling is initiated after a CV hold at 4.2 V, but then there is capacity decay rather than recovery.

6. Long-Term Compression Degradation - Mechanical

Credit to Mr Ian Campbell for his contribution to the work presented in Chapters 5 and 6. Including: Initial experimental design and scope definition, force sensor specification and verification testing and programming of the force sensor data logging software.

Chapter 5 covered the long-term compression experiment and the electrochemical results from it. This chapter reports the mechanical aspects of the experiment, namely:

- The measurements that were taken.
- How they were taken.
- The mechanical results.

The long-term compression experiment cycled eight Li-ion batteries 2000 times, at different compression magnitudes, under fixed displacement conditions. The batteries tested were 5 Ah Kokam power batteries, with a stacked electrode configuration. Reasons why the fixed displacement configuration was chosen are given in Section 5.2. Under this configuration, the magnitude of the compression was measured, and the thickness (displacement) of the battery was assumed to be constant throughout the experiment. The first part of this chapter looks in detail at the pressure (force) measurements and the validity of the fixed displacement assumption.

The mechanical results first look at how the battery pressure changed during cycling by tracking the maximum, minimum and mean pressures of the 2000 2C cycles. This is followed by looking at the changes in the ‘resting pressure’ of the battery, not only during cycling but also throughout the set-up of the experiment. These results lead into the discussion of defining the mechanical state of batteries when compressed. This chapter concludes by introducing the pressure hysteresis that occurs during cycling and how compression has changed the volumetric energy density of the batteries tested.

6.1 Pressure Measurement – Method and Error

This section introduces the compression jigs and how the pressure (force) magnitude was measured. Following this, the error in the measurements is quantified and the choice of sensors that were used is justified. The section concludes with a discussion of the errors and the limitation they put on the interpretation of the pressure results.

Figure 61 shows a CAD rendering of the compression jigs, showing the button load-cells located between the base and floating plates.

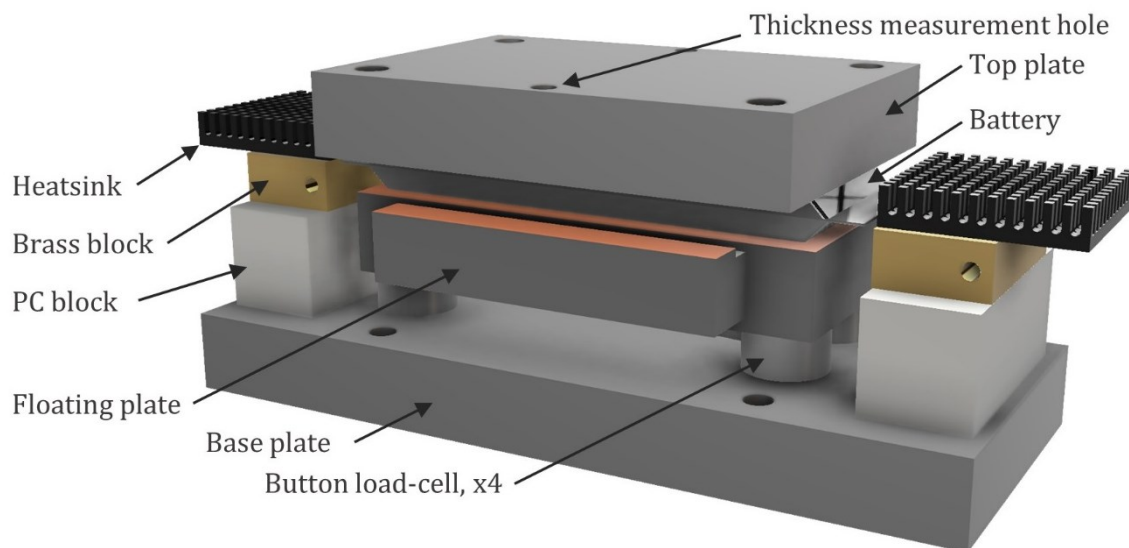


Figure 61: CAD rendering of battery compression rig used in the long term compression experiments. Key components labelled. Four bolts (not shown) are placed through each corner of the top plate and are threaded into the base plate. Note the thickness measurement holes in the top plate. This CAD rendering was generated in collaboration with Mr I. Campbell.

6.1.1. Load-cell type, quantity and error

Button type load-cells were used for taking the force measurements. These small (20mm diameter x 10 mm cylinders) were small enough to fit in a compact compression jig. This

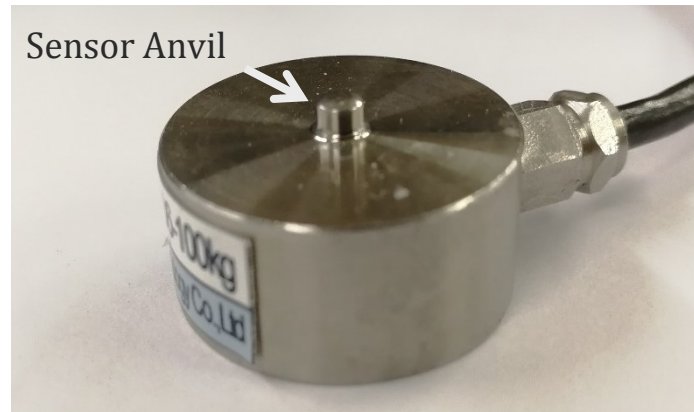


Figure 62: HTC-TAS606 button load-cell (107). 20 mm DIA. Sensor anvil highlighted by annotation.

enables multiple rigs to be fitted into the same thermal chamber. An example of one of the load-cells that were used is shown in Figure 62. These sensors use a Wheatstone-bridge strain gauge configuration, to measure very small displacements in the sensor anvil. These correspond to an equivalent force.

A total of four sensors was chosen, for two reasons:

- To limit the degrees of freedom of the float plate. The sensor anvil acts a pivot point for the float plate. One or two load sensors would allow the float plate to pivot about a single point or line, respectively. This would enable non-uniform expansion of the battery. Potentially, current inhomogeneities could occur and different regions of the battery then expand at different rates.
- Four sensors enable the uniformity of the pressure to be monitored throughout the duration of the experiment.

Load cell Full Scale Range (FSR)

The FSR of the load cell is the maximum force that can be measured by the sensor. This value is important as it limits not only the force range but also affects the error of the force

measurements, because the sensor error is proportional to the FSR. In these experiments, the magnitude of the force that the sensors would be measuring at the end of the experiment was unknown. This is due to the battery expanding as it ages, as seen by Cannarella and Arnold (2).

Cannarella and Arnold results were used as a guide to set the minimum FSR for each rig. The ‘Low’ battery in their work reached a maximum compression of 0.5 MPa. A 1.3 safety factor was applied to this to give the minimum FSR. Converting this pressure value into the force applied to the Kokam battery tested here, gives a total compressive force of 3000 N, resulting in 750 N per load-cell. Commercial button load-cells having an FRS equal or greater than 750 N were 1 kN load-cells. The batteries tested at a higher initial pressure required load-cells with a larger FSR. The load-cells used for each battery are given in Table 20.

Table 20: Button load-cell specification for each compression jig.

Initial Pressure	No. of load-cells	Load-cell FSR	Error	Load-cell model/manufacture
0.022 MPa (CSTR)	4	1 kN (250 lbs)	± 6 N (0.6 %FSR)	S400/SMD sensor (106)
0.043 MPa	4	1 kN (250 lbs)		
0.065 MPa	4	1 kN (250 lbs)		
0.13 MPa	4	1 kN (100 kg)	± 9 N (0.9 %FSR)	TAS606/htc-sensor (107)
0.20 MPa	4	1 kN (100 kg)		
0.26 MPa	4	2 kN (200 kg)	± 18 N (0.9 %FSR)	
0.65 MPa	4	2 kN (200 kg)		

Large FSR for the initial compression

The ratio of FSR to measurement magnitude is the most important variable when considering the measurement error. The load-cell error is proportional to the FSR and thus, small measurements compared to the FSR will have a proportionally much larger error. The load-cells in Table 20 were chosen based on the estimated high pressure that might be reached at the end of experiments. This limits the accuracy of the force measurements at the beginning of the experiment, because the forces being measured then are small compared to the FSR. For this reason, load cells with the smaller error from SMD were chosen for the three batteries with the lowest initial pressures.

The pressure data from the ageing battery was considered to be more valuable than the absolute accuracy of measurements at the beginning of the experiment.

Force measurement error

Calculating the error in the force measurements from the data sheet was not a trivial task, as the experiment was a complex application for the load-cells. The major complexities were:

- Unknown and varying region of the FSR (Nonlinearity error)
- Force Cycling (Hysteresis)
- Creep

Thus, calibration curves were used to estimate the error in the force measurements. This method had the advantage of accounting for further sources of uncertainty, apart from those in the sensor hardware, within the force measurement:

- Error introduced by the sensing equipment.
- Operating temperature.

The load-cells were calibrated using an Instron tensile testing machine (4466 Universal Testing System) at 40 °C with four force sweeps from 0N to the FSR and four sweeps from the FSR to 0N. From this the straight-line fit was calculated as the calibration curve. The residuals from

these fits were used to estimate the error in the force measurements. The estimated errors in the force measurements were: ± 6 N in the SMD sensors, ± 9 N in the 1 kN HTC sensors and ± 18 N in the 2kN HTC sensors, as shown in Table 20.

This error estimate does not include the effects of creep in the load-cells. It was decided that quantifying the effect of creep on the force measurements would not be possible without disrupting the experiment. So, it was accepted that load cell creep was an unquantified source of error, to be considered during analysis of the results.

Non-linear load-cell response

For most of the load-cells' range, the output signal will be linearly proportional to the force applied. When the force applied to the sensor drops below $\sim 5\%$ FSR, the linear relationship breaks down and the calibration curve is no longer valid. During this experiment some of the batteries will be under little to no compression, when the battery has contracted at low SOC. Thus, the error within these regions will be large.

6.1.2. Pseudo fixed displacement constraint

The constraint on the batteries is described as fixed-displacement. This means that once the initial compression had been applied, the thickness of the battery remained constant for the duration of the experiment. To achieve this, the bolts were prevented from loosening by the application of thread lock. In theory constant thickness might be assumed. In reality the thickness of the battery will have changed during the experiment due to:

- Compliance in the compression rig.
- Deflections in the load-cells

The compliance in the compression rig was minimised by using 20 mm thick aluminium plates.

The tensioning bolts were specified appropriately. For the 0.182 MPa and 0.434 MPa rigs M12 bolts were used, and for all other rigs M8 bolts were used.

The small deflections in the load-cells were unavoidable, as the sensor measures the force from the strain that results from these small defections. To understand the magnitude of the deflections with respect to the thickness changes in the battery during cycling, the anvil deflection was measured for the FSR of all load-cells. The displacements of the load-cell anvils at 100% FSR for the three different load-cell models are shown in Table 21.

Table 21: Load-cell anvil displacement

Load-cell model	FSR	Sample size	Mean anvil displacement at 100% FSR ($\pm$ SD) / mm	Maximum proportion of FSR used
S400/SMD sensor	1 kN	12	0.042 ($\pm$ 0.009) mm	33 %
TAS606/htc-sensor	1 kN	8	0.082 ($\pm$ 0.018) mm	46%
	2 kN	8	0.078 ($\pm$ 0.016) mm	48%

The load cell compliance measurements were taken from the load cell calibration data sets. The Instron tensile testing machine not only outputted the force measurement but also the crosshead displacement data sets. The crosshead displacements have been corrected for machine compliance.

The experiments in Section 4.6 showed that the magnitude of the thickness change in the batteries during cycling is ~ 0.18 mm. The anvil displacements in the load-cells are comparable to the battery thickness change. The full FSR of the load-cells was not used during the experiment. The fifth column in Table 21 shows the maximum proportion of the FSR used for each load-cell type. Assuming a linear force-displacement relationship for the load-cells, the largest load-cell anvil displacement that occurred during the experiment was 0.046 mm. This corresponds to 25% of the thickness change of the battery that occurred during cycling.

Battery Thickness Measurement Method

Thickness measurements were taken to enable a comparison of the battery thickness at the different pressures. To measure the thickness of the batteries during the experiment, the compression jigs were designed with two measurement points. These can be seen in Figure 61 and are two holes drilled into the top plate, one on each side of the battery. The depth gauge of digital callipers (accuracy of 0.02 mm) was used to measure the distance between the top of the floating plate and the top of the top plate. Six measurements (three on each side) were taken during each battery thickness measurement. From these measurements, the thickness of the top plate was subtracted, to find the battery thickness. The top plate thickness was measured using a manual micrometer with an accuracy of 0.02mm. These measurements were repeated six times, with the mean of these measurements being taken.

Thickness measurements were taken between each group of 200 cycles. The battery voltage was recorded with each measurement, 3.76V (nominal 50% SOC). To physically take the measurements, the compression rigs had to be removed from the thermal chamber. The time taken to perform the measurements was short enough that insufficient temperature change occurred to have affected the thickness measurements.

6.2 Constrained Degradation – Mechanical Results

The mechanical results are broken down into 5 sections:

1. Changes in the maximum, minimum and mean pressure during the 2C cycling.
2. Resting pressure changes throughout the experiment.
3. Defining the mechanical state of Li-ion batteries.
4. Pressure hysteresis during cycling.
5. Battery thickness during the experiment.

6.3 Minimum-Mean-Maximum Pressure Changes

To track the mechanical changes in the batteries as they degrade, the minimum, maximum and mean pressures that occur during each of the 2000 2C-cycles are plotted in Figure 63 - Figure 65. Figure 63 and Figure 64 show the plots for the batteries compressed up to 0.182 MPa. with Figure 65 being a larger plot of the results from the 0.434 MPa battery. The maximum pressures occur at 100% SOC and the minimum at 0% SOC.

The 5% FSR horizontal line in each figure is the pressure equivalent to 5% of the FSR of the load-cells in that testing rig. As discussed in Section 6.1.1, below 5% of the FSR the Force-Output signal relationship for the load cell becomes non-linear. Hence values below the line will have a large associated error. In Figure 63 and Figure 64 a large proportion of the pressure data is below this value in all six plots. Thus, limited conclusions discussing general trends will be drawn from these data sets, because of this large associated error.

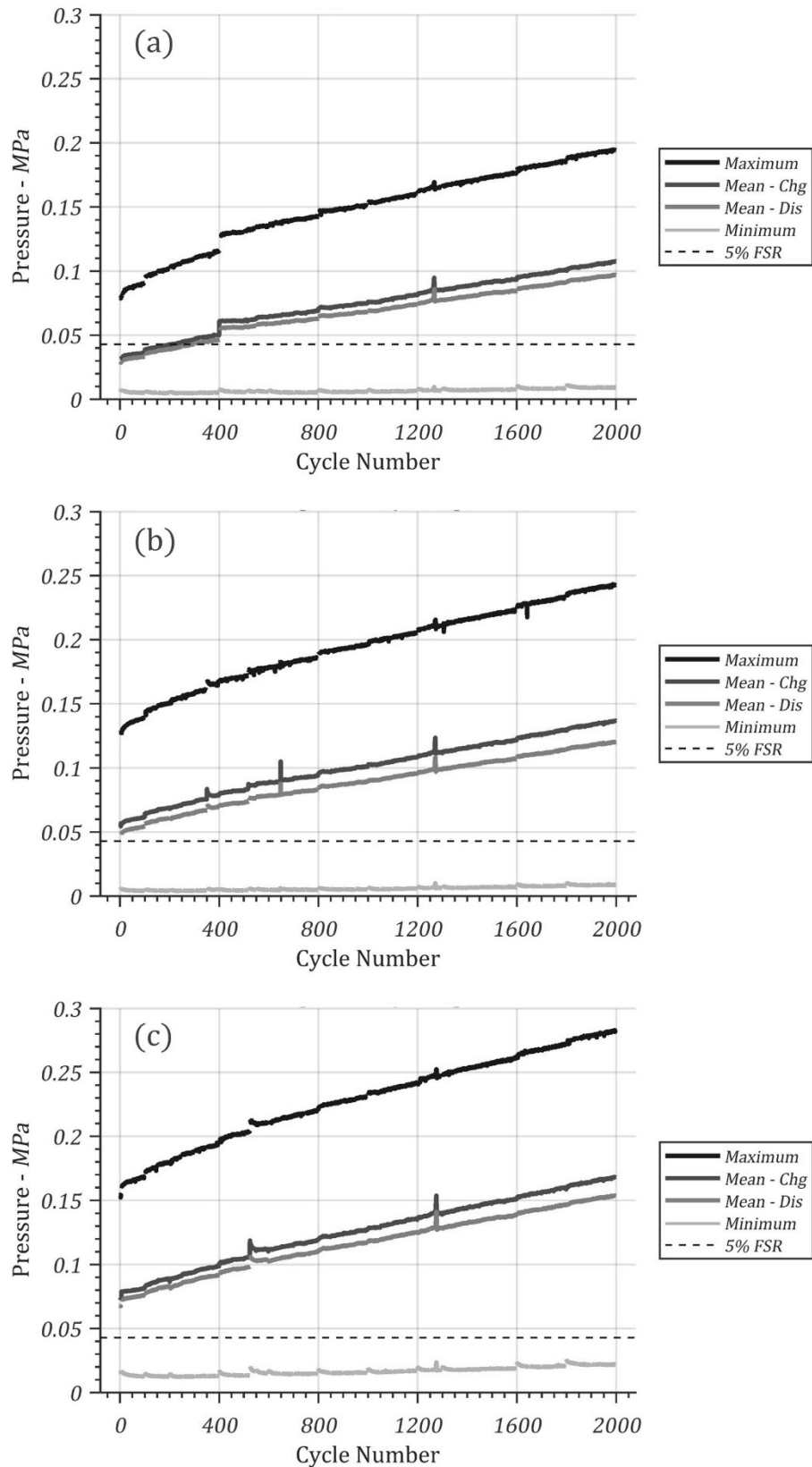


Figure 63: Minimum, maximum and mean pressures from all 2C cycles (CSTR, 0.040 MPa, 0.056 MPa). Maximum occurs at 100% SOC, minimum at 0% SOC. (a) Constrained [0.019 MPa], (b) 0.04 MPa, (c) 0.056 MPa. Horizontal line at 0.043 MPa represents 5% of the FRS of the load-cells. Below this line the data has a large associated error.

Key features of Figure 63:

- The batteries show a net increase in pressure as the batteries age, with the maximum and the mean pressures increasing.
- Visual inspection of the shape of the cycling data shows that the battery was always completely unloaded at low states of charge. This is due to the initial compression magnitude, applied at 50% SOC, being so small that thickness reduction in the battery as it is discharged completely relieves the compression. Figure 63 (c) shows the minimum pressure values above zero but this is a manifestation of the large error within this region of the sensor range.
- The maximum pressure values reached by the batteries show a similar trend. An initial higher rate of pressure rise per cycle occurred until approximately 400 cycles. Beyond 400 cycles the maximum pressure in each cycle increases linearly.

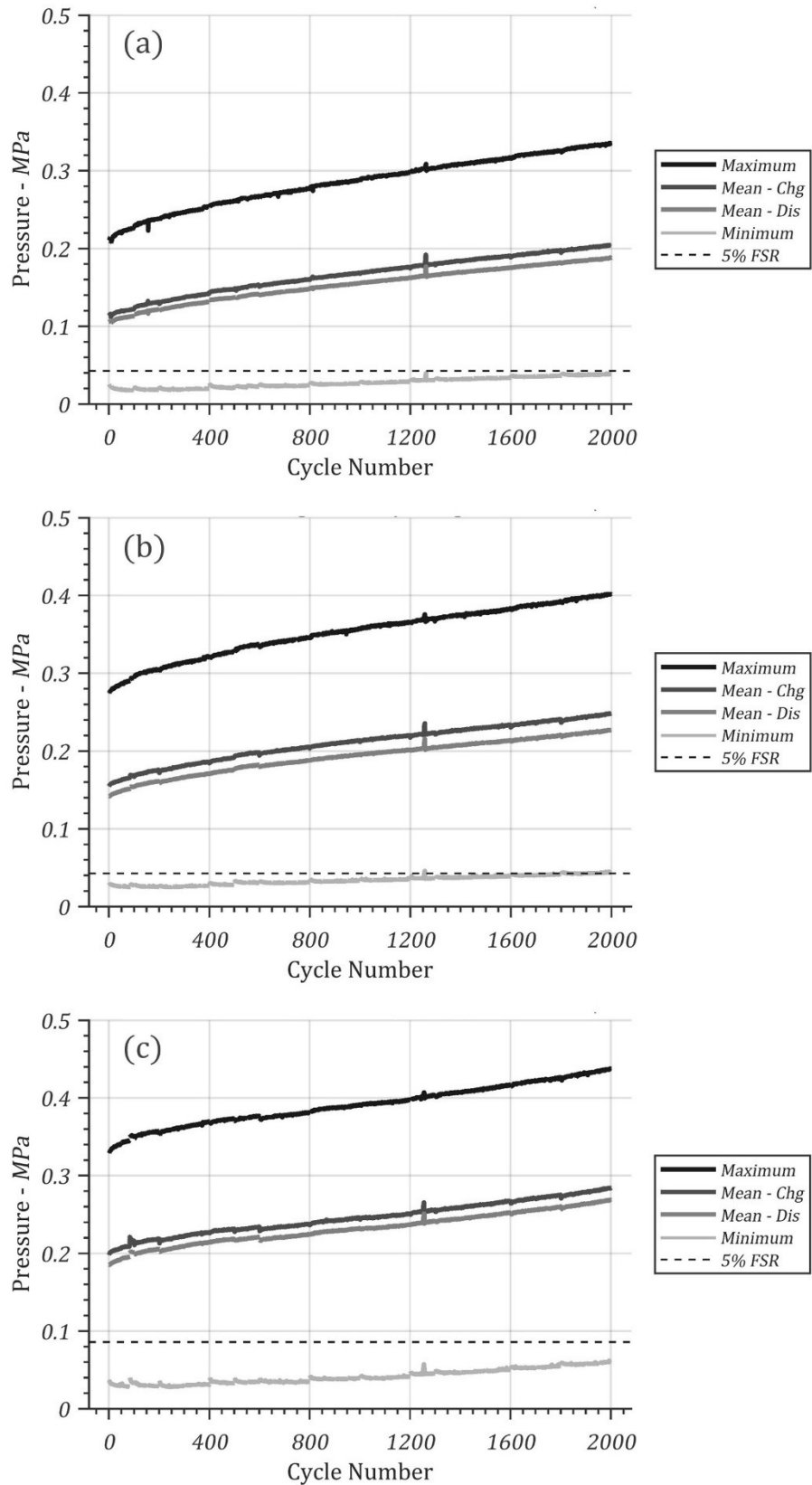


Figure 64: Minimum, maximum and mean pressures from all 2C cycles (0.097 MPa, 0.134 MPa, 0.182 MPa). Maximum occurs at 100% SOC, minimum at 0% SOC (a) 0.097 MPa (b) 0.134 MPa, (c) 0.182 MPa. Horizontal line at 0.043 MPa [0.086 MPa in (c)] represents 5% of the FRS of the load-cells. Below this line the data has a large associated error

Key features of Figure 64:

- The batteries show the same trend in pressure change as the batteries in Figure 63, with a gradual increase in the maximum and mean pressures.
- With the higher initial pressures, the batteries in Figure 64 are not always uncompressed at 0% SOC. For the 0.097 MPa battery, after approximately 600 cycles of being uncompressed at 0% SOC, the batteries are under compression throughout the whole cycle. The 0.134 MPa and 0.182 MPa batteries are never fully uncompressed.
- The maximum values show the same trend as in Figure 63, with an initial higher rate of pressure increase followed by a linear increase after approximately 400 cycles.

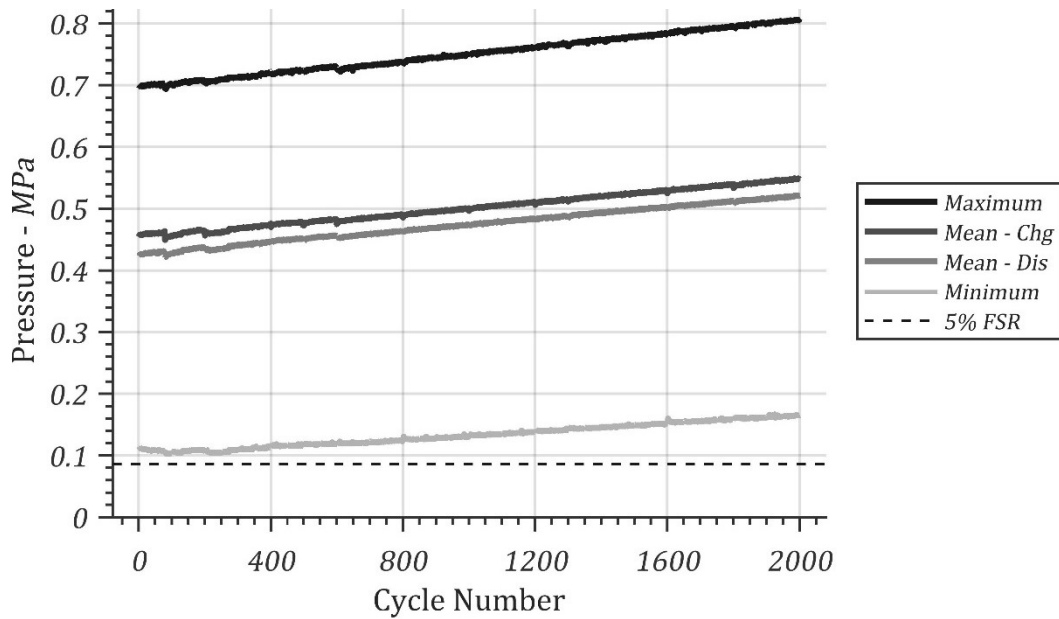


Figure 65: Minimum, maximum and mean pressures from all 2C cycles for the battery compressed to 0.434 MPa. Maximum occurs at 100% SOC, minimum at 0% SOC. Horizontal line at 0.086 MPa represents 5% of the FRS of the load-cells. Below this line data has a large associated error

Key features of Figure 65:

- The battery in Figure 65 was compressed to a nominal pressure of 0.434 MPa. This was the only battery test where all the pressure data measured occurred above 5% of the FSR of the load-cells.
- There is a linear increase in the pressure magnitudes as the battery ages for all four parameters, so all the pressure data is accurate.
- There is a slight divergence between the minimum and maximum pressure that the battery reached during cycling, as the battery ages (increasing from 0.59 MPa at 0 cycles to 0.65 MPa at 2000 cycles).
- The mean pressure during charge is higher than that of the discharge and the difference between the two is constant. This is discussed in Section 6.6, covering the pressure hysteresis that occurred during the experiment.

6.3.1. Minimum-mean-maximum pressure change – discussion

The changes in the minimum, mean and maximum pressure during the 2C cycles are consistent with the results in the literature (2) where batteries were compressed to a similar magnitude. A linear increase in the mean pressure and a gradual increase in the difference between the minimum and maximum pressures for a given charge/discharge are seen. The maximum pressure occurs at 100 % SOC and the minimum pressure occurs at 0 % SOC, as expected. It is agreed with that the gradual pressure increase is due to irreversible volumetric expansion of the electrodes resulting from SEI layer growth and cycling induced structural changes, as stated in the literature (2).

The magnitudes of the pressures on the batteries are lower than expected, so the load-cells had a significantly higher FSR than was required. This resulted in a large proportion of the pressure data being gathered within the non-linear portion of load-cells' output. Thus, most of the pressure data cannot be used directly for detailed analysis of the changes in pressure during individual cycles. The data set for the battery compressed to 0.434 MPa is the exception, as it was always under more than 5% FSR. For a more detailed analysis of the pressure changes from this experiment, only the 0.434 MPa battery data will be used.

6.4 Resting Pressure

The values of the minimum, mean and maximum pressures in a cycle provide a good understanding of how the pressure varies over the full SOC window. They cannot however be used to compare the pressure change to the initial pressure applied to the battery because there were no equivalent data points for the battery pressure prior to the 2C cycling commencing. Battery pressure changed from the initial pressure throughout the entirety of the experiment, including the two initial characterisations (outlined in procedure in section 5.3.3). Thus, to investigate this, the battery pressure during the periods of inactivity between electrochemical processes, was used. These 'Resting pressure' measurements are shown in Figure 66 and Figure 67. The larger plot, Figure 66, shows the resting pressure for the 0.434 MPa battery, with the remaining six battery data sets shown in Figure 67 (a)-(f). The salient features highlighted in Figure 66 are applicable to Figure 67 (a)-(f). The following features of these figures are of note:

Battery conditions

Both the temperature and the SOC of the battery significantly affect the pressure. Hence all data points in Figure 66 and Figure 67 are taken at the following temperatures and the fixed terminal voltage:

- $40\text{ }^{\circ}\text{C} \pm 1.5\text{ }^{\circ}\text{C}$ (or $25 \pm 1.5\text{ }^{\circ}\text{C}$ for the first three data points)
- $3.760\text{ V} \pm 0.006\text{ V}$

Resting at 25 °C

For the first three data points the batteries were at 25 °C, for all subsequent points the batteries were at 40 °C, in Figure 66 and Figure 67.

Lack of data points around 200 cycles

As discussed in Chapter 5, during the first 600 cycles there were several software crashes. The crashes resulted in the resting SOC not being adequately controlled. Once a crash was discovered, the batteries were returned to 50% SOC. This was not accurate enough to meet the battery voltage requirements stated above. Hence, there was a lack of data points around 200 cycles.

Error Bars

The error bars in Figure 66 and Figure 67 are equivalent to the load-cell error listed in Table 20. The first three data points have the additional error because the temperature was not that at which the load-cells were calibrated (with the additional error calculated from the load-cell data sheets (106,107)).

Pre-Cycle-Group, Post-Cycle-Group

To detect any changes in pressure during the inactive periods, the resting pressure at the beginning and end of these periods is shown in Figure 66 and Figure 67. These two data sets are very close to each other and a small x-axis offset has been applied to allow the data points to be distinguishable. The 'pre' and 'post' in the figure legends refer to the cycling groups and not the inactive period.

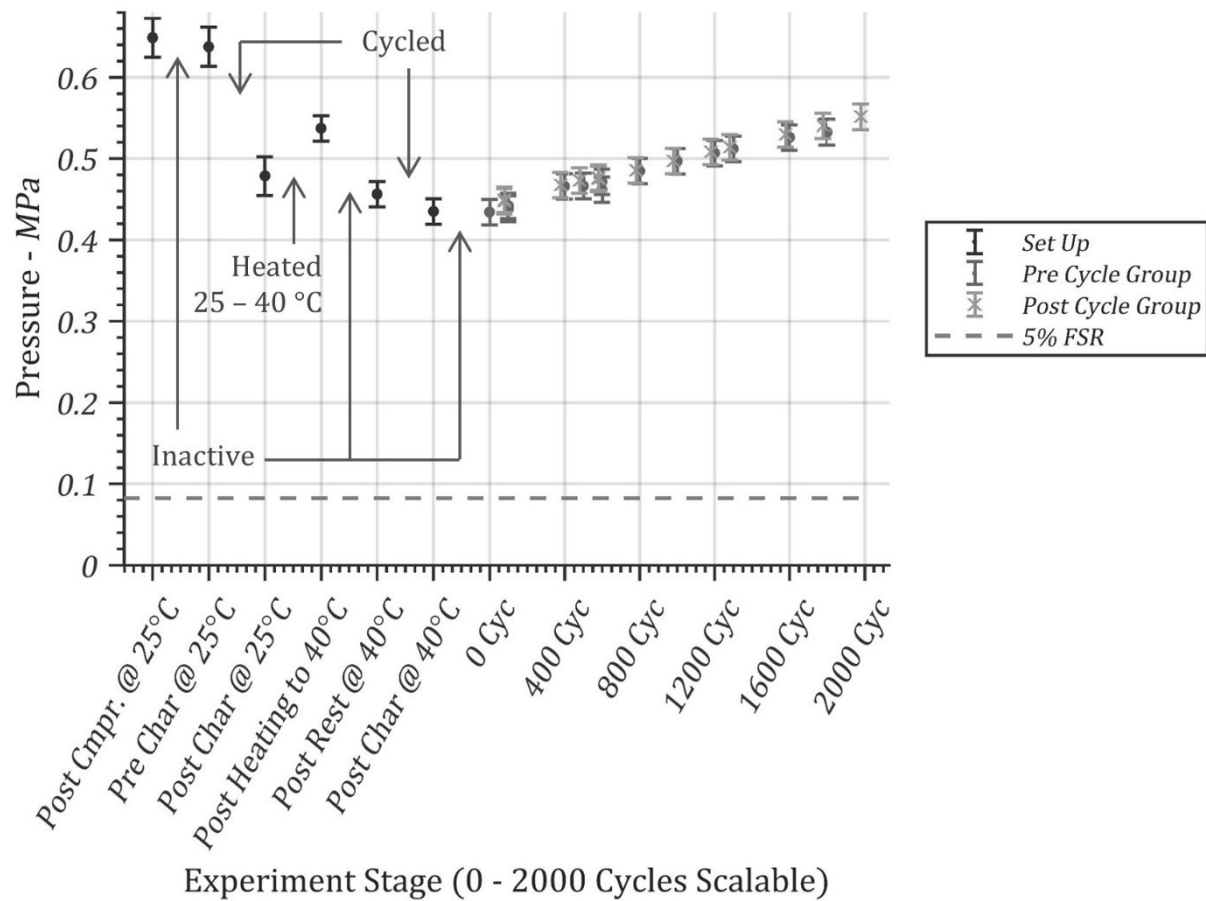


Figure 66: Battery pressure during periods of inactivity for the battery compressed to 0.434 MPa. Battery at 50% SOC and 25°C or 40°C for data points. Error bars show load-cell error from Table 20. On x-axis, the region from '0 Cyc' to '2000 Cyc' is scalable. All values to the left of '0 Cyc' (set-up) are declaring a battery state and the x-axis is not scalable. The processes that occurred between the set-up data points are highlighted.

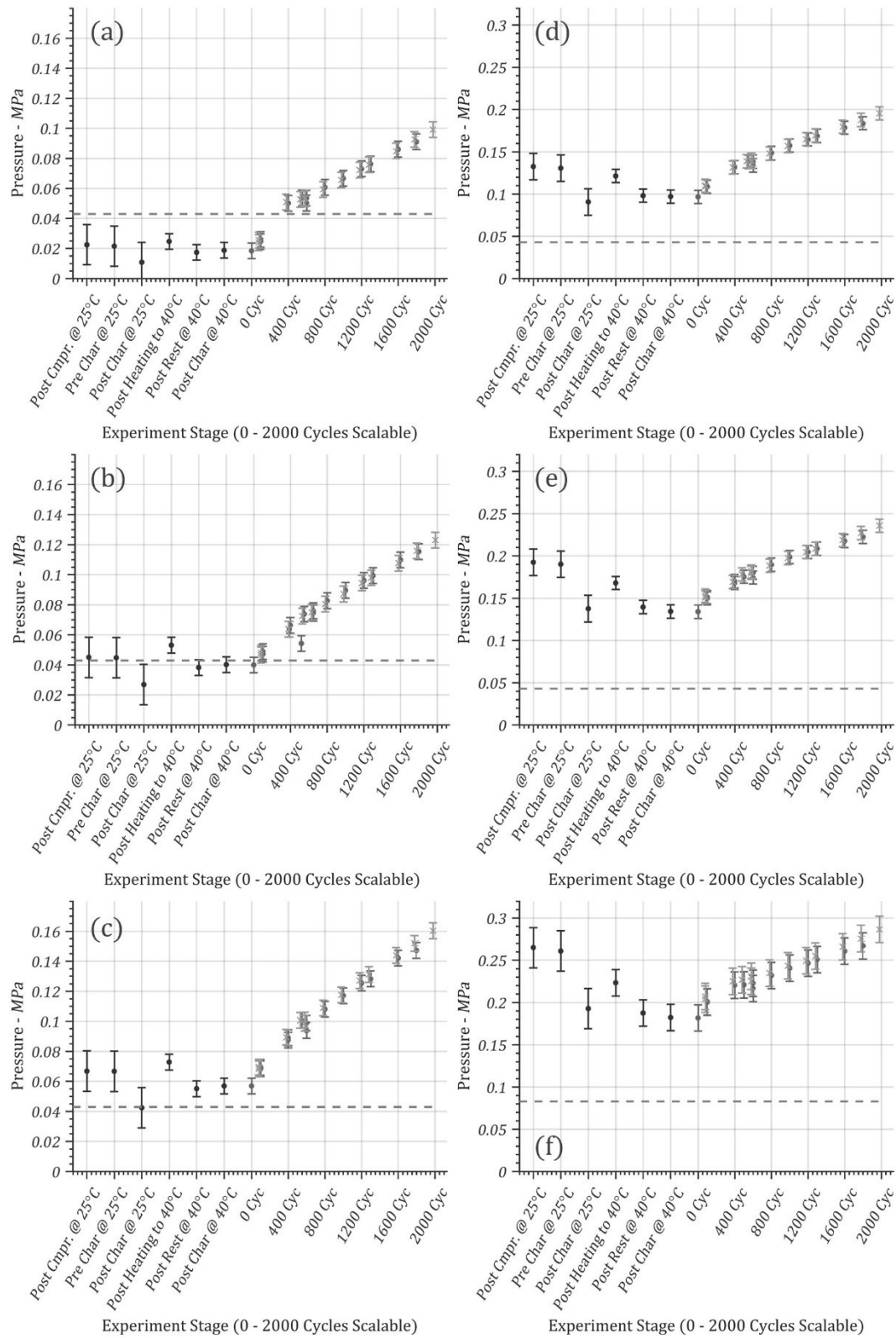


Figure 67: Battery pressure during periods of inactivity (all batteries except 0.434 MPa). Plots for different compression levels, (a) Constrained [0.019 MPa], (b) 0.040 MPa, (c) 0.057 MPa, (d) 0.097 MPa, (e) 0.134 MPa, (f) 0.182 MPa. Battery at 50% SOC and 25°C or 40°C for all data points. Error bars show load-cell error from Table 20. On x-axis, the region from '0 Cyc' to '2000 Cyc' is scalable. All values to the left of '0 Cyc' (set-up) are declaring a battery state and the x-axis is not scalable.

Key features of Figure 66 and Figure 67:

- All batteries show the same trend in the resting pressure:
 1. Slight decrease in pressure after the initial compression was applied and prior to any electrochemical changes. (see Section 5.3.3 for details of the initial compression procedure.)
 2. Large drop in pressure after cycling the battery during the electrochemical characterisation of the battery.
 3. Pressure rise as the battery is heated from 25 °C to 40 °C.
 4. Decrease in pressure during the period of inactivity after the temperature rise.
 5. Decrease in pressure during the second electrochemical characterisation but of smaller magnitude than that during the first characterisation.
 6. Stable pressure between the second characterisation and starting cycling.
 7. Linear increase in pressure throughout the 2000 cycles of the experiment.
- During the periods of inactivity between groups of cycles there was consistently a very small drop in pressure.
- The rate of pressure increase is very similar for all batteries. The values for all the batteries are given in Table 22.
- The pressure at which the cycling of the batteries is started is significantly lower than the initial pressure. The difference in the magnitude is shown in Table 22.

6.4.1. Resting pressure – discussion

There are two important points to draw from Figure 66 and Figure 67:

- The decrease in pressure between the initial/target pressure and the pressure at the beginning of cycling.
- The rate of the increase in pressure during cycling.

The first of these is by far the more important, due to its potential application. This is discussed in detail in following section, Section 6.5.

Table 22: Initial and True pressures applied to the compressed batteries and the linear rate of pressure increase with cycling. Rate of pressure increase calculated from data at 50% SOC and 40°C. Initial pressure values show the pressure applied, with the target given in brackets.

Initial Pressure (P_{init}) @ 25°C	True pressure at zero cycles (P_{true}) @ 40°C	Pressure Ratio (P_{0cyc}/P_{init})	Rate of pressure increase with cycling - MPa cyc ⁻¹
0.023 MPa* (0.022 MPa- CSTR)	0.019 MPa*	0.83*	3.8×10^{-5}
0.045 MPa * (0.043 MPa)	0.040 MPa*	0.80*	4.0×10^{-5}
0.067 MPa (0.065 MPa)	0.057 MPa	0.85	4.8×10^{-5}
0.133 MPa (0.13 MPa)	0.097 MPa	0.73	4.5×10^{-5}
0.193 MPa (0.20 MPa)	0.134 MPa	0.69	4.5×10^{-5}
0.275 MPa (0.26 MPa)	0.182 MPa	0.66	4.2×10^{-5}
0.649 MPa (0.65 MPa)	0.434 MPa	0.67	5.5×10^{-5}

** Data gathered close to or below the 5% FSR of the load cells and has a large associated error.*

The fourth column in Table 22 lists the rate at which the pressure increases with cycle number.

These values were found from the gradient of a line fit to the ‘Pre cycle group’ and ‘Post cycle group’ data sets in Figure 66 and Figure 67. The line fit was performed using the ‘fit’ function in MATLAB, employing a least squares fitting method (105). The rate at which the pressure rises (as it ages) is larger for batteries with higher initial pressures. This trend agrees with work

by Cannarella and Arnold (2) and the conclusion that electrode volume expansion is the cause of this trend is agreed with. Within this pressure range, the battery stress-strain relationship is non-linear, meaning that the battery is more rigid at higher pressures (2,46). The irreversible volumetric increase in the electrode that occurs with ageing, will induce a higher pressure increase in any batteries that have been more heavily compressed.

6.5 Defining the Battery Mechanical State

Defining the mechanical state of the battery during experiments is a recurring problem. There needs to be a defined state in order to make comparisons between different tests and different batteries. This is a very important problem that needs to be addressed, both for an understanding of the validity of comparing different results from a single experiment and comparing results between different batteries. There is a consensus in the literature that an ‘optimum pressure’ can be applied to batteries to maximise the cycle-life, see Section 2.5. Currently there is no clear definition of what an ‘applied pressure magnitude’ means, as the original state under which the pressure is applied is not consistent or defined.

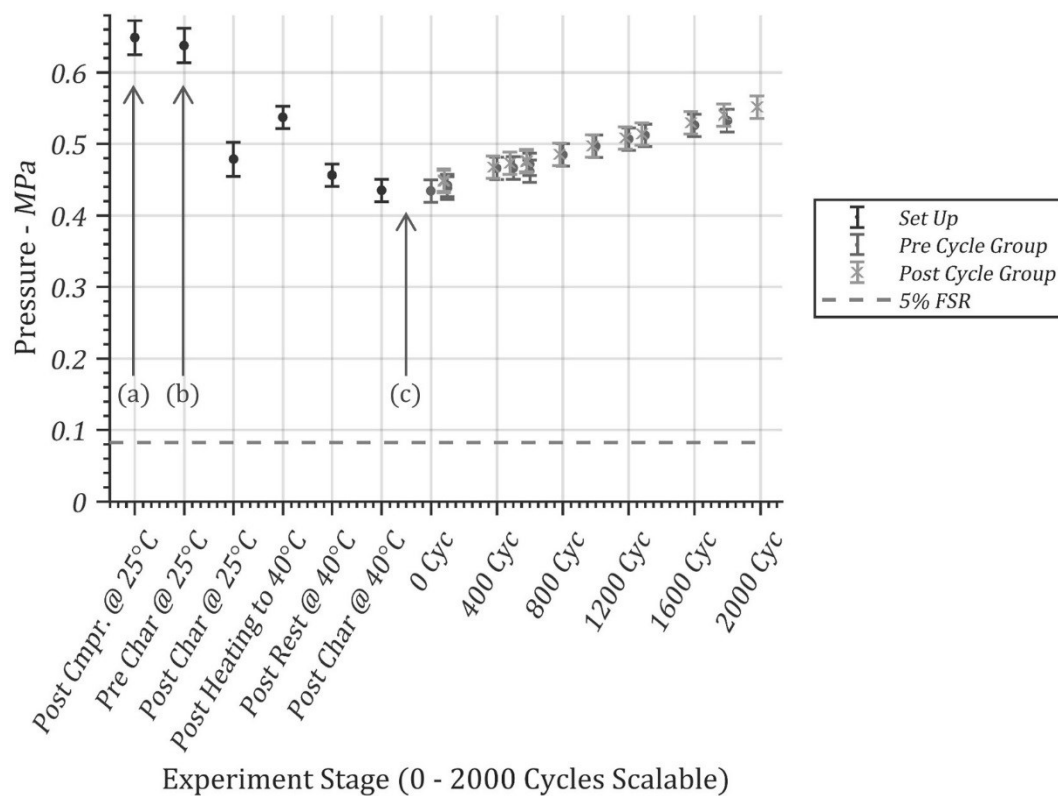


Figure 68: Battery pressure during periods of inactivity with key compressed states. Battery at 50% SOC and 25°C or 40°C for all data points. Error bars show load-cell error from Table 20. Three compressed states of interest highlighted (a) Initial pressure, (b) Pressure after viscoelastic stress relaxation and (c) True pressure.

The results shown in Figure 68 are a clear example of this problem. What pressure was the battery compressed to in this experiment? There are three possible pressure magnitudes highlighted in Figure 68:

(a) Target pressure

- The pressure on the battery immediately after the compression is applied and when the mechanical boundary conditions are fixed (i.e. the distance between the two plates constraining the battery is fixed.)
- Note that in this experiment, the constraint on the battery was incrementally increased to account for viscoelastic stress relaxation. (See Section 5.3.3 for details of the initial compression procedure)

(b) Pressure after viscoelastic stress relaxation

- After the mechanical boundary conditions have been fixed, the battery undergoes viscoelastic stress relaxation, changing the pressure from the target pressure.

(c) True pressure

- Further stress relaxation occurs because of electrochemical cycling and change in temperature.
- Pressure reaches a plateau, where the pressure does not relax further during electrochemical cycling.

All these pressures could be used as a description of the pressure applied to the battery during an experiment. The following section proposes a particular view on the mechanical response of batteries to compression. It explains why the pressure plateau (c) should be used to define the mechanical state of batteries, rather than state (a) or (b). This is followed by a discussion of future research that could be performed in this area.

6.5.1. Mechanical stages - assumptions

This discussion assumes the following:

No external changes to the mechanical boundary conditions

This is the most important condition for this discussion. For experiments and applications, external changes to the mechanical boundary conditions only occur at the beginning of tests and are fixed from that point onwards. All subsequent changes in the mechanical state of the batteries are the result of changes within the battery.

The above long-term compression experiment is an example of this, where the fixed displacement boundary condition was applied at the beginning of the experiment. The displacement was then maintained by applying Loctite 278 to the bolts, to prevent the bolts from loosening.

This assumption would also be valid for an experiment where active control is being used to maintain a constant pressure. Examples of this are the loading rate experiments in Section 4.3 and 4.5. Only through a constant pressure being held throughout the duration of the experiment, are comparable results obtained.

Temperature and SOC

Temperature and SOC significantly affect the mechanical state of batteries. For all pressure values it is assumed that the temperature and SOC are constant.

Constraint Configuration

Section 5.2 discussed the two different constraint configurations that can be applied to compressed Li-ion batteries:

- Fixed displacement
- Constant pressure

For consistency, throughout this chapter the discussion will be written using the terms relating to the fixed displacement constraint. This discussion is equally valid using any of the three constraints and their terms. They can all be used simply by interchanging the relevant terms listed in Table 23.

Table 23: Interchangeable terminology between the three different compression configurations

Fixed Displacement	Constant pressure
Pressure	Strain/Thickness
Stress Relaxation	Creep

6.5.2. Mechanical stages

Figure 69 shows the battery in different mechanical states and the changes between them, in a schematic form. This schematic follows the shape of resting pressures shown in Figure 68. These are the stages that Li-ion batteries undergo when being electrochemically cycled whilst being compressed.

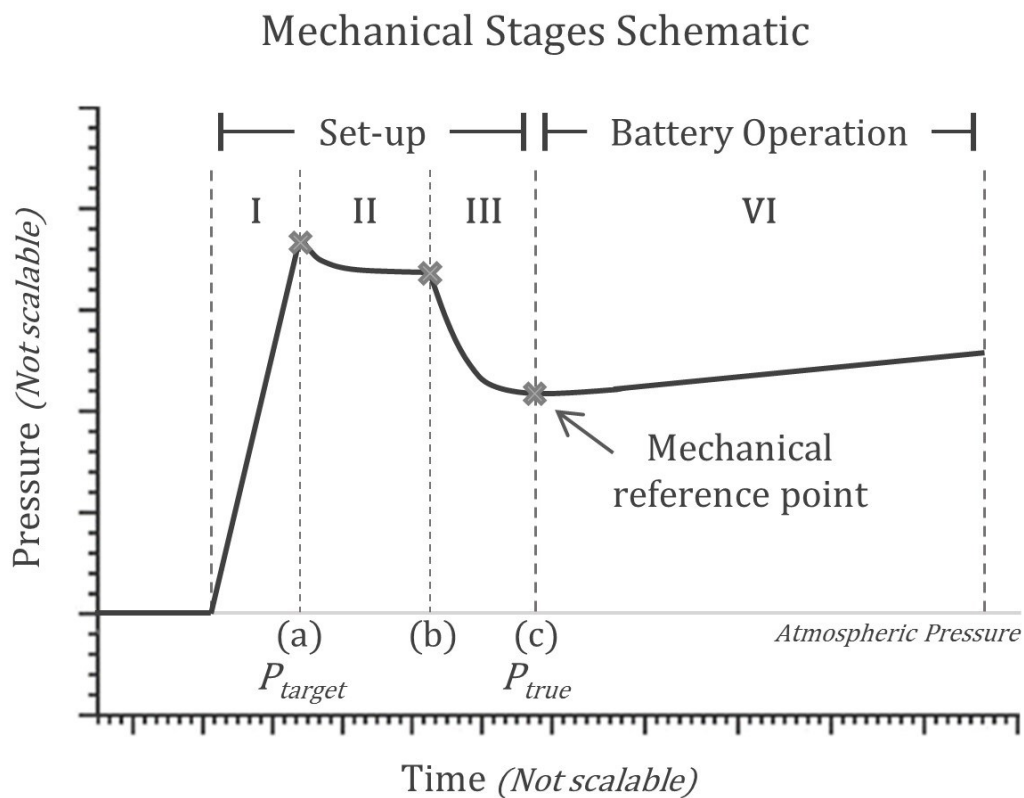


Figure 69: Schematic showing the four mechanical stages a Li-ion battery undergoes when operating under compression. Stages I, II and III are set-up. The set-up is comprised of: The initial compression (I), subsequent relaxation, without electrochemical cycling (II), further relaxation resulting from electrochemical cycling (III). Stage IV is the operational stage for the battery. Y-axis units are for a battery under fixed displacement constraint. Pressure can be replaced for strain for constant pressure constraint.

The three mechanical states labelled (a), (b), (c) in Figure 69 are the same as those in Figure 68 where actual measurements are given.

The four stages are defined as:

- I. **Initial compression to the battery:** - Pressure is applied from 0 MPa to a target pressure ($P_{initial}$).
- II. **Viscoelastic relaxation, with no change in SOC or temperature:** - Passive relaxation of the battery, i.e. pressure/strain relaxes depending on the constraint applied. The evidence for Stage II is in the loading rate experiments in Sections 4.3 and 4.5 There is also evidence of this stage in the literature (2,40). In this stage the pressure plateaus and the battery then reaches mechanical state (b).
- III. **Further relaxation of the battery as a result from electrochemical cycling:** - During electrochemical cycling, the pressure/strain of the battery reduces for any given SOC. The end of this stage is categorised as when no further notable reductions occur. This Stage is shown in Figure 29, in Section 4.5 and in the literature (2).
- IV. **The operational stage of the battery:** - upon completion of Stage III, increases in strain/pressure occur as the battery ages and continues to be cycled throughout its lifetime.

An important point to take from Figure 68 is that from both a scientific and engineering point of view, Stage IV is the main stage of interest. Stages I to III are the initiation steps of the operating life of the battery. State (c) is a 'mechanical reference point' at the starting point to Stage IV. At this transition point, the mechanical response of the battery is no longer being dominated by the relaxation after the initial compression. From this point (c), returning the battery to any given SOC and temperature, produces a consistent mechanical state.

Although a small distinction, this has large implications for both battery research and for the design of battery packs. Using this mechanical state to define the mechanical state of compressed batteries enables the following:

- Comparison of mechanical conditions and results between different tests within an experiment.
- Comparison of mechanical conditions and results between different experiments.
- Comparison of mechanical conditions and results between different batteries.
- Provision of a representative and comparable value for the pressure applied to a battery throughout its lifetime and when inside a battery pack.

6.5.3. Future research

Using the beginning of Stage IV to define the mechanical state of compressed batteries introduces new challenges for future research. Three possible areas are:

- Is the relationship between initial pressure (a) and the true pressure (c), consistent for different batteries of the same model?
- What procedure should be followed when transitioning between states (a) and (c)?
 - Can this procedure be standardised?
 - Can a standardised procedure be applied to different batteries?
 - Does this transition require electrochemical cycling, or can it be achieved using methods such as thermal cycling?
- Are the single battery results applicable when multiple batteries are compressed in a stack?

Note that these questions only cover trying to understand the transition from an uncompressed battery to a battery operating under a well-defined compressed state. Other future research into the effects of compression during operation (Stage IV) will be introduced in Section 7.3.

6.6 Pressure Hysteresis

Figure 63 - Figure 65 in Section 6.3 showed that the mean pressure during charging was higher than during discharge, indicating pressure hysteresis during cycling. This section looks at the pressure curves during cycling. All data in the section was taken from the 0.434 MPa battery results.

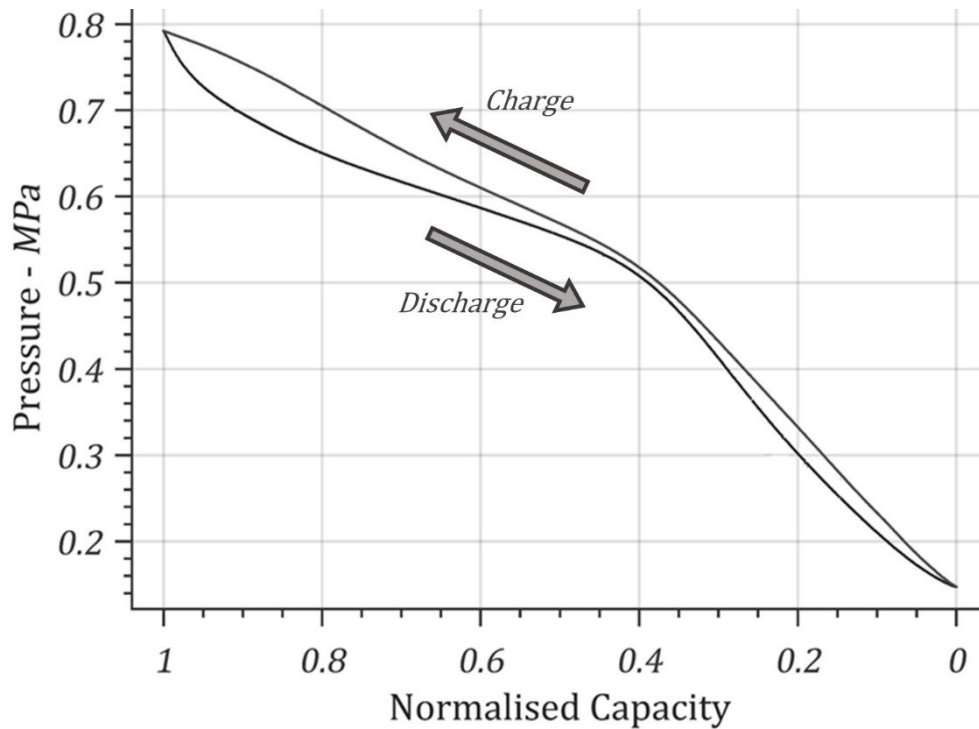


Figure 70: Pressure hysteresis during a 2C discharge and subsequent charge (cycle 1450 of 2000). There were no CV holds at the ends of either the discharge or charge. As shown by the annotative arrows the discharge pressure is lower in magnitude than the charge, at the same normalised capacity (SOC). Single cycle of the battery compressed to 0.434 MPa

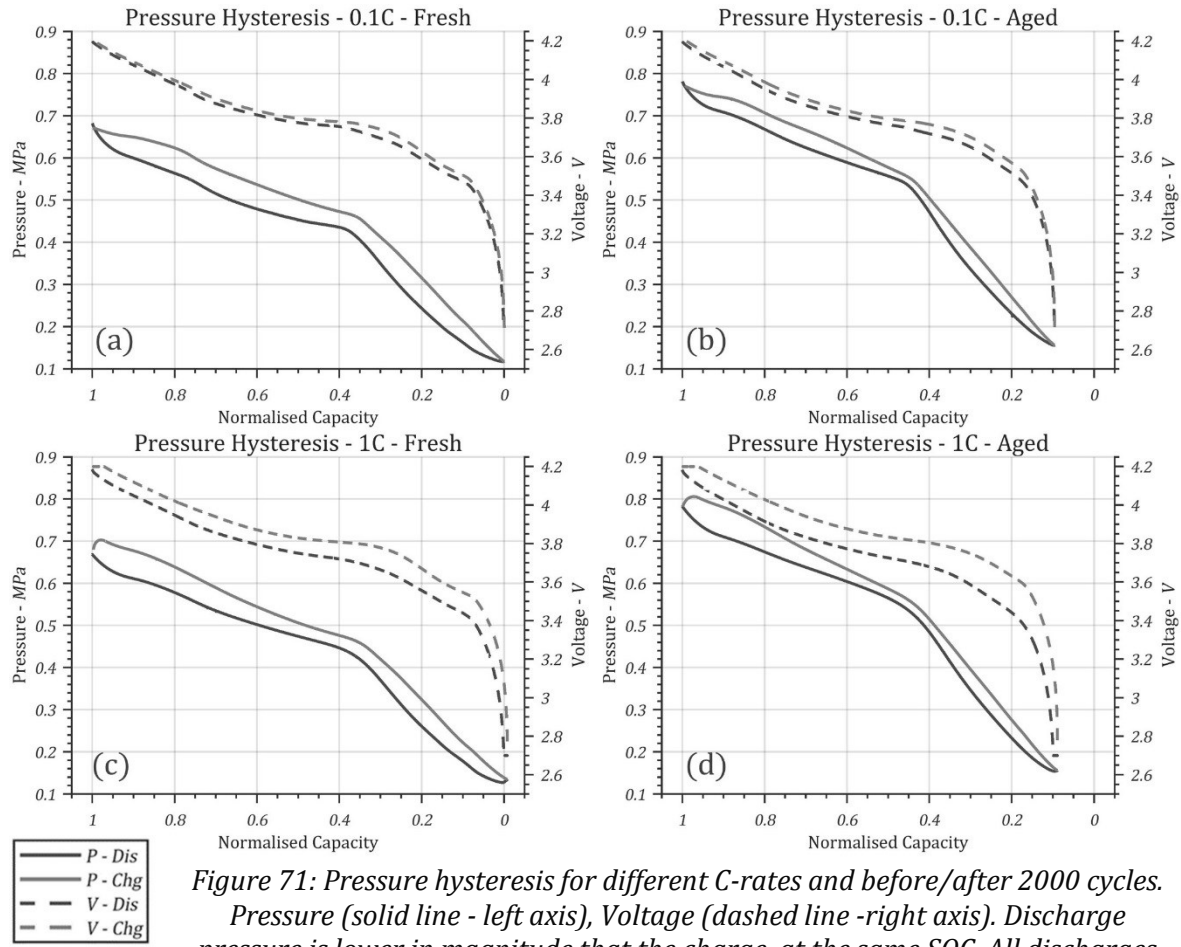


Figure 71: Pressure hysteresis for different C-rates and before/after 2000 cycles. Pressure (solid line - left axis), Voltage (dashed line - right axis). Discharge pressure is lower in magnitude than the charge, at the same SOC. All discharges and charges include a CV hold at the voltage limit.

Figure 70 shows the pressure change during a 2C discharge, followed immediately by a 2C charge. This clearly shows the hysteresis. At the same normalised capacity (SOC) there is a higher pressure for charging than discharging. There is a larger difference over the range of 100%-60% normalised capacity than below 60% SOC. Figure 71 shows the same data for the 0.1C and 1C discharges and charges and includes the corresponding voltage curves. The voltage curves also show hysteresis, which is to be expected due to battery internal resistance. Here the 'Fresh' plots, (a) and (c), refer to the characterisation at zero cycles. The 'Aged' plots (b) and (d) refer to the characterisation after 2000 cycles. The plots in Figure 71 also include the CV holds at 4.2 V and 2.7 V.

Bitzer et al. (108) found hysteresis when measuring the unrestrained thickness change (rather than restrained pressure changes) in an NMC-graphite Li-ion battery (109). Their work demonstrated hysteresis, but with the opposite effect, in that the thickness of battery was larger during the discharge than charge. This assumes that thickness and pressure under the different constraint configurations (unconstrained as opposed to fixed thickness) behave similarly. Increasing thickness when unconstrained is similar to increased pressure at fixed thickness. It should also be noted that the charge-discharge direction of the hysteresis curves is never explicitly stated in the body of the text by Bitzer et al. (108). The direction is assumed from annotative arrows in a single figure. It is therefore considered likely that the direction of the arrows is in error. Future work should be performed to confirm that battery thickness hysteresis is consistent across different conditions of measurement.

The detailed examination and discussion of the hysteresis and how it changes with ageing is beyond the scope of this body of work and needs to be assessed in future work.

6.7 Battery Thickness

The battery thickness was measured every 200 cycles during the inactive periods between the cycling groups, (3.76 V). The measurements can be used to compare the battery thickness when under compression and give an estimate of the relative Volumetric Energy Densities (VED) of the batteries. Figure 72 (a) and (b) show the same data, (a) with error bars and (b) without, for clarity. The error bars represent one standard deviation for the 6 thickness measurements performed at each data point.

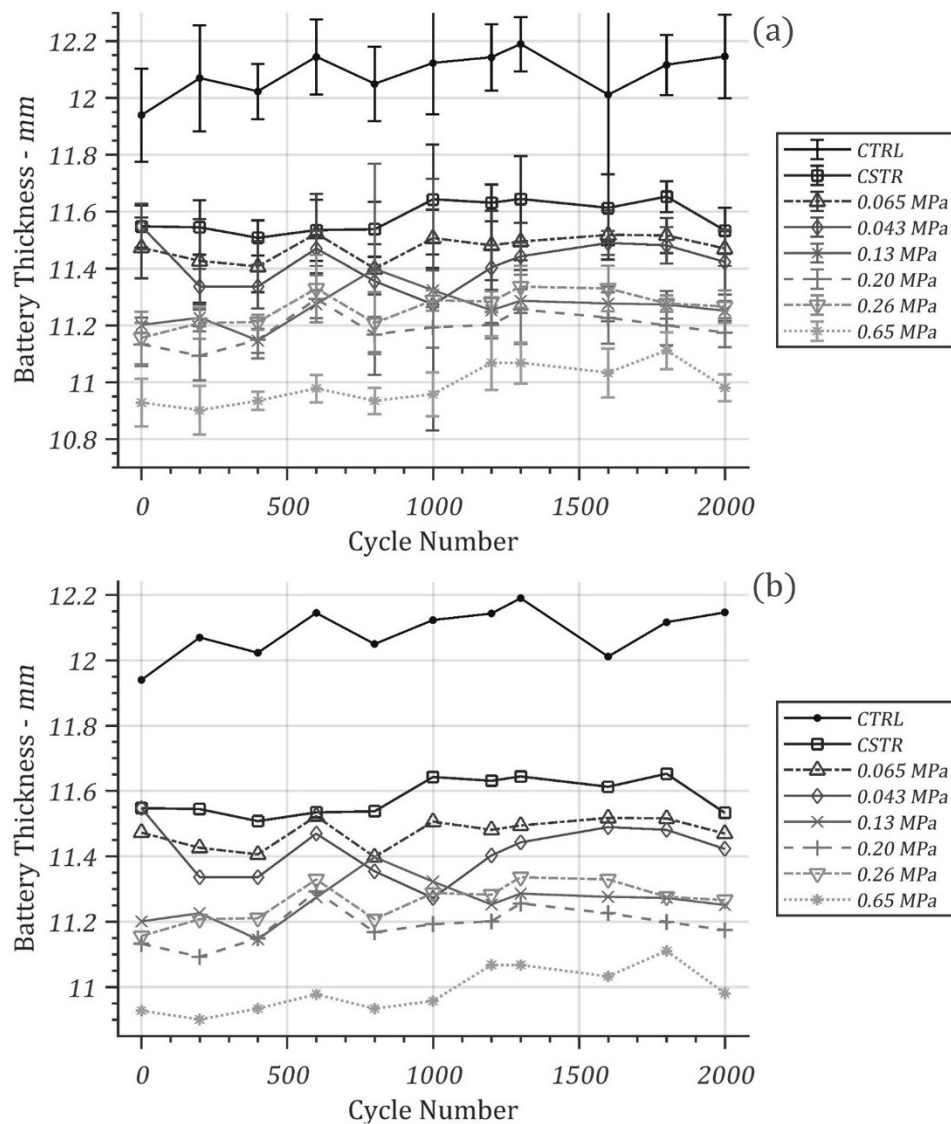


Figure 72: Battery thickness during inactive periods between cycling. Measurements taken at 40°C at 50% SOC. Plot (a) shows the thickness with the measurement error. (b) shows same data without the error bars for clarity.

The data in Figure 72 shows significant variability in the thickness measurements. Figure 72 shows the expected trend of greater compression resulting in thinner batteries, although this is not universal. The 0.057 MPa and 0.182 MPa do not follow the trend. This is thought to be due to variability between individual batteries.

For the purposes of estimating the VED of the batteries, the thickness is assumed to be constant throughout the experiment. Thus, VED can be calculated from the average of all the thickness measurements made throughout the duration of the experiment. The thickness measurements used are shown in Figure 73 against the pressure applied to the batteries. Table 24 shows the VED of the eight batteries at zero cycles and after 2000 cycles. These values were calculated using the following values:

- Battery thickness averaged from all thickness measurements taken throughout the duration of the experiment.
- Volume calculated by multiplying the mean thickness by the nominal electrode area, $4.6 \times 10^{-3} \text{ m}^2$. See Table 4 for battery specification.
- Energy calculated from a 0.1C discharge between voltage limits, 4.2 V and 2.7 V.
- Discharge preceded by CV hold at 4.2 V to $|i| < 0.01C$.
- 0.1C discharge performed at 40 °C.

The estimated values in Table 24 quantify the increased VED for the compressed batteries. As with the battery thickness, the VED does not always increase with increased compression. This is assumed to be a result of variability between the batteries, both in thickness and energy capacity.

The normalised VEDs show an increase of ~5% between the control battery and the constrained battery. As the pressure is increased the VED further improves to slightly more than 10% greater than the control battery. The results in Chapter 5 showed no significant difference in the rate of capacity fade between any of the batteries. Thus, compressing the

stacked electrode configuration battery can improve the volumetric energy density of the battery by ~10 %, with no effect on the cycle life of the battery.

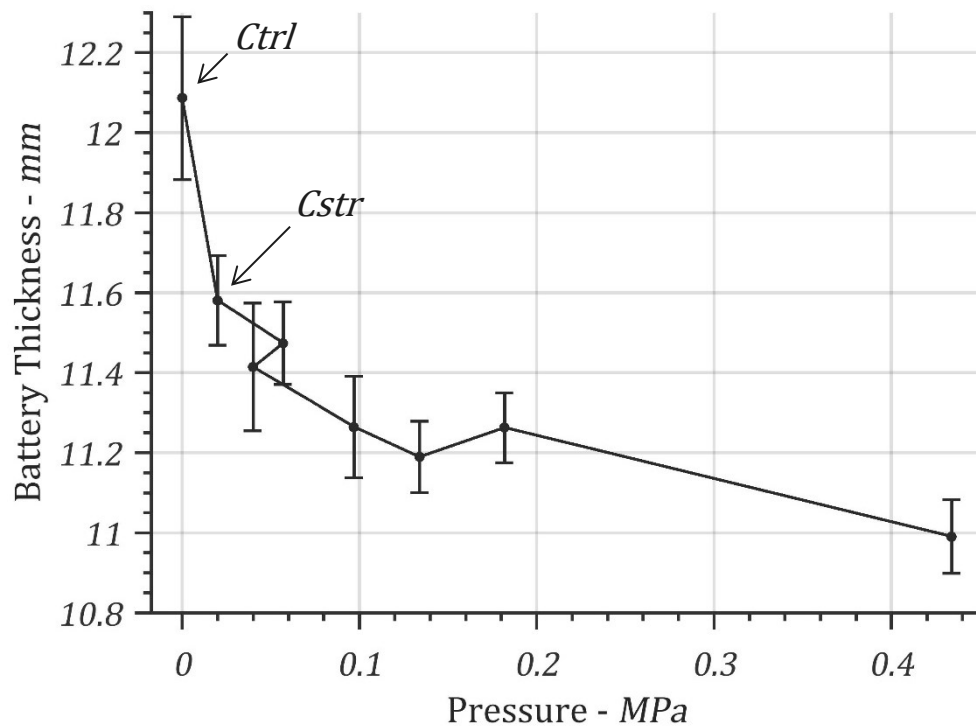


Figure 73: Average battery thicknesses throughout the 2000 cycle degradation experiment vs the true pressure initially applied. Error bars represent one standard deviation of all thickness measurements taken throughout the experiment.

Table 24: Energy density for the compressed batteries before and after 2000 cycles.

Pressure	Thickness mm	Volumetric Energy Density $Wh L^{-1}$	Normalised Volumetric Energy Density (vs. CTRL)	Volumetric Energy Density $Wh L^{-1}$	Normalised Volumetric Energy Density (vs. CTRL)
		0 Cycles		2000 Cycles	
CTRL	12.08	333	1.00	301	1.00
CSTR (0.020 MPa)	11.58	354	1.06	320	1.06
0.040 MPa	11.42	358	1.07	327	1.09
0.057 MPa	11.48	353	1.06	325	1.08
0.097 MPa	11.26	351	1.05	318	1.05
0.134 MPa	11.20	364	1.09	329	1.10
0.182 MPa	11.26	355	1.07	322	1.07
0.434 MPa	11.00	370	1.11	336	1.12

6.8 Mechanical Conclusion – Long-Term Compression

The mean of the thickness measurements taken throughout the experiment were used to estimate the difference in Volumetric Energy Density (VED) of the batteries. The thickness of the batteries decreased as the pressure increased. There was a ~5% increase in the VED between the uncompressed control battery and the constrained battery (0.020 MPa). The VED gradually increased with increased pressure to a maximum of ~10% improvement in VED for the battery compressed to 0.434 MPa. This shows that compression can be employed to significantly improve the volumetric energy density of certain types of battery, without impacting the battery ageing.

There has been no consistent method for defining the mechanical state of a battery that is compressed. Results from different experiments are difficult to compare to each other, without defining the mechanical state of the batteries. When operating under compression, batteries go through four mechanical stages.

- I. **Initial compression to the battery:** - Pressure is applied from 0 MPa to a target pressure.
- II. **Viscoelastic relaxation, with no change in SOC or temperature:** - Passive relaxation of the battery, i.e. pressure/strain relaxes depending on the constraint applied.
- III. **Further relaxation of the battery as a result of electrochemical cycling:** - During electrochemical cycling, the pressure/strain of the battery reduces for any given SOC. The end of this stage is categorised as when no further notable reductions occur.
- IV. **The operational stage of the battery:** - upon completion of Stage III, increases in strain/pressure occur as the battery ages and continues to be cycled throughout its lifetime.

Stage IV is the stage of interest operationally and Stages I – III should be considered as part of the set-up of the battery. The point at which the battery transitions between Stage III and Stage IV should be used to define the mechanical state of the battery.

The battery SOC and temperature also significantly influence the mechanical state, therefore these must also be declared whenever defining the mechanical state of a battery. A standard of 30% SOC and 20 °C is proposed when declaring mechanical states. The justifications for these values are:

- 20 °C is a common temperature used to describe ambient temperature.
- 30% SOC is a shipping standard (110), where the maximum SOC at which Li-ion batteries can be shipped is 30% (due to the additional expense of pre-cycling batteries prior to battery pack assembly, 30% can be considered a likely battery pack assembly SOC).

Thus, the use of this standard in defining the mechanical state means that results from different works can be directly compared and directly related to batteries being assembled into battery packs.

Button load-cells were used to measure the pressure applied to the batteries. The Full-Scale-Range (FSR) of the load-cells was found to be one of the most influential estimators of error in the experimental design used:

- The load-cell measurement error is proportional to the FSR.
- Below ~5% of the FSR, the sensor output is not linearly proportional to force, so linear calibration curves are not valid in this region.

The FSR for the load-cells was chosen to allow for a large pressure increase, expected from the ageing of the batteries. The large pressure increase did not occur during the experiments. Thus, the load-cells were over specified and only one of the seven compressed batteries had pressure data that remained above 5% FSR. Future work examining the pressure changes in Li-ion batteries requires initial experiments to specify the FSR required to generate high quality force/pressure data.

Investigation into how the load-cells measure force/pressure showed that the load-cells measure very small displacements of the sensor anvil. These are equated to a compressive force. The magnitudes of the anvil displacements were found to be ~25% of the change of thickness of an unconstrained battery between 0% and 100% SOC. It is concluded that this small displacement does not invalidate the fixed displacement assumption and the constraint configuration should not be considered compliant or constant pressure. Future work applying fixed displacement boundary conditions to compressed batteries should consider this displacement and confirm the validity of the constraint configuration. This would be more important when using a sensor with a proportionally smaller FSR as the anvil displacement linked to the proportion of the FSR used.

The changes in the maximum, minimum and mean pressures from the 2C cycles were consistent with the literature (2). These showed a gradual linear increase in the mean pressure with ageing. This is due to irreversible volumetric expansion of the electrodes resulting from SEI layer growth and cycling induced structural changes. The mean pressure during charge was higher than during discharge.

The pressure curves from the 2C cycles and the 1C and 0.1C characterisation cycles showed this pressure hysteresis. Part of future work stemming from this research (discussed in Section 7.3.) would be to investigate further the cause of the hysteresis and how it changes as the battery ages.

Visual inspection of the pressure curves showed that the volumetric changes in the batteries during cycling resulted in some becoming fully uncompressed at low SOC. The batteries compressed (at 50% SOC) to 0.020 (CSTR), 0.040, 0.057 MPa remained uncompressed at 0% SOC for the duration of the experiment. The 0.097 MPa battery was uncompressed at 0% SOC for approximately the first 600 cycles. Subsequently there was always some pressure applied to the battery. This is important if the pressure applied to the battery is required for securing/locating it. If this is the case the SOC and initial pressure must account for the pressure drop due to the battery being at low a low SOC.

The changes in the resting pressure of the battery led to the definition of the four mechanical stages described above. The resting pressures also showed that the rate at which the pressure in the battery increased with ageing was proportional to the compression applied to the battery. Within this pressure range, the battery stress-strain relationship is non-linear, meaning that the battery is more rigid at higher pressures (2,46). The irreversible volumetric increase in the electrode that occurs with ageing will induce a higher pressure increase in any batteries that have been more heavily compressed than in less pressurised batteries.

The thickness measurements taken throughout the experiment were considered to have too much variability and insufficient resolution to quantify any thickness changes that occurred during the experiment.

7. Conclusion

The aim of this work is to further the understanding of the effects of compression on Li-ion batteries. This chapter is in four sections:

- Results, Conclusions. Focused on the experimental results from this work and their contribution to the field.
- Methods and Data-processing, Conclusions. Focused on the experimental and data-processing methods employed.
- Future Work that could stem from this work.
- Engineering Focus. A concise summary of the key aspects of compressing batteries, as applied to battery pack design.

7.1 Results - Conclusions

Investigation of the effect of compression on the cycle life of stacked electrode batteries showed that the pressure range of 0 to 0.43 MPa (@ 40°C, 50%SOC) has no significant influence on the battery capacity fade. This was shown in the capacity fade, battery impedance and ICA curves. This result is in direct contradiction to the results in the literature (2), where obround jelly-roll batteries were tested. It is concluded that the electrode configuration of the battery has a significant impact on the effects of compression on batteries. A stacked electrode battery can be compressed to a larger magnitude without deterioration in performance, compared to an obround electrode battery.

The battery thicknesses were used to estimate the difference in volumetric energy density of the batteries. There was a ~5% increase in the energy density of the lightly constrained (0.02 MPa) battery over the uncompressed control battery. This increased with increased pressure to a maximum of ~10% improvement for the battery compressed to 0.43 MPa. This shows that compression can be employed to significantly improve the volumetric energy density of certain types of battery, without impacting the battery ageing.

The capacity fade and impedance results showed a marked stepped pattern, which coincided with the groups of 200 cycles applied to the batteries. The steps were attributed to calendar ageing that occurred during the inactive periods between the cycling groups. A calendar ageing rate was found. From this estimate, it was calculated that 40% of the total capacity fade could be attributed to calendar ageing.

The batteries were compressed under a fixed displacement configuration. The changes in the maximum (100% SOC), minimum (0% SOC) and mean cycling pressures were consistent with the literature (2). The mean pressure during charge was higher than during discharge,

showing pressure hysteresis. The pressure hysteresis was present at all C-rates, 0.1C, 1C and 2C.

The initial compression was applied to the batteries at 50 % SOC. At low SOC, the thickness of the battery is reduced, relieving the pressure. Batteries under lower initial compression were uncompressed at 0% SOC for the duration of the experiment. This is important if the pressure applied to the battery is required for securing/locating it. If this is the case the SOC and initial pressure must account for the pressure drop due to the battery being at a low SOC.

The resting pressures (during periods of inactivity at 50 % SOC) showed that the rate at which the pressure of the battery increases with ageing is proportional to the compression applied to the battery. The larger the pressure, the greater the rate of pressure increase.

7.2 Method and Data Processing - Conclusion

The experimental work highlighted the following points on the performance of compression experiments on Li-ion batteries and compressing batteries in general.

There has been no consistent method for defining the mechanical state of a battery that is compressed. Results from different experiments are difficult to compare to each other, without defining the mechanical state of the batteries. When operating under compression, batteries go through four mechanical stages. These are shown in Figure 74.

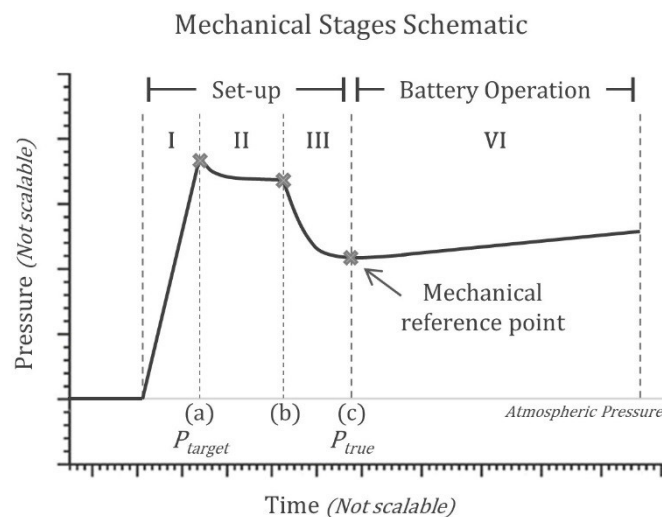


Figure 74: Schematic showing the four mechanical stages a Li-ion battery undergoes when operating under compression. Stages I to III are set-up and are the initial compression and the subsequent relaxation, without (II) and with electrochemical cycling (III). Stage IV is the operational stage for the battery. Y-axis units is for a battery under fixed displacement constraint. Pressure can be replaced by strain under a constant pressure constraint.

- I. **Initial compression to the battery:** - Pressure is applied from 0 MPa to a target pressure.
- II. **Viscoelastic relaxation, with no change in SOC or temperature:** - Passive relaxation of the battery, i.e. pressure/strain relaxes depending on the constraint applied.
- III. **Further relaxation of the battery as a result from electrochemical cycling:** - During electrochemical cycling, the pressure/strain of the battery reduces for any given SOC. The end of this stage is categorised as when no further notable reductions occur.

IV. **The operational stage of the battery:** - upon completion of Stage III, increases in strain/pressure occur as the battery ages and continues to be cycled throughout its lifetime.

Stage IV is the most important stage of interest in terms of performance, as this is the stage where the battery will spend its operational life. Stages I – III take place during set-up. The current assumptions that the pressures/strains at the beginning of Stage IV are similar to those applied in Stage I are incorrect. Stages II and III are also of significant importance. Unfortunately, pre-cycling is typically avoided during production as it is expensive. However, to define a more representative mechanical state of the cell, the conditions at the end of Stage III should be used and the SOC and temperature declared, with 30% SOC and 20°C proposed as a standard.

Experiments investigating the loading rate and subsequent creep contributed to the definition for the four mechanical stages. The strain at the end of Stage II showed no relationship to the loading rate. The mechanical state of the battery after initial loading and creep showed significant variability. A key conclusion from this work is that achieving a consistent mechanical reference state is not straightforward.

The battery strain that results from thermal expansion due to a 15 °C temperature rise was shown to be of the same order of magnitude as the strain due to a discharge from 100% to 0% SOC. Thus, when looking at the change in mechanical state of a battery during a single cycle, the temperature of the battery is an important variable. The effects of temperature on the electrochemical performance of the battery are significantly larger than those of any compression.

In performing compression experiments on Li-ion batteries there are two constraint configurations:

- Fixed displacement: Strain is constant, Pressure varies
- Constant pressure: Strain varies, Pressure is constant.

When using load-cells to measure the pressure changes in compressed batteries, there were two key considerations to be addressed. The first is specifying the full-scale range for the load-cells. The pressure the battery reaches at the end of the experiment is unknown. The load-cells used in this work were over specified, because the pressures never reached the magnitude anticipated. Much of the pressure data had a large associated error due to this. Future work examining the pressure changes in Li-ion batteries requires initial experiments to inform the full-scale range required, to enable the generation of higher quality force/pressure data. The second load-cell consideration is the anvil displacement. The force/pressure is sensed via the strain induced by small sensor anvil displacements. The magnitudes of the anvil displacements used in this work were found to be ~25% of the change of thickness of an unconstrained battery. This could be significant when assuming a fixed displacement constraint. When applying fixed displacement boundary conditions to compressed batteries, the sensor anvil displacement should be measured to confirm the validity of the constraint configuration.

A residual analysis methodology was used as a means of evaluating the quality of the smoothing of the noisy experimental data. Acceptable smoothed data was used to generate differential curves (such as ICA and DVA curves). The graphical methods provided very useful visual assessment of the quality of the smoothing. This data analysis process improves confidence in the resulting differential curves.

7.3 Future Work

Section 6.6 showed that pressure hysteresis occurs when cycling compressed Li-ion batteries, with the pressure being greater during charging. These results need to be expanded upon to explain both: why this occurs, and how the hysteresis changes with ageing. To help to understand this phenomenon, further work should be performed to generate a complimentary data set, measuring the hysteresis in battery thickness change.

The clarification of the mechanical Stages I - IV combined with the results showing the difference in compression tolerance of different electrode configurations opens several potential research avenues.

Mechanical Stages I to III

Using the end of Stage III to define the mechanical state of a compressed battery is very useful, as it is a representative description of the battery's mechanical state during operation. A problem with this definition is that it is unknown if nominally identical batteries that undergo an identical procedure in Stages I, II and III will achieve the same mechanical state. There is currently little to no understanding how a pre-defined mechanical state can be achieved repeatably. Two primary variables that can be controlled during Stages I - III are:

- Initial compression magnitude at the end of Stage I.
- The procedure applied to the battery during Stages II and III.

The research that could be performed includes:

- Studying the relationship between the compressions at the ends of Stages I and the repeatability of the mechanical state at the end of Stage III.
- Defining the procedure that can be performed to consistently transition from the ends of Stages I and III.

- Investigate if Stage III requires electrochemical cycling or can an equivalent result be achieved using methods such as thermal cycling or external cyclic pressure fluctuations?
- Assessing if the single battery results are applicable when multiple batteries are compressed in a stack.

Mechanical Stage IV (Operational Stage)

The results from this work showed that the electrode configuration significantly affects the compression tolerance of Li-ion batteries. There is scope for further research into the effects of higher compression magnitudes on batteries that are more compression tolerant, such as the stacked electrode configuration. This can be further developed to encompass the effects of non-uniform compression. This work should consider the following variables that will influence the results:

- Power battery vs. Energy battery.
- Electrode configuration.
- Constraint configuration. (defined in Section 5.2)
 - Fixed displacement.
 - Constant pressure.

This proposed future work would significantly expand the knowledge of:

- How to compress batteries to achieve a target compression magnitude.
- What compression constraint is best.
- How different compression magnitudes affect different batteries.
- What types of batteries are most suitable for applications where compression is required.

Different Battery Chemistries

Section 3.2.2 briefly discussed the effect of compression on batteries of a different chemistries to that tested here, particularly those with different anodes. Future work could

look at this and assess if the conclusions of this work are more widely applicable across the different battery chemistries.

7.4 Compressing Li-ion Batteries – Engineering Focus

This page is intended as a summary of the key points that battery engineers should consider when compressing Li-ion pouch batteries. It highlights what is understood and what is not understood within the scientific battery community.

The compression magnitude of a battery is a function of the SOC, temperature and the constraint configuration. All three of the above must be understood when comparing the results of different compression experiments. It is proposed a standard of 30% SOC and 20°C be used as a standard when defining the mechanical state of Li-ion batteries.

The separator is the most compliant material in the battery. When compressed, pore closure occurs in the separator, increasing the battery impedance (2,40–45).

During cycling the thickness of an uncompressed battery changes from a maximum at 100% SOC to a minimum at 0% SOC. When compressed, and depending on the constraint configuration applied, this change will manifest as either thickness change or change in pressure, or both. The magnitude of these changes will be battery and compression-magnitude dependent.

As the battery ages, its net thickness will increase gradually, as will the maximum and minimum pressures. The difference between the minimum and maximum pressures also diverges.

If applying a target compression magnitude to a battery, there are two key measurement points.

- The initial mechanical state. (*Initial-Mech-State*)
- The mechanical state after the subsequent relaxation. (*True-Mech-State*)

The large proportion of the relaxation occurs from electrochemical cycling of the battery. At the True-Mech-State, no further relaxation occurs with cycling. Returning to the same SOC returns the battery to the same mechanical state. This measurement should be used to define the mechanical state of the battery, as this is representative of the compression applied to the battery during operation. Currently there is no understanding of the relationship between the Initial and True Mechanical States. The procedural requirements to transition between them in a repeatable manner are currently unknown.

The electrode configuration impacts the compression tolerance of the battery. Stacked electrode configuration batteries are more tolerant than obround jelly-roll batteries. This has been shown for pressure magnitudes of up to ~0.5 MPa. The upper limit of compression tolerance of stacked electrode batteries is unknown. There is a consensus that an optimum compression magnitude exists for battery cycle life. There is insufficient research to understand how applicable this consensus is, given the huge variety of different batteries available.

Energy batteries have proportionally larger amounts of active material. Thus, the thickness changes during cycling are proportionally larger in these batteries. The effects of compression on energy-batteries compared to power-batteries is currently unknown.

8. References

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9. Appendix

The Appendix is broken into four parts, labelled A - D. Appendices A – C each provide additional information from three sections of the main document. Appendix D provides the permission documentation for the images used in this document, the copyright of which is owned by a third party.

9.1 Appendix A

In Section 4.1.4, residual analysis was performed on an example data set to display the functionality of the methodology. For this example, two smoothing parameters (shown in Table A1) were applied in the four possible combinations. The graphs show the results from the other two combinations that were not displayed in the main text.

- Figure A1: Large span – Few loops
- Figure A2: Small span – Many loops

Table A1: Smoothing control variable values

	Loops	Span (% of the total number of data points)
Low	1	100 (0.3%)
High	10	675 (2.0%)

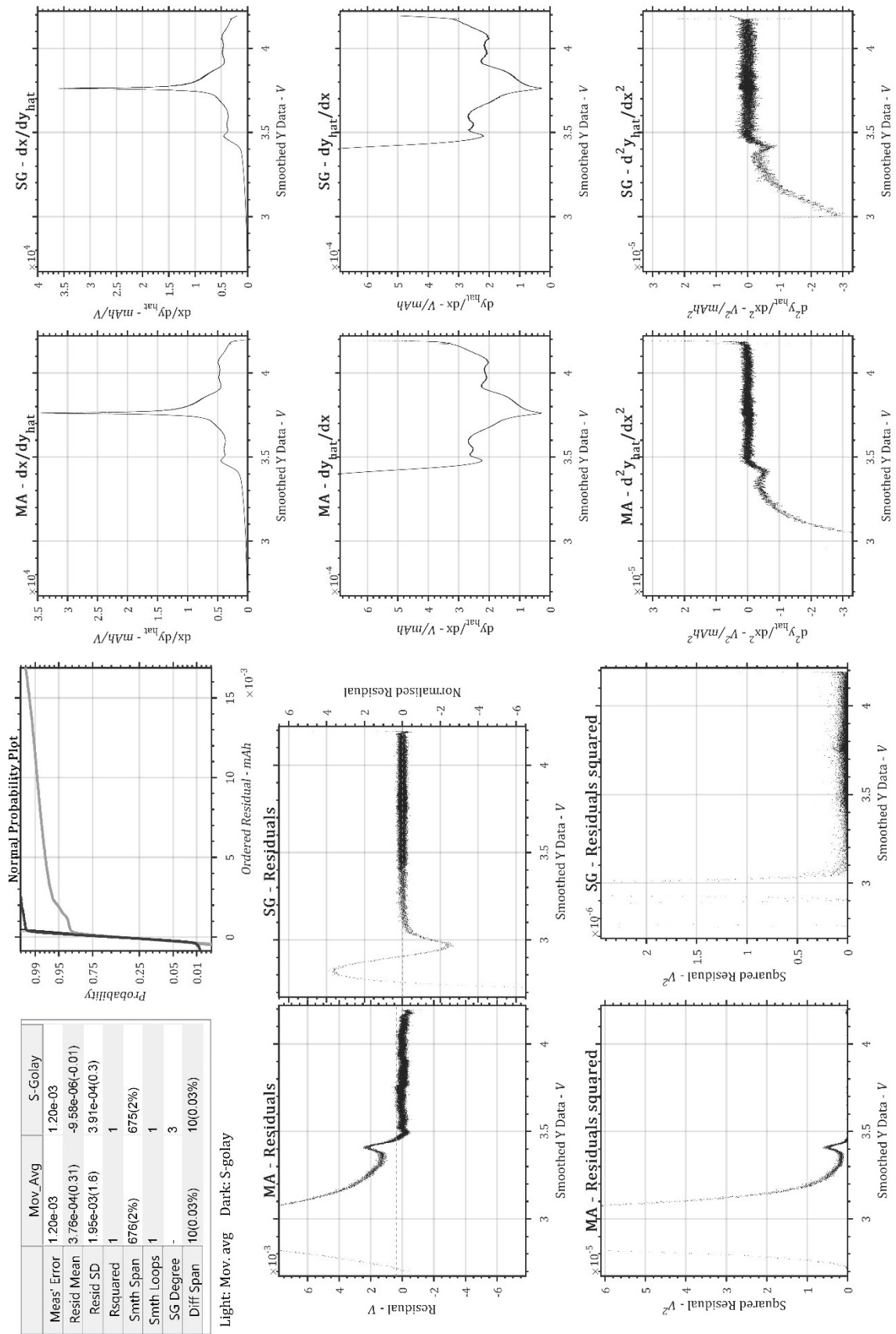


Figure A1: Residual analysis – large span, few loops

	Mov Avg	S-Golay
Meas' Error	1.20e-03	1.20e-03
Resid Mean	1.49e-04(0.12)	-7.44e-07(-0.00)
Resid SD	1.18e-03(1.0)	1.31e-04(0.1)
R-squared	1	1
Smith Span	102(0.3%)	101(0.3%)
Smith Loops	10	10
SG Degree	-	3
Diff Span	10(0.03%)	10(0.03%)

Light: Mov. avg Dark: S-golay

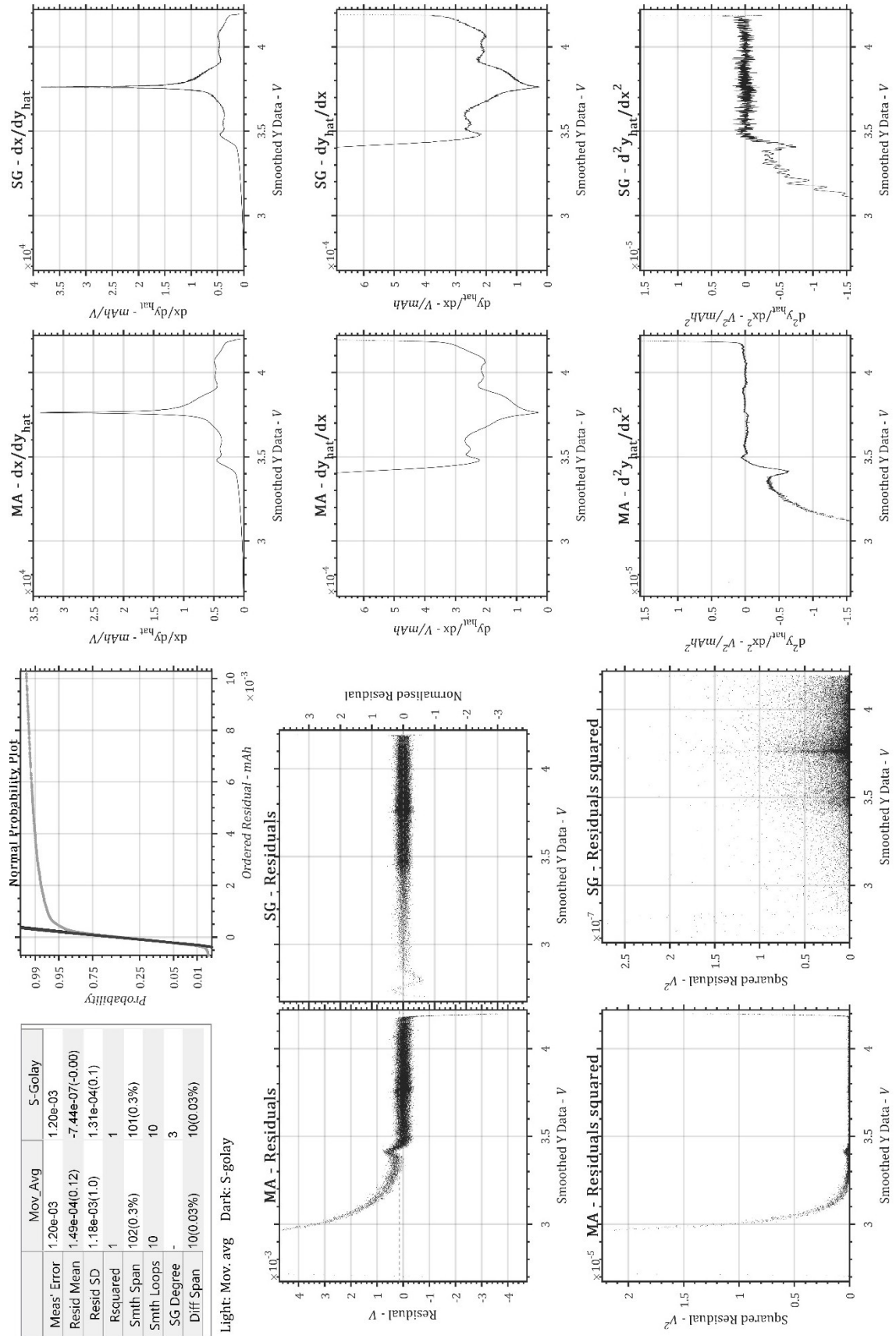


Figure A2: Residual analysis – small span, many loops

9.2 Appendix B

In Section 4.6.2, smoothing and the calculation of the derivative of the strain curves for four tests was performed. Residual analysis was performed to assess the smoothing of the four data sets. The graphs show the Residual analysis plots from the three data sets that were not shown in the main text.

- Figure A3: Fresh battery at 41°C
- Figure A4: Aged battery at 25°C
- Figure A5: Aged battery at 41°C

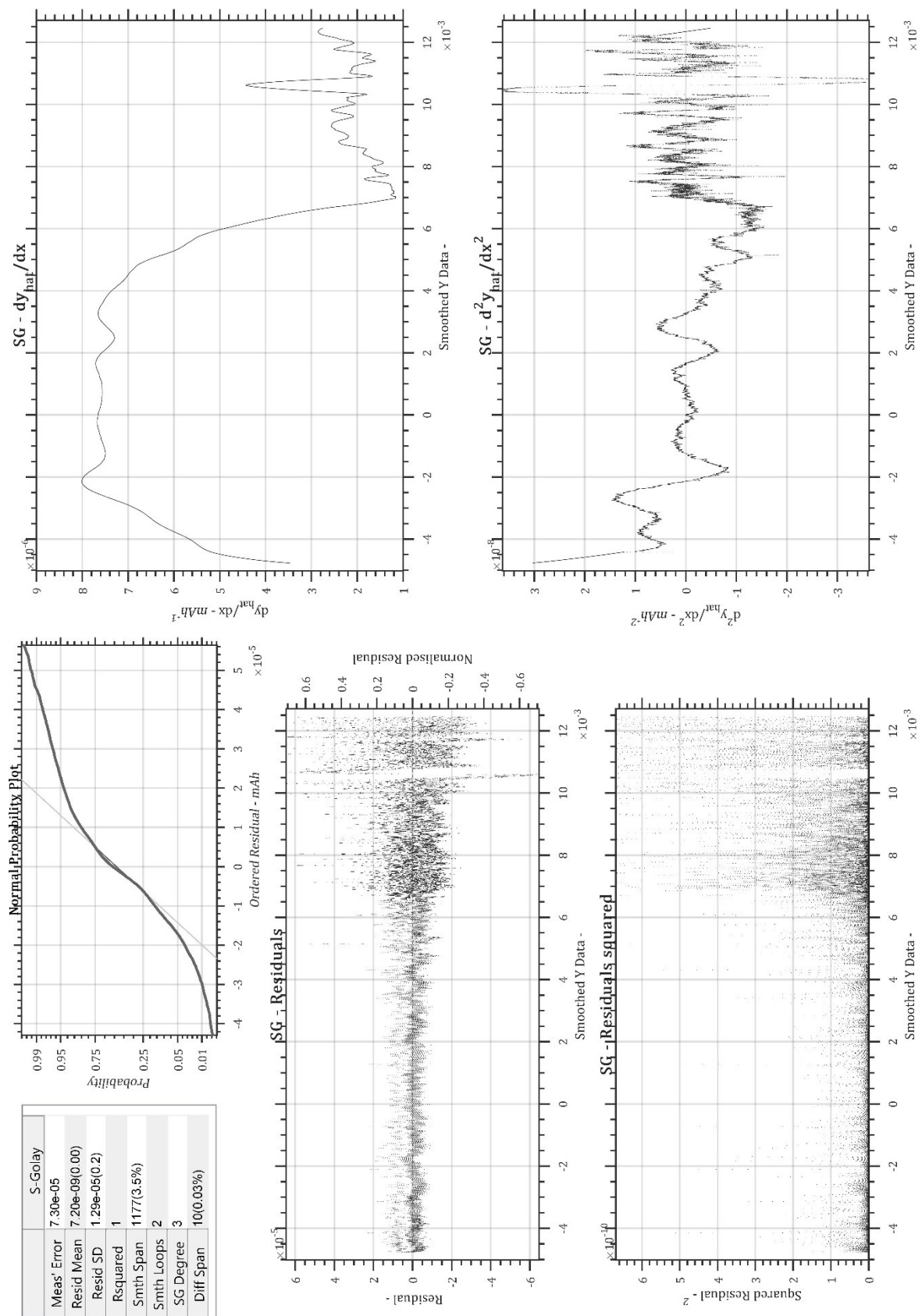


Figure A3: Residual Analysis plots for the smoothing and differential of the strain curve from 0.1C discharge of a fresh battery at 41 °C.

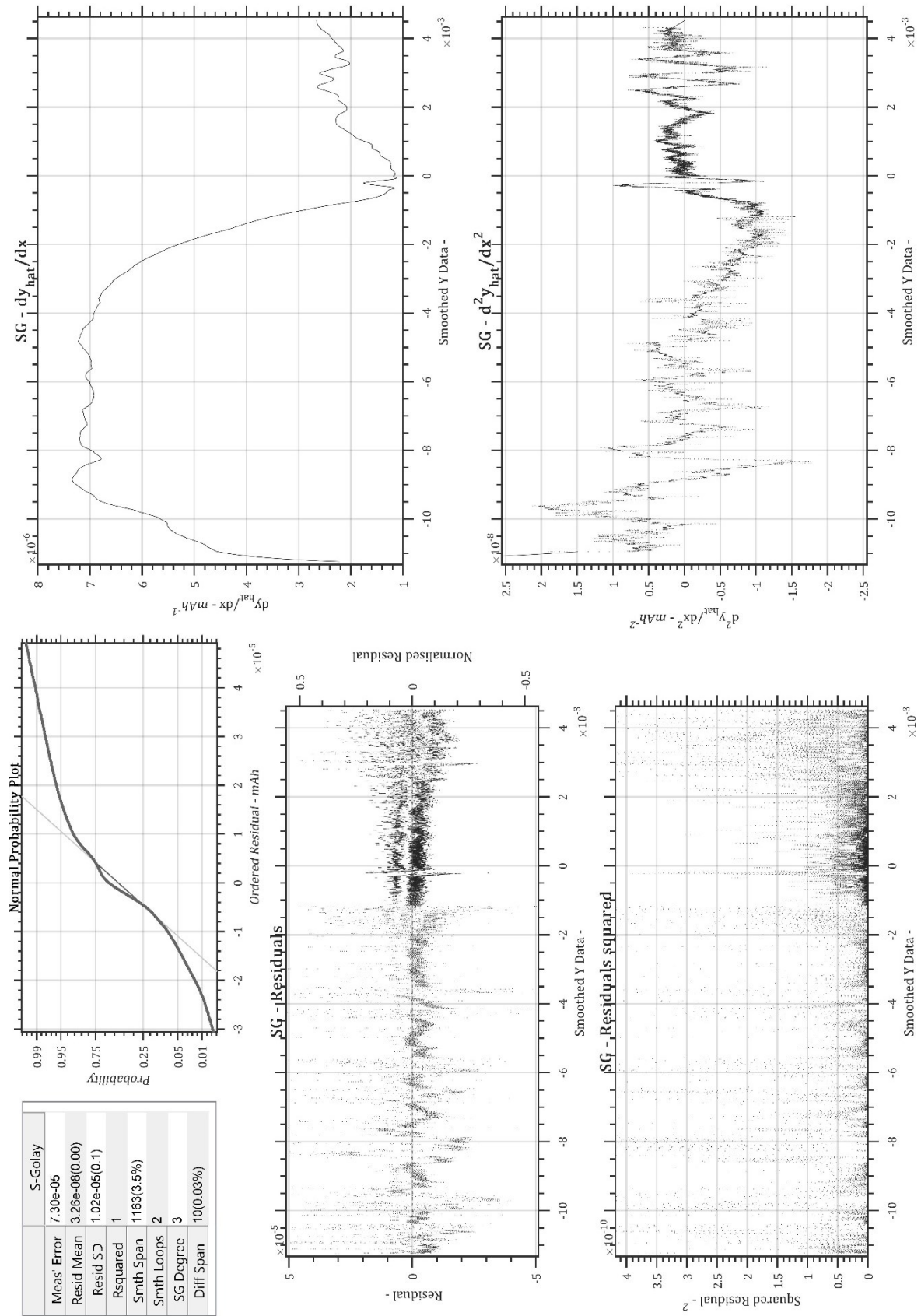


Figure A4: Residual Analysis plots for the smoothing and differential of the strain curve from 0.1C discharge of an aged battery at 25 °C.

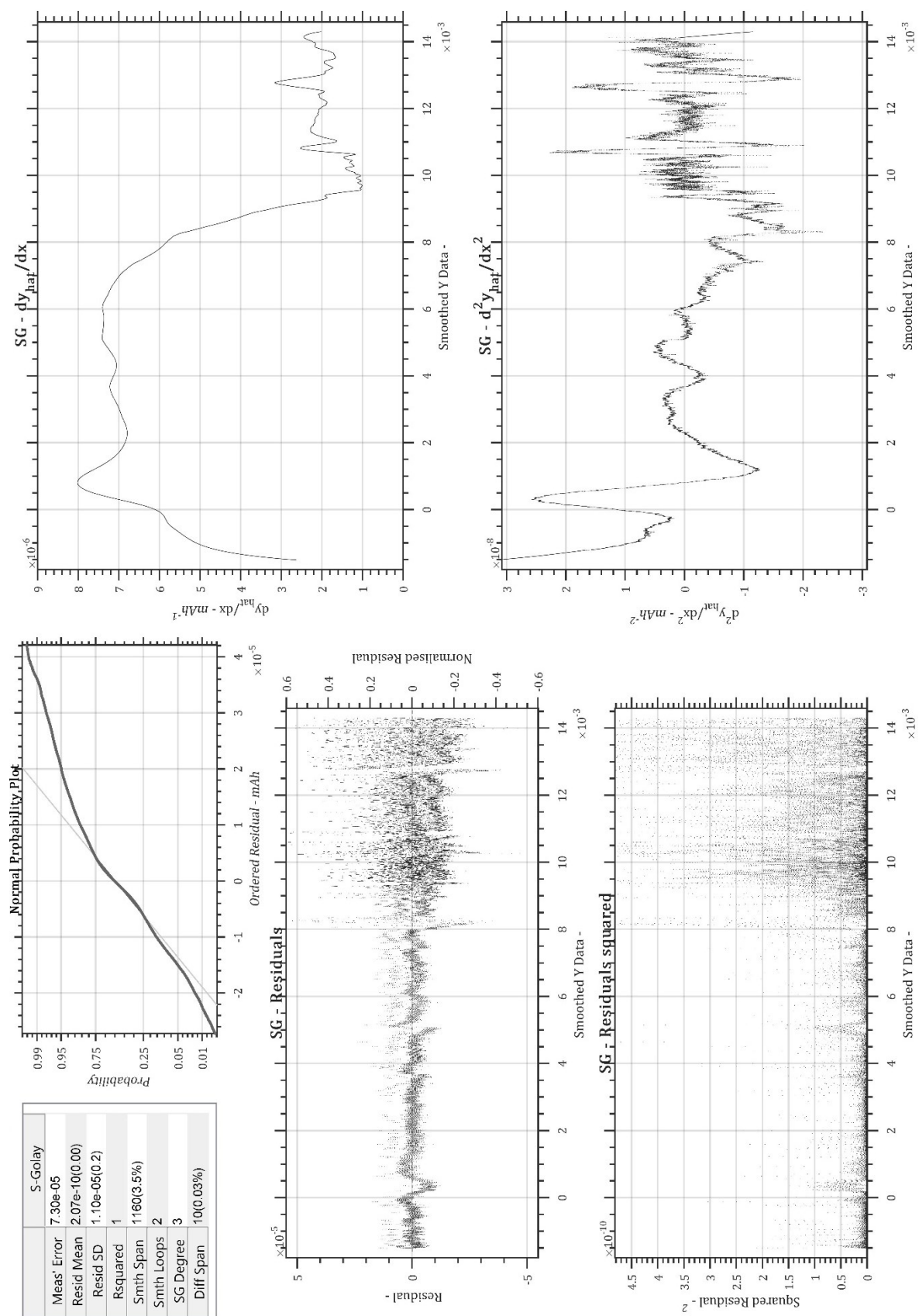


Figure A5: Residual Analysis plots for the smoothing and differential of the strain curve from 0.1C discharge of an aged battery at 41 °C.

9.3 Appendix C

In Section 5.5.1 it was stated: “All charging processes were isothermal and at 40 °C. All except three passed the isothermal test with a target temperature of 40 °C ± 1.2°C”.

To programmatically verify that experiments were performed under isothermal conditions the following pass-fail testing method was applied to the temperature data. The flow diagram of the test is shown in Figure A6.

Each temperature channel is tested individually.

There are three test inputs, Temperature data (T_{data}), Target temperature (TRG_T) and the acceptable temperature band ($\pm$) about the target temperature (Err_T).

There are three tests performed on each temperature channel. If any of the three tests for any channel are failed then the whole isothermal-test fails and visual inspection of the temperature data is required to determine if the experiment can be considered isothermal.

The three tests are applied to each channel individually and are described below and in Figure A6 with labels (a), (b) and (c).

- (a) Does the mean of the channel ($\bar{T}_n$) lie within the acceptable error band about the target temperature? Pass/Fail.

$$(TRG_T + Err_T) \geq \bar{T}_n \geq (TRG_T - Err_T)$$

The channel temperature data is then split into 50 equally-sized, consecutive ‘chunks’ and each chunk is individually tested in (b) and (c).

- (b) Do all Chunk-means lie within an error margin of $\pm 0.5Err_T$ of the channel mean? Pass/Fail for all chunks, if one fails the test is failed.

$$(\bar{T}_n + 0.5Err_T) \geq \bar{T}_{n,p} \geq (\bar{T}_n - 0.5Err_T)$$

- (c) Perform a Runs Test on the means for the 50 chunks to check for systematic patterns in the temperature. Pass/Fail.

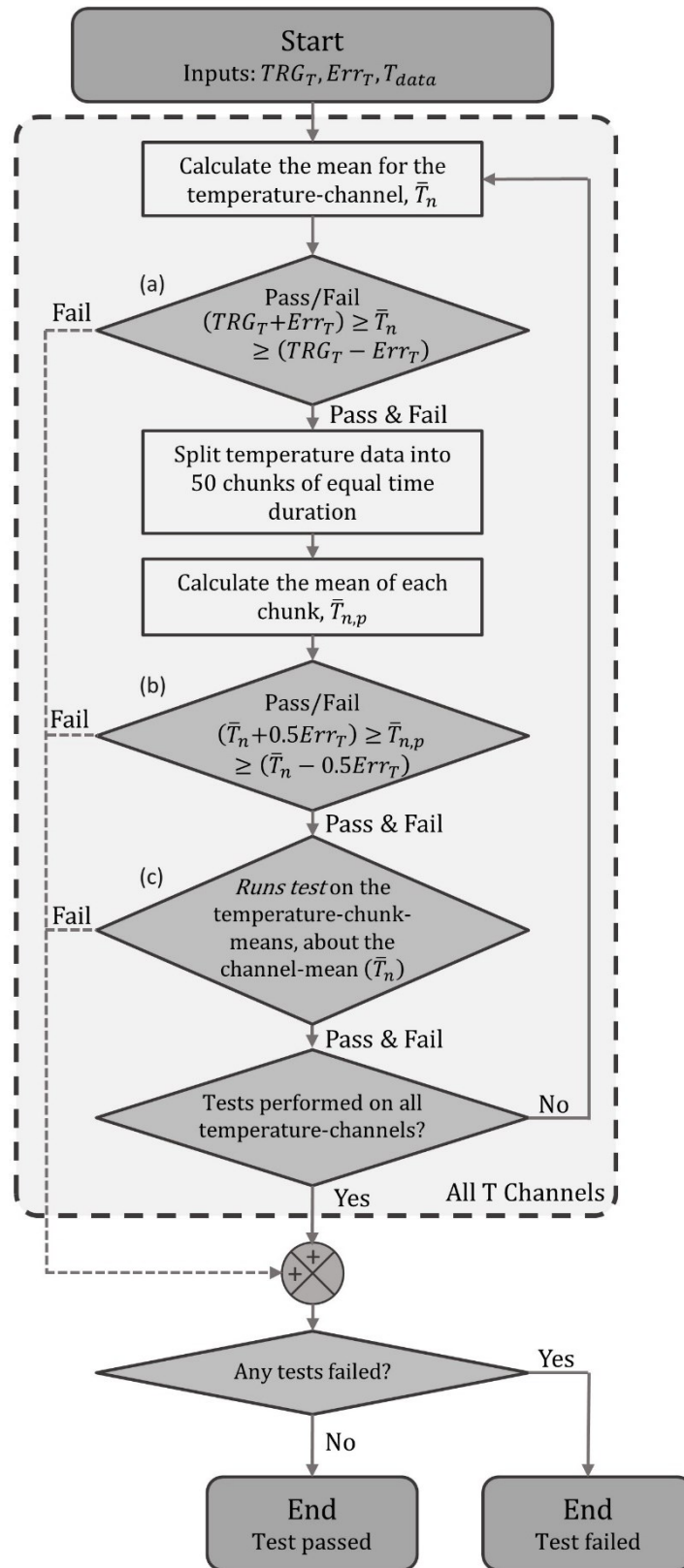


Figure A6: Programmatic isothermal test, flow diagram.

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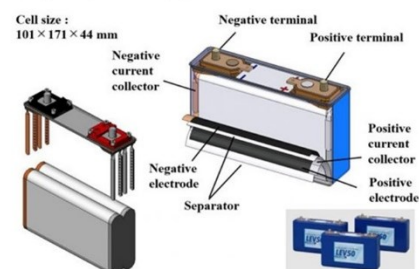
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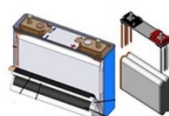
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