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Ultrasonic Calendering for Lithium-ion Battery Electrodes

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Abstract

The goal of high energy density and high power density lithium-ion batteries necessitates optimised electrode architectures with an efficient pore network. While calendering is the current industry standard for adjusting electrode porosity, the process offers limited control over the resulting microstructure. This thesis introduces a novel mechanical technique, termed *ultrasonic calendering*, as an alternative to traditional calendering. Inspired by ultrasonic welding technology, this method employs ultrasonic vibration to compact dry electrodes for the first time. The ultrasonic calendering of nickel cobalt manganese (NMC) cathodes resulted in enhanced electrochemical performance at high C-rates without compromising specific capacity. This improvement is attributed to a reduced tortuosity attained from alterations in pore size distribution, and the emergence of a unique carbon binder domain (CBD) morphology induced by the ultrasonic compaction. Conducted on industrially relevant film loadings, the performance of the ultrasonically calendered cathode was extrapolated to pouch cell format and demonstrated greater energy density and greater energy density at high rate. Whilst this work presents a technology in its infancy, a mechanistic understanding is proposed, and the process is demonstrated in detail. Valuable insights are provided towards the potential of ultrasonic calendering as it offers a new versatile platform to increase electrochemical performance through tuning both the pore structure and CBD phase. The results also support the prospects of harnessing mechanical processes for next-generation lithium-ion battery manufacturing.

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Abbreviations

Abbreviation	Definition
BSE	Backscattered electrons
C45	A carbon black powder from Imerys
C65	A carbon black powder from Imerys
CBD	Carbon binder domain
CEI	Cathode-electrolyte interphase
DEC	Diethyl carbonate
DEM	Discrete element method
DMC	Dimethyl carbonate
DSC	Differential scanning calorimetry
EC	Ethylene carbonate
ECM	Equivalent circuit model
EDX	Energy dispersive x-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EMC	Ethyl methyl carbonate
EV(s)	Electric vehicles
LFP	Lithium-ion phosphate (LiFePO_4)
LIB	Lithium-ion batteries
LVDT	Linear variable differential transformer
MIP	Mercury intrusion porosimetry
NMC	Nickel cobalt manganese (LiNiMnCoO_2)
NMP	N-methyl-2-pyrrolidone
PVDF	Polyvinylidene fluoride
SE	Secondary electrons
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SoC	State of charge
SoH	State of health
TBAClO ₄	Tetrabutylammonium perchlorate
VC	Vinyl carbonate
XRD	X-ray diffraction

1. Introduction Chapter

1.1 Introduction

Lithium-ion batteries (LIB) are at the forefront of our energy storage technologies ¹. Batteries have been a critical advancement for portable devices, and our global reliance is on a growing trajectory as we further develop our symbiotic relationship with technology ^{2,3}. Previously restricted to portable devices, recent advancements have indicated LIBs to be the future in transport as electric vehicles and for power grid supplementation as battery energy storage systems ^{4,5}. These expanded roles have become possible due to the high power and energy density applications possible with lithium-ion chemistries ^{6,7}, and the economic feasibility granted from the recent advancements in manufacturing despite the energy-intensive nature of production ⁸.

Lithium-ion batteries offer significant advantages, leveraging intercalation reactions to achieve high energy density, excellent reliability, and long cycle life ^{9,10}. These reactions were first identified in the 1970s, paving the way for the commercialization of lithium-ion cells by Sony in 1991 ¹¹. Sony's cell used a lithium metal salt cathode and a carbonaceous anode, the cell chemistry technology still widely utilised today ¹². While this stands as a testament to remarkable potential of LIBs, it also highlights a stagnation in manufacturing methods. Slurry casting of cathodes using polyvinylidene fluoride (PVDF) binder and N-methyl pyrrolidone (NMP) solvents, introduced in the 1970s, remains the industry standard ¹³. To meet the demands of the growing global market for electric vehicles ¹⁴, large-scale innovation in LIB manufacturing is urgently needed.

The primary barrier to the widespread commercialization of electric vehicles (EVs) remains their cost, with a substantial proportion attributable to the battery ^{15,16}. The UK automotive council recognise reducing the cost of large-platform batteries is crucial for enhancing EV adoption ¹⁷. Although battery costs have consistently decreased each decade with industry maturity ¹⁸, this progress is hindered by high energy demands ¹⁹ and reliance on scarce minerals ²⁰. Furthermore, concerns about driving range persist in the commercial EV sector ²¹, necessitating the development of high-capacity batteries whilst being capable of rapid charge and discharge cycles to support fast acceleration and reduced recharge times ²². This dual challenge of high power and high capacity has always been at the heart of battery engineering ²³. Fortunately, global decarbonization goals and net-zero targets have recognised EVs as a

potential solution ^{24,25}. This has spurred significant research efforts ²⁶, and is providing the opportunity to deepen the comprehensive understanding of the interconnection between material properties, manufacturing processes, and battery performance ^{27–30}. This relationship is critical in the development of next-generation LIBs for EVs.

1.2 Motivation

While novel battery chemistries continue to be a research priority, increasing emphasis has been placed on advancing manufacturing processes and understanding intrinsic process mechanisms at levels ^{31–33}. There are challenges associated with retrofitting novel materials to existing industrial methods ³⁴, which has narrowed the choice of viable chemistries, and difficulties with translating the intrinsic energy storage properties of active material into the performance characteristics of the final battery product. Performance losses are observed at the electrode, cell, and module and whole-system levels, with energy density at the system level often reducing to approximately 50 % of the cell-level energy density or less ³⁵. Packs and modules require structural support and thermal management considerations ^{36,37}. Improving efficacy across all stages of manufacturing is critical, with electrode production presenting significant opportunities for advancement. Cathode manufacturing in particular is more expensive and poses greater challenges compared to anode production ^{38,39}. Graphite anodes produced via slurry casting have demonstrated consistent and relatively uncontested production over time, offering practical gravimetric capacities starting at 372 mAh g⁻¹ ⁴⁰. Their primary emerging competitor, silicon, exhibits significantly higher performance, with capacities reaching up to >3000 mAh g⁻¹ ^{41,42}. In contrast, cathodes face more complex manufacturing challenges, including the use of a highly toxic solvent (NMP) ⁴³, and typically achieve lower gravimetric capacities in the range of 160-220 mAh g⁻¹ ⁴⁴. Focusing on optimizing cathode production is a route to unlocking the necessary improvements in battery performance.

Electrodes are complex porous structures that must support multiple electrochemical processes and pathways. Upon electrolyte immersion, the large microporous channels serve as lithium-ion diffusion pathways, while the surface area of the active material exposed to the electrolyte functions as the reaction interface ⁴⁵. The carbon binder domain (CBD), comprising a conductive additive and polymer binder, establishes the electronic network and ensures structural integrity ⁴⁶. However, it also disrupts the pore structure by forming a moss-like phase

that coats active material particles and occupies pore space. These considerations highlight the reliance of the electrochemical processes on both nanoscale and microscale structure ⁴⁷.

To enhance energy density, the industry employs calendering to densify porous electrode films by reducing pore volume ⁴⁸. Calendering offers electrochemical advantages, yielding higher-performance electrodes, particularly in terms of volumetric capacity, as the film volume is minimised, and the electrochemically active material is densified ⁴⁹. However, calendering induces significant structural changes within the electrode, adding complexity to the already limited understanding of electrode architecture ⁵⁰. The next progression in manufacturing necessitates a dual focus on comprehending electrode structure and the mechanisms by which it is modified to address this knowledge gap ⁵¹. This will advance the relationship with design choices and enable electrode optimization beyond empirical knowledge and iterative success approach.

1.3 Objectives

Porosity is a critical characteristic influencing electrode performance, playing a key role in determining both high-capacity and high-power capabilities. Calendering is currently the state-of-the-art industrial process to adjust electrode porosity. This research introduces an alternative approach, utilizing ultrasonic methods, to address the limitations of traditional calendering. The proposed technique aims to offer improved control over pore distribution and the structure of the conductive binder domain while effectively managing overall electrode porosity. These advancements would enable more precise manipulation of electrode architecture, enhancing its performance and functionality. The aims and objectives within scope:

- 1) To consolidate a polymer binder specifically designed for battery systems that is fully compatible with ultrasonic processing techniques.
- 2) To utilise ultrasonic calendering to produce a densified cathode film, followed by characterization of its physical properties and evaluation of the ultrasonic calendering process mechanism.
- 3) To assess the electrochemical performance of ultrasonically calendered cathode and correlate its performance with its physical and structural characteristics.

2. Literature Review

2.1 Lithium-ion Batteries

2.1.1 Electrode Composition

Lithium-ion batteries have two main elements, a cathode (a positively charged electrode) and an anode (a negatively charged electrode) ⁵². Both electrodes contain three different materials with distinct roles, displayed in Figure 2.1: An electrochemically active material, a polymer binder and a conductive additive ^{53,54}. The electrochemically active material serves as a chemical storage for the lithium-ions as they increase or decrease in chemical potential energy between the two electrodes. Common cathode active materials are lithium iron phosphate (LiFePO_4) or lithium nickel manganese cobalt oxide (LiNiMnCoO_2) ⁵⁵. Graphite is typically used for the anode ⁵⁶. The polymer binder forms bonds between particles to impart mechanical strength to the electrode ⁵⁷. This makes the electrode more resilient to physical distortion and expansion during electrochemistry ⁵⁸⁻⁶¹. PVDF is the primary choice for cathode binder ⁶². The conductive additive is an electrically conductive particle which reduces the ohmic impedance of the electrode. Carbon blacks are commonly used conductive additives ^{63,64}. Dispersing the carbon black to form an electronically percolating network is essential to create a complete electrical circuit and reduce electronic resistivity ⁶⁵⁻⁶⁷. Successful mixing will produce an electrode with these three materials distributed as homogeneously as possible, and ensure there is a uniform distribution of binder and conductive additive around the electrochemically active material (AM) ^{68,69}.

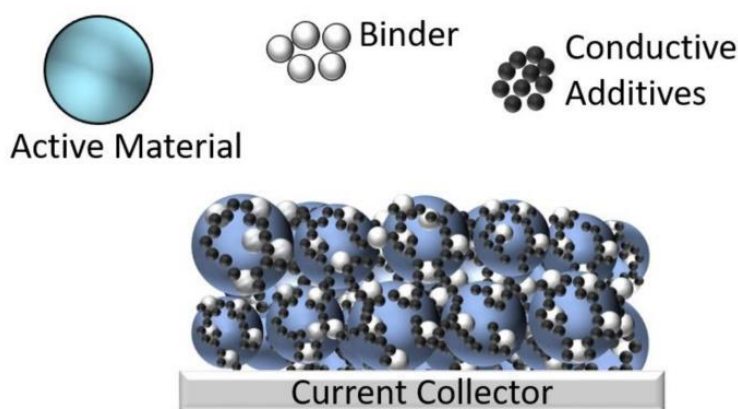


Figure 2.1 Diagram of a slurry cast electrode. ⁷⁰

Once a homogeneous mix has been achieved it is deposited onto a current collector. This is the contact point for conducting electrons between the electrodes ⁷¹. Copper is used for an anode

current collector. An aluminium current collector is required for the cathode because the cathode environment is more corrosive ⁷².

2.1.2 Battery Cell Architecture

Lithium-ion cells are constructed from an anode, a cathode, a separator and an electrolyte ⁷³, displayed in Figure 2.2. The electrodes are isolated from each other by the separator and the whole system is submerged in electrolyte. The electrodes are also orientated in parallel to minimise the average distance between their coatings. The electrolyte provides a transport medium for lithium ions to diffuse between the two electrodes ⁷⁴. The separator and the electrolyte have high electronic resistivity which prevents electrons from transferring directly between electrodes ⁷⁵. Once the battery is placed within a closed circuit, the electrons will have access to external circuit between the two current collectors; this higher electronically conducting path promotes the electrons to flow through this alternative route to the ions ⁷⁶. The circuit being incomplete until a load is connected prevents the battery from functioning until desired. The two different transfer routes for the lithium ions and electrons are critical for function; the isolated flow of electrons around the external circuit provides the electric current which is used to power the connected load ⁷⁷.

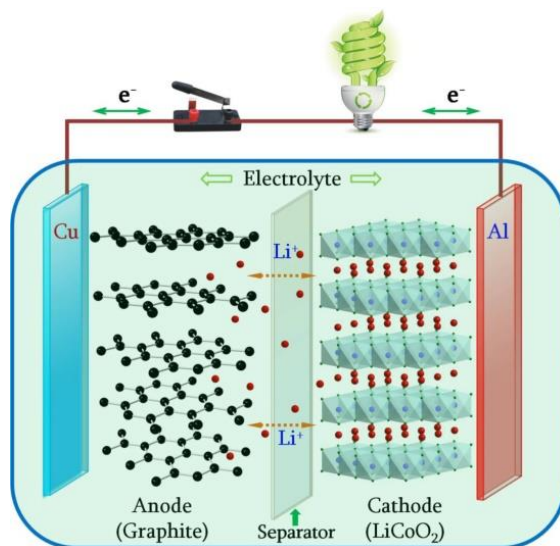


Figure 2.2 Schematic of a lithium-ion battery. ⁷⁸

2.1.3 Electrochemical Function

At the most fundamental level, a lithium-ion battery functions as an electrochemical energy storage system by converting stored chemical potential energy into electrical energy on demand ⁷⁹. This process is facilitated by the cathode and anode being able to react with electrons and lithium ions at different chemical potential levels. The anode stores the reactants

at a greater chemical potential energy level and the cathode stores the reactants at a lower energy level ⁸⁰. External electrical energy is required to drive the migration of ions from the cathode into the anode and increase the total chemical potential energy of the system. In this state the battery is charged. When the charged battery is included within a completed electrical circuit, the lithium ions and electrons will return to the cathode. During this, high voltage electrons will be conducted through the external circuit. The flow of electrons is known as a current. This cycle is repeatable which is imperative to lithium-ion being reusable energy storages devices.

The voltage produced by the battery, known as the open circuit voltage (V_{OC}) is dependent on the chemical potential difference between the anode (μ_A) and the cathode (μ_C) ⁸¹. Equation 2.1 displays this relationship, (e) represents electron charge.

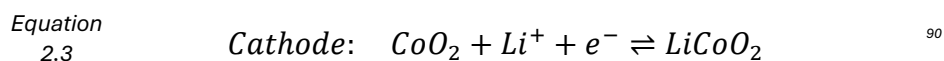
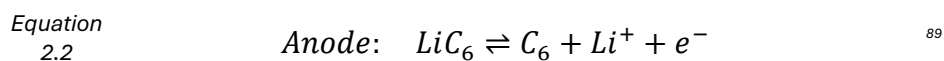
$$\text{Equation 2.1: Open Circuit Voltage} \quad V_{OC} = \frac{\mu_A - \mu_C}{e} \quad 81$$

2.1.4 Charging and Discharging

A lithium-ion battery cycle consists of two functions: discharging and charging. Charging and discharging are antagonistic. Charging involves a net intake of electrical energy from an alternate source to increase the chemical potential energy of the system, the electrons and lithium ions move from the cathode to the anode and are stored at a higher potential energy ⁸². Discharging uses the gained chemical potential energy to release electrons to power a connected load, converting chemical potential energy to electrical energy. This is the premise for how a battery functions as an energy storage system. The efficiency of the two functions is important because it dictates the performance of the storage system ⁸³.

Oxidation and reduction reactions asynchronously occur at both electrodes. During charging, one electrode will be oxidized whilst the other electrode will be reduced. The inverse occurs during discharging. A charged lithium-ion battery will have most lithium ions chemically reacted and stored in the graphite anode. During discharge an oxidation reaction occurs within the anode to release lithium ions and electrons. After the reaction, a graphite intercalation compound will be formed as the unbonded ion remains between the layers of graphite ⁸⁴. The lithium ion will deintercalate out the graphite and diffuse into and through the liquid electrolyte ⁸⁵, via the solid electrolyte interphase (SEI) layer. The electrolyte has a high ionic conductivity allowing the lithium ion to diffuse through the bulk of the electrolyte. The lithium ion will diffuse through the electrolyte surrounding the anode, to the separator, permeate the separator and

diffuse through the electrolyte surrounding the cathode until it reaches and diffuses through the cathode-electrolyte interphase (CEI) layer at the cathode ^{86,87}. The lithium ion intercalates into the cathode and reacts with an electron and the active material salt to form a lithium salt by a reduction reaction ⁸⁸. This can be summarised into two reversible half-cell reactions ¹⁰. Equation 2.2 and Equation 2.3 display the reaction in a graphite anode and lithium cobalt oxide (LCO) cathode during discharging. For charging, these reactions will be inverted.



The electrolyte exhibits high electronic resistivity and high ionic conductivity ⁹¹, preventing the direct transport of electrons generated during redox reactions across this medium, whilst allowing ionic transport. In contrast, the conductive additive incorporated within the electrode possesses high electrical conductivity ⁹¹. Electrons released from the active material are conducted to the nearest conductive additive and subsequently propagate throughout the percolating conductive network to the respective electrode's current collector ⁹². As the current collectors are electrically connected via an external circuit, the electrons are then conducted to the opposite electrode's current collector. An effective conductive additive network requires sufficient distribution throughout the electrode; this facilitates efficient electron transport and ensures the availability of electrons for redox reactions across the active material. The resistance that lithium ions and electrons encounter during this process and the chemical potential of the redox reactions are primary factors influencing the cell's capacity and overall energy efficiency.

2.2 Important Battery Characteristics

2.2.1 Specific Capacity

Specific capacity and energy density are two important metrics of batteries. Specific capacity represents of how much capacity can be discharged per unit mass (mAh g⁻¹). The difference between the theoretical and practical capacity of the active material arises because the theoretical capacity assumes full utilisation of the active material. However, this requires maximal extraction of lithium which is difficult to practically achieve. For NMC662, the practical

capacity is 160-180 mAh g⁻¹. Specific capacity is always dependent on the voltage window of the cell ⁹³. Typical lithium cells function between a lower limit of around 2.7 volts and an upper limit of 4.3 volts. Specific capacity is also highly influenced by the active material chemistry ⁹⁴. Nickel in NMC releases more lithium than cobalt and manganese within the typical voltage window; therefore, if the NMC salt has a higher nickel content it will have a higher specific capacity. NMC881 represents a stoichiometry of 8:1:1 nickel, manganese, cobalt. It is made of 80 % nickel, compared to a nickel content of 60 % in NMC622. Compared to NMC622, NMC811 produces a greater capacity. This is demonstrated in NMC811's 220 mAh g⁻¹ practical capacity ⁹⁵.

2.2.2 Energy Density

Lithium ion chemistries are favoured for their high energy density ⁹⁶, a metric which represents how much energy is contained within a given volume of battery ⁹⁷. The automotive industry is primarily interested in the volumetric energy density ⁹⁸. This interest originates from the fact that the battery must conform to the spatial limitations imposed by the vehicle's design. Cells made from the electrodes are arranged into modules which are further arranged into packs to make the complete battery. This vastly reduces the electrochemically active volume inside the battery, reducing the capacity ³⁵. The electrode composition includes electrochemically inert components, such as binders and conductive additives, which are essential for structural integrity and electronic conductivity but reduce the overall fraction of electrochemically active NMC material. Furthermore, the electrode coating must be deposited onto a current collector. Extending beyond electrodes, the cell architecture comprises of separators and external casings, which contribute to mechanical stability and safety but do not participate directly in electrochemical reactions ⁹⁹. The arrangement of cells in modules also creates void space as the tessellation of cells is not 100 % effective ⁹⁹. The effective volumetric energy density of batteries can be more than halved compared to the electrode level, with some displaying a volumetric-cell-to-pack ratio of approximately 0.4 ¹⁰⁰. The current pack level of NMC batteries reaches 250 Wh L⁻¹, despite using cells with a 500 Wh L⁻¹. This reflection drives the goal of increasing the cell level of batteries to 1000 Wh L⁻¹ by 2030, in order to allow EV to meet EUCAR's range requirements ¹⁰¹. Energy density is commonly used as a metric for packs because the cell pack architecture can be more influential than the electrode performance.

The specific capacity of electrodes and volumetric energy density of the cell are both important and usually positively correlate because increasing the available capacity provides more

current which provides a greater energy output. This attracts interest to improve either aspect and encourages similar design principles in electrode manufacturing: to create the most efficient and homogeneous electrode practically possible ^{102,103}.

2.2.3 Power Density

Power refers to the ability of the battery to charge or discharge a large amount of energy at a high rate ¹⁰⁴. Batteries supply energy to a circuit however the load of the circuit may increase or decrease depending on its function. Batteries must be able to compensate the surges in demand. Electrochemical processes within an electrode are more efficient at low power rates; increasing the power demand increases the rate of the processes and reduces the efficiency. Kinetic limitations of the electrochemical reactions and diffusion of lithium ions arise at high power ^{105,106}. This leads to more polarisation and less transfer of energy ¹⁰⁷.

2.2.3.1 C-rate

C-rate quantifies the rate at which the battery charges or discharges. This is important because it indicates how quickly the battery is charging from 0-100 % state of charge. A battery operating at 1C will discharge in 60 minutes. A high c-rate of 5 will conclude the charging in 12 minutes. A low c-rate of 0.1C will charge in 600 minutes. Evaluating battery performance in terms of C-rate provides a standardised framework which enables direct comparison across different systems. This accounts for the relationship between the power delivered and the battery's capacity and normalises performance irrespective of cell size or chemistry. It is more demanding for a 1 kWh battery to deliver 10 kW of energy compared to a 1000 kWh battery; c-rate considers this factor; these batteries would be functioning respectively at 10C and 0.01C.

$$\text{Equation 2.4} \quad C \text{ rate} = \frac{\text{current (A)}}{\text{capacity (Ah)}} = \text{discharge time}^{-1} \text{ (hours)}$$

2.2.3.2 Polarisation

The redox reactions of the half-cell reactions within the cell dictate the theoretical voltage output of the full cell, shown in Equation 2.1. The change in chemical potential energy causes an overpotential in the half cells. An overpotential is the increase in voltage over the equilibrium potential of the cell to drive the processes. The difference between the two overpotentials in the anode and cathode will equate to the voltage each electron possesses. Polarisation is a minimisation of the overpotential in either of the half-cell reactions, caused by internal resistances in the process ¹⁰⁸. This results in a smaller voltage difference between the

electrodes and the yield of lower voltage electrons, Figure 2.3 displays the voltage decrease and the attributable processes for the voltage loss. The consequence is a reduction in electrical energy produced per equivalent chemical potential energy. The greater the sum of internal resistance, the greater the drop in voltage. An additional consideration is the voltage window of cells. Cells have a lower voltage cut-off, therefore the high resistance manifested from large current densities lead to underutilisation due to a premature reaching of the cut-off voltage ¹⁰⁹.

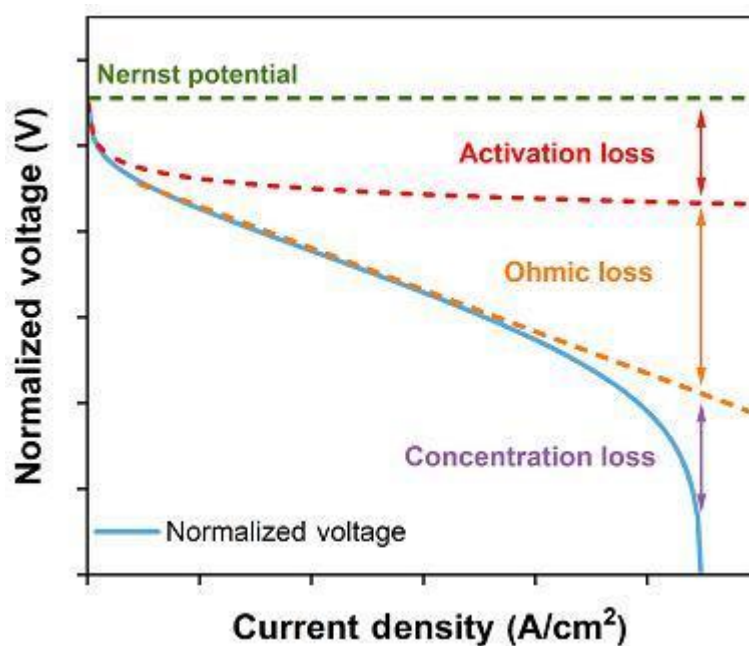


Figure 2.3 Polarisation curve for aqueous redox batteries. Indicates a lower voltage increasing with current density. ¹⁰⁸

2.2.3.3 *The antagonistic relationship between power density and energy density*

A battery capable of high-power demands design constraints which reduces the resistances of both lithium ions and electrons. Electrodes with high resistances at high c-rates suffer from underutilisation because ions are prevented from diffusing and intercalating towards the base of the electrode ¹¹⁰. The diffusivity of lithium is much greater through the electrolyte than through the active material ¹¹¹. Cells operating at the upper limit of kinetics will invoke the accumulation of ions around the active material and cause large ionic concentration gradients ^{112–114}. The high concentrations are formed from the build-up of ions accumulating near the active material interfaces occurs because the ions cannot diffuse/intercalate into the active material particles fast enough ^{115–117}. This causes an ionic wave front and inhibits the access of ions to the base of the electrode ^{118,119} due to depletion of ions along the longer pores ¹²⁰. A basic solution to this has been to increase the porosity in the electrode. This provides better ionic pathways however sacrifices energy density due to the decrease in electrode material density.

2.3 Industrial Lithium-ion Battery Production

2.3.1 Overview

The production of cells encompasses the manufacturing of cell components from raw materials to construction of the final cell ¹²¹. The overall process, as seen in Figure 2.4, shows the approach for manufacturing electrode before using these components to create a cell at the cell assembly. The production of cathode and anode share similar aims and objectives however because anode is manufactured from different materials to the cathode, the process parameters and the specific challenges faced in manufacturing vary ¹²¹. Cathode manufacturing is the primary focus in this explanation but both electrode fabrications involve a mixing, casting, drying and calendering stage.

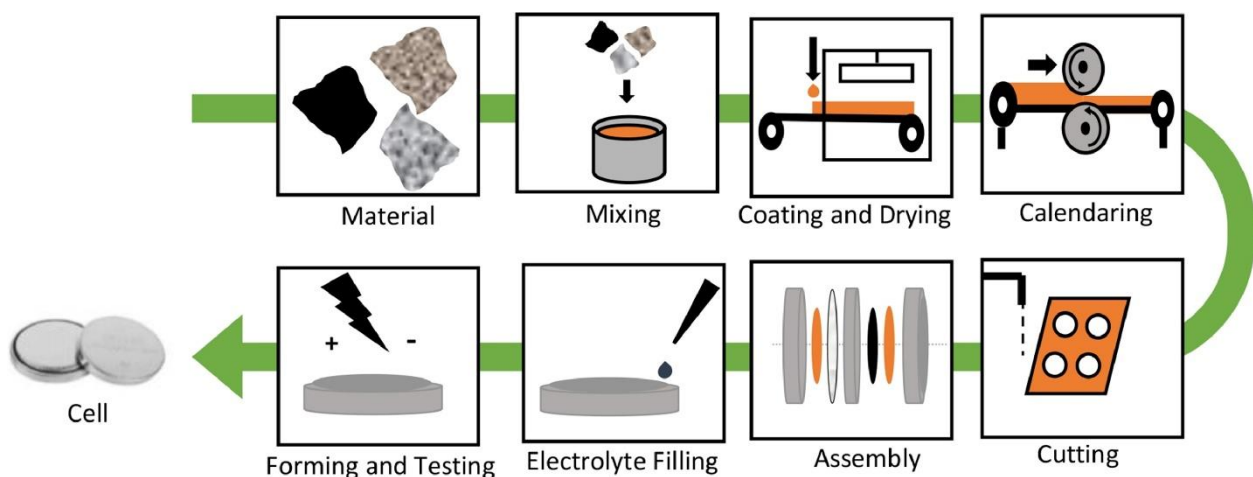


Figure 2.4 Lithium-ion cell manufacturing process using slurry casting methods. ¹²¹

The microstructure during the manufacturing process is finalised during calendering. The microstructure is initially formed during mixing and alters during every stage until calendering. The properties of the microstructure changes significantly, starting in solution and finishing out of solution. The manufacture of the electrode in series also complicates the process, upstream processes influence downstream processes and add additional design considerations at each stage.

2.3.2 Upstream of Calendering

2.3.2.1 Mixing

The purpose of mixing is to create the desired slurry for an electrode. Mixing is primary process towards creating a homogeneous slurry, as downstream processes introduce separation forces and do not have dispersive mechanisms ^{122,123}. Quality assurance of this process requires the

formulation of the correct electrode composition and effective mixing to disperse the different materials. The components: active material, binder and conductive additive can be difficult to mix. The cathode active materials used are typically reactive with water and will degrade in the presence of non-anhydrous conditions; therefore an organic solvent must be used within anhydrous conditions ⁹⁵. PVDF, the typical polymer binder, is highly resilient and requires a volatile solvent to dissolve. NMP is employed to fulfil this challenge, a toxic organic solvent capable of dissolving PVDF ¹²⁴. The particle size of NMC is much greater than PVDF and carbon black (approximately 10 μm compared to 100 nm). This poses problems because dispersion is more difficult with a multitude of particle sizes ¹²⁵ and agglomeration of materials is especially favoured for nanoparticles. This is because particle size is inversely proportional to surface area; therefore, smaller have a much larger surface area for interfacial forces ^{126,127}. Particles and aggregates of carbon black surround the NMC particles and flocculate ¹²⁸. A large amount of shear force is necessary to break up these agglomerates because the NMC, which makes up more than 90 % of the solid content in the mixture, cannot penetrate these agglomerates due to being significantly larger than the carbon black. Formulations with a high solid content of NMC helps towards increasing the shear strain rate to break up the carbon black agglomerates ¹²⁹. This is achieved by implementing a low mass of solvent because NMC already contributes to a large percentage of the solid loading. The carbon black agglomerates also form highly porous structures. NMP can be drawn into these structures reducing the effective solvent in the mixture. This solvent will be locked up until the agglomerate disintegrates. This also increases viscosity which affects casting. It is also desirable to break down the carbon black agglomerates to form a percolating carbon black network. The aim is to use the minimal amount of carbon black to form an effective electronic network. Adding additional carbon black to compensate for ineffective mixing will decrease the capacity of the cell and hinder the rheology of the slurry, potentially generating defects ¹³⁰. Electronic percolation can be achieved with relatively additive low content in polymers (<1 %) ^{131,132}, and in electrodes (<3 %) ¹³³.

Effective mixing involves preventing agglomerates from forming, the breakdown of pre-formed agglomerates and equal dispersion of all the components throughout the solution. This creates a homogenous mixture and prevents components being isolated or potentially destructive ¹³⁴. A homogeneous mixture is advantageous because, by definition, the components will be equally distributed. This standardises the mixture and creates uniform properties. This is critical to electrode manufacturing because electrode chemistry involves transport processes that traverse networks – the porous channels for ionic conductivity and the carbon black

networks for electronic conductivity ¹³⁵. Homogeneity promotes the connectivity of these networks and ensures the entire mixture possesses the same properties ¹³⁶. Should this criterion be unfulfilled, the electrode will be non-uniform and possess different properties and electrochemistry at different local points across the structure ¹³⁷.

2.3.2.2 *Casting*

Casting involves distributing the slurry across a current collector. In industry, a slot die will distribute a fine even coating across an aluminium current collector for the cathode. Ideal casting aims to uniformly distribute the slurry across the current collector. However, the mixture may not be homogeneous; there may be large agglomerates from the mixing process that unsettle the mixture and cause a structured profile of the cast slurry ¹³⁹. They can accumulate near the edges of the casting, known as “heavy edges,” demonstrated in Figure 2.5. The consequence of additional thickness can deform the shape of the cell once assembled ¹³⁸.

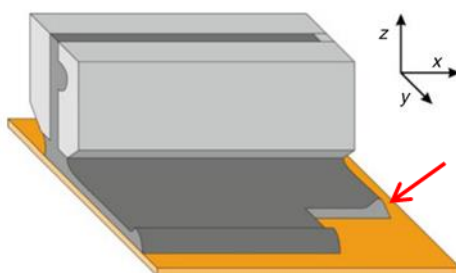


Figure 2.5 Slot die casting of slurry highlighting “heavy edges.” ¹³⁸

Casting causes particle alignment and separation of components. This is due to the slurry contents being dissolved in solution or in suspension; the two phases may be manipulated by different interactions or have different affinities for specific interactions. The suspended particles are free to move and are influenced by gravitational settling ¹⁴⁰. Gravity acts as a uniaxial force which moves particles to the base of the slurry. The greater the density of the particle, the greater the force generated. This causes the slurry to grade itself by density. NMC has a skeletal density around 4.70 g cm^{-3} . PVDF has a density of 1.78 g cm^{-3} . These are both greater than that of NMP 0.98 g cm^{-3} . Carbon black has a density of 0.18 g cm^{-3} , much lower than NMP. Sedimentation affects the particles differently because the particles have different densities, disrupting the microstructure between the large dense NMC particles and the carbon black. PVDF is initially; however, once precipitated, it will experience sedimentation. This demonstrates that gravitational forces overcome the buoyancy forces for NMC and PVDF; however, the buoyancy force of carbon black surpasses its gravitational force. This will cause

carbon black to rise to the surface whilst NMC and PVDF will settle towards the current collector.

The viscosity of the solution can be increased to reduce sedimentation as it would increase the resisting forces to particle rearrangements. This involves reducing the solvent used or increasing the proportion of the PVDF binder. This would align with the industry goal of reducing NMP usage, however, the viscosity of slurries is relatively high for the process. Increasing the viscosity further increases the risk of casting failures¹²⁸. Excessively viscous slurry is susceptible to forming agglomerates, suffers from low pumpability and struggles to be distributed to the boundaries of the current collector¹⁴¹. Low viscosity slurries can have too excessive flowability and be distributed too far, spreading beyond the current collector boundaries. The NMP slurry solution having shear thinning properties (becoming less viscosity with flow rate) helps with the handling of the slurry and the coating process^{142,143}.

2.3.2.3 *Drying*

Drying is an energy-intensive process and requires a large portion of infrastructure at an industrial scale¹⁴⁴. NMP is a highly volatile, expensive and toxic solvent. Disposal is regulated and economically disadvantageous. Slurries possess a solid content of approximately 60-70 %¹⁴⁵. Therefore, for a given throughput of electrode, the NMP used in the production will be equivalent to more than 30 % of the slurry mass. The disposal of NMP at this scale would introduce excessive waste and encourages the recycling of NMP. Industrial drying is conducted in atmosphere-controlled dry rooms. The higher temperatures and air filtration system remove NMP, keeping the partial pressure of NMP high. This leads to an increased rate of vapourisation for rapid drying. The closed system contains the NMP vapour released. The NMP is cooled, condensed and re-used continuously. Due to the cyclic use of NMP limiting usage is crucial¹⁵; the quantity of NMP used directly correlates to the energy expenditure required for slurry drying. The volume of the dryer is influenced by the mass of NMP solvent incorporated into the slurry. The complete removal of NMP must be achieved for the final dry electrode product and because drying is a continuous process, conducted on a moving belt (approximately 60 m min⁻¹¹⁴⁷), a quicker vapourisation stage enables the use of a more compact dryer. This reduces the drying infrastructure footprint. Drying temperatures can exceed 150 °C²⁰ to encourage a higher vaporisation rate, which is beyond optimal on a microstructural level. The rapid drying promotes binder migration to the electrode surface^{148,149} and reduces coating cohesivity¹⁵⁰, but is more economically viable by increasing electrode throughput. The high temperature in drying

are combined with air filtration to decrease the partial pressure of NMP in the surrounding gas phase. This maximises the NMP pressure gradient between the solution and the air, which encourages gas exchange as the vapourised NMP is quickly removed from the system. Industrial-scale drying can be completed in less than a minute, at a roller rate of 1 m s^{-1} ¹⁴⁷, this demonstrates the need for >60 m long vacuum dryer. An intense drying stage is necessary for electrodes because the porous structure makes vapourisation difficult; half of the drying time is used to remove the final 10 % of the solvent¹⁵¹.

The drying process can greatly alter the electrode microstructure and introduce defects, especially inhomogeneity. Drying is a complicated process because it involves mass transfer between gaseous, liquid and solid states. The bulk solvent vapourises into a gas, shrinking the volume of liquid and receding the liquid boundary. This occurs until the active particles come into contact at the boundary and the superficial layer of liquid is vapourised. This is known as the film shrinkage stage¹⁵². The second stage is pore emptying, the solvent is currently only retained in the pores of the structure¹⁵³. Convection currents and vapourisation will draw the solution to the surface prior to be vapourised. The rapid vapourisation and convection currents of solution redistributes binder to the surface of the electrode, known as binder migration^{154–}

¹⁵⁶.

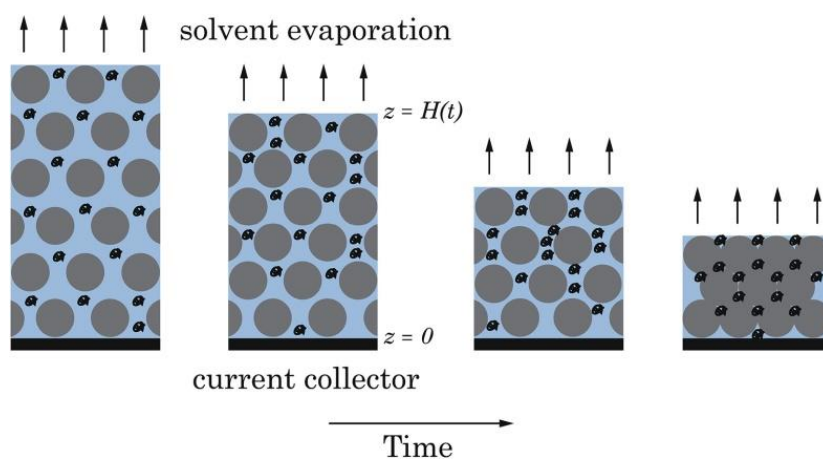


Figure 2.6 Diagram Illustrating the Binder Migration During Solvent Vapourisation.¹⁵⁷

PVDF is soluble of in NMP unlike carbon black and NMC. The mass fraction of PVDF in industrial cathodes approximate 2 %. This causes the PVDF to begin precipitating out during the pore emptying phase of drying. During this stage, the PVDF-rich NMP solution is convecting through the pores and evaporates at the surface of the cathode. This introduces a migration of PVDF towards the top of the cathode, away from the current collector because the solvent is

convected towards the top before vaporising and precipitating out the PVDF ¹⁵⁸, displayed in Figure 2.6. This redistribution of PVDF towards the top of the electrode introduces heterogeneity and reduces the electrochemical and mechanical performance of the film ¹⁵⁹. Adhesion strength between the electrode and the current collector reduces due to less PVDF present at the interface ¹⁶⁰. The lack of binder at the current collector inhibits sufficient bond formation ¹⁶¹. Good adhesion is imperative because degradation of the cathode and mechanical forces can shear the electrode from the current collector ¹⁶², disassembling the cell and permanently severing the electronic circuit, known as delamination ¹⁶³.

The higher distribution of binder at the electrode surface also increases the ionic resistance of the cell. Binder exhibits a pore blocking behaviour ¹⁶⁴, decreasing the effective diffusivity of the electrolyte ¹⁶⁵. Binder at the surface of the electrode will restrict the lithium ions diffusing into the electrode through the pores and will reduce the available NMC particle interface for intercalation ¹³⁸. Carbon black also experiences a migration towards the surface during drying. This is due to the carbon black being in suspension ¹⁴². This creates heterogeneity and less favourable electrochemical properties as there may be more ohmic resistance at towards the base of the cathode ¹⁶⁶.

The industrial drying process differs significantly to the laboratory-scale literature. Lab-scale experiments frequently will dry their electrode for up to 24 hours in a vacuum oven ¹⁶⁷ compared to a maximum of minutes in an industrial vacuum dryer. Ovens will operate around 100 °C with considerably less airflow than dryers. The vapourisation pressure of NMP in these ovens will be significantly lower. This results in a considerably lower vapourisation rate which minimises particle surface migration; Brownian motion is able to redistribute the migrated PVDF back towards the current collector ¹⁵⁷. The redistribution effect of Brownian motion is more impactful the slower the rate of NMP vapourisation.

Rapid drying also causes structural defects. ‘Mud-cracking’ can be an issue, especially with thick coatings ¹⁶⁸. The removal of the NMP causes film shrinkage which can cause local regions within the film to contract. This forms cracks as these regions contract, straining the cohesive forces of the film between them ¹⁶⁹. The cracks can act as larger electrolyte pores, increasing the effective ionic diffusivity of the film ¹⁷⁰; however, the cracks compromise the mechanical integrity of the coating.

2.3.2.4 *Upstream of Calendering Summary*

The stages upstream of calendering and some design considerations for each stage have been highlighted above in this section. It provides insight surrounding how the optimal decision for each choice is variable, why the ideal condition for processes can be antagonistic, and how NMP content in the slurry consequently effects the stages. The amount of solvent used was directly linked to mixing, casting and drying stages. How solvent mass influences agglomeration, sedimentation and binder migration, three causes of electrode microstructural defects, was also elaborated.

The most significant observations: the drying stage promotes minimisation of NMP however the coating and mixing stages requires NMP for homogeneous mixing. Sufficient NMP must be present to dissolve the PVDF binder and form a solution of sensible viscosity for processing; an incorrectly viscous solution reduces the capability of the mixer to produce enough shear forces to break down any agglomerates ¹⁷¹. Agglomerates vastly reduce homogeneity and effectively change the local proportions of NMC, PVDF and CB in the slurry and effect the final viscosity ¹⁷². A too low viscosity will enable high pumpability, but the slurry may distribute over the boundaries of the current collector. Viscosity also plays a critical role in the sedimentary effect of particles during the casting step, and the influence of binder particle migration and carbon black migration to the surface during drying ^{123,173}. These alterations negatively impact electrode homogeneity and electrochemical performance. Rapid drying employed for greater throughput also encourages dryers to be operated at high temperature to promote fast of the electrode. This exacerbates binder migration ^{122,148,174}.

2.4 Calendering

2.4.1 Aims

Calendering is the process that compresses the electrode to decrease the void volume in the electrode ¹⁷⁵. The final product after drying the slurry is a highly porous structure of the larger active material particles surrounded by the smaller conductive additive and polymeric binder particles. The porosity of the dried uncalendered electrode is approximately 50-60 % ¹⁷⁶. This shows on a volumetric basis, half of the electrode is pore space, providing no active material to store lithium ions. Energy density is one of the most important electrode metrics and can be optimised by manipulating the pore network with calendering ¹⁷⁷. Calendering also adheres the

electrode matrix to the current collector ^{178,179}, increasing the lifespan of the electrode due to higher adhesion bonding ^{180,181}. The contact resistance also decreases with higher contact between the electrode and current collector ^{182,183}.

2.4.2 Process

A compressive force is applied onto the cast electrode by passing the electrode through two rollers. The roller gap is less than the thickness of the electrode, leading to an increase in pressure, compacting of the electrode ¹⁸⁴. The electrode structure condenses as the electrode material and bonds deform whilst the electrode is forced between the smaller gap ¹⁸⁵. The particles rearrange themselves to occupy previous pore space and share more surface contact as the inter-particle distance shrinks ¹⁸⁶. Elastic and plastic deformation of both the polymer and active material particles occurs as the electrode is compressed into the smaller volume ¹⁸⁷. After passing through the rollers, the compressive load is removed from the electrode, and the electrode relaxes. During this relaxation, the elastic deformation reverses causing a minor increase in porosity, known as spring-back ¹⁸⁸. The plastic deformation is irreversible and will remain causing the final product's porosity (ϵ_{final}) to be lower than the initial porosity (ϵ_0) ¹⁸⁹. The restructuring of the particles into a smaller volume arrangement causes permanent densification of the structure. This change is demonstrated in Figure 2.7, the overall result is a higher material density and energy density as the new electrode occupies a smaller volume, retaining its mass but with less porosity ¹⁹⁰.

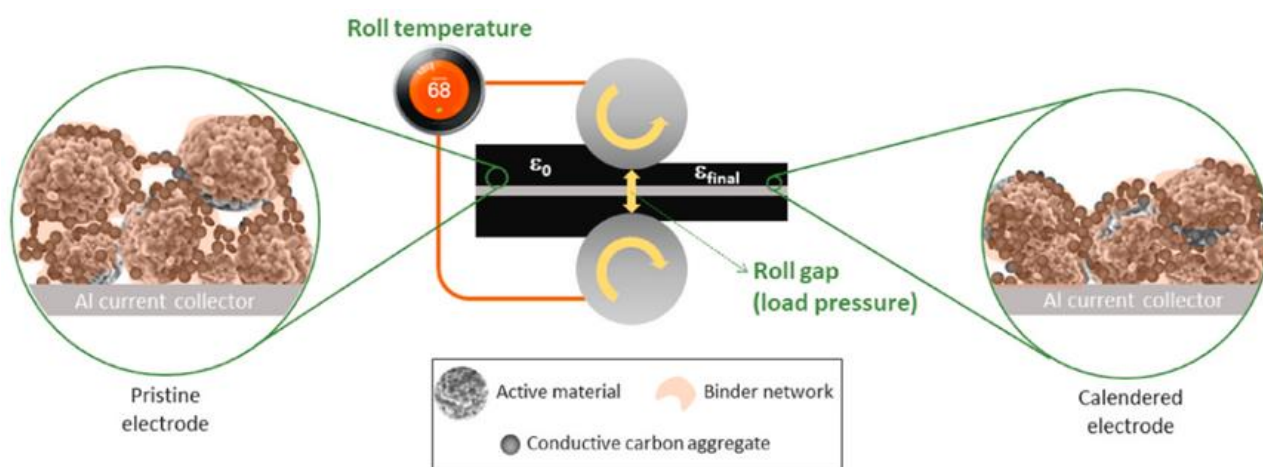


Figure 2.7 Calendaring of an electrode. ¹⁸⁹

At an industrial level calendering is a rapid process; the electrode belt is continuously fed through the rollers at speeds up to 60 m min⁻¹ ^{147,191}. This will be the same speed the belt traverses through the dryer. The rollers exert a compressive force of 50 to >150 MPa and operate at raised temperatures of >90 °C ^{183,189}. The elevated temperature encourages the electrode coating to be less brittle. The high pressures serve as the necessary mechanical force to deform the electrode from its initial porosity to target porosities ¹⁹². It is possible for calendering to cause damage and fracture the active material particles so the pressure and the time under load must be controlled ¹⁹³.

2.4.3 Electrode Changes During Calendering

2.4.3.1 *Microstructure Progression*

The electrode structure undergoes changes during calendering. This causes different properties to manifest depending on the final porosity ¹⁹⁴. Figure 2.8 documents a typical morphological progression of an electrode and the changes to its properties over progressive calendering.

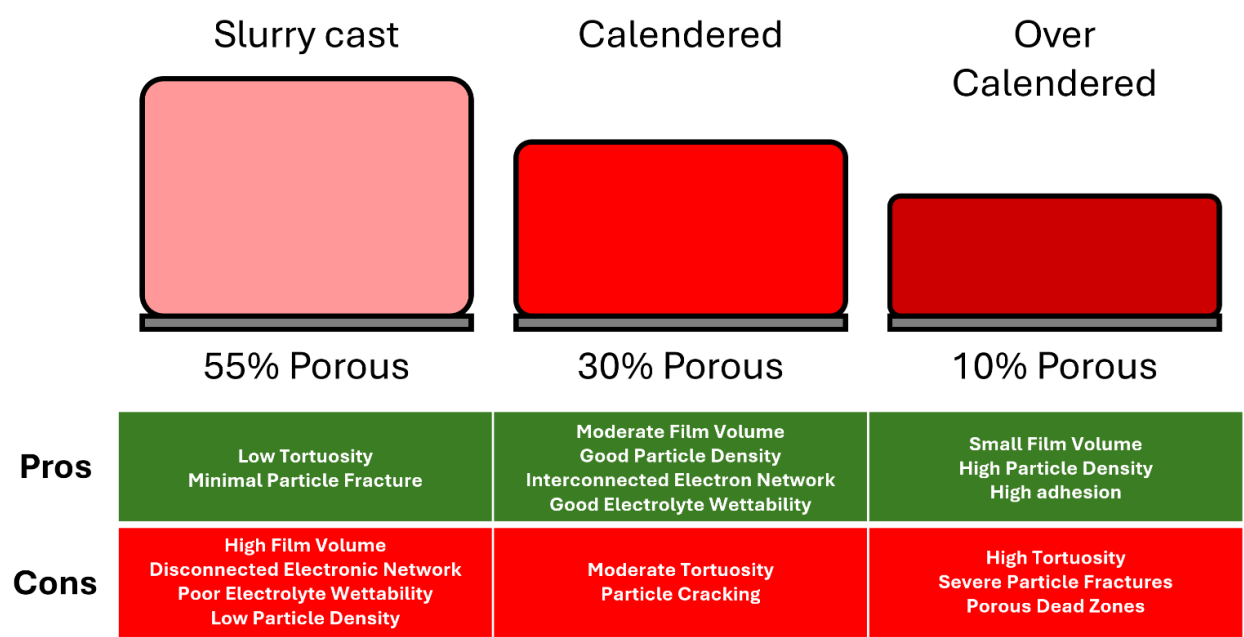


Figure 2.8 Electrode structure and characteristic progression during calendering. The slurry cast electrode has not been calendered.

Electrodes immediately after slurry casting occupy the largest volume. This is attributable to the initial microstructure of electrodes containing an abundance of pores ¹⁹⁵. The electrode has a high volume, a low particle density and a high surface area to volume ratio ¹⁹⁶. Compressing

via calendering compacts the particles together and eliminates pore space¹⁹⁷. This reduces the electrode's volume and creates more contact points between the NMC particles and the CBD phase¹⁹⁸, reducing the total exposed area of NMC within the electrode¹⁹⁹. This reduction increases the density of the film and increases the convolution (tortuosity) of the microporous network^{200–202}. It also compresses and restructures the PVDF and carbon black matrix^{203,204}, causing carbon black percolation throughout the structure if not previously achieved prior to calendering^{123,205}. This forms a more connected carbon black network, reducing electronic resistivity²⁰⁶. The large active material secondary particles are embedded into the PVDF network from the pressure, increasing cohesion from more contact points. The entire electrode is also pressed into the current collector, increasing adhesion between the electrode and the current collector²⁰⁷. Optimal calendering increases the cycle life of the electrode^{177,181,208}, despite some active material particles fracturing from the pressure²⁰⁹.

Electrodes can be overprocessed during calendering. The pressure to exerted during this compression causes excessive active material cracking²¹⁰; a defect which accelerates battery capacity loss^{211,212}. The excessive calendering also decreases the effectiveness of the electrode; the minimal electrode film volume is achieved at the expense of eliminating too much porous space. The increases the tortuosity of the porous network as pathways are constricted or sealed entirely. Dead zones are also created when active material is isolated from the bulk electrolyte and become electrochemically inert²¹³. There are some benefits to

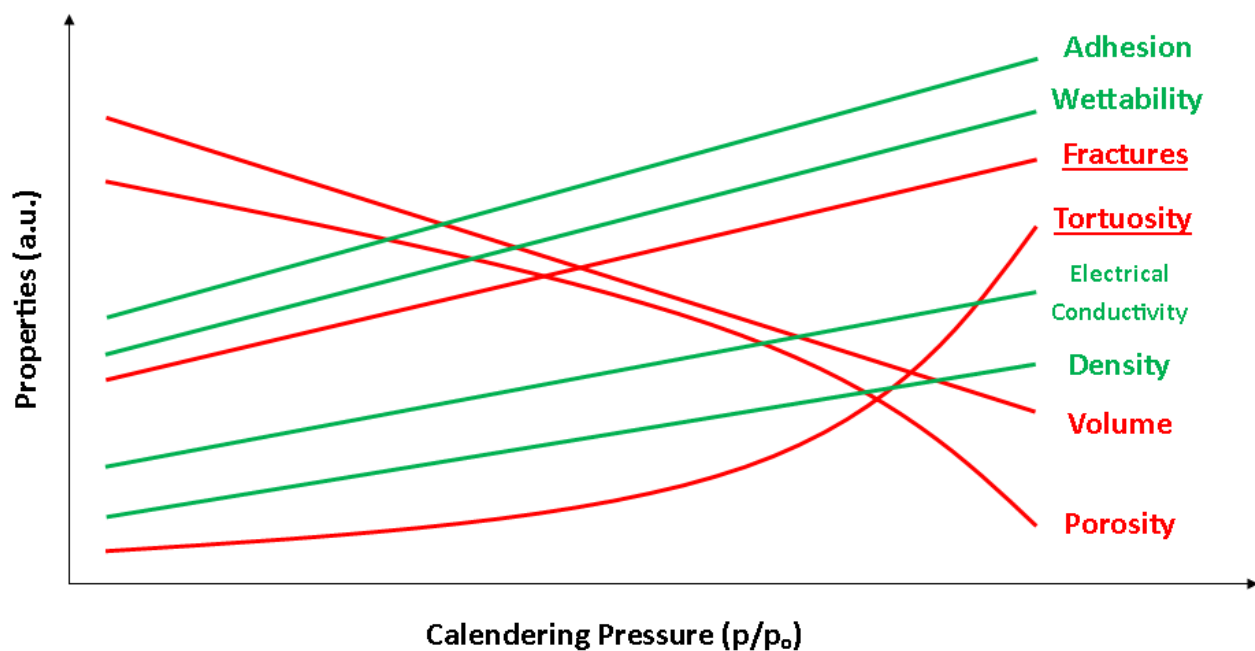


Figure 2.9 Illustration showing the property trends of electrodes with respect to calendering pressure. Green properties are desired to be maximised and red properties are desired to be minimised. Underlined properties have an undesirable correlation with calendering pressure. Trend lines are simplified: they only show an increase or decrease, not if the property changes linearly, exponentially or logarithmically.

the over compaction. The film occupies the smallest volume and adhesion is improved as the active material particles embed greatly into the current collector and interlock ^{214,215}, however, the previously explained drawbacks are too disadvantageous to warrant the benefits of the maximised electrode density and dissuades the calendaring of electrodes to this degree.

2.4.3.2 *Simplified Properties Overview*

Some important electrode properties are listed in Figure 2.9. The y-axis shows how each property progresses over increasing loads of calendaring. The property is coloured green if the ideal trend is for an increase with pressure and the property is coloured red if the ideal trend is coloured red. The figure shows that almost all the properties are improved with calendaring with the exception of particle fractures and tortuosity; the underlined two properties. Calendaring provokes particle fractures and increases the tortuosity of the porous network; both are detrimental to the electrochemical performance of the electrode.

2.4.4 Calendaring Pressure, Cracks and Porosity

Calendaring involves subjecting an electrode to intense pressures. The electrode can be traversing at 60 m min^{-1} on a continuous belt ^{147,216}. During calendaring, the cathode may need to be subjected to pressures of 300 MPa to compress the electrode to 30 % porosity ²¹⁴. This pressure is aggressive and may surpass the compressibility limit of the active material particles. This causes the large AM particles to deform and fracture ²¹⁷. This compromises the structure and adversely impacts the integrity and the electrochemical properties of the electrode ²¹⁸, e.g. cracks accelerating capacity fade ^{219,220}. The fracturing of particles becomes more prevalent with greater calendaring pressure, because more particles are subjected to pressures exceeding their fracture strength ²²¹. Despite this negative association with pressure, it is still beneficial to use employ relatively high pressure to reduce the electrode toward an optimal porosity. Work conducted by C. Meyer displays the relationship between line load and porosity for different compressibility factors, as shown in Figure 2.10 ²¹⁴. The cathode with a compaction resistance of 309 N mm^{-1} decreases from 57% to 26 % porosity after being subjected to a line load of 1050 N mm^{-1} .

The rate of porosity reduction diminishes with increasing calendaring force. This is a consequence of structural rearrangement increasing the surface contact between particles in the coating. Friction and bonds within the coating resist the compaction force. The increased

surface area during calendering promotes friction which resists the compressive force, known as compaction resistance. The surface area of particles in contact exponentially increases the denser the electrode becomes. This leads to the compaction resistance exponentially increase with decreasing porosity.

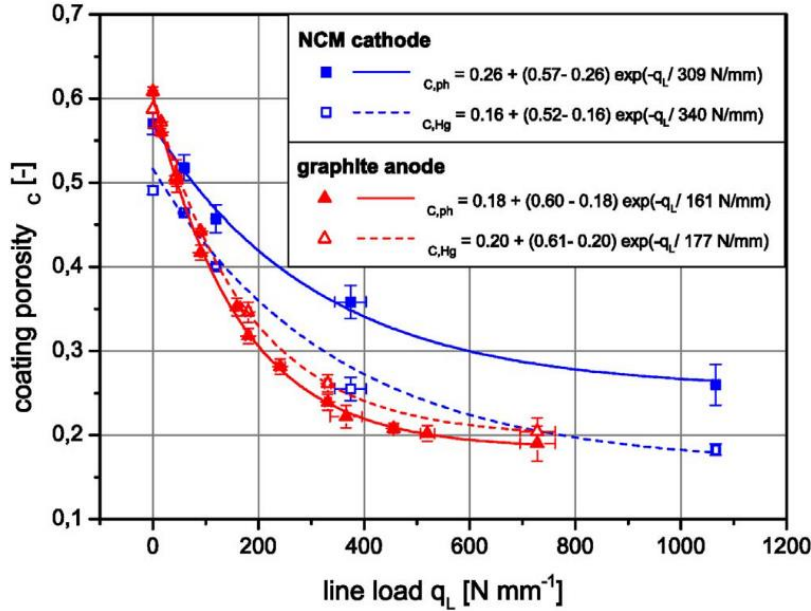


Figure 2.10 Line load relationship to coating porosity exhibited in C. Meyer's work. ²¹⁴

2.4.4.1 Compaction Resistance

Compaction resistance is the term used to describe the opposing forces generated when applying pressure during calendering. It can be used to estimate the maximum achievable electrode density and to correlate how much compaction will occur for a given line load (the calendering pressure). Equation 2.5 defines the relationship between electrode coat density (ρ_c), line load (q_L) and compaction resistance coefficient (γ_c). Increasing the line load results in an initially rapid decrease in coating density, followed by progressively smaller changes. This is importance because to reach a specific coating density, the line load may have to be increased dramatically. To reduce the electrode porosity from 35 % to 30 %, the line load may have to be increased by a factor of 1.5 ²¹⁴. This is highly detrimental because these high pressures invoked during calendering fracture the larger NMC particles. If the pressure exceeds the compressibility limit of the particle it will cause the particle to crack and deform, leading to fragmentation ²²². Calendering to a porosity of 30 % introduces significant active material cracking. Most of the cracks occur at the electrode surface, displaying random cracking within the structure and cracks in half of the surface particles; however, further decreasing the porosity to 18% cracks nearly all the particles at the surface of the electrode and half of the internal particles within the electrode ²²³. Cracking is more prevalent at low porosity because

the calendering forces are greater and the particles can no longer redistribute under compression and absorb the force ²²⁴. This mechanical degradation causes performance and longevity issues. The extra surface area exposes the active material to more electrolyte providing accelerated parasitic reactions and rapid capacity fade ²²⁵.

$$\text{Equation 2.5} \quad \rho_c = \rho_{c,max} - (\rho_{c,max} - \rho_{c,0}) \exp\left(-\frac{q_L}{\gamma_c}\right) \quad 214$$

2.4.4.2 Increasing Compressibility

The compaction resistance coefficient (γ_c) predicts how quickly the electrode can converge to its maximum density ($\rho_{c,max}$) in response to a line load (q_L). The lower the coefficient, the quicker the convergence. The compaction resistance coefficient is a constant as it represents the resistance to particle arrangement. A low coefficient indicates a system which is receptive to particle rearrangement; therefore, changing the system to lower the coefficient will decrease the pressure necessary to achieve a specific porosity. There are several parameters and conditions which facilitate this: increasing the temperature of the electrode during calendering increases compressibility and changes to electrode composition.

Temperature change during calendering has been explored by C. Meyer; heating the electrode reduces compaction resistance because the PVDF in the conductive additive and binder matrix has greater flow properties ²¹⁵. Calendering temperatures within industry are typically $>90^\circ\text{C}$ ¹⁸³. This temperature makes the polymer binder less rigid and pliable and promoting active particle embedment into the current collector to increase adhesion ²¹⁵.

The electrode composition has a great effect on the compaction resistance. Carbon black is a vastly smaller particle than the large secondary NMC particles (size difference of 10nm to 5um). This creates a scenario where the carbon black acts as a lubricant for the NMC particles because the particles are smaller and more mobile. Carbon black content inversely correlates with compaction resistance. Despite this, only a minimum quantity of carbon black to facilitate good electronic conductivity is added to the mixture. Surplus is not added to increase lubrication because it reduces the proportion of active material in the slurry. This lower proportion of active material would reduce electrode energy density. The chosen active material also plays a significant role in compaction resistance. Lithium ion phosphate (LFP) electrodes struggle to calender to high particle density due to their submicron particle size ²²⁶. LFP electrodes frequently delaminate or experience current collector fracture under the high pressures necessary in the pursuit of packing densities similar to NMC systems ²²⁷. The

compaction resistance is too great for sub-micron LFP; the minimum practical porosity is still relatively high.

2.4.5 Adhesion and Cohesion

Adhesion and cohesion are both important mechanical properties for an electrode. Mechanical stability is paramount to performance ²²⁸. Lithiation and delithiation during electrochemical cycling causes the crystal structure to expand and contract as the lithium ion is incorporated into the lattice structure ^{229,230}. Cohesion is fundamental to the integrity of the film and resists spalling, film cracks and fragmentation ^{150,231,232}. Adhesion binds the film to the current collector ²³³. This is imperative to completing the electronic network; severance of active material from the current collector causes leads to electrochemically inactive material. Adhesion displays a more complicated relationship with calendering pressure and porosity than cohesion. Adhesion between the electrode film and current collector decreases from high to medium levels of porosity before increasing from medium to low level of porosity, displaying a U-curve relationship ¹⁸³, Figure 2.11. This has been attributed to the shear strain experienced between the electrode film and the current collector the calendering rollers induce shear stress to the entire electrode ¹⁸³. Additionally, the electrode film and current collector have different Young's moduli ²³⁴ and expand at different rates during the calendered pressure, reducing the bonding. This leads to a decrease in adhesion with increasing pressure and porosity loss; however, a new mechanism emerges at higher pressures: the embedment of the active material into the current collector ²¹⁵.

Elevated temperatures also promote the active particle embedment. Calendering temperatures in the range of 90-120 °C display increased adhesion which is attributed to greater interlocking behaviour between the electrode film and current collector ^{183,235}. Temperatures exceeding 120 °C can lead to a reduction in adhesion and cell performance due to approaching the melt temperature of PVDF (approximately 160 °C) ^{51,183}.

Comparing calendering to uniaxial pressing highlights the impact of shear stresses. Uniaxial pressing sees a linear increase in adhesion with pressure as porosity increases ²³⁶. This shows the elimination of shear stress removes the initial loss of adhesion with calendering. High adhesion at low porosities and active particle embedment is also demonstrated with uniaxial pressing. The shear stress in calendering is reduced by increasing the diameter of the calender

roller. Expanding the diameter of the roller increases the circumference and results in a lower velocity gradient between the substrate in contact with each roller and the substrate centre ²³⁷. Figure 2.12 displays the velocity gradient as a substrate passes through a calender roller.

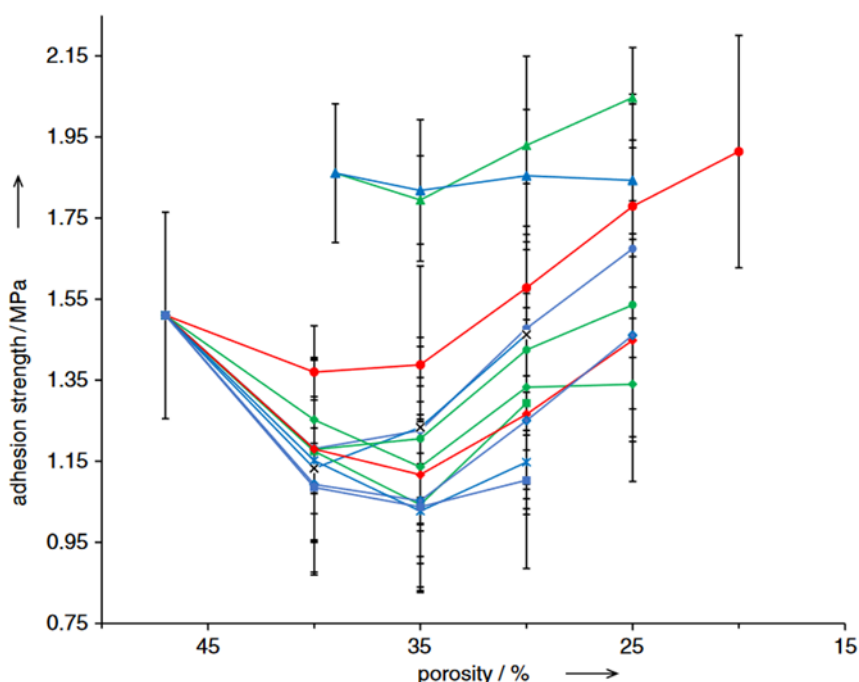


Figure 2.11 Adhesive strength for graphite anodes at different roller sizes, temperatures and porosities. Different calender roller sizes of 400mm 465mm and 600mm (blue, green, red). It can be seen a decrease before an increase in adhesion as porosity decreases. ¹⁸³

Cohesion increases inversely with porosity. Cohesion primarily correlates with the abundance of contact points between particles in the electrode, especially contact surface area between the active material and the CBD phase. The elimination of porosity reduces the available pore space which is achieved by rearrangement of the microstructure and a reduction of the interparticle distance between all particles in the film. Adhesion strength and cohesivity of the film appears to be independent of calender roller velocity. Electrodes have displayed no difference in performance characteristics at roller speeds of 1, 5 and 10 m min⁻¹ ¹⁸³.

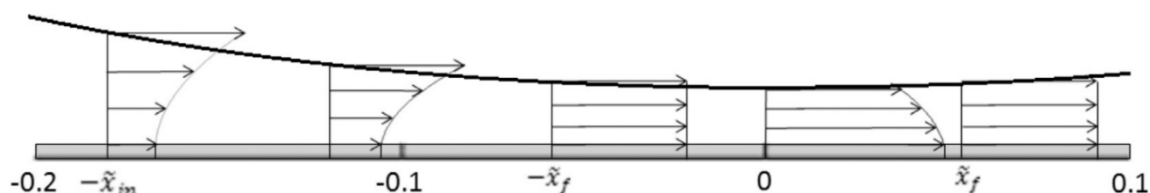


Figure 2.12 Diagram of the Velocity Gradient Experienced During Calendaring ²³⁷

Adhesion and cohesion both positively correlate with binder content and inversely correlate with conductive additive ²³⁸. High binder content enhances the mechanical properties by promoting the formation of more interconnected PVDF bonds. In contrast, shifting the additive

content ratio toward the conductive additive reduces binder content and introduces more carbon black, which interferes with the polymer chains and bonding of PVDF^{238,239}. Carbon black interrupts the interconnected chains of PVDF²⁴⁰ and reduces the strength of the bonds between the PVDF; this decreases the breaking strength of the electrode, Figure 2.13.

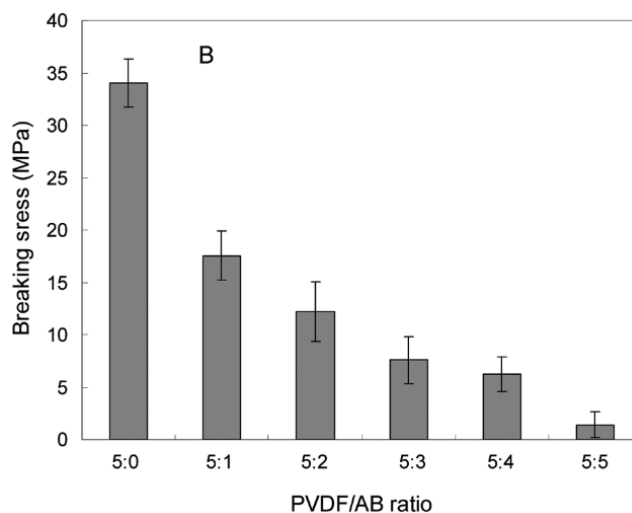


Figure 2.13 Binder content (PVDF) to conductive additive content (AB - acetylene black) ratio and the breaking stress of the electrode. Increasing the binder content increases the breaking stress of the electrode.²³⁸

Other works have shown swapping the conductive additive from carbon black to a mixture of graphite and carbon black increases film cohesivity. Cohesivity was increased by a factor of 4, swapping the 6 % carbon black ($62 \text{ m}^2 \text{ g}^{-1}$) to 1.5 % carbon black and 4.5 % graphite ($17 \text{ m}^2 \text{ g}^{-1}$)²⁴¹. This out was attributed to the of the lower surface area of graphite relevant to carbon black. The lesser surface area boosts cohesivity because it minimises the surface area the binder will coat²⁴². This promotes a thicker coating of binder in lower specific surface area films²⁴¹. This was also not at the expense of electrical conductivity which increased from 0.54 to 0.76 S cm^{-1} with the substitution of 4.5 % graphite.

2.4.6 Rate Capabilities, Charge-transfer and Porosity

The electrochemical reaction in lithium ion systems involves the transferal of a lithium ion from the solvation shell across the active particle-electrolyte interface before intercalating into a vacant spot within the active material²⁴³. The charge-transfer resistance is the impedance relating to the kinetics of this electrochemical reaction. The kinetics of the lithium ions are often the rate limiting step in the electrochemistry of lithium-ion cells because it involves the transfer of a lithium ion, which are significantly slower than electrons due to their greater mass

²⁴⁴.

Studies have indicated charge-transfer resistance decreases as porosity decreases^{245,246}, shown in Figure 2.14. The capacity of the batteries is also improved when discharging at high c-rates after calendering²⁴⁷. This evidence of calendering improving the rate capabilities of the electrode. The improvement to the charge-transfer resistance has been suggested to be a better coating of the CBD phase around the active particles; this has a geometrical effect and increases the electrochemical activity of the particles²⁴⁸.

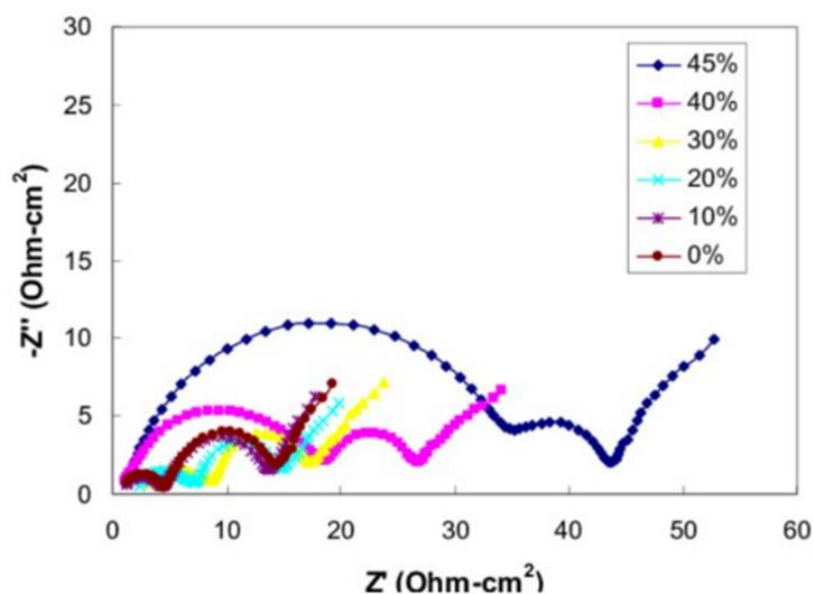


Figure 2.14 EIS Nyquist plot for NMC111 at a range of porosities.²⁴⁸

Charge-transfer is one of the larger internal resistances within cells; therefore, a reduction leads to a significant electrochemical performance improvement²⁴⁹, increasing reversible capacity and specific capacity^{250–252}. This is shown in Figure 2.15, work by Kang et al.²⁴⁶. Electrodes at all densities display similar capacities at 0.1C but the highest density (3.2 g cm^{-3}) and the lowest density (1.9 g cm^{-3}) electrode experience a reduction in capacity at 1C. The capacity reduction exaggerates at 4C, at this discharge rate the 1.9 and 3.2 g cm^{-3} electrode are not able discharge more than 10 mAh g^{-1} , only the moderately calendered cell has any performance within this voltage window at 4C. It indicates the cell has the lowest impedances. This lesser resistance reduces the voltage drop and increases the available current within the voltage window.

Kang et al. demonstrates the electrochemical benefits of calendering electrodes. The highest density electrode also experienced a charge-transfer resistance reduction²⁴⁶, correlating with Figure 2.14. However, this does not represent the complete understanding, as high-density electrodes exhibit diminished effective ionic conductivity²⁵³, another impactful resistance. This

resistance arises from the exponential increase of ionic pathway tortuosity induced by electrode densification ²⁵⁴. Tortuosity and effective ionic conductivity is reviewed in depth in 2.4.7.

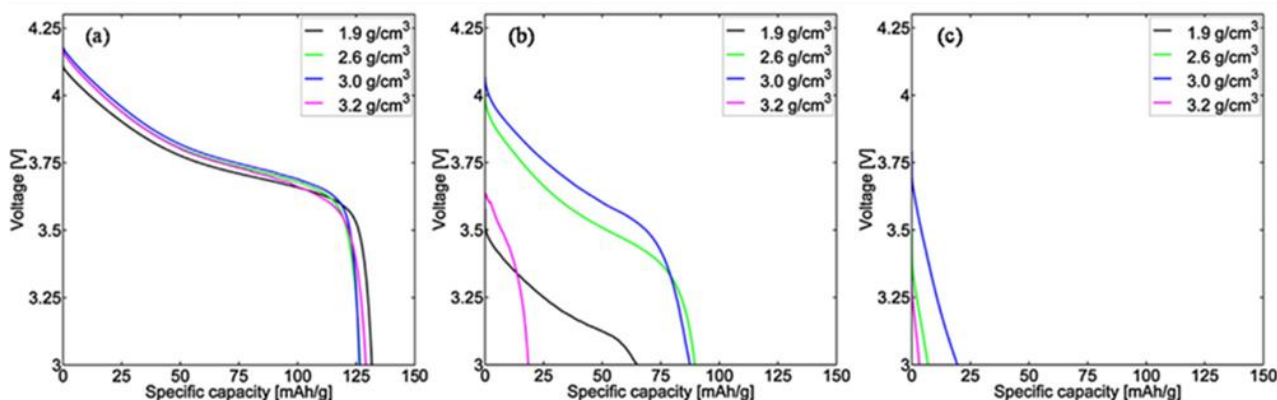


Figure 2.15 Voltage profiles indicating discharge capacities for NMC333 cathodes at different film densities, a) 0.1C b) 1C c) 4C. Performance indicates similar capacity at 0.1C but deterioration of the capacity for both the low and high densities at 1C and 4C. ²⁴⁶

2.4.7 Diffusion Pathways and Tortuosity

Ionic diffusion is a relatively high resistance process within electrode-electrolyte systems; therefore, minimising the diffusion pathways is critical to achieving greater performance ^{255–257}. Lithium-ion transport is constrained porosity in the microporous network ²⁵⁸. The morphology of the electrode is determined predominantly by the active material particles geometry; this encompasses the active material particle shape, size and interparticle spacing ²⁵⁹. The pores within this structure form around these particles, creating a complimentary shape ²⁶⁰. These pores are filled with electrolyte in the final battery product; therefore, the structure of the pore space determines the diffusive routes the lithium-ions traverse because ions diffuse through this electrolyte to traverse between the electrodes ²⁶¹. The electrolyte possesses a high ionic conductivity which is desirable for mass transfer; however, it still presents an ionic resistance ²⁶² and causes a polarisation, leading to lesser capacity ²⁶³. This highlights the dependency of lithium-ion diffusion on the geometry of the electrodes and the cell architecture ²⁶⁴. To minimise the polarisation, the pore structure must be optimised to reduce the average distance ions must traverse between the active material of the two electrodes ^{265–267}. The linear distance between the electrode materials is easy to evaluate however tortuosity within the electrode increases the true diffusion distance.

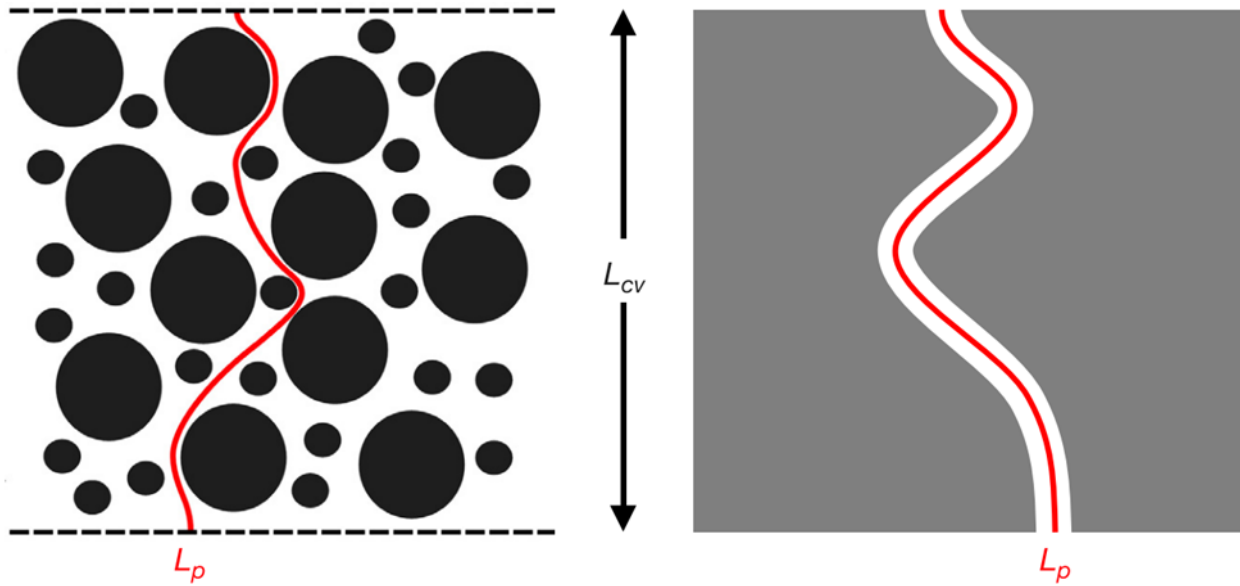


Figure 2.16 Tortuosity diagram; pore length (L_p) is shown to be longer than the control volume length (L_{cv}).²⁶⁸

Electrodes are submerged in electrolyte, the transport medium for the ions. Due to this nature, the ions diffusion path weaves between the particles, extending the distance the ions must travel. Tortuosity quantitatively describes how convoluted the pathway are. Figure 2.16 displays a tortuous path through an electrode structure and the tortuosity for this system is described in Equation 2.6. A tortuosity of one would represent a direct linear path; a tortuosity of ten would represent a system where the true distance travelled is tenfold greater than the linear distance.

$$\text{Equation 2.6} \quad \tau = \frac{L_{pore}}{L_{control\ volume}} \quad 268$$

Tortuosity is an important consideration in calendaring because particle rearrangement and compaction reduces pore volume and may seal off some previously accessible pores. This convolutes the ionic pathways and explains the negatively correlation between tortuosity (τ) and porosity (ϵ), Figure 2.17. This correlation has been modelled in various literature^{269,270}. The impact of tortuosity is substantial. High tortuosity hinders the capabilities to transport lithium ions through the porous network²⁷¹.

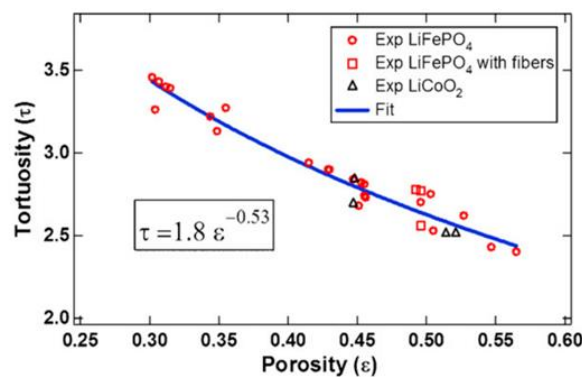


Figure 2.17 Tortuosity measurements from LFP electrode modelling.²⁶⁹

Bruggeman did a lot of work illuminating the fundamental relationships between tortuosity and porosity in porous structures and created the Bruggeman relation ²⁷², Equation 2.7. It shows how a reduction in porosity rapidly increases tortuosity ²⁶⁸. The application of this tortuosity model to electrode systems is unideal due to its assumption of monodisperse and perfectly spherical particles. Co-precipitation of the of NMC622 (a widely adopted synthesis method) ²⁷³ produces ellipsoid particles over a range of sizes; it does not produce a monodisperse product ²⁷⁴. A batch of monodisperse particles requires excessive filtration; this standard of quality assurance comes at a high cost. The effect of active particle polydispersity in electrodes increases tortuosity; spatial inhomogeneity caused by polydispersity can create local volumes of high tortuosity within the electrode and can increase the overall system tortuosity by 13 % ²⁷².

Equation 2.7: Bruggeman Relation for monodispersed particles

$$\tau = \varepsilon^{-0.5}$$

²⁷²

Whilst there is discrepancy between literature values and the literature and the Bruggeman relationship both reveal the great influence of porosity on tortuosity. For a cast electrode of 50 % porosity, the tortuosity would be 1.41, predicted by the Bruggeman equation. A calendered electrode with a porosity of 25 % is modelled to have a tortuosity of 2.00, an increase of 41 %. The equivalent tortuosities would be 2.60 and 3.75, 44 % increase, for 50 % and 25 % using the tortuosity equation from Figure 2.17. Despite the differences, both ultimately reveal compacting an electrode structure makes the network convoluted, yielding significantly extended transport paths, and therefore larger transport losses due to polarisation. The relationship indicates reductions to electrode porosity leads to much greater ionic transport resistance. Figure 2.18 illustrates the arrangement of pores within three-dimensional porous structure.

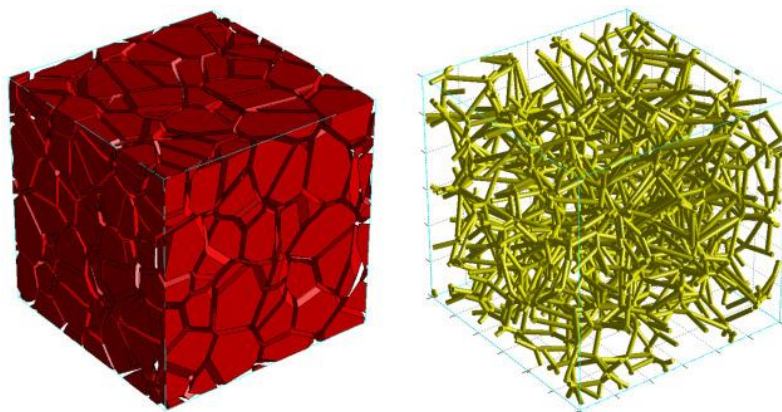


Figure 2.18 Diagram of a porous structure (left) and a diagram displaying the porous channels and their orientation of the porous structure (right). ²⁷⁵

2.4.7.1 Z-Plane Anisotropy Tortuosity

A key consideration in cell design is the directional flow of ions. This is demonstrated when aligning the electrodes in parallel during cell construction and extends to the structure of electrodes; slurry is cast onto a current collector, therefore the ionic pathways are going to traverse along the z-axis from the surface of the electrode to the active material in contact with the current collector. This becomes increasingly important when the simplification of perfectly spherical NMC particles is reconsidered. Particles will generally orientate to lie along their longest axis. NMC particles may have a slightly longer axis; NMC particles range from ellipsoidal to spherically shape (Figure 2.19) ²⁷⁶. This ellipsoidal geometry introduces anisotropy and will make it more difficult for ions to traverse the through-plane (z-axis) of the electrode ²⁷⁷.

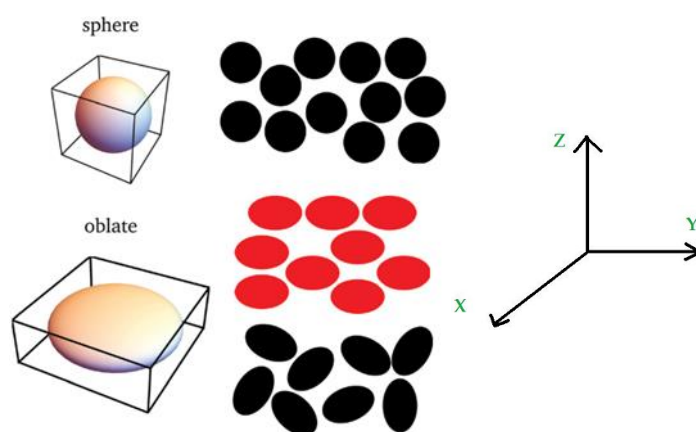


Figure 2.19 Diagram comparing the tessellation of spherical and oblate particles. ²⁷⁶

X-ray tomography conducted by Ebner et al. demonstrated the trend between particle anisotropy and tortuosity anisotropy in several different electrode materials; the NMC particles exhibited axial Bruggeman exponents of 0.528 (x-axis), 0.544 (y-axis), and 0.573 (z-axis), reflecting directional dependent transport behaviour ²⁷⁸. This variation is significant and causes the tortuosity to change by 6 % dependant on which axis is being analysed (x-axis tortuosity: 2.08, z-axis tortuosity: 2.21, for a porosity of 25 %). The influence of anisotropy is more impactful in graphite particles. Natural graphite particles have a flake-like shape, with two significantly longer axes than the third ²⁷⁹. This encourages particle rotation which promotes particles to orientate in parallel and frequently overlap. As a result, pathways through the electrode are greatly hindered. Graphite has an a-axis Bruggeman factor of 0.591 compared to 1.914 in the z-axis. This invokes a 6-fold difference in tortuosity, from 2.3 to 14.2, for a given porosity of 25 %. The difference is significant and highlights the importance of particle geometry and the evaluation of electrode properties by each axis, as the diffusion routes for

lithium ions travelling through the graphite anode are fourteen times longer than the linear distance in respect to the z-axis due to its convoluted structure. Figure 2.19 depicts arrangements of spherical particle and oblate arrangements and demonstrates how oblate particles can reorientate; the spherical particles resemble NMC particles and oblate particles resemble graphite particles.

2.4.7.2 Symmetrical Cell EIS, CBD and Tortuosity

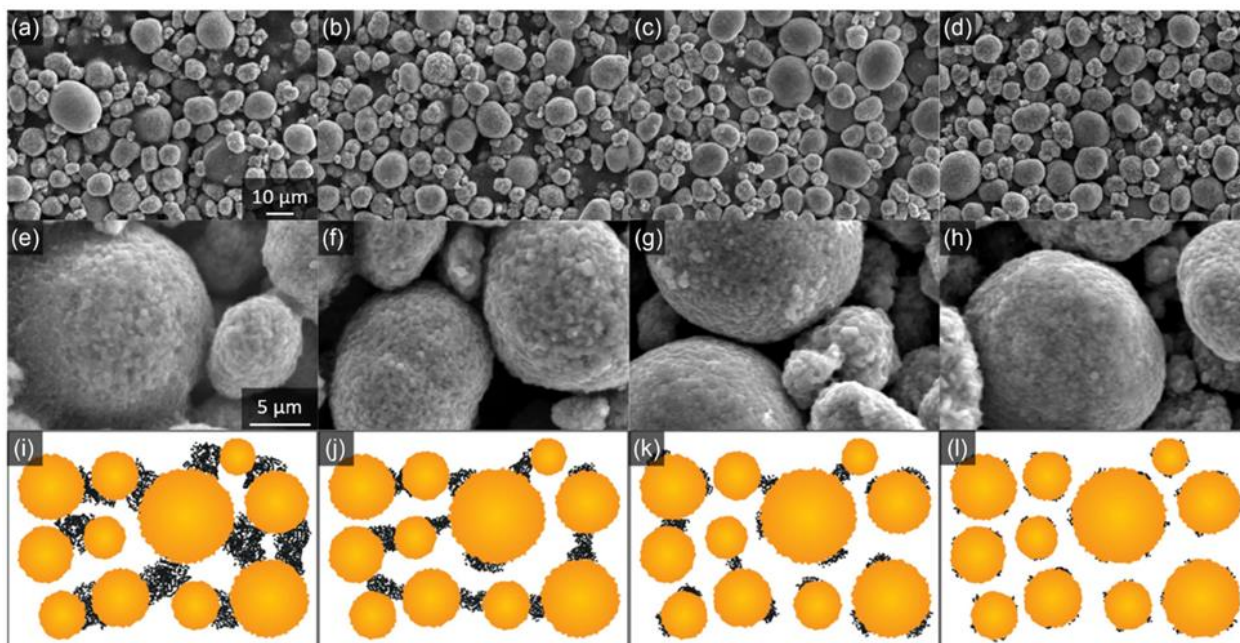


Figure 2.20 Microscopy of electrodes progressively less inactive material in the formulation. (a)(e)(i) have the greatest inactives and show a bridge-like CBD structure, (d)(h)(l) has the least inactives content and display a film-like structure.²⁸⁰

It has been demonstrated the modelling of tortuosity in electrode systems is complex and varies with electrode geometry. Alterations to porosity and particle shape significantly changes the tortuosity. This has recently been found to extend into the carbon-binder domain (CBD) phase. The CBD phase has pore-blocking behaviours and reduces the effective diffusivity of the electrolyte, as the lithium ions must flow around the structure or through the nanostructure¹⁹⁵. The CBD is nanoporous and can exhibit as multiple shapes and morphologies. CBD structure has been demonstrated to fall between a film-like structure or a bridge-like structure. Film-like CBD structure coats the active material in the electrode and effectively acts as an additional surface layer. The CBD follows the dimensions of the NMC particles and does not branch out into the larger pore network. Bridge-like CBD structures form bulkier masses of CBD which has large contact points between two NMC particles. This causes a the mass of CBD to be suspended away from the NMC particles in the microporous region, forming the ‘bridge’ structure displayed in Figure 2.20²⁸⁰. Comparing the two structures shows the geometry of the CBD invokes different pore-blocking behaviour. This has been shown in other works modelling

tortuosity: the tortuosity is seen to be to be 6 to 30 % greater depending on the morphology of CBD (Figure 2.21) ²⁸¹ and comparing the tortuosity of the system without the CBD region to the system when regarding the CBD region increased the tortuosity 1.4 to 1.8 times in a NMC622 system ²⁸².

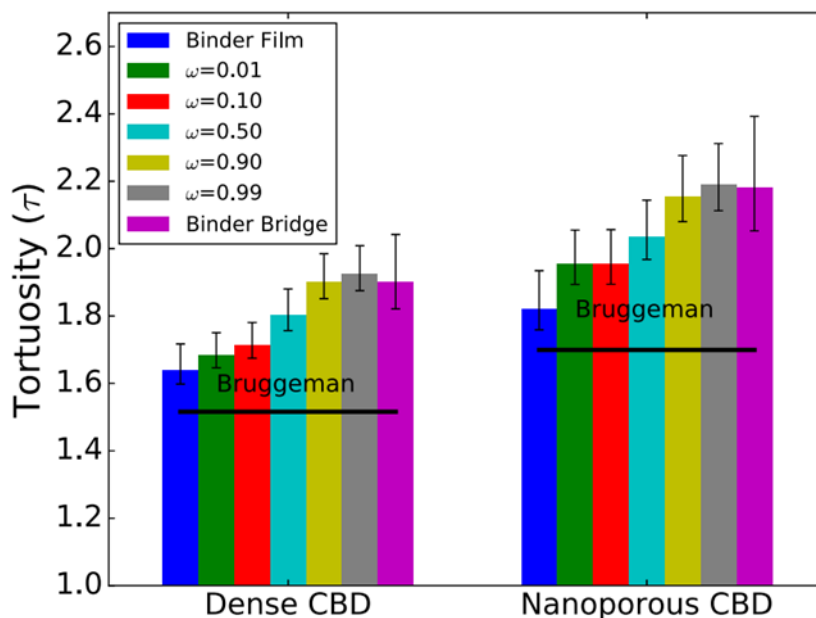


Figure 2.21 Tortuosity of electrode considering the CBD influence. ω represents the morphology, a low value indicates a film-like CBD coating, a high value indicates protrusive bridge-like structure. ²⁸¹

The demonstrated the increased tortuosity in modelling due to the CBD phase also correlates with the results seen measuring the diffusivity in symmetrical cells. Landesfeind et al. performed electrochemical impedance spectroscopy with symmetrical NMC622 cells ²⁸³. This involved cell construction with two identical NMC cathodes with a tetrabutylammonium perchlorate electrolyte. This electrolyte blocks intercalation which eliminates the process from the impedance response. This simplifies the response and shows a more resolved ionic diffusion component. The effective ionic resistance of the symmetrical cell is easily interpretable which can be used to determine the tortuosity. His results suggested the tortuosity to be 1.77 ± 0.06 when imaging with x-ray tomography but the symmetrical cell EIS indicated a tortuosity of 3.1 ± 0.3 ²⁸³. The EIS tortuosity is a 1.5 to 2.0 factor times greater compared to the tomography. The tomography was not able to resolve the CBD phase and therefore does not have a tortuosity contribution from the CBD ²⁸⁴. Symmetrical cell EIS is a physical process and is affected by the CBD. This concluded pronounced underestimation of tortuosity during tomography of the NMC cathode system is due to the unresolved binder and conductive additive. A second conclusion was the EIS tortuosity measurement was unequivocally accurate after confirming the technique to accurately predict the tortuosity for a

steel ball system ²⁸³ and proves the previous Bruggeman relationships fail account for the tortuosity induced by the CBD phase.

The development of the relationship between porosity and tortuosity and its adverse effects on transport resistance is important. It illustrates highly porous, less compressed electrode will have a large volume presenting a longer linear distance for the lithium-ions to diffuse through the electrode, however the pathways will not be very convoluted. In contrast, a calendered electrode will have a lesser volume but the diffusion pathways will be convoluted ^{110,285}, causing a significant difference between the linear distance and the practical distance of the pathway. This is evidence for calendering being necessary to maximise performance whilst demonstrating there is a limit to calendering, otherwise the lithium-ion transport resistance increases exponentially ²⁸⁶.

2.5 Alternatives to Calendering

The battery field has actively explored alternatives to calendering however they present limited improvement, limitations greater throughput or have insufficient demonstration at pilot and industry scales. Uniaxial compression was introduced during the review of calendering on adhesion (section 2.4.5). This involves the compression of the electrode under increasing static load. It was displayed to have the advantage of reduced shear-force which yields greater adhesion however the greater adhesive properties of the electrode manufactured by uniaxial compression did not merit the difficulty surrounding scaling the technique. Pressing can only be conducted as a batch process which severely limits throughput. The continuous processing of calendering is scales to industrial processing effectively. The higher throughput is valued more than the greater adhesion.

Densification of cathode prior to calendering has also been attempted. This involved ultrasonically vibrating the slurry during the drying process at lab scale; conducted by Ren et al ²⁸⁷. The LFP cathode slurry of 48 % solid content was cast onto 16 μ m aluminium foil before being transferred to oven with an ultrasonically vibrating shelf. The oven was set to 120 °C and vibrated at a frequency of 40 kHz during the first 10 minutes of drying. After this period, the vibrations ceased, and the electrode was dried for six hours to dry off all the NMP. The vibrational work during drying successfully increased the density of the electrode from 1.48 to 1.65 g cm⁻³ compared to slurry dried without any ultrasonic work. This also corresponded to a

measurable reduction in the thickness of the vibrated electrode from 207 μm to 187 μm . Ren's hypothesis was inspired from ultrasonic vibration-assisted compaction used in ceramic and metal powder processing industries. The motivation for Ren to ultrasonically vibrate the cathode during drying in conjunction to calendering was cited to be that 'blindly' increasing the pressure of the calendering process, or equivalently increasing the number of passes, will increase the vulnerability of the active particles to fragmentation from the greater exposure to force ²⁸⁷. Therefore, they aimed to increase the electrode density during drying prior to calendering. Ren's work is a new and novel instance of using ultrasonic work to change the morphology of electrodes in batteries.

Ultrasonic work does have a typical role within the battery sphere outside of ultrasonic welding, the adopted technique used to weld tabs onto the current collector of pouch cells ¹⁹. This shares a lot of similarities with the ultrasonic welding of thermoplastics ²⁸⁸. Ultrasonics are mostly commonly utilised across industries for measurement techniques such as imaging in the medical field ^{289,290} or sensing for gas leakage ^{291,292}. These techniques use ultrasonic vibrations as signals rather than as a means of exerting force or inducing change. Likely inspired by this, the battery industry is exploring state-of-health monitoring which can be measured with ultrasound ^{293,294}. The secondary use of ultrasonics across industry does utilise ultrasonics in the manipulation of material. It is a lesser market but it can be very advantageous, especially working with small particles such as emulsions ²⁹⁵.

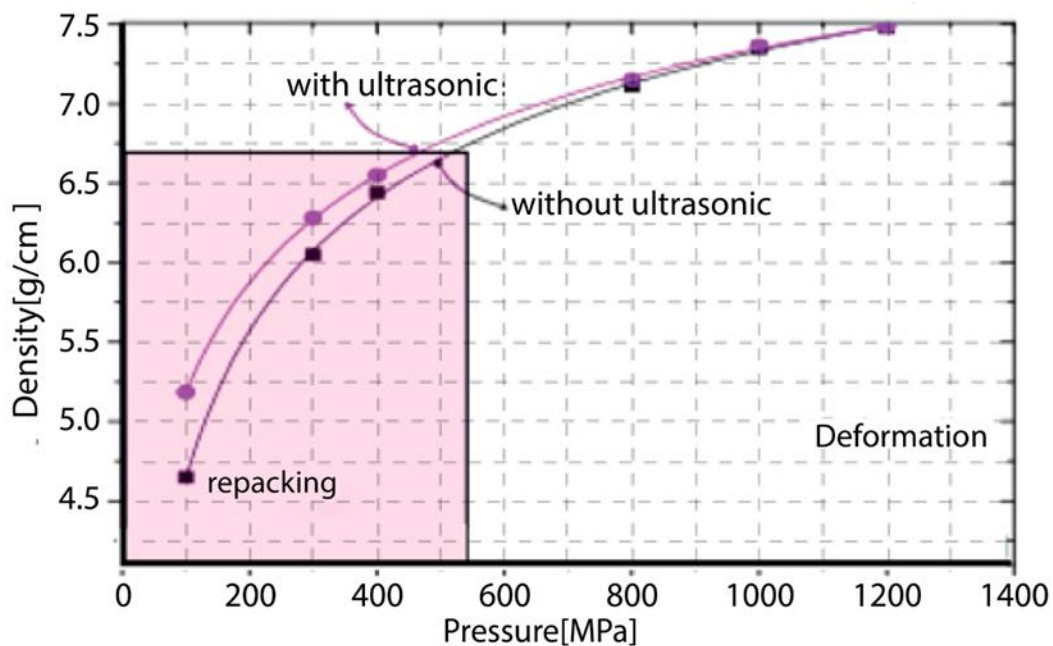


Figure 2.22 Density profiles of iron powders for two compaction methods, with and without ultrasonic vibrations. ²⁹⁶

Hwang investigated densifying soft magnetic composites through ultrasonic-vibration compaction ²⁹⁶. The composite powder is pure iron coated in a thin layer of electrically insulating material. The purpose of the insulating material is to prevent eddy currents. Typical processing of the composites involve compaction and sintering but the high temperatures involved in sintering would break down the insulating coating. This paper attempts to increase the mechanical strength of the particles by substituting the compaction and sintering processes for an ultrasonic-vibration assisted compaction. Their results, displayed in Figure 2.22, exhibit a higher density profile with ultrasonic activity; the particles have a greater density for all given pressures for ultrasonic methods. The result is more impactful during the repacking stage of compaction and is associated with the high frequency vibrations reducing particle friction and the lower frictional forces to promote particle rearrangement and slipping which increases particle density ²⁹⁷⁻²⁹⁹. It also achieves their goal of reaching a given density under less pressure.

Figure 2.23 depicts a force balance model of the compaction process. Motion occurs whenever the resultant forces on an object do not equate zero. The applied force is analogous to the load applied to compact the sample. The barrier friction represents the resistance force between the particle and the containment object; the interior particle friction represents the resistance force between other particles and the power formation force. The aim of the applied force is to move the particles into unoccupied voids and a different arrangement, but friction opposes this force. During static loading the applied load is greater than the resistant forces therefore the sample begins compacting. The particles begin rearranging and the frictional forces increase with more areal contact; friction is proportional to surface area contact. Compaction will proceed until the applied load and resistive forces equalise. This will inevitably occur because frictional forces will increase with compaction, but the applied load is constant; therefore, the final density is dependent on the applied load. In static compaction, the final density can only be overcome by increasing the applied force, resulting in further compaction. Henceforth, there is a positive correlation between applied load and the compacted particle density, as observed in Figure 2.22. The introduction of ultrasonics to the system can increase the maximum compaction because it reduces the internal friction which is an opposing force to the applied load. The barrier friction forces and the interior particle friction forces are reduced (supported by other literature ^{297,298}). This makes promotes particle movement and rearrangement. The oscillations also provide kinetic energy and the opportunity for particles to make bigger rearrangements. This is primarily due to the reduced interior particle friction, allowing particles

to slip past each other into unoccupied space. This results in a greater compaction and more areal contact before the frictional forces equate to the applied load. The result is a final compaction density greater than the static system.

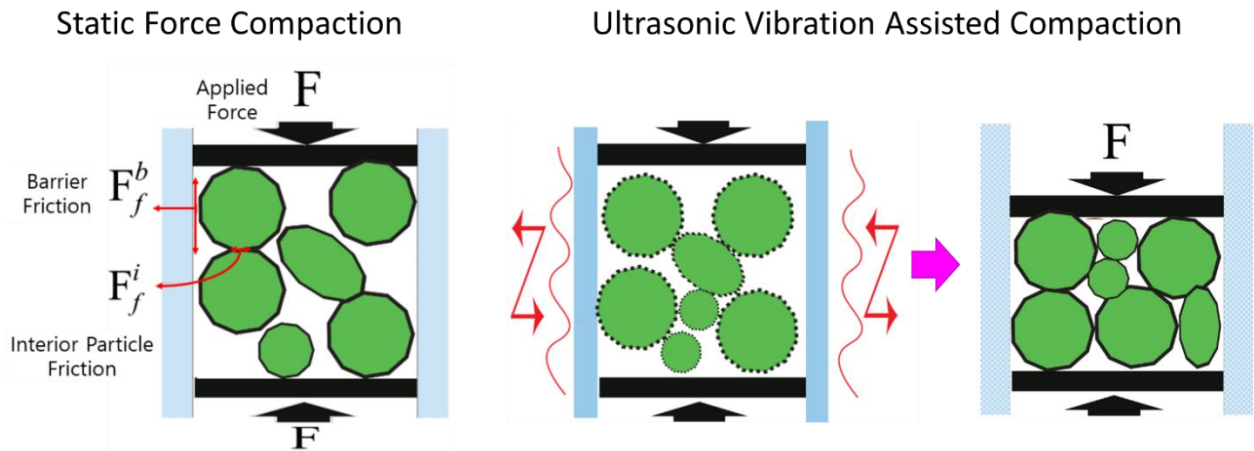


Figure 2.23 Force balance for the compaction under a static pressure and a process diagram for the ultrasonic vibration assisted compaction. ²⁹⁶

This model also assumes the particle and objects are incompressible however the particle may elastically or plastically deform. The elastic deformation will be an opposing force to the applied load, reducing total compaction. Particles which exceed their compressibility limit will also fracture leading to a permanent change to the shape of the particle; this was a concern in Hwang's work and is a concern with battery materials). Other literature has cited excessive work, or excessive vibration amplitude, leads plastic deformation of the material rather beneficial work to system e.g. reducing friction ²⁹⁸.

Similar systems involving nanosized zirconia ceramic particles indicated applying an ultrasonic forcing during compaction lead to less aggregates, and fracturing of the particles along grain boundaries; as a result, the ultrasonic work became an essential element to the compaction process ³⁰⁰. Another source showed 21.5kHz ultrasonic compaction of zirconia yielded greater densities and the density of the zirconia was greater with increasing ultrasonic energy input into the system ³⁰¹. The volume of the zirconia was reduced up to 35 % with the introduction of ultrasonic energy, compared to just uniaxial compression. The influence of the ultrasonic vibration was more influential during the compaction at lower pressures, increasing the rate of densification.

3. Materials and Methodology

3.1 Materials

Information on materials has been sourced from the technical data sheet ^(TDS) of the supplier, have been experimentally measured ^(EM) as part of the project or referenced if sourced from existing literature.

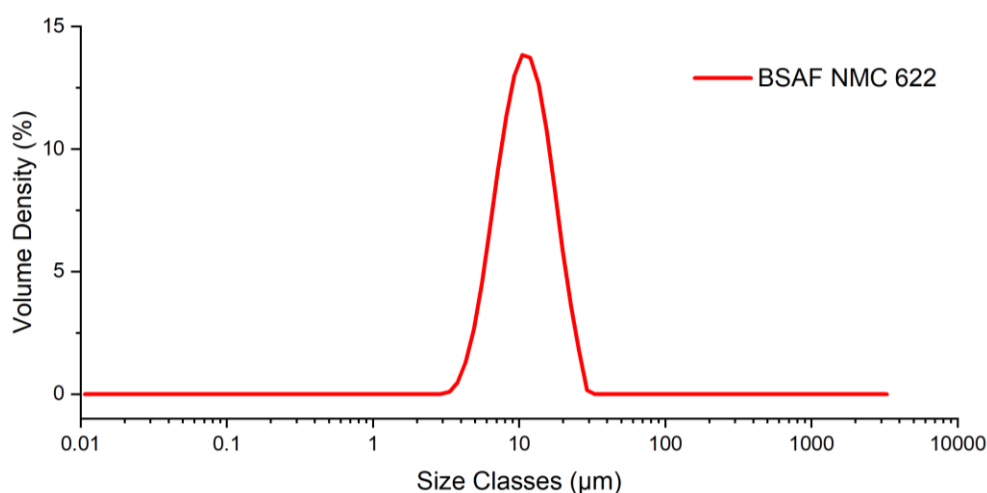


Figure 3.1 Pore size distribution of BSAF NMC 622, measured with a Mastersizer.

NMC622 – Lithium nickel manganese cobalt oxide is an active material for lithium storage. The nickel manganese cobalt stoichiometry ratio is 6:2:2. This has a higher nickel content than the other two transition metals. Nickel is a good transition metal for high voltage applications ³⁰², but suffers from lower stability. Manganese is a good thermal regulator and prevents dissolution of transition metal ions into the electrolyte ³⁰³, a cause of capacity loss and impedance rise ³⁰⁴. Cobalt is a good voltage stabiliser and bolsters ionic conductivity ³⁰⁵. The active material can come in other stoichiometry e.g. NMC111 or NMC811.

NMC622 was chosen because of its industrial relevance due to its higher nickel and electrochemical performance, surpassing NMC111 which has been phased out of the battery industry. NMC811 is used in the battery industry but has significantly less stability, suffering from irreversible reactions to water and oxygen in the atmosphere. This creates handling challenges compared to NMC622 which can be redried after exposure to atmospheric components. NMC622 is used as the active material in slurry cast cathodes in this work. The supplier is BSAF.

Table 3.1 NMC material properties.

Material	Skeletal Density [g cm ⁻³]	Particle Size (d50) [μm]
BASF NMC622	4.70 ^{TDS}	11.1 ^{EM}

C65 – Carbon black is an electronic conductivity enhancer. They are nanoparticles which can be dispersed in a system to create an electronic network to promote low ohmic resistance electron conduction. C65 is a carbon black with a specific surface area of $62 \text{ m}^2 \text{ g}^{-1}$. This boasts a high Brunauer-Emmett-Teller (BET) surface area to mass ratio. C65 is used as the conductive additive in slurry cast cathodes in this work. The supplier is Imerys. Literature has cited C65 to possess an electrical conductivity in the 50 S cm^{-1} ¹³³. NMC cathodes, depending on the stoichiometry have been reported to possess electrical conductivity around $<1 \text{ S cm}^{-1}$ ³⁰⁶. This difference in electronic conductivity the importance of including a conductive additive to the cathode formulation.

Table 3.2 C65 carbon black material properties.

Material	Skeletal Density [g cm^{-3}]	Particle Size (d50) [nm]	BET Surface Area [$\text{m}^2 \text{ g}^{-1}$]	Electrical Conductivity at 1.1 g cm^{-3} [S cm^{-1}]
Imerys C65	0.16^{TDS}	32^{TDS}	62^{TDS}	50^{133}

PVDF – Polyvinylidene fluoride is a carbon-based polymer. It has a chemical formula $(\text{C}_2\text{H}_2\text{F}_2)_n$. The high fluorine content yields high stability and low volatility. It is used as the primary binder in slurry cast cathodes due to its resistance to high-voltage environments, thermal stability and high mechanical strength. PVDF is used as the polymer binder in slurry cast cathodes in this work. Supplier is Solvay. The grade chosen is PVDF 5130. This grade of PVDF is stable under high voltage, presents a good viscosity when dissolved in NMP during slurry casting, and has proven to produce electrodes with greater discharge capacity ³⁰⁷.

PVDF Sheets – PVDF sheets were used to ultrasonically weld and were mechanically tested. The sheet dimensions were $10\text{cm} \times 10\text{cm} \times 0.1\text{mm}$. Supplier of the PVDF sheets is Goodfellow.

Table 3.3 PVDF powder and polymer sheet material properties.

Material	Skeletal Density [g cm^{-3}]	Molecular Length [Da]	Tensile Strength [MPa]	Glass Transition (T_g) [$^{\circ}\text{C}$]	Melting Point [$^{\circ}\text{C}$]
Solvay PVDF 5130	1.78^{TDS}	$1,000,000^{\text{TDS}}$	-	-40^{TDS}	160^{EM}
Goodfellow PVDF	1.78^{TDS}	-	$25-60^{\text{TDS}}$	-40^{TDS}	163^{EM}

NMP – N-Methyl-2-pyrrolidone is an organic solvent. It is used to dissolve PVDF and create a cathode slurry by adding the active material and conductive additive to make a suspension. NMP is used as the slurry solvent for slurry cast cathodes in this work. The supplier is Sigma Alrich.

Table 3.4 Electrolyte material properties.

Material	Density [g cm ⁻³]	Molecular Weight [g mol ⁻¹]	Melting Point [°C]	Boiling Point [°C]
NMP	1.02 ^{TDS}	99 ^{TDS}	-22 ^{TDS}	202 ^{TDS}

1M LiPF₆ in 3:7 EC:EMC + 2 % VC additive - 1M LiPF₆ in 3:7 EC:EMC + 2 % VC is the standard electrolyte used in lithium-ion cells for this work. LiPF₆, lithium hexafluorophosphate, is the electrolyte salt. The salt binds with lithium ions to form a solvation shell which is capable of diffusing through the solvent to facilitate ionic transport between electrodes. The solvent ethylene carbonate (EC) and ethyl methyl carbonate (EMC) are used to facilitate rapid diffusion of the electrolyte salt. It is a volatile and combustible solution. EC plays a pivotal role in the development of interphase layers around the active material to resist capacity fade. Similarly, vinyl carbonate (VC) is a sacrificial component which reacts with the active material to form stable interphase layers which is the reason for the low 2 % concentration. There are alternatives to EMC, DMC (dimethyl carbonate) and DEC (diethyl carbonate). These are similar molecules with either shorter or longer molecular chain length. DMC has better diffusive properties but has greater volatility. DEC has lower volatility but has of lesser diffusive properties due to its larger molecular weight. The supplier of the pre-mixed electrolyte is Targray.

4 mM/50 mM TBAClO₄ in 1:1 EC:DEC – Tetrabutylammonium perchlorate (TBAClO₄) is an electrolyte that is too large to facilitate intercalation in lithium-ion systems and can be used to test the cells under intercalation-blocking conditions. This electrolyte was used for a specialised test: electrochemical impedance spectroscopy of symmetrical cells. This electrolyte formulation was mixed in the lab. The supplier is Sigma-Alrich for all components.

Lithium Chips – Lithium metal chips were used for constructing half cells. Lithium is useful in a half cell because it serves as a reference electrode. This allows testing of just an anode or a cathode. 250 micron-thick chips were used. The supplier is Cambridge Energy Solution Ltd.

3.2 Ultrasonic Welding

Ultrasonic welding is a technique that uses ultrasonic vibrations to create heat through friction. This heat melts the surface of the parts, which allows bonds to form and join the parts. Ultrasonic welding requires no additional components to be included in the design, e.g. nuts or bolts, or the addition of another substance, such as an adhesive ^{308,309}. The prevention of any additions keeps the profile of the weld low and does not add any potential fault points; a nut and bolt can rust or be mechanically compromised if struck and adhesives may contain chemicals that may not be ideal to introduce into the system or may restrict the operating parameters e.g. some adhesives have less pH resistance than plastics. Limiting foreign substances is always beneficial. The technique is also extremely rapid, as it only requires heat conduction. This establishes ultrasonic welding for mass production, which is why it has been adopted by the automotive industry to weld wires rapidly ³¹⁰. Vibrations cause heat generation at interfaces therefore surface damage is minimised. The process also does not release any fumes, sparks or material, meaning it does not contaminate the near vicinity or the environment ³¹¹. The cleanliness and simplicity of ultrasonic welding make it advantageous to most joining techniques, however there are drawbacks. A limitation of ultrasonic welding is the inability to weld some materials; the properties of a material greatly affect how effectively vibrations are converted to thermal energy. Common usable materials are metals, plastics and fabrics. Welding parts thicker than 6mm has been proven challenging due to the long propagation of vibrations. The joint design must be simple e.g. an overlapping or shear joint ³¹². These disadvantages can be overcome by selecting appropriate materials and implementing correct weld design.

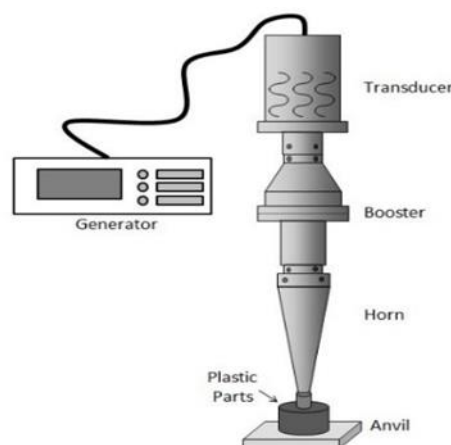


Figure 3.2 Ultrasonic welder with annotated components. ³¹³

3.2.1 Device

An ultrasonic welder is a device that is designed to generate and control ultrasonic oscillations and apply this energy for a set time and pressure. This creates work and heat to weld multiple parts together. It is important to be able to control these parameters because the joining of different materials requires varying amounts of work. There are four primary components in an ultrasonic welder: an ultrasonic generator, a transducer, a booster and a sonotrode. These are displayed in Figure 3.2. There are also secondary components in an ultrasonic welder which are pivotal for its function: a pneumatic chamber, which creates the pressure; a processor, which informs the generator; and an anvil, which is a base to weld onto.

3.2.1.1 Ultrasonic Generator

The goal of the generator is to convert the mains supply of electricity into power of the correct frequency and voltage necessary for the transducer. Ultrasonic welders have an interface to control the process parameters. The inputs from the user will be analysed by a processor in the machine which will output the frequency and voltage each time the machine operates.

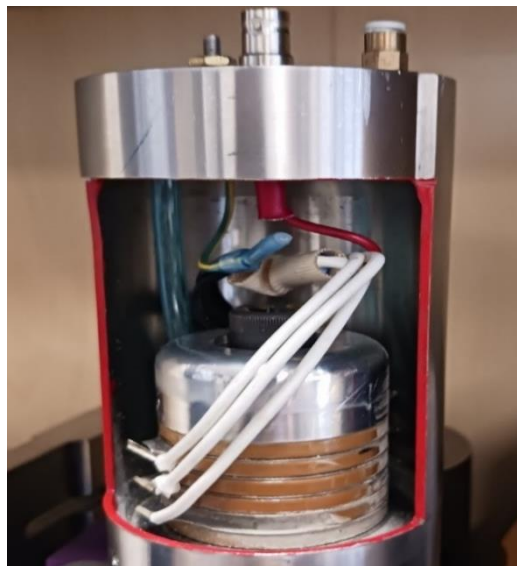


Figure 3.3 A skeletonised booster showing the transducer. The piezoelectrics discs can be seen which expand during voltage.

3.2.1.2 Transducer

A transducer converts the electrical energy from the generator into kinetic energy. The transducer contains piezoelectric discs which are connected to metallic surfaces and expand or contract in the presence of an electric field. This is critical because the discs change size and shape in the presence of electricity. The expansion is controlled because it correlates with the voltage. Due to the output of the generator, the electricity supplied to the transducer will

have a frequency and voltage to stimulate this expansion and contraction thousands of times a second. This is how the oscillations are created.

3.2.1.3 Booster

The booster's objective is to amplify the oscillations produced by the transducer and to propagate the vibrations to the sonotrode. The mechanical vibrations produced will be of the specified amplitude and frequency, so the booster is the ideal mounting point for the sonotrode. Due to the vibrations being ultrasonic, the booster must be fashioned to resonate at the same frequency range the machine is designed to operate at.

3.2.1.4 Sonotrode

The sonotrode (also known as a welding horn) is the sample contact point for the device. Its purpose is to transfer mechanical energy produced by the machine to the sample. The shape of the horn must be considered greatly. Effective design will maintain frequency and amplitude of oscillations whilst propagating the vibrations to the sample. Improper design will lead to oscillations with different frequencies or amplitude, leading to welding with parameters that have not been chosen, or it could completely fail to weld.

3.2.2 Ultrasonic Welding Parameters

A welding cycle consists of hold time, weld time and cool time; these are given as inputs. The times refer to the time from applied static force to initiation of ultrasonics, the timeframe ultrasonics occur for, and the time length after ultrasonics have occurred until relief of the static force.

3.2.2.1 Hold Time

Hold time is the time period prior to the ultrasonic vibrations in which the static force is loaded onto the sample. This timeframe will initiate after a threshold pressure has been reached. This ensures good sample contact prior to the work. This can also be set to a target force instead of a timeframe (e.g. 10 N). This will cause the work to be instantaneous after reaching the force threshold.

3.2.2.2 Weld Time

Weld time is the length of time that ultrasonic vibrations will occur and be transferred to the sample. A realistic weld time would range between 0.3 and 2.0 seconds. A longer weld time is

necessary when the material does not have good weldability, or the desired temperature is high. Weld time has a linear relationship with the energy transferred to the sample.

3.2.2.3 Cool Time

Cool time is the time length the static force is held onto the sample after ultrasonics. This is the timeframe during which the sample begins cooling and bonds anneal. Releasing of the pressure before annealing can compromise the weld strength.

3.2.2.4 Frequency of Vibrations

Frequency of vibrations is the rate at which oscillations occur; usual units are Hertz, which denotes how many oscillations occur per second. The minimum frequency used in ultrasonic welding is 20 kHz. A frequency less than this would not be ultrasonic; however, higher frequencies can be used. The upper echelon of frequencies used is approximately 200 kHz. It has been cited that the frequency range between 40-90 kHz typically performs better³¹⁴. Frequency is one of the factors in controlling how much energy is transferred to the sample.

3.2.2.5 Amplitude of Vibrations

Amplitude of vibrations quantifies the distance travelled in one full oscillation. The greater distance travelled causes more displacement and therefore energy transferred per oscillation. Amplitude can range from 10 to 100 microns.

3.2.2.6 Static Force

Static force indicates the load applied to the sample. The pressure generated in the pneumatic chamber will correspond to the applied force on the sample. The total time the sample is under the static load will be the sum of hold, weld and cool times.

3.2.2.7 Geometry of Energy Director (ED)

Energy directors are sacrificial segments on the sample which are subjected to higher temperatures and are intended to deform and spread over the welding interface; the melted energy director heats the welding interface at a rapid rate²⁸⁸. A successful weld will sacrifice the energy director; the material will completely melt and be incorporated into the weld interface. Energy directors do not need to be structured. A smooth surface, termed a flat energy director, is an option. Figure 3.4 displays a triangular energy director.

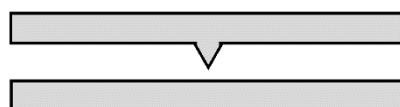


Figure 3.4 A triangular energy director.

3.3 Ultrasonic Welding of PVDF Strips

Two PVDF pieces were ultrasonically welded together using a TMAX-VS-40A welder (Figure 3.5). The bonding area for this test was a 4mm x 4mm square; the standard welding face supplied for the ultrasonic welder. The size of the welding head is proportional to the welded area, which directly correlates with the force necessary to fracture the joint. To standardise weld size, the force (newtons) was divided by the welding area to yield stress (pascals). Stress offers a more accurate comparison, since it normalises force to welded surface area; larger welds inherently require greater breaking forces, making direct force comparisons misleading.

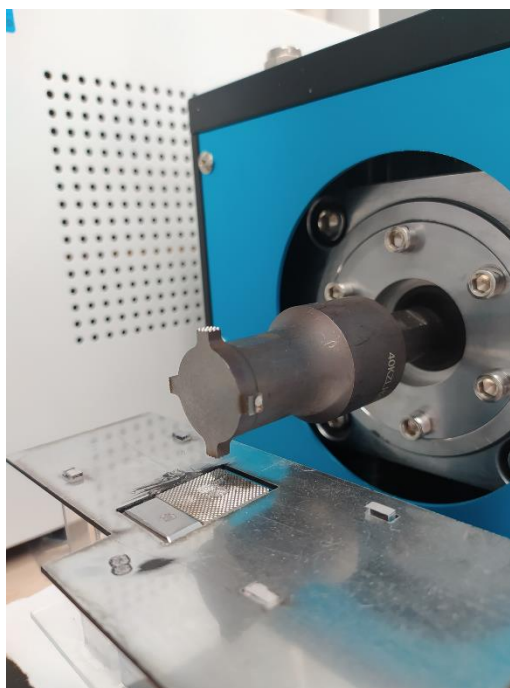


Figure 3.5 Pouch cell ultrasonic welder (TMAX-VS-40A) with a 4x4 mm square weld face sonotrode attached.

A 0.1mm thick PVDF sheet (Goodfellow) was cut into 50 mm x 6 mm rectangular strips to weld together. The process parameters were then input into the ultrasonic welder. The strips were aligned with an overlap of material underneath the welding head. Upon activation, the welding head pressed onto the two overlapping strips, compressing the material between the welding face and the anvil. This ultrasonically welds a 4 mm x 4 mm section of the two strips together to form a lap joint. The product is a 90 to 95 mm long sample with a weld in the middle, shown in Figure 3.8. The samples had two independent variables: weld time (range: 0.20 - 0.65 s) and amplitude (range: 50 - 100 %).

3.4 Stress-Strain Testing of PVDF

The experiment selected for a bonding strength test was a lap shear tensile strength test. A lap joint involves bonding overlapping material for a given area. This was selected because it is the simplest joint design. A shear tensile strength test is also a simple method to conduct in the Hounsfield machine.

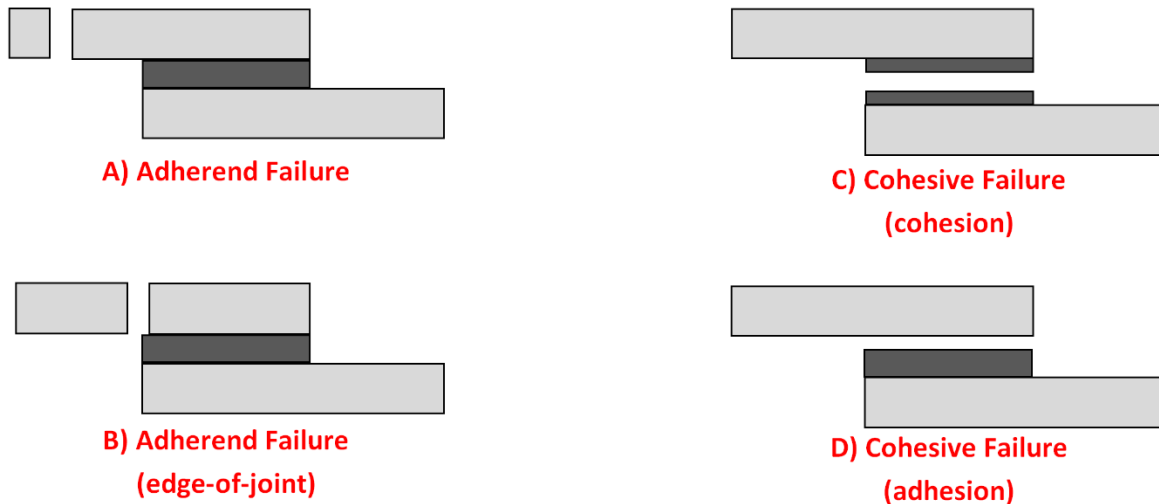


Figure 3.6 Strain Failure Diagrams indicating the four failure modes. a) adherend failure – a fault outside of the joint. b) an adherend failure on the edge of the joint. c) a cohesive failure – a failure within the joint. d) an adhesion failure – a failure to anneal the join to one side.

The Hounsfield machine, Figure 3.7, is an ideal piece of measuring equipment. It has a movable platform which can be mechanically moved closer or further from a second, fixed platform. The distance traversed by the moving platform can be measured whilst simultaneously measuring the resistive force that the machine is overcoming to enable the movement. Therefore, a sample attached to both platforms can be elongated until failure, and the distance from the original position is measured in tandem with the force necessary to elongate the material. This provides the data to plot a stress-strain curve for the sample.

An appropriate load cell is fixed into the Hounsfield machine and attached to the top, movable platform. A clamp is then fixed to the bottom of the load cell and the bottom fixed platform. The top platform is lowered until the distance between the clamps spans the length of the sample. The sample is then fixed into both clamps. The top platform is slowly extended away from the base until the sample is under tension and experiences a negligible load. The distance and the load are zeroed on the interface. The test is then ready to be initiated. The initial distance and the rate of extension are input to be conducted by the machine. The load will gradually increase whilst measuring the distance until there is a sudden loss in resistance and load due to the sample failure. This will cease the machine and end the test. This is carried out for each sample.

The distance between the two clamps was 80 mm before initiating the test. This controls the initial length and is used to calculate the strain of the material.

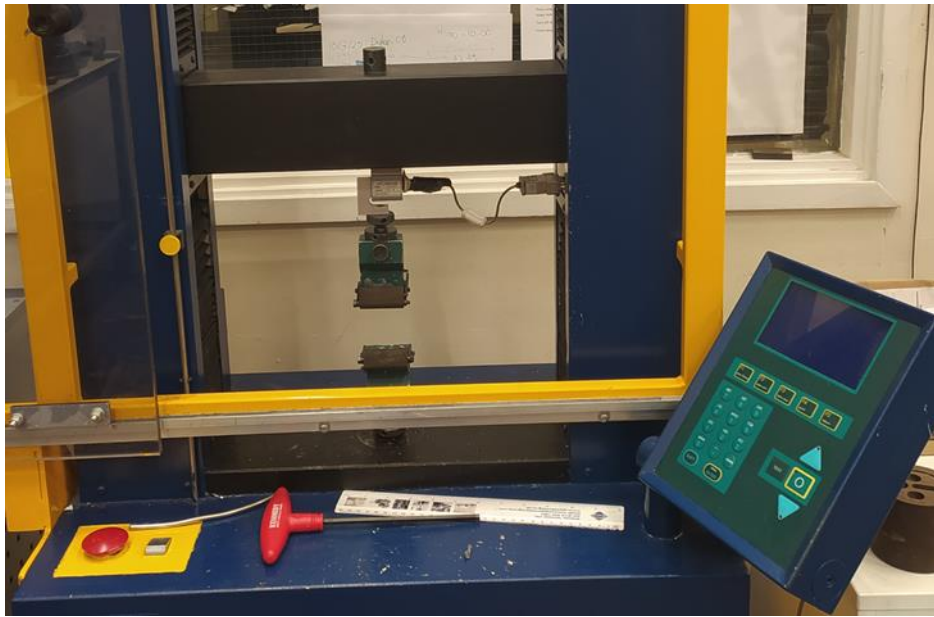


Figure 3.7 Hounsfield tensile tester with two clamps for the testing of PVDF strips.

All the samples were subjected to sufficient stress to cause fracture. The failures exhibited can be categorised into two different types: an adherend failure or a cohesive failure. An adherend failure involves a breakage in the material not involved in the bonding. A cohesive failure is a breakage of the material involved in the bonding. Adherend failures can be further detailed into two separate categories: a generic adherend failure or an edge-of-joint adherend failure, which



Figure 3.8 Clamp arrangement for the Hounsfield tensile tester with an ultrasonically welded PVDF strip product held in position, under tension, ready for mechanical testing.

involves the fracture of material not involved in the bond, but material close to the bonding material. This would typically occur when the bonding process causes a weakness in the sample. Cohesive failures could be categorised into adhesion or cohesion failures; however, it is difficult to distinguish between these two breaks due to the thickness of the samples. These failure types are detailed in Figure 3.6. Destructive testing involves straining the sample until failure. An adherend failure would be considered a successful weld; however, a cohesive failure would be considered a failed weld. An adherend failure is an indication of good bonding because the weld withstood a strain that caused the base material to fail. This is a simple qualitative analysis, but it serves to demonstrate if the bond formed was strong enough for the welded sample compared to a single continuous piece of PVDF.

3.5 Ultrasonic Calendering

This section details the preparation and the process to ultrasonically calender the 20 mm diameter sections of cathode. The main equipment was a Branson 2000X ultrasonic welder, Figure 3.9. This welder was selected for its size and its operating frequency of 40 kHz. The larger size accommodates larger compatible welding horns. This allows the ultrasonic calendering of a larger surface of cathode per operation. The 20 mm diameter circular welding horn was attached to the purple booster for the Branson 2000X welder. This booster has a 0.75 amplitude conversion; it reduces the amplitude of the ultrasonic oscillations received at the top of the booster to 75 % before being transferred to the welding horn.

The anvil, shown in Figure 3.10, was polished to remove surface roughness and texture. The welding horn was also polished similarly. The objective behind polishing the surfaces was to reduce less damage to the electrode film, despite the greater risk of the electrodes slipping³¹⁵. A clamp on the anvil reduced cathode slippage and movement during operation, Figure 3.10. The clamp would be less necessary if the film was larger and had more mass to resist movement. Weld parameters (e.g. weld time and amplitude) were adjusted with the control unit, Figure 3.11.

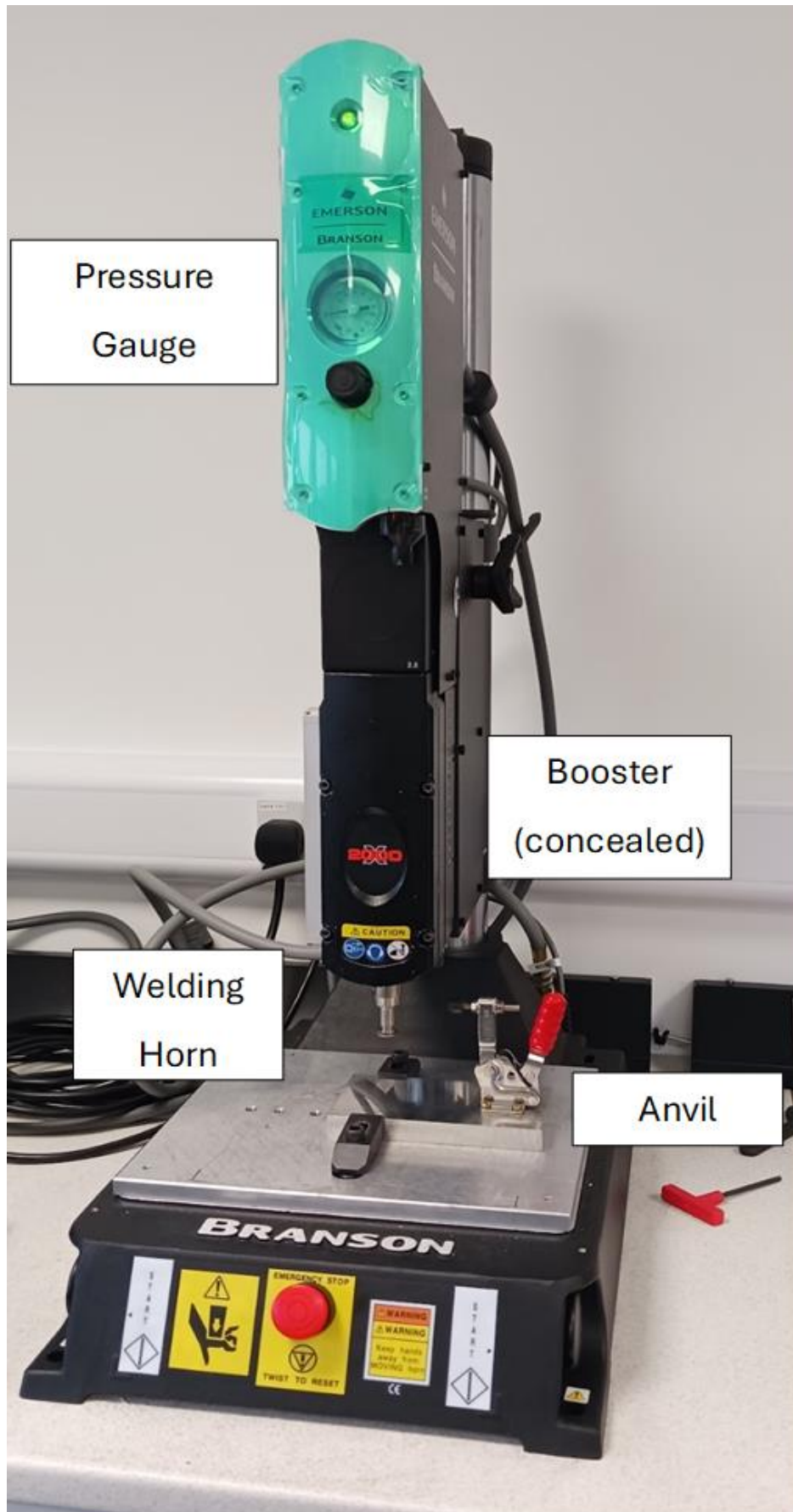


Figure 3.9 Branson 2000X ultrasonic welder with the 20 mm diameter welding horn and the anvil fixed in position.

3.5.1 Procedure

The electrode film is clamped down onto the anvil (Figure 3.10). The parameters are selected with the control unit. The space between the film and the welding horn is checked and cleared of obstructions. The welder is ready for activation. The welder is engaged by the two buttons until the sample have been ultrasonically welded. To prepare the next section of cathode, unclamp the electrode, inspect the anvil and welding horn for debris (clean if necessary), and shift the electrode until a fresh electrode section is below the welding horn. Reclamp the electrode to the anvil. If necessary, alter the welding parameters prior to proceeding.

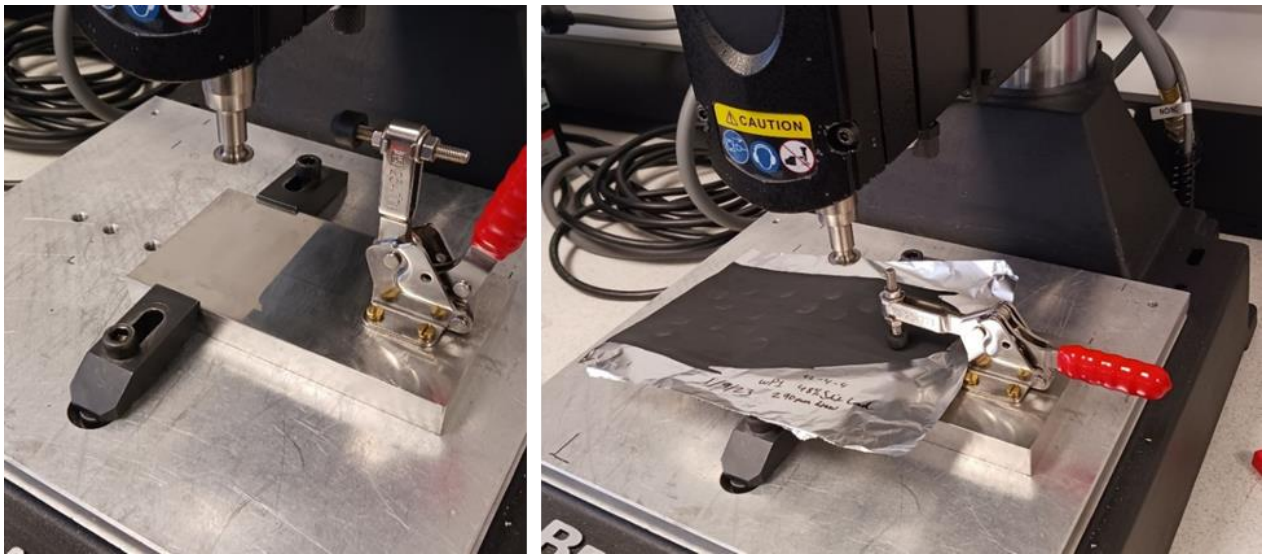


Figure 3.10 The anvil fixed for use with the ultrasonic welder and some NMC622 cathode clamped to the anvil during operation.

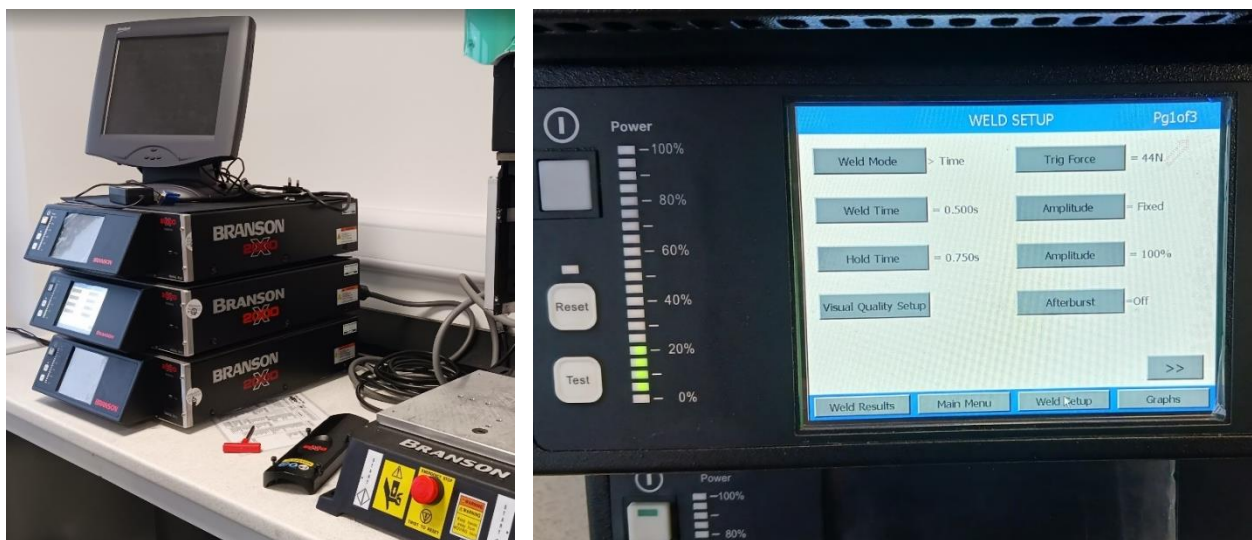


Figure 3.11 The controller and encoder for the Branson 2000X ultrasonic welder, the display on the control unit showing process variables.

3.5.2 Limitations and Considerations of the Parameters

Welding time, welding pressure, and oscillation amplitude are three important parameters defined in ultrasonic welding literature^{316–327}. These parameters were also observed to impact the quality of ultrasonic welds in the preliminary results, the welding of the PVDF sheets. A range of weld times and welding pressures were chosen in ultrasonic calendering of cathode with the 2000X welder. Welding gauge pressure was varied between 10 and 22 psi, and the weld time was varied between 0.30 and 1.25 seconds. It was estimated that the amplitude at the tip of the welding horn (the amplitude of oscillation transferred to the sample) was approximately 12 microns when the machine is set to 100 % amplitude, using of the 0.75x purple booster and polished welding horn, Figure 3.12. Unfortunately, oscillation amplitude could not be varied or explored due to machine error messages. Amplitudes of less than 100 % were attempted to be input into the machine however it did not initiate any welding. The welding head would lower to the film, but no ultrasonic motion started. It was suspected a safety shutdown feature was engaging, resulting from altering the amplitude from 100 %. Amplitude is reduced by intermittently cutting electrical power. The machine operates on an alternating current (AC). This means that the power is supplied in a sinusoidal waveform. To reduce amplitude, the lower and upper voltages are cut off to reduce the amplitude of the AC sinusoid. The machine's self-preservation algorithm can engage when welding samples which are not as feasible or expected to damage the welder; for an undetermined reason, this was engaging whenever the voltage was altered.

Literature indicates that a weld time above 2 seconds is uncommon and under a second is sufficient energy to initiate an ultrasonic weld³¹¹. For this reason, 0.3 s was chosen as the lower and 1.25 s as the upper limit. Regarding pressure, increasing the pressure beyond 25 psi caused a machine to automatically engage the safety shutdown mechanism. This occurred after contact with the cathode film, but before the initiation of any ultrasonic work. Pinpointing the cause of the safety and how to overcome it was difficult due to the engagement of the shutdown early in the welding process; it was challenging to determine what the machine was measuring and why it was concluding that readings were outside the normal range, causing it to fail the check needed to continue the process (similar to the error exhibited during reduced amplitude).



Figure 3.12 Branson 2000X ultrasonic welder with the booster removed, ultrasonic welder pressure gauge, the 0.75x gain purple booster with the welding horn attached, the welding horn in position.

3.6 Slurry Casting

All slurry castings were performed using the same procedure. The mixing and drying procedures were consistent across all batches. Different electrode film thicknesses were examined in this thesis. To achieve this the doctor blade gap was increased. Excluding this step, the casting procedure was consistent across all slurry castings.

3.6.1 Procedure

Weighing steps are performed in an argon-controlled glovebox with an atmosphere of < 0.1 ppm water and oxygen. A 4-point balance is used to measure mass. The Thinky mixer was outside the glovebox in ambient conditions. Prior the mixing steps, any involved powders were dried over 24 hours in a 120°C vacuum oven overnight until anhydrous. The materials were then moved into the glovebox; this involved leaving the material under vacuum in the glovebox antechamber for 3×5 minutes; filling the chamber with argon between each vacuum. All solvents and powders added during mixing were dispensed into the Thinky pot inside the glovebox and sealed, maintaining the argon environment before being removed from the glovebox and mixed in the Thinky mixer. The Thinky pot was not opened outside the glovebox until the final mixture was prepared for casting.



Figure 3.13 Slurry casting of NMC622 slurry on aluminium foil using a doctor blade.

The PVDF (Solvay) was added to a Thinky pot followed by NMP (Sigma-Aldrich) to make a solution of 8 % PVDF. The mixture was mixed for 1 minute at 500 rpm, before being mixed at 2000 rpm for 15 minutes. The solution should appear colourless and fully dissolved. C65 (Imreys) and half of the remaining NMP were then added to the Thinky pot and mixed for 1 minute at 500 rpm,

followed by 2000 rpm for 5 minutes. The NMC (BASF) was added to the pot with the remaining NMP. This final mixture was then mixed at 500 rpm for 1 minute and 2000 rpm for 10 minutes. The solution was then degassed at 2200 rpm for 3 minutes. The slurry mix was then ready to be cast.

Aluminium foil (15 microns thick) was placed over surface of the draw-down coater. The slurry was moved to the drawn down coater. A doctor blade height was then set to 180 microns using a shim over a glass plate. The doctor blade was placed onto the foil, and the slurry mix was deposited onto the foil ahead of the blade, in the shape of a femur. The doctor blade was then drawn across the draw-down coater at 1.4 m min^{-1} . The doctor blade was then removed, and the overhead heating elements were moved over the slurry and set to 80°C . The casting was dried for 1 hour before being transferred to an 80°C vacuum oven overnight.

After the overnight drying was complete, the dry casting was removed from the vacuum oven and punched with EL-CELL cutters. Cathodes were cut to a diameter of 14.8 mm to yield coin-cell-sized electrodes.

3.6.2 Quality Control of the Cathodes

This section evaluates the slurry-casting methodology conducted in this thesis and compares them to electrodes produced at pilot-plant or industry scale. Pilot-plant and industry-scale production involves slurry preparation under stricter quality control to eliminate vulnerabilities associated with electrode manufacturing e.g. hygroscopic materials. These processes and facilities differ from those made in laboratory environment, in which these electrodes were made.

The performance of the uncalendered electrodes exceeded expectations, particularly at high c-rates during electrochemical testing. Additionally, the conventionally calendered cathodes had a good rate performance, as expected; however, the impedances measured during EIS, did not reflect this improvement compared to the uncalendered cathodes. The charge-transfer resistance is expected to decrease with the lower porosity of the conventionally calendered cathode³²⁸, but this was not observed in the EIS Results (Section 4.5.2.1).

3.6.2.1 *Atmosphere*

The electrodes used for the data presented in these results were exposed to a far less controlled environment than industrial or pilot-plant electrodes. The industry standard for

electrode production is a dry room. This involves removing moisture and gases from the atmosphere to reduce interaction with the electrodes.

The cathodes in this project experienced a much less controlled and not always inert atmosphere from slurry casting through cell sealing:

The slurries were prepared in a glove box, an argon controlled environment. This prevents the introduction of contaminant gases and the re-introduction of any water removed during the vacuum oven drying. All work in the glove box was only conducted with readings of <0.1 ppm water and <0.1 ppm oxygen. Once mixed, the slurry is cast outside the glove box in a fume cupboard. Once dried, the cast electrode is cut into sheets and transferred into a vacuum oven overnight to ensure the complete removal of NMP. This concluded the slurry casting and drying stages. The dried electrode sheets were then transferred, with a heat sealer, into the glove box. The electrodes were sealed in an airtight bag. This created an argon-filled, closed environment for the electrodes to travel to the off-site lab in Crawley. The electrodes were opened at the lab in Crawley, ultrasonically calendered and then placed back in the bag without heat sealing; the Crawley site did not have an inert source of gas to seal the bag. The transport of electrodes took approximately 6 hours before being returned to the vacuum oven. This process involved significant exposure to an uncontrolled environment. The exposure should have been identical for the ultrasonically calendered cathode and controls because all the electrodes used in the experiments experienced the same slurry casting procedure and transport related to the Crawley site; however, identical exposure doesn't guarantee that the contamination risk impacted every sample in the same way.

3.6.2.2 Production Quality and Quantity

Pilot plants can produce slurries on the order of kilograms. This creates a large batch of electrode material that has been mixed and cast under identical processing conditions. This is far more consistent than laboratory-made electrodes. The electrodes in this thesis were produced in several batches due to draw-down coater surface area and Thinky pot volume limitations.

3.6.2.2.1 Drying Bed Surface Area and Thinky Pot Capacity

The vacuum dryer imposed a surface area limitation of about 1.5 m length of drying space. This created a fixed length for the slurry casting. This is combined with the fixed width of the doctor blade. This limits the producible surface area of coating per drying session. Additionally, the

Thinky mixer utilised 125 ml Thinky pots. This restricts the volume of slurry which could be made in a single batch. Slurries are made of several components, each with different densities and solubilities. The drying process took an hour before transferral to the vacuum oven, making the mixture is vulnerable to separation during time frame. As a result, only one electrode could be cast per batch of slurry.

3.6.2.2.2 Drying Bed Heat Retention

An additional consideration is the high heat capacity of the draw-down coater. This resulted in slurries having to be mixed and drawn down on consecutive days to allow for cooling. If cooling was disregarded, replacing a newly dried electrode with current collector and a doctor blade would transfers heat to the current collector and the doctor blade, elevating the temperatures of both. Attempting to slurry cast with the elevated doctor blade and current collector temperatures would cause rapid drying of the slurry upon contact with the current collector and the doctor blade. Slurry will build up on the hot doctor blade, leading to agglomerations, should dry electrode pieces break off and fall into the wet slurry, and to a non-uniform drawing of the slurry, leading to an inhomogeneous and textured film because the wet slurry is in contact with a textured, dried electrode rather than the smooth, metallic doctor blade. The rapid drying also changes the final thickness of the electrode; as slurry is drawn down and meets the heated current collector, it dries almost instantly. This will alter the course of the doctor blade, mostly in the z-axis, because the solidified coating resists the inertia of the doctor blade more than a liquid.

These additional considerations resulted in multiple slurries being mixed and cast over several days. Despite operator experience in these processes and the adherence to a precise and robust SOP practice, mixing, coating and, drying are complicated processes that are still not fully understood, and may not have resulted in identical products. The variables involved in these processes are difficult to recreate exactly for each slurry, and simple factors such as relative humidity or ambient temperature of the laboratory will affect the slurry casting.

3.7 Calendering

Conventional calendering in this project was conducted by placing a punched electrode between two stainless steel plates before feeding this stack between two rollers of an MTI heated electrode calender. The roll speed was 1 m min^{-1} . The calender did not have line-load

measuring capabilities. The roller gap was measured and controlled by two micrometers attached to the top roller and zeroed when there is no roller gap. The rollers were set to a temperature of 40°C. Calendering was conducted in four passes: forwards, backwards, inverted forwards and inverted backwards. The electrode, sandwiched between two stainless steel plates, underwent four passes to reduce shear strain from the rollers and minimise non-uniform compression of the electrode film. Porosities were calculated using micrometer thickness measurements and density values.

3.8 Coin Cell Construction

Cathode half cells are assessed in this work. Half-cell assembly adhered to a strict protocol to ensure comparable data between cells and batches.

Cell components are kept in an 80 °C vacuum oven overnight before being transferred to a glovebox. The glovebox is argon-controlled and maintained at <0.1 ppm oxygen and water. Coin cell parts are vacuumed in the antechamber while hot from the vacuum oven for three 5-minute cycles, refilling the antechamber with argon between vacuums. Once moved into the antechamber, the cell assembly begins. One 250 µm lithium chip is scrubbed with a toothbrush to remove surface oxide and placed into the base of the cell, the negative can. A full cell separator (Celgard H1609) of 16 mm diameter is placed onto the lithium chip. 80 µL of 1 M lithium hexafluorophosphate (LiPF₆) in 3:7 EC:DEC with 2 % VC additive is dispensed onto the separator with a micropipette. The cathode is placed coating-down, followed by a 1.0 mm spacer and a 0.5 mm spacer. A wave spring is added before the positive cap is placed onto the cell stack with a vacuum pen and gently pressed to compact the cell. The cell is flipped and placed into a cell crimper with plastic tweezers and subjected to 70 kg m⁻² of force to crimp the cell. Cells are then transferred to small plastic pouches to electrically isolate them whilst they are removed from the glove box and placed in a cell-cycler.

3.9 Cell Cycling

Cells are tested using a Maccor cell-cycler. Cell tests are managed in the MIMSCClient software. The cell rate test is performed in two parts: a pre-EIS procedure, and a post-EIS procedure. The pre-EIS test involves formation cycles at C/20 and charging up from 3.0V to 4.2V for EIS. The

post-EIS test is a rate-capacity test progressively increasing the discharge c-rate from 0.1 to 5C. Charges are performed at 0.1C or 0.2C when the discharge c-rate exceeds 0.1C. Constant current constant voltage (CCCV) charges are employed to ensure cells reach their maximum capacity for 4.2 V. Increasing the upper voltage limit beyond 4.2 volts would increase the available capacity of the cell ³²⁹. All discharges are galvanostatic with constant current; they do not have a constant voltage step, and terminate once the voltage reaches 3.0 V. There are 30-second rest intervals seconds after charging or discharging, prior to the next step. The cells are placed in cell-holders within 25 °C ovens to control the temperature during the cycling; this regulates the temperature-sensitive kinetics of the cell's electrochemistry ³³⁰.

3.10 Scanning electron microscopy (SEM)

3.10.1 Theory

A scanning electronic microscope (SEM) uses a beam of electrons to image a sample. This employs a field emission gun to generate the electron beam. Electrons generated by the source are known as incident electrons. These electrons are then accelerated, giving the electrons more energy ³³¹. The acceleration is achieved by applying a voltage to the electrons, known as an accelerating voltage. Typical accelerating voltages range from 5 to 20 kV. The SEM has multiple rings of electromagnets that act similarly to lenses in optical systems: to focus and concentrate the electron beam from the source onto the sample at the correct angle for reflection onto a detector for measurement. There are multiple sources of signal sources generated from the interactions of the incidence electrons with the sample. Secondary electrons (SE) are electrons ejected from the atomic shells of the sample following a collision with an incidence electron. Multiple secondary electrons (in the thousands, positively correlating with accelerating voltage) can result from one incident electron. Backscattered electrons (BSE) are incident electrons which have interacted with the sample and have been redirected toward the detector. There is at most one backscattered electron for each incident electron, which leads to a very low signal ratio of BSEs to SEs; however, BSE signal intensity increases steeply with sample atomic number and can be used to identify heavier elements ³³². X-rays are also generated. When secondary electrons from inner atomic shells are ejected, electrons from the outer rings drop down to fill the vacancy; the electron loses energy from the shell drop, which is released in form of an x-ray ³³³. Electron shell gaps are unique for each

element; therefore, the wavelength of the x-ray corresponds to the energy released, making each x-ray characteristic of a particular element. This enables elemental differentiation of the sample.

3.10.2 Experimental

3.10.2.1 *Microscope*

The scanning electron microscope used was an FEI Inspect F50 equipped with an Oxford Instruments 80 mm² silicon drift detector for energy dispersive x-ray spectroscopy (EDX). Electron microscopy was conducted at 5 kV to yield more surface information and at a spot size of 3.5. A working distance of 10 mm was also employed for all samples.

3.10.2.2 *Resin Impregnated Cross-sections*

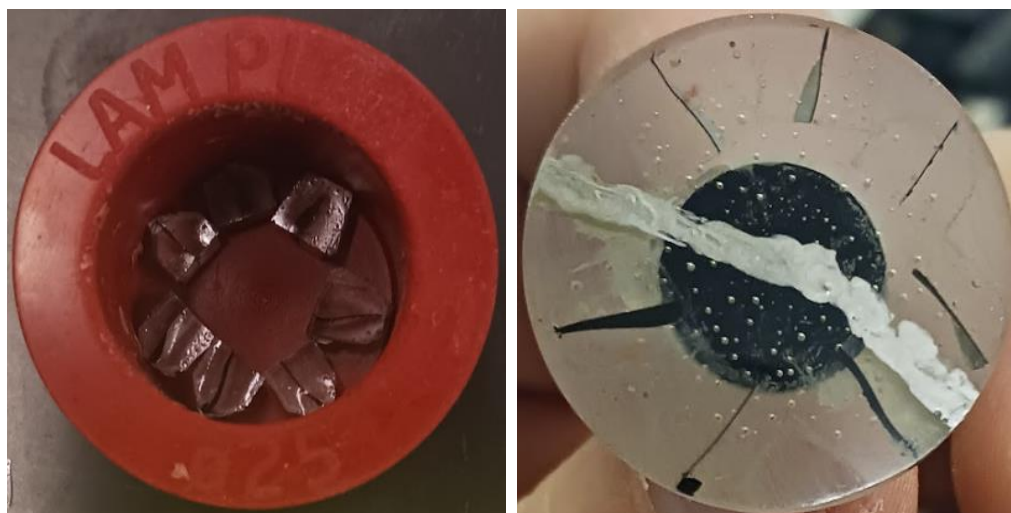


Figure 3.14 Resin tombs which have been placed into the 25mm circular die and the final polished tomb, earthed with silver paint which connects the surface to the metal stub. The black lines are cathode cross-sections.

Resin casting was conducted by cutting pieces of electrode and placing them into a mold to create individual resin tombs. The resin (EpoFix Resin with EpoFix Resin Hardener) was mixed by pipetting 10 g of resin into a Thinky pot before adding 1.2 g of resin hardener (1.2:10 weight ratio of resin hardener to resin). The mixture was hand stirred and folded for 30 seconds before mixing in the Thinky mixer for 8 minutes at 1500 rpm with 3 minutes of degassing at 2200 rpm. The resin mix was then pipetted into the mold to cover the electrodes. Pipette discipline involved avoiding bubbles in the mix and slow dispensing to not introduce bubbles. Once covered, the mold block was transferred to a glovebox antechamber and vacuumed over 10 minutes, held at vacuum for 1 minute, before re-pressurizing the antechamber over 20 seconds. This removed gas from the mixture and impregnated the resin into the pores of the electrode. The mold block was monitored for resin spill, topped up if needed, and re-vacuumed down if too much resin was lost. If only a small amount was lost, the refilled resin did not need

to be vacuumed. The resin block was transferred to a fume hood and left to set overnight (12+ hours).

Once set, the tombs are removed and placed into a circular 25 mm diameter mold (Figure 3.14), as these dimensions are compatible with the VibroMet. The same resin composite is reused to set the tombs into a block at the base of the mold. This presents a 25mm diameter circular face to polish. A polished finish is required to resolve the microstructure under SEM³³⁴.

Polishing was conducted by hand with silicon carbide grit pads, diamond polishing paste and then with a VibroMet vibratory polisher coated with 0.05 μm aluminum oxide solution: The stub was polished on silicone carbon pads of 2500 grit, followed by 4000 grit. This yielded a 4 to 5 μm finish. Imperfections could be seen by looking under an optical microscope; observing the current collector is the best measure. 1 μm diamond paste was worked into a damp velvet cloth and the resin block was polished until at a 1 μm finish (checkable with an optical microscope). The stub was then mounted into the VibroMet circular holder. MasterPrep Alumina 0.05 μm aluminum oxide solution was dispensed to coat the microcloth mat in the VibroMet. The VibroMet was turned on and set to 30 % oscillation strength. The resin block in the sample holder was placed at the centre of the mat and allowed to polish. The block was polished for 60 minutes. If the block orbited to the edge of the polishing mat, it was placed back into the centre. How quickly the block orbits to the edge of the mat indicates how level the sample is.

3.10.2.3 *Bladed Cross-sections*

Bladed cross-sections were prepared by slicing the electrode film with a razor blade. This method promotes sample pull-out, causing a non-uniform, rough cut but results in less fragmentation of the NMC particles. Bladed cross-sections were employed to look at the CBD. The sample was also carbon-coated with 5 ng cm^{-2} .

3.11 Optical Microscopy and Topography

To assess the surface roughness of the electrodes, a Keyence 7000N digital microscope was employed to image the cathodes. This microscope can image samples in three dimensions yielding x, y and z-axis data. This data can be used to produce 3D topography of the electrode. To produce high-resolution imagery of whole-scale electrodes, a panoramic image was employed with z-stitching. Panoramic imaging takes multiple images in sequence with a slight overlap. This allows the microscope to render all the images together, providing a large image

covering the whole electrode. Z-stitching involves taking images at multiple heights to focus the entire field of view. Light has a relatively long wavelength^{335,336}, meaning its short depth-of-field is shorter than the height range of the sample. Z-stitching takes multiple photos along integers of the z-axis before assessing each pixel in each photo. When a pixel is in focus, it will have a higher light intensity, due to the reflecting light converging on the detector instead of to scattering. The microscope analyses every pixel at all the heights and compiles each pixel in focus into a final image. This provides an image entirely in focus despite the depth-of-field limitations. It also provides topography data, as the height at which each specific pixel is most focused can be associated with the height of the sample.

3.11.1 Imaging Procedure

Individually, each electrode sample was placed in the centre of the microscope base. The electrode was covered with a glass slide to help eliminate topography contributions from the electrode's convexity or concavity. The weight of the glass slide flattened the electrode against the microscope base. The sample was brought into focus at the default 20x magnification before increasing to 100x magnification. The 100x magnification provided topography data at single-micron resolution. However, this did not provide a field of view large enough to capture the entire electrode; therefore, panoramic imaging was used. The panorama boundaries were defined using a rectangular function, selecting a start point to the bottom left of the electrode and an end point to the top right of the cathode. To gather topography data at multiple heights using Z-stitching, the lowest point of the sample (the electrode base plate) was brought into focus and selected as the low focus limit, and then the highest point (the surface of the electrode) was brought into focus and selected as the high focus limit. This provided a z-axis range in which the microscope took multiple images to render the sample in focus. After the panoramic and z-stitch ranges were defined, the imaging was initiated. The microscope imaged the sample and, upon completion, provided a 3D model.

3.11.2 Line-scans and Analysis

Line-scan topography data was collected by selecting two points using the '2-point' tool after opening the 3D model of the sample. A point off the electrode, on the base, was selected and another point on the base, on the other side of the electrode was selected for measurement. The tool is shown in Figure 3.15. This provides the height of the electrode. To account for the inhomogeneity, which is common in any electrode, four line-scans were conducted for each

sample; transecting the sample horizontally, vertically, and along two diagonals. This provides the z-axis height along the four transects.

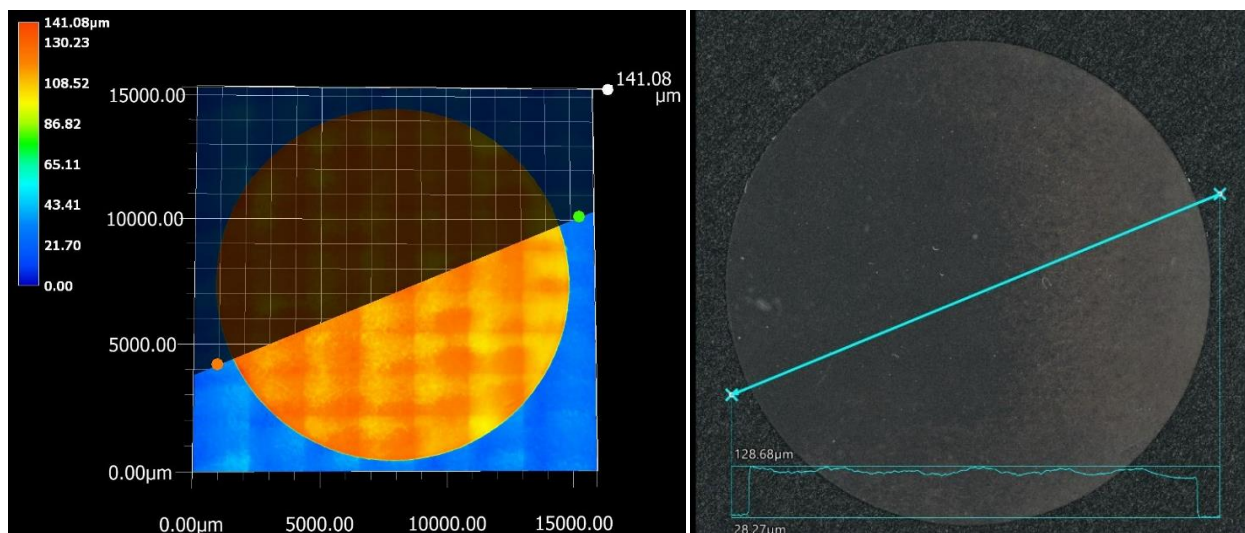


Figure 3.15 Electrode line-scan topography tool. Two points are selection either side of the electrode to measure the height and topography of the sample.

It was observed that the electrodes were concave, especially towards the edge of the electrode. This was likely due to the cell punching procedure and general electrode manual handling. To reduce the effect, the topography was only considered over a diameter of 11.5 mm within the electrode, excluding the edge. Because the undulation consisted of increases in height followed by decreases, the roughness of the electrode was calculated by squaring and then square-rooting the change in height. This causes positive changes and negative changes in height to be recorded as a positive value. The total change over the transect can be summed and a greater value indicates more undulation from greater changes in height and averaged over the line length, dZ/dX . This is a suitable substitution for surface roughness and allows a quantitative comparison in the results.

3.12 Electrochemical Impedance Spectroscopy (EIS)

3.12.1 Theory

Potentiostatic electrochemical impedance spectroscopy functions by applying a sinusoidal voltage of multiple frequencies through an electrochemical circuit and measuring the responsive sinusoidal current. Due to Ohm's law relating resistance voltage and current, the current will change due to the resistance in the system. This will manifest as an offset in the signal known as a phase shift. The phase shift is effectively a delay in time between the peaks

of the voltage and current sinusoids. The phase shift indicates the impedance of the system for the given frequency. Measuring the system at a range of frequencies indicates the impedances of the system which can be modelled as an equivalent circuit. This is possible because the components in the equivalent circuit react differently and present different impedances for each frequency.

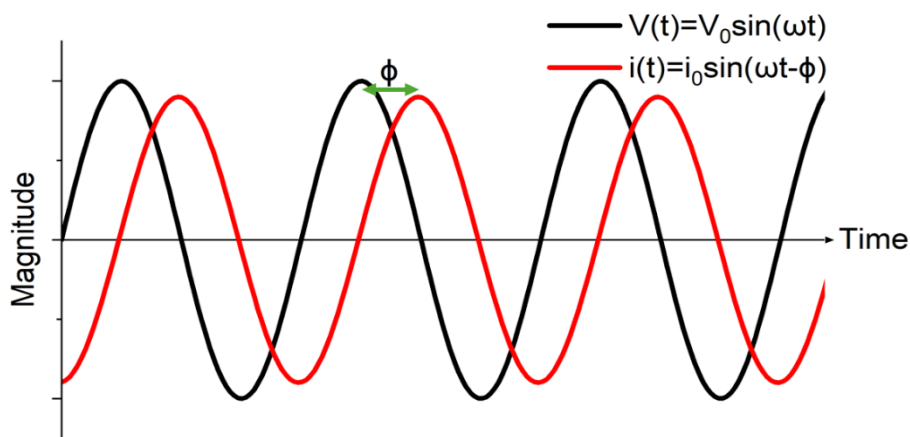


Figure 3.16 Input (voltage) and output (current) of potentiostatic EIS, ϕ indicates the phase shift between the voltage and current.

Performing a Fourier transform of this data, inverting the data from time to frequency and then plotting the data in Cartesian coordinates yields data points with a real resistance (x-axis) and an imaginary resistance (y-axis) which can be plotted as a Nyquist plot.

3.12.2 Experimental

3.12.2.1 Experimental Set-up

Electrochemical impedance spectroscopy was used to measure the impedances of the cells. To conduct the EIS fairly, the cells were formation cycled from 3.0 to 4.2 volts twice at a c-rate of 1/20 before being charged to 4.2 V in the Maccor cell-cycler. This ensures similar aging and open circuit voltage for all the cells because state of charge (SoC) and state of health (SoH) both influence battery impedance^{337–340}. Cells were loaded into the cell-holders for a Solartron 1470E, which are housed inside a Faraday cage within a temperature-controlled oven set to 25 °C. This configuration regulates the cell's temperature and provides shielding from external frequency interferences produced by other electronics. The EIS protocol involves holding the cells at their OCV for 15 seconds before initiating the voltage sweep from 1,000 kHz to 0.01 mHz at a sweep rate of 10 mV.

3.12.2.2 *EIS for Half Cells*

In this project, the EIS of the cathodes was conducted after two complete formation cycles and the reaching 4.2 volts (charging and discharging at 0.05C between 3.0 to 4.2 volts before being charged to 4.2 V at 0.1C). This ensures that the cells are all measured at the same voltage. The equivalent model used involves a resistance, a resistance and capacitor in parallel followed by a Warburg Diffusion. The system would typically yield an offset semi-circle followed by a 45-degree flick, which can be observed in the results, excluding anomalous readings. There were two motivations to choose 4.2 V for the EIS: The charge-transfer resistance will be smaller when the cells are charged to 4.2 V compared to 3.0 V. This is because the NMC is highly oxidised and the lithium ions with their respective electrons have transferred from the cathode to the lithium metal anode. This results in the cathode having a high affinity for lithium ions as there is a chemical potential energy from intercalating the lithium ions back into the cathode. In this state, the resistance regarding intercalation of lithium ions is reduced. It is also easier to control for because the charge to 4.2 V is CCCV, whilst the discharge to 3.0 V is only constant current.

A typical response from a freshly constructed half-cell would be modelled with an equivalent circle of $R_b - R_{ct}/C_{dl} - Z_w$ and is demonstrated in Figure 3.17. This model is also common in multiple works exploring the EIS of cathode half cells^{341–345}. Bulk resistance (R_b) is a high frequency resistance at the beginning of the semi-circle³⁴⁶. This is associated with the electrical resistance of the system³⁴⁷. Electricity can be described by a flow of electrons; electrons are extremely fast and are therefore represented first in EIS measurements during the high frequency response. The resistance includes the coin cell casings, electrolyte, and the coin cell holder. The semi-circle (R_{ct}/C_{dl}) involves a resistance and a capacitance in parallel, the resistance is denoted by the x-axis intercepts of the semi-circle, and the capacitance is denoted by the height of the semi-circle along the y-axis. R_{ct} denotes the charge-transfer resistance, representing the kinetically limited chemical reaction of a lithium ion and an electron to insert into the lattice of lithium metal salt. The capacitive component is a double layer capacitance attributed to a formation of orientated solvation shells at the active material interface. The lower frequency portion of the response is associated with the diffusion of ions through a semi-infinite system (Z_w). It is portrayed as a 45° line before the response begins to tend to 90° asymptotically. The ions have a large amount of electrolyte they can diffuse through. The movement of ions through a solution is one of the slower processes in a cell, which is why the process is portrayed at low frequencies. It should be noted that lower frequencies of EIS are less reliable and are increasingly vulnerable to noise and error. This is of particular concern with

Li-ion systems being transient systems and displaying OCV hysteresis^{348,349}. It can lead to unusual behaviour, presenting a non-straight Warburg line in some cells.

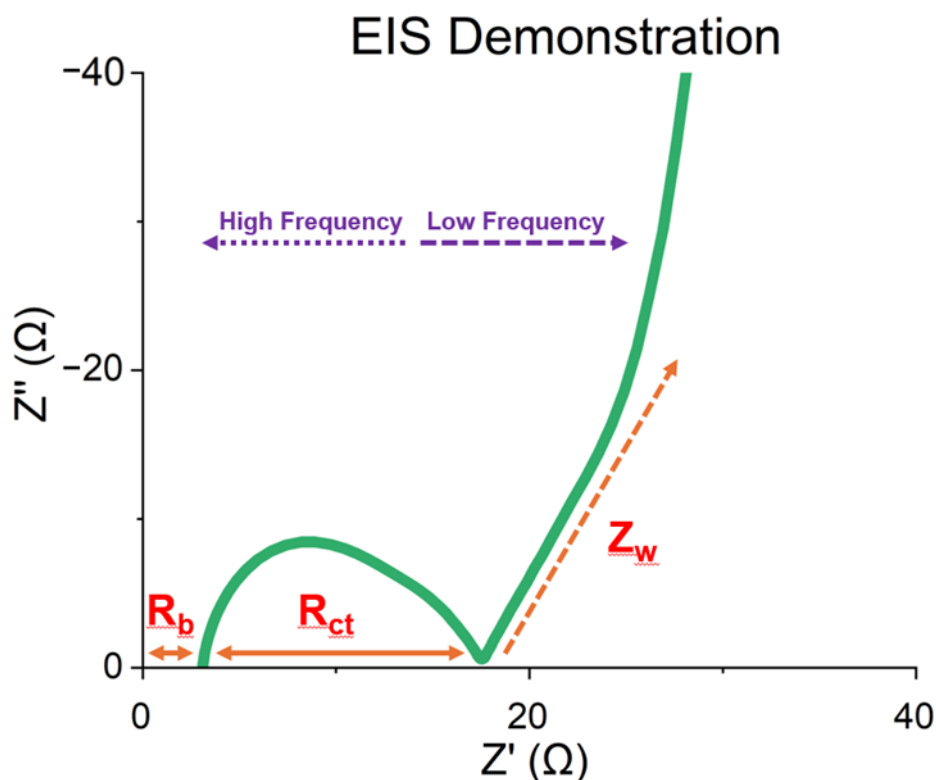


Figure 3.17 Annotated EIS response seen for cells using a model of R_e - R_{ct}/C_{ct} - W_o . Electrical resistance (R_e), charge-transfer resistance (R_{ct}) and Warburg Diffusion Element (Z_w). This circuitry is known as Randles Cell.

The Randles cell equivalent circuit could be applied to the system; however, it could be advocated that the more appropriate equivalent circuit model (ECM) would be a double Randles cell (R_b - R_{cei}/C_{cei} - R_{ct}/C_{dl} - Z_w). This is due to the knowledge of the cells having undergone formation cycles and the shape of the semicircle being skewed to one side. This indicates that the semicircle could be two semi-circles in series but cannot be resolved and therefore shows as an irregular semi-circle, demonstrated in Figure 3.18(1). It can be confirmed that two semi-circles are present by observing the results of the cells in Figure 4.15 and Figure 4.16 showing responses similar to Figure 3.18(2); portraying two similarly sized semi-circles which can be confidently resolved. Double semi-circle (two R/C's in parallel) is a common EIS responses for cells^{350,351}. The first semi-circle could be the impedance surrounding the traversal of the solid-electrolyte interphase at the cathode (CEI)³⁵². This resistance is similar amongst the cathodes as it increases depending on primary particle surface area and the age of the cell. The primary particle surface area should be highly similar amongst all the cathodes providing they have similar porosities. The age of the cells is the same; all cells in this analysis were constructed and then moved to the Maccor cell cycler to begin electrochemical testing. The cell cycle and time since cell construction are the same; therefore, aging is a controlled variable. The control

of both these variables indicates the CEI impedances are expected to be negligibly different between the cells. In this model, the second semi-circle will be the charge-transfer resistance of the cathode (R_{ct}).

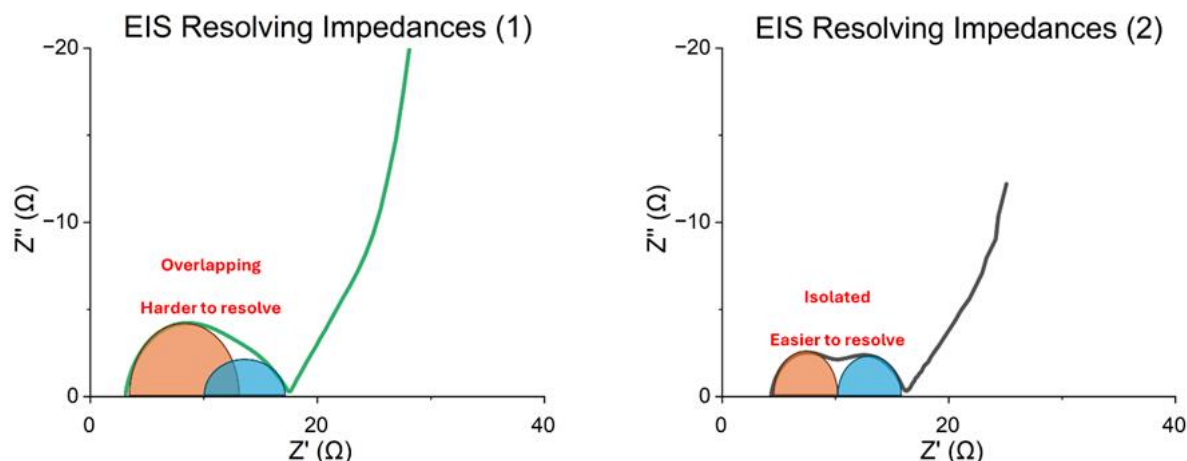


Figure 3.18 EIS responses measured for two different cells. They both have $R_b-R_{cei}/C_{cei}-R_{ct}/C_{ct}-W_o$ models. The $R_{cei}/C_{cei}:R_{ct}/C_{dl}$ ratio in (1) is skewed towards a larger R_{cei}/C_{cei} . (2) represents a $R_{cei}/C_{cei}-R_{ct}/C_{dl}$ ratio of 1. It can be observed it is easier to resolve (2).

R_{cei} and R_{ct} both involve the movement of lithium ions through a medium while experiencing attractive and repulsive forces. This consequently will manifest the impedance response at similar frequencies. Processes of similar speeds and impedances will manifest as two semi-circles which overlap but can be resolved, Figure 3.18(2). Time constants indicate the characteristic frequency at which the impedance will manifest the greatest in the response. A time constant correlates to the product an impedance's capacitance and resistance. Therefore, impedances of the same time constants are unresolvable and manifest as one impedance. Two processes with a similar time constant, but with one impedance larger than the other will present as one large semi-circle encroaching on a smaller semi-circle and will be difficult to resolve as they overlap, Figure 3.18(1). When the time constants of R_{ct} and R_{cei} differ more, the response will be illustrated as two semi-circles with greater separation. This response, Figure 3.18(2), is easier to resolve.

R_{cei} is expected to be similar or only slightly different amongst the cells, because despite CEI being a complicated phenomenon, the cell protocols and chemistry are similar³⁵²; however, the corresponding impedances in the results differ. R_{cei} is also a significant impedance towards reducing the rate capabilities of the cells³⁵³. Some results also have poor separation between the two impedance semi-circles.

The evidence suggesting that the first semi-circle in the EIS of the NMC half cells is not electrolyte-ionically related is the frequency at which the semi-circle response is measured. The circle peaks near the 10 kHz regime which is indicative of a far faster process than an ionic process³⁵⁵. A frequency of 10 kHz indicates the process is more likely to be related to the electronic regime, ohmic processes tend to present at frequencies above 1000 kHz³⁵⁶. Ionic processes range from 1000 Hz to 1 Hz^{357,358}. There are works in literature portraying this resistance as contact resistance^{283,354,359}. Contact resistance would be a significant resistance within cells at their porosity⁴⁸, and would decrease with further compaction.

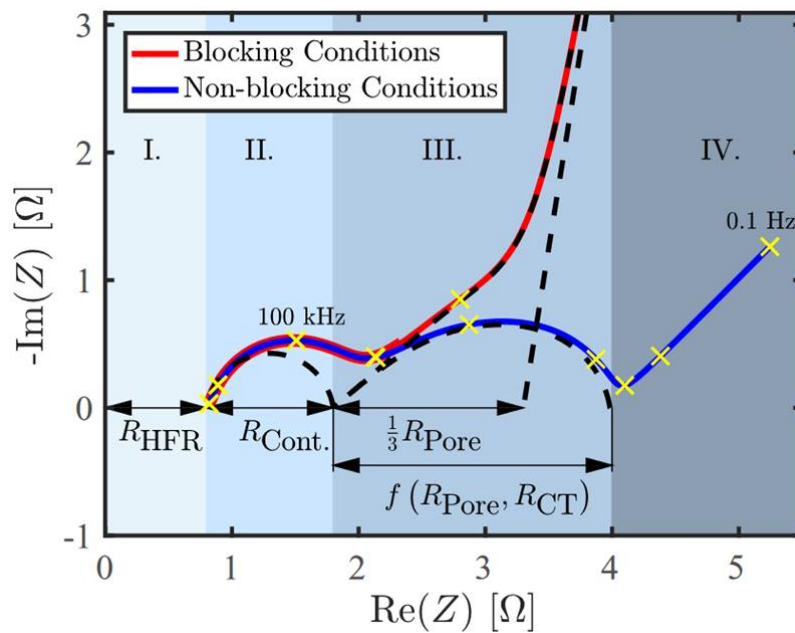


Figure 3.19 EIS responses for ionically blocked and nonblocked cells. The suggested model for non-blocking conditions is a high frequency resistance, followed by a contact resistance impedance and a charge-transfer and porous resistances.³⁵⁴

There is also evidence in this work advocating for contact resistance, following the ECM detailed in Figure 3.19. The half-cell EIS and the symmetrical-cell EIS both portray an initial semi-circle around 10kHz. Symmetrical cells are explained in detail in the next section; however, in this system the ionic resistance is high due to the 50 mM salt concentration, so the electronic components manifest earlier, at a much lower time constant than any ionic processes. Therefore, this first semi-circle can confidently be labelled as the contact resistance, and is accepted in the symmetrical cell EIS literature^{354,359,360}. The similar impedance at the same frequency is strong evidence for contact resistance in the cells is creating the initial semi-circle for both the symmetrical and standard half-cells.

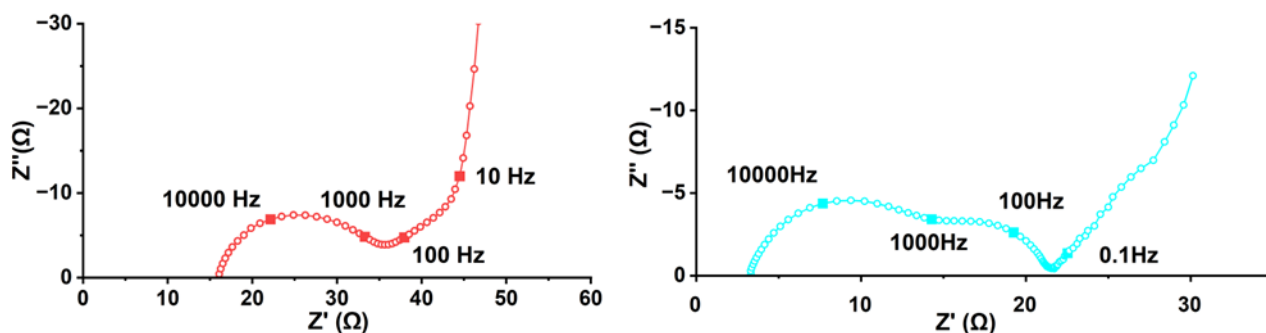


Figure 3.20 50mM TBAClO₄ symmetrical cell EIS response (red) and a conventional NMC 662 half cell (blue). Both involve an initial semi-circle around the 10000 Hz frequency which is suspected to be contact resistance.

It can also be observed the semi-circle in the symmetrical cell is twice the imaginary and real resistance compared to the half-cell, Figure 3.20. This is explained in the cell architecture, the symmetrical cell will be measuring the EIS of two NMC cathodes, compared to the EIS of the standard half-cell, which only contains one cathode and has a lithium chip as an anodic counterpart; the measurement of the two electrodes with similar contact resistances will manifest a twice-as-large response for the symmetrical cell. It is important to understand the literature also elaborates that the relatively low impedances in battery systems can lead to difficulty in assigning the impedance to the elements of battery reactions ³⁶¹. This had led development to the model over time ³⁶² and multiple suggested models for similar EIS responses of battery systems ³⁶³.

3.12.2.3 *EIS for Symmetrical Cells*

Electrochemical impedance spectroscopy was performed on symmetrical cells with a non-intercalating electrolyte. The non-intercalating electrolyte prevents intercalation within the cell and eliminates the charge-transfer component of the ECM. This simplifies the ECM to a high frequency resistance followed by a Warburg diffusive term, presenting as a 45-degree tail, measuring the diffusion of lithium ions, before finishing with a low-frequency capacitive tail which tends to infinite imaginary impedance ³⁶⁴. An exemplary response is shown in Figure 3.21.

Due to the symmetrical geometry, the EIS response yields a more resolved Warburg component with greater accuracy, which indicates the effective ionic resistance of the system. Knowledge of the effective ionic resistance of the electrodes, spatial characteristics (coating thickness, porosity), and the effective diffusivity of the electrolyte for the given temperature allows the calculation of tortuosity for the cathodes.

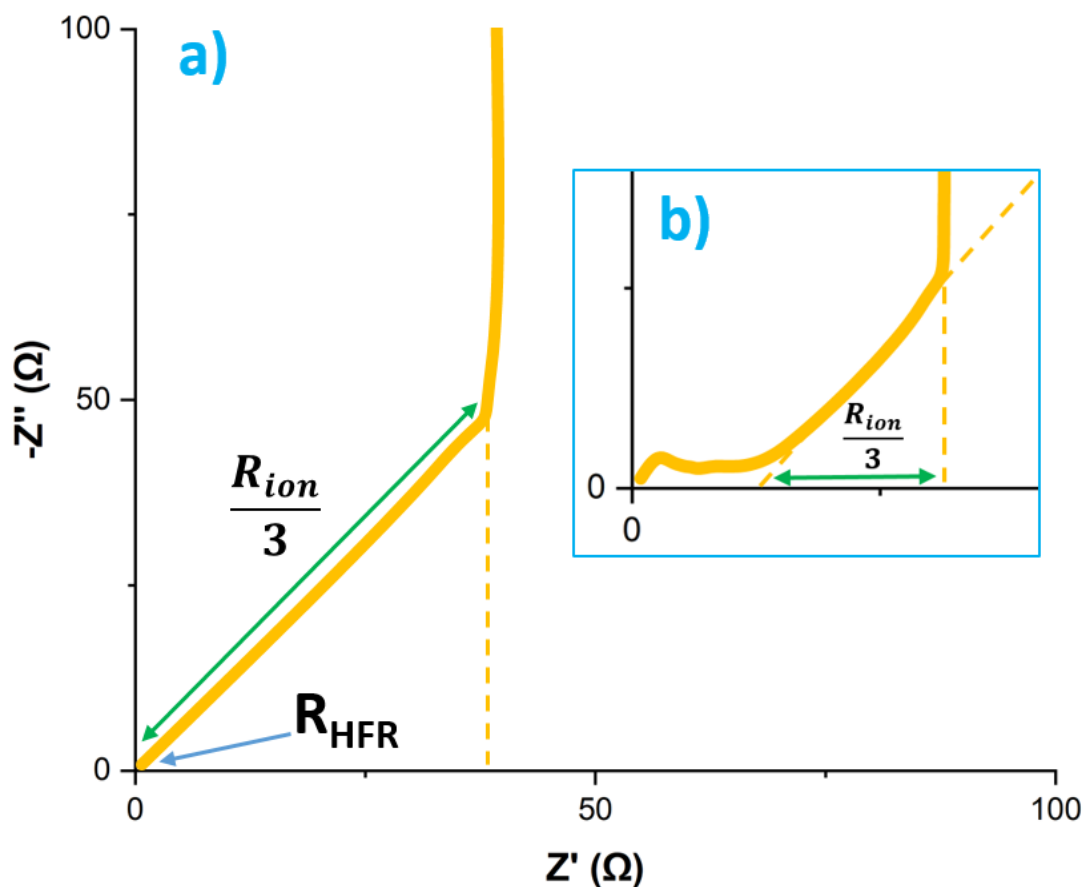


Figure 3.21 Symmetrical cell EIS responses with a non-intercalating electrolyte. a) indicates a system with a high electronic conductivity. b) indicates a system with non-negligible electronic resistance, contact resistance between the electrode coating and current collector manifests an additional component after the high frequency resistance.

3.13 Mixing of tetrabutylammonium perchlorate electrolyte

An electrolyte mixture of 4 mM and 50 mM TBAClO₄ in 1:1 EC:DEC was made in the lab. This mixture and components are air sensitive, so they were transferred into an argon controlled glovebox for mixing, <1 ppm water and oxygen. The TBAClO₄ and EC are solid at room temperature and were left in the antechamber under vacuum for 3 x 5 minutes, refilling the antechamber with argon in-between each vacuum. The DEC was delivered in a sealed container with a syringe permeable top and was transferred through the antechamber immediately due to volatility. To measure the components, a container to mix the electrolyte was placed onto a 4-point balance. The mixture was made by adding the DEC to the container using a syringe. EC is solid at room temperature. For optimal handling, the EC was heated on an 80 °C hot plate until fully molten (approximately 2 hours). It was then pipetted into the container as a liquid. The melting temperature of EC is 37 °C; however, the addition of the TBAClO₄ salt to the EC:DEC mixture raised the melting temperature of the solution above ambient. The TBAClO₄ was added using a spatula into the mixture before the solution could

cool. The mixture was then slowly rotated on an offset axis to agitate the mixture before being allowed to cool and homogenise over time.

3.14 Mercury Intrusion Porosimetry (MIP)

Mercury is a highly non-wetting material with a very high surface tension. This causes mercury to form droplets on the surface of a material rather than spread out and adhere to a surface. This intrinsic property of mercury makes it usable for determining the properties of a porous structure. Mercury will only wet a pore once the pressure forcing the mercury into the pore is greater than the surface tension exhibited by the mercury. You can increase the ability of mercury to wet a pore by expanding the diameter of the pore or by increasing the pressure. Mercury intrusion porosimetry utilises this principle. A substrate will be submerged in mercury before being pressurised to hundreds of megapascals. This causes the mercury to progressively intrude and wet increasingly smaller pores it has access to. Monitoring the loss of mercury from the bulk as it intrudes, in tandem with the pressure exerted at that moment, yields data revealing the porosity of the material at progressively smaller pore sizes. The lower limit of the technique approaches 2 nanometres. The ability of MIP to measure pore sizes from the micrometre range to a few nanometres proves why MIP is effective in determining the pore size distribution of battery electrodes; electrodes have microporous and nanoporous domains.

3.14.1 Process

To compare the pore size distribution in this project all samples were from the same electrode films. Uncalendered sample was just uncompressed electrode cut from the casting. Calendered electrodes were punched and calendered to target porosity in the MTI heated roller calender at 40 °C. Details about calendering cathodes conventionally are described in section 2.4 (Calendering). The punched 14.8 mm electrode discs were pinched into a concaved position to reduce contact surface area between samples, Figure 3.22. Ultrasonically calendered samples were punched from the electrode film into 14.8 mm discs.

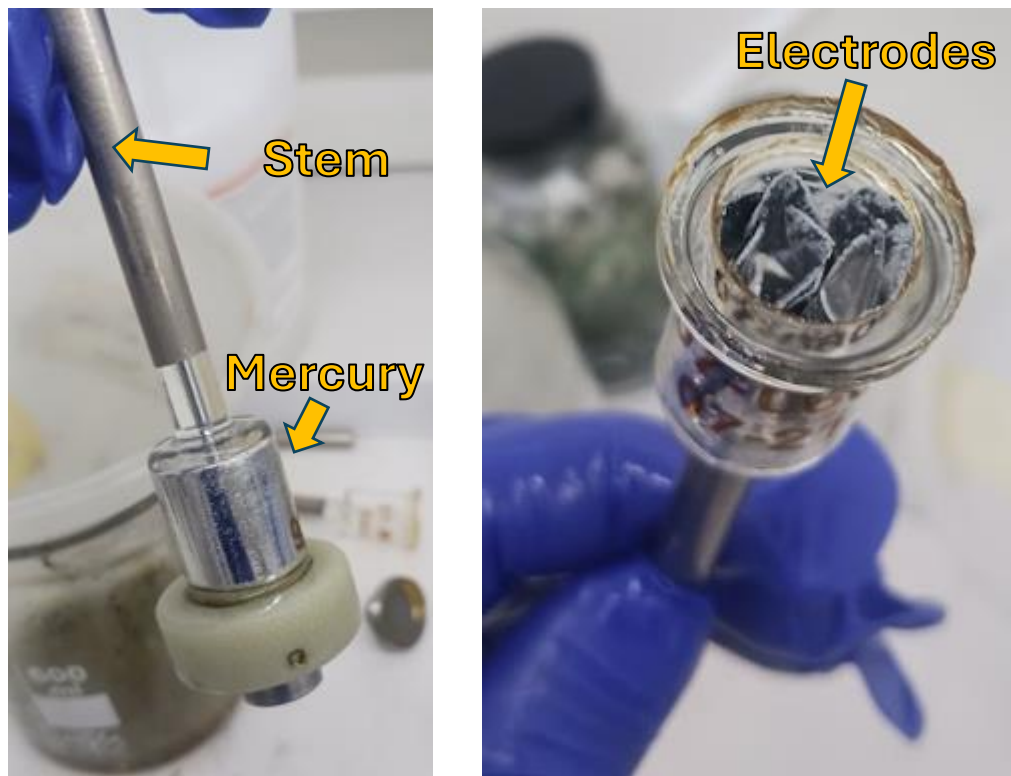


Figure 3.22 MIP penetrometers filled before the high pressure analysis and emptied of mercury after the high pressure analysis to show the electrode packing geometry.

Electrodes were placed into the penetrometer, capped and placed into the low-pressure analysis port to fill the penetrometer with mercury. The filled penetrometer is then moved to the high-pressure analysis port to measure porosity from the micrometre to nanometre scale. It required approximately 0.5 g of electrode for a 7 ml penetrometer vessel. The greater the electrode mass measured, the more reliable the results; therefore, the aim was to maximise the amount of electrode used without creating excessive contact area between the electrodes, and between the electrodes and the penetrometer. During the high-pressure analysis, the mercury-filled penetrometer is pressurised, and the mercury will intrude into the electrode drawing the mercury from the penetrometer stem. To ensure a reliable measurement, the minimum acceptable penetrometer stem volume was 20 %; if less than 20 % of the mercury in the stem intruded, the measurement was repeated with more electrode. Creating excessive surface area in the penetrometer by cramming too much electrode into the vessel will create artificial pores which reduce the surface area of the electrode available until the pressure rises sufficiently to force mercury between the surface area in contact. This overpacking can create artificial pore space and shift the pore size distribution to larger diameters by requiring greater intrusion pressures, resulting in a compromised pore size distribution measurement.

3.14.2 Calibration

To validate the results of MIP and create a pore size distribution dataset for the cathodes used in this project, a baseline cathode coating was taken and calendered to a range of porosities to be analysed with MIP. These results can be seen in Figure 3.23 and were compared with literature. Our data proves to be consistent with literature. In this literature report they have observed an alteration in pore size distribution and total porous volume for a given film calendered to different thicknesses⁵⁰. The report used a graphite formulation 95:1.5:1.5:2 (graphite:SBR:carboxymethyl cellulose:acetylene black) which was drawn down onto 18 μm copper foil to create a 59 μm thick anode. As the film was calendered to 55, 53, 49, and 41 μm thicknesses and progressively deformed, the total pore volume, indicated by the integrated area underneath the curve, was reduced. This is in addition to the peak in the multi-micron region frameshifting towards a smaller average pore diameter. This is because, as the electrode compresses, the void volume decreases as the pores become constricted. Calendering does not destroy old voidage and create new voidage of the electrode; it restructures the existing voidage. Therefore, the compressed, smaller porous network will always resemble the previously uncalendered pore network.

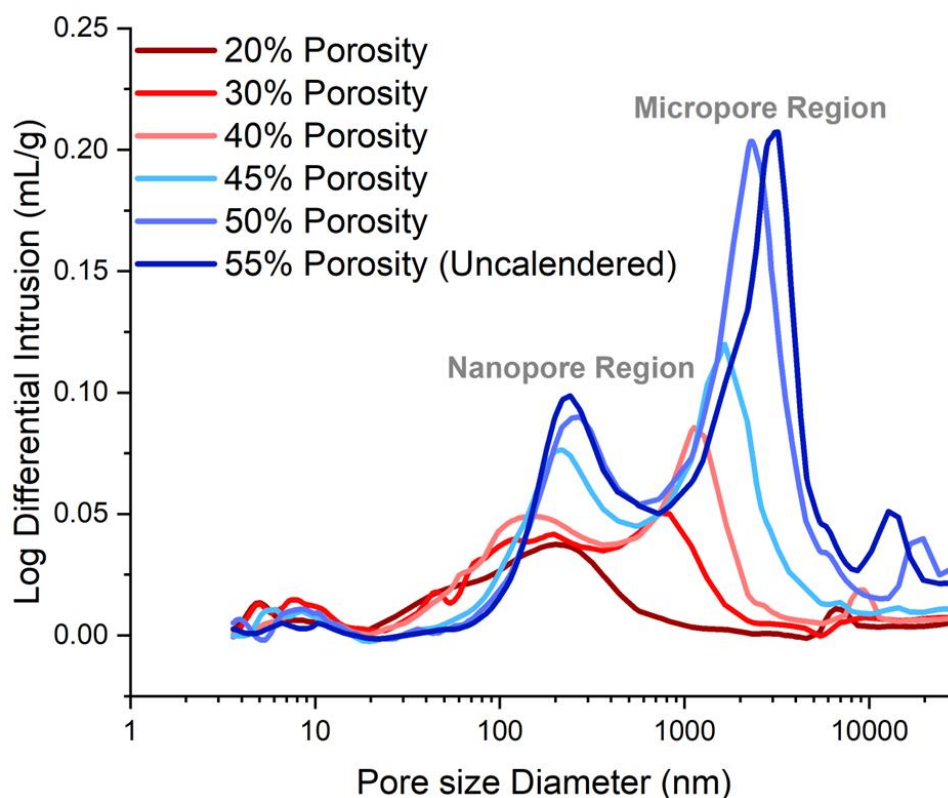


Figure 3.23 Pore sized distribution curves attained from MIP of a baseline cathode calendered over a range of porosities, 20 % to 55 %.

The results from MIP in this project are considered to be accurate because of the rigorous sample preparation, in addition to MIP being well-accepted technique within the battery sphere^{365,366}. Despite this, there are limitations to be considered. MIP cannot measure sealed-off porous volume (dead-zones), because the mercury requires a physical channel for intrusion²²³. However, this rarely affects electrodes due to their highly porous structure with good pore connectivity. These qualities are desirable for electrolyte diffusion and therefore pore connectivity is an attribute the electrode manufacturing optimises for. Dead-zones are common only in excessively dense, over-calendered electrodes, which would be sub-optimal for electrochemical performance, and even then mainly in the active material particles, not the interparticle spaces²²³. This is not expected to be significant in the electrodes within this project because the porosities are not towards the over-calendered range.

Additionally, if larger pores are only connected to the surface of the electrode by smaller pores, the smaller pores will have to be intruded before the larger pores are able to be intruded³⁶⁷⁻³⁶⁹. This will skew the pore size diameter for this measurement. This relationship is known as the throat-cavity ratio and is important when considering the flow of mercury through the structure³⁷⁰⁻³⁷². Akin to the dead-zones, the highly connect pore network with multiple pathways helps prevent restricted flow to specific volumes in the electrode when the porosity has not been overly reduced³⁷³.

4. Experimental Chapter: Approaching and Conducting Ultrasonic Calendering

4.1 Chapter Introduction

This chapter investigates the preliminary work, exploring the ultrasonic weldability of PVDF and how the process parameters affect bond strength, before taking this information forward to assess the ability to calender cathode with an ultrasonic welder. It examines the outcome of the technique the technique, how the ultrasonically calendered cathode varies under different machine parameters, and the electrochemical performance of cells made the cathode. This chapter explores aim 1 in detail and works towards aims 2 and 3.

- 1) To consolidate a polymer binder specifically designed for battery systems that is fully compatible with ultrasonic processing techniques.
- 2) To utilise ultrasonic calendering to produce a densified cathode film, followed by characterization of its physical properties and evaluation of the ultrasonic calendering process mechanism.
- 3) To assess the electrochemical performance of ultrasonically calendered cathode and correlate its performance with its physical and structural characteristics.

4.2 Ultrasonic Welding PVDF

This section investigates the ultrasonic weldability of PVDF. PVDF is the primary choice for a binder in slurry-cast cathodes due to its mechanical, thermal and electrochemical stability. The binder provides mechanical stability to the electrode film; therefore, understanding the effect of ultrasonic work on PVDF and its mechanical properties is critical.

Table 4.1 details the results of the PVDF mechanical testing, and Figure 4.1 plots the responses. All six parameters have repeats which are labelled as A and B. The control samples were single pieces of PVDF. The graph shows that most parameters performed similarly and that the repeats of each parameter experience similar behaviours. The Appendix shows the results with both controls.

The weld parameters are listed in the Appendix. Adherend failures occurred for 1A, 2A, 2B, 4A, 4B, 5A, 5B, 6A, 6B (failing for 1B, 3A, 3B). This is a successful weld for nine of the twelve samples and a successful weld from five of the six chosen parameter sets. The welds which failed had the lower range of pressure and amplitude. It is probable that these welds had insufficient energy to form a strong bond. The high success rate of all the welds which had greater pressure and amplitude is a promising result. A broad range of parameters produced good bonding which suggests PVDF has good ultrasonic weldability.

The data does not portray the theoretical ideal behaviour of a thermoplastic. This is common and has been cited in literature; thermoplastics do not always display a linear relationship between stress and strain in the elastic region due to dislocations and material imperfections^{374–376}. A normal to the curve at low stress is often used as a substitute to calculate a Young's modulus. Points of interest in the curve have been identified and will be compared. The elastic limit (the upper region of the elastic region) has been identified alongside the fracture point and ultimate yield strength.

4.2.1 Results

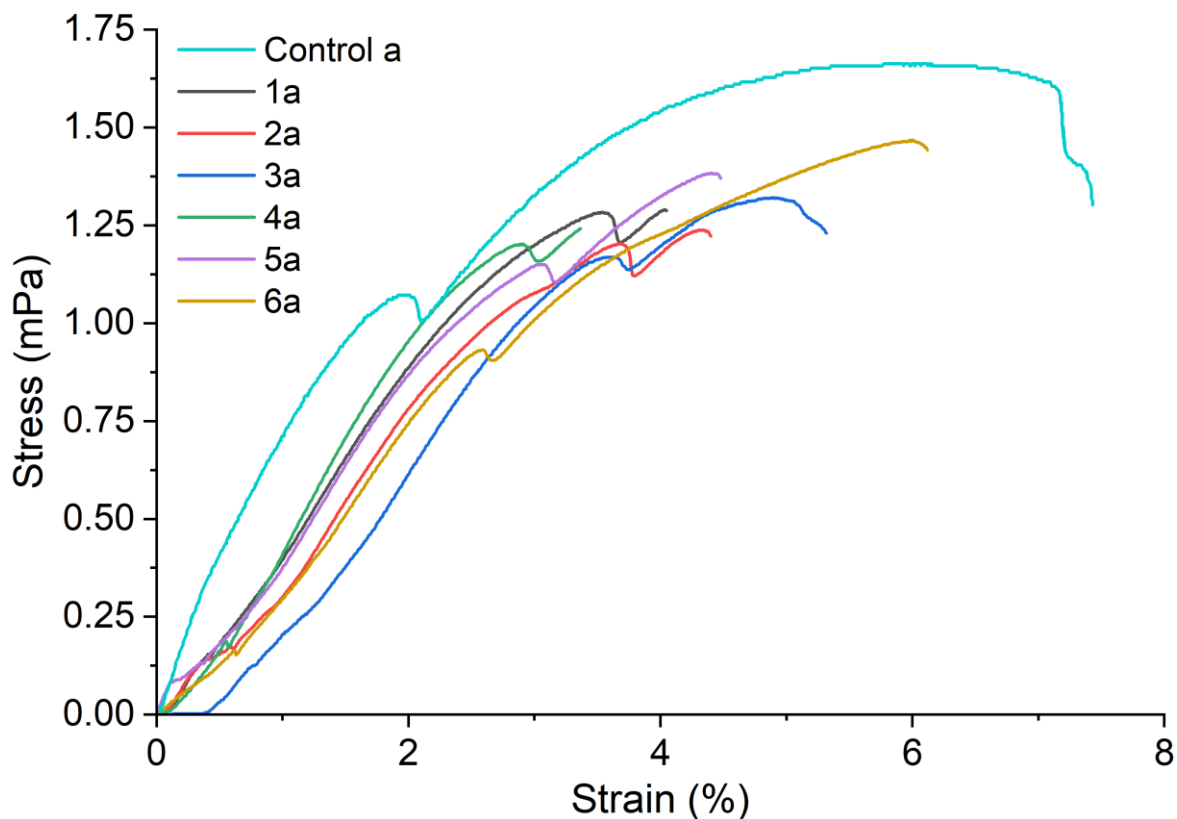


Figure 4.1 Stress-Strain Curve for PVDF Samples; each number represents a different set of parameters, detailed in the Table 4.1. Each parameter was conducted twice and labelled A or B, this graph only shows the first repeat (A). Both repeats are shown in the Appendix. Necking behaviour (the small sharp decrease before increasing again) and a greater ultimate tensile strength is common for all the samples.

Table 4.1 Data Yielded from the mechanical testing of the PVDF strips. Upper yield points are the peaks before the yield point. Ultimate tensile strength is the highest stress measured. Fracture points are the stress as the PVDF strips fail – the final measurement.

Sample	1a		1b		2a		2b		3a		3b		4a	
	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)
Upper Yield Point	1.28	3.58	1.2	3.7	1.2	3.71	1.36	4.43	1.17	3.62	1.1	3.32	1.2	2.9
Ultimate Tensile Strength	1.29	4.05	1.24	4.33	1.24	4.34	1.56	6.4	1.32	4.905	1.28	4.91	1.24	3.37
Fracture Point	1.29	4.05	1.22	4.4	1.22	4.4	1.56	6.4	1.23	5.32	1.2	5.81	1.24	3.37
Break Class	Adherend		Adherend		Adherend		Edge-of-joint		Cohesive		Cohesive		Adherend	
Weld Verdict	Success		Anomalous		Success		Success		Failure		Failure		Success	

Sample	4b		5a		5b		6a		6b		Control a		Control b	
	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)	Stress (mPa)	Strain (%)
Upper Yield Point	1.22	3.19	1.15	3.09	1	2.62	0.93	2.61	1.14	3.46	1.07	1.99	1.06	2.43
Ultimate Tensile Strength	1.42	4.45	1.38	4.39	1.53	5.88	1.47	6	1.14	3.46	1.66	5.97	1.7	5.97
Fracture Point	1.42	4.45	1.37	4.48	1.53	5.88	1.44	6.12	1.12	3.73	1.3	7.43	1.62	6.2
Break Class	Edge-of-joint		Adherend		Adherend		Adherend		Edge-of-joint		Cross-section		Cross-section	
Weld Verdict	Success		Success		Success		Success		Success		N/A		N/A	

4.2.1.1 Elastic Region

A material with a larger elastic limit will be more resilient to small mechanical manipulations. This is because its bonds can elongate and contract without irreversible change to the material. This is advantageous for an electrode binder because the large active material particles (NMC) expand during lithium-ion intercalation. It is sensible to hypothesise the mechanical durability of the electrode would increase if the stress induced on the binder by lithiation does not exceed its elastic limit.

Due to the samples' nonideal behaviour, the elastic region was difficult to analyse because the initial strains are non-linear. To simplify this issue, a comparison of the yield points has been substituted for the elastic region. The yield point, which describes the point where some plastic deformation has occurred and is just prior to necking behaviour, is distinct in this dataset. Since the samples are of the same material, the yield points will correlate to the elastic region. This was the rationalisation for analysing yield points.

The yield points of the controls were 1.07 MPa and 1.06 MPa at 2.53 % and 2.43 % strain for controls A and B. In comparison to the ultrasonically welded samples, there was a relatively even distribution of yield points above and below this yield point. Similarly for the ultimate strength analysis, a sample which displays a strength that of the control sample (± 25 %) will be considered a successful weld. All but two samples (1B and 6A) have a yield point above this threshold. This concludes 10 out of the 12 samples and their parameters yielded successful welds.

4.2.1.2 Ultimate Strength

The fracture and ultimate tensile yield points provide quantitative measures of bond integrity under shear, with higher values indicating more robust welds and greater electrode cohesion. The mechanical stability of the electrode is built upon highly cohesive inter-particle bonds between NMC particles and high adhesion of the NMC particles to the current collector. Fracture and ultimate yield point are indicators of the force necessary to shear bonds in the electrode. Exceeding these forces in an electrode would lead to spalling of the coating or delamination from the current collector.

The controls exhibited an ultimate tensile strength of 1.66 MPa and 1.70 MPa, both at strain rates of 5.97 % for controls A and B. Welded samples produced a range of ultimate tensile strengths between 1.14 MPa and 1.56 MPa, shown in Table 4.1. Three welds: 2B, 5A, 5B yielded

an ultimate strength within 80 % of the highest control sample (control B). Seven of the twelve welded samples: 1A, 2B, 3A, 3B, 4B, 5A, 5B, 6A yielded an ultimate strength within 75 % of the control samples' average ultimate strength (1.26 MPa). Considering the limitations of lap joints and potential experimental errors, exhibiting a strength within 75 % of the control sample was considered a success. Several welding parameters produced a weld within this range and serves as evidence towards the weldability of PVDF. The result shows a broad range of parameters can produce a joint between the substrates which approaches the mechanical performance of a single continuous piece of material.

4.2.2 Limitations and Anomalous Results

4.2.2.1 *Joint Design*

The ultimate tensile strength measured for the welded PVDF samples were substantially lower than provided from the material supplier data sheet, which lists values of 25-60 MPa. The maximum ultimate strength yielded from a welded sample was 1.56 MPa and the strongest control strip was 1.70 MPa. This is smaller than a tenfold reduction, despite also being tested at ambient temperatures.

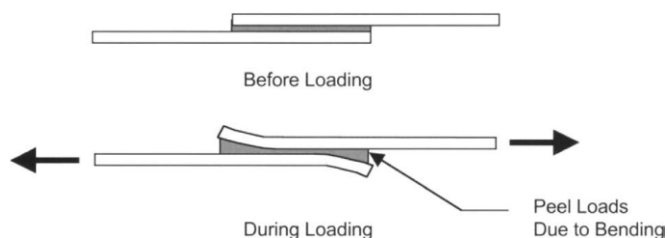


Figure 4.2 Peel Loading Diagram.³⁷⁷

A portion of this reduce can be attributed to methodology using lap joints; idealised joint design is should ensure failure in one of the adherends rather than a failure within the bonded plane³⁷⁷. An adherend-type failure did occur in some of the welded samples, although the joint design was not optimised to do this. A lap joint is expected to be weaker than other joints and will consequently fail at lower stresses, underrepresenting the strength of the weld.

Lap joints were the chosen joint for feasibility and simplicity. They are a minimalistic, simple design used to fuse two pieces of material; it is not an optimal design because it suffers from peel loading. Peel loading occurs due to bending in the material, demonstrated in Figure 4.2. Additionally, the inherent flexibility of PVDF as a polymer makes the sample vulnerable to peel

loading; it is not rigid or brittle. To mitigate peel loading, tapered ends should be designed into lap joints to feather out the edge-of-joint stresses ³⁷⁷. Alternatively, adopting an alternate joint design that mitigates peel loading would be advantageous.

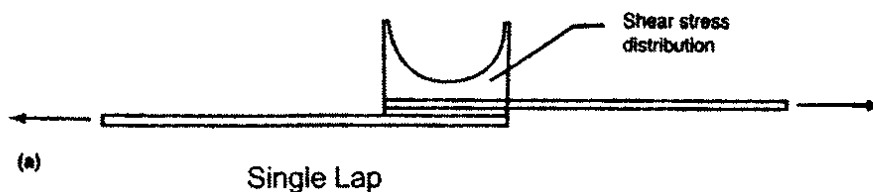


Figure 4.3 Non-Uniform Stress Distribution in Lap Joints. ³⁷⁸

Peel loading should be avoided because the uneven force generated causes an uneven stress across the bonded interface. This causes premature breakage in the joint because some locations on the sample are experiencing more stress over a given surface area than expected under the measured pressure. Figure 4.3 displays the uneven stress distribution. This leads to an inaccurate measurement and results in the measurement of force values lower than the actual value. This is important because it provides results that under-represent the bond strength, leading to lower recorded strength in the material. This is a problem because these values are standardised per unit area, so they can be compared; the underestimation compromises the assessment of PVDF's welding performance. A thesis by S. Raza comparing the ultrasonic welding of other crystalline thermoplastics (acrylonitrile butadiene styrene and polypropylene) reported lap shear strength values lower than expected. The measured values represented 34 % and 15 % of the base material strength ³⁷⁸. The primary cause for the severely reduced material strength was concluded as the joint design. This highlights the limitations of lap joints; they cannot withstand much force.

4.2.2.2 Material and Method Limitations

The material supplier's data sheet claimed a strain of 50 % before failure. This indicates that the material should not reach its fracture stress until the strain rate is approximately 50 %. This vastly exceeds the greatest strain achieved by any of the samples in the experiment. The maximum strain was 8.00 %, in sample 2B, suggesting the presence of factors which severely limited the characteristics of the material.

Causes for this discrepancy could be temperature related. The glass transition temperature of PVDF is -40 °C, and the laboratory room temperature was 22 °C. The reported strain rate on the datasheet is for 25 °C, ambient conditions. Both temperatures exceed the glass transition

temperature, meaning the material should not be brittle, it should be flexible. The Hounsfield machine could have also contributed to the discrepancy. A miscalculation or a misread of the measurements could also result in a low strain reading. If the machine is underestimating the elongation, the increase in length would be underrepresented. This would lower the percentage increase in sample length, giving a lower strain measurement.

4.2.3 Overview

A qualitative and quantitative analysis was conducted across a range of different ultrasonic welding parameters to identify the ultrasonic weldability of PVDF. The qualitative analysis evaluating the failure type of each sample during testing indicated good weldability of PVDF; breakages in the samples typically occurred in the adherend or at the weld edge. This is significant because a joint strength surpassing the inherent strength of the material indicates a successful joint. A quantitative analysis of the ultimate tensile strength and the yield strength showed some instances of welded samples surpassing the yield stress of the control samples and almost all the samples presented a yield stress greater than 80 % of the control sample. The ultimate tensile strength of the control samples was greater than all welded samples; however, most of the samples had a strength within 80 % of these values, which was deemed acceptable. Both results provide strong evidence towards PVDF as a viable polymer in ultrasonic welding. Whilst the observed mechanical performance of the material did not match the properties cited on the material datasheet, several plausible explanations have been proposed. The conclusion was that PVDF is a suitable polymer for ultrasonic welding and therefore will be the primary choice for the polymer binder in ultrasonically calendered cathodes.

4.3 Ultrasonically Calendering 96 % Active Material Cathode

Cathode 96 % active material NMC, 2 % PVDF binder, and 2 % carbon black conductive additive (96:2:2) was prepared. It is preferable to have the highest percentage of active material in the formulation as possible to give the electrode greater lithium storage and therefore energy capacity. The binder and conductive additives are essential for electrode performance however having more than necessary wastes energy density, which is highly undesirable. 96:2:2 is a common formulation within the field and is the baseline formulation for this project.

The ultrasonic calendering of the 96:2:2 cathode was considered a failure. The material did not compress as desired. The material was brittle and sustained damage under the load. Some areas were more effected than others (hot spots). A few hot spots breached through the current collector and can be seen on the underside of the electrode. It can also be seen that the aluminium was deforming, which is a negative application of the ultrasonic energy. The cause of this brittle behaviour was deemed to be due to the lack of PVDF present in the formulation. The PVDF was affected by the ultrasonic motion however the NMC was not and act as hard surfaces for the PVDF to contact and cause friction.

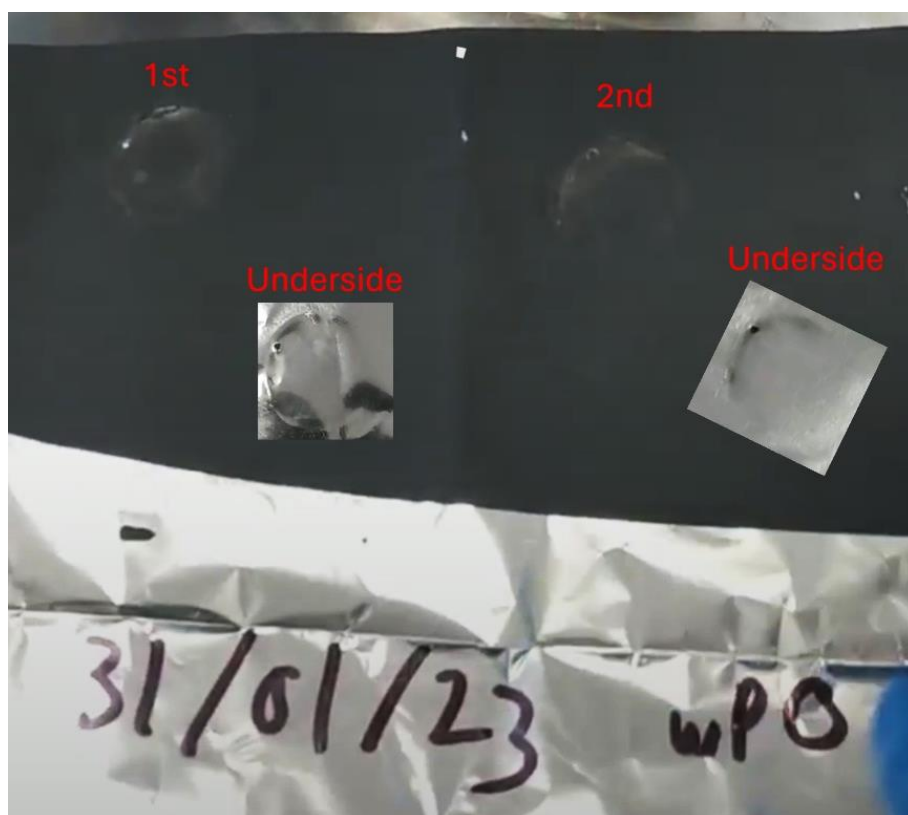


Figure 4.4 96:2:2 Cathode. Two locations have been ultrasonically calendered, and their respective undersides have been imposed onto the image.

An observation from this experience showed that PVDF sheets behaved differently under the ultrasonic welder compared to cathode, which appeared to response poorly to any ultrasonic work. Whilst not unexpected, it showed greater consideration of welding parameters would be necessary. Additionally, a decision was made to double the PVDF present in the mixture to 4 % to decrease the rigidity of the cathode and increase cohesion ²³⁸. Changing electrode formulations can have complex consequences to the final electrode product and the slurry processing steps. Literature has cited that decreasing ratios of conductive additive can cause loss of electrical conductivity or loss of mechanical strength ²²⁴. To keep the additive ratio the same, the conductive additive was also doubled to 4 % to invoke the similar behaviour from the additives in the processing steps and the final CBD phase performance. This led to forming a cathode formulation of 92:4:4 (NMC:PVDF:C65).

4.4 Ultrasonic Calendering of 92 % Weight Active Material Cathode

This analysis considers the electrode during the ultrasonic calendering, before electrochemical data was conducted, focusing on the thoughts and observations made conducting the ultrasonic calendering and provides insight and predictions surrounding electrochemical performance and feasibility of manufacturing cells with the cathode.

4.4.1 Design of Experiments

The relationships between the parameters are detailed in Section 3.5 along with some equipment limitations and ranges of parameters for the ultrasonic welder, Table 4.2.

Table 4.2 Welder presets and their respective settings. 7 different parameter sets were used. A hold time of 0.1s was constant and a cool time of 0.25s before the ultrasonic energy is applied and before the pressure is released after the work.

Welder Preset	Amplitude (μm)	Gauge Pressure (psi)	Weld Time (s)	5C Discharge (mAh g^{-1})
1	12	15	0.5	114
2	12	22	0.3	33
3	12	10	0.3	22
4	12	15	0.8	67
5	12	10	1	60
6	12	10	1.25	15
7	12	10	0.8	106
Uncalendered	-	-	-	36
Calendered	-	-	-	43

4.4.1.1 Setting #1 – 15 psi 0.5 seconds

Setting one utilised an amplitude of 12 μm , a gauge pressure of 15 psi and a weld time of 0.50 seconds. These were the first attempts at ultrasonically calendering the 92:4:4 electrode and seemed to be effective. An initial observation, which became common among all the ultrasonically calendered electrode, was their significantly shinier than expected appearance. The working area was good, circular in shape and appeared to be somewhat uniform from visual inspection. Little damage was sustained. The change in micrometre measurements also showed there was a compression of the electrode. This initial result seemed promising and indicated the welder was having the desired ultrasonic effect on the cathode to invoke positive change. This was significantly better than the effect seen ultrasonically calendering the 96:2:2 electrode, which had caused damage. This validated the decision to increase the additive content from 4 % to 8 %; the cathode was benefitting from the increased mechanical stability from the additional binder. The parameters used in setting #1 seemed to be a good match and suggested that they could approximate the midpoints of the weld time and gauge pressure limits.

4.4.1.2 Setting #2 – 22 psi 0.3 seconds

Setting two utilised an amplitude of 12 μm , a gauge pressure of 22 psi and a weld time of 0.30 seconds. These results were the first to indicate the potential of the technique to work non-uniformly across the working area. Visual inspection showed a circular area of motion; however, it was distinctly affecting a crescent-moon-shaped section, towards the edge, more than the centre (observable in Figure 4.5). The weld area was also non-uniform, presenting spots which seemed to incur more work. The non-uniformity was consistent throughout the ultrasonically calendered cathode produced from setting #2. These results suggested the pressure was either too high for the material or too high for the short weld time. It was assumed the highly worked areas were the result of a cathode being worked too quickly with excessive force. A longer welding time with less pressure would allow rearrangement and compression of areas in initial contact with the sonotrode and create a more uniformly worked area.

4.4.1.3 Setting #3 – 10 psi 0.3 seconds

Setting three utilised an amplitude of 12 μm , a gauge pressure of 10 psi and a weld time of 0.30 seconds. Parameters in setting #3 were based on the results of setting #2. The area seemed to be worked too aggressively because of high pressure. The pressure was reduced from 22 to 10 psi between these settings, to compare with setting #2, which had the same weld time. This

was chosen to indicate if 22 psi is near the upper limit of pressure or if the weld time was too low to create the desired ultrasonic behaviour in the samples. Setting #3 did not seem to produce as much work on the sample. Estimations with the micrometre showed little compression. Visually the electrode did not seem to accumulate as much worked surface area. The deduction was 0.30 seconds is insufficient weld time to induce acoustic movement in the sample, preventing rearrangement of the sample. This indicated that setting #2 could be damaging the NMC particles and the cathode structure during the ultrasonic calendaring.

4.4.1.4 Setting #4 – 15 psi 0.8 seconds

Setting four utilised an amplitude of 12 μm , a gauge pressure of 15 psi and a weld time of 0.80 seconds. This mirrored setting #1 but with an elongated weld time from 0.50 to 0.80 seconds. Setting #4 behaved similarly to setting #1. These parameters were chosen to induce a result which differs from setting #1; however, it also produced an observable uniformly worked area whilst not incurring any damage or hot spots. The current collector was intact. This result indicated that a good weld could be produced from this range of weld time for the given pressure. Setting #1 and 4 showed similar potential.

4.4.1.5 Setting #5 – 10 psi 1.0 seconds

Setting five utilised an amplitude of 12 μm , a gauge pressure of 10 psi and a weld time of 1.00 seconds. Setting #5 and the next three settings were conducted at the lowest gauge pressure with progressively extended weld times. Setting #3's weld time (0.30 s), was taken as the lower limit. Parameters in setting #5 seemed to produce a successful weld. There were no indicators of damage.

4.4.1.6 Setting #6 – 10 psi 1.25 seconds

Setting six utilised an amplitude of 12 μm , a gauge pressure of 10 psi and a weld time of 1.25 seconds. Setting #6 had the longest weld time and overworked the sample. The cathode appeared to accumulate the most damage of the entire 92:4:4 sample set. The sample damage was inconsistent across the calendered area but some of the electrode was severely damaged. The damage would not be acceptable for use in a coin cell.

4.4.1.7 Setting #7 – 10 psi 0.8 seconds

Setting seven utilised an amplitude of 12 μm , a gauge pressure of 10 psi and a weld time of 0.8 seconds. The results from setting #6, with a 1.25 second weld time, prompted the reduction of weld time to 0.80 seconds rather than a further increase. Visual inspection yielded no sign of

damage and use of the micrometre indicated compaction of the electrode. These parameters were concluded to be successful.

4.4.1.8 *Significant observations*

The manufacturing of the ultrasonically calendered cathode for each of the parameters yielded different results. The samples shown in Figure 4.5 vary from underworked, not converting the kinetic energy to alter the cathode (#3; 10 psi, 0.3 s weld time) to overworked from the supply of excessive kinetic energy (#6; 10 psi, 1.25 s weld time). Settings #1 and #7 both appeared to be successful, which was promising because they had similar parameters. Setting #1 (15 psi gauge pressure and 0.5 second weld time) and setting #7 (10 psi gauge pressure and 0.8 second weld time) approximately mirror each other; 10 psi is 66 % of 15 psi and 0.5 seconds is 63 % of 0.8 seconds (100 % pressure, 150 % weld time compared to 150 % pressure, 100 % weld time). It indicated setting #1 and #7 had received similar amounts of ultrasonic energy, suggesting that they have both been similarly transformed and have comparative performance.

The damage sustained in setting #6 can be observed in electron microscopy of cathode cross-sections, detailed in Figure 4.7. Overworking is demonstrated in the obliteration and fragmentation of a significant amount of the NMC structure towards the surface of the cathode coating. Comparing all the electrodes cross-sections between Figure 4.6 and Figure 4.7 attests to the damage sustained in setting #6 not being due to upstream processes e.g. mixing, because the cathode produced from other settings have not experienced nearly as much NMC damage. The damage also appears to have a gradient through the z-axis, being worse at the surface and compared to the bulk coating ²²³, supporting the ultrasonic calendering cause of the damage.

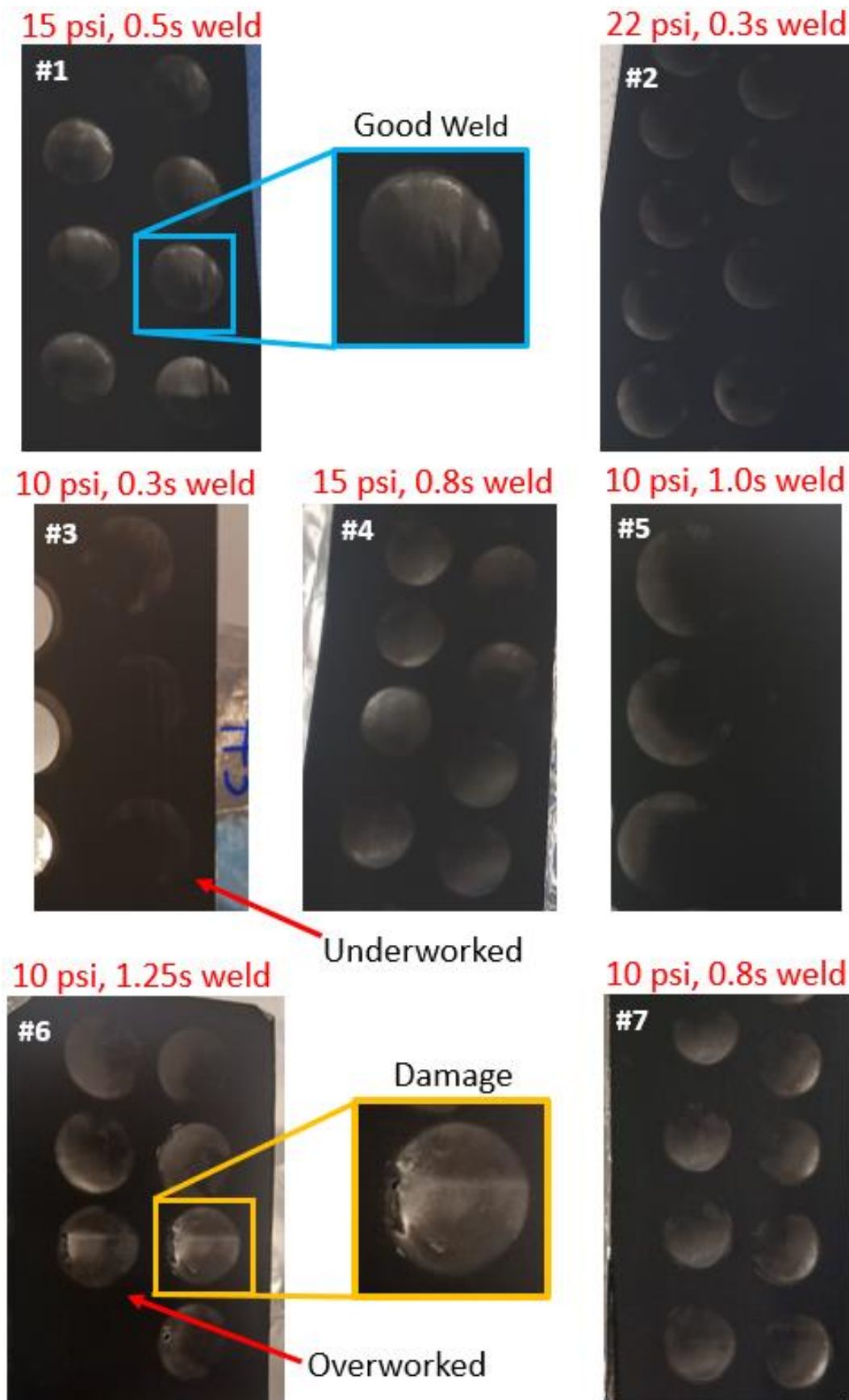


Figure 4.5 Ultrasonically calendered cathode for each welder preset. All samples had an amplitude of 12 microns and a hold time of 0.2 seconds. The figure details the gauge pressure psi and the weld time in seconds. It is demonstrated there are visual differences. #1 are good welds with good effect by the ultrasonic welder. #3 has not received much work and #6 has been overworked, damaging the film and breaking the current collector.

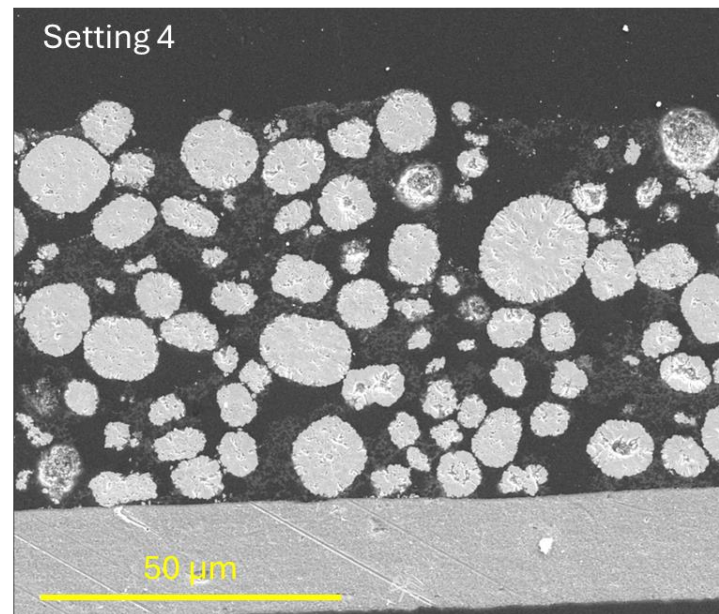
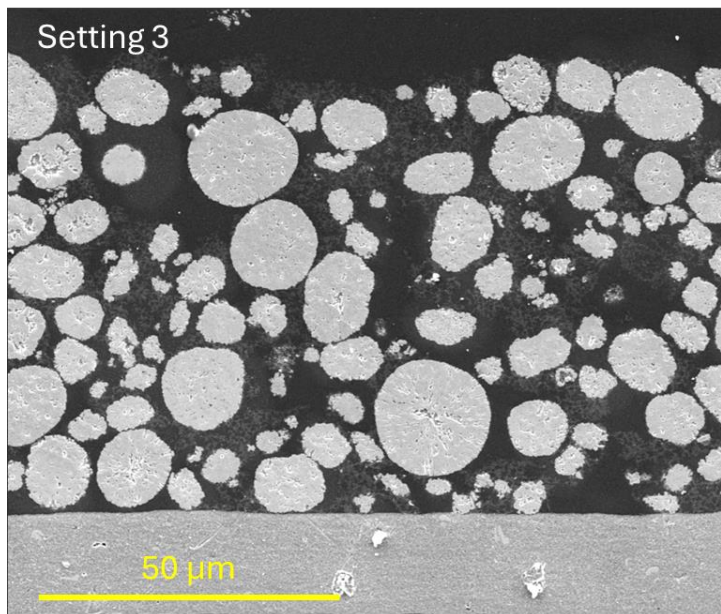
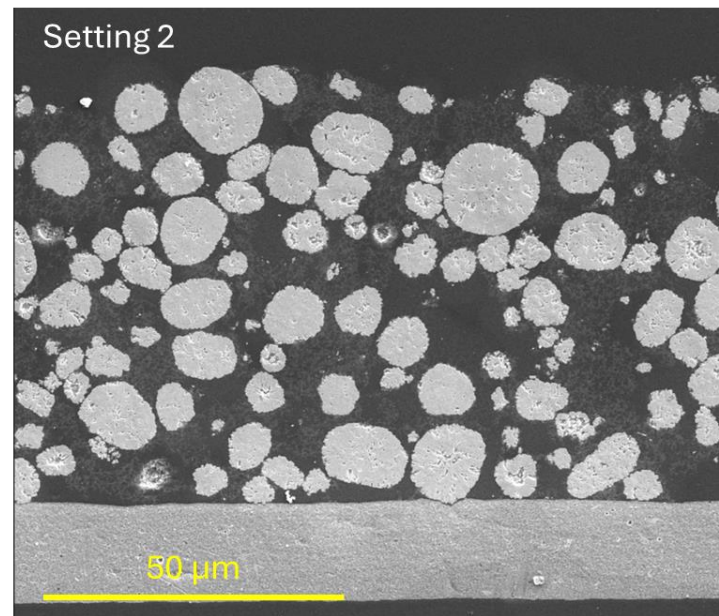
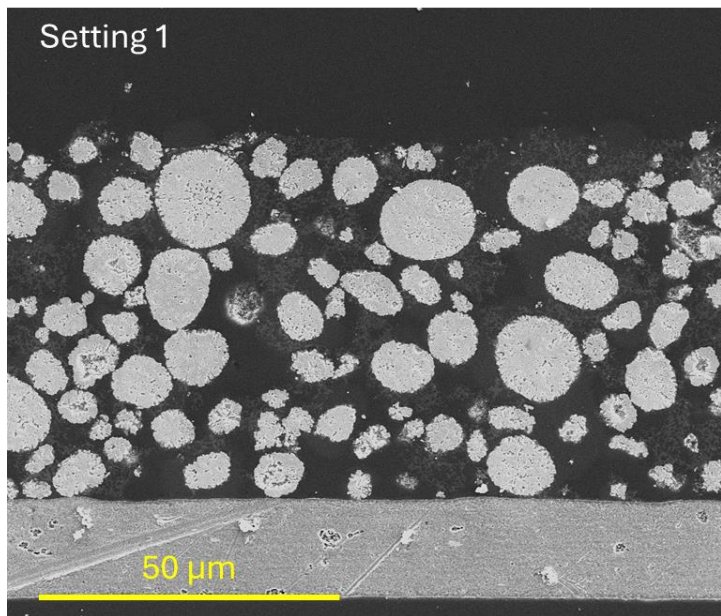


Figure 4.6 SEM Image of ultrasonically calendered cathodes (setting #1 to 4). Cross-sections prepared with resin impregnation and polishing.

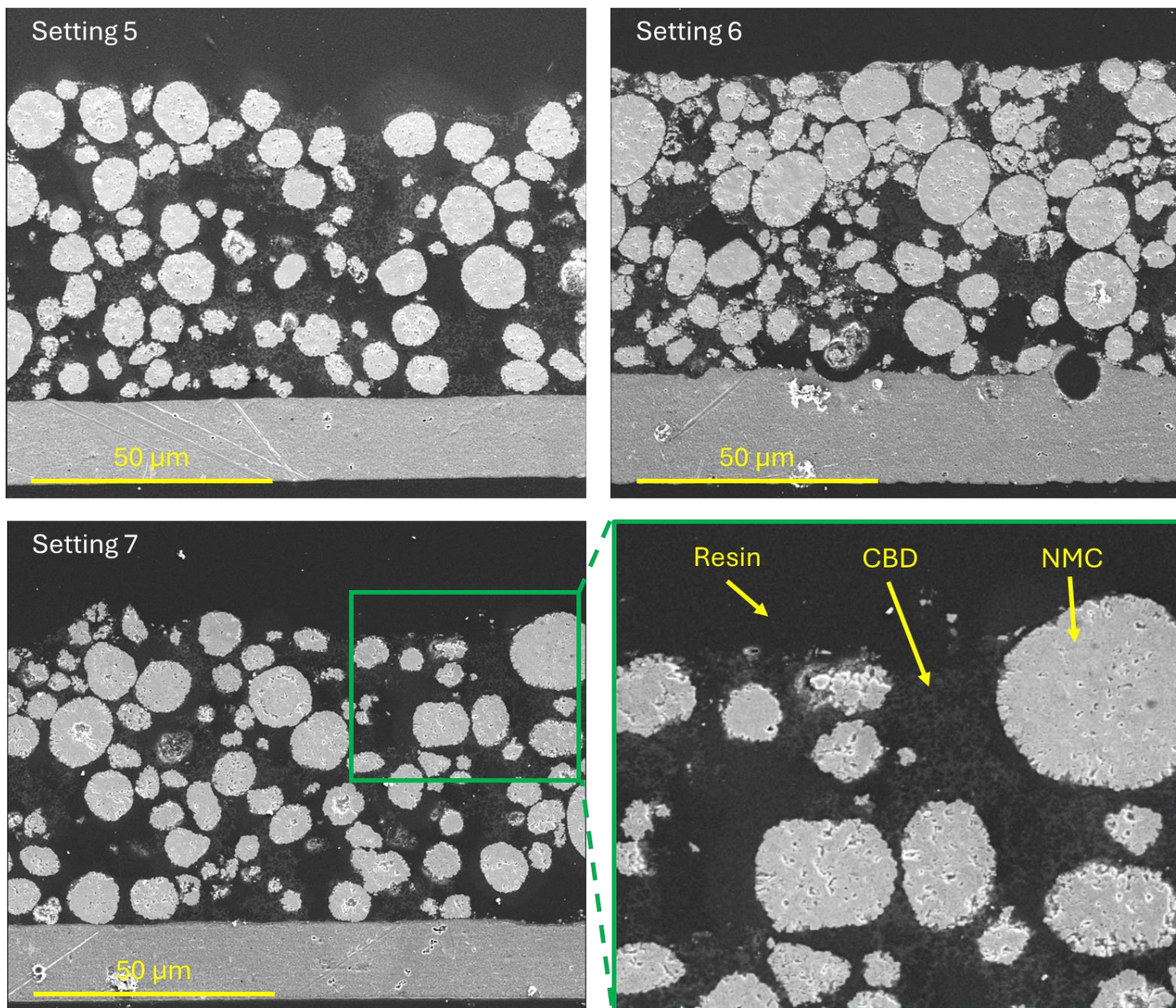


Figure 4.7 SEM Image of ultrasonically calendered cathodes (setting 5 to 7) and an annotated inset differentiating the materials (material-free resin, CBD and NMC). Cross-sections prepared with resin impregnation and polishing.

4.4.2 Welder Data and Process Analysis

Table 4.3 shows the data received from the encoder during several welds performed under two parameters. This data is taken from the encoder display in Appendix. The data displayed is: the cycle count, weld time (s), weld collapse (mm), absolute weld (mm) and energy (J). The duration of ultrasonic oscillation is weld time (s), which is programmed into the control unit. Weld collapse (mm) is the relative displacement of the weld stack during the weld, which is effectively a measurement of the total plastic and elastic deformation into the cathode. The weld abs (mm) is the absolute depth at which the welder engages ultrasonic motion and therefore measured the height the machine has reached sufficient detectable force in order to assume sample contact (minimum threshold of force (N)). This threshold was approximately 10 N. Energy (J) denotes the electric energy expended for the weld. In theory this can be used to calculate the energy utilised during ultrasonic calendering for each parameter. However, this data proved difficult to utilise due to a large deviation and an unexpected outcome of ineffective welds causing a spike in energy consumed.

Table 4.3 Weld results for multiple setting #1, cycle #197-202, and a single setting #2 weld cycle #203. Data gathered from encoder display featured in Appendix.

Cycle	Time (s)	Weld Collapse (mm)	Weld Abs (mm)	Energy (J)
203	0.3	0.02	22.66	30.3
202	0.5	0.04	22.68	70.7
201	0.5	0.04	22.67	72.9
200	0.5	0.04	22.67	72.6
199	0.5	0.04	22.67	68.8
198	0.5	0.04	22.67	71.7
197	0.5	0.04	22.64	67.5

4.4.2.1 Non-uniform Ultrasonic Calendering and Cathode Damage

Some welds suffered extreme hot spots. This involved a small specific portion of the affected cathode receiving most of the work. This could be due to non-uniform coating thickness, leading that section of the cathode to receive work before other areas of the cathode are subjected to force; a high surface roughness leads to hot spots³⁷⁹. Another cause could have been the adhesion of some cathode material to the sonotrode. This creates an artificial texture to the welding face, an energy director, which acts as a focal point for pressure. The welds which had a hot spot and left most of the surface area unaffected typically had an increase in energy consumed during the weld. The increase in energy reached an additional 100 % in some cases. The suspected reason was the weld being inefficient, as the energy director will not invoke the desired ultrasonic motion but instead pulverise the material. Pulverisation was observed in

some ultrasonically calendered electrodes, Figure 4.5 and Figure 4.7. The observation indicated the effectiveness of the weld seemed to affect energy consumed by the weld in addition to the amplitude, weld time and gauge pressure; complicating the relationship between the energy consumed and these parameters. It may have been possible to correlate a 'good' and 'bad' weld upon visual inspection for each parameter, however this would consume more time and require prior awareness before the experiment. The observation was made around setting #5, quite far into the lab session.

4.4.2.2 Encoder data: force verses displacement

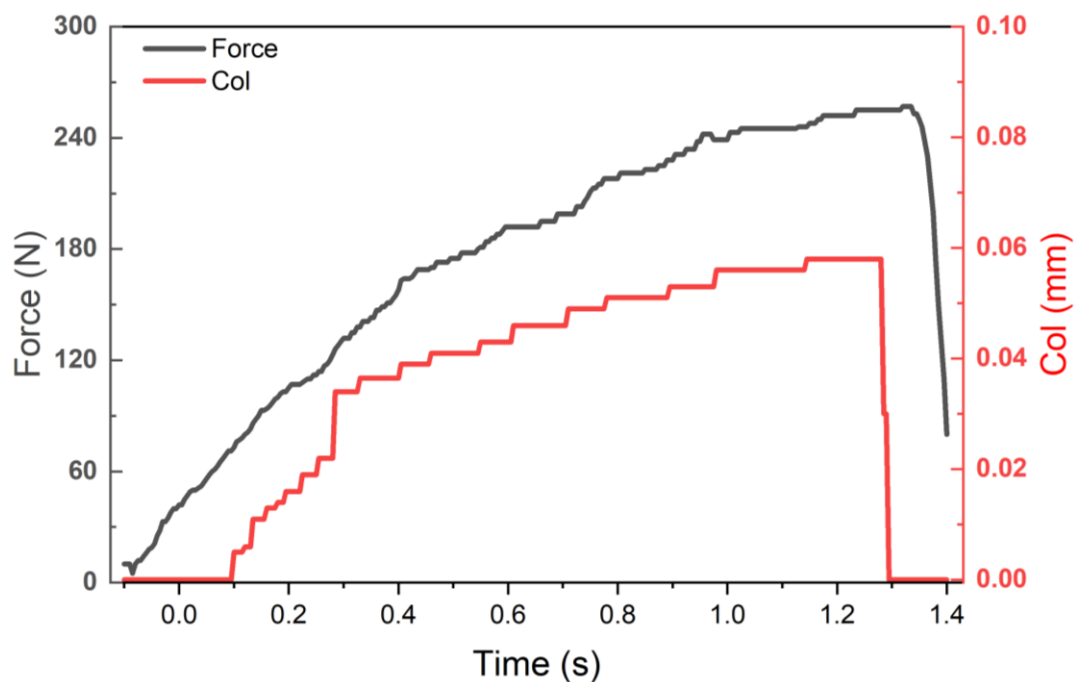


Figure 4.8 Encoder data detailing the force (N) against collapse distance (mm) for setting #6 (10 psi gauge pressure and 1.25 second weld time).

Analysis of the encoder data shows a timeline progression of the process. The data is taken from the ultrasonic calendering of the cathode using setting #6 (12 μm amplitude, 10 psi gauge pressure and 1.25 second weld time). The graph shows data for -0.1 seconds to 1.4 seconds. The weld actuates from 0 seconds to 1.25 seconds, showing information during the preload time, from -0.1 seconds to 0 seconds, where the sonotrode is in contact with the sample but no ultrasonic motion is being actuated. Then during the hold time at the end, between 1.25 and 1.4 seconds, where the ultrasonic motion has been completed, but pressure is still exerted by the sonotrode onto the sample. There are some noticeable correlations between the two variables on the graph, the force (N) measured by a load gauge within the stack, and the micrometre measuring displacement of the stack, collapsed distance (mm).

4.4.2.3 *Results and Discussion*

4.4.2.3.1 Timeline Analysis of Ultrasonic Calendering

Figure 4.8 shows the exerted force and the sonotrode displacement over the ultrasonic calendering process; this was analysed with consideration of its impact on the film:

The sonotrode meets the sample between -0.1 and 0 seconds. It begins recording at 10 N for a first measurement at -0.1 s. The force can be seen to increase to approximately 50 N. The gradual increase to 50 N is due to the sonotrode pressing into the film. The film storing a small amount of elastic energy which then relaxes and resists the sonotrode after the initial contact is the probable cause for small decrease and subsequent increase to 50 N after contact.

Between 0 and 0.1 seconds, the ultrasonic motion has been initiated, and the load is increasing; however, there is no displacement in the stack. After 0.1 seconds, and for the rest of the calendering, there is displacement in the stack. This shows a lag time of displacement after initiating the ultrasonic work. This lag time could be indicative of the electrode resisting compression until sufficient energy has been transferred to the film. This would correlate with the hypothesis of the ultrasonic motion mobilising the PVDF through friction-generated heat by oscillating the particles in the film. The PVDF will then have greater flowability after heating and allow the NMC particles to rearrange. If this proves true, it would indicate the electrode film is oscillating, the PVDF is heating during this elapsed time (0 to 0.1 seconds) and becoming more mobile prior to any arrangement.

Between 0.1 and 1.25 seconds, the force exhibited in the stack and the displacement of the stack increase over time. This would be attributable to the electrode film experiencing more work, further increasing in temperature and compacting under the load as the film rearranges. The load also increases over time, correlating with the displacement. The load is expected to increase as displacement occurred because as the film is compressed, the contact surface area between the particles will increase and impart pressure on each other and resist the movement of the sonotrode. The resistance of the sonotrode movement will lead to a higher measured force. The literature review detailed work by Meyer et al., which demonstrated the rigidity and resistance to compaction increasing as porosity is lost from the film (2.4.4). This would be a behaviour also seen during ultrasonic compaction.

The final part of the ultrasonic calendering is the ceasing of ultrasonic motion. This causes the weld interfaces to rapidly cool. This is feasible because one benefit of ultrasonic welding is that

only the superficial points of contact experience a significant increase in temperature during operation, due to the heat generation occurring through friction. This leads to the PVDF, CBD and the outer surface area of NMC particles reaching high temperatures, while the core of the NMC particles remains at approximately the initial temperature. Once the ultrasonic motion ceases, the supply of motion and heat will end. The interfaces will have the highest temperature and now begin to cool as the heat dissipates, being conducted into the core of the NMC particles, to the current collector and through the current collector. The cooling provides the opportunity for the PVDF binder to anneal and retain a new arrangement the particle, consolidating the microstructure and the nanostructure of the electrode coating. This loss of film height leads to a low force reading as the sonotrode is retracting and returning to the initial position.

4.4.2.3.2 Points of Interest

Static pressure alone was shown to be insufficient to deform the film; the sample does not immediately deform during the hold time. This shows the film resists the force and will only begin compressing once the PVDF has become less rigid; it is necessary for the PVDF to become more fluid to allow the compression, but this is only possible certain after a certain amount of energy has been transferred to the sample to heat the PVDF.

The force experienced on the sample increases throughout the process. Due to the worked area being constant, it indicates that despite a maintained gauge pressure of 10 psi during for the ultrasonic calendering the sample experienced a dynamic pressure. The gauge pressure is a static force per unit area; however, the force gauge showed onto the sample experiences a dynamic load per unit area.

There is a notable rapid increase in displacement at 0.3s, which may provide insight into the mechanism occurring in the cathode. During this section of the process, the force is gradually increasing whilst the displacement jumps approximately 10 μm . This may be evidence in support of sudden, significant NMC particle rearrangement. The average diameter of the NMC particles (d_{50}) is 12 μm . The initial structure of the electrode (uncalendered) is highly porous with large network of approximately 3 μm channels (demonstrated in section 3.14.2: Mercury Intrusion Porosimetry Calibration). Ultrasonic motion is exceptional at causing a bulk of powder to rearrange to their lowest gravitational potential^{298,299}, moving the particles closer together and down through the z-axis. The 10 μm jump in displacement could be due to a

similar movement of the NMC particles shifting and rearranging to occupy the larger space in the film towards the current collector. These would be major changes to the structure and are only possible while the pore diameters are large. Smaller pores are too narrow in relation to the NMC particles to be occupied. This would correlate with the hypothesis of the tortuosity reducing by more favourable NMC particle rearrangement. This hypothesis details particles forming a more orderly arrangement, distributing the pore spaces. The large compression at 0.3s could be indicative of a large arrangement of NMC particles in this manner. After some porosity loss, only initial minor changes to the structure would be possible. Small adjustments to the ordering and particle may be possible; however, a given particle would not be expected to shift past another particle - the NMC particles will not make large traverses to fill a pore, instead, the interstitial space between the NMC particles will gradually shrink under progressive compression. This correlates with the trend of the displacement curve, which progresses with a series of minor increases followed by plateaus as the force curve increases. The NMC particles are moving closer together, but the porous network is not experiencing any significant alterations, the pore spaces are only reducing in diameter.

The maximum reported displacement of the stack is 0.062 mm, equivalent to 62 μm . This distance is almost 75 % of the coating thickness, assuming total rigidity of the 15 μm aluminium current collector. This shows that there is considerable deformation of the cathode during the ultrasonic calendaring. Measuring the final thickness with a micrometre shows that the permanent change in thickness is significantly lower, indicating the work conducted by the ultrasonic welder is primarily elastic with some plastic deformation.

It should be considered within this observation that the entire stack of the welder is under load will elastically deform. To more accurately assess the compression of the cathode alone, a linear variable differential transformer (LVDT) should have been included within the set up. The LVDT micrometre would not be directly connected to the micrometre-welder-sample stack and therefore does not receive the load. This eliminates any deformation of material in the welder from the displacement measurement. It would be recommended this be done should this project be taken further; it would require time and adapting of the 2000X welder, which could not be modified at the time.

4.4.3 Optical Microscopy – Roughness and Hotspots

Microscopy was undertaken to identify differences in topography across the different cathodes after observing the potential inhomogeneity in the ultrasonically calendered cathode and a difference in surface finish compared to the conventionally calendered cathode. Three samples were examined: a conventionally calendered, an uncalendered and an ultrasonically calendered cathode (utilising setting #1: 0.15 psi, 0.8 s). Each sample was punched out using a 14 mm diameter coin cell punch and placed under the microscope. Uncalendered electrode coatings do not have a smooth surface. Calendering will minimise undulations in the topography to create a smoother finish. Calendering can also resolve some defects, such as cracks and pinholes by rearranging the structure. This is a particularly important consideration for the ultrasonically calendered cathode because the surface finish is inconsistent. It can be observed that there is a shiny region of the cathode which is novel to this manufacturing method. This indicates the ultrasonic calendering may be causing an uneven topography. To assess this, two analyses were done: The surface roughness of the conventionally calendered cathode was compared with the ultrasonically calendered cathode; uncalendered cathode was used as a baseline. Secondly, regions of shinier appearance on the ultrasonically calendered cathode were compared with less shiny region to provide insight into inhomogeneity.

Table 4.4 Calendering Method Surface Roughness Data from Optical Line-scans.

Sample	Uncalendered				Conventional				Ultrasonic			
	1 st	2 nd	3 rd	4 th	1 st	2 nd	3 rd	4 th	1 st	2 nd	3 rd	4 th
Total dZ (µm)	266.9	268.3	245.7	272.3	188.7	198.5	178.5	157.6	204.8	204.9	214.8	249.6
dZ/dX	0.023	0.023	0.021	0.024	0.016	0.017	0.016	0.014	0.018	0.018	0.019	0.022

Comparing topographical line-scans of the cathode showed the variance in surface roughness. The height topographies are plotted in Figure 4.10, and the height changes are detailed in Table 4.4. It can be visually observed that the uncalendered cathode has a much greater spread and deviation in the height values across the cathode. Both the calendered electrodes, by conventional or ultrasonic methods, have a narrower spread of height and undulation across the electrode. It is important to consider the handling and manufacturing of the punched electrode being imaged; it can crease the electrode, which will convolute the surface roughness of the calendering after the slurry casting and (if applied) the calendering. This is the surface roughness of interest; therefore, to diminish the effect of the creasing on surface

topography, the change in height across each micron of the line-scan was assessed. This provides insight into how the surface changes on a microscale, and not the larger scale creasing. A dZ/dX analysis (the change in height per unit of length) indicated the conventionally calendered cathode had a total change of 181 μm (mean average) over the 11.5 cm length assessed. Comparatively, the uncalendered cathode had a total change of 263 μm and the ultrasonically calendered cathode had a total change of 218 μm across the same length. This indicates conventional calendering reduces the surface roughness of the cathode by 31 % and is advantageous for surface finish compared to ultrasonic calendering which reduced the surface roughness of the cathode by 17 %. These findings suggest conventional calendering may have a more uniform force distribution across the electrode surface compared to ultrasonic calendering, because the electrode surface is comparatively more homogeneous in height. It was also discussed in the literature review, calendered electrode are more uniform in terms of defects, even potentially eliminating some ¹⁹⁸.

This interpretation also runs under the assumption of the ultrasonically calendered cathode possessing a uniform finish. It can be visually observed in Figure 4.5 and Figure 4.9, the ultrasonically calendered electrode exhibits gradient within the electrode finish. Figure 4.9 shows the right of the cathode has a more reflective, less dark appearance, compared to the left of the electrode which has a more conventional, matt, non-reflective finish. This is novel in ultrasonic calendering.

Table 4.5 Ultrasonic Calendering Surface Roughness Comparison Data from Optical Line-scans.

Sample	Dull	Reflective
Total dZ (μm)	89.1	52.6
dZ/dX	0.019	0.011

To quantitatively assess the finish differences across the ultrasonically calendered cathode, two line-scans, one in each section (reflective and dull), were conducted (Figure 4.9). Similarly, a dZ/dX comparison was conducted over the two transects and to reveal the difference in roughness, Table 4.5. The reflective side of the cathode demonstrated a dZ/dX of 0.011, almost half of the dull side which displayed a dZ/dX of 0.019. This shows for a given length of cathode, the reflective section has nearly half the undulation and micron-level texture compared to other ultrasonically calendered cathode section. Interestingly, the dZ/dX yielded from the reflective side was significantly lower than the average dZ/dX yielded from the conventionally calendered (0.016) and less than half of the uncalendered cathode (0.023). This displays a significant

reduction in surface roughness specifically for the reflective area of the ultrasonic calendered cathode. The values in Table 4.5 are also validated by their similarity to the dull section of the ultrasonically calendered cathode, equating to the average dZ/dX (0.019) of the ultrasonically calendered cathode, detailed Table 4.4.

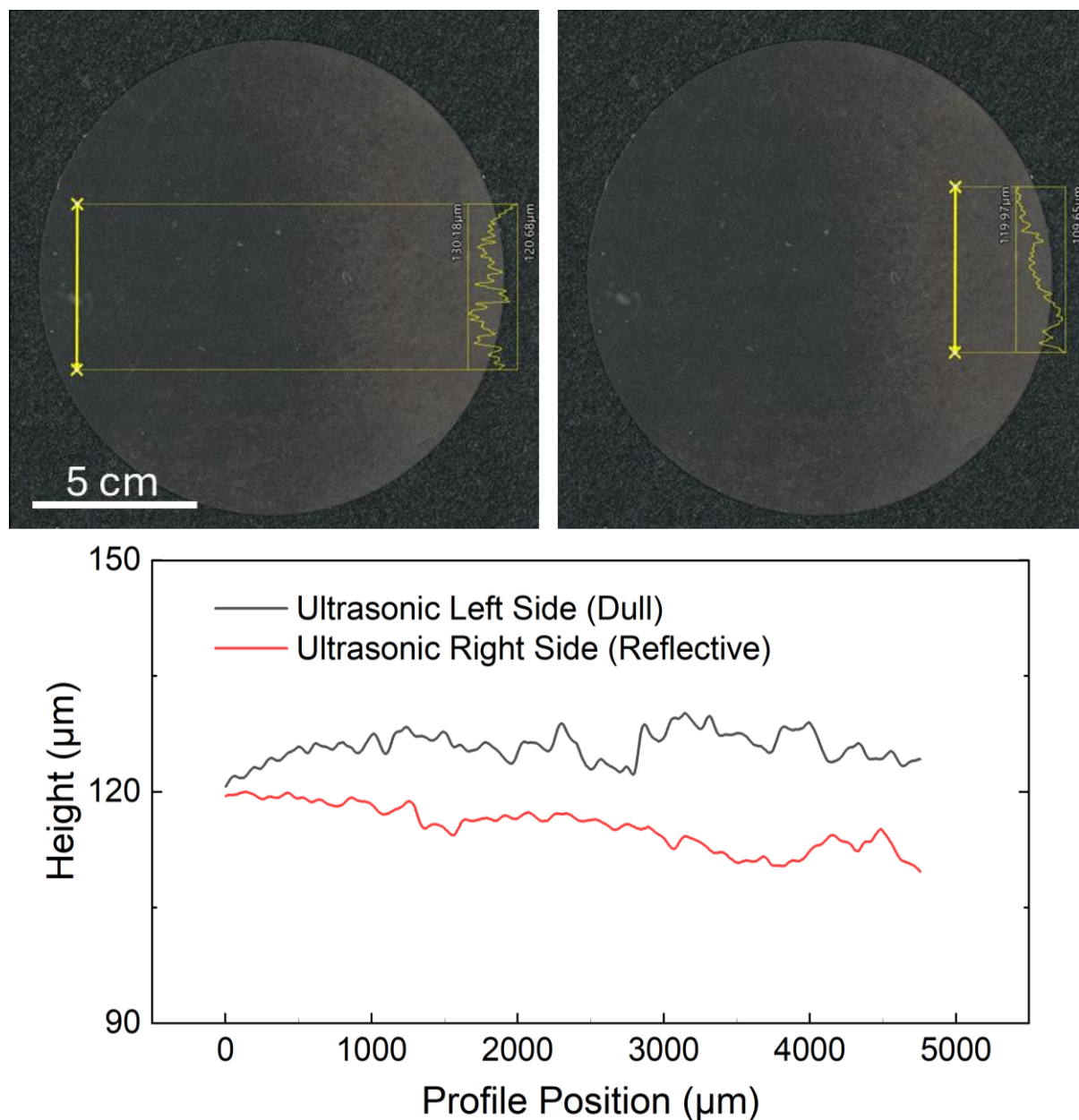


Figure 4.9 Line-scan selection for comparing the dull and more reflective areas on the ultrasonically calendered cathode and the topography for the selected line-scans. It can be observed the left side (dull) undulates more displaying greater roughness.

Visual microscopy of uncalendered cathode and calendered cathode by ultrasonic and conventional means has highlighted significant alterations in the surface roughness of the cathode after calendering. The uncalendered cathode was measured to possess the greatest surface roughness. The conventional calendered cathode exhibited a uniform smoothing of the topography. This behaviour was expected. Ultrasonic calendering was shown to smooth the electrode compared to uncalendered cathode; however, it was demonstrated to non-uniformly

effect the cathode. Defined into two sections, dull and reflective: the reflective side displayed the least surface roughness of the sample set; however, it did show a significant difference to the dull side. This shows the potential for ultrasonic calendering to advantageously reduce surface roughness but has revealed an imperfection of the current set-up, resulting in non-homogeneity. Optimisation and additional improvements to the standard operating procedure could unlock greater homogeneity and allow greater utilisation of the novel cathode surface created via ultrasonic calendering.

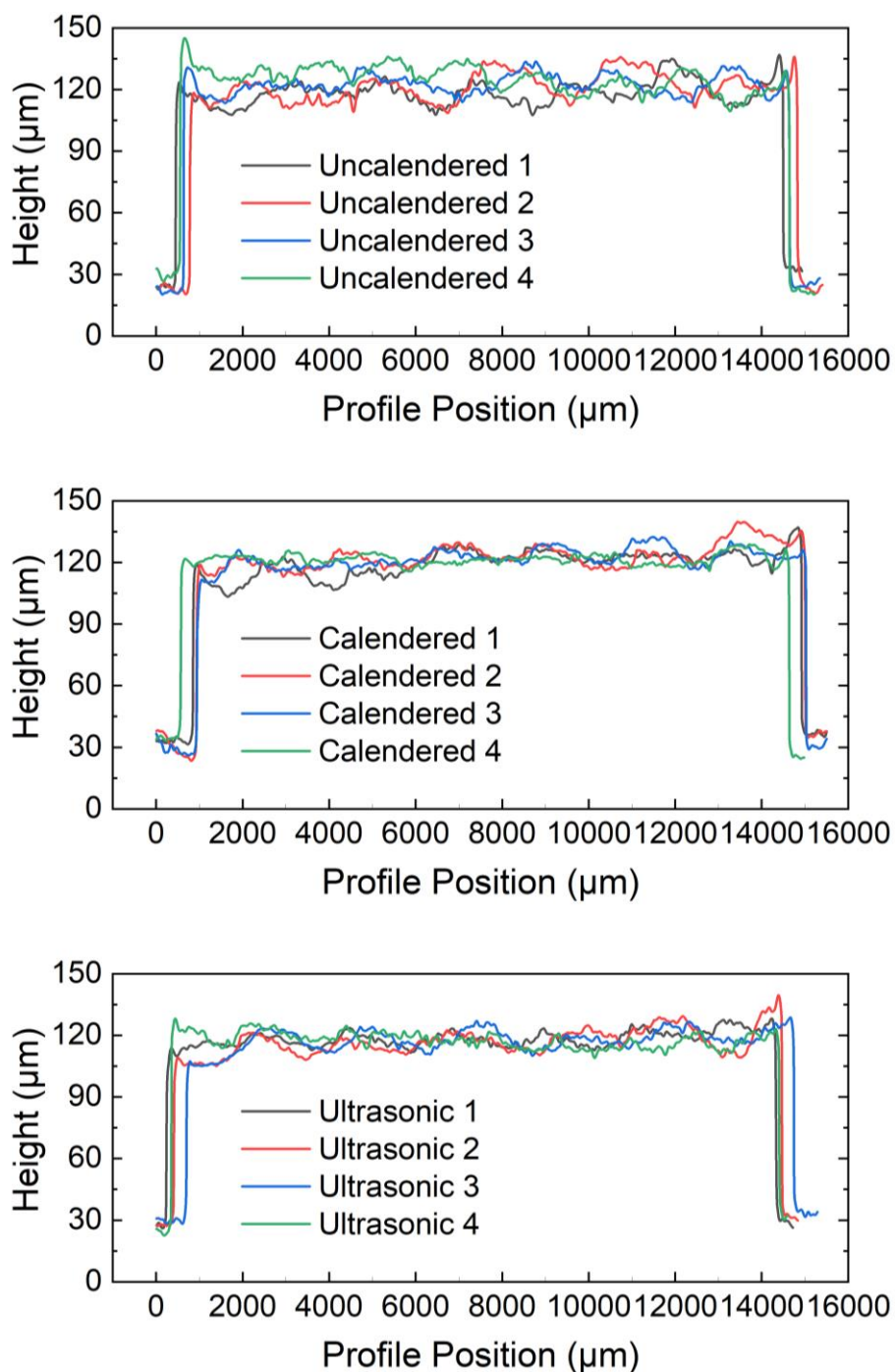


Figure 4.10 Topographies for the line-scan transects for the uncalendered, conventionally calendered and ultrasonically calendered electrodes (setting #1: 0.15 psi, 0.8 s).

4.4.4 Practical Insights and Summary of Conducting Ultrasonic Calendering

The ultrasonic calendering of 96:2:2 cathode was conducted and concluded as unsuccessful. The cathode subjected to the welder mechanically failed due to exfoliation and delamination from the current collector. It was deemed that the cathode was not transferring the acoustic energy and breaking apart. Whilst it may be possible to ultrasonically calender a 96:2:2 formulation, a decision was made to double the additives to 92:4:4 with the intention of making a more flexible and pliable cathode. The ultrasonic calendering of 92:4:4 formulation saw both positive and negative results. The cathode was successfully calendered yielding a compacted cathode. A displacement of 62 μm was measured with the encoder of the welder. It indicated that the cathode was being compacted similarly to conventional calendering and then slightly relaxing due to reversible elastic deformation and irreversible plastic deformation. It was observed that the parameters of the welder were critical to the product of ultrasonic calendering. Some cathodes did not see much work, while other cathode samples suffered damage, which would not be acceptable for use in cells. Contrasting these negative results, some cathode was beneficially worked, producing compacted cathode similar to conventional calendered cathode. This result indicated ultrasonic calendering is more challenging than the ultrasonic welding of PVDF strips. This was expected and increasing the additive content assisted in reducing the difficulty; however, the importance of the parameters was demonstrated to be far more stringent when dealing with cathodes. The ultrasonically calendered 92:4:4 cathode looks promising for cell testing.

4.5 Electrochemical Assessment

This section looks at the electrochemical data collected for each setting for comparison and insight into how the parameters affect the cathode and electrochemical processes. This analysis will predominantly consider rate capacities of the cathodes and the electrochemical impedance measured during EIS but will also acknowledge the observations and results of the ultrasonic calendering of these electrodes in the lab.

It has been extensively documented that calendering has two great benefits to electrodes. It increases the specific volumetric energy density of the electrodes by compacting the coating into a thinner volume and it increases the adhesion of the coating to the current collector, which increases electrode lifetime, resisting electrode delamination. Another benefit to

calendering is the increase to the electrode's rate capabilities. Compressing the electrode into a smaller volume improves the performance of the electrode at high current densities. The internal resistances are smaller, increasing the efficiency. This is especially relevant to fast charging cells.

Rate performance of an electrode measures the effectiveness of the cell at different current densities. The specific capacity of a cell indicates the capacity of the cell if fully charged or discharged. However, there are situations where a charge or discharge needs to be performed quickly.

An effective method to assess the rate performance of an electrode is conduct a rate performance test. A rate performance test involves to charging the electrodes to the same capacity each time and then discharging at increasingly progressive currents to assess the effectiveness. This can span 0.1 to 10C, with respective discharge times of 10 hours to 6 minutes. The effectiveness of these cells will be an expression of the inherent internal resistances of the cell. These resistances increase as the current density increases; therefore, cells with the lowest internal resistances experience higher current densities maintain a greater capacity at higher c-rates.

The internal resistance of a cell can be measured with electrochemical impedance spectroscopy (EIS). This response can be analysed and modelled against an equivalent circuit model to show the resistances within a cell. Accurate modelling allows quantitative measurements of these resistances.

4.5.1 Rate Performance Test

This section examines the results of the rate performance test, shown in Figure 4.11 and Figure 4.12. The procedure is detailed in section 3.9: Cell Cycling. In the analysis, five repeats (A-E) were made for each electrode excluding setting #1, #6 and #7. Four coin cells were constructed (A-D) for setting #6 due to only 4 sections of cathode being sufficiently undamaged. Three cells (A-C) were made for setting #1 and setting #7 due to cathode quantity restrictions. Construction of these cells was at an earlier time, during preliminary cell testing. In this experiment, the calendered controls performed similarly to the calendered controls in this dataset (detailed in Appendix); therefore, a decision was made that the data is meets the

threshold to be reproducible and have been included in the dataset. Anomalous or faulty cells have been removed from the graphs, but for transparency, these cells have been documented in the Appendix and kept their alphabetical assignment e.g. if cell B is not included in the graph, it was not representative or failed.

4.5.1.1 Rate Performance - 5C Comparison

A c-rate of 5 was the upper limit of current density in the rate capacity test. This occurred over cycles 28 to 32, producing five data points. Due to logarithmic increase in internal resistances of these cells with current density ³⁸⁰, leading to more polarisation ³⁸¹, the greatest manifestation of rate performance is displayed at 5C. Therefore, discharge capacities at 5C have been used to compare the rate performance of the cells.

The average rate capacity at 5C for the uncalendered electrode was 36 mAh g⁻¹. The calendered controls produced a rate capacity of 43 mAh g⁻¹. This is a 20 % increase in capacity at 5C. This shows the benefits of calendering on rate capacity. The uncalendered controls performed significantly better than expected. This seems to be attributable to the formulation being 92:4:4. The carbon black appears to already be electronically percolating in the uncalendered cathode structure.

Three different parameters of ultrasonically calendered cathode underperformed with respect to uncalendered and calendered controls. These cells underperformed; their 5C capacities were less than 43 mAh g⁻¹ (the 5C capacity of conventional calendering) and they were below the uncalendered 5C capacity of 34 mAh g⁻¹. This implies it would have been more beneficial not to alter the cathodes by ultrasonic calendering, because the process was detrimental to electrochemical performance (setting #2 - 32.5 mAh g⁻¹; setting #3, 21.6 mAh g⁻¹; setting #6, 15.3 mAh g⁻¹).

Contrasting the detrimental electrochemical performance of the previous ultrasonically calendered samples, other ultrasonic calendering settings yielded a beneficial rate capacity at 5C (setting #1 – 114.1 mAh g⁻¹; setting #4 – 66.7 mAh g⁻¹; setting #5 – 60.5 mAh g⁻¹; setting #7 – 106.1 mAh g⁻¹). These show a minimum of 70 % improvement in the 5C capacity compared to the uncalendered cathode, and a minimum 5C capacity improvement of 39.4 % compared to the conventionally calendered cathode.

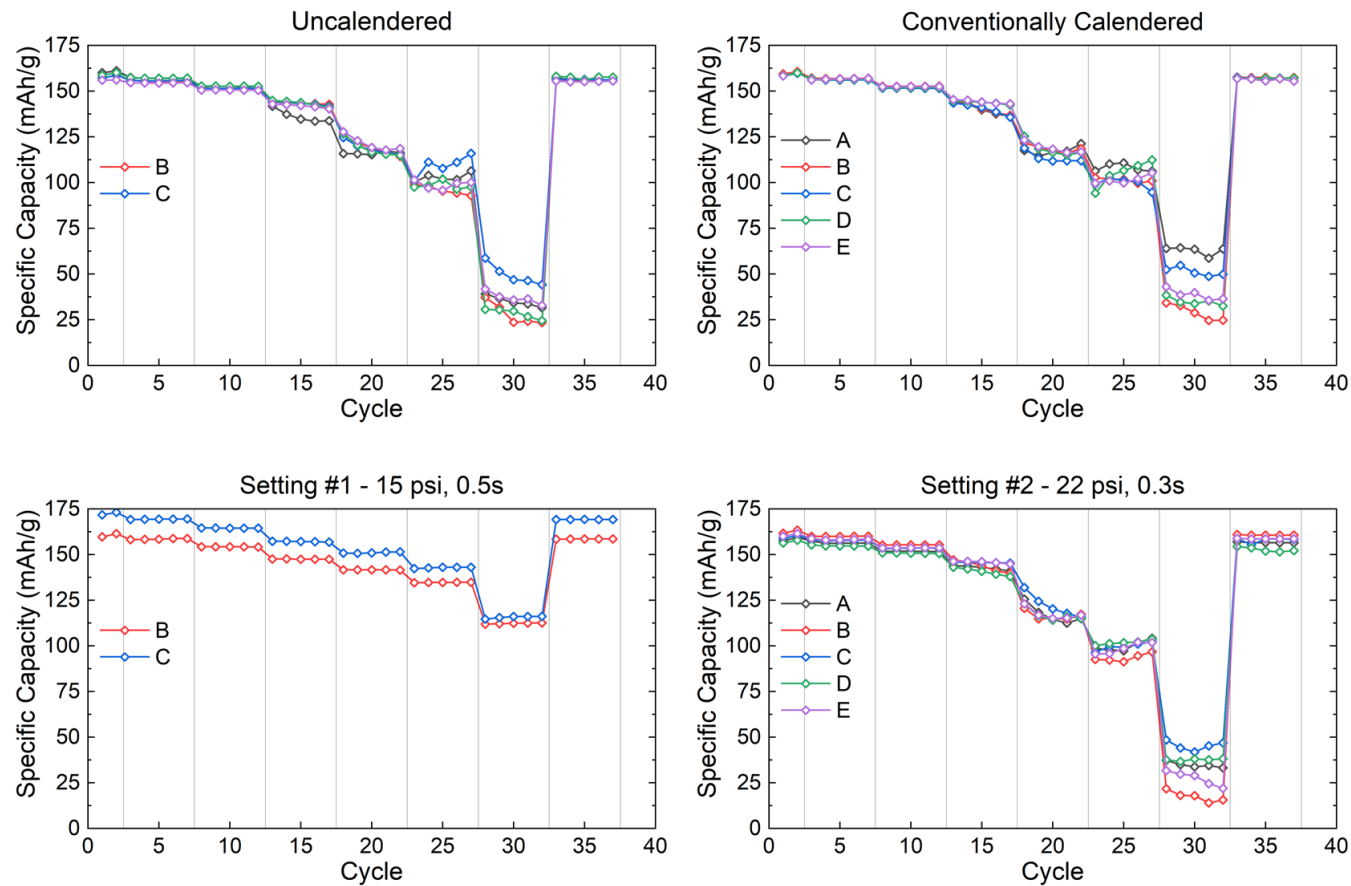


Figure 4.11 Rate performance test results for ultrasonically calendered cells and two control groups; uncalendered and conventionally calendered. Ultrasonically calendered cells are titled with their parameter setting (#) with the gauge pressure in psi and the weld time in seconds; an amplitude of $12\mu\text{m}$ was consistent between settings.

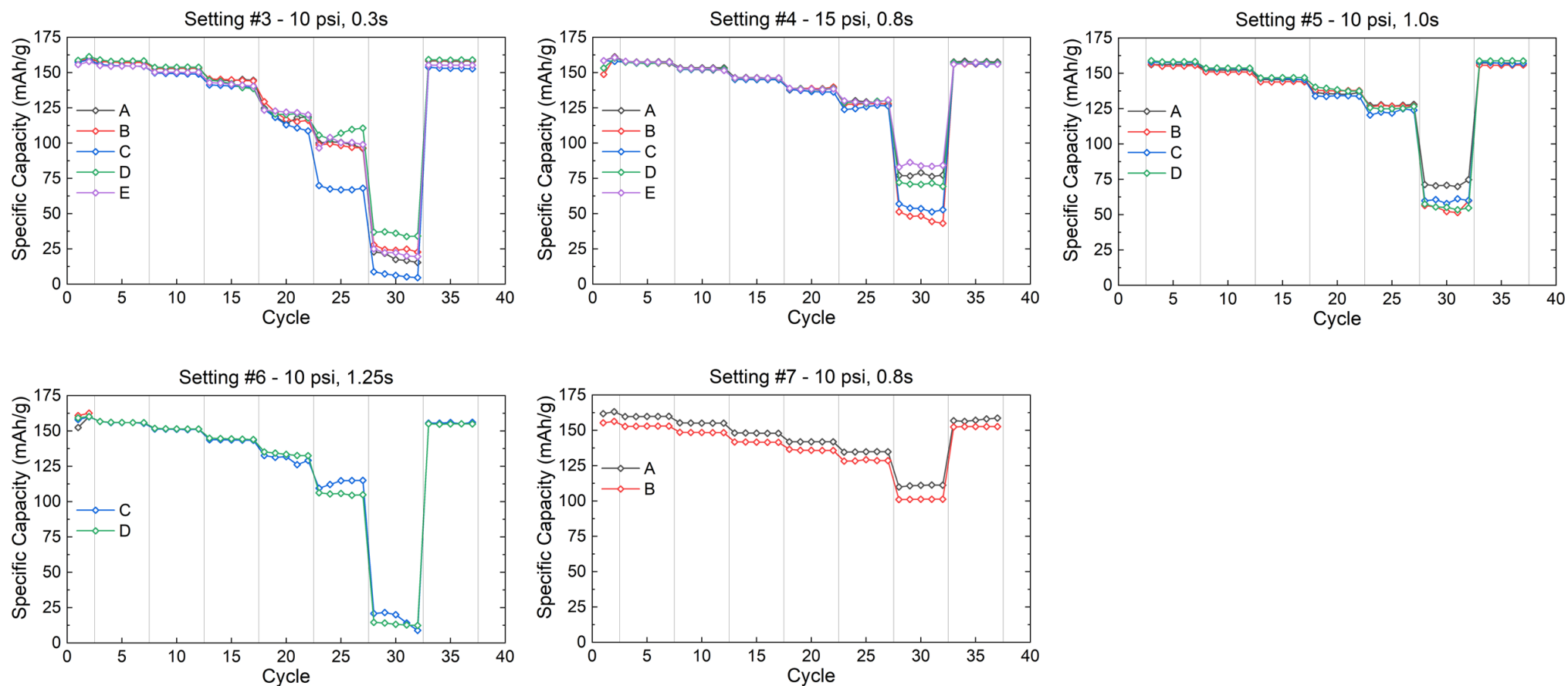


Figure 4.12 Rate performance test results for ultrasonically calendered cells. Ultrasonically calendered cells are titled with their parameter setting (#) with the gauge pressure in psi and the weld time in seconds; an amplitude of $12\ \mu\text{m}$ was consistent between settings.

4.5.1.2 Rate Performance - Specific Capacity (0.1C) Comparison

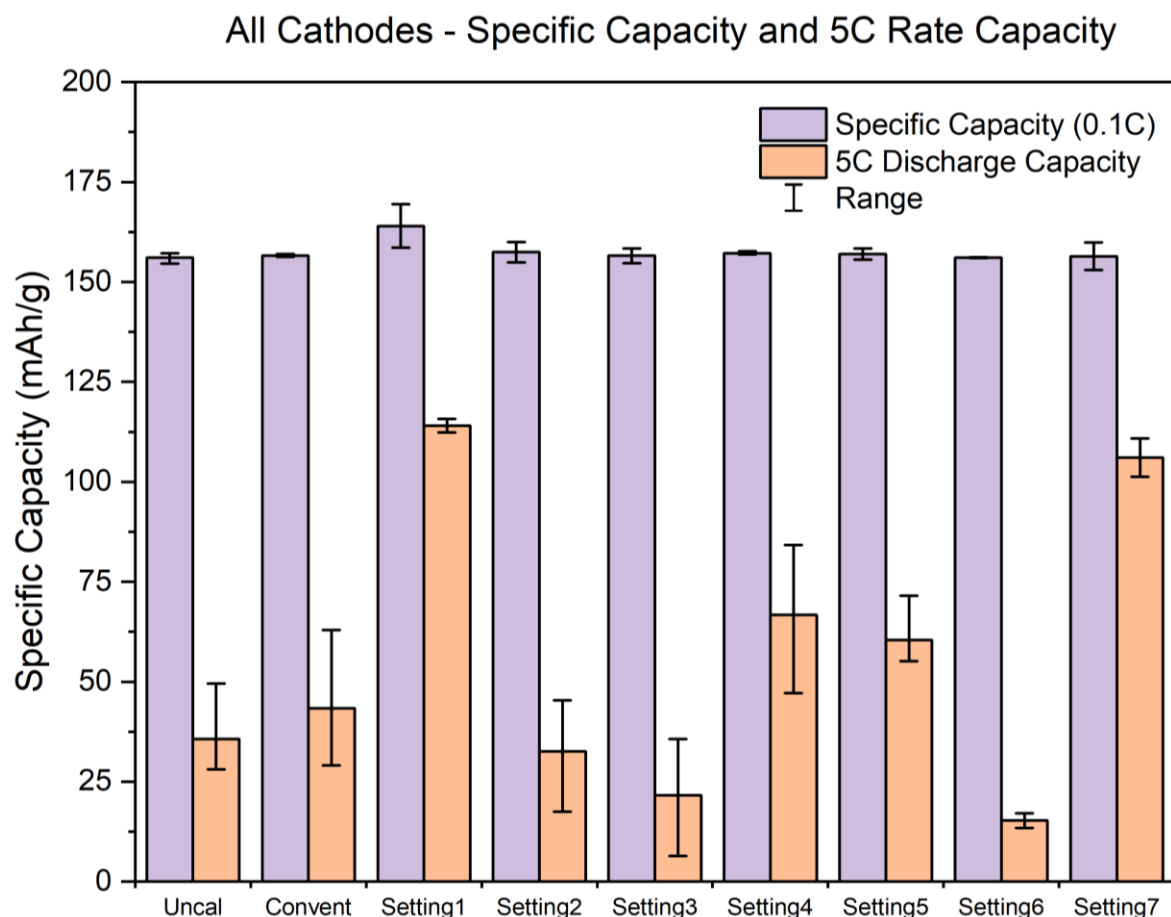


Figure 4.13 Comparison of the specific capacity and rate capacity of cells from the rate capabilities test. The specific capacity is greater than the rate performance and similar for all cells but the rate capacity at 5C has a much greater difference. This indicates that the specific capacity of the cells is the same and unaltered by the calendaring methods, however, the rate capabilities of the cells is greatly impacted by the calendaring method.

The specific capacity of the cells is assessed after formation cycles (cycles 3-7). Specific capacity is used as the baseline to compare capacity changes at higher current densities, because specific capacity is the storage capacity limit for the cell. It can be observed that the mean specific capacity of the cells in this data is consistent among the cathodes and has low variability. The mean ranges from 156.0-157.2 mAh g⁻¹, excluding setting #1 (163.9 mAh g⁻¹), which is slightly anomalous.

4.5.1.3 Voltage Profile Analysis

Plotting the voltage versus specific capacity for individual discharges are shown in Figure 4.14. The initial voltage and the decrease of voltage during discharge indicates internal resistance and consequently reveal its effect on the discharge capacity. The voltage profiles plotted extracted from the rate capacity test. Three different samples are compared: ultrasonically calendered cathode, with setting #4, cell E (4E); conventionally calendered cathode, cell A (conv.A) and uncalendered cathode, cell E (Uncal.E). These cells exhibited the best rate

capabilities of the two control groups (uncalendered and conventionally calendered) and from setting #4, which has been identified as a high-performing ultrasonically calendered cathode.

Three rate capacities are shown on the graph; discharge cycles at 0.1C, 1C and 5C. This exhibits the behaviour for a slow discharge current, a moderate discharge current, and an aggressive discharge current. The purpose of these is to indicate the rise in internal resistance and loss of discharge capacity associated with current density. The test involves five cycles at each c-rate. The greatest discharge capacity for each cell at the c-rates is shown on the graph. These correspond to setting #4's 3rd, 22nd, 29th discharge; calendered A's 3rd, 20th, 22nd discharge; uncalendered E's 3rd, 18th, 28th discharge.

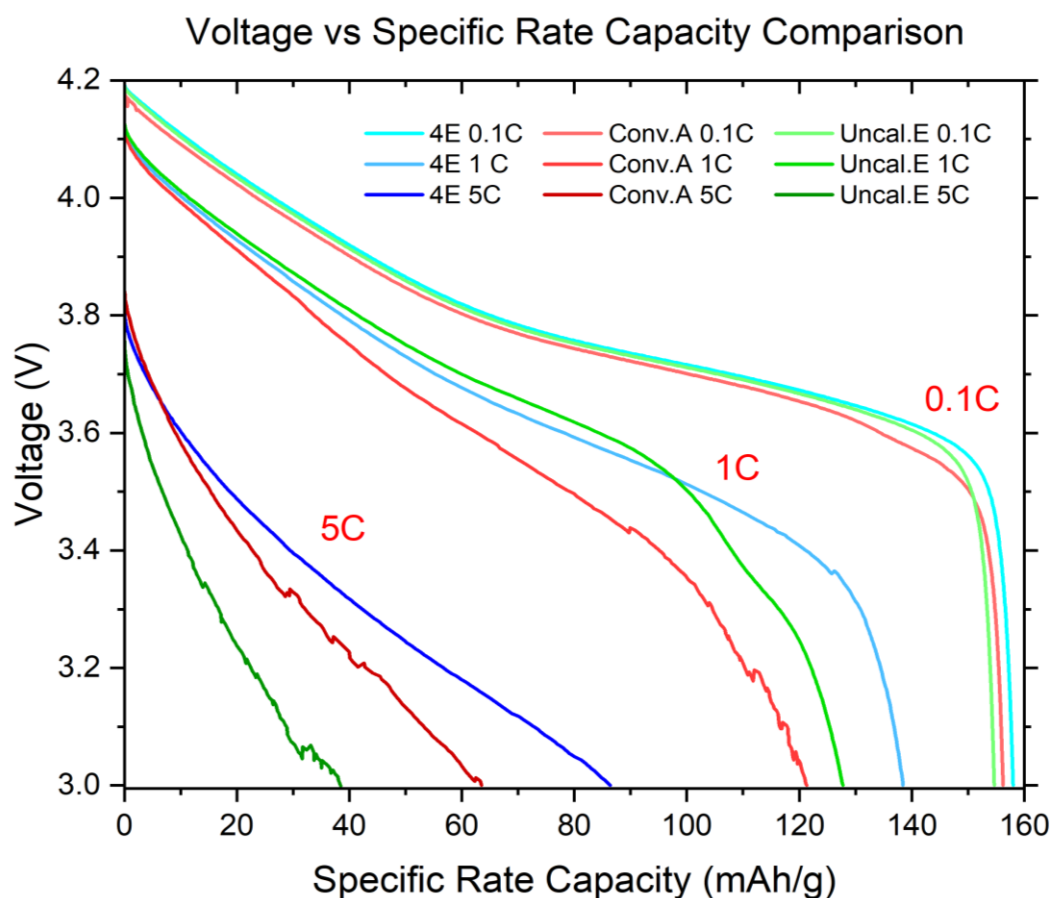


Figure 4.14 The voltage during discharges at several rates for the best cells within the uncalendered, conventionally and ultrasonically calendered (15 psi gauge pressure, 0.8s weld time) cells. Points of interest are the initial voltages, which inversely correlate with internal resistance. The cells perform similarly and low c-rate (0.1C) but have different initial voltages and capacities at 5C. 4E represents cells E from ultrasonic setting #4, conv.A – conventionally calendered cell A, uncal.E – uncalendered cell E.

An important comparison is the initial voltage at which each cell begins discharging current. The electrochemical test is a constant-current discharge from 4.2 to 3.0 V. Therefore, any voltage deviation from 4.2 V represents internal resistance of the cell. Polarisation due to internal resistance causes the voltage to drop, the initial voltage drop corresponding to Ohm's law, Equation 4.1.

$$I = \frac{V}{R} \quad \text{current (Amps)} = \frac{\text{voltage (Volt)}}{\text{resistance (Ohms)}}$$

All cells at 0.1C begin discharging at a voltage of 4.15 V or greater. This demonstrates the low inherent resistance of the cells. These cells cycle well and are electrochemically active. The distribution of capacities for this low current density is narrow, ranging from 152 to 157 mAh g⁻¹. This reflects the consistent specific capacity of the cell seen in the 5C vs specific capacity plot, Figure 4.13. The cells have the potential to reach high capacities if they are cycled non-aggressively.

1C discharge shows the first significant drop in voltage during initial discharge. The cells output energy at approximately 4.1 V, 0.1 volts lower than each cell's OCV before cycling (4.2 V). This demonstrates the increase in internal resistance associated with a more demanding discharge. Despite this increased demand, initial voltages show negligible difference. The rate capacity at 1C has a broader distribution than at 0.1C, ranging from 122 to 138 mAh g⁻¹. This is the first indication of differing rate capabilities of the cells as 16 mAh g⁻¹ has been lost.

The initial voltage at 5C shows the drop from 4.2 V to 3.75-3.85 V. This is a significant loss of voltage. The active material, NMC622, has a nominal voltage of 3.7 V. Nominal voltage represents the voltage these cells are going to predominantly discharge at and can be considered the average voltage. The initial voltage output by all these cells at 5C is on the threshold of the nominal voltage and then rapidly decreases. This is normal expected electrochemical behaviour, following an S-curve discharge shape between 4.2 and 3 volts for lower current densities. Analysing the cells at 5C shows the greatest difference between the samples. The uncalendered electrode is providing the least performance, initial discharge at 3.75 V. This is inferior to the calendered samples. The ultrasonically calendered sample's initial output is ~3.85 V, slightly higher than conventional calendering, outputting 3.8 volts. This is evidence for the uncalendered calendered electrode having the highest internal resistances, surpassed by both the calendered electrodes. The conventionally calendered electrode displays lower internal resistance but is inferior to the ultrasonically calendered electrode which displays the lowest internal resistance.

The rate capacity differences have manifested within the cells at this current density. The rate capacities at 5C range between 38 mAh g⁻¹ and 88 mAh g⁻¹. This is a significant difference. The ultrasonically calendered cells possess more than 200 % of the discharge capacity of the uncalendered cathodes and exceed the calendered control (64 mAh g⁻¹).

4.5.2 EIS

Electrochemical Impedance Spectroscopy is a technique used to quantify the internal impedances of a cell. The impedance response can be fitted to an equivalent circuit model (ECM) which is comprised of resistances, capacitances and inductances. EIS measures the impedance response of the cell, and with a suitable equivalent circuit model (ECM), an ECM is fitted to the impedance response to separate out the impedance and assign each impedance to their respective electrochemical process. The methodology and ECM selection is detailed in section 3.12.2.

4.5.2.1 Results

The EIS data, displayed in Figure 4.15 and Figure 4.16, are fitted using the Randles circuit model (circuit modelling detailed in section 0) and isolated into three resistances R_b , R_{cont} and R_{ct} , shown in Table 4.6.

R1 (R_b): The initial impedance which is mainly resistive, is the bulk resistance (R_b), which can also be known as the electrical resistance because it is associated with ohmic processes³⁸³. Electrical resistance of electrodes has been documented to negligibly change by calendering for high-additive-content electrode¹⁸⁹; however, it is seen in the data to vary between 2.7 and 11.3 Ω . This is a significant difference in resistance.

R2 (R_{cont}): The 2nd resistance in the response, correlating to the contact resistance between the coating and the current collector (R_{cont}) ranges from 4.6 to 17.8 Ω between individual cells. This indicates a significant resistance variation within the cell dataset. Uncalendered cells averaged a mean of 7.5 Ω compared to conventionally calendered cells with a mean resistance of 8.6 Ω . Both controls are surpassed by ultrasonically calendered cathode with setting #4 (15 psi gauge pressure, 0.8s weld time), possessing a mean of 5.8 Ω . This presents the lowest resistance of the cells; 77 % and 68 % of the uncalendered and calendered controls.

R3 (R_{ct}): Charge-transfer resistance has been documented to decrease, with an optimum around 30 % porosity²⁴⁵. The charge-transfer resistance dataset ranges from 4.6 to 13.0 Ω . The uncalendered cathode had the lowest mean charge-transfer resistance in the dataset. This was followed by ultrasonically calendered cathode setting #5 (10 psi gauge pressure, 1.0 s weld time) with a mean of 7.0 Ω , and ultrasonically calendered cathode setting #4 (15 psi gauge pressure, 0.8s weld time). This is lower than the conventionally calendered cathode, with a charge-transfer resistance of 7.9 Ω . Setting #4, exhibited 96 % of the calendered control's

charge-transfer resistance. Additionally, setting #4 had a much narrower standard deviation, setting #4 R_{ct} ranges from 6.3 to 9.1 Ω . The conventionally calendered control R_{ct} ranges from 6.2 to 11.0 Ω . The uncalendered cathode yielded a surprisingly low mean charge-transfer resistance exceeding both the conventionally calendered control and the ultrasonically calendered samples, despite having the highest porosity.

Several ultrasonic settings: 2 (22 psi, 0.3 s), 3 (10 psi, 0.3 s) and 6 (10 psi, 1.25 s) had a detrimental impact regarding charge-transfer resistance; measuring mean charge-transfer resistances of 9.2 Ω , 8.6 Ω and 8.6 Ω , compared to 7.9 Ω . This would indicate that the parameters in setting #2, 3, and 6 involved a cathode compression that produced a structure which does not facilitate lithium-ion intercalation as effectively.

4.5.2.2 *Errors and Repeats*

It is important to note that EIS can produce noise or errors during measurements. Repetition of the EIS measurement could eliminate these anomalies; however, it is difficult to identify which are anomalies and which are faulty cells at this stage (4.2V in the 3rd cycle). Repeating the EIS is time consuming and if only 'faulty' cells are repeated it would be changing the SOP for specific cells, which could be perceived as biased laboratory practice. At the time of EIS, the rate performance test had not been conducted to generate the data to determine which cells are functional or dysfunctional, and if the cells had noticeable performance, either superior or inferior. Due to this, there are some anomalous measurements in EIS readings for important cells in this analysis. Should the EIS be repeated, they may show a more conventional measurement, however, repeats for these cells would have to occur after cycle 37 to avoid interrupting with the rate performance test. This measurement at cycle 37 would not be comparable with the bulk EIS data collected at cycle 3 due to aging^{384,385}. Cell degradation and the thickening of interphase layers lead to increased resistance and consequently increased impedance measurements³⁸⁶. Significant changes may even advocate for a change to the ECM. These factors limit EIS comparisons and indicate the importance of performing EIS under the same conditions e.g. temperature, cell cycle, and cell charge.

Table 4.6 EIS processed data using the Randles circuit model. Uncalendered, conventionally calendered and ultrasonically calendered (#2-6) cells are detailed. Parameters for the ultrasonically calendered cells are detailed in Table 4.2 and the characteristics of the cells are detailed in the Appendix. Red cells have been concluded inaccurate due to the unreliable EIS fitting.

Cathode	Rb (Bulk) [Ω]	Rcont (contact) [Ω]	Rct (Charge-transfer) [Ω]	5C Discharge (mAh/g)
Uncal1	4.4	10.6	5.5	35
Uncal2	8.3	8.5	5.1	28
Uncal3	9.5	6.3	7.1	50
Uncal4	3.7	5.2	8.2	28
Uncal5	4.5	5.7	8.2	37
Uncal Average	5.2	7.5	6.7	35.6
Conv.1	4.1	5.6	6.5	63
Conv.2	11.3	10.9	6.2	29
Conv.3	5.1	7.7	6.6	51
Conv.4	4.6	6.1	13.1	35
Conv.5	3.1	7.2	11.0	39
Conv. Average	6.5	8.6	7.9	43.4
#2a	7.6	4.6	9.2	35
#2b	4.8	13.7	7.1	18
#2c	11.8	2.3	14.2	45
#2d	3.5	5.1	10.7	38
#2e	3.7	6.2	9.6	27
#2 Average	4.9	7.4	9.2	32.5
#3a	5.8	12.2	7.3	19
#3b	4.0	13.2	5.9	25
#3c	3.9	17.8	11.9	6
#3d	3.9	10.6	4.7	36
#3e	3.2	8.0	13.0	22
#3 Average	4.2	12.4	8.6	21.6
#4a	4.2	7.1	6.3	77
#4b	5.8	3.8	11.9	47
#4c	2.7	5.8	9.1	54
#4d	3.6	4.6	7.6	71
#4e	4.4	1.9	13.8	84
#4 Average	3.5	5.8	7.7	66.7
#5a	5.1	7.1	8.5	71
#5b	5.4	5.5	7.4	55
#5c	3.1	11.7	4.6	60
#5d	3.0	6.9	7.6	55
#5e	2.9	50.9	96.5	-
#5 Average	4.1	7.8	7.0	60.5
#6a	3.5	7.3	8.0	-
#6b	6.2	10.4	8.6	-
#6c	3.7	7.6	8.5	17
#6d	3.1	8.5	9.2	13
#6 Average	4.1	8.4	8.6	15.3

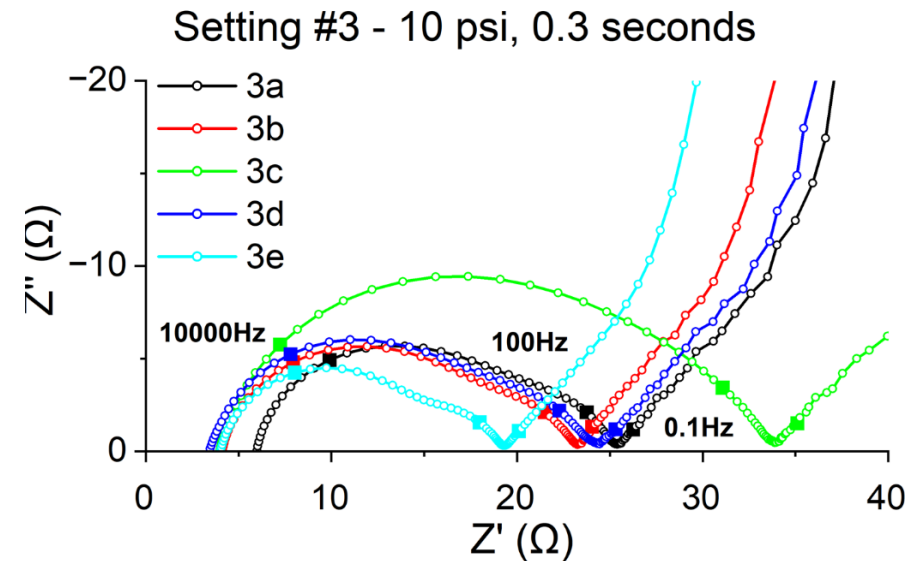
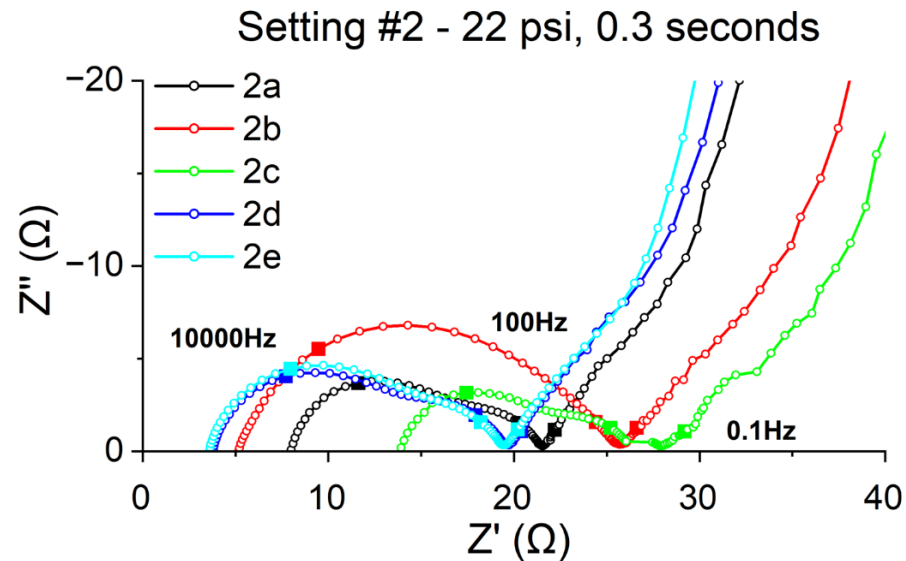
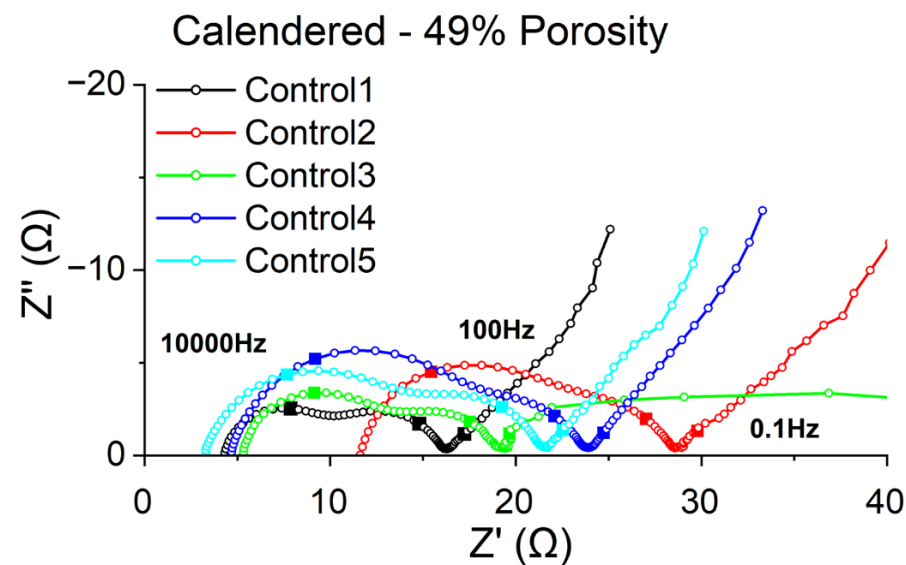
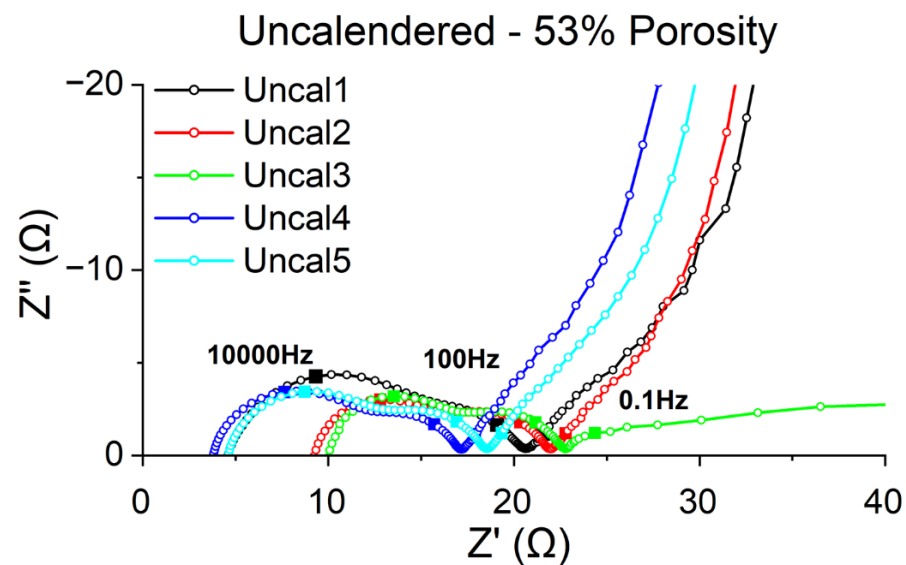


Figure 4.15 EIS responses for ultrasonically calendered cells and two control groups; uncalendered and conventionally calendered. Ultrasonically calendered cells are titled with their parameter setting (#) with the gauge pressure in psi and the weld time in seconds; an amplitude of $12\text{ }\mu\text{m}$ was consistent between settings. Three frequencies have been highlighted: 10000Hz, 100Hz, 0.1Hz.

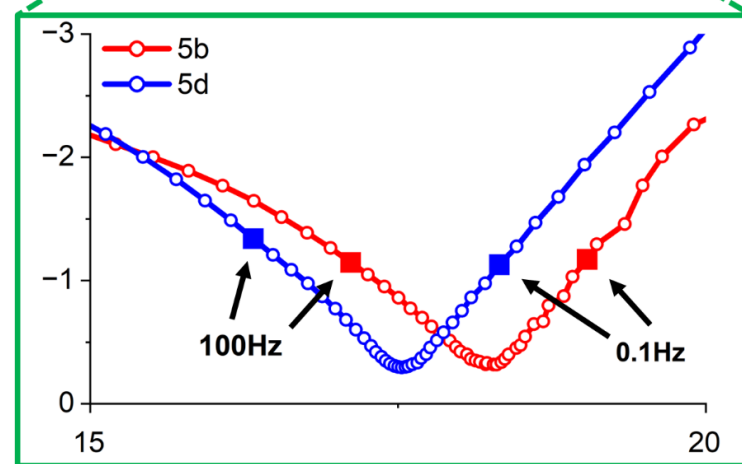
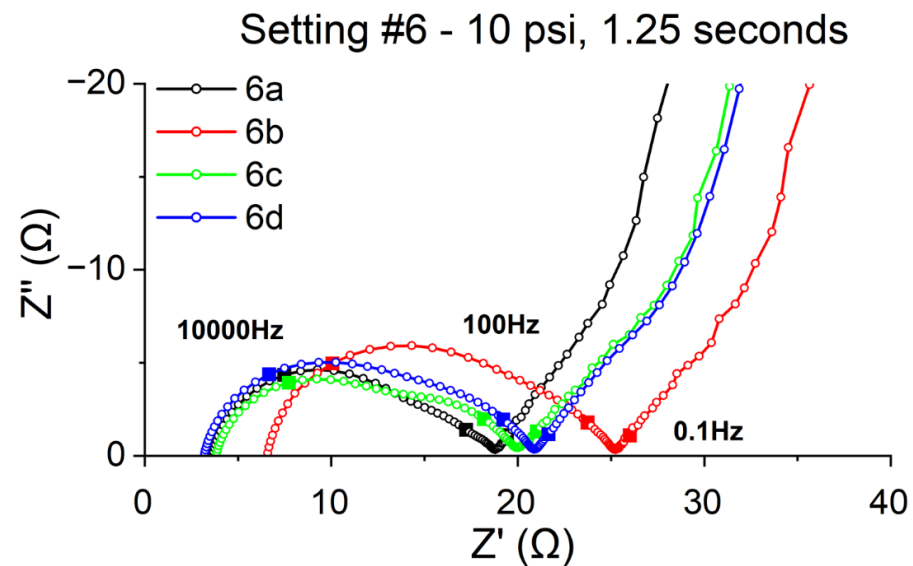
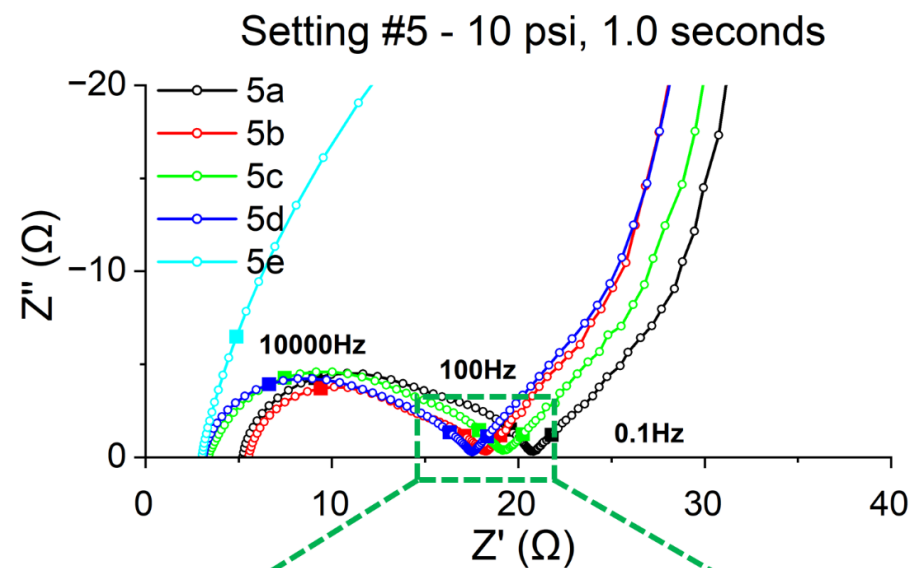
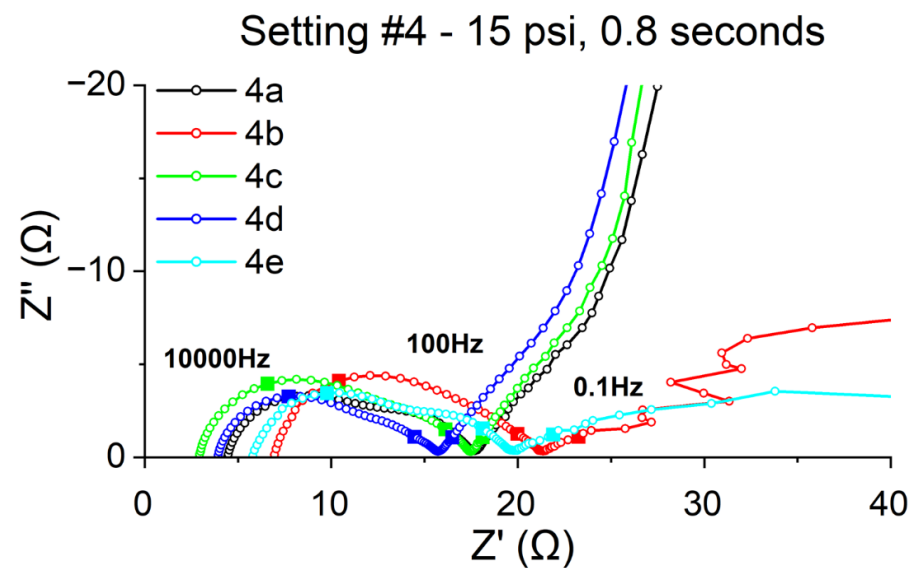


Figure 4.16 EIS responses for more ultrasonically calendered cells. Ultrasonically calendered cells are titled with their parameter setting (#) with the gauge pressure in psi and the weld time in seconds; an amplitude of $12 \mu\text{m}$ was consistent between settings. Three frequencies have been highlighted: 10000 Hz, 100 Hz, 0.1 Hz.

4.5.3 Electrochemical Discussion

4.5.3.1 *Rate performance and internal resistance*

The results from the rate performance test suggest that ultrasonically calendaring does affect the rate capabilities of the cathode. There is evidence of beneficial change in the rate capabilities of the ultrasonically calendared cathodes; a greater capacity at 5C was achieved for four out of the seven settings utilised (setting #1, #4, #5, #7). The remaining three settings (setting #2, #3, #6) have shown a detrimental change to the rate capabilities, yielding a lower rate capacity than the uncalendered and calendared controls. These changes are also not insignificant. Setting #6 possessed a 5C discharge capacity of 15 mAh g⁻¹ compared to 36 mAh g⁻¹ and 43 mAh g⁻¹ produced from the uncalendered and conventionally calendared cathodes. This is a relative capacity of 43 % and a 36 %. There is a significant loss to the capacity of setting #6 indicating the changes to the cathode made by the ultrasonic process have detrimentally impacted the rate capabilities of the cell.

Ultrasonic calendaring using setting #4 produced cathode which had a 5C rate capacity of 67 mAh g⁻¹, this is 186 % of the uncalendered cathode's capacity and 156 % of the conventionally calendared cathode's capacity (similar porosity). Analysing the voltage profile from the voltage vs discharge capacity plots of the best cells (Figure 4.14) indicated there is a significant decrease to the internal resistance of setting #4 which yielded the increased 5C capacity. All the cells possess a similar initial voltage around 4.2 V, the upper voltage cut-off of the charge, and discharge to approximately 155 mAh g⁻¹ at 0.1C. However, this differs at 5C; the ultrasonically calendared cathode of setting #4 has an initial voltage of 3.85 V and a discharge capacity of 87 mAh g⁻¹. The control possesses initial voltages of 3.75 V and 3.8 V when uncalendered and conventionally calendared, with capacities of 38 mAh g⁻¹ and 64 mAh g⁻¹. All the cells were charged to 4.2 V before the discharge therefore the lower initial voltage is caused by voltage drop due to overpotential. This overpotential is an excessive driving force which is necessary to function the cells at the current density. This indicates the sum of internal resistance in the uncalendered cells is greater than the conventional counterpart, which is expected behaviour, and the ultrasonically calendared cells have the lowest sum of internal resistances.

Demonstration of the 5C discharge capacities as a 3D surface plot with respect to welder pressure and weld time reveals a conical shape, Figure 4.17. This shape indicates that gauge

pressure and weld time both approximate a bell curve distribution; within the tested range of these parameters, a weld time or gauge pressure which is too small or too great leads to a poor cathode capacity. This indicates the potential of the ultrasonic calendering to positively transform the cathode, provided sufficient energy is supplied and too much energy is not transferred to the cathode.

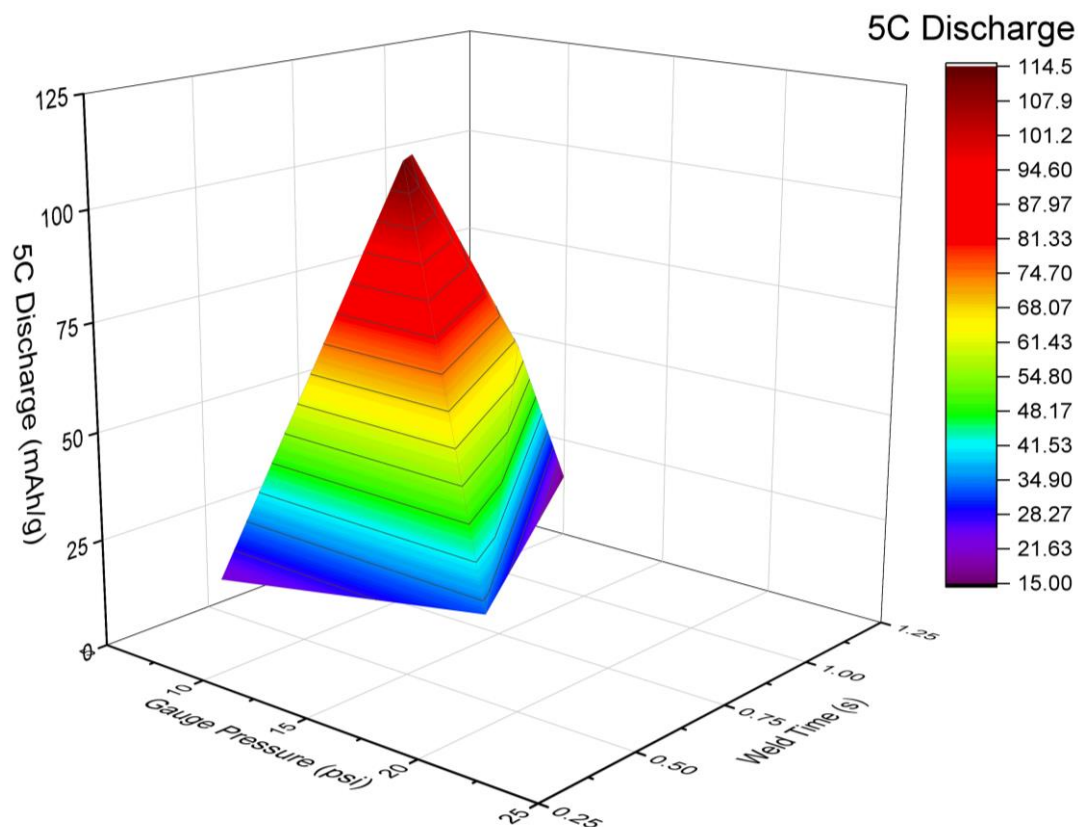


Figure 4.17 3D surface plot of specific discharge capacities comparing gauge pressure and weld time of the Branson 2000X welder. The conical shape indicates that there the optimal value between two related bell curves, excess or minimal gauge pressure and weld.

4.5.3.2 Charge-transfer Resistance and 5C Rate Performance

EIS provided further insight into the internal resistances. A suitable equivalent circuit model was used, separating the impedance response into the electrical resistance, contact resistance and charge-transfer resistance and a Warburg diffusion term. This ECM was applicable to all of cells and yielded impedances values which could be compared.

The observed changes in resistance were predominately in contact resistance and charge-transfer resistance. The cathode manufactured via ultrasonically calendering possessed a range of transfer resistances, depending on the ultrasonic calendering parameters; ultrasonic setting #5 yielded a mean R_{ct} of 7.0 Ω and ultrasonic setting #2 yielded a mean R_{ct} of 9.2 Ω . This provided additional evidence highlighting the importance of optimising the ultrasonic calendering parameters. The uncalendered cathode exhibited a mean charge-transfer

resistance of $6.7\ \Omega$ and the conventionally calendered cathode yielded a mean of $7.9\ \Omega$. These EIS results show that charge-transfer resistance can be reduced by ultrasonically calendering. Two ultrasonic calendering parameters (setting #4 and #5) exhibited a lower charge-transfer resistance and a greater 5C discharge capacity than the conventionally calendered controls; demonstrating the potential of ultrasonic calendering to outperform current methods. This serves as evidence towards ultrasonic calendering being an advantageous compaction process for cathodes.

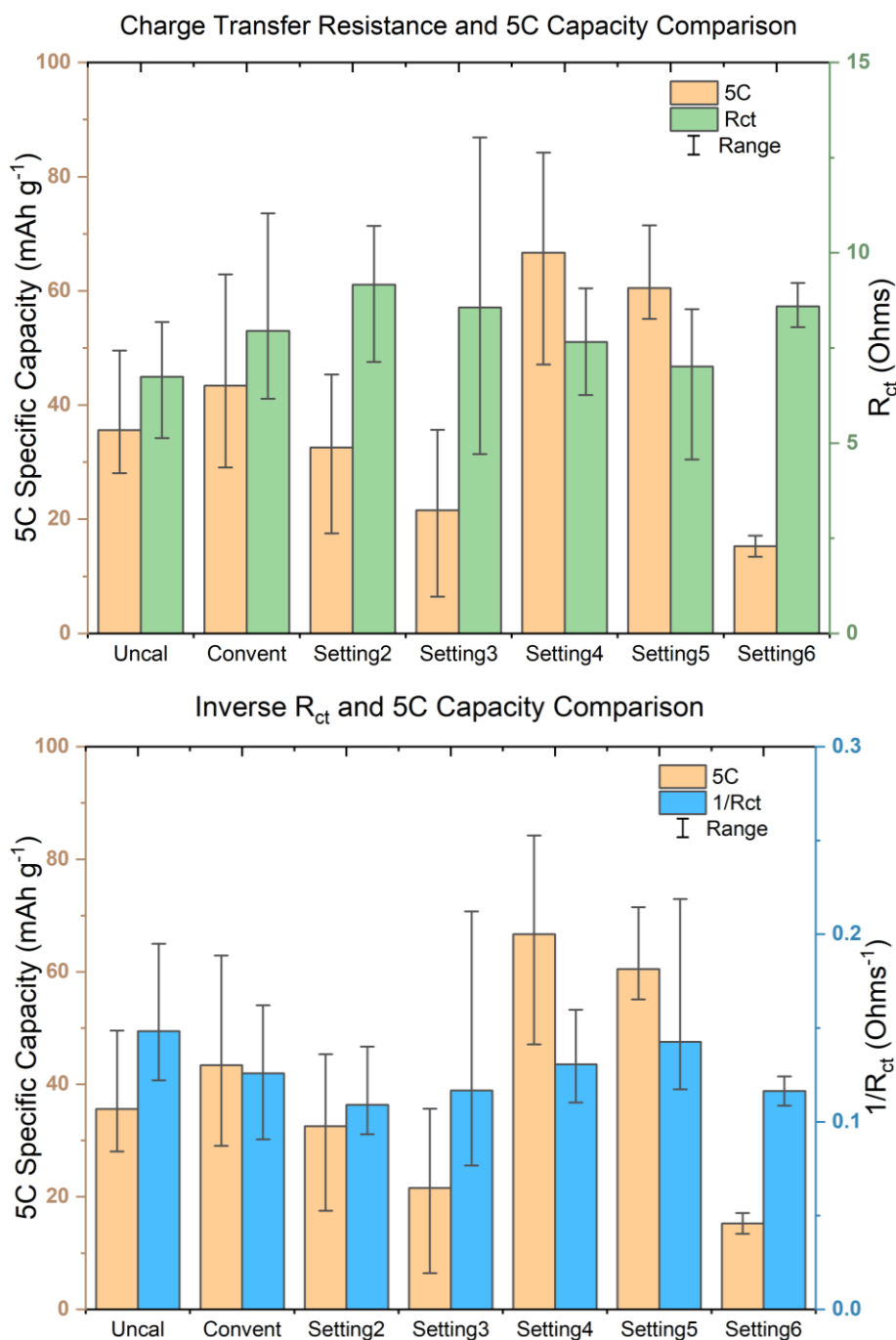


Figure 4.18 Two graphs showing the relationship between the charge-transfer resistance (R_{ct}) and the 5C discharge capacity the cathodes. The relationship is inversely correlated, so $1/R_{ct}$ has been demonstrated for trend observation. EIS had been conducted for the two controls, uncalendered and conventionally calendered and for setting #2, #3, #4, #5, #6; excluding setting #1 and #7.

This observed relationship between lower charge-transfer resistance and higher rate capabilities, as seen in these results, is also reported in the literature; the rate capacity at 5C and the charge-transfer resistance of the given cells should exhibit an inverse correlation^{330,387-391}. Larger charge-transfer resistances are expected to increase internal resistance, leading to a reduced capacity at high current densities. Figure 4.18 demonstrates the average charge-transfer resistance and the average 5C discharge capacity for the cells; the greater the charge-transfer resistance (green column), the lesser the 5C discharge capacity (orange column). This indicates an inverse correlation. For ease of comparison, Figure 4.18 also details $1/R_{ct}$ (purple column). The relationship between 5C discharge capacity and $1/R_{ct}$ should be a positive correlation, and this is portrayed in the results: higher $1/R_{ct}$ cathodes typically yielded a greater 5C capacity, as demonstrated in setting #4 and setting #5. Setting #3 also follows this trend, demonstrating the smallest $1/R_{ct}$ and nearly the lowest 5C discharge capacity.

This analysis shows the impact of charge-transfer resistance on facilitating high current density in lithium-ion cathodes. It also shows that charge-transfer resistance is a dominant impedance within a cell and that ultrasonically calendaring can intrinsically lower charge-transfer resistance.

4.5.3.3 *Cell Stability and Specific Capacity Retention*

Comparing the voltage profiles, Figure 4.14, at 0.1C indicates that the specific capacities of the cells were similar, 155-157 mAh g⁻¹. This confirms that differences in the capacities at higher rates are due to internal resistances. The cells reach the same capacities when charged and discharged low c-rates, 0.1C, showing the performance differences at high rates arise from their behaviour under high-rate conditions. This insight is bolstered by the specific capacity analysis, Figure 4.13, which showed negligible capacity difference between all the cells discharged at 0.1C. At low current densities, the internal resistances in the cell are minimised; therefore, the capacity of the cell at this c-rate correlates directly with the amount of electrochemically active material in the electrode. The mass of active material is also normalised by converting to the specific capacity (mAh g⁻¹). This illustrates that greater specific capacity of the cell correlates to more optimal utilisation of NMC in the electrode.

The similar specific capacities of the cathodes across the dataset, Figure 4.13, signify that they are not affected by the calendaring method; the available lithium and the amount of electrochemically active NMC in the cathodes are not reduced by ultrasonic calendaring. This

is important because it validates the analysis of the cells at different rate capacities; the difference in capacity at high current densities in cathodes can be attributed to differences in the rate capabilities, and not differences in specific capacity.

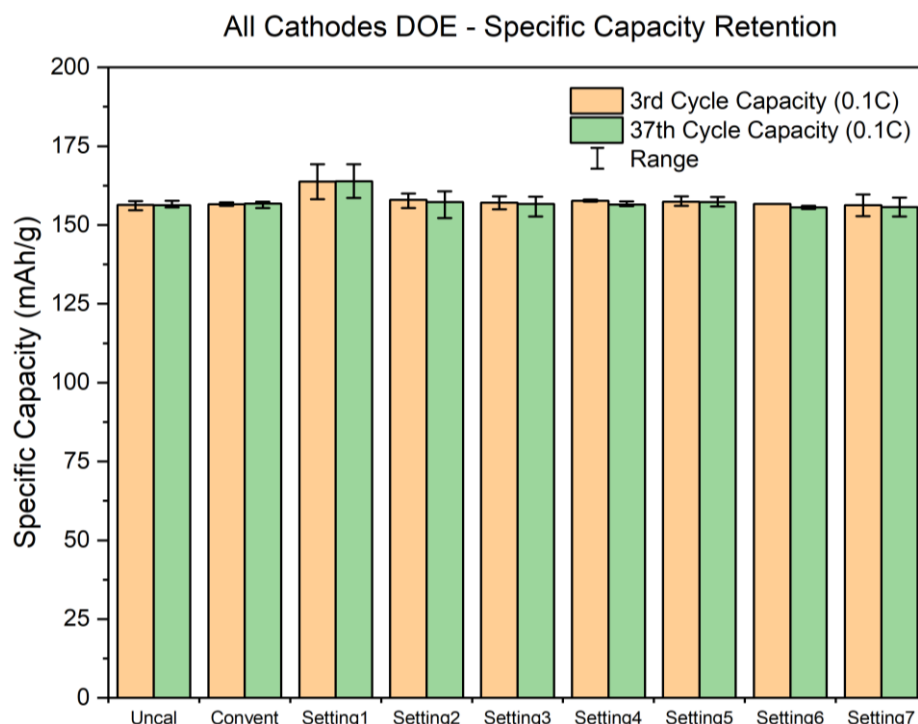


Figure 4.19 Specific Capacity for two cycles; cycle 3 is a discharge at 0.1C and cycle 37 is the final discharge in the rate performance test, also at 0.1C. Indicates changes to specific capacity during cycling are negligible.

The voltage profiles also indicate an absence of unexpected side reactions. Some voltage instability is observed at 1C and slightly more at 5C; however, no unanticipated peaks from undesired chemical reactions are present. Figure 4.19 shows similar specific capacities measured at cycle 3 (the 0.1C cycle after the formation cycles), and cycle 37 (the final cycle at 0.1C in the rate capacity test after the high c-rates cycles). This specific capacity retention from cycle 3 to 37 also indicates that capacity loss has not occurred, further illustrating that the performance differences at high rates is due to the high current density. If there have been any dramatic capacity changes or capacity loss, it would have suggested excessive lithium consumption, cathode electrolyte interphase build-up or active material cracking.

4.5.3.4 Compliance with Literature

4.5.3.4.1 Lithium-Ions and Limitations on Rate Performance

Ions are the slowest component of the system and slow processes present large impedances³⁹². Two large internal resistances associated with the lithium ions are the charge-transfer resistance and the diffusion resistance^{393,394}. These resistances be equal, or one may dominate³⁹⁵. In thin electrodes, the diffusion pathway is shorter and therefore has a smaller diffusion

resistance ³⁹⁶. Charge-transfer resistance is a large impedance ³⁹⁷, and will dominate in low-diffusion-resistance systems ³⁹⁸. In contrast, thick electrodes, larger than 100 μm , have long diffusion pathways ³⁹⁹. The long pathways, combined with the inherent tortuosity experienced in electrodes, will cause the ionic diffusion resistance through the electrolyte to dominate ^{400,401}. In these thicker electrodes, compressing the electrode can reduce the average diffusion distance, providing the increased tortuosity does not cancel out the reduction in electrode depth ⁴⁰².

Zheng et al investigated these resistances across a broad range of porosities ²⁴⁵. The study considered electrodes at 0 %, 30 % and 50 % porosity. These porosities are significant because they represent a completely compacted, a moderately calendered, and an uncalendered electrode. A completely compacted cathode, at 0 % porosity, is evidently going to experience high lithium-ion diffusion resistance because the lack of porosity and porous network will severely limit the wetting of the electrode ^{403–405}. It is likely the only way this electrode functioned was because the formulation contained a high mass of inactive additives (8 % PVDF binder and 7 % acetylene black conductive additive). The electrolyte can slowly diffuse through the CBD phase because it is nanoporous. The EIS results indicated that compressing the electrode from 50 % to 30 % porosity reduced R_{ct} , but decreasing the porosity beyond 30 % increased R_{ct} . 0 % porosity presented the largest resistance, and 10 % porosity had a resistance greater than the uncalendered electrode. This trend shows an inverted bell curve centred around 30 %; the largest resistances experienced at high or low porosities. This is good evidence that the charge-transfer resistance measured is a representation of the real resistance exhibited in cells. The resistance does increase as the electrode becomes overcalendered; too much porous volume loss is detrimental ⁴⁰⁶. Zheng also states that charge-transfer resistance dominated the cathodes. The cathodes ranged from 100 to 188 μm (0 % porosity to uncalendered).

Ogihara et al investigated the relationship between electrode thickness and performance. In this work, the electrodes were classified into thin-electrode regions and thick-electrode regions. In the thin-electrode regions, R_{ct} is greater than R_{ion} . In the thick-electrode regions R_{ion} , is greater than R_{ct} ³⁹⁵. In his work, the critical electrode thickness of 40 μm was identified, defining the transition between the thin and the thick electrode regimes. Isolating the resistances revealed the trends of R_{ct} and R_{ion} : R_{ion} has a linear relationship which increases with electrode thickness, and R_{ct} has an exponentially decaying relationship. R_{ct} dropped from 150 $\Omega\text{ cm}^{-2}$ at 20 μm to 37 $\Omega\text{ cm}^{-2}$ at 35 μm and <20 $\Omega\text{ cm}^{-2}$ at 75 μm . These are important

considerations for cell resistances and how they are manifest in EIS. His work concluded the internal resistance of electrodes are dominated by the resistance charge-transfer of lithium ions; however, with increasingly thicker electrodes, the resistance of the ion diffusion through the electrolyte increases and can exceed the charge-transfer resistance ^{407–409}.

The charge-transfer resistance denotes the resistance of the ions to intercalate and react within the active material particles. The ions are in bulk within the ionic solution. To react, they must traverse the crystal lattice until a vacant active site is available before combining with a free electron to form an oxidised crystal. There are a multitude of factors which affect charge-transfer resistance: inherent characteristics such as chemical stoichiometry, the mass of the intercalating ion, and the oxidation state of the cathode. This study is limited to lithium-ion systems with a cathode active material of NMC622; this controls for these inherent characteristics as they are constant. Physical factors such as temperature and state of charge affect the charge-transfer resistance ⁴¹⁰. Higher temperatures provide more kinetic energy for the charge-transfer and higher oxidation states allow higher capacity by utilising more chemical potential energy ^{411,412}. Both temperature and oxidation states were controlled in this project: all electrochemical testing was conducted in 25 °C temperature chambers, and the voltage window for all tests was limited to 3.0-4.2 volts.

4.5.3.4.2 The Impact of Charge-Transfer Resistance on Rate Performance

Literature and this project used EIS to deduce the charge-transfer of the electrodes. In the experiment, the resistance of the cells can be very similar and sometimes within a negligible range. An opinion could be formulated that the difference is small and may have little or negligible effect on cell performance; however, discharging of the cells demonstrates the effect of the cells' resistances and how it greatly impacts performance at higher current densities. Efficiency at high current rates is critical for fast discharging; however, due to the internal resistance of a cell increasing logarithmically with current density, it can be challenging. Therefore, having the electrodes' inherent charge-transfer resistance being minimal is desirable.

Equation 4.2: Butler-Volmer

$$i = i_o \left(e^{\frac{\alpha_a F \eta}{RT}} - e^{-\frac{\alpha_c F \eta}{RT}} \right) \quad 413$$

The Butler-Volmer equation, Equation 4.2, explains how current density relates to overpotential ^{413,414}, but it is only applicable at low current densities. At higher current densities, a derivative of the Butler-Volmer equation, the Tafel equation (Equation 4.3), is applicable ⁴¹⁵.

$$\eta_s = a + b \log(i)$$

$$\text{If current is doubled: } \eta_2 = a + b \log(2i_1)$$

$$\Delta\eta = \eta_2 - \eta_1 = [a + b \log(2i_1)] - [a + b \log(i_1)]$$

$$\Delta\eta = b \log(2i) - b \log(i) = b \log(2) \quad \therefore \text{logarithmic relationship}$$

This logarithmic behaviour can be seen in the results; Figure 4.20 shows the capacity for all the cells decreasing with increasing discharge c-rate. This shows how c-rate represents the demand of the cells and consequently increasing the c-rate leads to additional charge-transfer resistance which causes a loss of specific capacity⁴¹⁷; as the c-rate increases there is a greater-than-linear loss of capacity. The discharge c-rate axis is displayed logarithmically.

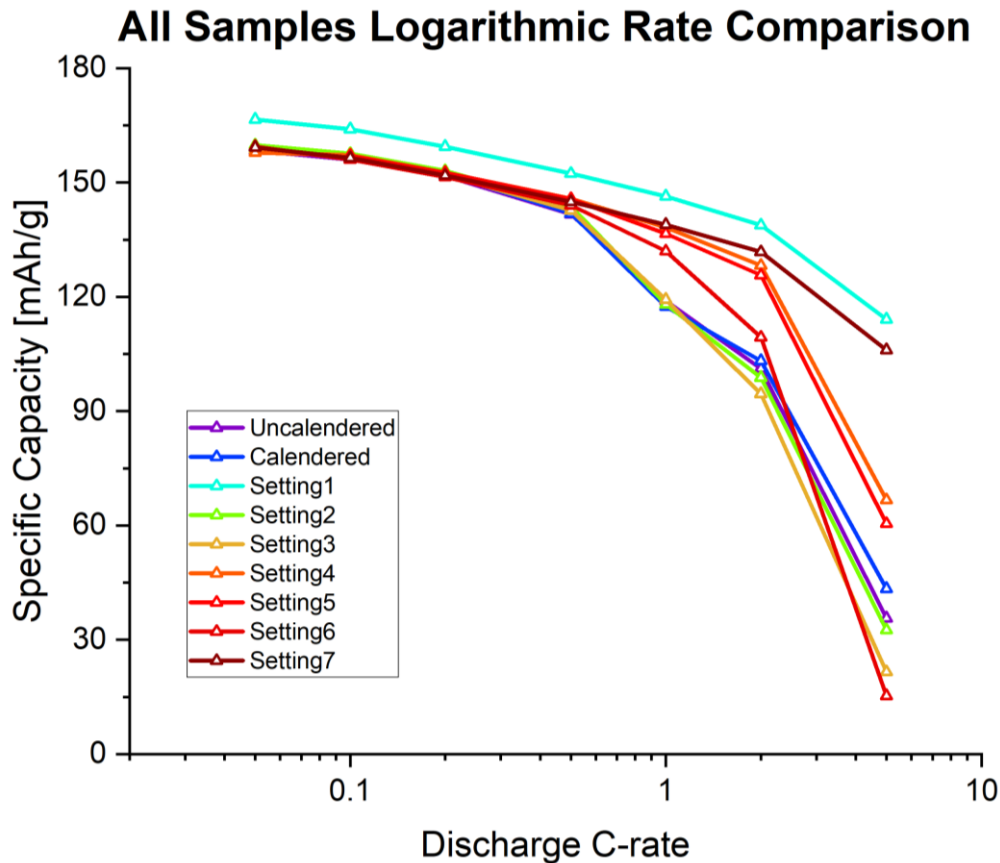


Figure 4.20 A logarithmic rate comparison of two controls at free standing and calendered to 45 % porosity, compared with all the different welder parameters used. Each data point is the mean average of the cells produced. Some anomalous results have been eliminated from the capacity average. The graph shows the relationship between c-rate and capacity is a logarithmic relationship. The drop off at 2C and 5C can be seen for all cells. The higher specific capacity for setting #1 is unexpected and assumed anomalous.

It can be observed that the specific capacity decreases steadily and linearly from 0.05C to 0.5C before rapidly decreasing from 0.5C to 5C. At the lower c-rate, the ohmic resistance provides the most significant contribution to the total resistance, because there is not a great demand on the cells, the diffusion concentrations are not large, and the intercalation reactions are slow

⁴¹⁸. The internal resistance will follow Ohm's law at low c-rate ¹⁰⁷. At high c-rates (0.5C to 5C) the trends of the graph show that the specific capacity progressively decreases as the c-rate is increased. This is indicative of ionic processes becoming significantly impeding ⁴¹⁹ which presents as a logarithmically decreasing relationship defined and exhibited in the literature ^{420–424}. At this current density, the charge-transfer resistance and the concentration gradients are causing greater internal resistance and creating a larger overpotential, following Tafel. This leads to the change from the linear decrease during Ohm's law regime (<0.5C) to the exponentially decreasing capacity at >0.5C. This observation shows that the cells in this analysis behave as expected and adds to the evidence that the ultrasonically calendered cells exhibit improved but orthodox electrochemical performance.

4.5.3.5 *Limitations and Anomalous Results*

This section investigates potential weaknesses of the work conducted in this electrochemical analysis. The insights cover rationalisations and suggestions for the replication or future work.

The most concrete evidence of the ultrasonic calendering being competitive with the conventional calendering is setting #4. Setting #4 had all five cells perform consistently without a short-circuiting or failure. The cells cycling is also highly consistent, for each of the given cells, the capacity deviation at every c-rate is similar. The initial 0.1C cycling data (cycle 3-8) had the same capacity as the final five cycles at 0.1C (cycle 33-37). This shows that the cells have not changed in specific capacity over the cycles. This is strong evidence of no side reactions or unusual electrochemical behaviour. The specific capacity of setting #4 is equivalent to the calendered control; however, it exhibits a greater rate capacity at 5C of 67 mAh g⁻¹. This is a 56 % increase in discharge capacity at the same c-rate. The average coating weight of the cathodes in setting #4 is 0.0270 g compared to 0.0259 g for the calendered samples. All capacity data presented is normalised by active NMC weight to produce specific capacities and specific rate capacities. Thinner cells have less internal resistance and greater rate capacities because of better ionic diffusion pathways ^{118,425,426}. The 5 % greater coating loading for setting #4 rules out differences in coating thickness as a driver of the increased performance. Setting #4 cells were also constructed in the same lab sessions and placed in the cell cycler chamber at the same time as the control cells. Setting #1 and #7 performed better than setting #4, but they were made at a different time with slightly different protocols and therefore had different control cells. EIS measurements were also not performed. These control cells performed better than the controls involved in this analysis, therefore taking setting #4 further seems more authentic

and has more data available. Setting #1 and #7 also had slightly less coating loading, at 94 % and 88 % of the film loading compared to the uncalendered controls. Thinner coatings are known for lesser internal resistance ⁴²⁷. This correlates with the greater specific capacities at 5C of 114 and 106 mAh g⁻¹. Considering these points, it would be advantageous to focus on setting #4 to eliminate thinner coatings as a contributor to the better rate performance in ultrasonic cells ^{428,429}.

Setting #4 is appealing to take further in analysis because it produced stable, consistent cells, which did not fail during electrochemical testing. The coating weight of the cells is towards the upper range, EIS measurements were conducted, and, ultimately, the cells had better electrochemical performance than both the uncalendered and the conventionally calendered control cells.

Regarding anomalous results, factors for quality control of the cathode have been identified and discussed in the methodology chapter (3.6.2). Sources of potential errors in the manufacturing process were identified and discussed. Importantly, the travel of the cathode from the off-site lab exposes the cathodes to uncontrolled atmosphere and the limitations on the slurry casting process prevented the production of sufficient film in one casting, leading to the casting of multiple slurry batches over several days. It is hard to attribute these reasons to specific behaviours; however, it should be acknowledged that there are additional considerations with the cathodes in this project.

4.5.3.6 *Discussion Summary*

The different parameters of the ultrasonic calendering were electrochemically assessed. Two sets of controls were tested alongside these cells, uncalendered (53 % porosity) and conventionally calendered (49 % porosity). The rate performance test involved cycling from low c-rate to high c-rates (0.1C to 5C). The data showed that the specific capacity of all the cells approximated 160 mAh g⁻¹, indicating that the cells had the same capacity at low current densities, when the internal resistances are minimised. The similar performance did not hold true at high current densities; at a c-rate of 5C the cells experienced a large range of capacities (from 13 to 116 mAh g⁻¹). EIS and a voltage profile analysis suggest a reduction in internal resistance is the cause of the differing capacities at 5C. The initial voltage at 5C indicated that the uncalendered cells generate a much larger overpotential compared to the ultrasonic and

traditionally calendered counterparts, which is indicative of greater internal resistance, requiring more voltage to drive the discharge. The ultrasonic cells had the lowest voltage drop. EIS also supported the ultrasonically calendered cells possessing greater rate performance, measuring the cells to have a lower charge-transfer resistance (7.0Ω) compared to conventionally calendered cells. This would concur with the ultrasonically calendered cells' greater capacity at 5C. Unexpectedly, the uncalendered cells had a lower charge-transfer resistance than the conventionally calendered cells. This indicates that there may be another contributor to the high-rate performance. This is also supported by the specific capacity decreasing more than logarithmically with increasing c-rate, suggesting the charge-transfer resistance, the main kinetically limiting process, may not be the only significant contributor to internal resistance.

4.6 Chapter Conclusion

This chapter explored the ultrasonic weldability of PVDF. A multitude of different ultrasonic welding parameters were utilised to bond two PVDF strips. The bonded strips displayed comparable tensile strength to longer, singular pieces of PVDF. This serves as evidence of PVDF being successfully ultrasonically welded despite being performed at room temperature, above the glass transition temperature of PVDF, which makes materials difficult to ultrasonically weld. This indicated PVDF to be a viable polymeric binder for ultrasonic calendering.

The 96:2:2 cathode formulations, containing NMC622, PVDF and C65 carbon black, proved too brittle to be ultrasonically calendered; however, the ultrasonic calendering of a 92:4:4 formulation resulted in a net compression of the electrode from 55 % porosity to within the range porosity of 45-52 %. The variable porosity was dependent on the ultrasonic calendering parameters. This shows an ultrasonic welder can be used to ultrasonically calender 92:4:4 cathode films. This is evidence of a new, novel manufacturing technique to fabricate calendered cathode.

A rate performance test and additional electrochemical analysis showed varied capacities at 5C but negligibly capacities difference at 0.1C, indicating similar specific capacity but differing rate performance amongst the cells. Altering the ultrasonic calendering parameters was proven to affect the rate capabilities of the cathode. Multiple parameter sets produced cathodes that had greater rate capabilities than both uncalendered cathode and conventionally calendered cathode of comparable porosity (welder setting #4 and setting #5). The increased rate

performance was attributed to a reduction in internal resistance. Charge-transfer resistance was identified as the main contributor to the reduction in internal resistance; charge-transfer resistance was measured lower in cells with good rate capabilities and measured higher in cells with poor rate capabilities. Further electrochemical results which support the increased rate performance are explained in section 5.3 and the mechanism producing this effect is explained in sections 5.4 and 5.5.

5. Experimental Chapter: Ultrasonic Calendering – A Mechanistic Understanding

5.1 Aims and Objective

In the previous chapter a beneficial rate capability for the ultrasonically calendered cathode was observed but not fully justified. The aim of this chapter is to delve deeper into how ultrasonic calendering changes the cathode. This works towards the following aims:

2. To utilise ultrasonic calendering to produce a densified cathode film, followed by characterization of its physical properties and evaluation of the ultrasonic calendering process mechanism.
3. To assess the electrochemical performance of ultrasonically calendered cathode and correlate its performance with its physical and structural characteristics.

5.2 Porosity and Pore Size Distribution

Electrodes are composed of a porous network of active material and additives. Electrodes will typically have micron-sized pores between the active material particles due to the particles being ellipsoidal and having a 12 μm average diameter (d_{50}). The additives comprise of a polymeric binder, PVDF, and a conductive additive, carbon black. Carbon black is a highly porous nanoparticle. Imerys C65 carbon black has a high surface area to volume ratio ($65 \text{ m}^2 \text{ g}^{-1}$ and a density of 0.18 g cm^{-3}). This indicates the particle is highly porous. PVDF is a polymer and can become almost infinitely long during precipitation as the NMP is vapourised.

The smaller nano-sized binder and carbon black form networks and are inherently nanoporous, which contributes to a nanoporous part of the electrode. Additionally, the pore space between the active particles and the CBD can be nano-sized⁵⁴. These regions are described as short-range contacts, the CBD directly in contact with the active material particles, imparting strength and forming a short electronic network⁴³⁰.

Due to the micron-sized pores attributed to the active material and the nanoporous regions formed in relation to the CBD network, the pore size distribution of an electrode is bimodal.

There is an abundance of multi-micron-sized porosity and a secondary fraction of porosity which is submicron.

Compression of the electrode causes permanent plastic deformation which has been demonstrated to decrease the total porosity of the electrode. Additionally, as porosity is eliminated the two bimodal peaks typically shift towards a smaller value, as the diameter of pores in the electrode shrinks under deformation. This is demonstrated with a control group in 3.14.2 - the MIP results in Figure 5.1. It can be seen the uncalendered electrode has a peak at a pore diameter of 3.3 μm . It shows an abundance of porosity in the largest microporous region seen, above 0.20 mL/g. The nanoporous region is also the most abundant and is predominantly sized above 100 nm in diameter. This suggests the CBD has not been compressed or forced to additionally cover/coat the NMC particles. The integrated area under the curve between the 10 nm and the 4 μm is also the largest, which is consistent with the structure being uncompressed and the total pore volume being the largest; this observation is expected for the uncalendered cathode.

The two ultrasonically calendered cathodes display different structure with respect to the uncalendered cathode. For the ultrasonic setting #7 (10 psi, 0.8 s weld time), the pore sizes are mostly narrower than 3 microns, having shifted to centre over 2.6 microns. This shows a compaction of the microstructure, specifically the porosity between the NMC particles. The integrated area underneath the curve is also smaller than the uncalendered sample, indicating permanent plastic deformation is present in the cathode because of ultrasonically calendering. The nanoporous region has also been compressed but is more akin to the uncalendered electrode. The electrode in this sample was estimated to be approximately 45 %.

For the ultrasonic setting #1 (15 psi, 0.5 s), the pore sizes are narrower than 3 μm with a microporous peak centred over 2.0 μm . The shape of the microporous region peak is much broader than the other samples. This may indicate a non-uniformity in the compression, as the peak could be comprised as a peak at 1.5 μm and 2.25 μm . The integrated area underneath the curve appears smaller than the ultrasonic setting #7 and the uncalendered cathode, showing a greater loss of total pore volume. This sample was also estimated to be 45 % porous from micrometre thickness measurements and density calculations. Regarding the CBD region, the nanoporosity exhibited in the sample has been compacted, reducing the peak at 200 nm. There

is also a smaller tail from this peak into the sub-100 nm region. This could indicate less NMC particle cracking; however, it is difficult to assess this solely with MIP.

The two ultrasonically calendered cathodes having similar porosity but displaying slightly different curves allude to possibility of different pore structures. Typically, as discussed in the literature, the pore size distribution of an electrode only changes with porosity. It is atypical for two cathodes from the same coating to have a different pore size distribution if compressed to the same porosity.

The purpose of conducting mercury intrusion porosimetry was to identify if ultrasonic calendering was causing the cathode permanent plastic deformation and to quantify how it was affecting the porous network. A total loss of porosity was observed, which demonstrates the technique compacts the electrode. Additionally, the porosity in the structure constricts and frameshifts towards a smaller average pore diameter. This is consistent with conventional calendering and indicates that the loss of thickness after the technique is due to restructuring of the electrode. The two novel cathodes, which were estimated to have a porosity of approximately 45 %, show a curve that fits between the 45 % and the 50 % porosity peak. An observation regarding the CBD was identified, which may indicate that the CBD behaviour could be different compared to conventional calendering. The CBD does not appear to compress as much; however, it should be considered that some of the calendered samples are compressed to a greater degree. Literature involving the compression of NMC cathodes suggested that an increase of pore volume below the 100 nm region is indicative of NMC particle cracking²²³. The most notable observation is the difference between the curves of both the ultrasonically calendered cathodes, despite possessing the same porosity. This difference in pore size distribution may indicate that ultrasonic calendering creates a different electrode microstructure compared to conventional calendering methods. This is important because the ability of the ions to flow through the structure greatly influences the electrochemical performance of electrodes at high c-rates. The effective ionic resistance is significant contributor to overall cell resistance. Reducing this via electrode restructuring would be electrochemically advantageous.

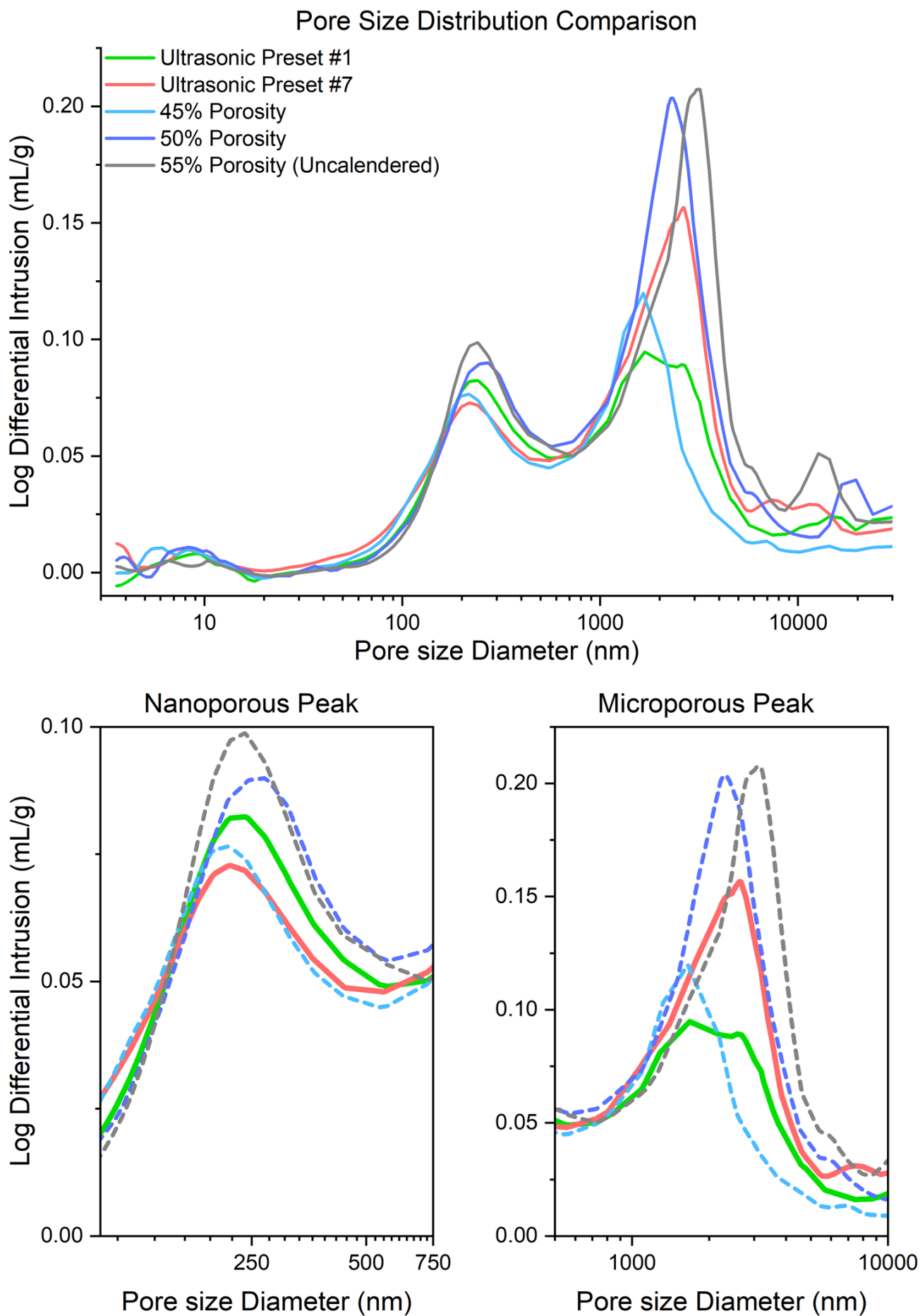


Figure 5.1 Pore sized distribution curves attained from MIP of two ultrasonically calendered samples and 3 controls. Ultrasonic preset #1 (15 psi gauge pressure, 0.5s weld time) and #7 (10 psi gauge pressure, 0.8s weld time). PSDs from controls at 45 % and 50 % have been added to compare.

5.3 Tortuosity and Effective Ionic Diffusivity Analysis

5.3.1 Objective

MIP demonstrated the ultrasonically calendered cathodes may exhibit different pore size distributions and microstructures compared with those produced by conventional calendering methods. This result prompted investigation into whether the effective lithium-ion diffusivity has changed. The effective lithium-ion diffusivity can be increased by heating the cell ⁴³¹, using a less viscous electrolyte mix or by reducing the tortuosity of the system. Increasing tortuosity has always been one of the significant drawbacks to calendering, hindering ionic transport ⁴³². Providing a compressive technique which reducing tortuosity could provide a new method to reducing electrode resistance and achieving higher rate capabilities ^{433,434}.

5.3.2 Introduction

5.3.2.1 *Cell Resistances*

The two biggest resistances in cells are the lithium-ion diffusion resistance and the charge-transfer resistance. Both these processes involve the transport of lithium ions which are significantly slower than the processes involving electrons transport. The slow ionic processes consequently provide the most resistance. Lithium-ion diffusion resistance relates to the traversal of the lithium, contained within a solvation shell through the electrolyte, along pore channels. Charge-transfer resistance encompasses the intercalation reaction of the lithium ions, moving from the electrolyte to the surface of the active material and then throughout the crystal lattice before bonding with an unoccupied reaction site and an electron.

5.3.2.2 *Measuring R_{ion} with Symmetrical Cells*

Effective ionic diffusivity is difficult to compare between cells because it is a slow process. EIS presents impedances based on their response to a progressively decreasing frequency pulse. Fast processes within the cell are presented first in the response, within the high-frequency range. This is typically the electrical resistance of the cell. As the frequency decreases, slower cell processes are measured. The charge-transfer resistance will follow the electrical resistance and precede the Warburg impedance in the low-frequency region. The Warburg impedance represents the ionic diffusivity within a semi-infinite system. Whilst Warburg impedance indicates the ionic diffusivity, it is in the low-frequency regime, which is less

accurate and prone to greater error. More importantly, it is at the end of the equivalent circuit model, which means it needs to be deconvoluted/resolved from the previous components. The combination of these factors leads to great difficulty obtaining an accurate representation of ionic diffusivity in electrochemically active cells (half-cells and full cells).

Symmetrical cells with an inhibited charge-transfer process can be used to more accurately measure R_{ion} compared to conventional half or full cells. This is because the EIS response and equivalent circuit model simplifies to an electrical resistance and an ionic resistance; the elimination of R_{ct} eliminates the impedance from the EIS response.

There are two methodologies for eliminating charge-transfer from the system. The charge-transfer component can be eliminated by making a symmetrical cell with two electrodes of equal voltage. The equal voltage will prevent charge-transfer because the energy difference between the electrodes is insufficient to exchange current. This presents challenges because inhomogeneities in cells cause voltage differences between local regions of the electrode which can accumulate to a slightly different total cell voltage. The cells also need to be assembled into functional a cell to charge the electrode to a specific voltage. These two cells are then disassembled to access the cathodes and made into symmetrical cells. This methodology is significant, complex work, which can introduce errors.

Alternatively, the use of an electrolyte containing salt(s) that cannot intercalate into the cathode can be employed to eliminate charge-transfer. The lithium ions and electrolyte salt need to be able to bind to form a solvation shell. This is significantly larger than an isolated lithium ion. The solvation shell helps the intercalation of lithium ions from the electrodes and their transport through the electrolyte.

The tortuosity was calculated by measuring the resistances within the symmetrical cells via EIS and Equation 5.1 using the electrodes' properties.

Equation 5.1 Tortuosity Relation for EIS

$$\tau = \frac{R_{Ion} \times A \times \varepsilon \times \kappa}{t}$$

435

This is applicable for any electrolyte solution, as it considers the electrolyte conductivity, and the measured resistance (R_{ion}) will vary depending on the electrolyte conductivity. It should be noted that the equivalent circuit for this model is an electrical resistance followed by a Warburg impedance. The EIS responses show a semi-circle at high-frequency, a 45-degree line and an asymptotic line at low-frequency, Figure 5.2 and Figure 5.4. The start of the semicircle at high

frequency is an electrical resistance and the semicircle is a capacitive component due to the electrical resistance (R_e) being a significant portion of the cells' resistances. This causes the two resistances to overlap and become challenging to resolve. In situations where the electrical resistance is comparable to the ionic resistance, the measured R_{ion} has contributions from R_e , inflating the value. The portion of the contribution can be determined with analytics and models; however, in an ideal situation, the R_e is sufficiently small that the contribution to the R_{ion} measurement is negligible. In the literature, was identified that having a relationship of R_e/R_{ion} equal 100 has been sufficient for the measured R_{ion} value to truly represent the actual R_{ion} resistance³⁵⁹.

5.3.3 Results

5.3.3.1 50 mM Analysis

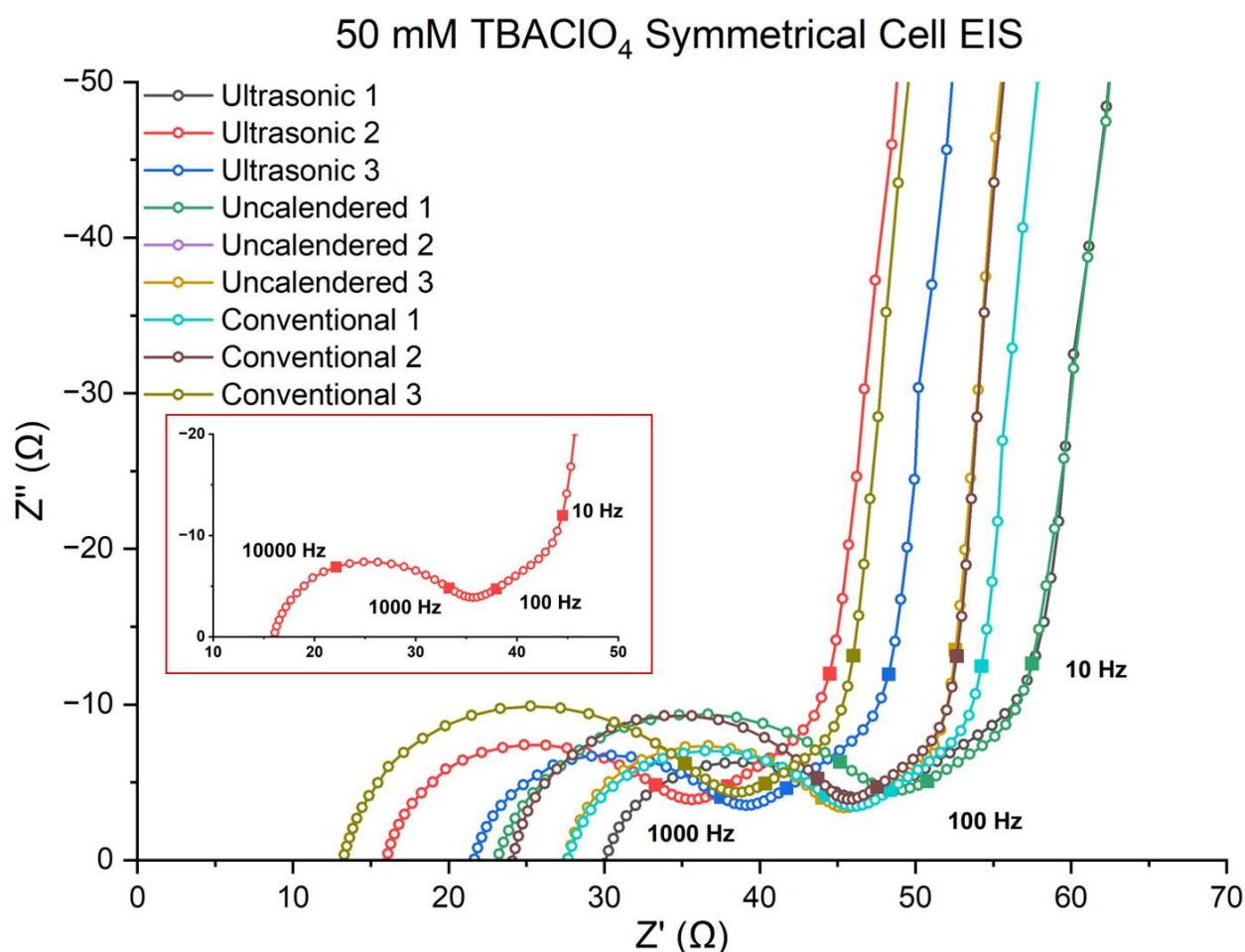


Figure 5.2 Solartron EIS response for 50 mM tetrabutylammonium perchlorate symmetrical cells. Conventional, uncalendered and novel (ultrasonically calendered) cathode are shown. Inset shows a typical response with frequencies at 10000, 1000, 100 and 10 Hz, indicating the contact resistance is before 1000 Hz.

R_e to R_{ion} for 50 millimolar TBAClO₄ has ratio of approximately 1:1, which causes the capacitance to be so large that it inflates the R_{ion} resistances. To prove that the values are not an accurate representation, the tortuosity values were calculated to indicate how inaccurate the values are. The mean average porosities in the dataset were 52 %, 50 % and 47 % for the uncalendered, ultrasonically calendered, and conventionally calendered. The least calendered cell had a porosity of 53 % (uncalendered cell 2). For a porosity of 53 %, the tortuosity calculated by the Bruggeman equation (Equation 2.7) for a sphere would be 1.37. Therefore, the minimum tortuosity expected in the dataset should be 1.37; however, there were cathodes in each of the three cathode types that measured below this tortuosity threshold. This indicates the values are not accurate because they are lower than achievable.

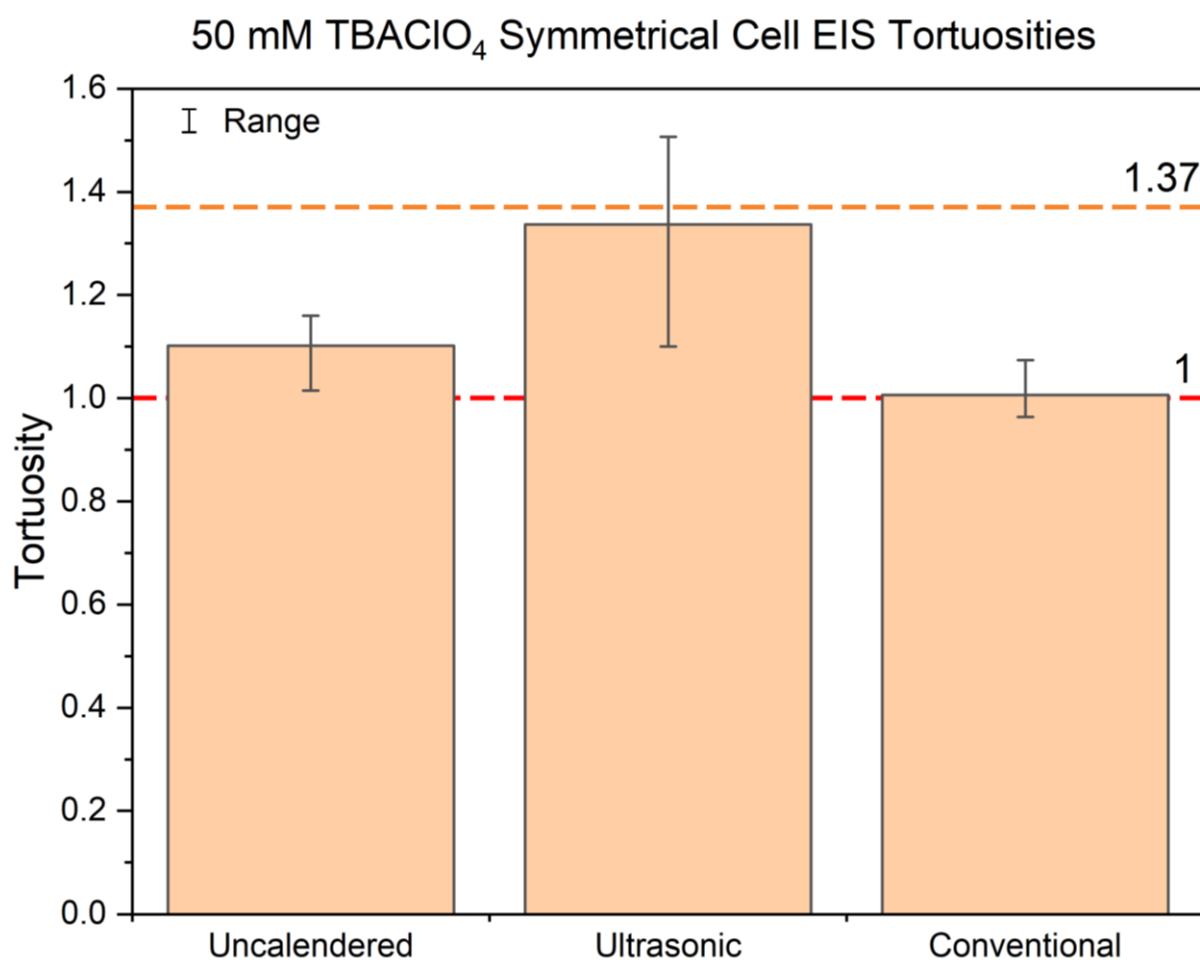


Figure 5.3 Calculated tortuosity measurements from the 50 millimolar 4mM tetrabutylammonium perchlorate symmetrical cells EIS. Tortuosity values of 1 and 1.37 are labeled on the graph. A tortuosity of 1.37 is the lowest tortuosity possible for the highest porosity used in this dataset (53 % porosity) if following the Bruggeman tortuosity relation. This data indicates that tortuosity values are measured lower than possible.

To further this inaccuracy argument, a lower tortuosity can be achieved in a system by manipulating particle orientation or adding macropores. However, tortuosities must always equal or exceed one because a tortuosity of one indicates a directly linear path with no deviation or convolution. A tortuosity of less than one would hypothetically indicate a traversal

distance which is less than the direct linear distance. This is impossible, but despite this, the lower range for the conventionally calendered electrodes yielded a tortuosity of 0.96, lower than 1.

To reduce the impact of R_e on the symmetrical cell EIS response, a solution containing a lower concentration of TBAClO₄ was prepared. The lower concentration decreases ionic conductivity, causing the $R_e:R_{ion}$ ratio to decrease. This makes Warburg impedance more resolved for attaining a more accurate R_{ion} value. A 4 mM tetrabutylammonium perchlorate was prepared and used to repeat these results.

5.3.3.2 4 mM Analysis

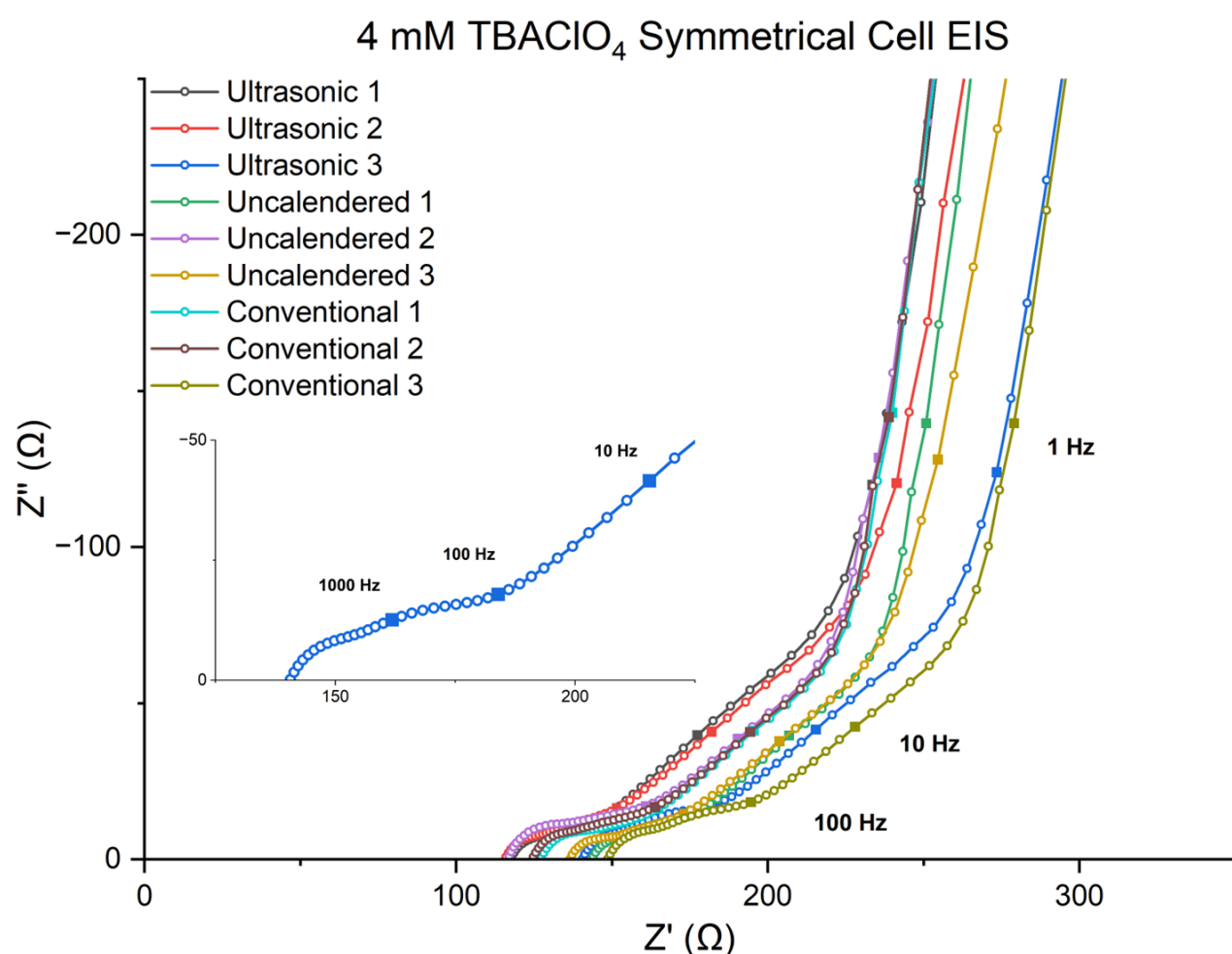


Figure 5.4 Solartron EIS response for 4 mM tetrabutylammonium perchlorate symmetrical cells. Conventional, uncalendered and novel (ultrasonically calendered) cathode are shown. Inset Shows a typical response with frequencies at 1000, 100 and 10 Hz, indicating the contact resistance is before 1000 Hz.

Analysis of the 4 mM tortuosities TBAClO₄ symmetrical cells indicated that the lowest tortuosity belongs to the ultrasonically calendered cathodes, followed closely by the uncalendered cathode, the conventionally calendered cathode possessed the highest, significantly higher than the others. The range of values measured were the most compact for the uncalendered,

the ultrasonically calendered had slightly more variance and the conventionally calendered electrode had the most range of response. The uncalendered and ultrasonically calendered tortuosities overlap; however, the conventionally calendered symmetrical cell that had the least tortuosity lies above the range of both the uncalendered and ultrasonically calendered cells. The ultrasonically calendered cells had a mean tortuosity of 3.29 with an upper range of 3.50. The uncalendered cells had a mean tortuosity of 3.49 with an upper range of 3.62. The conventionally calendered mean was 5.05 with a lower range of 4.36. This result replicates literature for conventional calendering; the tortuosity during the conventionally calendered process has increased from the initial uncalendered tortuosity^{436,437}, however the ultrasonically calendered cathode's tortuosity had not increased as significantly, or potentially, has not have increased it beyond its original, uncalendered tortuosity.

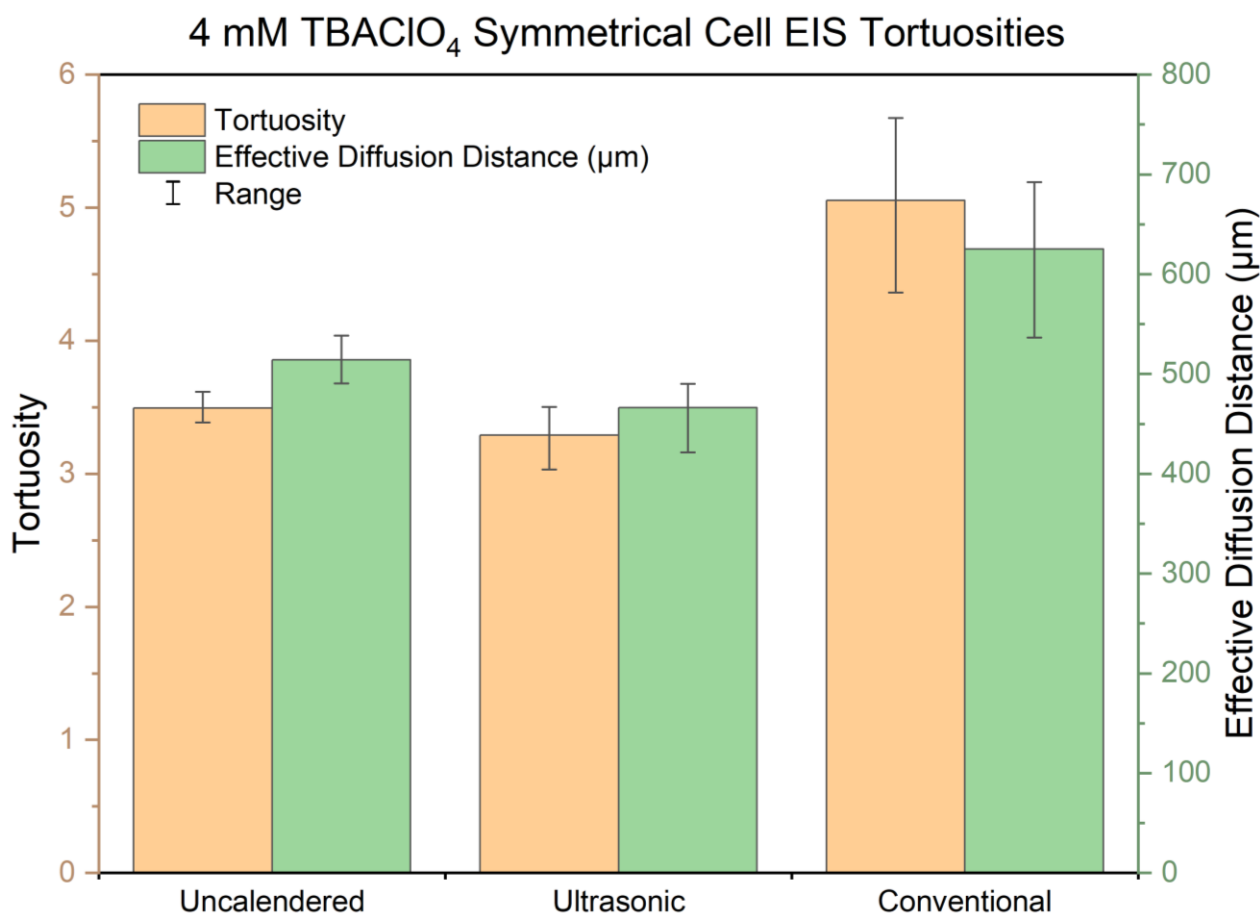


Figure 5.5 Results of symmetrical cell analysis using 4 mM tetrabutylammonium perchlorate. The range bars include three repeats for each cell type. All electrodes are NMC-622 with 92 % loading and 4 % binder and conductive additive (92:4:4). Uncalendered coating averages – 142 μm 54 % porosity; ultrasonically calendered coating averages – 147 μm 48 % porosity; conventionally calendered coating averages – 124 μm 48 % porosity.

5.3.3.3 Analysis of the Ultrasonically Calendered Cathode Compared to Uncalendered

The uncalendered and ultrasonically calendered cathode tortuosity measurements being so close could indicate multiple situations. A disadvantage within this chapter has been the need

to use a 4 mM solution of tetrabutylammonium perchlorate in EC:DEC (1:1). This electrolyte concentration was necessary to decrease the ionic conductivity of the solution in an effort to make the ionic resistance significantly greater than the electronic resistance in the symmetrical cells. This significantly increased ionic resistance makes the response more resolvable and reduces the contribution of the electronic resistance being incorporated into the ionic resistance. However, by reducing the salt content, the solution has become diluted. There is not much salt in the solution, which gives rise to greater interference from impurities. Impurities will affect the intrinsic conductivity of the electrolyte, which would change the tortuosity values calculated in Equation 5.1 if the has solution's conductivity deviated from the used 0.156 mS cm^{-1} (for a 4 mM solution). Ideally, the impurities would have been negligible in the solution, since the substrates used to make the solution were 99.9 % pure and recommended for electrochemical analysis. Should there be non-negligible impurities, hopefully the impurities distributed homogeneously. This would cause a relative inflation or deflation to the measured tortuosities of the cells by the same factor. In this situation, drawing comparisons between the different cells should still indicate the same trends and therefore should not affect the conclusion.

Alternatively, the measurements could be a real representation of less resistive lithium-ion diffusion within the cells. This finding would contrast literature which shows as the porosity of a system decreases, the tortuosity increases leading to longer effective pathways^{285,438,439}. There are exceptions, such as templating; however, this is not employed in this project^{440–442}. This holds true not only for battery electrode coatings but other materials containing pore space^{443–446}. However, in the context of these electrodes, it would indicate increases as the porous material is compacted, the effective lithium-ion diffusion pathways become longer. This trend is the opposite to what is exhibited in the results: the ultrasonically calendered cathode decreases in tortuosity as porosity is reduced. The ultrasonically compressed cathodes are going from a highly porous structure, 54 % porosity, to an average porosity of 48 %. The decrease in void volume is not too extensive to fall into the expected trend. Uncalendered coatings also have the largest pore volumes, largest pore diameters, and the least consistent pore size distribution; the uncalendered coatings occupy the largest volume of space and have the least orderly structure. This creates some plausibility for the tortuosity to decrease as the NMC particle arrangement becomes less heterogeneous^{200,443} and initial large pore spaces are eliminated, providing the elimination of the pore space does not

eliminate the reduction in tortuosity yielded from the better ordering ⁴⁴⁷. These larger pore spaces are not fully utilised during electrolyte transport, shifting an NMC particle to encompass some of this void would give rise to a more orderly and structured arrangement which greatly decreases the tortuosity for this localised space. A net decrease of tortuosity in small regions over the electrode would lead to a reduction in the average tortuosity of the electrode which would lead to a lower ionic diffusion resistance measurement yielded in the symmetrical EIS ⁴⁰⁸.

5.3.3.4 *Addressing the High Tortuosity Values from Symmetrical EIS*

The use of symmetrical cells has been commonly utilised in literature to measure the tortuosity of electrodes. In the literature, the tortuosities of graphite anodes, LFP cathodes and NMC cathodes have been measured. This technique has been identified to produce tortuosities much greater than expected from the properties of the active material. For spherical particles, the Bruggeman equation (Equation 2.7) uses an exponent of 0.5 to predict tortuosity. This would yield a tortuosity of 1.91 for an electrode of 40 % porosity; however, this has been reported to be greater than 3 in the literature ⁴³⁵. This holds true at lower porosities in other works too: an electrode of 30 % porosity (an expected tortuosity of 2.43 with Equation 2.7) was reported to have a tortuosity between 4 and 5 ⁴⁴⁸.

An attributable factor to this inflated tortuosity is the anisotropy of the particles. NMC particles are not completely spherical, they possess a slightly ellipsoidal shape with a framboidal surface texture. This leads to a different tortuosity through the coating, depending on the direction of measurement ⁴³⁶. Non-sphericity will induce a different electrode structure ²⁷⁸. The settling of the particles changes as gravitational potential energy and buoyancy in the slurry will no longer be uniform across the particle. A great example of this rearrangement is graphite anode slurry coatings. Graphite particles have a flake-like structure ²⁷⁹, they have a much smaller z-axis length compared to their x and y dimensions. This leads to the graphite particles lying lengthwise across the current collector and other adjacent particles. The results in the pore channels being less convoluted and nearly straight (tortuosity ~ 1) when in plane with the current collector; however, when traversing from the surface to the current collector, through the z-axis, the pore channels are significantly more convoluted. The lithium ions have a much greater diffusion distance to traverse. This, by definition, shows a greater tortuosity and is with respect to the z-dimension. Tortuosity anisotropy is not as impactful in coatings which contain

ellipsoidal NMC particles compared to platelet graphite particles; however, NMC coatings have been modelled to have a non-negligible increase ²⁷⁸.

The mass of the electrodes in the symmetrical cells is approximately 0.035 g per cathode. This means each cell is measuring around 0.070 g of coating material for a tortuosity measurement. This is a small amount of active material and is recognized as one of the disadvantages of coin cells; only a small amount of electrode material is being tested. The coin cells have a capacity in milliampere-hours (mAh) range compared to ampere-hour (Ah) capacities of pouch cells ⁴⁴⁹. This can increase the susceptibility of particle size distribution and particle polydispersity affecting the cells.

The literature exhibits multiple examples of higher-than-expected tortuosity ⁴⁵⁰ which suggest the tortuosities are accurate and have led to the hypothesis that the higher values due to the influence of the CBD phase ⁴⁵¹. One study measured a 3.69–3.83 tortuosity for an 88 micron-thick coating at 37 % porosity ²⁸² (90 % NMC532, 5 % PVDF, 5 % C45). They estimated their experimental tortuosity values to be 1.4 to 1.8 times higher compared to models considering only active material structure. The 1.4 to 1.8 factor range depended on the CBD being film-like or protrusion-like ²⁸². It was shown that CBD creates smaller pores and blocks pore diffusion paths ^{195,282}. This reveals considerable insight about how the CBD affects lithium-ion diffusion in an electrode. Each segment of CBD can be contemplated as a smaller porous network that the lithium ions must diffuse through or around. The effective lithium-ion diffusion within this nanoporous structure depends on several factors: the volume of the CBD ⁴⁵²; the location of the CBD volume with respect to active material particles and micropore network ⁴⁵³; the porosity of the CBD and the tortuosity of the CBD pore network ^{54,454}.

In summary, the primary reason for the high tortuosity values obtained in these experiments is believed to be the same as that identified by numerous studies that also report high tortuosity values. Whilst the CBD phase was never considered to not be affecting the lithium-ion diffusion through electrode, the recent literature has proven the CBD to be dramatically more impactful on tortuosity than previously thought, especially when compared to a system consisting solely of active material. A second, profound reason for the high tortuosity values is the R_e - R_{ion} overlap. The tortuosity results being slightly inflated due to inflation of the R_{ion} measurement has been discussed previously. Fortunately, this is a drawback of conducting the experiment on NMC622 cathode (low electronic conductivity) and should provide a consistent relative inflation for all

the cells because the electronic conductivity across all coatings is similar irrespective of ultrasonic or conventional calendaring. This was validated with four-point-probe electronic resistance measurements. These explanations account for the high values and indicate that the comparison of tortuosity among the different coatings is accurate.

5.3.4 Conclusion

To measure the effective ionic diffusion resistance of the cells, symmetrical cell with a non-intercalating electrolyte (TBAClO₄) were assembled. Two solution strengths were used 50 mM and 4 mM. The 50 mM solution provided inaccurate R_{ion} and tortuosities compared to the 4 mM solution, which was more accurate, due to the minimization of the $R_e:R_{ion}$ ratio. The 4 mM solution yielded tortuosities in the range of 3.2 to 5.5, with the ultrasonically calendered cathode possessing the lowest average tortuosity despite being more compressed than the uncalendered control. This suggests ultrasonically calendaring adapts the structure to provide a less tortuous path for the lithium ions. The tortuosity values attained from the measurement are higher than expected compared to the Bruggeman relationship (Equation 2.7), however, this has been attributed to the pore-blocking influence of CBD and to the influence of non-negligible R_e values associated with NMC622 cathodes. These rationalizations indicate the dataset is accurate for analysis between cells and similar to literature, yielding tortuosities of 3.69–3.83 for similar cathode films.

5.4 Hypothesis 1: Ultrasonic Calendaring Induces More Orderly NMC Rearrangement

The hypothesis (Figure 5.6) illustrates the idea that the ultrasonic oscillation of the cathode melting the PVDF which allows the NMC particles to rearrange more freely, shifting into less heterogeneous geometry with more orderly pore spaces during the compaction. The intent of the ultrasonic motion is to create friction between the particles in the coating this will convert kinetic energy into thermal energy and heat the particles. The heating and melting of PVDF will increase the deformability of the polymer and impart less strength and rigidity to the electrode film. The PVDF holds the NMC particles in place; therefore, as the PVDF becomes more pliable, the NMC particles will be able to move from their local position in the film. The NMC particle

movement will be assisted by gravitational potential energy and the lowered friction coefficient. This allows the NMC particles to shift and settle into unoccupied pore space.

The electrode film is entrapped between the welding face and the anvil during the ultrasonic work; therefore, the z-axis dimension will decrease and prevent the coating from expanding in this direction as the material will be confined within the spatial limits of the anvil and welding face. This will direct the movement of the NMC particles into adjacent spaces along the x-y plane, compacting the coating depth (z-axis length).

As the ultrasonic motion ceases, there will be no source of temperature generation, allowing the heat to dissipate. The molten PVDF will be able to cool below its melting point and solidify. This will bond the PVDF to any NMC particles in contact.

The final product will have a different ordering and arrangement of the NMC particles after eliminating the pore space and relocation of NMC particles. This is also the goal of conventional calendering; however, the difference in calendering is that the particles are held together by PVDF whilst being pressed by rollers at an insufficient temperature to melt PVDF. This allows the film to compact and eliminate pore space, but the NMC particles are not as mobile compared with ultrasonic calendering. This results in the ordering and arrangement of the NMC particles during conventional calendering being more resilient to reordering as the film is more rigid.

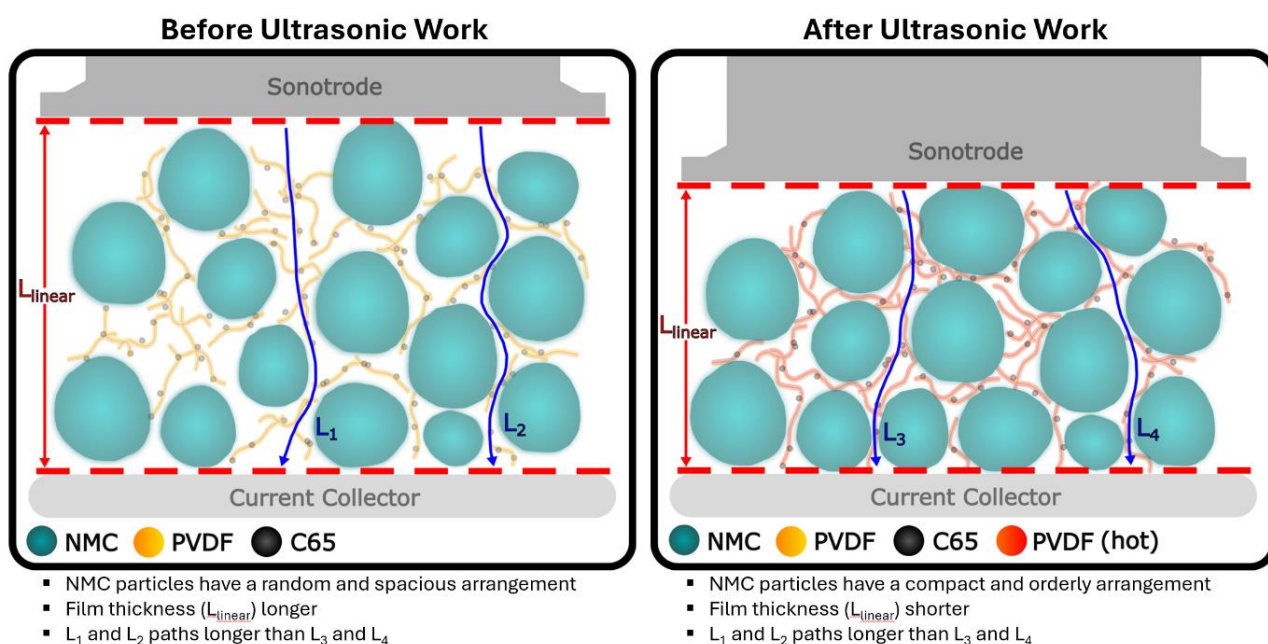


Figure 5.6 Illustration of hypothesis 1. The cathode is compressed and the NMC particles rearrange as the PVDF is melted, causing a smaller coating thickness. The lithium-ion diffusion pathways are shorter and less convoluted after the ultrasonic calendering.

This hypothesis of the ultrasonic compaction mobilizing the PVDF and allowing the arrangement of NMC particles into a more orderly structure would reduce the ionic resistance by creating more accessible and less convoluted lithium-ion pathways throughout the structure; the less convoluted and more accessible ionic pathways lower the tortuosity. This would correlate with the results found in the symmetrical cell EIS; the ultrasonically calendered cells having a lower average tortuosity than the uncalendered and conventionally calendered cathodes.

5.5 Hypothesis 2: Ultrasonic Calendering Alters CBD phase in Favour of Lower Tortuosity

Electrode structures are primarily made of large dense ellipsoidal active material particles which create a tortuous pore structure, however, the CBD phase within the coating should not be neglected^{450,455}. CBD is an amorphous low density random structure containing PVDF polymer chains and dispersed aggregates of C65 carbon black. The formulation used within the electrodes in this project is 92:4:4 by weight. C65 is nanoporous and has a density approximating 0.16 g cm^{-3} . PVDF is denser and spaced more orderly in chains yielding 1.78 g cm^{-3} . NMC possesses a density of 4.7 g cm^{-3} , significantly higher than PVDF and C65. This means the mass ratio of 92:4:4 correlates to a volume ratio of 20:2:25. The volume ratio shows that despite the cathode mass being predominately NMC, the cathode volume is shared more equally amongst all the components. This highlights the importance of considering the additives.

Table 5.1: Relationship between the volume fraction and mass fraction of 92:4:4 cathodes. It is important to consider the bulk density of C65 is very low and does not directly correlate the true density of the C65 and how it will exist in the electrode as CBD. This is difficult to measure, but it will act as a higher density, towards its true density and exhibit a lower volume fraction for the mass fraction portrayed in this table.

Material	NMC622	PVDF	C65 Carbon Black
Mass Fraction	92.0	4.0	4.0
Bulk Density (g cm^{-3})	4.70	1.78	0.16
Volume Fraction	19.6	2.2	25.0

The volumetric fraction of the CBD phase, which shows the system is more affected by additives, correlates with the recent discovery of the CBD phase having a much greater impact

on tortuosity than expected ^{282,451}. This has been discovered in more recent modeling and measurement of the ionic resistance in symmetrical cells:

- The ionic resistance from symmetrical cells has been measured much higher than expected in literature and this project. This revelation shows that the system is more tortuous than expected with standard Bruggeman relationships when the impact of CBD is considered. This finding is reliable because all the variables which are considered in the relationship (ionic resistance, effective ionic diffusivity, electrode porosity, and thickness) can be measured accurately with a high degree of certainty.
- Accurately modelling the porosity and the local tortuosity of the CBD regions has been a challenge as it requires understanding of the CBD nanostructure. Submicron measurements have always required extensive efforts because research is limited by physics and imaging machines. However, continual effort and technological advancement have finally led to models which can consider the CBD phase, and these models also demonstrate a tortuosity higher than expected with previous Bruggeman relationships.

This analysis of the greater impact of CBD on structure and tortuosity indicates the greater potential for alteration of the CBD phase to change the tortuosity of the system. The greater impact of CBD on tortuosity shows a greater potential to manipulate the CBD to decrease the tortuosity of the electrode. Therefore, this hypothesis proposes that the CBD phase is being altered to promote a higher rate capability in the cell by reducing tortuosity and consequently reducing the ionic resistance of the cathode.

CBD structure and its consequences on performance has been detailed in the literature review, section 2.4.7.2 and elaborated on in section 5.3.3.4, a summary of finding is:

- The distribution of the CBD in relation to the NMC particles proves to have a high-rate capability if the CBD assumes a film-like structure opposed to a bridge-like structure ⁴⁵⁶.
- The CBD is prone to aggregation which can form large agglomerates ⁴⁵⁷. These large agglomerates are detrimental to the performance as they have pore blocking behaviour whilst proving no additional structural strength or electronic conductivity ⁴⁵⁸.

The hypothesis, demonstrated in Figure 5.7, suggests that the PVDF in the CBD phase changes morphology due to the melting and solidifying of PVDF. As the PVDF becomes molten, the CBD can form film-like structures from originally bridge-like CBD structures. This is achieved by the CBD's ability to coat around the NMC particles as the electrode is compressed and NMC

particles exert force on the surrounding materials ¹⁸³. Alternatively, the new CBD structures may present less pore-blocking behaviour. This outlines two changes: a more geometrical adaptation, altering the geometry of the CBD to envelope the NMC particles, reducing the pore blocking of the CBD; and a more structural CBD change, as the CBD structure melts from a flocculent CBD structure to a denser structure to exhibit less pore blocking behaviour. Either of these two adaptations would lead to a lower tortuosity.

Two hypotheses have been described: one illustrates a rearrangement of the NMC particles to form a more orderly structure during the ultrasonic calendaring. This reduces the linear thickness of the electrode whilst promoting a more orderly arrangement, leading to shorter convoluted lithium-ion pathways. The other hypothesis illustrates alteration of the CBD phase to yield a lower tortuosity. The CBD experiences pore blocking behaviour, increasing the convolution of the ionic pathways. It suggests that the ultrasonic calendaring alters the CBD phase in favour of less pore blocking behaviour. The two mechanisms proposed in the two suggested hypotheses both involve the heating and melting of PVDF to invoke structural changes to the coating. Therefore, an analysis of the PVDF and CBD phase before and after ultrasonic calendaring and a comparison to the conventionally calendared cathode would provide insight into alterations to the PVDF.

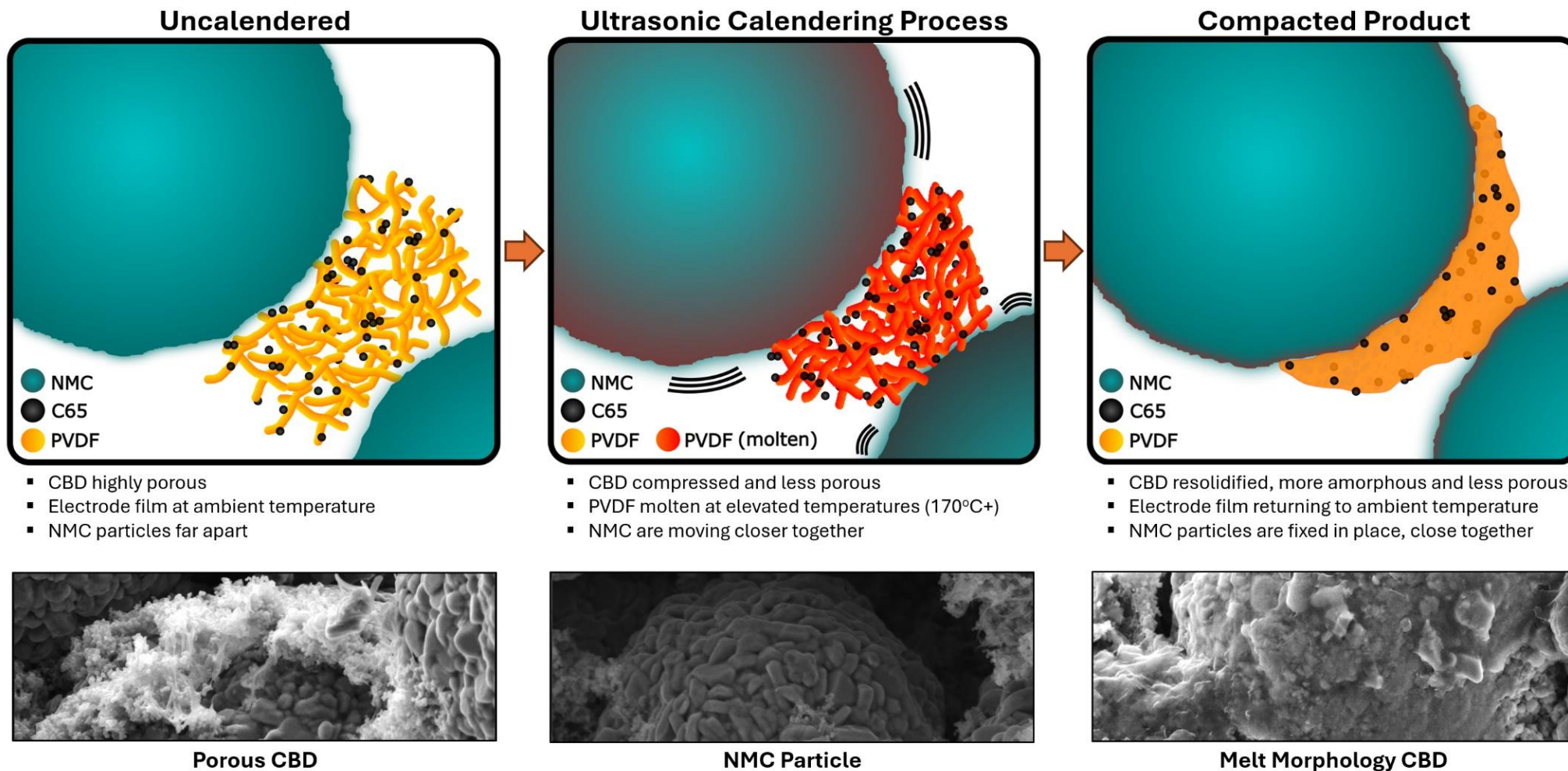


Figure 5.7 Illustration of hypothesis 2. The ultrasonic calendering causes ultrasonic oscillation of the particles in the electrode film. This causes friction and melts the PVDF in the CBD. This allows the CBD to change shape and change morphology as the PVDF solidifies. The final CBD structure resembles a more film-like structure and possesses a denser structure, promoting less pore-blocking behaviour.

5.6 Conductive-Binder Domain (CBD) Microscopy

The role of CBD is described in section 2.1.1 (Electrode), its importance to mechanical properties and how these change during calendering are outlined in sections 2.4.3.1 and 2.4.5 (Microstructure Progression, Adhesion and Cohesion), CBD microstructure and its effect on pore structure is explained in section 2.4.7.2 (Symmetrical Cell EIS, CBD and Tortuosity). The literature detailed in section 2.4.7.2 both simulated and experimentally determined how varying CBD structures altered the electrochemical performance of the electrode. It was reported that film-like structures are more likely to produce a less tortuous lithium-ion diffusion path opposed to protrusive structures ^{280,281}. A film-like structure possesses better rate capabilities, which are attributed to a reduced tortuosity. This section aims to identify differences and similarities in the cathode and explore if it can provide insight into the hypothesis regarding lower tortuosity from CBD changes.

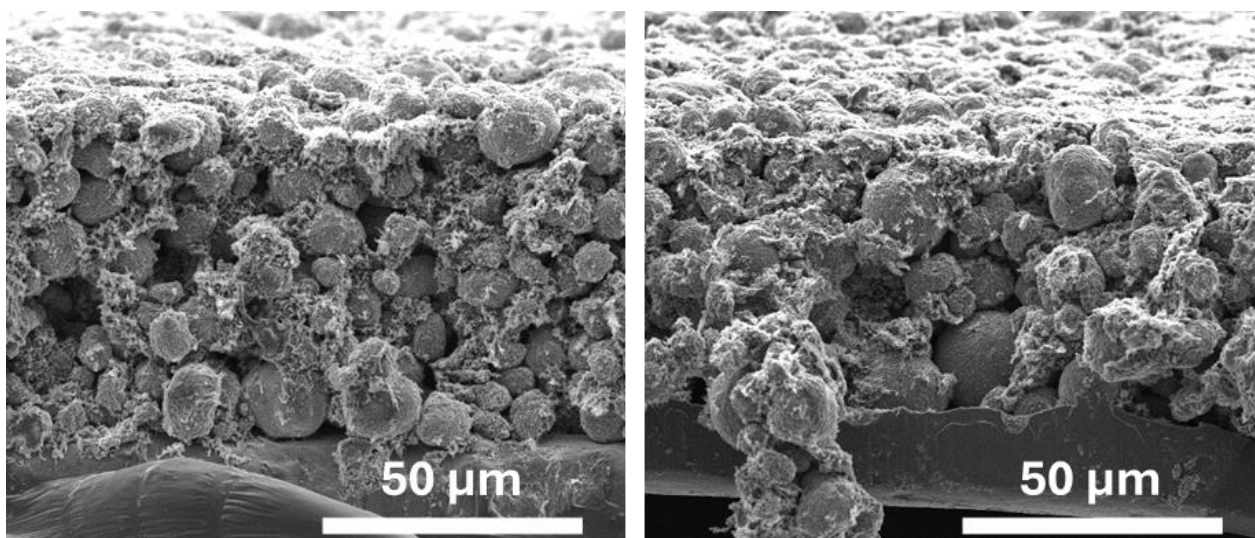


Figure 5.8 Cross-sections of ultrasonically calendered cathode (left) and conventionally calendered cathode (right). Sample preparation involved incision with a blade to avoid particle cracking but will display of sample pull-out and shearing.

In any given cathode there will be a mixture of film-like and bridge-like CBD structures; there will be a blend of the two different CBD structures throughout the electrode. All the cathodes in this project were produced from the same formulation and therefore should possess the same CBD throughout the sample after slurry casting. This means it should be expected to see the same blend of bridge to film-like CBD in each cathode prior to calendering methods which can alter the structure. Therefore, any noticeable alterations to the CBD between the uncalendered, the ultrasonically calendered and the conventionally calendered cathode will be the consequence of the calendering method. It would be expected that the CBD phase in these cathodes are closer on the spectrum towards bridge-like structures because the

formulation is 92:4:4. It has been shown that the additive content in an electrode formulation correlates with more the fractal and bridge-like CBD structure^{189,280}.

Electron microscopy cross-sections of cathodes were conducted to show the surface of the NMC particles and how the CBD coats them, as shown in Figure 5.8. The presence of bridge-like CBD structures, demonstrated in Figure 5.9(a), can be observed in the cross-section for both cathodes. The CBD spans a multi-micron gap from one NMC particle to another adjacent particle. Film-like structures can also be seen as particle coatings over the surface of the NMC particles, demonstrated in Figure 5.9(b). CBD agglomeration is also observed. Large CBD nodes, which may have previously bridged over to particles removed during the cross-sectioning, are seen branching off from the NMC particles. The agglomerated CBD, large three-dimensional CBD nodes, and the examples of bridge-like structures indicate that the uncalendered cathode (prior to any calendering) has a more bridge-like CBD morphology; film-like structures would present the CBD phase as a thinner morphology.

5.6.1 Melt Flow Morphologies

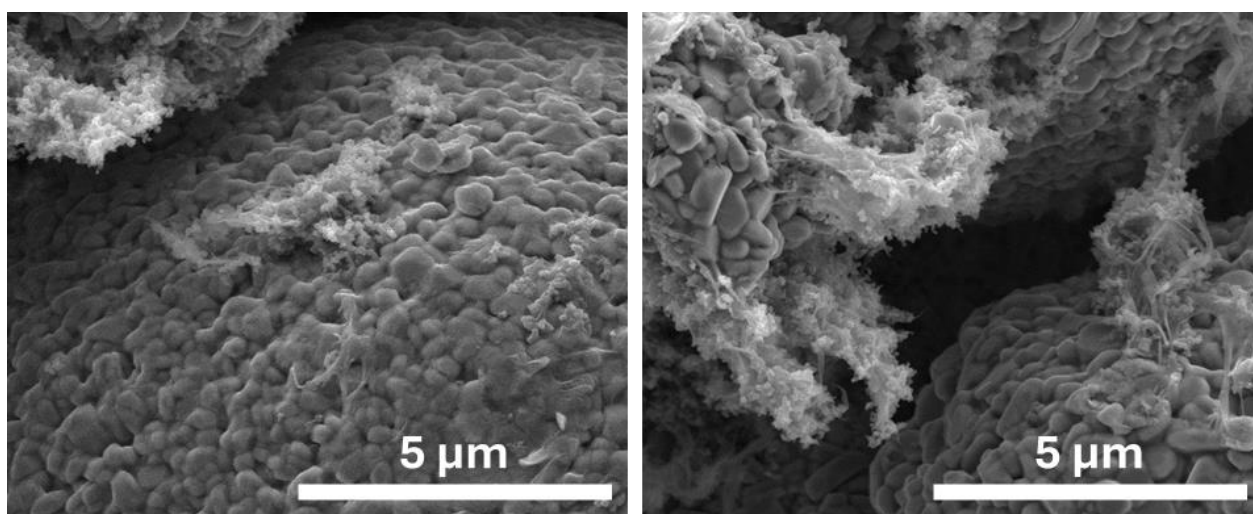


Figure 5.9 Cross-section of conventionally calendered cathode exhibiting film-like CBD structure (left) and bridge-like CBD structure (right).

Novel CBD structures were identified during the bladed cross-section of the ultrasonically calendered cathode and are detailed in this section. These structures do not present as flocculent compared with the conventional appearance of CBD. The structure is smoother with a less porous, waxy appearance. This structure is suspected to be a melt morphology. This would form if the CBD has reached the temperature to cause the PVDF to melt. Its structure

and phase would change to a viscous liquid and upon cooling the liquid PVDF would solidify to create a new morphology.

Melt morphologies are a possible consequence of work done by the ultrasonic welder. The work imparted by the welder is intended to cause ultrasonic motion within the coating. This causes heat generation at the particle interfaces due to friction. This friction will cause the PVDF to increase in temperature. This will reduce the rigidity of the PVDF and cause melting if the temperature exceeds the PVDF's melting temperature. The introduction of sufficient heat to melt PVDF in the CBD phase could lead to a new CBD phase structure during solidification. As the PVDF solidifies as a more film-like structure, it is possible to decrease the local tortuosity of the CBD within that region. Multiple occurrences of this behaviour would contribute to a significant structure-wide reduction in tortuosity. This change would be manifested as a smaller R_{ion} value produced from the results in the symmetrical cell impedance spectroscopy and consequently result in a smaller tortuosity value when calculated using Equation 5.1.

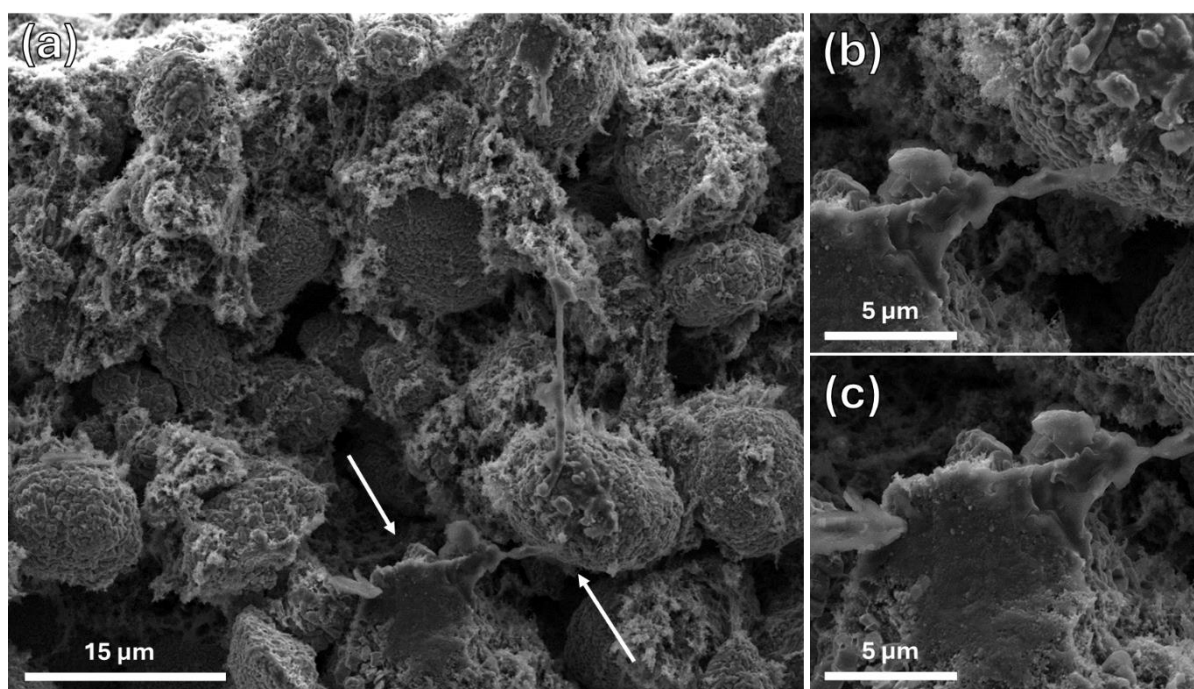


Figure 5.10 Additional cross-section of ultrasonically calendered cathode. (a) The whole cross-section. (b) a waxy appearance bridge CBD structure. (c) a waxy concaved plane of CBD.

Analysis of Figure 5.10 shows a cross-section of an ultrasonically calendered cathode. In this cross-section, several points of interest show unexpected CBD structure. There is some typical CBD appearance, bulbus and flocculent, as seen in Figure 5.9; however, Figure 5.10(b) and (c) show a waxy CBD bridge structure spanning across two NMC particles. It has a triangular base which then extends as a large fibre across to another NMC particle. This fibre attaches to the NMC and transitions to a half-waxy, half-bulbus and flocculent appearance. There is also the regular flocculent CBD surrounding and connected to the bridge contact point. This base and

bridge structure is novel, and at the right-side point of contact it appears to be in a transition state halfway between conventional flocculent CBD structure and the new waxy appearance. It suggests the bridge may have originally been of regular CBD structure, however, has now transitioned during ultrasonic calendaring to a melt morphology.

In addition to this bridge, there is a large waxy plane of CBD which lies upon an NMC particle below it (Figure 5.10(c)). This CBD plane is of interest because it appears as a particularly large and smooth plane. It also possesses a concave nature. The top half of the structure is perpendicular to the field of view, whilst the bottom half of the structure is at a 45-degree angle to the field of view. This shape indicates that this section of CBD was previously attached to an NMC particle which has been removed during cross-section preparation. This is plausible because of the nature of the sample preparation; cross-sectioning of the cathode by a blade is rudimentary and makes the sample susceptible to pull-out. When the blade hits a NMC particle, the force of the blade will either overcome the tensile strength of the CBD attaching the particle to the coating and pull the particle out of the sample, or slice through the NMC particle, which is less likely due to the hardness of NMC. This leads to the extremely rough, uneven cross-section, demonstrated in Figure 5.8 and Figure 5.10(a).

The smooth, flat face of CBD seen in Figure 5.10(a) and (c) is suspected to be present due to being previously connected to a CBD particle prior to pull-out. This indicates that this plane was previously an NMC-CBD interface which has been sheared. The waxy structure of the CBD at this interface suggests that the CBD connected to the NMC particle has undergone melting during ultrasonic calendaring and formed a melt morphology, coating the NMC particle. This would be an instance of evidence indicating that the PVDF is melting under the ultrasonic motion due to friction between the NMC and the CBD phase. The molten CBD is then solidified and bonds to the NMC particle.

The CBD taking a complementary shape to an NMC particle also indicates that in addition to a morphology change, the CBD may have also changed dimensions and enveloped the NMC particle. This is supported by the size of this section of CBD. The CBD is a network and provides electrical connectivity throughout the coating. The shape of this network has nodes and specific areas of voluminous CBD phase which will present as spherical or ellipsoidal. This is accompanied by thinner, connective CBD strands. The CBD plane seen is the largest node of CBD in the structure. This indicates this plane of CBD would have previously been a node or bridge structure which had been melted and reshaped into the complementary concave shape

of the NMC. The driving force of this process would be the ultrasonic motion of the coating during ultrasonic calendaring. The entire coating experiences motion and additional pressure. This would be able to partially embed and spread the molten CBD phase over and around the NMC particle. This would give rise to envelopment of the NMC by the CBD, which once pulled by the cross-sectioning tool, leaves the CBD phase behind as a concaved plane.

5.6.2 CBD Melting and Cooling Morphology Change – Understanding the Melt Morphologies

This section investigates the difference between conventional CBD and the changed morphology under the proposed melting and solidification. PVDF is a semi-crystalline thermoplastic polymer. Semi-crystalline polymers have crystalline and amorphous regions. Crystalline regions involve ordered polymer chains with distinct intermolecular spacing due to the orderly polymer chains and a repeating pattern of how the chain is orientated with functional groups. Amorphous regions have a disorderly and random arrangement of polymer chains which leads to a range of intermolecular spaces and polymer density.

Conventional CBD is flocculent and with bulbus parts. It is formed from carbon black in suspension and PVDF dissolved in NMP. The solvent, NMP, is evaporated over an hour in a fume cupboard before being transferred into a vacuum oven overnight. This drying over an hour gives the PVDF plenty of time to precipitate out of the solution and crystallise as the NMP is removed from the system. The term for PVDF precipitating out as the solvent is evaporated is “crashed out.” This yields long chains of PVDF which are orderly and crystalline. These ordered chains bring a high true density but a low bulk density to the CBD phase. This is because crystalline polymers have a high true density, as the chains are ordered and have had an opportunity to exert attractive and repulsive forces on other chains; these forces will cause the molecules to have smaller average intermolecular distances, yielding the high true density. However, the polymer has precipitated out in fibres, on a nanoscale basis, and these fibres possess a lot of free space in a random arrangement. The result is a porous structure, of dense polymer with free, convoluted space in between the fibres. The presence of this free space dramatically lowers the bulk density. During ultrasonic motion of the welder, the PVDF is heated via friction to melting temperature, heating the CBD phase and the superficial NMC. This rapidly melts the PVDF in the CBD phase. The crystalline structures breakdown as the PVDF becomes molten,

creating an unordered liquid plastic. The ultrasonic motion then ceases. This eliminates the source of friction and heat. The heat accumulated in the CBD and the superficial NMC then dissipates as the electrode equilibrates in temperature. Heat is conducted to the core of the NMC particles and the current collector. Due to the mass of the superficial NMC and CBD being smaller than the total mass of the system, the decrease in temperature is quick and dramatic. This rapid drop in temperature leads to rapid cooling, and solidification of the PVDF. Quenching denotes cooling at high rate. Quenching the PVDF will create a polymer with a bias towards amorphous regions because some regions of the polymer which would become crystalline do not have time to form and attract or repel other chains and therefore cannot form an ordered structure. The formation of crystalline regions takes time. The quick reduction in temperature reduces the thermal energy of the polymer causing the polymers then lack the kinetic energy to vibrate and re-arrange as the polymers have limited mobility. After a sufficient reduction in mobility, the polymers will become pinned, fixing the structural arrangement. This leads to a loss of crystallinity and an increase of the amorphous region ⁴⁵⁹. The product is an amorphous region which may have equilibrated to a crystalline region if cooled more slowly. Unless exposed to a low cooling rate (1–10 °C/min), crystallinity is lost in semi-crystalline polymers ⁴⁶⁰.

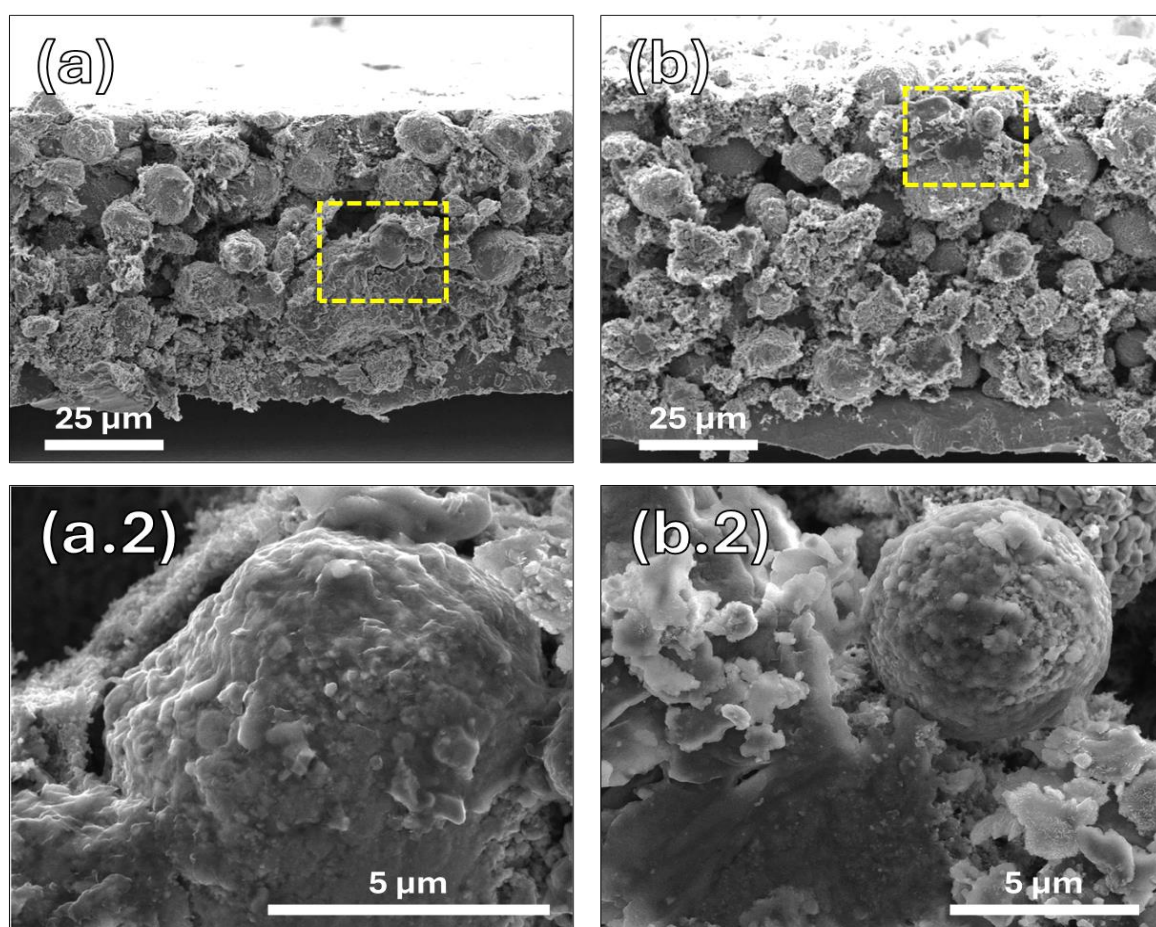


Figure 5.11 Cross-sections of Oven-heated (a) and Ultrasonic Cathode (b). Both figures have a POI highlighted which show CBD envelopment of NMC particles and a more film-like CBD structure and are magnified in a.2) and b.2).

5.6.3 Melting Validation – Baked Electrodes

Both hypotheses infer that CBD is being exposed to a temperature to melt the PVDF to form new structures CBD. To identify if melting is involved in the morphology change, an uncalendered cathode was heated to the melting temperature of PVDF in a controlled environment, without compression or exposure to processes which can cause microstructure alterations and compared with the ultrasonically calendered cathode for similarities.

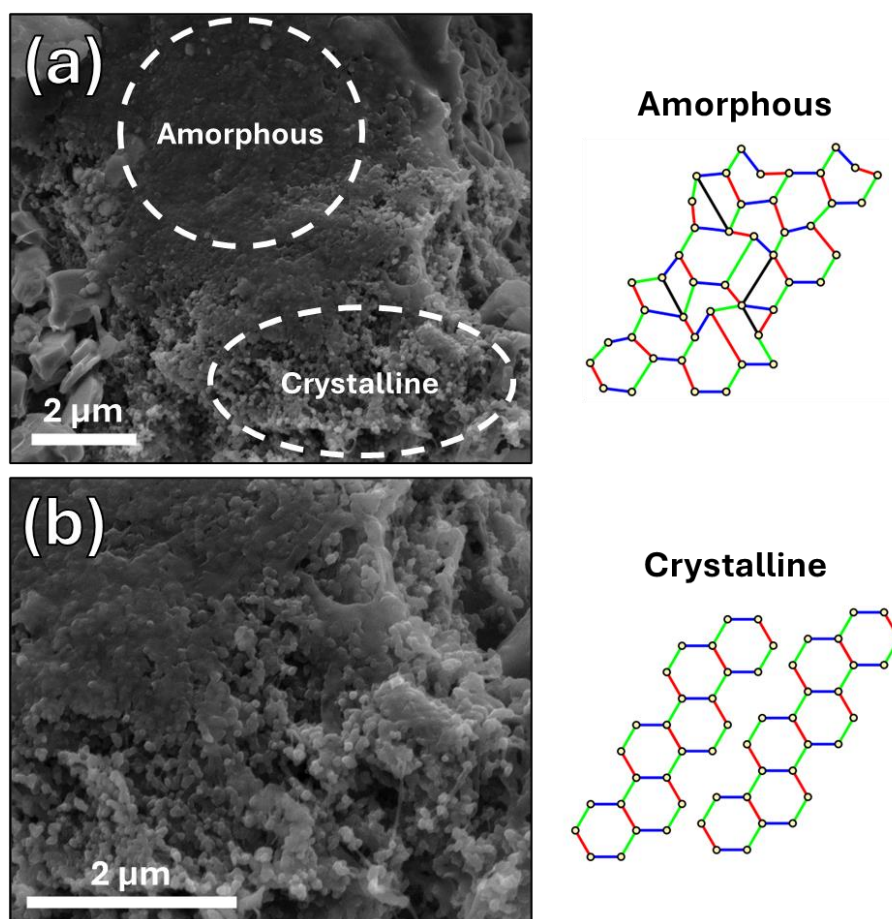


Figure 5.12 Cross-section from ultrasonically calendered cathode. (a) Full view (b) magnified view. Amorphous PVDF CBD regions and crystalline PVDF CBD regions have been labelled. Lattice structures of PVDF in amorphous and crystalline formations have been demonstrated.

Uncalendered cathodes were placed into an oven which was heated to 180 °C for 24 hours. This was conducted with the intention of heating the PVDF within the cathodes beyond the melting temperature. Once 24 hours had passed, the cathode was pulled out of the oven into ambient conditions to cool the sample. Microscopy would be needed to reveal alterations; therefore, the oven heated electrode was prepared for SEM. Sample preparation involved slicing with a razor blade, replicating the same methodology for the ultrasonic and conventionally calendered cross-section.

It can be observed that the oven-baked electrode possesses dissimilar CBD to conventional CBD, showing more similarities to the ultrasonically calendered electrode. The CBD in the

oven-heated electrode has a waxy appearance, Figure 5.11 and Figure 5.13. This is conducive to more amorphous PVDF structure in the CBD, achieved by heating the PVDF beyond the melting temperature, before being exposed to ambient conditions. This would have provided a temperature gradient beyond 150 °C. This would induce relatively rapid cooling, especially through the crystallisation temperature of PVDF (131-145 °C) ⁴⁶¹. Leading to an amorphous PVDF formation bias. The oven-baked cathode and ultrasonically calendered cathode both show the melt morphology CBD. The CBD no longer has a flocculent appearance and has a less porous, waxy appearance. CBD can also be seen to coat around the NMC particles with high surface area contact, Figure 5.11, in the oven-baked and ultrasonically calendered cathode. This moulding around the NMC particles is achieved by melting the CBD phase, providing lower rigidity of the CBD phase, allowing the envelopment of the NMC particle. This CBD structure is distinctive and novel to these electrodes, it has not been observed in uncalendered or conventionally calendered cathode. This could contribute towards the ultrasonically calendered cathode's lower tortuosity; the novel CBD resembles more of a film-like CBD structure, known to promote lower tortuosity.

5.6.4 CBD Comparison Summary

Scanning electron microscopy of cathodes indicated multiple morphologies of CBD. Conventional flocculent CBD was observed in all cathode samples. In addition to this CBD, another alternative CBD morphology was observed in the ultrasonically calendered cathode samples. This CBD has a waxier and dense appearance, which indicates the PVDF is more amorphous than in conventional CBD. The PVDF in the uncalendered cathode is more crystalline and has been 'crashed out' of the NMP during drying of the electrodes. The drying takes place over an hour and gives the PVDF time to orderly arrange and form crystalline structures. This indicates that the waxy, amorphous CBD is due to melting before solidifying to bias the PVDF towards amorphous. This was confirmed by heating uncalendered cathode for 24 hours before cooling to yield the same structures present in the ultrasonically calendered cathode. This shows the novel CBD structure in the ultrasonically calendered cathode could be a consequence of melting and cooling the PVDF and it serves as evidence that the CBD has been exposed to temperatures sufficient to melt PVDF during ultrasonic calendering.

Ultrasonic

Oven-heated

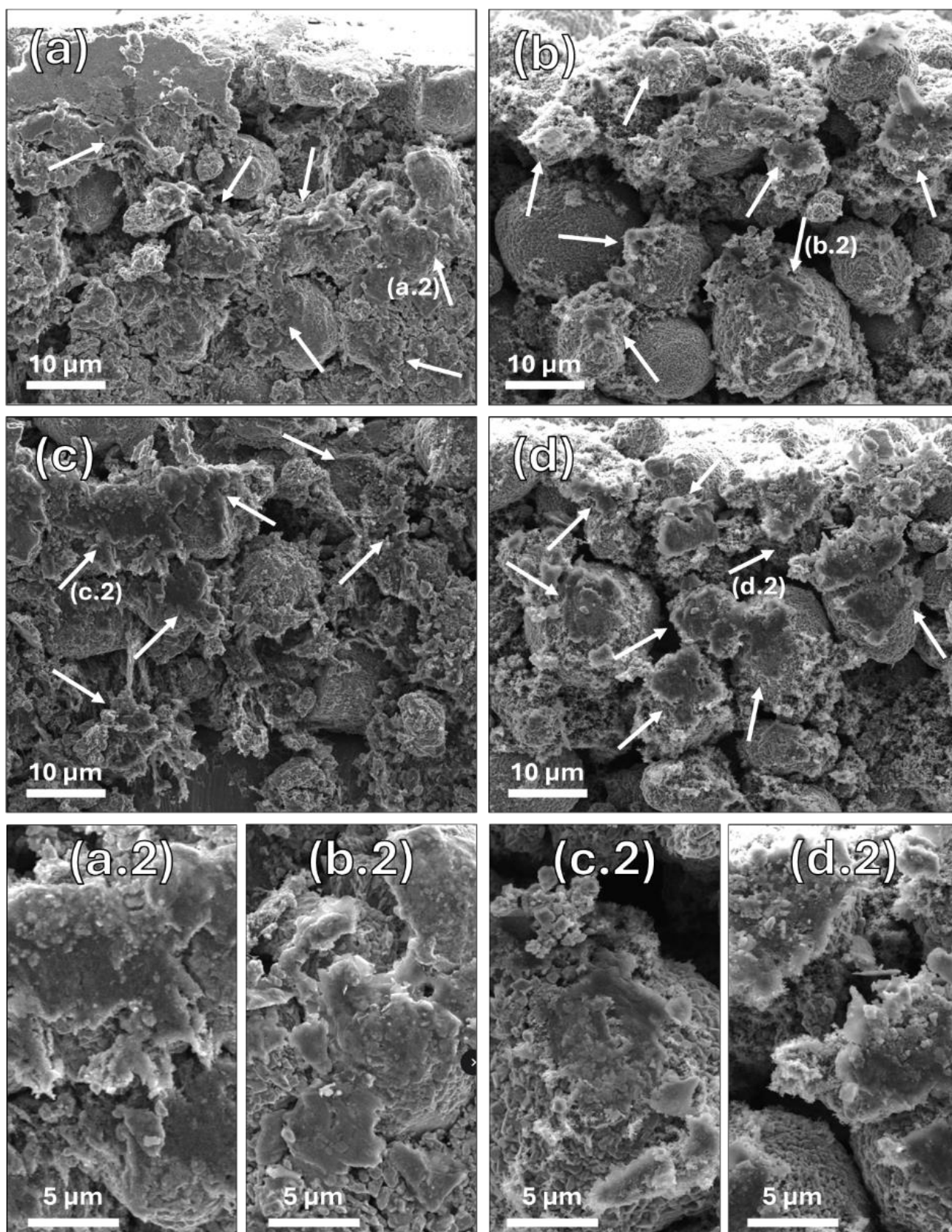


Figure 5.13 Cross-sections showing melt morphology CBD in the ultrasonically calendered and oven-heated cathodes. (a) and (c) are ultrasonically calendered. (b) and (d) are oven-heated. Arrows indicate instances of melt morphologies. Each figure has one POI labelled as (x.2) which has been scaled up to compare the morphology. It can be seen the melt morphologies are common thorough both cathodes and show similar structure.

5.7 Melt Morphologies - Heat Analysis

To assess if the PVDF in the ultrasonically calendered cathode is reaching melting temperature of PVDF, a heat analysis was conducted. This was inspired by the oven-heated cathode and ultrasonically calendered cathodes both exhibiting melt morphology CBD. Two analysis methods were available and have both been analysed. A FLIR thermal imaging camera was taken to the lab, and the ultrasonic welder comes with an encoder that can detail the energy expended in a weld.

5.7.1 Differential Scanning Calorimetry

Differential scanning calorimetry was performed on both the Solvay 5130 PVDF and the Goodfellow PVDF sheets. The results of the temperature change both show a peak heat flow peak around 160 °C: 163 °C for the PVDF sheet from Goodfellow and 160 °C for the 5130 PVDF powder from Solvay. The result shows over elevated temperature from 50 °C to 225 °C, both samples experience only one change in structure. This peak is the melting temperature (T_m). This is the minimum temperature for the α -crystalline regions in the semi-crystalline polymer to undergo melting⁴⁶². At this temperature the crystalline regions have become liquid. It indicates that the PVDF sheet may have slightly higher molecular weight, as the melting temperature is marginally greater⁴⁶³.

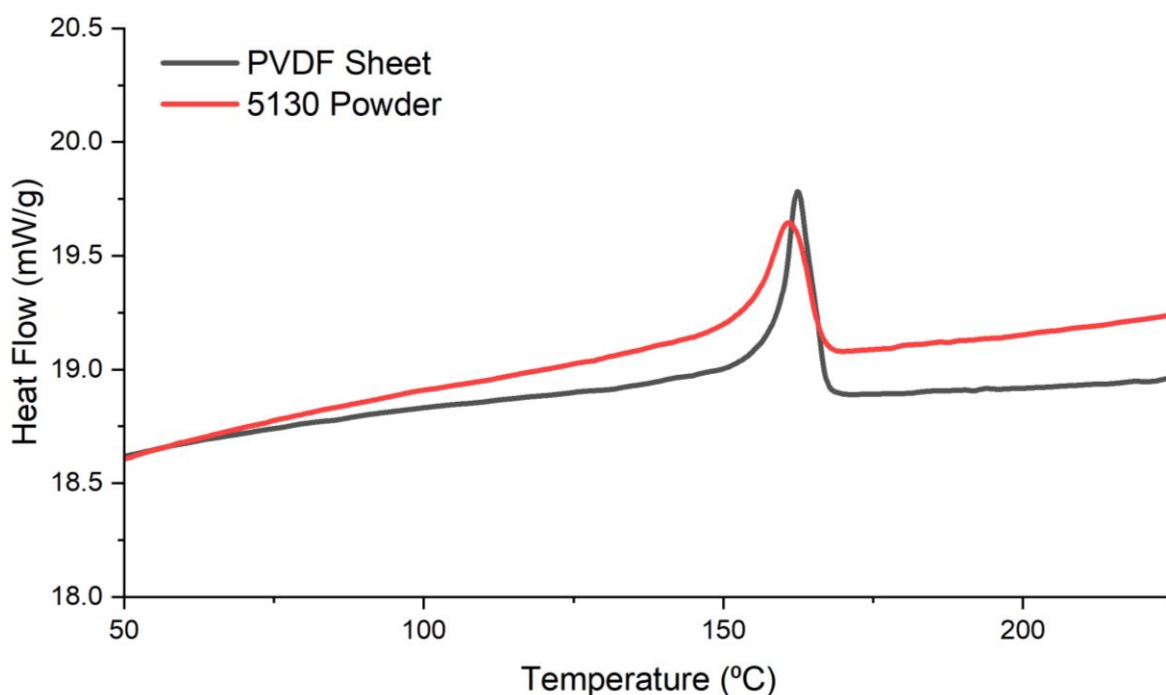


Figure 5.14 Differential scanning calorimetry (DSC) result indicating the heat flow of Solvay 5130 PVDF powder and Goodfellow PVDF sheet across 50 to 225 °C, one heat flow peak is observed for both at approximately 160 °C, indicating the melting temperature (T_m).

The glass transition temperature (T_g) is temperature at which the amorphous regions of the polymer become fluid-like and pliable. Under the glass transition temperature, the polymer is brittle and hard. PVDF's T_g is approximately $-40\text{ }^{\circ}\text{C}$, which is why there is only one heat flow peak within the $50\text{ }^{\circ}\text{C}$ to $225\text{ }^{\circ}\text{C}$ temperature range.

The greater creep in heat flow outside of the peak for the 5130 PVDF powder could be attributed to the geometry of the sample. This behaviour is also present in the literature ⁴⁶⁴; the addition of carbon nanotubes, which add structure, reduces the effect ^{465,466}. The 5130 PVDF is powdered, compared to the other PVDF sheet. This could lead to rearrangement of the powder during the measurements. This could manifest in the DSC reading as heat flow. Ideally, both materials would have been processed to the same geometry. However, the results prove sufficient to indicate these materials have similar intrinsic properties. After controlling for geometry, they would react similarly to ultrasonic welding and ultrasonic calendaring.

5.7.2 FLIR Thermal Imagery

Multiple thermal images were taken using the FLIR infra-red camera. The substrate had a temperature of approximately $24\text{ }^{\circ}\text{C}$ after being acclimatised to the ambient temperature. The photo which was taken during the weld indicates that the hottest part of the image is the cathode underneath the welding horn. Also importantly, the welding horn is shown to not be at the elevated temperature of the cathode. This shows the heat generation is within the cathode and whilst it may be conducted to the horn, it is not generated significantly at the interface between the cathode and the welding face. The heat generation originates from within the cathode matrix. This is evidence that the cathode does have acoustic properties and can propagate the ultrasonic vibrations.

The highest recorded temperature was $44.9\text{ }^{\circ}\text{C}$ on the photo captured during operation and indicates the cathode as this is the hottest section of the image. This temperature can be considered low. At face value a reading of $44.9\text{ }^{\circ}\text{C}$ would not support melting of the PVDF within the sample. This is not reaching the $170\text{ }^{\circ}\text{C}$ melting temperature and could serve as evidence against these hypotheses. However, it is important to consider the source of heat generation in this technique because the intention of an ultrasonic welder is to impart work and heat specifically at the interfaces of the substrate whilst simultaneously avoiding heating of the entire substrate.



Figure 5.15 Images taken during ultrasonic calendering of NMC cathodes. (a) visual spectrum image of set-up (b) FLIR infra-red thermal image prior to activation (c) FLIR infra-red thermal image during actuation of the ultrasonic calendering. The cathode shows the peak temperature of 44.9 °C during actuation. The welding horn does not match this temperature rise.

The principle of ultrasonic welding functions by ultrasonically oscillating interfaces. This causes friction which generates heat. This heat expands the interatomic spacing of the materials which allows the atoms to interlock and bond. The significance of this process when considering a heat analysis is the friction occurs at the interfaces, therefore it superficially heats the materials. The heat generation occurs on the outer atoms. This is a well-utilised advantage of ultrasonic welding. Two interfaces can be welded by using a fraction of the energy necessary to heat the whole substrates to the minimum bonding temperature, only the superficial atoms at the interface are required to reach the temperature threshold. The superficial surfaces are heated to the high threshold temperature during the weld and then this heat naturally dissipates, leading to the core of the substrates not reaching the bonding temperature thresholds. The outcome of this is the substrate in its entirety does not reach the peak welding temperature reached.

The thermal imagery in Figure 5.15 displays pronounced heat generation within the cathode during ultrasonic calendaring. This heat is generated at the interfaces between the CBD and other NMC particles. The CBD and superficial NMC experience a temperature rise surpassing the melting temperature of PVDF during the welding process, before this heat is dissipated or distributed throughout the substrate. Additionally, the minimum energy required to raise the CBD phase to the melting temperature of PVDF can be estimated, and then the final temperature of the electrode when this energy is distributed throughout the whole structure can be estimated. The CBD content is 8 % of the cathode, in equal parts PVDF and C65 (4 % each). The CBD phase is a small partition of the cathode and does not demand much energy to melt. The energy required to heat the CBD phase from ambient (20 °C) to its melting point (174 °C) is approximately 0.7 J. If it is assumed that no energy is lost from the system and that the energy is contained within the cathode coating, 0.7 J of thermal energy would heat the coating by 12 °C. This estimation does not account for NMC being heated; however, it indicates that targeting the CBD phase with the thermal energy only requires a small fraction of energy and the total temperature change of the system from this energy would not be significant. The concept of heating the CBD and superficial NMC to the melting point of PVDF, to create melt morphologies, is plausible within the data interpreted from the thermal imaging.

It was identified that the thermal imaging showed a temperature increase during the ultrasonic calendaring of the cathode. The heat rise was localised to the cathode, indicating the heat generation is from within the cathode matrix. Considering the mechanism of the process not

being necessary to heat the whole substrate to the melting temperature of PVDF to ensure the local melting of the PVDF binder in the CBD, and the measured temperature change providing sufficient energy if targeted to the PVDF to melt the PVDF within the cathode, it is plausible to expect the creation of melt flow morphologies of PVDF in the cathode.

5.7.3 Encoder Data

The encoder is an additional unit which can record the operation of the welder. It provides an information log of the force on the welding horn (N), the displacement of the horn (mm) and the electrical energy expended by the welder (J). Recording the electrical energy expended is useful because it indicates the maximum possible amount of energy transferred to the cathode. It was recorded that setting #4 utilised 120 J of energy when ultrasonically calendering. The mass of the cathode and the heat capacity of the material is known; therefore, the temperature increase can be calculated.

Equation 5.2 Heat Capacity

$$Q = mC_p\Delta T$$

$$\Delta T = \frac{Q}{m_{cathode}C_{p,cathode}}$$

467

The weld face has a 20 mm diameter weld face. Therefore, the surface area of the electrode affected is a 20 mm diameter circle. The average cathode mass for this surface area is 0.0619 g of which 0.0126 g is aluminium current collector (20 %). Considering only the cathode matrix being heated, 120 J would cause a temperature rise of 2026 °C, assuming a heat capacity of 1.2 J/g/K for the NMC material ⁴⁶⁸.

Considering the PVDF and C65 would only increase this value, as they have lower heat capacities. Eliminating the assumption that only the NMC matrix is heated, if 120 J were converted to heat in the cathode and current collector, the expected temperature increase would be 1701 °C. This uses a composite heat capacity of 1.14 J/g/K (0.9 J/g/K for aluminium which approximates 20 % of the electrode mass, and 1.2 J/g/K for the NMC material which approximates 80 % of the mass). This is a substantial heat increase in both scenarios.

There needs to be an acknowledgement of the many variables and unknown efficiencies involved in converting the raw electrical energy consumption of the welder directly to thermal energy produced in the cathode. These variables include: the acoustic properties of the cathode (e.g. elasticity of the medium and dissipation of kinetic energy), the efficiency of the

ultrasonic welder, and the conversion of work to other forms of energy (e.g. sound). Due to these many variables and unknown efficiencies, an overall efficiency of 15 % conversion of electrical energy into heat energy has been assumed. For this efficiency, the temperature rise would be 337 °C for just the NMC coating and 284 °C when considering the NMC and current collector. All four of these temperatures (two considering the displayed electrical value, and the two assuming the reduced efficiency), the melting temperature of PVDF (173 °C) has been surpassed. This would indicate that the PVDF has been exposed to sufficient energy to melt. This would indicate occurrence of melt flow during ultrasonic calendering and the presence of melt morphologies in the ultrasonically calendered cathode.

The data from the encoder indicated that the electrical energy utilised in the technique when would be able to heat the cathode to extremely high temperatures directly converted towards heating the cathode. A total process efficiency of 15 % was employed to account for unknown efficiencies and losses. Even under this assumption, there is sufficient theoretical electrical energy to heat the cathode above 300 °C, surpassing the melting temperature of PVDF. This would yield the opportunity to create melt morphologies within the cathode. The intention of this analysis was to approximate quantitative temperature change to understand if it is possible to have melted some regions of PVDF in the cathode. It has been demonstrated that there is more than sufficient energy consumed by the machine, it just requires that sufficient electrical energy be converted to thermal energy via the process.

5.7.4 Heat Analysis Summary

The objective of this section was to identify if the melting of PVDF is plausible with ultrasonic calendering. Two methods were employed to illuminate the temperature change and thermal energy involved in the technique. The encoder details the electrical energy expended by the welder during the ultrasonic calendering. An average of 120 J was recorded for the ultrasonic calendering of the cathode using the 20 mm circular welding face. The heat capacity of the individual coating components and the whole electrode were considered, and indicated a fully efficient process would theoretically reach temperatures above 1700 °C. The melting temperature of PVDF is 173 °C. This demonstrated that more than the minimum energy is supplied to the system. There was difficulty in confirming what fraction of electrical energy was being converted to thermal energy in the cathode because the losses and efficiencies were not measured; however, a total technique conversion of 15 % would have still yielded a

temperature rise of the coating and electrode beyond the melting temperature of PVDF, due to the low heat capacity and low mass fraction of CBD in the cathode. It was calculated that <1 J of thermal energy would be able to heat the CBD (excluding the NMC) to the melting point of PVDF. The dissipation of this heat would only yield a temperature rise of 12°C to the total coating. The thermal imagery captured during the ultrasonic calendering supported the plausibility of melting the PVDF. The temperature fluctuated from ambient temperature to 45°C . The focal point of the high temperature was also localised to the cathode. The surroundings and welder parts did not experience the temperature rise.

These results validate the suggested process model of ultrasonic calendering: The electrical energy supplied to the welder is converted to kinetic energy at the actuator of the welder. This kinetic energy oscillates the welding horn, which induces the ultrasonic movement within the cathode. The movement converts the kinetic energy to thermal energy via friction. The coating is heated from the increase in thermal energy.

5.8 Chapter Conclusion

5.8.1 Experimental Summary

Cell rate performance tests indicated a favourable rate performance for ultrasonically calendered cells of similar cathode loadings and porosity in the previous experimental chapter. Mercury intrusion porosimetry showed an alternative pore size distribution and cathode microstructure. Further electrochemical testing indicated that there may be a lower tortuosity in the ultrasonically calendered cathodes which promotes a lower effective ionic resistance. A lower effective ionic resistance would be sufficient to yield the increased rate performance seen in ultrasonically calendered cathodes. The lower effective ionic resistance was measured by performing EIS of symmetrical cells using a non-intercalating electrolyte. A reduced resistance was measured which suggests the cells possess a different structure causing the reduction.

Scanning electron microscopy showed the ultrasonically calendered cell possess evidence of CBD that has changed morphology. The mechanism of the ultrasonic welder creating friction, and the nature of PVDF being semi-crystalline, alluded to the CBD rapidly melting under the ultrasonic work of the welder, and then cooling to create a CBD phase with a more amorphous crystallinity. A heat analysis indicated a significant temperature change over the ultrasonic

process, confirming the potential to melt PVDF. The melting of PVDF enables two potential structural changes which could have resulted in the lower tortuosity. Either the NMC particles have rearranged to yield a better ionic path, made possible by the lowered rigidity of the PVDF once melted, or the melted CBD phase possessing a higher bulk density has improved tortuosity through or around localised sections of CBD, lowering the average cathode tortuosity. Alternatively, the melt morphologies changing the CBD regions from bridge to film-like have been documented to alter tortuosity and c-rate performance ⁴⁶. This would also align with the lower tortuosity measured in this chapter and the greater c-rate performance demonstrated in the previous chapter.

5.8.2 Objectives and Milestones

MIP showed that there is manipulation of the active particle positioning and the micropores throughout the structure for ultrasonically calendered cathodes. One cathode provided a narrow distribution of pores, while the other had a much broader microporous region distribution. This difference indicates the potential of ultrasonic calendering to manipulate the pore size distribution to yield greater control over pore structure. This requires further exploration to confirm; however, it is suggested. Conventional calendering provides great control over the volume of the cathode but provides no control over the pore size distribution. Conventional calendering eliminates porosity by narrowing the porous network leading to the frameshift of the PSD. To reduce the average pore size, the electrode must be compressed. The ability to produce two cathodes of similar porosity but different pore size distribution is novel to the ultrasonic calendering and shows the potential for greater micropore control.

Ultrasonic calendering provides a new technique to alter the CBD phase and is able to create a novel CBD morphology. Conventional calendering compresses the NMC particles closer together and forces CBD from between the NMC particles. This can agglomerate and bunch the CBD phase in the interstitial spaces of the NMC ²⁴⁵. This is undesirable; agglomeration is detrimental to the electronic and ionic conductivity of the electrode ⁴⁶⁹. Ultrasonic calendering has shown potential to create melt morphologies in the coating. This has transformed some of the CBD bridge structures, creating a denser structure. There have also been indications of a melted CBD phase, and partially enveloped NMC particles where the CBD has been in contact. This is a novel behavior of the CBD, indicating the ability to manipulate the CBD in relation to the NMC particles through means other than squeezing and compression.

Insight into the mechanism behind ultrasonic calendering has been demonstrated. Ultrasonic calendering was inspired by ultrasonic welding which uses friction to create heat and interlock the superficial atoms of two substrates, bonding them. Electrode coatings contain thousands of particles with multiple points of contact. In ultrasonic calendering the work targets the coating, oscillating the particles and elevating the temperature of the particles through friction. The temperature rise is sufficient to melt the PVDF in the CBD phase. The kinetic energy supplied by the ultrasonic welder in tandem with the lowered CBD rigidity from elevated temperatures and melting allows the coating to plastically deform. The cathode deforms into a smaller volume constrained between the welding face and the anvil. This shape and new structure of the ultrasonically calendered cathode is retained after cooling.

6. Experimental Chapter: Coating Loading and Pouch Cell Format Extrapolation Study

6.1 Introduction

Uncalendered cathodes with an increased thickness of 110 μm were made to investigate the influence of thickness on the results of ultrasonic calendering. A large batch of ultrasonically calendered thick cathode was produced using one set of parameters, setting #1. This decision was made to minimise time spent on specialist equipment and to focus on one ultrasonic calendering condition. Repeating all settings of the thinner cathode analysed in the previous chapter would expand the resources and time needed. The disadvantage of this approach was the uncertainty surrounding setting #1 (15 psi, 0.8 s weld time) being optimal or suboptimal for the thick cathode. The selection of a single ultrasonic calendering setting enabled the production of a larger quantity of identical thick cathode, eliminating the need to conserve material. This facilitated testing using mercury intrusion porosimetry and supported the production of larger, more statistically robust cell datasets.

The thicker cathode is 20 mg cm^{-2} , compared to 16 mg cm^{-2} examined in the previous chapters. 20 mg cm^{-2} is a coating thickness that produces the greatest energy densities before diminishing returns⁴⁷⁰. Scale-up aspects such as affecting sufficient area to create a pouch cell or continuous ultrasonic calendering (instead of batch processing) was of interest; however, proved to be beyond the scope achievable in this project. A pouch cell extrapolation was demonstrated as an alternative.

The larger cathode coating loading provides more medium for the ultrasonic vibration to transfer through; therefore, increasing the mass of the coating may affect the mechanism of ultrasonic calendering. The extra mass may attenuate or propagate the kinetic energy provided by the ultrasonic welder; therefore, the physical and electrochemical properties of thick cathode ultrasonically calendered are investigated, working towards the following objectives:

- 2) To utilise ultrasonic calendering to produce a densified cathode film, followed by characterization of its physical properties and evaluation of the ultrasonic calendering process mechanism.
- 3) To assess the electrochemical performance of ultrasonically calendered cathode and correlate its performance with its physical and structural characteristics.

6.2 Experimental: 110 μm Thick 92 % Active Material Cathode

6.2.1 Microscopy and Coat Loading Comparison

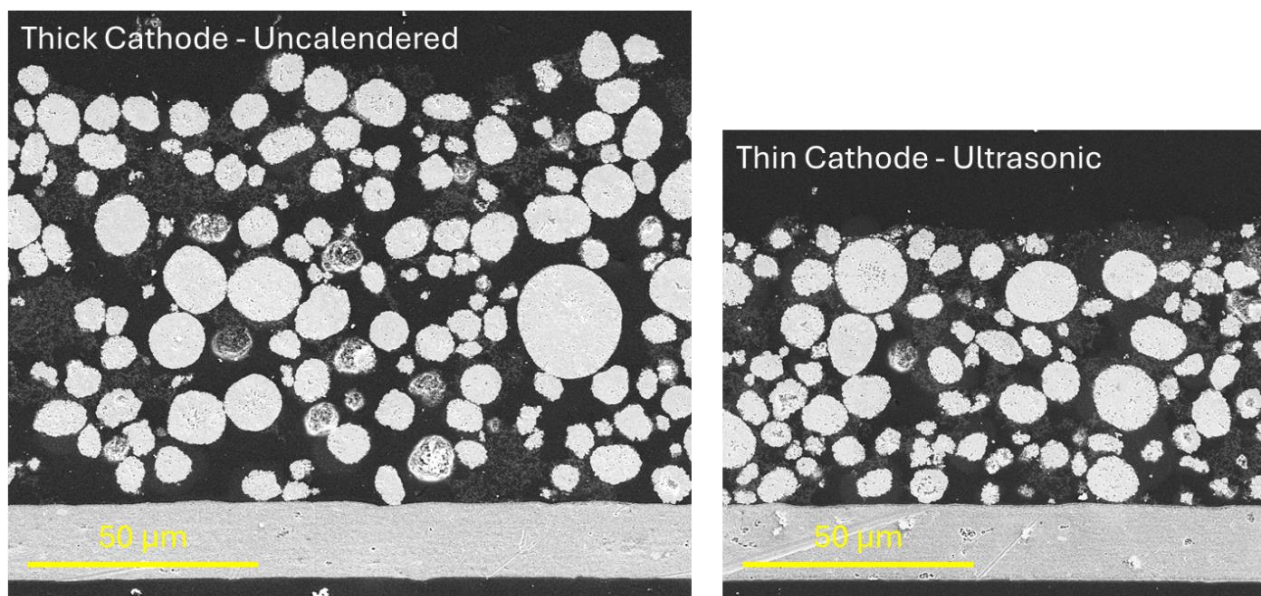


Figure 6.1 Uncalendered thick cathode (112 micron coating) compared to the ultrasonically calendered thinner cathode (setting #1), with a coating of 62 microns. The coating thickness and material density is thinner and more compact for the thin ultrasonically calendered cathode. The figures have consistent magnification ($\times 2000$) and scale bars.

Images from scanning electrode microscopy in Figure 6.1 displays the morphological differences between the cathodes of this chapter and the previous work in chapters 2 and 3. An uncalendered coating with a loading of 20 mg cm^{-2} shows a much greater z-axis height compared to the thin cathode with a coating loading of 16 mg cm^{-2} . Visual analysis of the two cathodes also indicates the density of the thin cathode to be greater; the proximity of the NMC particles to the resin containing CBD phase is much closer. Additionally, there is a lower relative surface area of free-resin within the cathode. Both observations indicate the thin cathode to have a lower porosity. This is expected, and an intension of this work. The thin cathode has been subject to ultrasonic calendering to reduce the porosity of the electrode. The porosity of the thin cathode is approximately 46 % and the porosity of the thick cathode in its uncalendered state is around 56 %.

6.2.2 Pore Volume and Pore Size Distribution

Mercury intrusion porosimetry is a technique which has been covered in section 3.14 and had results discussed in section 5.2. It is a valuable technique in characterising the porous volume in a structure. MIP analysis of battery electrode can reveal the total porosity of the structure and calculate the pore size distribution of the film.

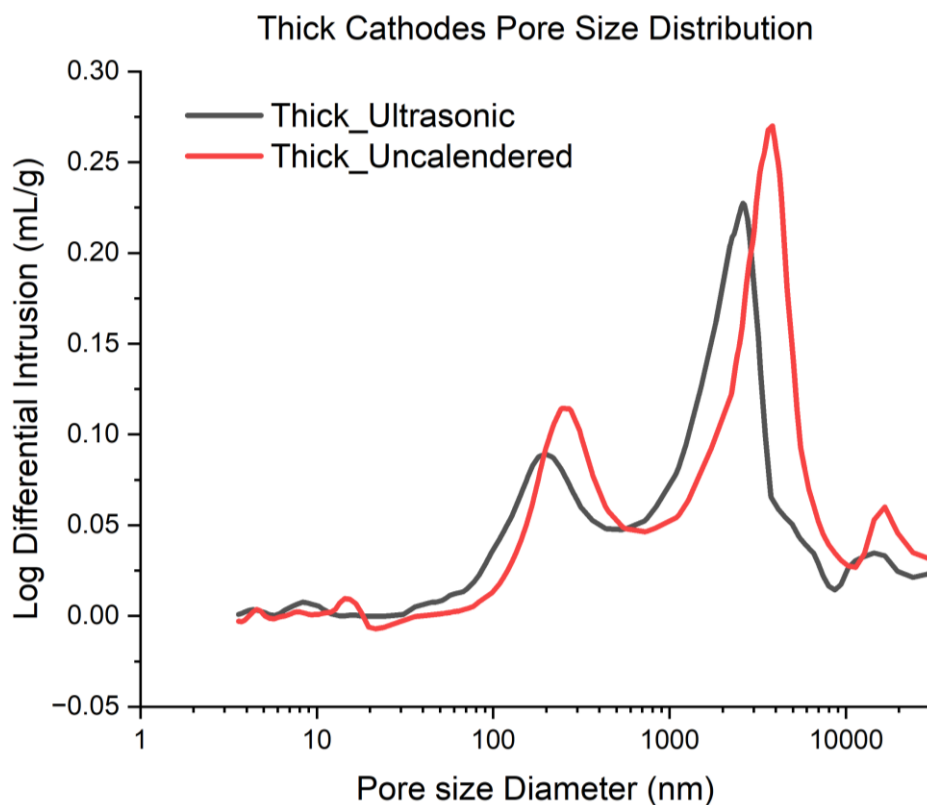


Figure 6.2 MIP pore size distribution for uncalendered thick cathode and ultrasonically calendered thick cathode (15 psi, 0.8s weld time).

The data indicates a bimodal distribution for both samples. It can be observed that the largest peak in the samples' intrusion curve correlates with the microporous region of the cathode. The uncalendered thick cathode is centred at 3.8 microns compared to 2.6 microns for the ultrasonically calendered thick cathode. This is a reduction of 32 % in the median diameter size of the larger peak. The narrowing of the micrometre sized pore peak indicates the micron regime pores have been compressed and plastically deformed to a smaller structure. Visual analysis of the graph indicates the total pore volume to be lower in the ultrasonically calendered electrode. This is confirmed by integrating the curve to quantify the area. Integrating the ultrasonically calendered micron peak measures a mercury intrusion of 659 mL nm g^{-1} of cathode. By comparison, the uncalendered cathode measures an intrusion of $1056 \text{ mL nm g}^{-1}$ of cathode, corresponding to a 62.2 % reduction.

The smaller peak of the bimodal distribution demonstrates the nanoporous region (200nm), which represents the pores related to the nanoparticles in the cathode. There is also a reduction in the median pore size. The nanoparticles are carbon black and PVDF binder. They form a CBD phase which is amorphous and coarse. This CBD phase forms a network throughout the electrode to impart strength and to reduce electrical resistivity by enabling an electronically percolating network. Pores in the CBD phase are attributable to the spaces

between the coarse nodules of CBD and the spaces between the CBD in contact with active materials. The nanoporous peaks are centred over 190 nm and 260 nm for the ultrasonically calendered and uncalendered cathode. This represents an average reduction of 27 % in the median diameter pore size due to ultrasonically calendering. The area of the peak can also be visually observed as lower after ultrasonically calendering, which is backed up by integration of the peak yielding an intrusion of 28 mL nm g⁻¹ for the ultrasonically calendered cathode compared to 41 mL nm g⁻¹ for the uncalendered cathode. This corresponds to a 67 % reduction.

6.2.3 Thick Cell Cathode Characteristics and Reliability Assessment

Coin cells made from the same slurry and with the same cell construction can yield different performances. This means single-cell testing is suboptimal practise and produces unrepresentative data, which may lead to inaccurate conclusions. In addition to the sample size, it is notorious that coin cells have variable performance^{242,471}.

Six cells for each calendering method were punched and constructed into coin cells. Table 6.1 details the mass, thickness, porosity and theoretical capacity of each cell. The cell with the thickest coating (conventionally calendered thick cell 6) has a mass of 42.04 mg. The cell with the least coating (ultrasonically calendered cell 1) has a mass of 36.62 mg. This is a non-negligible difference in mass, which will influence performance. The ultrasonic cell coating has 84.6 % of the mass compared to the conventional cell. This will result in a better rate performance and create more variation in the results, which will further increase the poor repeatability of the cells. To illustrate this, a box plot with ± 1 standard deviations is shown in Figure 6.3. The thin cathode cells from earlier chapters (full dataset of 5) were compared with the thick cathode cells (full dataset of 6) and the thick cathode cells restricted to a minimum mass of 40 mg (3 of the full 6 dataset).

The performance at higher C-rates will have more variation because the internal resistances of the cells are increased and have a greater influence on electrode capacity. This will inherently lead to greater data deviation at 5C. This relationship is displayed in all the data; the standard deviation is the greatest during 5C discharges for all three calendering subsets. At 5C, all three subsets have 1 or 2 outliers, data points exceeding 1 standard deviation. However, the full thick cell dataset presents more outliers at 2C and 0.1C compared to the thin cathodes and the reduced thick cells dataset; it shows more datapoints existing outside of a single standard

deviation. This is the consequence of the variation in coat loading. Due to this, the data in this chapter considers the reduced dataset of 3 cells for each cell type in the thick cathode data – reduced from 6. Cells with mass less than 0.04 g are disregarded. Only green cells within the relative coating weight column of Table 6.1 are considered.

Table 6.1 Thick Cathode Coin Cell Characteristics. The relative coating weight is compared to the largest mass. Green indicates a selected cell for the thick cathode data, yellow indicates an unselected cell with a mass >90 %, red indicates a mass <90 %, a cell which would greatly increase the deviation of results.

Cathode	Raw Mass (g)	Final Thickness (μm)	Coating Weight (g)	Final Porosity (%)	Theoretical Capacity (Ah)	Relative Coating Weight (%)
Uncalendered Thick 1	0.04149	111	0.03461	52.6	0.0056	98.4
Uncalendered Thick 2	0.03947	111	0.03259	55.4	0.0052	92.7
Uncalendered Thick 3	0.03884	106	0.03196	53.8	0.0051	90.9
Uncalendered Thick 4	0.04064	113	0.03376	54.7	0.0054	96.0
Uncalendered Thick 5	0.03993	111	0.03305	54.7	0.0053	94.0
Uncalendered Thick 6	0.03782	107	0.03094	55.8	0.0050	88.0
Conventionally Calendered Thick 1	0.03786	99	0.03098	51.5	0.0050	88.1
Conventionally Calendered Thick 2	0.03932	104	0.03244	52.1	0.0052	92.3
Conventionally Calendered Thick 3	0.04196	108	0.03508	50.4	0.0056	99.8
Conventionally Calendered Thick 4	0.03815	100	0.03127	51.6	0.0050	88.9
Conventionally Calendered Thick 5	0.03995	99	0.03307	48.2	0.0053	94.1
Conventionally Calendered Thick 6	0.04204	102	0.03516	46.9	0.0057	100.0
Ultrasonically Calendered Thick 1	0.03662	92	0.02974	49.2	0.0048	84.6
Ultrasonically Calendered Thick 2	0.04049	104	0.03361	50.3	0.0054	95.6
Ultrasonically Calendered Thick 3	0.04003	101	0.03315	49.3	0.0053	94.3
Ultrasonically Calendered Thick 4	0.03854	94	0.03166	47.3	0.0051	90.0
Ultrasonically Calendered Thick 5	0.03705	100	0.03017	53.3	0.0049	85.8
Ultrasonically Calendered Thick 6	0.04004	99	0.03316	48.1	0.0053	94.3

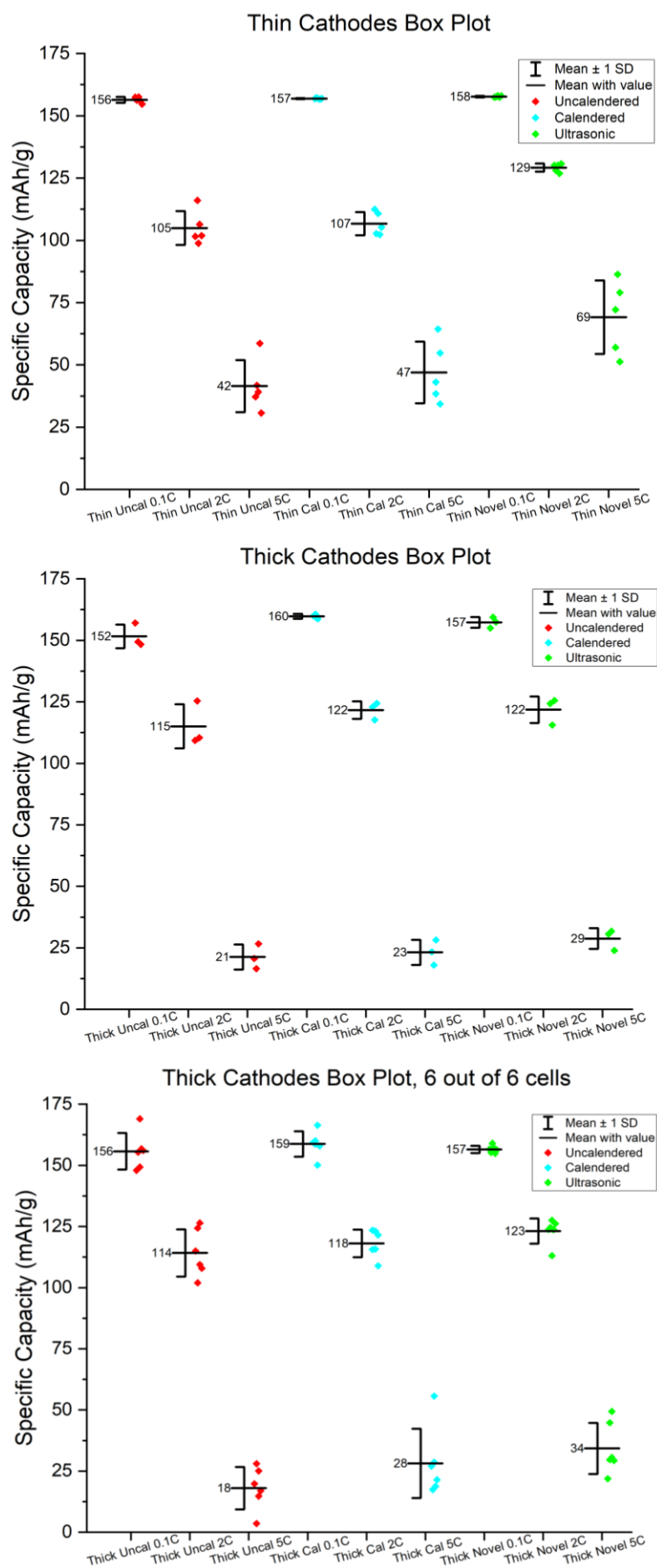


Figure 6.3 Analysis of the thin cathode cells (dataset of 5), the thick cathode cells (dataset of 3, cathodes > 0.04g) and the thick cathodes (dataset of 6, no mass restriction). Cells in the 3 cell thick dataset fall between 94 % and 100 % coat loading. The full dataset of 6 cells spans 84 % to 100 % loading, which is a large enough range to see significant performance variance. It can be seen the mass restricted dataset has less variance in the standard deviation.

6.2.4 Rate Capacity

Analysis of the rate capacity tests provides 5 discharge rates for each of the 3 cells per sample at different c-rates, seen in Figure 6.5. A mean average taken for each of the cells at 0.1C, 2C, and 5C. These discharges can then be averaged for all the cells in the uncalendered, conventionally calendered and ultrasonically calendered electrodes.

At a discharge rate of 0.1C the uncalendered thick cathode, conventionally calendered thick cathode and the ultrasonically calendered thick cathode possess capacities of 151, 159 154 mAh g⁻¹, respectively. This shows a narrow distribution and consistency between the capacities at low current density. At 2C, >75 % of the specific capacity is retained across the cells; capacities of 114, 120, and 119 mAh g⁻¹ are demonstrated. At 5C the rate capacities of the cells have differentiated with capacities of 20, 22 and 27 mAh g⁻¹ for the uncalendered thick cathode, conventionally calendered thick cathode and the ultrasonically calendered thick cathode. It also shows the decrease in performance of the thick cells at high-rate capacity, maintaining only 13-18 % of the 0.1C specific capacity.

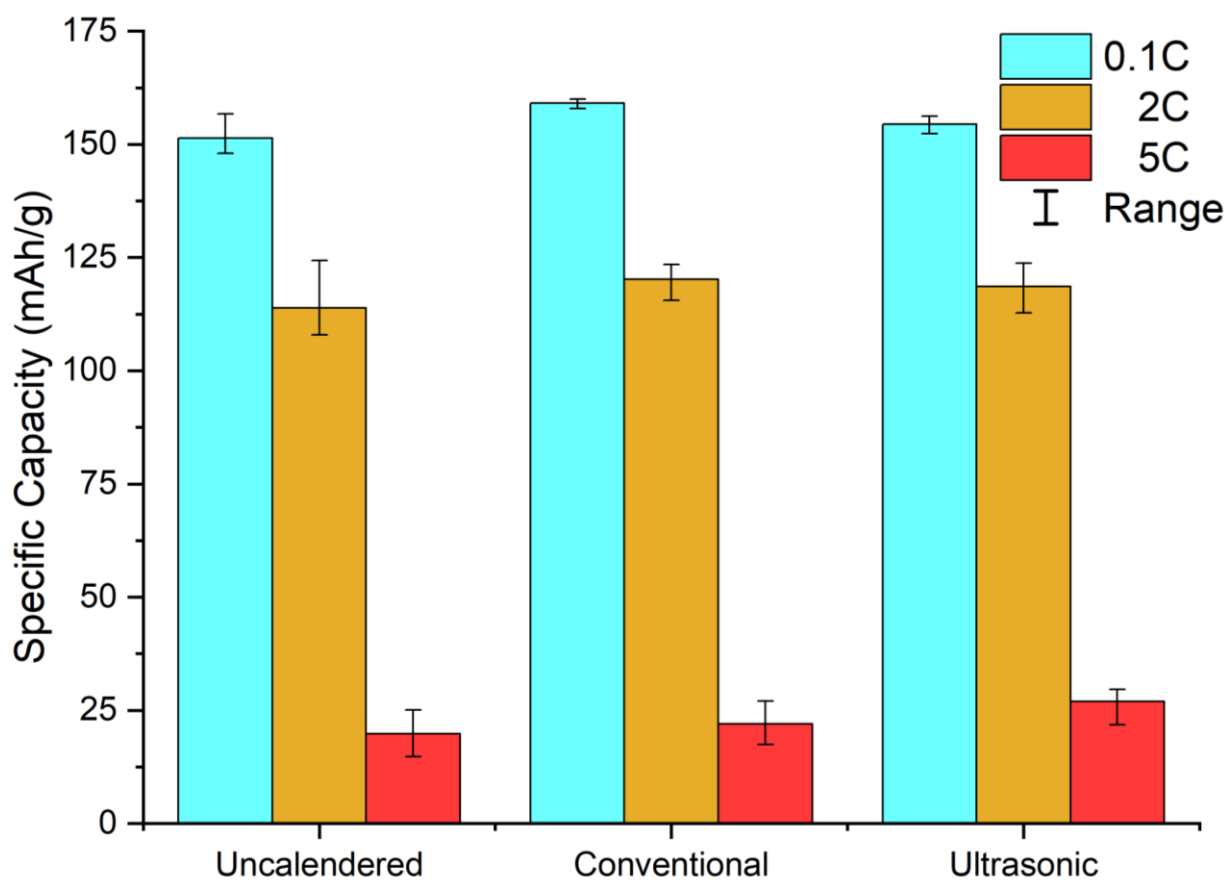


Figure 6.4 Rate capacity comparison for the thick cathode cells. Uncalendered is uncalendered thick cathode (54.0 % porosity average). Conventional is conventionally calendered thick cathode (48.5 % porosity average) and ultrasonic is ultrasonically calendered cathode (49.2 % porosity average).

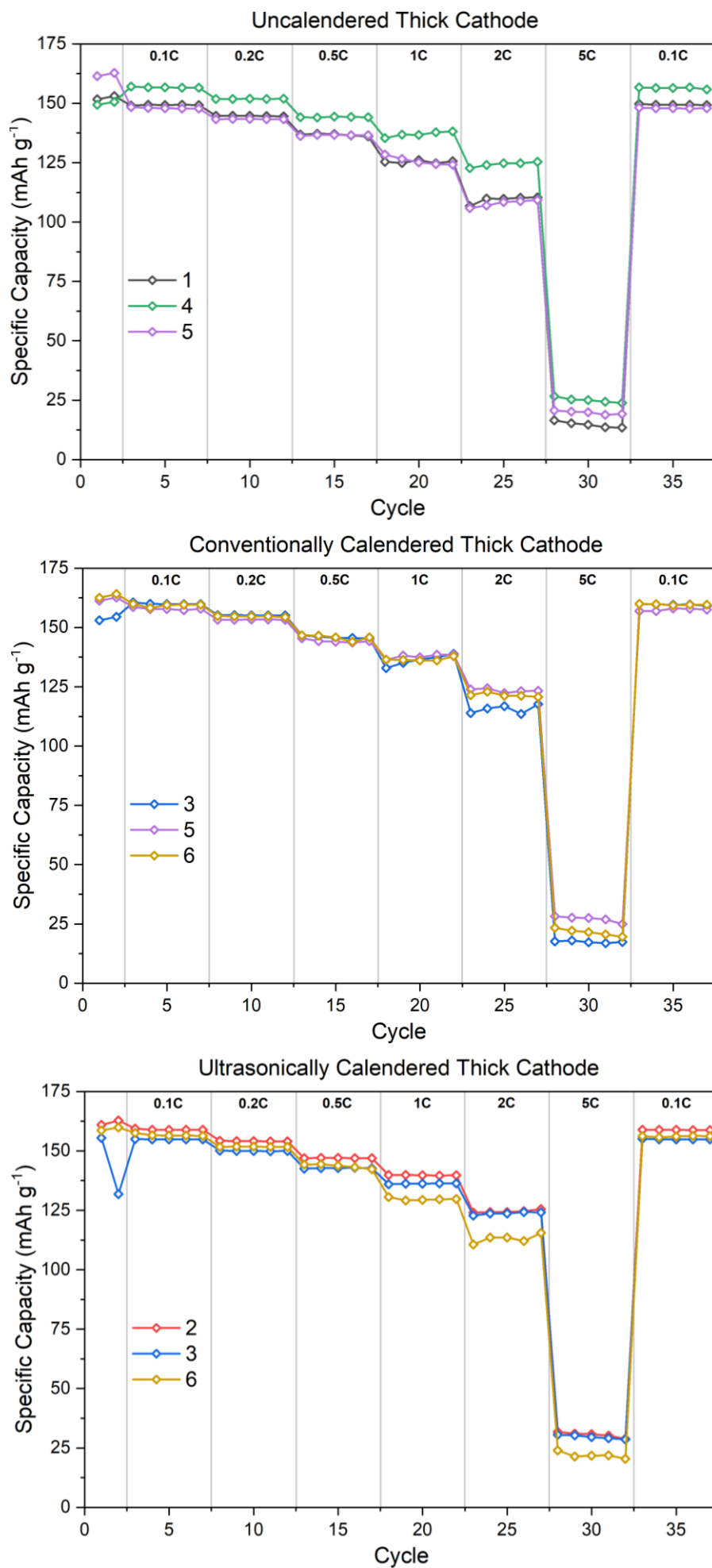


Figure 6.5 Rate capacity performance test results for the thick cathodes. Uncalendered, conventionally calendered and ultrasonically calendered cells are displayed. The 3 thickest cells of the batch are shown in accordance with the reliability assessment.

6.2.5 Electrochemical Impedance Spectroscopy

EIS was conducted to identify the impedances which make up the internal resistances in the cathodes. The technique of EIS has been explained and the equivalent circuit model has been explained in previous chapters (section 0) Figure 3.17, with results in section 4.5.2. The results indicate the difference in impedance between the calendering methods and can be compared with their thinner cathode counterparts. This is reliable, as all the cathodes in this chapter were subjected to the same electrochemical procedure: a formation cycle, an EIS measurement once fully charged at cycle 3, before a rate capability test.

Table 6.2 Results of the thick cathode cells EIS. Double Randles cell ECM applied to the data shown in Figure 6.6.

Cathode	R_b (Bulk) [Ω]	R_{cont} (contact) [Ω]	R_{ct} (Charge-transfer) [Ω]	$R_{cont}+R_{ct}$ [Ω]	5C Discharge (mAh/g)
Thick Uncalendered 1	15.4	12.0	8.1	20.0	14.8
Thick Uncalendered 4	4.4	11.6	7.9	19.5	25.0
Thick Uncalendered 5	3.4	12.0	6.3	18.3	19.8
Thick Uncalendered Mean	7.7	11.8	7.4	19.3	19.9
Thick Calendered 3	3.6	12.8	6.3	19.1	17.4
Thick Calendered 5	3.4	12.4	5.3	17.7	27.0
Thick Calendered 6	3.5	10.7	5.9	16.5	21.4
Thick Calendered Mean	3.5	11.9	5.8	17.8	22.0
Thick Ultrasonic 2	3.5	9.0	5.9	14.9	29.3
Thick Ultrasonic 3	4.0	6.9	6.5	13.5	29.6
Thick Ultrasonic 6	4.2	7.3	6.0	13.3	21.8
Thick Ultrasonic Mean	3.9	7.8	6.1	13.9	26.9

The results show the high frequency resistance (R_b) is similar across the dataset, excluding an outlier, uncalendered cell 1 at 15.4 Ω, the resistances span 3.4 to 4.4 Ω. The charge-transfer resistances see variation. The uncalendered thick cathode cells possess the greatest charge-transfer resistance, with the highest mean at 7.4 Ω and the greatest resistance in the set at 8.1 Ω. The conventionally calendered and ultrasonically calendered cells have a reduced resistance; a mean average of 5.8Ω and 6.1Ω. This indicates the charge-transfer resistance has been reduced by both calendering methods. The conventionally calendered cells exhibit the lowest charge-transfer resistance. It requires noting, the average porosity for the conventionally calendered cells is 48.5 % and the ultrasonically calendered cells average a porosity of 49.2 %. The ultrasonically calendered cells have a higher charge-transfer resistance but do have an increased porosity.

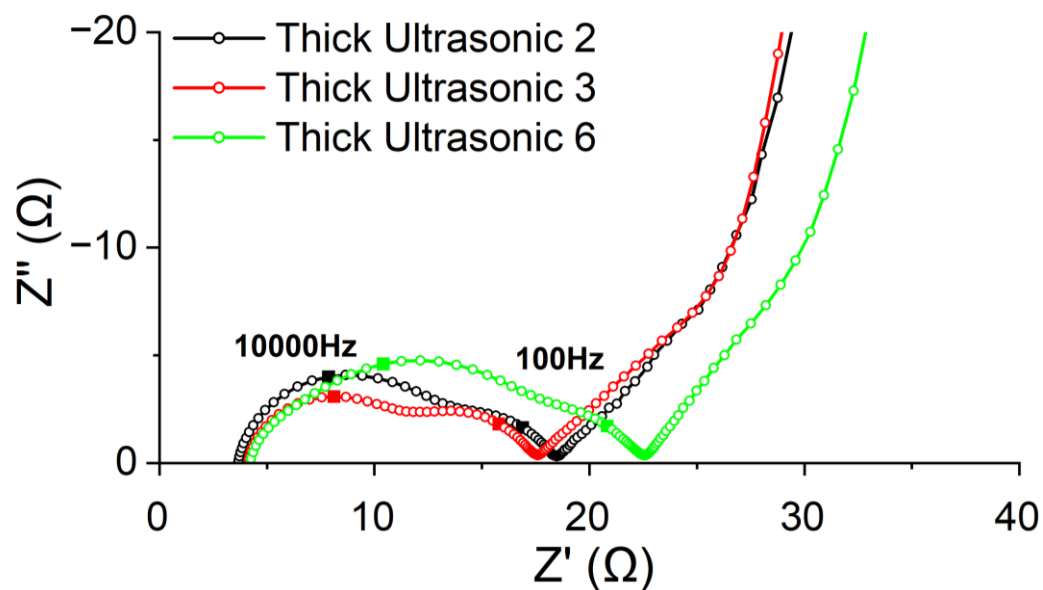
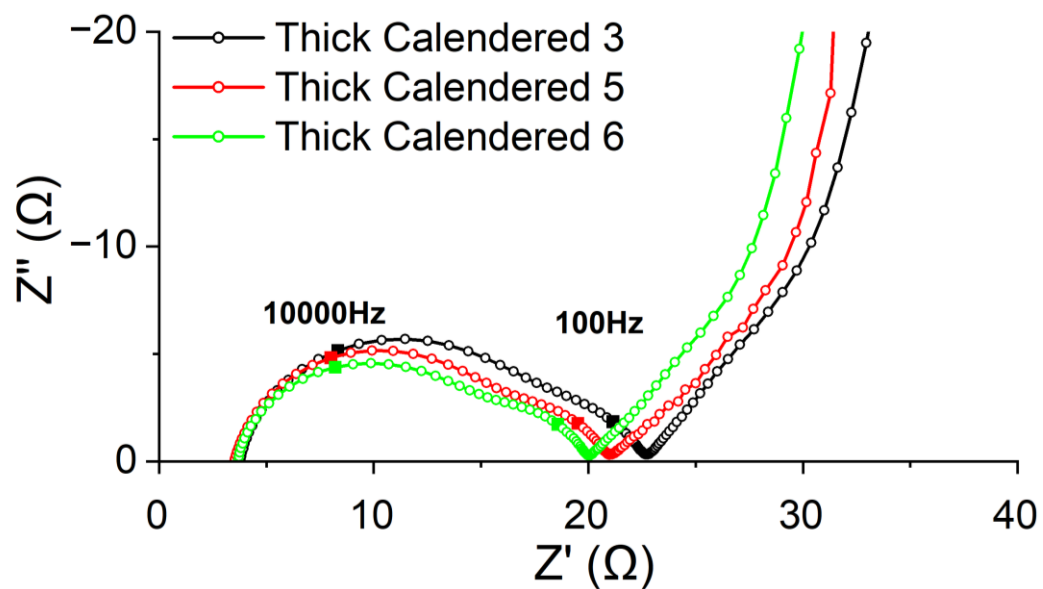
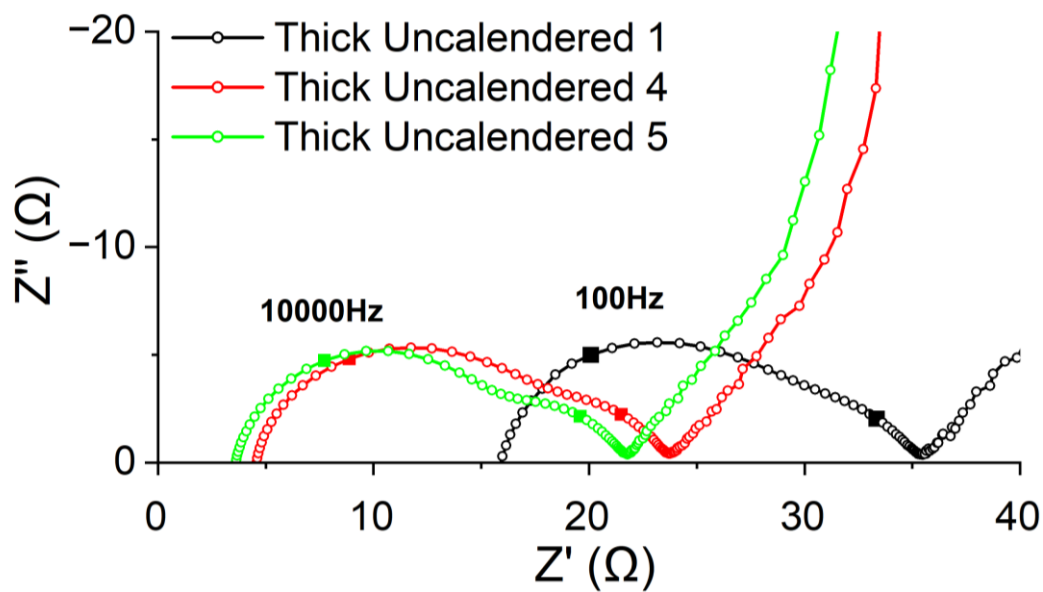


Figure 6.6 EIS response for the thick cathode cells (the 3 selected cells – mass >0.04 g).

6.2.6 Voltage Profiles: Thickest Cells

Figure 6.7 details the voltage profile and discharge capacity for three cells at 0.1C, 1C, and 5C. The cell selected has the highest coating film loading out of the thick cathode dataset for the uncalendered, conventionally calendered and ultrasonically calendered cells.

It can be seen at 0.1 C the initial voltage drop is small and all approximate 4.18 V. The capacities of the ultrasonically calendered and the conventionally calendered cathode are identical at 159 mAh g⁻¹, the uncalendered cathode has 149 mAh g⁻¹. These show comparable specific capacities at low rates. The specific capacities are reflected in these capacities, the uncalendered cell has a slightly lower specific capacity.

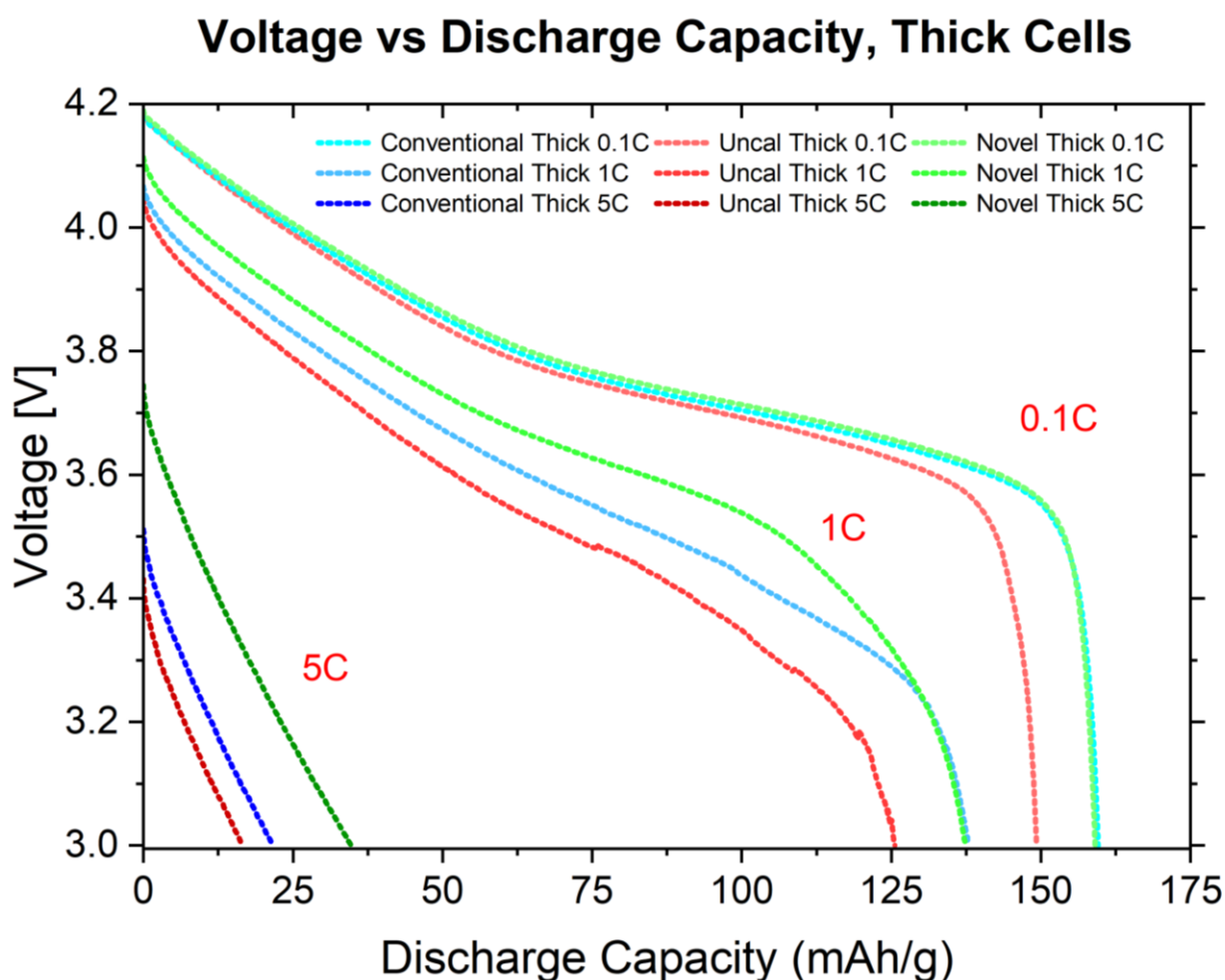


Figure 6.7 Voltage profiles of the thickest cells in the thick cathode dataset.

At 1C, the discharge capacity of the ultrasonic and the conventionally calendered cells are also identical, at 137 mAh g⁻¹. This is a good indication of similar rate performance as they share the same capacities at both 0.1 and 1C. The uncalendered cell has a capacity at 125 mAh g⁻¹; however, in relation to the 0.1C discharge capacity, the relevant decrease in discharge by increasing the current density is similar to the other cells. The initial voltages are 4.11 V, 4.07 V

and 4.03 V (ultrasonic, conventional and uncalendered). Indicating similar internal resistances however there is a difference in the resistance displayed at this c-rate.

At 5C, the rate performance in the cells has differentiated the discharge capacity and the initial voltages. The uncalendered cell has the lowest rate capacity at 16 mAh g⁻¹ and an initial voltage of 3.43 V. The ultrasonically calendered cell has the highest discharge capacity at 34 mAh g⁻¹ and the highest initial voltage (3.74 V). The conventionally calendered cathode performs between the uncalendered and ultrasonic cathode with a midpoint initial voltage and discharge capacity of 3.51 V and 21 mAh g⁻¹. Conventionally calendering the cathode increases the capacity by 31 %, however ultrasonically calendering the cathode increases the cathode rate capacity by 112 %. This increase is significant.

6.2.7 Discussion

The ultrasonic calendering of the thicker cathode was successful. The average porosity of the uncalendered thick cathode was 54.5 % and this was reduced to an average of 49.6 % porosity after ultrasonically calendering with a gauge pressure of 15 psi and 0.5 seconds of weld time. This porosity change, estimated by micrometer readings, was confirmed by mercury intrusion porosimetry which evidenced a reduction in the median pore diameter from 3.8 to 2.6 μm and a significant reduction in the total pore volume of the film. This indicates the ultrasonic calendering on the thicker cathode to be physical effective on the microstructure.

The electrochemical analysis also indicates a positive effect of ultrasonic calendering on the thick cathode; the rate capabilities of the cells were improved. The performance at low current densities (0.1C) was almost identical, indicating the inherent characteristics of the NMC particles and electrolyte wettability (the primary influences at slow discharge rates) are highly similar. This is to be expected because the internal resistance at small currents is low; electrode thickness and electrode porosity have little impact at low current densities. All the electrodes have been produced from the same slurry and only differ at the penultimate stage of calendering. However, this is compelling evidence to confirm ultrasonic calendering has not altered the specific capacity of the cells and simultaneously indicates the differing performance at higher c-rates is the consequence of the rate capabilities of the cathode, because all the cathodes have similar electrochemical storage capabilities.

The rate capabilities of the electrodes at high c-rates have severely diminished and have manifested an observable difference in performance, compared to 0.1C. The most underperforming electrode is distinctly the uncalendered electrode. The uncalendered cathode had a 5C discharge of 20 mAh g⁻¹. This is a consequence of the high internal resistances seen in the voltage profile exhibiting an initial voltage of 3.4 V, a reduction of 0.8 V from 4.2 V. The high resistances have accumulated from the high effective ionic diffusion associated with thick cells and the high charge-transfer resistance (18.9 Ω average), measured during EIS. This result correlates with literature^{472,473}; large mass coatings have long diffusion pathways from the electrode surface to the current collector⁴⁴². This produces a high effective ionic resistance for the ions to traverse the electrode and would benefit from compaction and corresponds with the performance of the calendered electrodes^{258,474}. Both the conventionally calendered cathode and the ultrasonically calendered cathode displayed a higher 5C discharge capacity, a higher initial voltage at 5C and a lower charge-transfer resistance. The conventionally calendered cathode had an initial voltage of 3.5 V at 5C, a mean discharge capacity of 22 mAh g⁻¹ and had a charge-transfer of 17.6 Ω. These are all electrochemical performance increases from the uncalendered thick cathode; however, they are inferior to the ultrasonically calendered thick cathode, which boasts the greatest 5C mean discharge capacity of 27 mAh g⁻¹. This was attributable to the lowest initial voltage drop 3.6 V displaying the least internal resistance. The charge-transfer resistance was reported the lowest, a mean of 13.9 Ω. This appraisal of the data demonstrates the uncalendered cathode has the worst rate capabilities and that ultrasonic calendering increases the electrochemical performance and the rate capabilities of the thick cathode.

6.3 Modelling: Energy Density Extrapolation to Pouch Cell Format

6.3.1 Introduction

This section will look at the modelling of the selected thin and thick electrodes into pouch cell formats. Coin cells have terrible volumetric density; most of the coin cell volume consists of non-porous parts of steel to form a linear electrical circuit from the base of the negative can to the top of the positive cap. The Wh L^{-1} of a coin cell would be an extreme underperformer because electrodes cannot be multilayered and the electrode will not make up more than 400 μm of the 3.2 mm depth, approximately an eighth. A pouch cell consists of an electrode stack surrounded by an aluminium envelope. This design is flexible and allows the stack to be inserted, filled with electrolyte and then vacuum sealed, reducing the unused pouch volume. As a result, the depth of the pouch cell is composed predominantly of the electrode stack, except for the envelope casing. This advantageous in terms of volumetric packing and promotes a 90-95 % packing factor. A packing factor indicates the fraction of the properties the cell has compared to the electrode level. An electrode producing 200 Wh L^{-1} at electrode level would have a cell level of 190 Wh L^{-1} when sealed in a pouch cell assuming a packing factor of 95 %.

The electrode performance of the coin cells produced in this project can be extrapolated to estimate their performance in a pouch cell by defining a few assumptions and characteristics. This can then be compared with literature or the latest industrial battery products.

6.3.1.1 Assumptions

The cells made in this project have been primarily NMC 662 half cells. The electrochemical testing has been conducted with a lower voltage cut-off of 3.0 volts and an upper cut-off voltage of 4.2 V. The nominal voltage of the cells has been 3.7 volts.

The inert thicknesses of the electrodes are one 15 μm aluminium current collector on the cathodic side; the separator is a tri-laminate polypropylene mesh which possesses a 15 μm thickness; the copper current collector is more robust than aluminium and is 9 μm thick on the anodic side.

Half cells use a metallic lithium chip; however, this is only practical in coin cells. The lithium chip should be substituted with a graphite anode for pouch cells. Graphite inherently has a lower gravimetric density than NMC but has a greater capacity to store lithium (325 mAh g^{-1}).

This superior capacity offsets the lower density. The anode to cathode ratio is a manufacturing decision which requires optimisation; however, an acceptable ratio is 1.1:1.0. This indicates a 2 mAh cm⁻² cathode would be paired with a 2.2 mAh cm⁻² anode. This translates to a coating thickness of 1.1:1.0 due to the higher gravimetric capacity but lower particle density relationship of the anode material discussed above.

Assumption summary:

- Anode coating loading is 110 % of cathode ⁴⁷⁵
- Inert thicknesses are 15 µm, 15 µm and 9 µm for the aluminium current collector, separator, and copper current collector
- The nominal voltage of the cell is 3.7 volts ⁴⁷⁶
- The packing factor of a pouch cell is 95 % ⁴⁷⁷

6.3.1.2 *Limitations*

This model is rudimentary. There are two potential fallacies in converting the half-cell coin data to a pouch cell: the scaling of a half cell to a full cell, and the scaling of a coin cell to a pouch cell. The scaling to a full cell from a half cell provides a different system with difference internal resistances and pouch cell systems introduce more dynamic factor such as thermal inhomogeneity.

A lithium chip is a bulk of lithium with which the lithium ions can interact, and it provides an interfacial resistance from the formation of a lithium metal oxide layer. A graphite anode has a lattice structure, which involves an intercalation reaction and has an associated charge-transfer resistance. These are two different impedances. The rate performance of the cells cannot be assumed to be identical. The advantage of half cells is lithium chips act as control variables for cell performance. This allows performance and analysis to be associated to the cathode (in a cathode half-cell) which is valuable and was utilised in this project.

A pouch cell has a vastly different architecture from a coin cell. A coin cell is primarily stainless steel and voidage/electrolyte, which presents a high heat capacity of adjacent material to the electrode stack. The stack also has spacers and is compressed with a spring to increase the pressure of the system. A pouch cell is primarily an electrode stack, encased in a thin pouch. This presents thermal complexities to the pouch cell system and can often lead to overheating issues. Reaction kinetics and degradation are highly influenced by cell temperature ^{478,479}. Additionally, a pouch cell provides a non-pressurised system and therefore must be

compressed between two plates. It has also been demonstrated in literature that pouch cell pressure dramatically affects performance ⁴⁸⁰. Other work has also shown the impedance of pouch cells can be lower when comparing identical coin cell and pouch cell systems, leading to greater c-rate and less lithium plating ⁴⁸¹. These pouch cell advantages result in a better electrochemistry and longer cell life ^{482,483}.

Table 6.3 Cell specifications modelled in the pouch cell scale up. Thin novel cell 4E was manufactured with 15psi gauge pressure and a weld time of 0.8s.

	Sample	Coating Weight (g)	Porosity (%)	Total Thickness (μm)	Theoretical Capacity (Ah)	Relative Coating Mass (%)
Thick	Uncalendered (Uncal Cell 1)	0.03461	52.6	111	5.6	98.4
	Conventional (Cal Cell 6)	0.03516	46.9	102	5.7	100
	Ultrasonic (Novel Cell 4)	0.03367	48.5	101	5.4	95.8
Thin	Uncalendered (Uncal Cell E)	0.02613	51.3	86	4.2	74.3
	Conventional (Cal Cell A)	0.02592	49.6	82	4.2	73.7
	Ultrasonic (Novel Cell 4E)	0.0268	50.1	85	4.3	76.2

6.3.2 Results

The relationship between the performance of the thick and thin cells, indicating the effect of coating loading, and the performance between uncalendered, conventionally calendered and ultrasonically calendered cells can be observed in Figure 6.8.

6.3.2.1 *Low Rates*

The 0.1C rate capacities resemble the specific capacity. Energy densities at this current density have the least relative distribution, from 683 Wh L⁻¹ to 814 Wh L⁻¹. This is an increase just shy of 20 %. The largest variance in 0.1C performance belongs to the thick cells. This is because inert materials, e.g. current collectors and separators do not contribute electrochemically and provide no storage capabilities to the cell. The thin cathodes will inherently have more layers for a given cell thickness and consequently have more inert material for a given volume; therefore, any difference in the electrochemical performance of these electrodes will not manifest as prominently.

The uncalendered thick electrode possesses a capacity of just under 694 Wh L⁻¹ at 0.1C. This is inferior to both calendered thick electrodes. The ultrasonically calendered electrode has 778 Wh L⁻¹, and the conventionally calendered cathode has 814 Wh L⁻¹. This difference is primarily the result of the uncalendered electrode having the highest porosity and the thickest coating; the electrode has a 53 % porosity and is 110 µm. This large, but ineffectively packed, electrode volume presents a low energy density. The two thick calendered electrodes have both been compacted (both to approximately 100 µm from 110 µm). This reduces the total thickness of the electrode, allowing more electrodes per litre. The coating is also more compact, porosities of 46.9 % and 48.5 % for conventional and ultrasonic. This increases the packing density of the NMC particles and consequently increases the volumetric energy density of the cell. The conventionally calendered electrode has approximately 70 Wh L⁻¹ more than the ultrasonic cathode. At low current density, differences in internal resistance will have negligible effects on the capacity of the cell; therefore, the calendered cathode having 1.6 % less porosity may be the primary advantage

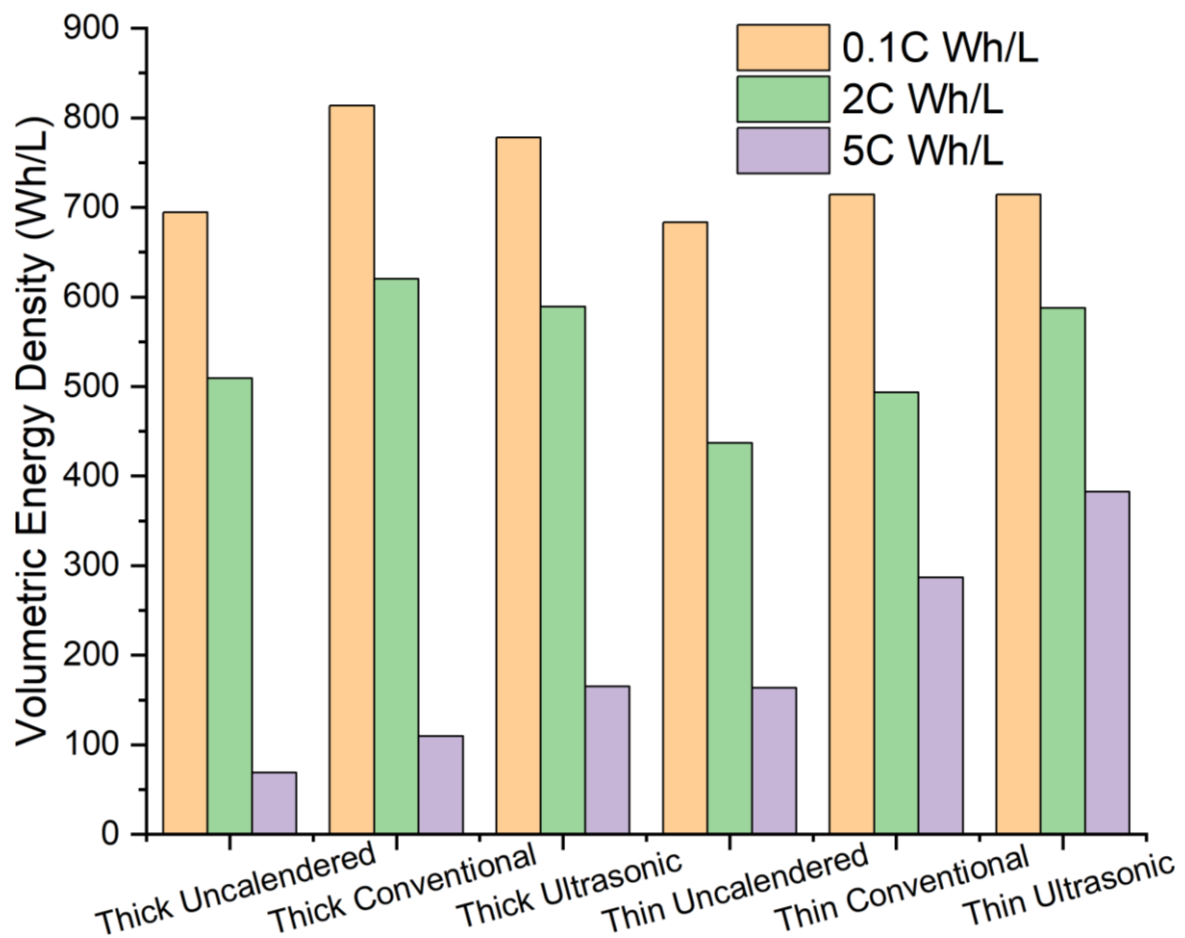


Figure 6.8 Pouch cell model energy densities for c-rates at 0.1C, 2C and 5C. The best rate performing thin cathode cells have been compared with the thickest film loading cells from the thick cathode. Thick uncalendered – uncalendered cell 1. Thick conventional – conventionally calendered cell 6. Thick ultrasonic – ultrasonically calendered cell 2. Thin uncalendered – uncalendered cell 5. Thin conventional – conventionally calendered cell 1. Thin ultrasonic – ultrasonically calendered cell 5.

yielding the greater volumetric energy density. In summary, it is shown that calendering, via either method, is effective at increasing the volumetric energy density at low rates.

The thin cathodes indicate the same relation exhibited in the thick regime. The uncalendered cathode has the lowest volumetric energy density; 683 Wh L⁻¹ compared to 715 and 714 Wh L⁻¹ for the ultrasonic and conventionally calendered cells. This is also mainly due to the greater volumetric density of the cathodes. The uncalendered cells are the thickest of the set and have the lowest density, resulting in fewer layers being possible per litre, and less active material being packed per layer. The ultimate result is less NMC material being included within the cell-level volume.

6.3.2.2 *High Rates*

All the cells demonstrated a high percentage of capacity retention at 2C. The worst performing cell was the thin uncalendered cell which retained just over 63 % of its specific capacity at 2C. The best relative capacity retention at 2C was from the thin ultrasonically calendered cathode cell, maintaining greater than 82 % of its specific capacity. The performance of uncalendered cells appear poor in comparison to the any of the compressed electrodes at high rates. This outcome is expected, as uncalendered cells typically have greater resistances and lesser rate capabilities. The internal resistances of both thick calendered cells in this analysis aren't sufficiently different to manifest a significant difference in capacity 2C, the average capacity retention is 73 % for the dataset.

Table 6.4 Pouch cell scale-up energy densities at increasing c-rates.

	Cathode Sample	0.1C (Wh L ⁻¹)	2C (Wh L ⁻¹)	5C (Wh L ⁻¹)	2C Retention (%)	5C Retention (%)
Thick	Uncalendered	694	509	69	73	10
	Conventionally Calendered	814	620	109	76	13
	Ultrasonically Calendered	778	589	165	76	21
	Mean Average	762	573	114	75	15
Thin	Uncalendered	683	437	163	64	24
	Conventionally Calendered	714	493	287	69	40
	Ultrasonically Calendered	715	587	382	82	53
	Mean Average	704	506	277	72	39
	Total Average	733	538	196	73	27

At 5C, the thick cathode cells had the worst energy densities, ranging from 69 to 165 Wh L⁻¹. The uncalendered cell had the lowest density and the ultrasonically calendered had the best energy density (10 % vs 21 % capacity retention). The thin cathode cells energy densities at 5C ranged from 163 to 382 Wh L⁻¹; the poorest performance by the uncalendered cathode and the best performance by the ultrasonically calendered cathode (24 % vs 53 % utilisation). The trend shows 5C having the greatest variations in energy ranging from 69 to 382 Wh L⁻¹. This represents a greater than 5-fold increase by substituting the uncalendered thick cathode with the thin ultrasonically calendered cathode for energy density at 5C. The dataset shows the rate capabilities of the cells greatly differ at 5C.

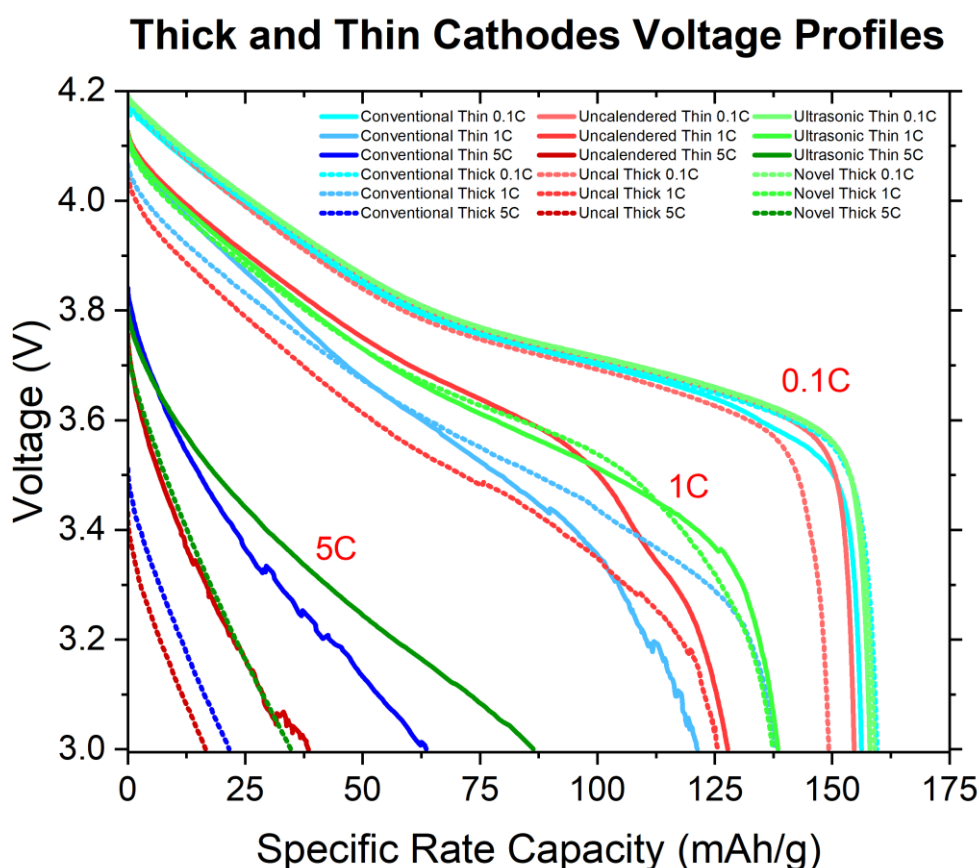


Figure 6.9 Voltage profiles thick and thin cathodes. Dataset shows the thickest cells from the thick cathode and the best performance cells from the thin cathode.

Comparison of the voltage profiles at 0.1 C indicates highly similar performance. Excluding the uncalendered thick cathode cell, all the cells, either thick or thin cathodes, possess a specific capacity of around 160 mAh g⁻¹ and have a similar initial voltage around 4.19 V.

For a discharge of 1C, the early-stage voltage profiles of the thin cathodes drop to approximately 4.10 V, compared to the thick cathodes drop to 4.05 V (excluding the thick ultrasonic cathode also only drop to 4.10 V). This indicates the greater increase in internal resistance leading to voltage loss in the thick cathodes. The average of capacity of the thick

cathodes have also decreased to 120 mAh g⁻¹ from the 138 mAh g⁻¹ average capacity of the thin cathodes at 1C.

The capacity for the cells at 5C spans 87 mAh g⁻¹ to 16 mAh g⁻¹ and displays a greater than 5-fold increase in 5C discharge capacity when comparing the ultrasonically calendered thin cathode (best capacity) with the uncalendered thick cathode (worse capacity). The initial voltages of the thin ultrasonically and conventionally calendered cathode are both the greatest at 3.80 V. The uncalendered thin cells have a lower initial voltage at 3.70 V. The thick ultrasonically calendered cathode also has an initial voltage of 3.70 V; however, the other two thick cathodes, the uncalendered and the thick conventionally calendered cathode, have the lowest initial voltages of 3.5 V and 3.4 V, indicating the greatest internal resistances.

6.3.3 Discussion

At 5C, the internal resistances were the dominant influence on energy density. The differences in specific capacity do not have as great an influence on the rate capacity, but instead the differences are due to the effectiveness of the electrodes at high rates. Effective utilisation of the material is more influential on the 5C capacity than the inherent capacity of the electrode. The current density at 5C is enough to provoke significant internal resistances within the system. This causes a high overpotentials and lowers the initial voltage from 4.2V, as shown in Figure 6.9. The drop in initial voltage causes a premature reaching of the lower cut-off voltage, reducing the discharge capacity of the cell. Observing the voltage profiles, the thin ultrasonically calendered cathode has the highest initial voltage and the largest capacity at 5C, followed by the thin conventionally calendered cathode. These two cells also show the highest Wh L⁻¹ at 5C in Figure 6.8, and demonstrate the advantages of thinner cathodes and calendered electrodes at high rates: the ultrasonically calendered electrode possesses 380 Wh L⁻¹; followed by the conventionally calendered electrode, 275 Wh L⁻¹; and the uncalendered electrode, 150 Wh L⁻¹. These differences are significant; a cell possessing the uncalendered cathode would need more than double the volume of a cell possessing the ultrasonically calendered electrodes to output the same energy at 5C.

All the thick cells began to suffer dramatic performances decrease at 5C. The ultrasonically calendered thick electrode has a volumetric energy density of 165 Wh L⁻¹, the conventionally calendered has 109 Wh L⁻¹ and the uncalendered has 69 Wh L⁻¹. This pales in comparison to the

energy density at low discharge currents (762 Wh L⁻¹ average). The low performance of the thick cells at 5C is attributable to the high resistances provided by the coating thickness. Discharging these cells at 5C is pushing the capabilities of the electrodes to function within the voltage window. Despite this, it is worth noting that the relationship between the calendaring method and the electrochemical performance of the thick cells also applies to the thin cells. Both the ultrasonically calendared cathodes possessed the greatest capacities, surpassing the conventionally calendared electrodes at 5C. The uncalendered thick and thin cathodes had the worst performance, significantly inferior to the other electrodes. This analysis indicates that if a design criterion of a battery is to maintain performance at higher c-rates, the thinner cathodes should be recommended, and that this dataset indicates the usage of the ultrasonically calendared cathode for the greatest performance retention.

The specific capacities measured at 0.1C displayed in the voltage profiles indicate the gravimetric performance of the cells is near identical, Figure 6.9. Due to this, the relationship between specific capacity in the voltage profiles and the energy densities modelled in Figure 6.8 do not share the same strong correlation observed at 5C. At 5C, the specific capacities in the voltage profiles and the 5C Wh L⁻¹ follow the same trend, the greater the 5C capacity the greater 5C energy density. At 0.1C, the specific capacity and the energy density correlate less strongly because the cell thickness and film density are much more impactful. The energy density at 0.1C highly correlates with active material packing and the amount of active mass which is within the given cell volume; this contrasts the 5C discharge energy density, which highly correlates with rate performance and how effectively the material in the electrode can be utilised at high rate. This is the cause of the thicker cells possessing the best 0.1C energy densities because the electrode coating loading is greater. This greater loading decreases the volume of inactives (separator and current collector), increasing the volume dedicated towards the coating⁴⁸⁴. The ultrasonically calendared thick cathode has a marginally lower 0.1C energy density than the conventionally calendared thick cathode, 694 vs 814 Wh L⁻¹. The thicknesses are the same, however the coating is thicker for the conventionally calendared cathode, leading to a lower porosity. This greater coating loading and lower porosity is advantageous for active material packing and causes the conventionally calendared thick cathode to triumph at 0.1C energy density.

This analysis considered two design objectives, energy density at low rates and energy density at high rates. If high-rate capabilities are necessary, the thinner, ultrasonically calendared

cathode would be recommended due to the greatest 5C specific capacity and energy density. If the energy density of the cell at low rates is the design priority, the thicker cells would be recommended; the ultrasonically calendered thick cathode and the conventionally calendered thick cathode had the two best energy densities, with the optimum being the conventionally calendered thick cathode.

6.3.4 Model Summary

The energy densities were proven to be superior in the thick cathodes; however, this was not sustained at high current densities/c-rates. The thicker cathodes exhibited a much steeper decline in performance at 5C compared to their thinner cathode equivalent, which better maintained their energy densities. The calendered electrodes, manufactured by conventional and ultrasonic methods, both had superior energy densities at 0.1C and 5C, indicating an increase in energy density across the board. At 5C current densities, there was vastly more variance, 69 Wh L⁻¹ to 382 compared to 682 to 813 Wh L⁻¹, which demonstrates the benefit of calendering is more impactful for higher c-rates. The ultrasonically calendered thin cathode provided the best energy density at all rates, while the conventionally calendered thick cathode provided the greatest energy density (0.1C).

6.4 Chapter Conclusion

A higher coating loading, thicker cathode film (20 mg cm⁻²) of the same formulation (92:4:4) was ultrasonically calendered with ultrasonic setting #1 (15 psi gauge pressure, 0.8 second weld time). Mercury intrusion porosimetry indicated there was a decrease in total pore volume from 54.5 % to 49.5 % and the median pore diameter decreased from 3.8 μm to 2.6 μm. The electrochemical performance of the ultrasonically calendered thick cathode surpassed the uncalendered thick cathode and a conventionally calendered cathode of similar porosity during a rate capacity test, providing 27 mAh g⁻¹ compared to 20 and 22 mAh g⁻¹. This was bolstered by voltage profile analysis, which indicated a lower initial voltage drop for the ultrasonically calendered cell and a lower charge-transfer resistance mean for the ultrasonically calendered cells. This provides substantial evidence towards the effectiveness of ultrasonic calendering on thicker cathode (an increase in coating loading from 16 mg cm⁻² to 20 mg cm⁻²). A drawback, which was also observed in the ultrasonic calendering of the thinner

cathodes, was the lower limit of porosity being 45 %. This porosity level is suboptimal; porosity values below 45 % are considered more favourable for performance. Future work towards reducing the porosity below this threshold should be prioritised.

The electrochemical performance for the thick cathodes was input into a rudimentary pouch cell scale-up model, along with data for the thin cathodes assessed in chapter 1 and 2. The model indicated the ultrasonically calendered cathode provided better energy densities for both thicknesses compared to uncalendered cathode. The ultrasonically calendered cells had better energy retention at 2C or 5C for both thicknesses, and the ultrasonically calendered thin cathode provided the best energy density at a 5C discharge, indicating its superior performance for higher rates.

This chapter's results have shown promise in the feasibility of ultrasonically calendering different cathode loadings, ranging from high-rate performance films to thicker cathode films, which are expected to have higher energy densities at the expense of lower rate performance.

7. Conclusion

This thesis introduces a novel manufacturing method for densifying cathode films, offering an alternative to the traditional calendering process. For the first time, ultrasonic processing, adapted from ultrasonic welding, has been employed to restructure dried slurry cast electrodes. This technique provides a broader range of controllable parameters compared to conventional calendering methods and has been effectively utilised to modify the cathode microstructure. Ultrasonically calendered cathodes exhibit a restructured pore network and pore size distribution, morphological changes in the conductive binder domain (CBD) phase, and enhanced electrochemical performance. The improved performance is evidenced by higher capacity retention at high C-rates without compromising specific capacity, demonstrating the cathode's potential for greater utilization in high-power applications. Furthermore, a mechanistic understanding of the ultrasonic calendering process is proposed, offering valuable insights into its impact on electrode architecture and functionality.

An ultrasonic welder was employed to compact cathodes, with a design-of-experiments approach used to assess its impact on electrode structure and electrochemical performance. The results revealed a spectrum of outcomes: some cathodes experienced negative effects, such as delamination and reduced rate performance, while others demonstrated positive effects, including enhanced rate performance. These findings indicate that the cathode's response to ultrasonic processing is highly dependent on the applied energy. Insufficient energy led to negligible performance benefits, a constructive amount of energy improved performance through structural optimization, and excessive energy resulted in structural degradation, delamination and performance loss.

Further investigation into ultrasonically calendered electrodes revealed two distinct pore size distributions with comparable overall porosity. This marks the first demonstration of a method capable of modifying the pore size distribution of an electrode while maintaining controlled porosity. With the exception of electrode templating techniques, which do not calender the electrode; to date, no prior methods have been reported that enable independent adjustment of pore size distribution for a given porosity in dry slurry-cast electrodes, emphasizing the novelty and potential of ultrasonic calendering in electrode design.

Symmetrical cell electrochemical impedance spectroscopy (EIS) provided valuable insights into the improved rate performance observed in ultrasonically calendered electrodes. The

measurements revealed a lower-than-expected effective ionic resistance, suggesting that the process results in reduced tortuosity within the electrode structure. Drawing on this information, the principles of ultrasonic welding, additional insights from SEM analysis indicating a novel conductive binder domain (CBD) morphology and infrared thermal measurements demonstrating significant heat generation during ultrasonic calendaring, the mechanism of ultrasonic calendaring was proposed: Ultrasonic oscillations transfer kinetic energy to electrode particles, generating frictional heat that melts the PVDF binder. The molten binder and vibrating motion from the process enable the restructuring of the electrode's microstructure.

Ultrasonic processing was applied to two cathode film thicknesses, 90 μm and 110 μm , both representing industrially relevant coating loadings. Both thicknesses exhibited enhanced electrochemical performance, surpassing that of uncalendered cathodes. The dimensional and electrochemical performance data of the cathodes were extrapolated to estimate the energy density of pouch cells, a format more representative of industrial applications. Although not as rigorous as some models, the analysis demonstrated that the 90 μm ultrasonically calendered cathode achieved the overall highest energy density at high C-rates and the greatest energy density among thinner cathodes. Similarly, the 110 μm ultrasonically calendered cathodes yielded the highest energy density at high C-rates within their class. These findings further bolster the potential of ultrasonic calendaring to optimise cathode structure for high-power lithium-ion battery applications.

8. Future work

This work explores the potential novel manufacturing stage in the production of lithium-ion cathodes. Despite its infancy, this approach demonstrated promising advancements through an alternative technique by physically modifying the electrode structure. The recent focus on mechanical processes, particularly targeting fibrillation of the electrode binder, has facilitated the development of first-generation dry cathodes. This research, alongside the industry emergence of dry electrodes, highlights the opportunity for the battery sector to leverage mechanical processing techniques to enhance the productivity and performance of electrodes.

This project investigated instances of a novel CBD morphology, characterized by a film-like structure and referred to as *melt morphologies*. Evidence supporting the formation of this new structure was obtained, suggesting that the polyvinylidene fluoride (PVDF) polymer within the CBD phase becomes more amorphous due to the kinetic and thermal energy imparted during ultrasonic calendering. This behaviour aligns with the expected crystallinity changes of the polymer during rapid melting and cooling. However, further evidence is needed to substantiate this hypothesis. Currently, technological limitations hinder the ability to confirm these structural changes. While X-ray diffraction (XRD) is a potential technique, its application in this context is challenging due to the small domain of the CBD within the electrode and the dominant diffraction signals from the high content of NMC622. Isolating the novel CBD phase from the active material, which would be challenging due to its role in providing mechanical strength, or an advancement in diffractive technology may provide a pathway to verify the PVDF polymer's crystallinity in this new morphology.

One of the challenges encountered during ultrasonic calendering was the inability to reduce the cathode porosity below 45 %, even when applying high pressure and extended weld times. This limitation may arise because the uncalendered cathodes possess preferable acoustic properties for propagating ultrasonic oscillations; however, these properties may change or diminish as the electrode porosity decreases. A deeper understanding of the electrode's response to ultrasonic energy could enable further reductions in the lower limit of porosity.

The interaction of ultrasonic energy with electrode particles is not extensively studied in literature and is recognized as an area requiring further investigation. Modelling techniques, such as the discrete element method (DEM), have proven effective in replicating and validating

the traditional calendering process. Extending DEM modelling to ultrasonic calendering could provide valuable insights; however, this approach demands a thorough understanding of the forces and interactions within the system, which are currently not well defined for ultrasonic systems.

An unexplored aspect of this project was the impact of ultrasonic vibration amplitude. In ultrasonic welding, substrate roughness strongly correlates with amplitude. While the amplitude was minimised in the design of experiments, it is recommended that further reductions be investigated, as the lowest amplitude possible with the ultrasonic welder significantly exceeded the cathode surface roughness. Designing an ultrasonic welder from the ground up to accommodate this change could provide valuable opportunities to advance this technique. Additionally, a second phase of development could involve exploring amplitude ramps, in which the amplitude is progressively reduced as the film densifies. This approach could align the input ultrasonic energy with the decreasing porosity of the electrode, potentially enhancing the effectiveness of the densification process.

Scalability is a critical factor for the further development of any new process. Ultrasonic calendering has demonstrated performance improvements at the lab-scale; however, a key limitation is its reliance on batch processing. Continuous ultrasonic welding is a well-established technique in certain industries and offers advantages for applications suitable to continuous processing. Due to the significant effort required to adapt the available ultrasonic welder for batch processing of cathodes, continuous ultrasonic calendering was excluded from the scope of this work. Traditional calendering, on the other hand, is inherently scalable, with larger rollers operating seamlessly in a continuous manner at all scales. Translating the lab-scale success of batch-process ultrasonic welding to a continuous ultrasonic welding system could provide a viable pathway to greater scalability. This potential solution warrants further investigation to assess its feasibility and effectiveness in an industrial context.

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Appendix

PVDF welding

Sample		Amplitude (%)	Weld Time (s)	Hold Time (s)	Cool Time (s)	Sonotrode Pressure (MPa)
1	a	50	0.50	0.1	0.4	14.8
	b					
2	a	50	0.35	0.1	0.4	14.8
	b					
3	a	50	0.20	0.1	0.4	14.8
	b					
4	a	50	0.65	0.1	0.4	14.8
	b					
5	a	100	0.50	0.1	0.4	14.8
	b					
6	a	100	0.35	0.1	0.4	14.8
	b					

Ultrasonic welder encoder data

The photograph shows a handheld electronic device displaying 'WELD RESULTS'. At the top right is a 'Print' button. Below the title, it says 'Preset0 *' and 'RUN: TIME = 0.300'. A table of data follows, with columns for Cycle#, Time (s), Weld Col (mm), Weld Abs (mm), and Energy (J). The data is listed for cycles 197 through 203. A red arrow points to the top right corner of the screen.

Cycle#:	Time (s)	Weld Col (mm)	Weld Abs (mm)	Energy (J)
203	0.300	0.02	22.66	30.3
202	0.500	0.04	22.68	70.7
201	0.500	0.04	22.67	72.9
200	0.500	0.04	22.67	72.6
199	0.500	0.04	22.67	68.8
198	0.500	0.04	22.67	71.7
197	0.500	0.04	22.64	67.5

Coin cells rate capability test data

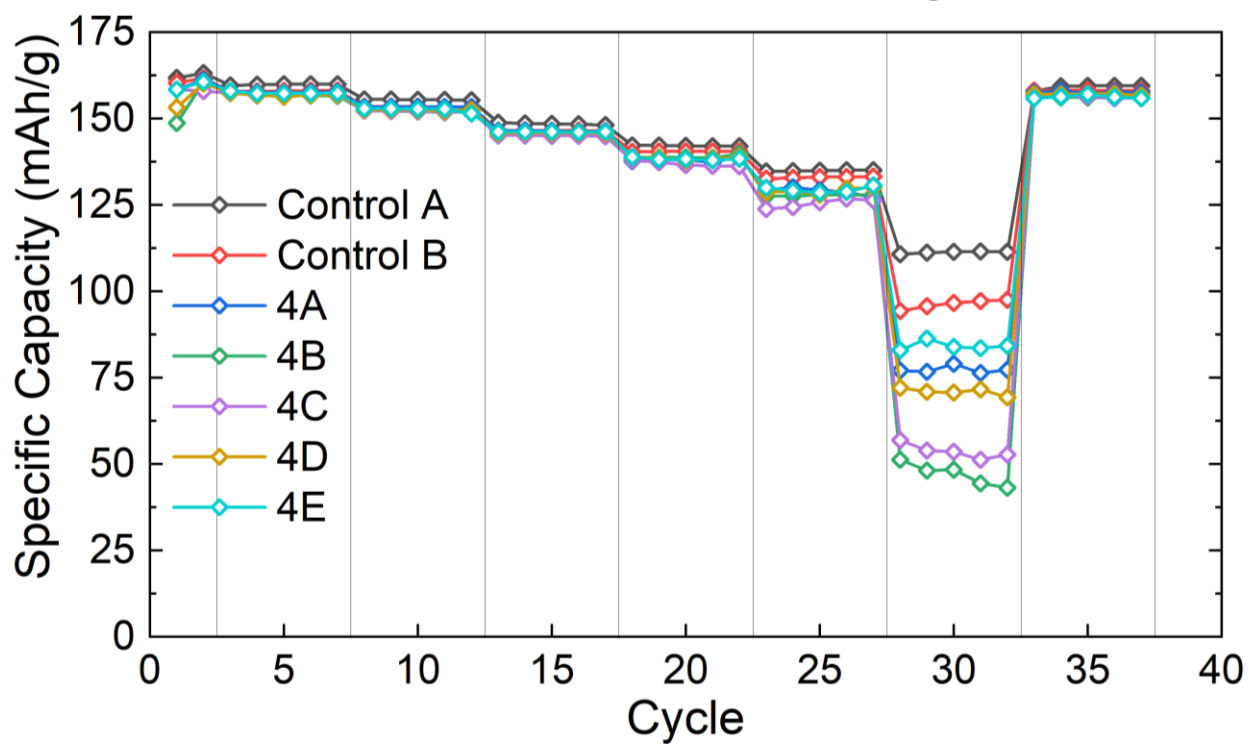
Cathode	Raw Mass (g)	Coating Weight (g)	Final Thickness (μm)	Final Porosity (%)	Capacity (mAh)
Uncal1	0.03293	0.02605	89	54.1	4.2
Uncal2	0.03334	0.02646	87	52.1	4.3

Uncal3	0.03310	0.02622	84	50.5	4.2
Uncal4	0.03381	0.02693	90	53.2	4.3
Uncal5	0.03301	0.02613	85	51.3	4.2
-	-	-	-	-	-
Conventional1	0.03280	0.02592	82	49.6	4.2
Conventional2	0.03267	0.02579	81	49.1	4.2
Conventional3	0.03311	0.02623	81	48.2	4.2
Conventional4	0.03301	0.02613	83	49.9	4.2
Conventional5	0.03243	0.02555	81	49.5	4.1
-	-	-	-	-	-
#1a	0.03010	0.02322	78	52.0	3.7
#1b	0.02982	0.02294	76	51.0	3.7
#1c	0.02985	0.02297	72	47.5	3.7
-	-	-	-	-	-
#2a	0.03430	0.02742	90	52.3	4.4
#2b	0.03398	0.02710	85	49.5	4.4
#2c	0.03481	0.02793	86	48.7	4.5
#2d	0.03367	0.02679	88	52.2	4.3
#2e	0.03465	0.02777	90	51.7	4.5
-	-	-	-	-	-
#3a	0.03489	0.02801	92	52.6	4.5
#3b	0.0339	0.02702	92	54.3	4.4
#3c	0.03478	0.02790	87	49.5	4.5
#3d	0.03398	0.02710	90	52.9	4.4
#3e	0.03480	0.02792	89	50.8	4.5
-	-	-	-	-	-
#4a	0.03404	0.02716	86	50.1	4.4
#4b	0.03415	0.02727	89	52.0	4.4
#4c	0.03427	0.02739	88	51.1	4.4
#4d	0.03337	0.02649	85	50.7	4.3
#4e	0.03368	0.02680	85	50.1	4.3
-	-	-	-	-	-
#5a	0.03167	0.02479	83	52.5	4.0
#5b	0.03234	0.02546	83	51.2	4.1
#5c	0.03208	0.02520	85	53.1	4.1
#5d	0.03192	0.02504	86	54.0	4.0
#5e	0.03195	0.02507	82	51.2	4.0
-	-	-	-	-	-

#6a	0.03214	0.02526	80	49.3	4.1
#6b	0.03600	0.02912	90	49.4	4.7
#6c	0.03588	0.02900	87	47.5	4.7
#6d	0.03736	0.03048	91	47.7	4.9
-	-	-	-	-	-
#7a	0.03164	0.02476	68	39.1	4.0
#7b	0.03130	0.02442	74	46.0	3.9
#7c	0.03239	0.02551	73	42.7	4.1

Old controls (made with setting #1 and setting #7 cells) and setting #4 cells rate performance

Old Controls Plotted with Setting 4 Cells



EIS Data for Cells (red indicates couldn't produce reasonable values for the response)

Cathode	R _b (Bulk) [Ω]	R _{cont} (contact) [Ω]	R _{ct} (Charge-transfer) [Ω]	5C Discharge (mAh/g)	R _b Error [%]	R _{cont} Error [%]	R _{ct} Error [%]
Uncal1	4.4	10.6	5.5	35	0.7	3.7	7.5
Uncal2	8.3	8.5	5.1	28	1.0	8.1	13.2
Uncal3	9.5	6.3	7.1	50	0.3	3.5	3.0
Uncal4	3.7	5.2	8.2	28	0.2	1.2	0.7
Uncal5	4.5	5.7	8.2	37	0.2	1.5	1.0
Uncal Average	5.2	7.5	6.7	35.6	2.1	14.6	22.5
Conv.1	4.1	5.6	6.5	63	0.3	2.5	2.4
Conv.2	11.3	10.9	6.2	29	0.6	5.0	8.7
Conv.3	5.1	7.7	6.6	51	0.4	3.3	3.5
Conv.4	4.6	6.1	13.1	35	0.2	2.3	1.0
Conv.5	3.1	7.2	11.0	39	0.3	2.0	1.2
Conv. Average	6.5	8.6	7.9	43.4	1.3	10.3	13.4
#2a	7.6	4.6	9.2	35	0.2	4.1	2.0
#2b	4.8	13.7	7.1	18	0.3	4.0	7.8
#2c	11.9	2.3	14.2	45	0.2	2.3	4.3
#2d	3.5	5.1	10.7	38	0.2	2.5	1.2
#2e	3.7	6.2	9.6	27	0.1	1.1	0.7
#2 Average	4.9	7.4	9.2	32.5	0.8	11.7	11.7
#3a	5.8	12.2	7.3	19	0.1	2.0	3.4
#3b	4.0	13.2	5.9	25	0.2	1.4	3.3
#3c	3.9	17.8	11.9	6	0.4	11.5	17.6
#3d	3.9	10.6	4.7	36	0.2	1.2	2.9
#3e	3.2	8.0	13.0	22	0.6	5.4	3.4
#3 Average	4.2	12.4	8.6	21.6	0.3	4.3	6.1
#4a	4.2	7.1	6.3	77	0.2	3.3	4.0
#4b	5.8	3.8	11.9	47	1.8	31.2	8.4
#4c	2.7	5.8	9.1	54	0.7	7.3	4.8
#4d	3.6	4.6	7.6	71	0.7	6.8	4.4
#4e	4.4	1.9	13.8	84	2.2	21.5	2.9
#4 Average	3.5	5.8	7.7	66.7	1.7	17.5	13.1
#5a	5.1	7.1	8.5	71	0.3	6.4	5.1
#5b	5.4	5.5	7.4	55	0.2	5.8	4.1
#5c	3.1	11.7	4.6	60	0.7	2.6	6.4
#5d	3.0	6.9	7.6	55	0.3	5.9	5.2
#5e	2.9	50.9	96.5	-	0.4	19.9	10.3
#5 Average	4.1	7.8	7.0	60.5	0.4	5.2	5.2
#6a	3.5	7.3	8.0	-	0.7	6.1	5.2
#6b	6.2	10.4	8.6	-	0.4	6.8	7.9
#6c	3.7	7.6	8.5	17	0.2	2.4	2.0
#6d	3.1	8.5	9.2	13	0.0	0.0	0.0
#6 Average	4.1	8.4	8.6	15.3	0.3	3.8	3.8

