

Effects of Stack Pressure on High Performance Lithium-Ion Batteries



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To my parents, who have never stopped encouraging me to find the path that makes me happy, no matter what country that leads me to.

To every mentor I have had over the years, thank you for pushing me to challenge my path and journey down the right one, even when it was the hardest.

To my partner, Brady, thank you for enduring every twist, turn, and reversal along this path without wavering in your support and encouragement.

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 20,000 words including appendices, bibliography, footnotes, tables and equations.

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Abstract

With the rapid acceleration of electrification in the automotive industry, the development of control systems and pack design must continue to keep pace. Pouch cells are a commonly used geometry in electric vehicles due to their high packing efficiency and therefore high volumetric energy density; however, the non-rigid casing provides an additional design parameter to consider. Previous works have shown that applying mechanical pressure to the through-plane surface of pouch cells can have both beneficial and detrimental effects on cell performance and lifetime. Despite this, there is little work exploring the implications of this performance difference when discussing battery models. Equivalent circuit models (ECMs) are a well-documented and frequently used battery modelling approach for lithium-ion cells due to their minimal parameterisation requirement, low computational complexity and flexibility compared to physics-based counterparts.

This thesis presents experimental results of two lithium cobalt oxide cells at different pressures. The experimental setup is presented alongside the considerations when designing the tests for pouch cells. The results for pressure variation, capacity measurements and resistance measurements are evaluated with a clear pressure dependency across all tests. The thesis then investigates the addition of pressure dependence to an ECM. The results presented show an improvement in fidelity of up to 68% when utilising a pressure-informed fitting method when compared to field standard implementation of the ECM that does not consider operating stack pressure. A single-RC model and a two-RC model are presented and compared, with the two-RC model showing improvement in fidelity, at the cost of computational cost, and execution time. Overall, this work provides justification that it is critical to consider the operating stack pressure when utilising equivalent circuit models for lithium-ion pouch cells.

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Acronyms / Abbreviations

MBPF Modular Battery Pressure Fixture

DCIR DC Internal Resistance

ECM Equivalent Circuit Model

HPPC Hybrid Pulse Power Characterisation

OCV Open-Circuit Voltage

P-OCV Pseudo Open-Circuit Voltage

PIECM Pressure Informed Equivalent Circuit Model

RC Resistor-Capacitor

RPT Reference Performance Test

SEI Solid Electrolyte Interphase

SOC State-of-Charge

SOH State-of-Health

Chapter 1

Introduction

1.1 Research Motivation

It is widely accepted that the effects of climate change that the world is experiencing require action to reduce carbon emissions across the globe. One of the ways to achieve this is through the electrification of the transport sector. Many governing bodies have committed to these initiatives, including the development of the Electric Vehicles Initiative coordinated by the International Energy Agency [1], which includes a commitment from 16 countries to support and accelerate the adoption of electric vehicles, particularly in the consumer sector [2]. In addition, many countries have made individual commitments to phase out sales of conventional combustion vehicles over the next few years. In the UK, sales of new petrol and diesel cars will be phased out by 2030 and all new cars and vans will be zero emission by 2035 [3, 4]. Figure 1.1 shows the commitments made by other governing bodies around the world. Many Original Equipment Manufacturers (OEMs) are following suit, focusing on the development and expansion of their electric fleets.

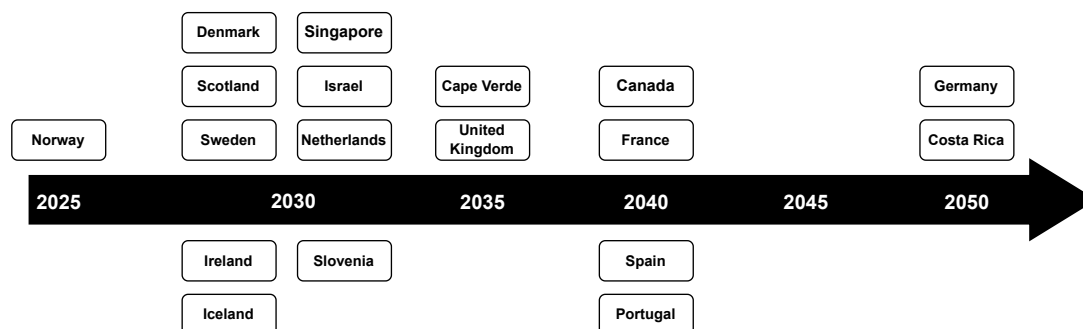


Fig. 1.1 Government targets for 100% zero-emission sales [2]

With this rapid adoption of electrification across the transport sector, it is incredibly important that new technologies are developed to keep up with this demand. Lithium-ion cells have been at the forefront of this movement due to their availability, cost-effectiveness, and integration into international electricity grids when compared to other energy storage solutions. The majority of electric vehicles on the consumer market currently use lithium-ion cells in their battery packs, but there are still concerns when it comes to developing reliable, performant, and safe battery systems that meet consumer needs [5]. These concerns often involve total cost and / or vehicle performance [6, 7].

Range anxiety, one of the most frequently cited concerns among consumers, is the worry that a vehicle will not be able to drive the necessary distance before requiring a charge or being stranded [6, 8]. This is because current lithium-ion batteries struggle to achieve both high energy density and high power density [9, 10] needed to achieve the desired energy requirements while maintaining consumer expectations when it comes to performance. Additionally, the lifespan of the battery pack is a major concern among consumers, as the degradation of lithium-ion cells is heavily dependent on the system's cyclic history and environmental conditions and therefore is difficult to predict exact capacity fade or catastrophic failure [11, 12, 13, 14]. Predicting the average use drive cycle and the accurate life of a pack is challenging due to the chaotic nature of human driving practices. Additionally, the complex nature of lithium-ion cells makes it difficult to extrapolate state-of-health estimations based on ageing tests completed in labs with degradation being highly path dependent [14, 12, 11, 13]. Path dependency is critical to consider across different applications with work being completed showing different mechanisms within battery testing resulting in different degradation results. Ma et al. [11] show a quantitative analysis of cell degradation being dependent on depth-of-discharge and frequency and severity of the thermal cycle. Su et al. [13] present results finding that degradation was dependent on temperature and state-of-charge in both static and non-static test conditions. Raj et al [14] identify that path dependency cannot look at calendar ageing or cyclic ageing independently.

Cost in both the economical and environmental sense remains the other key concern within the electrification of the transport sector. While the cost to produce lithium-ion battery packs has dropped and is projected to continue to decline over the next decade, there is still a large cost associated with the manufacturing of both cells and packs [15]. In addition to this, there is an environmental cost to many of the materials and processes that are required to manufacture these cells [15, 16, 17] including the emissions from the plants

that are manufacturing the cells and the emissions from mining of the materials [16]. While many researchers are working toward minimising both the economic and environmental cost, this confirms the need to also develop new solutions for current technologies that are available. It is well understood that the external stack pressure on lithium ion cells impacts the performance; however, quantifying these effects and investigating the impact on data-driven models has not been widely researched [18, 19, 20]. Evaluating these effects further and the modelling capabilities can provide a pathway to additional optimisation without changing cell chemistry or geometry.

Addressing these challenges can be sorted into two categories: cell chemistry and form factor, and pack design and control. Recent years have seen significant investment in cell chemistry and manufacturing research to produce cost-effective cells that are energy-dense and have a reasonable lifespan [2, 15]; however, it is important to acknowledge that there is still a long road to commercialising many of these solutions such as material availability and thermal and lifetime stability. As such, it is important to recognise the potential advancements that can be made with current technologies.

As there is a growing interest in electrification beyond commuting-level vehicles, there is a need for high-performance systems not only in consumer-level vehicles but also in hyper-cars, motorsport, and heavy-duty transportation. This demand has led to a need for high-performance lithium-ion cells that not only deliver high power but are also often weight-sensitive, necessitating high power density and high energy density. To address this issue, pouch cells are commonly used due to their high packing efficiency and stackable layer, as well as the resulting increased energy density [21]. As pouch cells become more prevalent due to these reasons, it is crucial that this additional design metric is not forgotten as it can have effects on not just the performance, but degradation as well. Pouch cells consist of a rectangular layered or wound electrode stack that is then packaged in a malleable metallic casing with a relatively low stiffness when compared to its cylindrical and prismatic counterparts, allowing for the benefits mentioned. The lack of stiff external casing requires the user to consider external stack pressure; however, external stack pressure is denoted as the pressure applied across the face of the pouch cell in the through-cell plane. As the cell is cycled this pressure will vary from factors as will be introduced later in this chapter. Despite this, there is little literature that considers this when developing models for lithium-ion cells, and the author is unaware of any data-driven models that currently consider stack pressure as a dependent variable within the model parameterisation. The work in this thesis addresses this gap through a methodology for experimental

data acquisition for data-driven parameterisation. In addition, it presents a pressure-informed equivalent circuit model. The remainder of this chapter will overview the necessary background information required to give context to the work presented.

1.2 Literature Review

Lithium-ion batteries are energy storage systems based on ion intercalation that facilitate energy exchange. They are an excellent solution for consumer electronics and automotive electrification due to their high energy density, relatively high safety, and low cost. The following subsection briefly introduces lithium-ion cell mechanics and chemistries to provide the necessary background for discussing the work within this thesis. Experimental methods and current modelling methodologies are then discussed and reviewed.

1.2.1 Lithium-Ion Cell Mechanics

Lithium-ion batteries provide an electric load through a redox reaction that sees a lithium-ion intercalate into porous electrodes, while the electron is supplied to the external circuit facilitated by an electrolyte. The following section provides an overview of each key component within a lithium-ion cell. A lithium-ion cell consists of five main components: the positive electrode, the negative electrode, the separator, the electrolyte, and the current collectors. Figure 1.2 shows a schematic, highlighting these components. The positive and negative electrodes will sometimes be referred to as cathode and anode; however, as this definition changes depending on the direction of the current, this work will maintain a positive and negative naming convention.

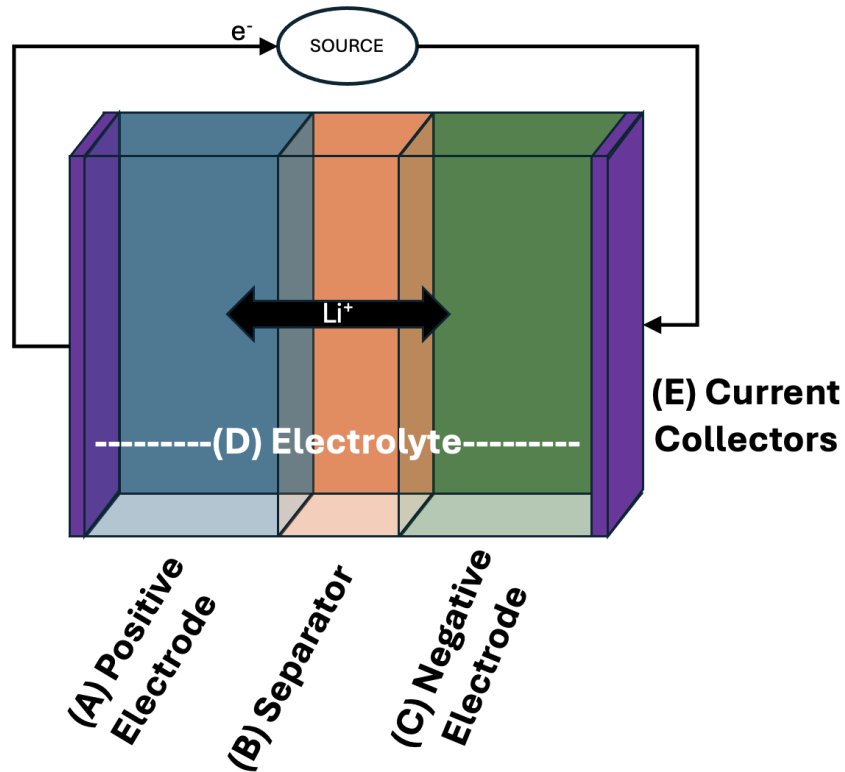


Fig. 1.2 Internal schematic of a single-layer lithium-ion cell showcasing the main components

The first two presented components are the positive and negative electrodes. Since the discovery of rechargeable Li-ion cells, there has been extensive research into electrode materials to improve performance and lifetime. Although not the focus of this thesis, it is important to cover the current state of the art and available materials for both the positive and negative electrodes as external stack pressure can have different effects based on electrode compositions. The positive electrode has been a key component in materials research over the years. Common material compositions include lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), and lithium nickel manganese cobalt oxide (NMC). Table 1.1 presents the average capacity, potential, and energy density for common positive active materials from Armand et al [22].

Table 1.1 Key parameters for common positive active materials [22]

Material	Practical Specific Capacity mAh g ⁻¹	Average Potential V vs. Li ⁺ /Li	Specific Energy Wh kg ⁻¹
LCO	150	3.90	402
LMO	110	4.10	337
LFP	165	3.45	379
NMC ₅₃₂	165	3.70	407
NMC ₈₁₁	190	3.70	448

Each material composition has advantages and disadvantages, but they all provide a method for lithium to (de)intercalate. In high-power applications, the focus is on increasing energy and power density while maintaining safety and operational stability. High voltage positive electrodes are a key candidate for achieving this goal by having a larger operating range, resulting in higher available energy thus a higher energy density. Li et al. provide an overview of recent progress in this area [23].

The negative electrode is typically a graphite composition, which consists of multiple layers of hexagonal C6 graphene stacked on top of each other. This structure allows lithium ions to be intercalated into these layers. A common alternative is a blended Silicon/Graphite electrode but comes with additional complications. While Silicon offers the opportunity of a higher energy density, it currently suffers a very low cycle life, partially due to volumetric expansion of up to 400% which results in significant strain within the material [24]. Although other negative electrode materials exist, such as niobium, tungsten, and silicon, they do not offer the energy and power densities required for high-performance applications or are not currently commercially available. The electrolyte facilitates the exchange of ions between the electrodes. The electrolyte is typically a liquid solution containing dissolved chemicals, often a salt, which provides the necessary conductivity. The electrolyte must not be electrically conductive and stable at operating voltages. An alternative solution that is currently being explored is solid-state electrolytes where the electrolyte is a solid instead of a liquid. Solid-state batteries provide the opportunity for a safer battery due to flammability and electrolyte leakage not being an issue while providing the opportunity to have a lithium-metal anode which would greatly increase the energy density of the battery [25]. There are still many challenges faced by this transition; however.

Notably, the requirements of very high stack pressures of up to 400 MPa to ensure cycle life and performance [26, 27]. This further emphasises the need to have a robust methodology for testing and modelling with external stack pressure within the system. The separator, although containing no active material, plays a vital role in the operation of the cell. The separator is a mechanical microporous material that electrically isolates the positive and negative electrodes and is also ionically conductive. This enables lithium intercalation while preventing short circuits within the cell.

Although lithium-ion cells share the above orientation, they can come in a variety of form factors. Four common commercial form factors are coin, cylindrical, prismatic, and pouch, as shown in Figure 1.3.

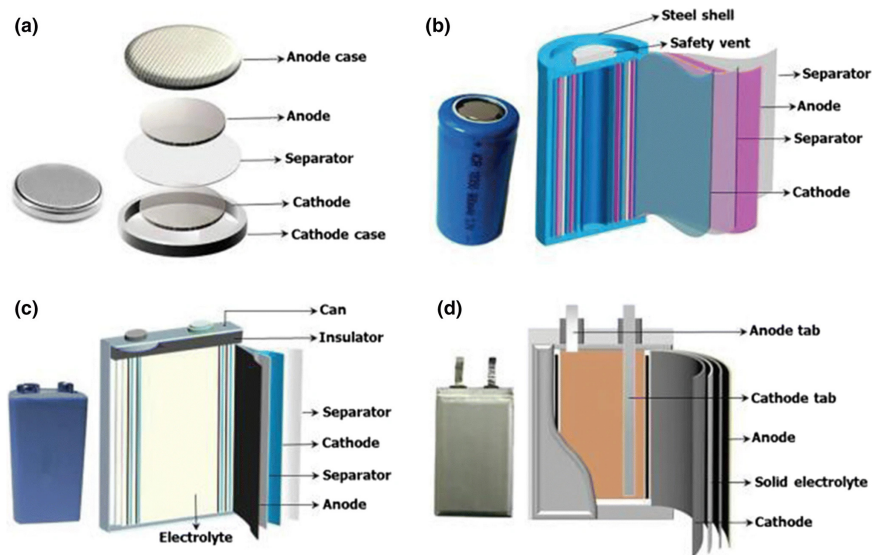


Fig. 1.3 Cross-sectional representation of lithium-ion cell form factors (a) coin (b) cylindrical (c) prismatic (d) pouch [28]

The first form factor discussed is the coin cell. Coin cells are typically single-layer cells that are often used as proof of concept and prototype cells. Cylindrical cells are currently one of the most common form factors for automotive applications. The stacks are assembled as a sheet and rolled to fit within the rigid can to contain the cell. This results in positive and negative tabs on opposite sides of the canister, often resulting in very high internal resistance due to tab placements. Additionally, cylindrical cells are cheap to manufacture on a production scale. One reason for this is the ability to create electrode stacks at large scale which is then wound and cut before being placed in a rigid casing. Prismatic cells are similar to cylindrical cells but are enclosed in a rectangular hard case. They are often used in high-power applications because of their high capacity, but they also

have high resistances and low power densities. The final form factor is the pouch cell, which is a flat cell that can have either stacked or wound electrodes and is contained in a soft pouch, typically made from an aluminium alloy. Pouch cells generally have lower internal DC resistances and can be assembled into packs with high efficiency due to their relatively soft casing and rectangular shape [21]. As a result of these advantages, pouch cells are common in high-performance situations. Conversely, pouch cells tend to have a much higher cost. One reason is an additional stack in the manufacturing process of releasing initial off-gassing from the formation cycles that is accounted for through pressure relief valves in cylindrical cells.

1.2.2 Stack Pressure Influence on Cell Performance

It is well documented that lithium-ion cells undergo expansion and contraction during cycling and cycle life [18, 19, 20]. A component of this is due to the intercalation of lithium into graphite [29, 30, 31]. In form factors such as cylindrical and prismatic, this expansion creates an inherent pressure across the electrodes as the casing prevents most expansion [32, 33, 34]. Furthermore, Mohan et al. observed stress in prismatic hard cases and used a bulk force model based on this stress to model the state of charge [20]. Mussa et al. showed a high likelihood of accelerated degradation as high-stress points within these electrodes [35]. Pouch cells present a unique situation as the constraint comes from the design of the pack rather than the design of the cell. Seigel et al. investigated the relationship between cell expansion and different cell mechanisms such as state of charge and current rate [36]. Wünsch et al. investigated three different methods of applying stack pressure to automotive pouch cells: fixed displacement (no expansion), six compression pads, and four springs, and compared them to an unpressurised system [37]. This study found that 80% more cycles could be achieved with a spring system compared to the unpressurised system. Mussa et al. investigate the effect of external stack pressure on the ageing of 1.4Ah pouch cells [35]. They show that the addition of stack pressure improves electrical contact within the cell; however, there is an optimum pressure and higher pressures can mechanically damage the cells. They also discuss the negative influence of inhomogeneous pressure across the electrodes. Leonard et al. investigate different methods of applying stack pressure, in particular, the effects of a constant displacement method compared to a constant pressure method using pneumatics [38]. They show that applying pressure reduces internal resistance measurements, with benefits in both systems. The study highlights the additional benefits of

the constant pressure method during cycling. While there is much evidence that applying stack pressure to pouch cells as discussed, further evidence suggests that high stack pressures can reduce ionic conductivity and lead to higher reversible lithium loss [35] and the likelihood of lithium deposition on the graphite surface of the negative electrode [39].

1.2.3 Lithium-Ion Battery Test Methods

Experimental testing is crucial for prototyping and validating cell performance, as well as providing parameters and boundary conditions for models. Parameter identification is necessary for all models at varying levels of complexity depending on the scale of the system. This work focuses on full-cell, non-destructive testing of lithium-ion batteries. Model characterisations from full-cell data involve cycling cells through a variety of test protocols to obtain an accurate representation of cell performance under various conditions. Non-destructive testing will limit the available data to externally measurable parameters including current, temperature, and voltage. Developing experimental processes for lithium-ion cells requires careful consideration of safety measures and accurate system representation. The equipment utilised for this work was not designed to handle catastrophic failures such as thermal runaway, and as such, significant safety margins were included. Guidance from the manufacturer was minimal with recommendations not to exceed 1 MPa. As the material of the separator was not known, external stack pressures were kept to below 50% of the recommended 1 MPa. The following subsections provide an overview of some of the current state-of-the-art methods within full-cell non-destructive testing needed for parameter identification of an equivalent circuit data-driven model. Throughout this section, C-Rate notation will be utilised as a normalising factor across cell models. C-Rate represents the amount of current load that will result in a cell being discharged in one hour and can be calculated as per equation 1.1.

$$C_{rate} = \frac{I}{Q_{cell}} \quad (1.1)$$

where I is the current load, and Q_{cell} is the capacity of the cell. Notationally, this is represented as xC, where x is the load value (i.e. 1C, C/40).

1.2.3.1 Open Circuit Potential Estimation

The test method presented is the open circuit potential (OCP) estimation. Open circuit potential is the voltage at equilibrium measured against state-of-charge and is presented at both the electrode level and full cell level [40]. At the electrode level, this represents the voltage against a reference, often lithium metal, and represents the lithiation within the electrode [40]. Full cell open circuit potential, referred to more commonly as open circuit voltage (OCV), is the difference between the electrode potentials at equilibrium [41]. As it is a function of the electrode design, OCV will be different for every cell model; however, there are often trends visible in similar chemistries [40]. All models will utilise some form of OCV, either at the electrode level or full cell level depending on the underlying mechanics present in the model with physics-based models such as the single particle model utilising electrode OCP and data-driven models utilising full cell. While electrode OCP provides a wealth of information, including degradation information, it is a destructive process and must be done in an inert environment [42, 43, 44, 40]. As such, utilising full-cell experimental data is very attractive and is what is used in this work. Conventionally, there are two experimental methods used to identify the OCV. The first is known as the pseudo-OCV test. The pseudo-OCV test performs a very slow discharge followed by a very slow charge. The goal of this is to minimise polarisation to represent the equilibrium state as closely as possible while also minimising losses due to ohmic heating. There is often a trade-off in pseudo-OCV testing between accuracy and time as most tests are completed at a rate between $C/20$ and $C/30$ [40, 45, 46, 47]. It is important to note that while low-rate cycling may minimise certain effects, hysteresis will still be present and must be accounted for, otherwise there will be an additional error in the identified OCV parametric function.

Alternatively, the Galvanostatic Intermittent Titration Technique (GITT) provides a method to capture OCV without the reaction dynamics through discharging at relatively slow rates to a known state of charge (SOC) and allowing sufficient time for the cell dynamics to relax, resulting in a voltage reading at a known SOC. This test provides a considerable amount of flexibility regarding fidelity as (dis)charge rate, SOC step, and relaxation time can all be varied to fit the needs of the user. The FreedomCAR standard recommended 10% SOC steps, with a relaxation period of 1-hour [48]; however, some literature contradicts this recommendation and suggests relaxation periods of up to 4 hours [41, 49]. Kindermann et al. presented results showing after 40 hours an LFP cell shows deviation from a relaxed state [50]. GITT testing can also cause

issues as interpolation must happen between achieved points and can result in an artificially smoothed curve. GITT testing can provide important information regarding diffusion into the electrodes that can be beneficial when developing a model parameterisation.

1.2.3.2 Dynamic Performance Tests

In addition to the more static open-circuit voltage testing, dynamic tests are also required. Lithium-ion cells have complex dynamics that must be captured across an array of operating conditions to provide the necessary responses for performance optimisation and modelling parameterisation. A commonly performed test is the high rate capacity test, also known as constant current or high discharge testing [40]. This test involves applying a constant current at different rates depending on the cell's design and chemistry. It is often conducted at varying depths of discharge and temperatures to provide insight into the cell's performance across a diverse operating space. High-rate capacity tests allow a relatively quick test that provides information into the dynamic response of the system at varying operating conditions. Additionally, it provides available energy at these differing operating conditions.

Another common dynamic test is the Hybrid Pulse Power Characterisation (HPPC), first introduced by the United States Advanced Battery Consortium LLC (USABC) in 1996 [51] as a peak power test. This test was developed to test performance over varying depths of discharge at high current rates. Since then the HPPC has been adopted by many in various iterations, most notably by the updated FREEDOMCAR regulations [40, 48, 47]. The HPPC uses a square wave charge pulse for 10 seconds followed by a 40-second rest, then a 10-second discharge followed by a 40-second rest. Bialon et al. investigated the use of a 60-second pulse due to the slower time constant of lithium iron phosphate cells [52]. Barai et al. present an in-depth review of the effect of time scale on pulse length with an experimental pulse time of 18 seconds [53].

The above tests are often combined to form a reference performance test (RPT). This test procedure provides a snapshot of the battery's state at a particular time. An RPT aims to provide insight into how a battery is degrading over time. This allows for a better understanding of design and control development as well as ensuring safe operation throughout. Timing reference performance tests is often a matter of desired fidelity and time available, as it typically take 2 - 4 days to complete, depending on the inclusion of an open-circuit voltage test. In addition, it can often be unknown with new cell developments as to what the

ideal RPT interval is, which can result in either missed key indicators such as a knee point, or unnecessary data collection. RPTs can also add artificial cycles to the cycle count as a cell will typically see 2-3 equivalent full cycles during the process.

It is important to consider and thoughtfully develop experimental procedures when testing lithium-ion cells. Capturing the required data while maintaining data integrity and cell safety is paramount to gathering high-quality data. The experimental procedures used in this work are described in detail in chapter [refchap:exp](#).

1.2.4 Lithium-Ion Battery Modelling

As discussed previously, lithium-ion batteries are complex electrochemical systems that are ideal for applications such as consumer electronics and e-mobility. Battery models are necessary for control optimization and safe operation, as well as design optimization. Currently, two main methods are in use: data-driven and physics-based. The following sections will introduce the fundamental principles for both types of methods and evaluate the current techniques used in the field and industry.

1.2.4.1 Data-driven battery models

Data-driven battery models utilise experimental data to systematically fit parameters to a representative model that reflects the behaviour of the battery. These models are typically simplified systems that focus on measurable parameters of the full cell and basic dynamics. Utilising data-driven models has many benefits, including the non-invasive parametrisation of the model and low computational costs. As a result, they are a popular choice for commercial manufacturers of battery management systems. Equivalent Circuit Models (ECMs) are the most widely used empirical model, as cited in several studies [54, 55, 56, 57, 58]. ECMs use standard electrical circuit components to create a model that accurately reflects the behaviour of a system. At its most basic, an equivalent circuit model consists of an Open-Circuit Potential (OCP) voltage source with a series resistor that represents the internal DC resistance of the cell. To capture the diffusion of the lithium ions through the electrolyte into the electrode, an RC circuit, which stands for resistance-capacitor circuit, is added. This simple circuit is shown in Figure 1.4 below.

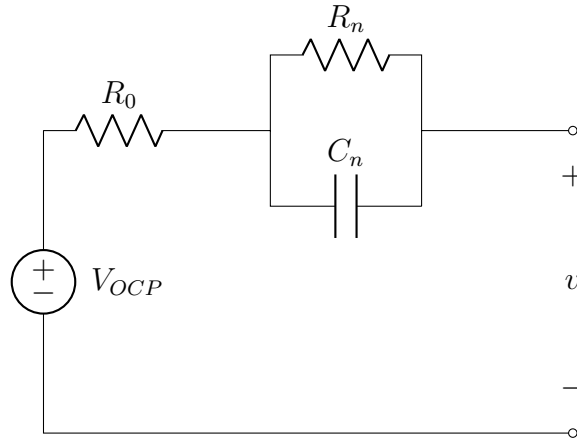


Fig. 1.4 Circuit diagram showing a basic equivalent circuit model with a single RC pair commonly used for control systems in the automotive industry

The theory and derivation of the governing equations are further developed in Chapter 3. Due to the popularity of this model, there have been many extensions to the model itself to increase fidelity and to better capture the dynamics within a lithium-ion cell. Plett has presented many of these model variations [55]. The first model presented here is the combined model, which uses the state of charge as a known battery state and fits polarisation resistance (K_i) and constants (K_1, K_2, K_3) into the model to predict the terminal voltage. Plett extends this to the Simple Model, which introduces a further dependence on current [55]. This is then extended to include hysteresis as a dependency within the model, again improving the accuracy of the model [55]. An additional method sometimes used to capture this phenomenon is to take an average of the charge and discharge open circuit potentials; however, this assumes that hysteresis is symmetric about each state-of-charge point and introduces further error into the model. Plett introduces the Enhanced Self-Correcting Model (ESC), which introduces a hysteresis element that acts as a correction factor to the predicted cell endpoint voltage [59].

ECMs are widely used in control optimization and development with varying degrees of complexity. Hu et al. presented a rapid calibration technique for optimizing the parameters of the model using a 2RC Thevenin circuit [57]. Although there have been many attempts at improvements, there are diminishing returns to the complexity of an ECM when evaluating fidelity versus computational load. Computational load is one of the key benefits of using an ECM. Hu et al. [58] conducted a comprehensive review of 12 different ECM models and concluded that a single RC model is optimal for LiNMC cells. Hu [58] also shows that

for LiFePO_4 , a single RC with 1-stage hysteresis is optimal due to increased hysteresis.

1.2.4.2 Physics-Based Lithium-Ion Battery Models

Although this work focuses on the data-driven side of modelling and experimentation, it is important to provide an overview of other modelling methods currently available. Therefore, a brief introduction to physics-based battery models is presented. In contrast, physics-based models derive the behaviour and mechanisms inside a cell and represent the behaviour through a series of partial differential equations. The Pseudo-2D (P2D) model, also known as the Doyle-Fuller-Newman (DFN) model, is the most common physics-based battery model. It was initially published by Fuller et al in 1994 [60]. The model is based on the Butler-Volmer kinetics, porous electrode theory, and concentration solution theory [61]. The text provides insights into the mechanisms within the cell, including lithium diffusion and electrochemical kinetics, and serves as the basis for many other models. However, the P2D model requires extensive parameterization that is both destructive and requires specialized equipment. Its computational complexity also makes it challenging to implement in real-time applications, such as battery management systems. Therefore, it and the common derivations are not considered for this work.

1.3 Thesis Outline

The rest of this thesis is presented as follows. Chapter 2 discusses the experimental methodology used, including the design of a novel fixture for high-quality data acquisition. It then discusses the results from two cell models and the performance effects of varied stack pressure. Chapter 3 then covers the derivation and implementation of an equivalent circuit model. Parameter fitting methodologies with pressure considerations are completed before the results are presented. Finally, a conclusion over-viewing the work is given.

Chapter 2

Experimental Methods

There are many considerations when developing test methods for lithium-ion cells. Test apparatus must be developed to ensure that repeatable, safe, and accurate results are obtained. For cylindrical and prismatic cells, ensuring a repeatable and relevant setup is relatively straightforward, with the main consideration being ensuring adequate connection to the terminals. However, for pouch cells, there is an additional consideration as there is no rigid casing to constrain the expansion. As discussed in the literature review in section 1.2, this can lead to premature degradation within the cells and even catastrophic failures such as electrolyte gassing and electrode delamination [19, 62]. While there has been a great deal of work demonstrating the benefits of stack pressure, there is still much debate about the optimum stack pressure for pouch cells [35, 63, 19, 64, 37]. It is essential to have a robust methodology to investigate this and to ensure that the data obtained is suitable for use in empirical models. This chapter discusses the experimental setup and methods developed to investigate the dependence of stack pressure on high-performance pouch cells and the results obtained.

2.1 Experimental Methodology

There are many methods of applying external stack pressure to a pouch cell, but they can generally be divided into two operating methods: constant displacement and constant pressure. A constant displacement fixture enforces a constant cell thickness, resulting in variable pressure across the cell face as the cell is cycled and ages [38, 19, 65]. This method can result in uncontrolled heterogeneous pressure across the cell surface as well as uncontrolled pressure throughout the operation. Despite these potential difficulties, this method is much easier to implement and requires minimal components, making it an attractive solution

at the OEM level. Constant displacement requires two main considerations: either the initial pressurised condition or the overall thickness, and stiffness of the constraining structure. The second method, constant pressure, also requires a method to account for both the cyclical expansion as well as the irreversible expansion from aging. This is most commonly a spring system [63, 66, 37, 64] or pneumatics [38, 67]. Leonard et al. [38] investigate the performance differences between constant pressure and constant displacement and present results from two different fixture setups. Constant displacement was chosen for this study due to its ease of implementation and adherence to current industry standard methods.

2.1.1 Cell Specification & Experimental Fixture

As pouch cells are often utilised as a high-performance solution as discussed in section 1.1, it was desired to have cells for the experimental testing that reflected this. Two cells were used in the experiments: a 5.5 Ah LiCoO₂/graphite cell and a 3.7 Ah LiCoO₂/graphite cell. These cells were selected for their high-performance capabilities and relatively short specified life of ≥ 100 cycles to 80% state-of-health due to the manufacturer prioritising performance over longevity, as this would help to achieve potential degradation results over a shorter time scale. The selected cells have the shorter life span due to the manufacturer prioritising high power, short term application such as motorsport over longevity making them a good candidate for this work. In addition, the 3.7 Ah cell is a high-voltage cell with a higher maximum operating voltage, providing a higher nominal energy density. The cell specifications are shown in Table 2.1. The data sheets for cell model (1) and cell model (2) can be found in Appendix A and Appendix B respectively.

Table 2.1 Rated cell specifications for Melasta SLPB7336128HV & Melasta SLPBA442124

	Cell Model	Chemistry	Nominal Voltage [V]	Initial AC Impedance [$m\Omega$]	Nominal Capacity [Ah]
Cell Model (1)	Melasta SLPB 7336128HV	LCO	3.8	≤ 2.6	3.7
Cell Model (2)	Melasta SLPB A442124	LCO	3.7	< 2.0	5.5

Currently, there is not a commercially available fixture for testing lithium-ion pouch cells that are constrained under an external stack pressure. To facilitate the work in this thesis, the Modular Battery Pressure Fixture (MBPF) [68] was developed for this work as a low-cost, robust method to complete constant displacement testing of lithium-ion pouch cells. The fixture prioritised safety, modularity, and repeatability to allow for a large design of experiments with one fixture. The fixture can be seen in Figure 2.1 with drawings and CAD available in the open-source GitHub repository [68].

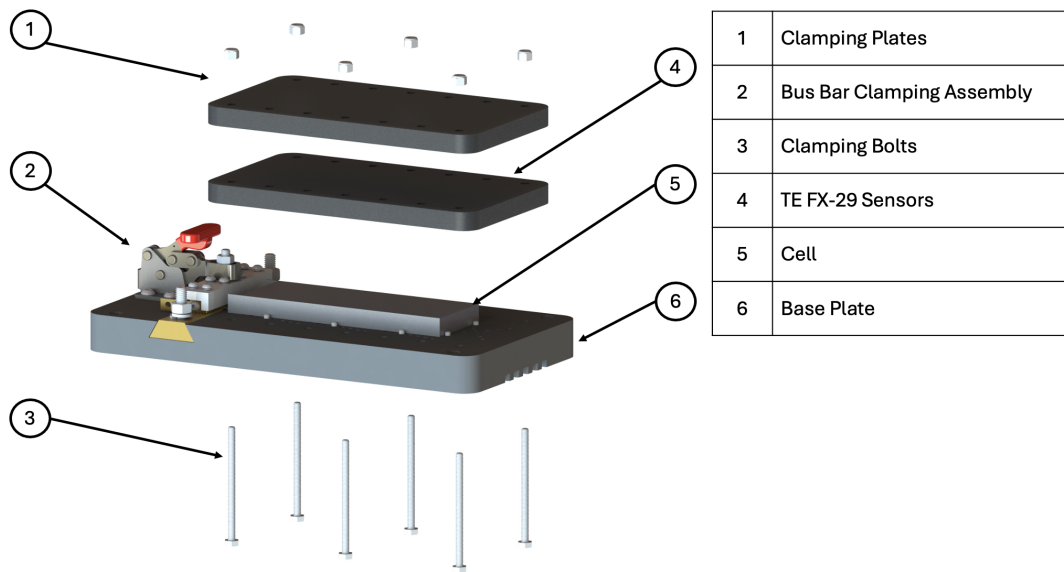


Fig. 2.1 Modular Battery Pressure Fixture Schematic

The fixture consists of 6 main components. Item (6) shows the base plate that constrains the bottom busbar and a toggle clamp that houses the upper busbar through spring force to ensure adequate contact (item (2)). In addition, the base plate is compatible with t-slots for rigid mounting into thermal chambers to provide further safety. A current load is provided through a busbar clamping system that connects to the equipment (2). The busbars are gold-plated copper to promote electrical conductivity with minimal oxidation. Two plates are used to apply pressure to the top face of the cells (1). Two TE FX-29 force sensors were used in this work with stainless steel disks used to improve force distribution through the plates and prevent damage to the pressure plates (4). A Teensy 4.1 microcontroller was used for sensor integration with all data collected on a microSD card [69]. Scripts were written utilising Arduino for data acquisition. A circuit diagram and the code developed can be found in Appendix C. The sensors were placed equidistantly from the top and bottom of the cell to ensure

adequate distribution when setting and measuring pressure as shown in figure 2.2.

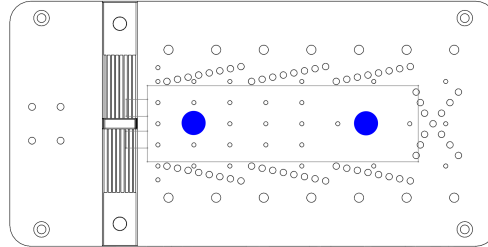


Fig. 2.2 Sensor placement for the MBPF [68]

The base and pressure plates were machined from Tufnol for the electric and thermal insulating properties. The base plate additionally provides channels that allow for thermocouple integration across the surface of the cell as seen in Figure 2.3. The holes are 2mm in diameter, allowing for type-T thermocouples to be used with minimal impact on the pressure being applied across the cells. Type-T thermocouples were chosen for their high accuracy and good relative linearity and in the operating regions of the testing. The author did not observe any visual markers at the locations of the holes across the cells throughout any of the experimental testing in this work but acknowledges that higher pressures could result in heterogeneous pressure across the base and 'hot spots' in the electrode materials at these locations. Minimal temperature variation is expected due to the low impedance of both cells and as such it is assumed the expansion is mainly due to intercalation and not temperature effects.



Fig. 2.3 MBPF base plate showing incorporated thermocouple channels

2.1.2 Experimental Procedure

The following section discusses the experimental protocol that was used to observe the performance effects of stack pressure across the two high-power pouch cells. Testing was completed using an Arbin LBT-21084-HC 60A 8-channel cell cycler with cells placed in a Binder KB115 thermal chamber with a minimum of 1-hour rest to allow for temperature saturation. Before performance testing, cells were subjected to five conditioning cycles that consisted of a 1C discharge and 0.5C charge. This promoted initial SEI growth, as well as verified that the manufacturing variance between the cells was low.

Testing was completed for both cells at three pressures. Initial testing was completed on cell model (1) at 47 kPa, 140 kPa, and 210 kPa to represent low, medium, and high pressures. Pressures were set at 100% SOC before allowing for 1 hour of relaxation to allow the system to come to an equilibrium state. Cell model (2) was tested at 0 kPa, 50 kPa, and 100 kPa. As constant displacement was utilised as the constraint method, there is variation over both charge & discharge, as well as over life which will further be reviewed in the results section. Testing conditions for each cell are shown in Table 2.2.

Table 2.2 External stack pressure test conditions for cell model (1) and cell model (2)

	Low Pressure	Mid Pressure	High Pressure
Cell Model (1)	47 kPa	140 kPa	210 kPa
Cell Model (2)	0 kPa	50 kPa	100 kPa

2.1.2.1 Pressure Variation

The first thing that was investigated was the variation in stack pressure across state-of-charge points due to negative electrode expansion from lithium intercalation. As graphite undergoes a large volume change when lithium ions are intercalated when compared to Lithium-Cobalt-Oxide, it is expected that cells will experience higher stack pressures at higher states of charge when the graphite is fully intercalated [31]. In addition, it is expected that as the cell ages, it will expand due to irreversible loss of lithium inventory into the electrodes due to SEI growth and lithium plating. A slow discharge was included within the reference performance test to provide a baseline to investigate pressure change over state-of-charge.

2.1.2.2 Hybrid Pulse Power Characterisation

As introduced in section 1.2.3, the Hybrid Pulse Power Characterisation (HPPC) test is a key protocol in characterising the available power in lithium-ion batteries over state-of-charge. As per the FREEDOMCAR standard [48], the charge pulse amplitude is determined from a 0.75 multiplier on the discharge pulse amplitude. Due to the high power nature of the cells being tested, the HPPC tests were performed at the maximum rate for both charge (C_{max}) and discharge (D_{max}) to better capture the cell dynamics at the cells maximum operating capabilities for applied current. A nominal representation of the square profile can be seen in Figure 2.4 with an example voltage response presented in Figure 2.5.

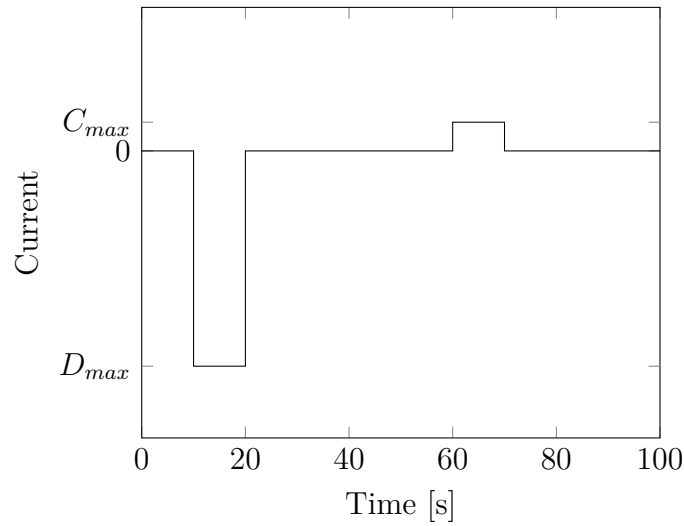


Fig. 2.4 Representative HPPC pulse

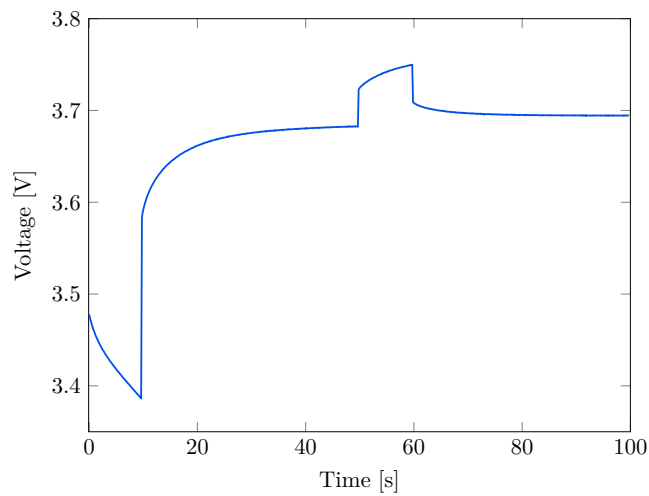


Fig. 2.5 Example Voltage Response from an HPPC Pulse

Initially, cell model (1) was tested every 10% SOC from 100% SOC to 10% SOC. Cell model (2) was tested every 5% SOC from 100% SOC to 5% SOC to provide additional data points for degradation investigation. After the pulse profile, the cell is discharged at C/2 to the next step. The test protocol for a standard HPPC test is presented in Table 2.3.

Table 2.3 Hybrid Pulse Power Characterisation test protocol

Step	Procedure
1.	Rest for 10 seconds
2.	Discharge at $D_{\max}$ for 10 seconds
3.	Rest for 40 seconds
4.	Charge at $C_{\max}$ for 10 seconds
5.	Rest for 40 seconds
6.	Discharge at C/2 until next SOC point
7.	Rest for 1 hour

This test provides a wealth of information often associated with state-of-charge estimation but also provides insight into internal ohmic resistance and charge transfer and diffusion kinetics [53]. It is important to note that this measurement is sensitive to many parameters, in particular temperature, pulse length, applied current load, stack pressure, and state of charge. For this thesis, temperature, pulse length, and load are normalised to allow the isolation of stack pressure effects.

There are two main parameters evaluated by HPPC pulses: resistance and power. When evaluating HPPC pulses for resistance, three main phases can be visualised: ohmic resistance, charge transfer resistance, and polarisation resistance [53]. It should be noted that these phases are difficult to identify accurately and are very sensitive to cell design. For this reason, the three resistances are combined and referred to simply as lumped resistance. Resistance (R) can be obtained by measuring the voltage response to the applied current. From this, the resistance can be calculated using Ohm's law as shown in the equation 2.1.

$$R = \frac{\Delta V}{\Delta I} \quad (2.1)$$

DC internal resistance (DCIR) will also be encountered later in this chapter. This term is taken directly from the Arbin cell cycler and the principle is the same; however, the user only specifies the current amplitude, not duration. The cycler takes the amplitude, applies it over a short period of time and will then provide the user with the calculated DCIR value. Both metrics are evaluated; however, as DCIR is only measured at 100% SOC, it will only be used to investigate the state of health.

Power can also be investigated throughout the pulse with stack pressure as a function. Whilst this is directly related to resistance, as increased resistance correlates with lost power, it is also often useful to visualise and investigate. This can be extracted from the test using the Equation 2.2.

$$P = VI \quad (2.2)$$

where P is the power, V is an instantaneous voltage, and I is an instantaneous current. This equation can be utilised to look at different power metrics depending on the current and voltage selected, such as maximum, average, or minimum power over a pulse, alongside the instantaneous power at any point. Particularly in high-power applications, state-of-power is often a critical design and control parameter. This becomes an increasing issue at high states of charge, which is a critical consideration when looking at fast charging situations, and at low states of charge for high power requirements such as heavy-duty vehicles or motorsport applications. In addition, this can inform cooling design requirements, which affects the use case at both a performance and safety level. In Chapter 3, HPPC pulses are used to fit empirical models.

2.1.2.3 Cyclic Ageing

As mentioned in Section 1.2, there is evidence that pouch cells have an extended life when stack pressure is applied; however, there is little evidence as to the optimal pressure to apply [21, 18, 19, 63, 35, 37]. Following the promising results of the cell model (1), cyclic ageing was added to the experimental protocol in an attempt to quantify the benefits of stack pressure when cycling cells. The cells used were rated for > 100 cycles at 0.5C charge and max discharge and were therefore considered to be good candidates for cyclic ageing experiments. There are two main components to cyclic ageing: Reference Performance Testing and

Aging Protocol. The first component, the Reference Performance Test (RPT), consists of varying tests that are repeated at different points in the ageing process to provide consistent performance metrics to compare. This often includes a standard charge and discharge, as well as a high-performance characterisation, in this case, an HPPC test. The RPT used in this work is presented in Table 2.4.

Table 2.4 Reference performance test protocol

Step	Procedure
1.	Discharge cell at 1C until $V_{\min}$
2.	Rest for 30 minutes
3.	Charge at 0.5C until $V_{\max}$, hold at $V_{\max}$ until C/20
4.	Rest for 30 minutes
5.	Perform HPPC as per Table 2.3

The second component of cyclic ageing is the cycling between RPT tests. Depending on the desired outcome of the test, this can vary greatly. For this protocol, the desire was to age the cells as quickly as possible in a safe and repeatable manner. As such, the cells were cycled slightly below the maximum specification to ensure safe operation. The protocol used can be found in Table 2.5.

Table 2.5 Cyclic aging performance protocol

Step	Procedure
1	Perform Reference Performance Test (RPT)
2	Rest for 30 minutes
3	Charge at 1.5C until $V_{\max}$, hold at $V_{\max}$ until C/20
4	Rest for 15 minutes
5	DCIR test at an amplitude of C/3
6	Rest for 2 minutes
7	Discharge at 10C until $V_{\min}$
8	Rest for 15 minutes
9	Repeat steps (3) to (8) for 20 total cycles
10	Perform Reference Performance Test

The protocol is repeated for 100 cycles or until cells have reached 80% state-of-health (SOH) as defined in equation 2.3.

$$SOH = \frac{Q_n}{Q_0} \quad (2.3)$$

Where Q_n is the measured discharge capacity at cycle n during the RPT and Q_0 is the measured discharge capacity at cycle 0.

2.1.2.4 Pseudo Open Circuit Potential

Finally, open circuit voltage (OCV) is required for most models, especially empirical models. True OCV is difficult to measure as it takes a considerable amount of time to reach equilibrium as discussed in Section 1.2.3. For this reason, pseudo open circuit voltage (P-OCV) is often used. This involves cycling the cell at a very low current for both charge and discharge to create a pseudo-equilibrium condition. C/20 for both charge and discharge was chosen for this test as a compromise between accuracy and test time. Discharge and charge P-OCV vs. state of charge curves can be generated from this data and fed into models, as will be discussed further in the results section. P-OCV was not used as a performance metric and was only tested at a nominal initial stack pressure of 10

kPa for model fitting. It is recommended that further investigation is undertaken to determine if stack pressure affects OCV.

2.2 Experimental Results

2.2.1 Pressure Variation During Cycling

As mentioned, the first investigation was into how pressure varied over a single discharge cycle. The expected behaviour was observed for the two pressurised experiments in cell model (2), with a gradual decrease in pressure as the voltage decreased; however, all three experiments with cell model (1) showed very peculiar behaviour. For all three pressures, a similar behaviour was observed with a plateau at around 55-70% SOC. The high-pressure and low-pressure tests also then show an increase in pressure, which is unexpected. The exact mechanisms for this behaviour are not confirmed, however, it is suspected that temperature is an additional input into the expansion and contraction system. Immediate correlation is not clear; however, further testing is recommended. Figure 2.6 presents pressure, voltage, and temperature over a C/2 discharge for each pressurised test.

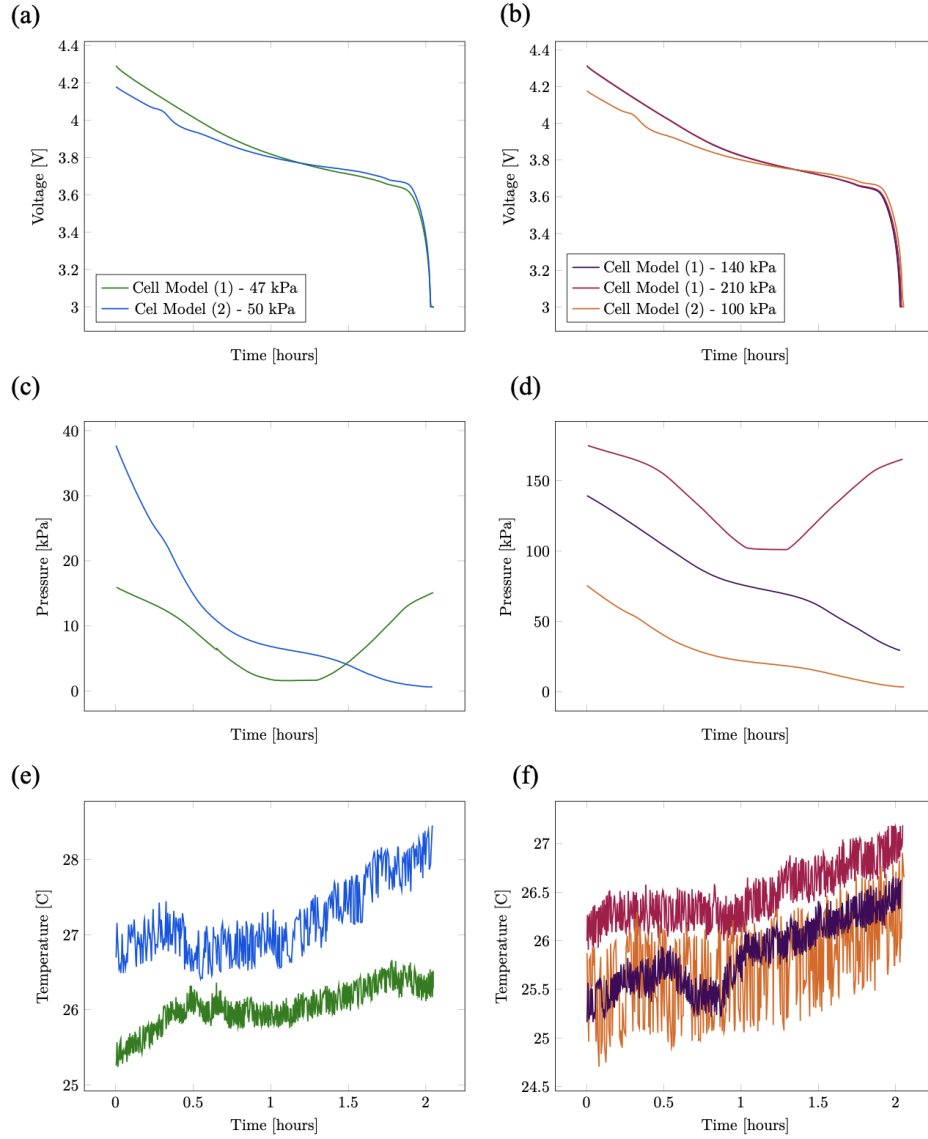


Fig. 2.6 (a),(b) Voltage vs. Time and (c),(d) Pressure vs Time and (e),(f) Temperature vs Time for each pressurised test

Furthermore, the HPPC testing provides an opportunity to observe pressure dependency on state-of-charge with relaxation time, providing pressure and voltage at a 'pseudo' equilibrium condition. Once again, cell model (2) presents a strong correlation between the C/2 discharge and the HPPC measurements during the first cycle of the testing as presented in Figure 2.7.

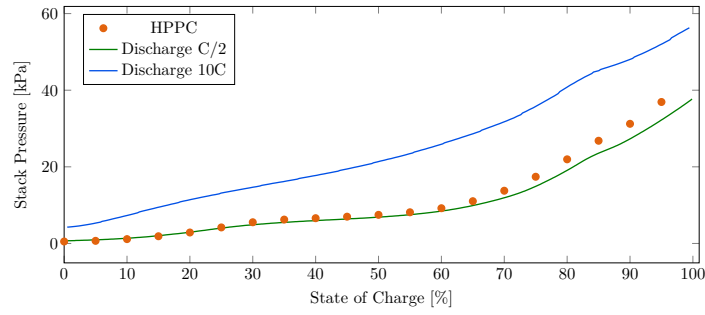


Fig. 2.7 Pressure vs. State-of-Charge comparison for discharge at C/2, 10C, and throughout an HPPC test for cell model (2) at 50 kPa

There is a fairly large discrepancy when looking at the 10C discharge, however. This provides an interesting perspective on the inverse relation noted when plotting the discharge curve concerning state-of-charge. Cell model (1) in contrast performs as expected in the HPPC testing, showing a gradual reduction of pressure over the full state-of-charge as presented in Figure 2.8.

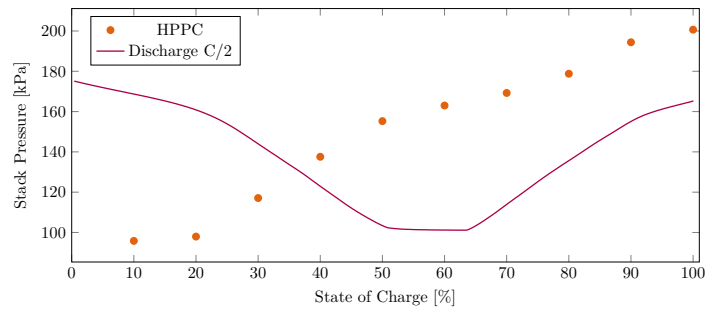
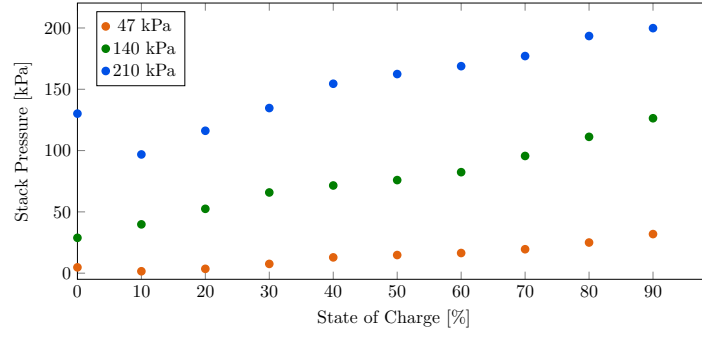


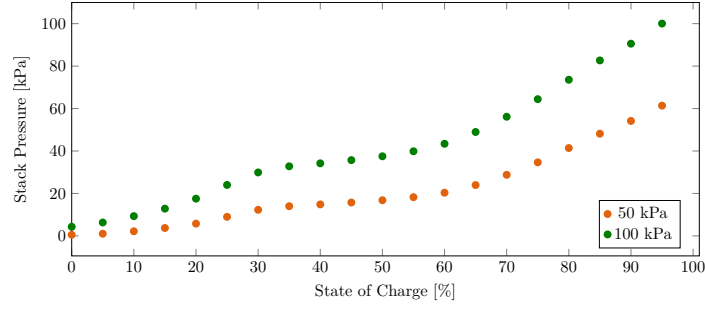
Fig. 2.8 Pressure vs. State-of-Charge comparison for discharge at C/2, and throughout an HPPC test for cell model (1) at 210 kPa

This leads to a hypothesis that the higher voltage cell is being quite heavily affected dynamically by the design of the cell and it is recommended that further destructive testing be completed to draw concrete conclusions. The 10C discharge data was not available for cell model (1) as it did not undergo degradation testing where the 10C data was pulled from.

The HPPC pressure comparisons can be completed for each cell model across all starting pressures. Figure 2.9 presents these comparisons.



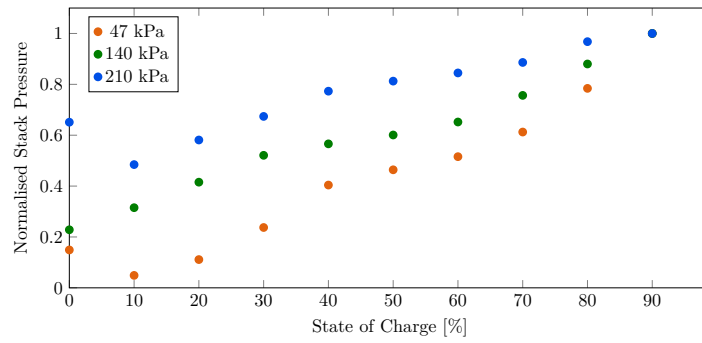
(a) Stack Pressure vs. SOC for varying initial stack pressures for Cell Model (1)



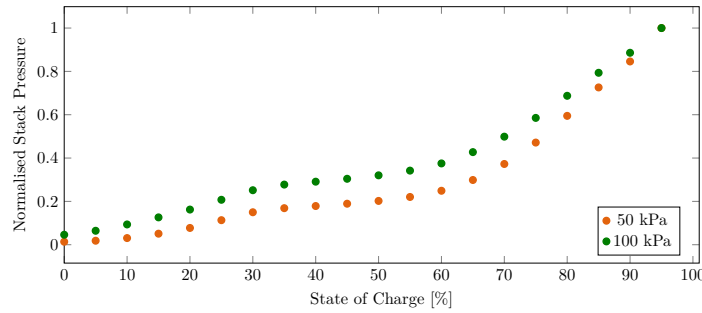
(b) Stack Pressure vs. SOC for varying initial stack pressures for Cell Model (2)

Fig. 2.9 Stack Pressure vs. SOC for varying initial stack pressures

Both cell models show expected behaviour over the state-of-charge range. To confirm the impact of stack pressure, these plots were then normalised. Figure 2.10 shows the normalisation and confirms that the effect of initial stack pressure is not a linear scalar.



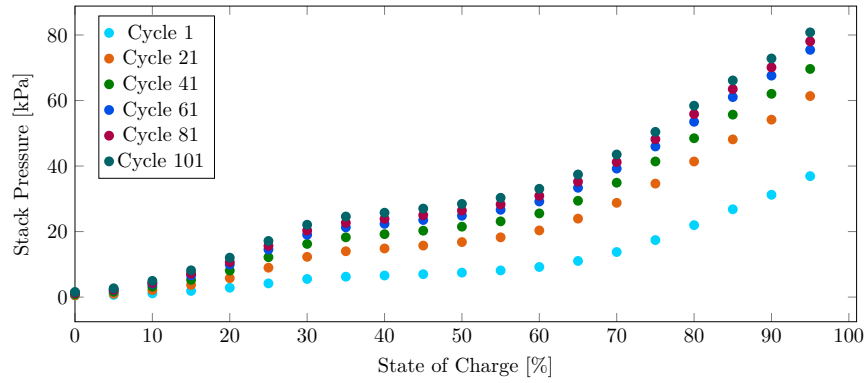
(a) Stack Pressure vs. SOC for varying initial stack pressures for Cell Model (1)



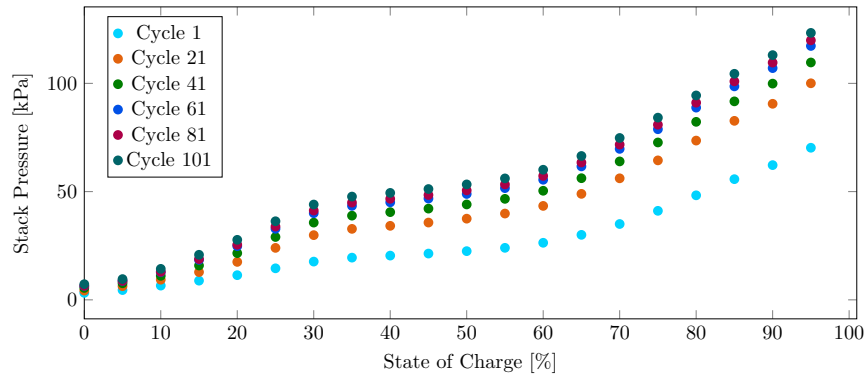
(b) Stack Pressure vs. SOC for varying initial stack pressures for Cell Model (2)

Fig. 2.10 Stack Pressure vs. SOC for varying initial stack pressures

The final aspect that needs to be looked at with pressure independently is the change in stack pressure over time. As previously mentioned, it is expected to see an increase in measured stack pressure due to irreversible losses of lithium into the negative electrode, resulting in irreversible swell within the cell. It is important to note that in this testing, electrode gassing is not considered as that is considered to be a catastrophic failure and results in cells not being usable. Figure 2.11 presents the reference performance test measure pressure vs. capacity at a 20-cycle interval with the expected behaviour of pressure increase over time for cell model (2).



(a) Stack Pressure vs. SOC at each RPT for cell model (2) at 50 kPa over 100 cycles



(b) Stack Pressure vs. SOC at each RPT for cell model (2) at 100 kPa over 100 cycles

Fig. 2.11 Stack Pressure vs. SOC at each RPT for cell model (2) over 100 cycles

Notably, there are diminishing increases as the cell ages with the largest notable jump during the first 20 cycles. It is predicted that there is still a solid-electrolyte interface being developed during those initial cycles, thus increasing the width (and stack pressure) of the cell. This leads to interesting correlations toward internal resistance aging which will be further discussed in the following section. This confirms the hypothesis that there is a benefit in modelling the predicted stack pressure to ensure that the plateau is achieved at the desired stack pressure.

2.2.2 Measured Capacity & Available Energy

Cell capacity and available energy are critical parameters for accurate and performant control systems. Individual discharge curves can be investigated at different discharge rates to determine the capacity vs voltage curve, providing key insight into available cell capacity and energy for given performance scenarios. Figure 2.12 presents discharge curves for voltage vs state-of-charge at two different discharge rates for the cell model (2).

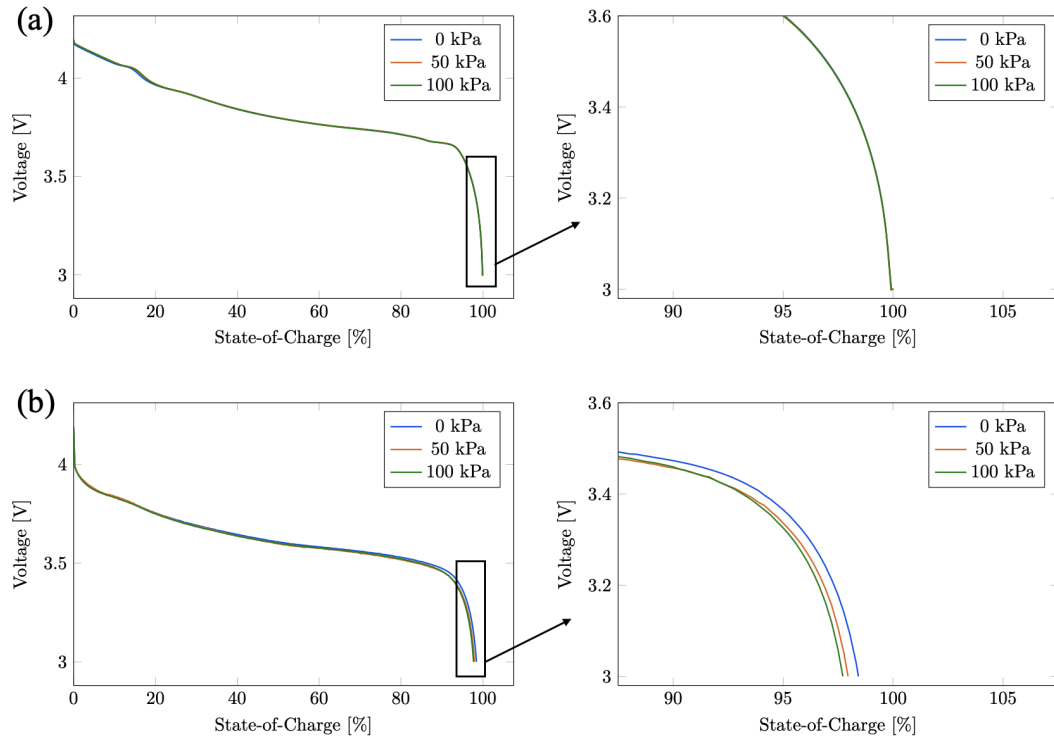
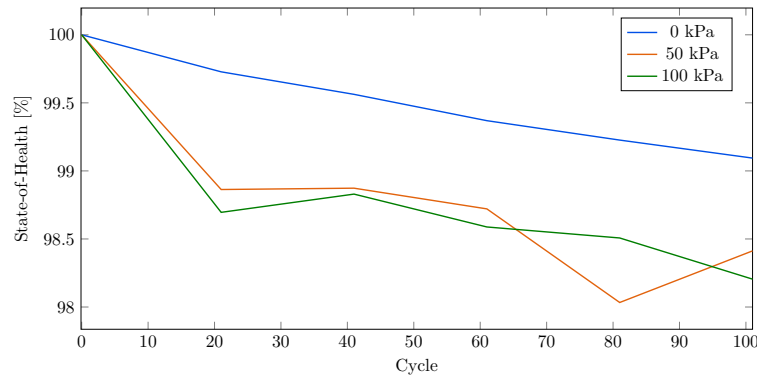
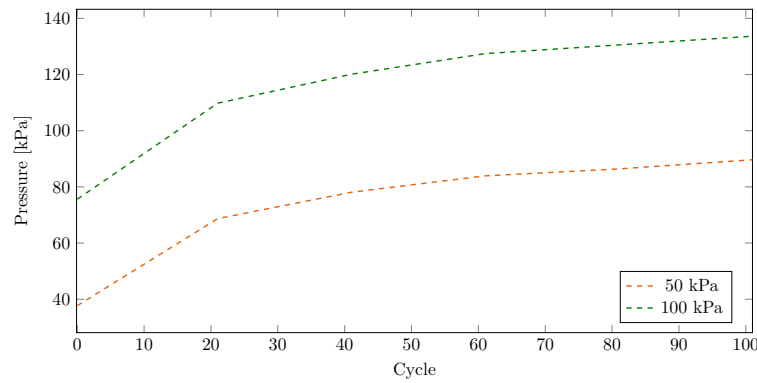


Fig. 2.12 Voltage vs. State-of-Charge for cell model (2) at each tested pressure for (a) C/2 and (b) 10C

It can be seen that as pressure is increased, there is less available capacity at the high discharge rates. Furthermore, the state-of-health can be investigated through RPT capacity measurements for the cell model (2). While the expectation was to see a significant fade as per the manufacturer's specification, very little capacity degradation is seen in all cases. It is interesting to note; however, that the ageing profile of the non-pressurised cell is very linear, with a more stochastic profile on both pressurised cells. Figure 2.13 presents the capacity fade and pressure evolution for cell model (2) over the first 100 cycles.



(a) State-of-Health vs. Cycle at each pressure for Cell Model (2)



(b) Stack Pressure vs. Cycle at each pressure for Cell Model (2)

Fig. 2.13 Stack Pressure and SOH vs. SOC for varying initial stack pressures

While the pressurised cells both experience a larger drop after the first 20 cycles, they exhibit half the degradation over the last 40 cycles that the unpressurised cell saw at 0.4% vs 0.8% respectively. Figure 2.13b does not include 0 kPa and the cell was unpressurised and therefore there are no pressure readings available. Further testing should be completed to determine the longer-term effects of added stack pressure. As Figure 2.13b presents, pressure gradually increases as the cell ages for both pressures tested. Both cells have very similar pressure vs. cycle curves with knee points at very similar points. This behaviour is reassuring; however, it is recognised that many more samples are needed to confirm the pattern holds; however, it provides a positive outlook toward the ability to model pressure vs. state-of-health in future work.

2.2.3 Resistance & Power Performance

Varying stack pressure is known to influence internal resistance in pouch cells due to the increased interfacial contact between layers when pressure is applied [63, 35]. Due to this, it is recommended that pressure be applied; however,

there is rarely a guideline on the exact quantitative measure of this. While it is near impossible to determine an ideal number for pressure across all operating conditions and cell models, it is important to investigate the impact. Cell model (1) experiences a large effect of initial set stack pressure on resistance vs state-of-charge. Figure 2.14 presents the correlation between lumped internal resistance and State-of-Charge showcasing a mean decrease of 10% across SOC with a maximum decrease of 17% at 100% SOC when varying stack pressure from 47 kPa to 140 kPa.

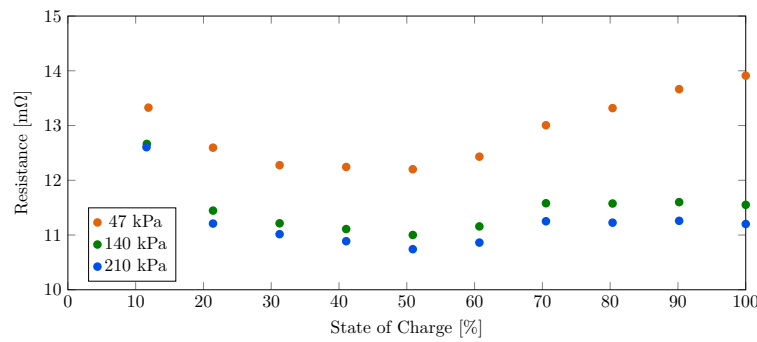


Fig. 2.14 Discharge internal resistance vs. SOC for varying stack pressures for discharge pulses for Cell Model (1) measured from an HPPC test

This dependency weakens with further applied stack pressure with results showcasing an additional 70 kPa providing a marginal decrease of 2%. In comparison, cell model (2) performs much differently. While there was a gradually decreasing resistance in cell model (1) as pressure increased, cell model (2) saw similar results at 0 kPa and 50 kPa and saw an increase in resistance when the pressure was increased to 100 kPa. This is counter-intuitive to what would be expected when comparing the pressure plots as presented in Figure 2.9 as a gradual decrease in pressure is not observed, but instead a saddle shape. Figure 2.15 presents measured internal resistance vs state-of-charge for the cell model (2).

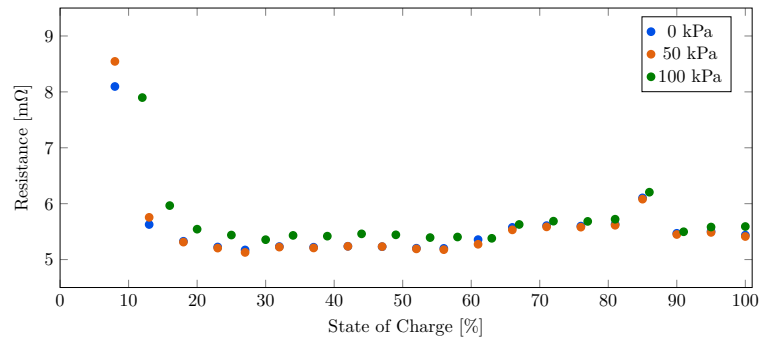


Fig. 2.15 Discharge internal resistance vs. SOC for varying stack pressures for discharge pulses for Cell Model (2) measured from an HPPC test

While this information alone does not conclude the exact relationship between pressure and resistance, it is clear that there is an effect on internal resistance from the external stack pressure and that it cannot be ignored. Furthermore, it emphasises the need to model specific fitting for pressure in a pouch, as two models from the same manufacturer with similar chemistries but different mechanical elements perform vastly differently. Further investigation into the HPPC results can provide insight into the dynamic behaviour of the different cell models and the impact that external stack pressure can have by isolating the pulse responses at differing state-of-charge. Figure 2.16 presents pulse profiles at 10% SOC and 90% SOC. As expected, there is a much more significant impact on the model (2) cells during both the discharge and charge pulses.

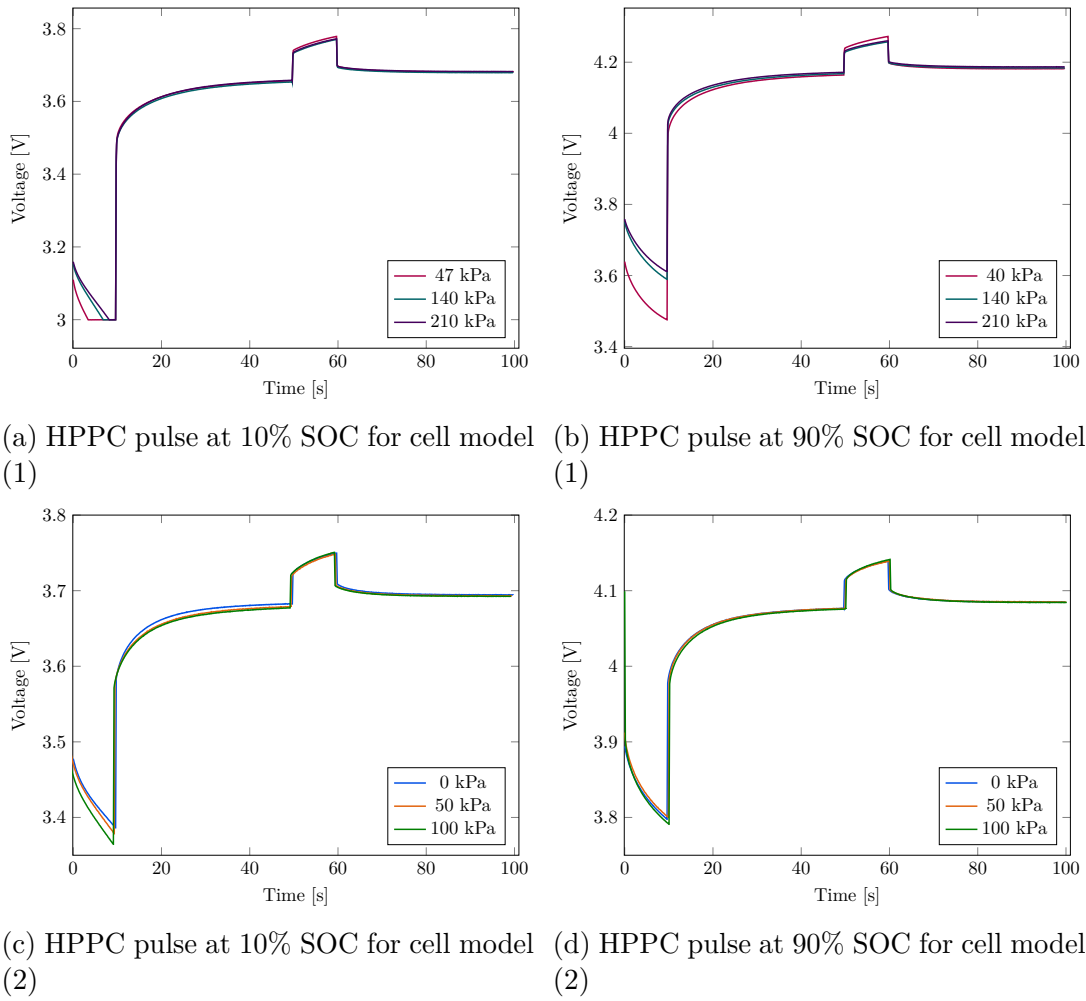


Fig. 2.16 HPPC pulses for both cell models at two different SOC points

Both cell model results reflect the resistance plots as expected, with cell model (1) having a much more significant impact at both high and low state-of-charge. An interesting observation is that due to the higher resistance in the high-voltage cells, at 10% SOC, the cell low-pressure cell reaches its minimum voltage cut-off very quickly, which can vastly impact the performance of the cell when compared to the medium and high-pressure cells as figure 2.16a shows. In contrast, cell model (2) is still relatively far from its minimum voltage, despite both cells experiencing a maximum pulse rate discharge pulse.

Finally, resistance change over cycle life can be investigated as a metric of health. Throughout the testing for this work, DCIR was measured utilizing the built-in function on the Arbin MITSPRO software as described in the section above. The measurements across the 100 cycles for each pressure condition are presented in

Figure 2.17.

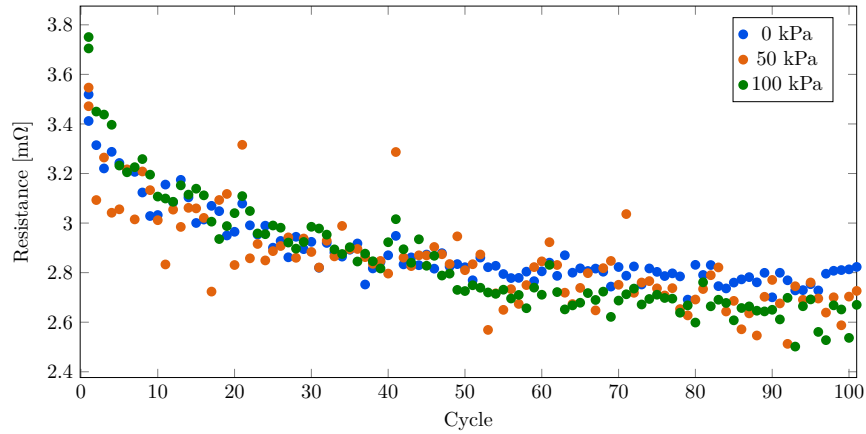


Fig. 2.17 Resistance vs. Cycle for 100 cycles of cell model (2) at three initial stack pressures

Similar behaviour to the pressure profile is seen with a decrease in resistance over the first 100 cycles and a plateau from approximately cycle 35 onward. Similar to the capacity fade presented in Figure 2.13a, the 0 kPa cell exhibits very linear behaviour with the 50 kPa cell having the most variation. Figure 2.18 shows the change in resistance over the first 100 cycles. It can be seen that the increase is relatively similar across the entire SOC range and that there is very similar behaviour exhibited to the pressure profile as shown in figure 2.11.

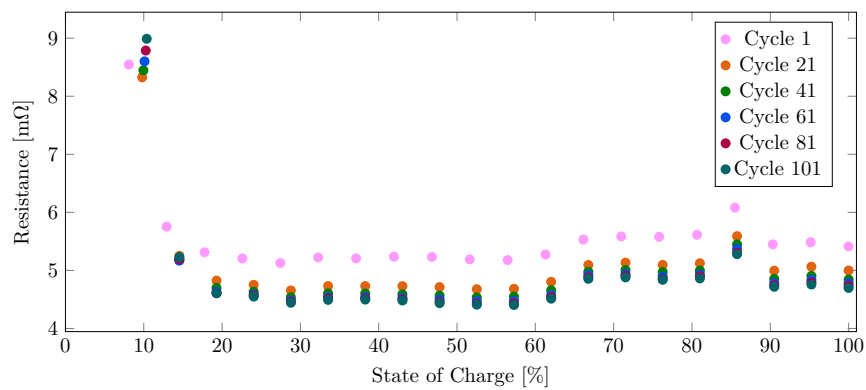


Fig. 2.18 Resistance vs. SOC for varying stack pressures for discharge pulses

It is recommended that further aging be completed to determine exact aging pathways.

2.3 Experimental Conclusions

A novel methodology was developed for the experimental evaluation of lithium-ion pouch cells. A modular fixture was presented that allows for pressure variation for multiple cell sizes utilising a constant displacement setup. Two LCO/graphite cells were tested under three pressure conditions each at low, medium, and high external stack pressures. Hybrid pulse power characterisation was utilised as the main evaluation test with degradation testing being completed on one cell model. The results show that expansion and contraction of the cell are dependent on initial stack pressure and rate of lithiation. Cell model (1) exhibited a plateau at all three pressures during a C/2 discharge; however, did not exhibit this behaviour during HPPC testing. Higher state-of-charge correlated with high pressure during all testing. During degradation testing for cell model (2), it was observed that pressure increased as the cell aged as expected. Capacity testing revealed further dependency on both stack pressure and discharge rate, with a higher discharge rate showing a larger variation of available energy across pressures. Finally, resistance and power were investigated. Both cell models showed resistance variation across the different stack pressures, with cell model (1) having a higher sensitivity with degradation testing showing different ageing paths with further investigation recommended. Power followed these trends. The experimental results show that there is a need to have representative testing conditions when developing methods. The presented results highlight the variations between different cell models and stack pressure configurations. They also present the further dependency of the current load and how the performance results are affected by these inputs.

Chapter 3

Pressure Fitted Equivalent Circuit Model

The previous section highlighted the additional complexity that pouch cells present when evaluating performance and designing test apparatus. The additional complexity extends beyond experimental testing, however. Models are a key component for the development of control systems such as for battery management. Parameterisation is an important aspect to consider when determining the best model for an application as many parameters are not observable. In addition, all models are an estimation, and as such the user must decide on the required fidelity. One of the most common model choices, particularly for control systems, is the equivalent circuit model (ECM) due to its non-invasive parametrisation, low computational cost, and moderate to high fidelity. The advantage of ECMs is largely due to their ease of parametrisation compared to their physics-based counterparts such as the Doyle-Fuller-Newman [70] and Single Particle Model [71]. Conventionally, the main operational considerations in the model are ambient temperature and state of charge [58, 59, 55]; however, as shown in the previous chapter, it can be seen that in addition to this, the external stack pressure can also affect performance, particularly for state of charge and state of health. For the work in this thesis, the ECM was chosen due to its industry relevancy, ease of parameter identification, and low computational cost.

In this chapter, an equivalent circuit model and its governing equations are presented. The Pressure Informed Equivalent Circuit Model (PIECM) is presented alongside the required data conditioning and analysis. The impact of external stack pressure on equivalent circuit model fitting and performance is investigated for a single RC pair and two RC pair ECM through a parameter

sweep to determine the sensitivity of the fit parameters. Finally, the two models are optimised, and error, computational memory, and computational fitting time are compared.

3.1 Equivalent Circuit Model Derivation

An equivalent circuit model (ECM) is composed of standard electric components such as voltage sources, resistors, and capacitors to replicate the behaviours of a lithium-ion cell. At the most basic, an ideal voltage source can be utilized to represent the voltage of a lithium-ion battery as shown in Figure 3.1.

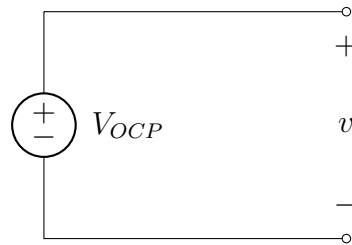


Fig. 3.1 Equivalent circuit model representing the voltage of a lithium-ion cell considering only open-circuit voltage

This voltage source represents what is referred to as the open-circuit voltage (OCV) and represents the voltage of the cell at complete equilibrium as a function of State-of-Charge (SOC). This term can be approximated through experimental testing as described in section 2.1.2.4; however, as mentioned in section 2.1.2.4, this is not an exact representation due to the cell not truly being at equilibrium during testing and the presence of hysteresis. The methodology of obtaining the open-circuit potential for this work is described in section 3.2.2. This representation is a static model, not considering any dynamics within the system. To capture this behaviour, the first step is to consider the instantaneous response of the system when a load is applied. A series resistor is added to represent the lumped internal resistance of the cell, as shown in figure 3.2.

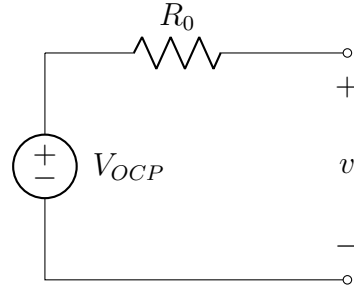


Fig. 3.2 Equivalent circuit model representing the voltage of a lithium-ion cell considering open-circuit potential and bulk resistance

While this does increase the fidelity of the model slightly, there is still the assumption of the single bulk resistance; when it is known that this is not accurate behaviour [53]. To account for this, a resistor and capacitor in parallel are added to the model thus providing the final proposed system as presented in figure 3.3. The system is shown with a single RC pair but it is possible to have any number n of pairs, connected in series. In the presented diagram V_{OCP} is the open circuit potential, R_0 is the fitted bulk cell resistance, and R_n and C_n are the fitted RC parameters for n number of pairs.

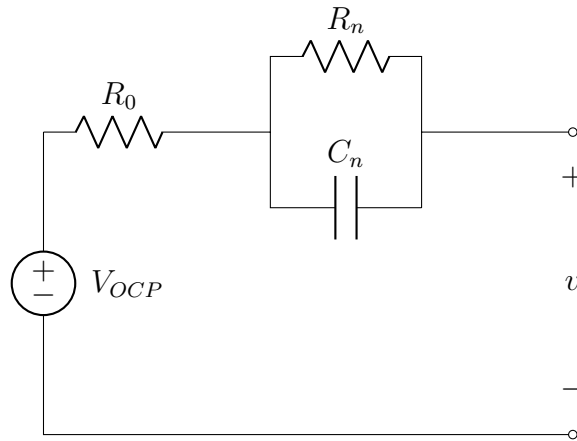


Fig. 3.3 Equivalent circuit model representing the voltage of a lithium-ion cell considering open-circuit potential, ohmic resistance, and a single RC pair

From here the governing equations are derived and then discretised. The following derivation and discretisation were originally presented by Plett [59] and have been modified to fit the notation from experimental data including adjusting the sign of the current such that positive current is defined as charge. The first dependency to derive is the state-of-charge (SOC) where the cell is defined as being fully charged at 100% state-of-charge and fully discharged at 0% state-of-charge. If

the cell voltage is somewhere between these two points, the state-of-charge can be defined as a function of the total cell capacity, and the capacity that has been added and/or removed during operation. The state-of-charge is defined as the ordinary differential equation presented below:

$$\dot{z}(t) = \frac{\eta(t)i(t)}{Q} \quad (3.1)$$

Where $\dot{z}(t)$ is the time derivative of state-of-charge, $i(t)$ is applied load current and is denoted as positive on the charge, η is defined as the coulombic efficiency and Q is the total cell capacity. When $i(t)$ is negative, ie. when the cell is being discharged, η is modelled as 1 and when the cell is being charged, ie. $i(t)$ is positive, η is the ratio of charge capacity to discharge capacity and should always be less than 1. This is due to parasitic side reactions with the electrolyte during the charging process [72]. This can either be calculated through measured capacity or approximated to 0.995, as the accuracy of most cyclers is not able to differentiate beyond this [72, 73]. It can be then observed that a discharge, or negative current, will result in a reduction in the state-of-charge. Integrating equation 3.1 then provides the means to estimate the instantaneous change in state-of-charge over a defined time interval as shown in equation 3.2.

$$z(t) = z(t_0) - \frac{1}{Q} \int_{t_0}^t \eta(\tau)i(\tau)d\tau \quad (3.2)$$

where $z(t_0)$ is the initial SOC and $[t_0, t]$ is the time interval. This equation can now be utilized to determine the V_{OCP} term within the voltage response. Typically, this can be completed through a polynomial function fitted to the experimental data or through a look-up table at standardised points that are then interpolated. For this work, a look-up table and linear interpolation were utilized, generated from the experimental data with 1000 SOC points. The ohmic resistance can then be added utilizing Ohm's law, previously presented in Chapter 2 as equation 2.1. This provides equation 3.3 to determine the terminal voltage of the system:

$$v(t) = V_{OCP}(z(t)) + i(t)R_0 \quad (3.3)$$

where R_0 is the equivalent system resistance, commonly referred to as the ohmic resistance. This resistance can be estimated through Ohm's law as described in equation 3.4 over any current pulse or identified through optimisation. Hybrid pulse power characterisation pulses provide an excellent starting point for this.

$$R = \frac{\Delta V}{\Delta I} \quad (3.4)$$

As the cell resistance is dependent on many factors such state-of-charge, stack pressure, and state-of-health the calculated resistance is only utilised in this work as the initial value for the optimisation and R_0 is fitted. It can further be seen that as the current goes negative, a reduction in terminal voltage would be observed as desired. The final component to add to the terminal voltage is the diffusion voltage, which is represented through the RC-pair(s). Adding this term to the terminal voltage provides us with the following:

$$v(t) = V_{OCP}(z(t)) + i(t)R_0 + i_{R_n}(t)R_n \quad (3.5)$$

where $i_{R_n}(t)$ is the current through the resistor R_n for the n th RC pair. To determine $i_{R_n}(t)$, Kirchhoff's current law is used, stating that the total current $i(t)$ is equal to the sum of current through the parallel pathways. This is presented in equation 3.6.

$$i(t) = i_{R_n}(t) + i_{C_n}(t) \quad (3.6)$$

where $i_{C_n}(t)$ is the current through the capacitor C_n for the n th RC pair. Furthermore, the current through the capacitor $i_{C_n}(t)$ can be defined by equation 3.7.

$$i_{C_n}(t) = C_n \frac{dv_{C_n}(t)}{dt} \quad (3.7)$$

The voltage term in equation 3.7 can then be substituted utilising Ohm's law once again, resulting in equation 3.8.

$$i_{C_n}(t) = C_n \frac{di_{R_n}(t)}{dt} R_n \quad (3.8)$$

Equation 3.8 can now be inserted in to equation 3.6 to provide the following:

$$i(t) = i_{R_n}(t) + C_n \frac{di_{R_n}(t)}{dt} R_n \quad (3.9)$$

Equation 3.9 can then be rearranged to provide the following differential equation:

$$\frac{di_{R_n}(t)}{dt} = -\frac{1}{C_n R_n} i_{R_n}(t) + \frac{1}{C_n R_n} i(t) \quad (3.10)$$

This then results in the following system of equations that can be simulated to provide $v(t)$, the terminal voltage of the cell.

$$\begin{aligned} z(t) &= z(t_0) - \frac{1}{Q} \int_{t_0}^t \eta(\tau) i(\tau) d\tau \\ \frac{di_{R_n}(t)}{dt} &= -\frac{1}{C_n R_n} i_{R_n}(t) + \frac{1}{C_n R_n} i(t) \\ v(t) &= V_{OCP}(z(t)) + i(t) R_0 + i_{R_n}(t) R_n \end{aligned} \quad (3.11)$$

This system can now be discretised to allow for simulation resulting in the system of equations utilised for the optimisation. A full discretisation can be found in Appendix D.

$$\begin{aligned} v[k] &= V_{OCP}(z[k]) + i[k] R_0 + \sum_n i_{R_n}[k] R_n \\ i_{R_n}[k+1] &= e^{-\frac{\Delta t}{R_n C_n}} i_{R_n}[k] + \left[e^{\frac{\Delta t}{R_n C_n}} - 1 \right] i[k] \\ v[k] &= V_{OCP}(z[k]) + i[k] R_0 + \sum_n i_{R_n}[k] R_n \end{aligned} \quad (3.12)$$

3.2 Model Development and Architecture

The presented discretisation was utilised for the implementation of the equivalent circuit model framework to investigate the effect of external stack pressure. The following subsection presents the model architecture, data conditioning, and

parameter identification methodology. An overview of the architecture and workflow is presented in Figure 3.4.

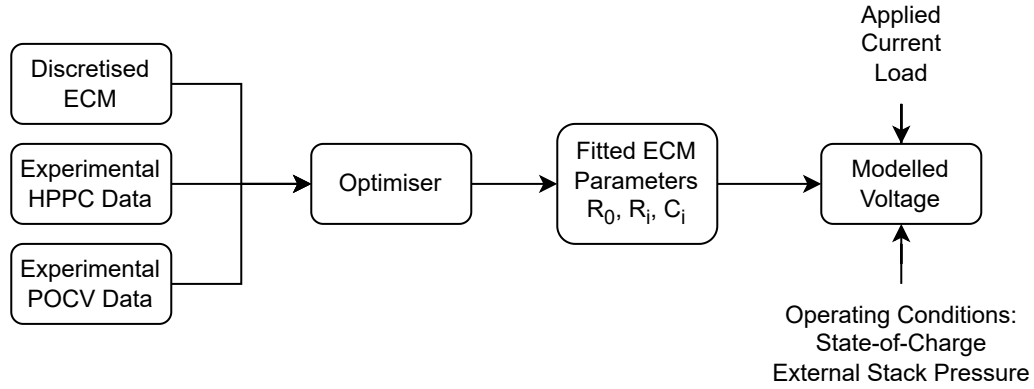


Fig. 3.4 PI-ECM workflow for parameter identification

3.2.1 Model Implementation

The model was implemented in the Julia programming language. Julia is a just-in-time compiled language that was developed at the Massachusetts Institute of Technology as a fast, dynamic scientific programming language [74]. There are many benefits to using Julia; however, the main reason it was chosen was the dynamic typeset and speed. The dynamic typeset provides a code set that is easy to understand and iterate on as well as is intuitive to read. In addition to this, having code that is reliably fast is increasingly beneficial when dealing with large datasets. As the PIECM is incorporating an additional fitting dimension on a traditional model, it was determined that the speed of the language was a key consideration. The model was implemented in Julia 1.9.2 and all of the code discussed in the following sections is available on GitHub [75].

3.2.2 Data Conditioning

The first step when developing the model was ensuring robust methods for conditioning and analysis of the experimental data. Figure 3.5 shows the unprocessed data from one of the experiments.

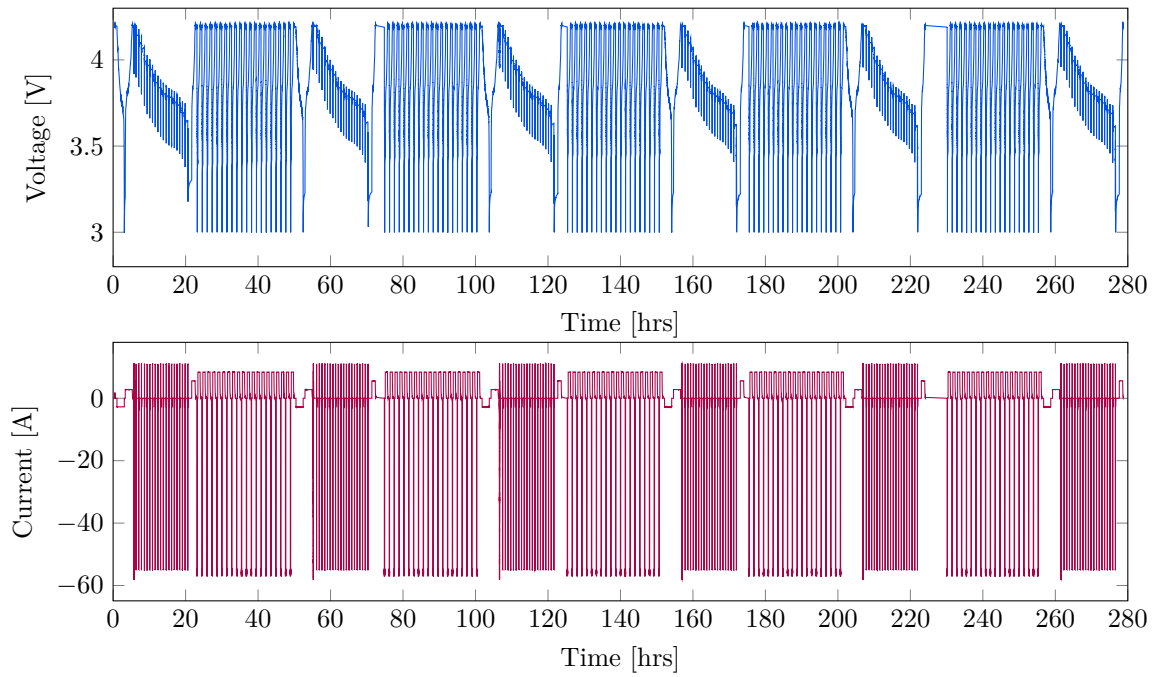


Fig. 3.5 Unprocessed experimental data for cell model (2) at 50 kPa

Data processing scripts were developed that automated data analysis to provide the experimental data required for this work. This includes extracting an open-circuit potential vs SOC relationship, isolating fitting data for each SOC point at each fitting pressure, and methods for data extraction for validation. An example of this isolated data is presented in Figure 3.6 as an isolated HPPC pulse that was utilised for fitting.

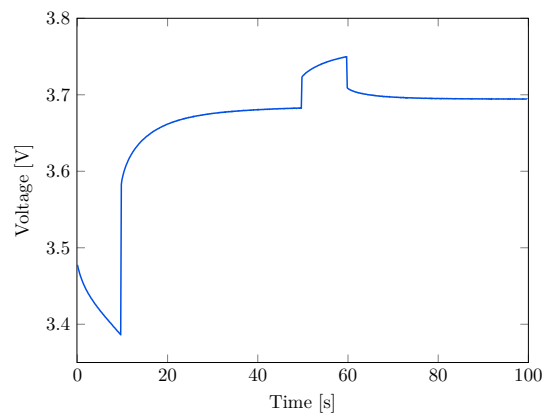


Fig. 3.6 Example data conditioning of a single HPPC pulse utilised for model fitting

The scripts were developed in Julia to allow for fast analysis of large data sets; particularly the cyclic aging. All post-processing scripts can be found in the

PIECM module on GitHub [75]. The scripts were developed to be modular and allow for easy modification to suit different datasets while remaining robust and accurate. A focus was put on modularity and functionality to minimize the effort required for the numerous fitting procedures that need to be completed. Throughout the data processing process, DataFrames.jl was utilized. DataFrames provide a framework to work with table-based data, allowing for ease of sorting, filtering, and plotting. First, data initialization was required to match the Arbin experimental output to the pressure output from the Teensy and was combined into a single data frame - with readings of common date time in the form of "yyyy-mm-dd HH:MM:SS". Where pressure data was not available, the DataFrame supplied a NaN value.

Once this is completed, filtering and conditioning of the data for usage in the model can begin. The Arbin data output provides a Step_Index that correlates each item in the test protocol schedule with a unique identifying number. This identifier was used frequently throughout the data processing to provide fast and repeatable filtering of data. It is acknowledged that the current data processing algorithms will only work alongside Arbin's data output.

The first item required for the ECM model is the open-circuit voltage term. As described in the previous chapter, pseudo-OCV testing was completed on the cells, and from there, an OCV vs SOC relationship can be gathered. In this work, hysteresis is accounted for by taking an average of the charge and discharge voltages at the calculated state-of-charge. First, state-of-charge is determined independently for the charge and discharge process based on measured capacity. The function has four inputs: raw data, discharge Step_Index, charge Step_Index, and SOC points. The final input, SOC points, allows for a standardized SOC vector for model implementation while allowing the user to determine the fidelity they need and weigh that against available memory and processing power. Hybrid Pulse Power Characterization pulses were extracted similarly for each SOC point tested and only contained the 100-second pulse profile for fitting. All code can be found in the open-source GitHub repository [75].

3.2.3 Pressure-Informed Equivalent Circuit Model Code Implementation and Parameter Fitting

As mentioned above, the framework for the ECM model was also built within Julia. The code relies on several inputs into the function to return the desired voltage prediction including user-defined inputs, fitted variables, and input data.

A cost function was implemented to determine the fitted parameters utilising the Sum of Squared Error method as defined in the equation 3.13.

$$\text{SSE} = \sum_{i=1}^n |a_i - b_i|^2 \quad (3.13)$$

The cost function utilizes normalized parameters to improve the fitting optimization by providing a stable fitting range when compared to the values themselves which vary in range from 0.001 to 75000 depending on whether it is a resistance term or capacitance term. The sum of squared error method was chosen as the minimization method to allow for a more robust comparison across the fitting parameter range. To account for the dynamic response of the system, the hybrid pulse power pulses are utilised as the fitting data. Within the fitting data, the critical area of concern is the dynamic voltage response to the applied current load. As there is a relatively large amount of rest time in the fitting data it was determined that least squares was the appropriate error calculation to ensure all error is equally considered.

There were two methods used for parameter identification for this work that focus on determining the effect of variations in stack pressure on an ECM. The first investigation involved a parameter sweep for a single RC model that investigated how the differing stack pressures affected the error across a single HPPC pulse at a specified state-of-charge. This activity provides insight into the sensitivity of each parameter. The parameter sweep was also completed for the two-RC model for the five fitted parameters. Once the parameter sweep was completed, optimization was performed utilizing the Optim.jl package and a bounded L-BFGS optimization algorithm [76].

3.3 Pressure Informed ECM Fitting Results

As discussed so far, ECMs require experimental data to fit the above governing equations. It is important that the data used is representative of the operating conditions and contains enough dynamics to capture the behaviour of the cell. Hybrid Pulse Power Characterization is often used to map out ECM parameters across the operating range. For this work, temperature will not be considered to isolate the effect of pressure across a single temperature before adding complexity. The reader is directed to alternative work for more information regarding temper-

ature dependencies within equivalent circuit models [56, 59, 77]. Once the model implementation within Julia was completed, the investigation into the effect of pressure on the model fitting and execution was completed. Initial investigations began with parameter sweeps across a single RC circuit for each pressure at ten SOC points. For the parameter sweep, ranges are set arbitrarily for R1 and C1; however, for R0 the range is set by taking the initial measurement from the HPPC pulse and taking a range $\pm 10 \text{ m}\Omega$. First, the impact of fitting R0 compared to using the calculated DCIR from the pulse is presented. Figure 3.7 showcases the three R0 values that provide the lowest error for the determined parameter range. A notable result is that the measured R0 through the HPPC pulse is $0.0107 \text{ }\Omega$ which results in a minimum error of 0.781 V^2 shown in Figure 3.7d, significantly higher than the other values presented.

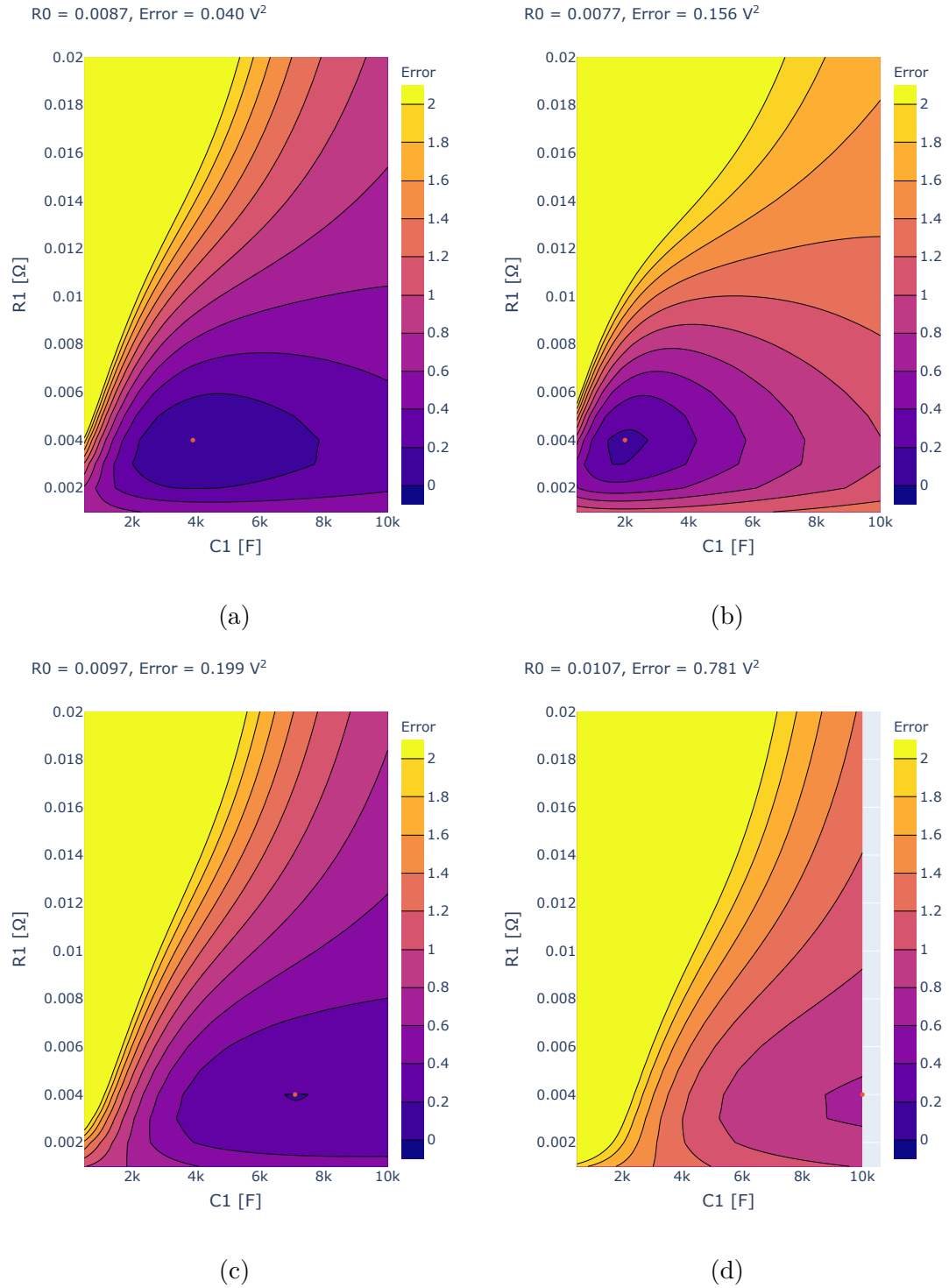


Fig. 3.7 R_1 vs C_1 Error plots for model (1) at 140 kPa for 50% SOC with R_0 equal to (a) $0.0087 \text{ } \Omega$ (b) $0.0077 \text{ } \Omega$ (c) $0.0097 \text{ } \Omega$ and (d) $0.0107 \text{ } \Omega$

This iterates the benefits of utilising a fitted and not a deterministic R_0 parameter. Further investigation can then be made regarding pressure variation. Contour

plots representing the error for the ECM function based on varying R_1 and C_1 values are presented in Figure 3.8 with the R_0 parameter also minimized; however, only the optimal R_0 is presented. All state-of-charge points return very similar results.

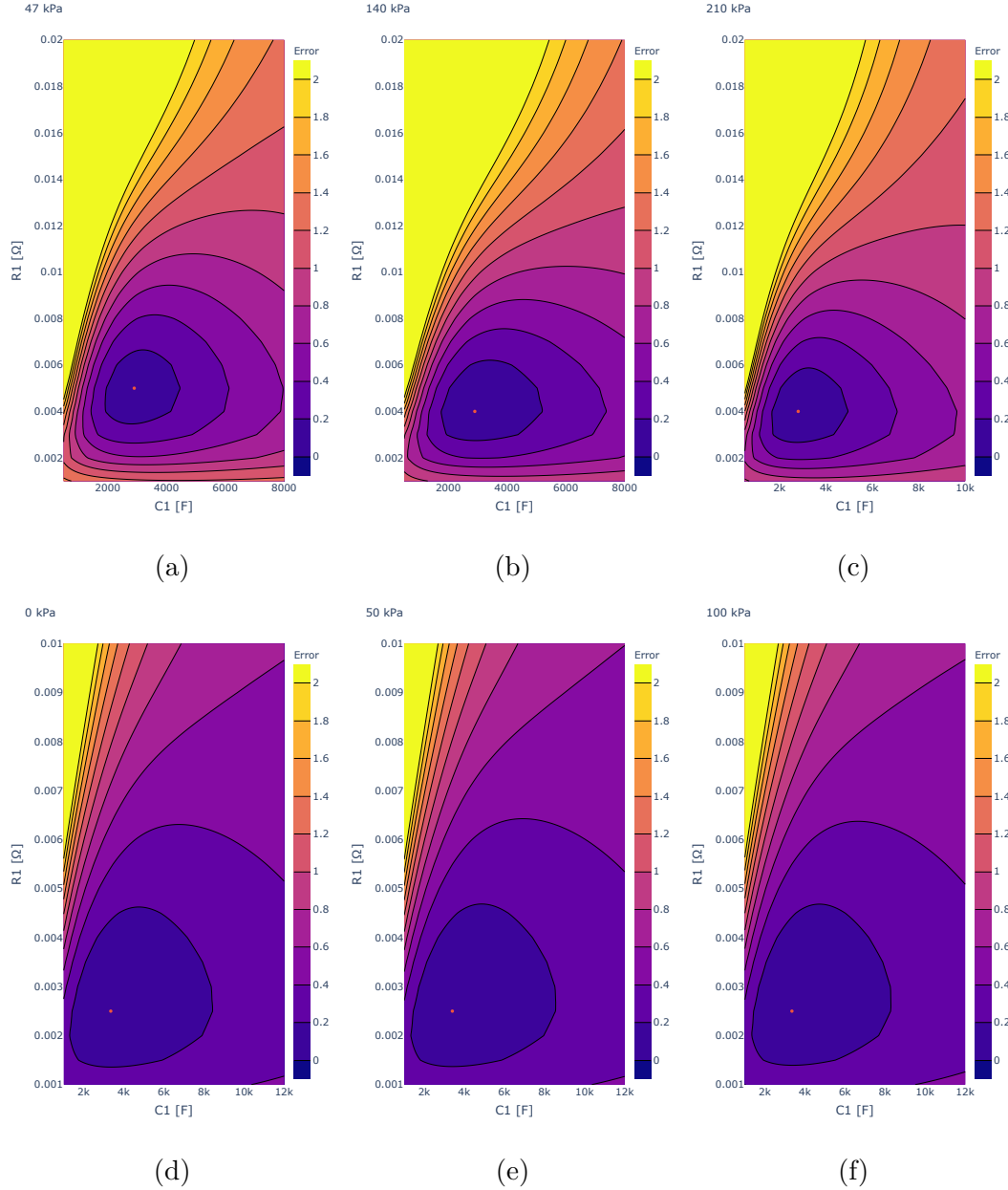
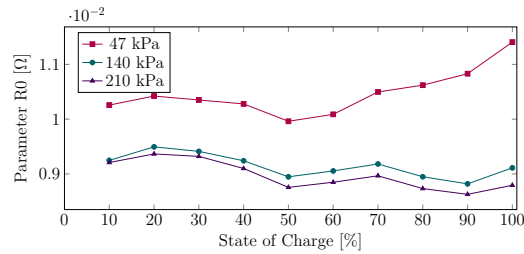


Fig. 3.8 Error contour plots at 90% SOC for cell model (1) at (a) 47 kPa (b) 140 kPa (c) 210 kPa and cell model (2) at (d) 0 kPa (e) 50 kPa (f) 100 kPa

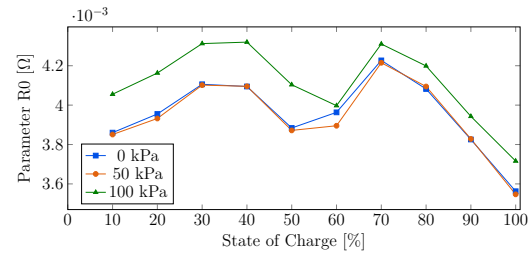
The contour plots in Figure 3.8 show sensitivity in both resistance values and capacitance fitted values. As expected, cell model (1) shows a higher sensitivity to pressure variation compared to the results from cell model (2). In addition

to the varying contour plots, the minimal error of the fitted parameter set is presented on the plots as the single scatter point. Similar to the contour plots themselves, it is also evident of the variation of optimal parameters with a more prominent difference in the high voltage model, cell model (1). This knowledge combined with the knowledge from the experimental testing is evidence that it is critical to optimise to relevant stack pressure.

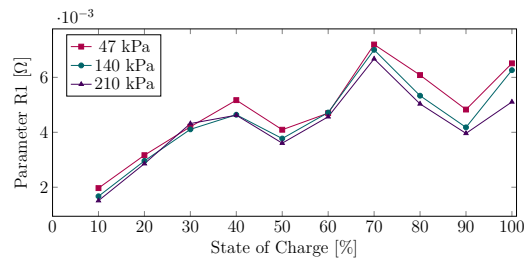
From here, the forward model was run through L-BFGS optimization as described earlier to determine the optimised parameter set for each condition across 10 measured state-of-charge points. These parameters were then plotted against state-of-charge and are presented in figure 3.9. The result at 0% SOC was excluded due to the pulse reaching a boundary condition and being an exceptional circumstance for fitting.



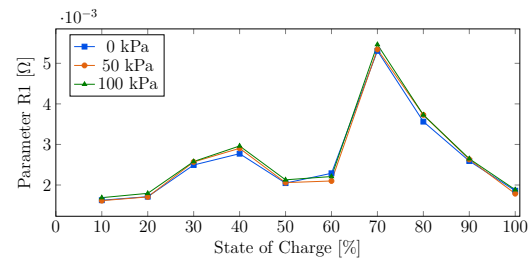
(a) Fitted R0 parameter for cell model (1)



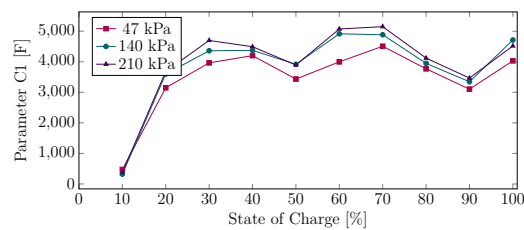
(b) Fitted R0 parameter for cell model (2)



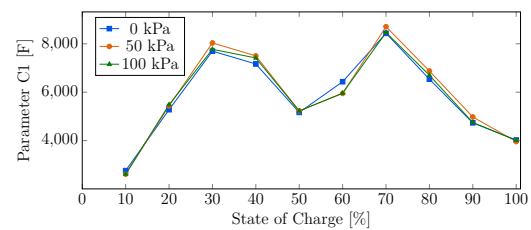
(c) Fitted R1 parameter for cell model (1)



(d) Fitted R1 parameter for cell model (2)



(e) Fitted C1 parameter for cell model (1)



(f) Fitted C1 parameter for cell model (2)

Fig. 3.9 Fitted Parameters vs State-of-Charge for a single RC equivalent circuit model

In all cases, there is some stochastic behaviour across the variation of parameters with cell model (1) showing a much more dramatic variation, presenting a justification for utilizing pressure as an input into ECM models. Furthermore, it can be seen that not only is there variation of these parameters, but that it is not a linear relationship, both across pressure and state-of-charge. The error across each pressure for the single RC model is presented in Figure 3.10.

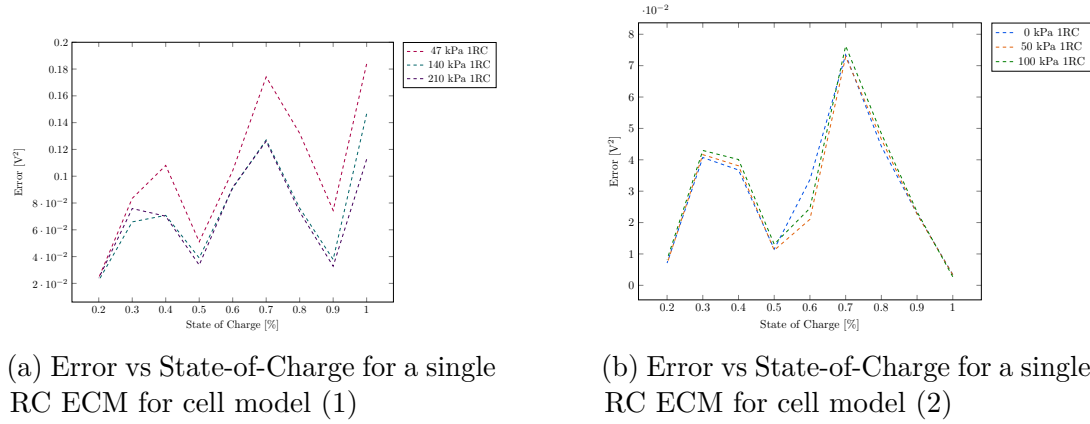


Fig. 3.10 Error vs SOC for a single RC ECM for each cell model at all tested pressures

It can be seen that there is significantly more error in the results from cell model (1) when compared to cell model (2) which accurately reflects the sensitivity that was seen in both the experimental model and the parameter sweep presented thus far. This is especially true at 100% and 70% SOC across all pressures; however, remains true at all state-of-charge points. Finally, investigating the forward model further, the voltage output at specific SOC points can be visualised as presented in Figure 3.11 and 3.12. Two state-of-charge points are presented for each model, and there is a benefit for fitting to the correct pressure.

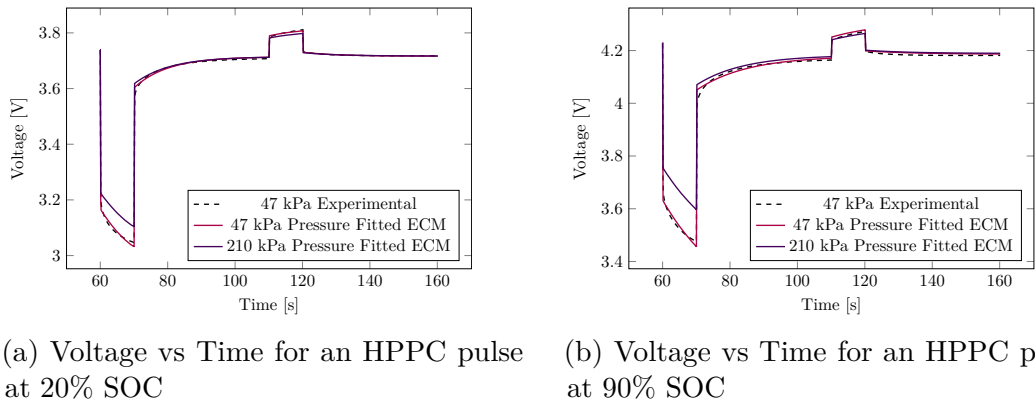


Fig. 3.11 Voltage vs Time for the Pressure Fitted ECM compared to experimental data at two SOC points for cell model (1)

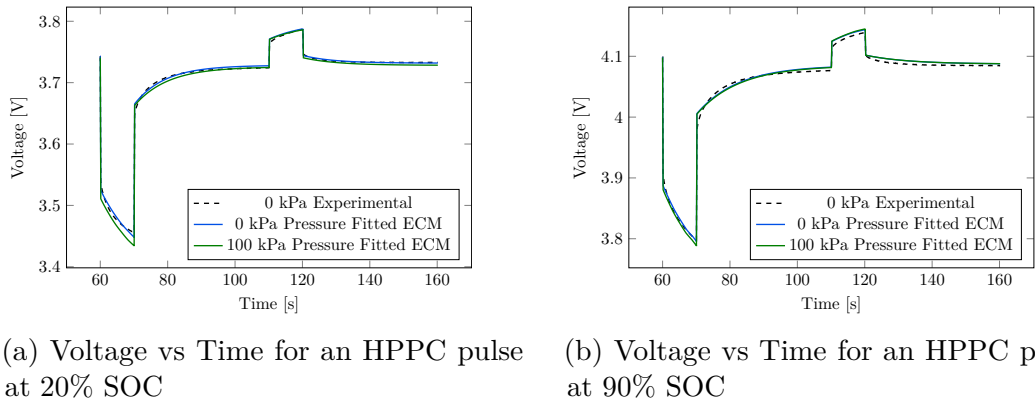
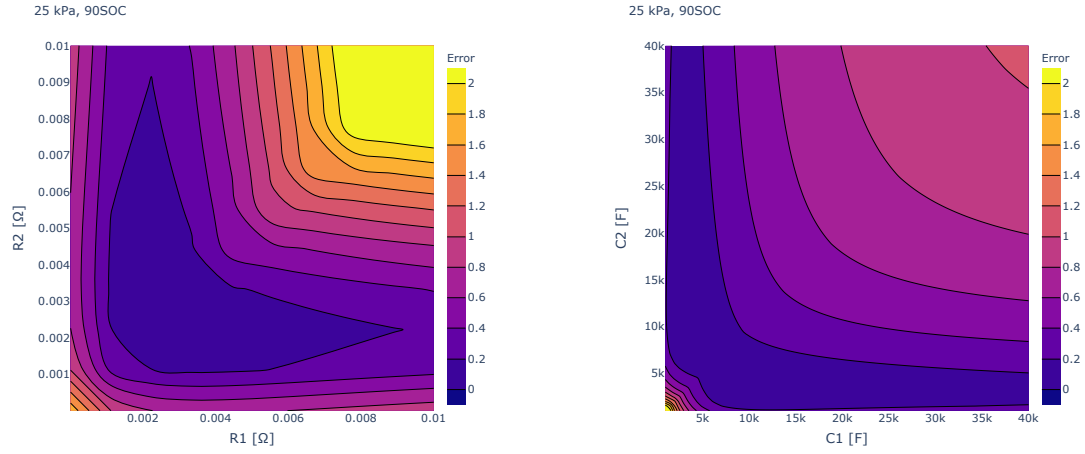


Fig. 3.12 Voltage vs Time for the Pressure Fitted ECM compared to experimental data at two SOC points for cell model (2)

The single-RC ECM shows a good improvement over not incorporating pressure when fitting the model. The error of cell model (1) increases from $0.012 V^2$ to $0.044 V^2$ when parameters from 210 kPa fitting are used at 20% SOC with an increase from $0.014 V^2$ to $0.025 V^2$ at 90% SOC. Across all SOC points, an average increase in error of 60% is observed for utilising the fitted parameters at 210 kPa for experimental data at 47 kPa. Error increase of up to 68% is observed for model (1). Conversely, cell model (2) sees a much smaller variation but still sees up to 27% increase in error when the incorrect pressure parameters are used. One methodology to improve the response of the system is to add an RC pair to the model; however, this comes with the trade-off of additional parameters to fit as well as longer run times. The optimisation was repeated at each state-of-charge point for the 5 required parameters: $[R1, R2, C1, C2, R0]$. The parameter sweep and optimisation process was then repeated for the two-RC model. To present

the results in a meaningful way, two slices of the parameter sweep are presented in Figure 3.13.

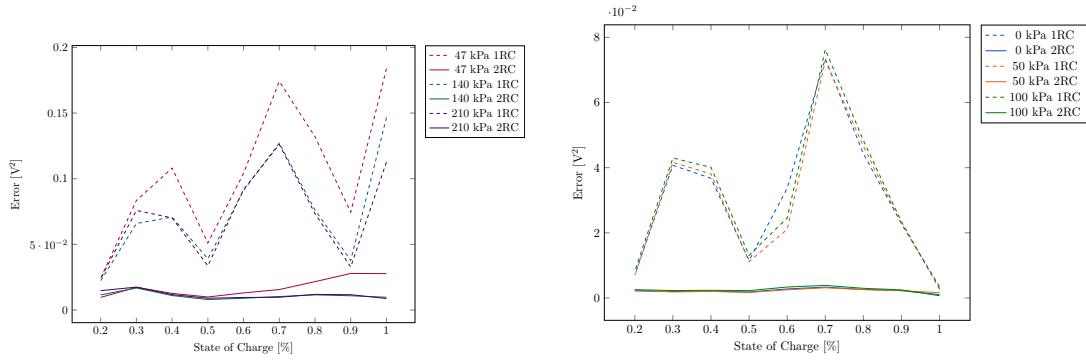


(a) Error contour plot for fixed C values

(b) Error contour plot for fixed R values

Fig. 3.13 Error contour plot for a second order ECM for minimum R_0 with slices through a fixed (a) capacitance and (b) resistance

Slices are taken at the minimum error for R_0 first. Slices are then taken through the minimum capacitance pair (Figure 3.13a) and the minimum resistance pair (Figure 3.13b). It is important to note that the system is not a true 5-dimensional problem, as the RC pairs are not sequentially dependent. The parameter sweep provided insight into the sensitivity of the parameters, as well as provided informed optimisation windows to minimize the time required for the optimisation process. From here, the optimisation was then completed in the same process with the normalised fit parameters, and the error was compared. Both models saw significant improvements across all SOC points with a mean improvement of 56.1% for cell model (1) and a mean improvement of 63.5% for cell model (2) as presented in Figure 3.14.

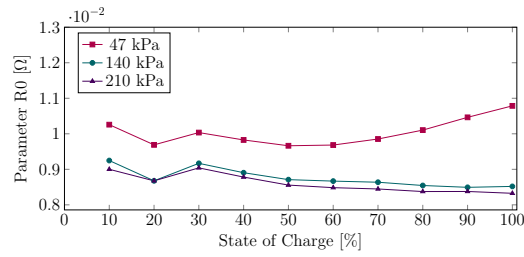


(a) Error vs SOC for a 1RC ECM and 2RC ECM for cell model (1)

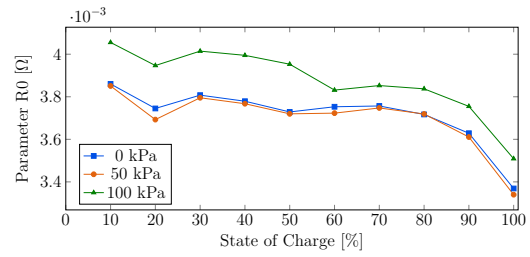
(b) Error vs SOC for a 1RC ECM and 2RC ECM for cell model (2)

Fig. 3.14 Least Squared Error vs SOC for single RC and two RC equivalent circuit models for each cell model

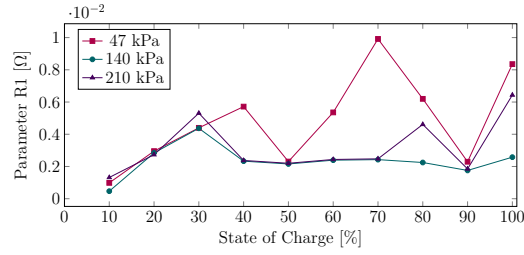
Plotting the fitted parameters against state-of-charge provides further insight into the stochastic behaviour of the fitted parameters. Unlike the single RC model, there is very little correlation between any of the RC parameters as presented in Figure 3.15.



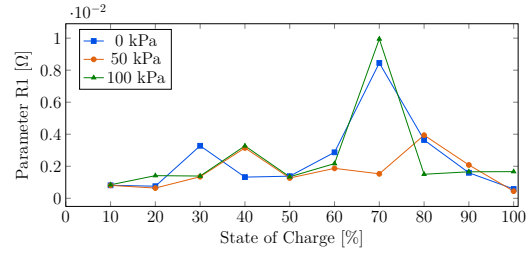
(a) Fitted R0 parameter for cell model (1)



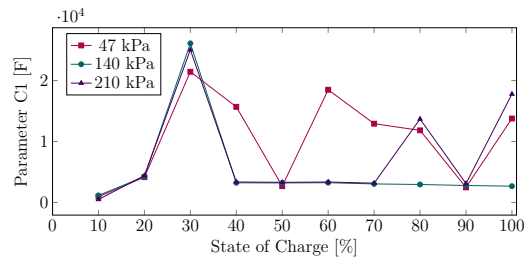
(b) Fitted R0 parameter for cell model (2)



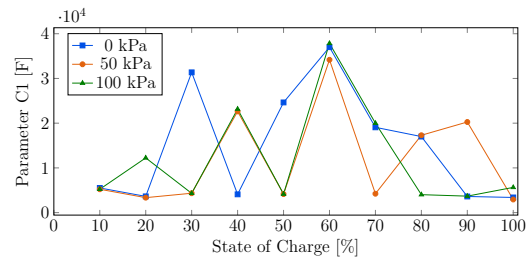
(c) Fitted R1 parameter for cell model (1)



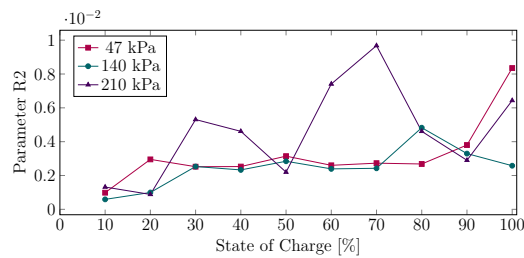
(d) Fitted R1 parameter for cell model (2)



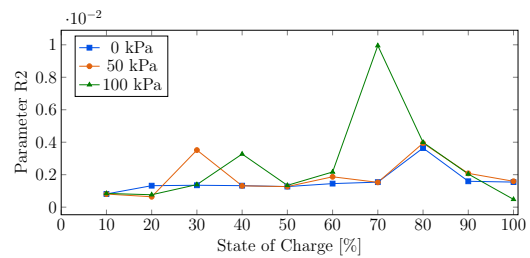
(e) Fitted C1 parameter for cell model (1)



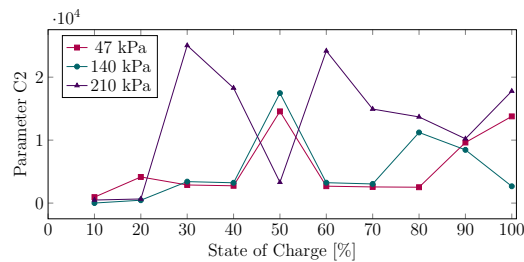
(f) Fitted C1 parameter for cell model (2)



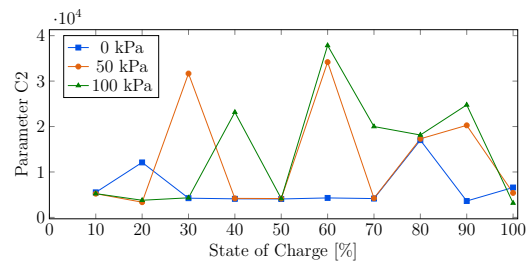
(g) Fitted R2 parameter for cell model (1)



(h) Fitted R2 parameter for cell model (2)



(i) Fitted C2 parameter for cell model (1)



(j) Fitted C2 parameter for cell model (2)

Fig. 3.15 Fitted Parameters vs State-of-Charge for a two RC equivalent circuit model

The 2RC model is an improvement for both cell models; however, it is important to consider the negative impacts of the increased complexity. Benchmarking was completed utilizing the BenchmarkTools.jl package in Julia with the parameters set to run for 60 seconds. This resulted in 5-8 simulations for each run. Each pressure was run at 50% SOC with the times and computational memory requirements averaged. For the single RC model, it took an average of 3.86 seconds with the total memory used throughout the calculation being 3.02 GB. The two-RC model took a mean time of 9.23 seconds with a total memory used of 5.02 GB.

3.3.1 Conclusions

Overall, there is a benefit to including the external stack pressure when developing equivalent circuit models with pouch cells. The single RC model sees improvement from using a pressure informed fitting methodology with up to 68% reduction in error. There is some correlation in the fitted parameters but it is not linear and varies between the two models evaluated. The two-RC model sees a further error reduction of up to 63.5% with the fitted parameters being highly stochastic with little correlation across the applied stack pressures. This comes at the cost of both time and required total memory, though. Depending on the required fidelity from the applications, both models provide a good improvement when utilising the pressure informed fitting methods when compared to pressure agnostic methods.

Chapter 4

Conclusions and Further Work

With the rapid adoption of battery electric vehicles and a large amount of governance toward the same objective, lithium-ion technologies must keep up. While many advancements are being made at the cell level, it is also important to consider current technologies and how to best optimise performance. One such consideration is accounting for how stack pressure affects performance on widely used high-performance pouch cells. Despite there being work confirming that cells expand and contract during intercalation as well as over the life of a cell and that this affects the performance of the cell [40, 62, 38, 63, 35], there is little available on testing and modelling methodology in this area. This work presents experimental methodology and results on how cell performance is affected by variations in stack pressure. It then presents how this affects a commonly used data-driven cell model. Two different cell models were tested under varying pressure conditions utilising a constant displacement methodology. The cells were tested under a cyclic ageing procedure that included a high rate charge and discharge at 100% depth of discharge. Reference performance testing included full-range SOC HPPC testing and a slow charge and discharge load. Evaluating pressure over the state-of-charge range showed that pressure was dependent both on charge rate and state-of-charge as well as initial pressure. Through capacity testing, it was also clear that initial stack pressure had an impact not only on available capacity but also on the state-of-health over 100 cycles. It was also clear that the effect of stack pressure is dependent on cell design as witnessed in the resistance and power evaluations. The high-power cell exhibited a higher sensitivity to pressure than the standard cell.

A pressure-informed equivalent circuit model (PIECM) was then presented. The model confirms the R_0 pressure dependency as concluded in previous chapter for both cell models. For model (1) there is also a clear dependency on the R_1

and C1 parameters; however, there is a less clear dependency on the R1 and C1 parameters for model (2). Additionally, the variation across all parameters is non-linear.

A second-order (2RC) model was also investigated and there was a further significant improvement to the model; however, there was also a large increase in both memory requirement and mean run time. While there was an improvement across all state-of-charge points in error for including pressure as a consideration, the returns on the additional computing times may be negligible based on the fidelity of the application.

Across this work, it is clear that initial stack pressure affects the performance and lifetime of lithium-ion pouch cells. This work shows that stack pressure should be a consideration when utilising pouch cells and that assembly can drastically affect the results achieved. It also highlights that relatively small changes in pressure can have a large impact on the performance. Finally, this work presents that pouch cell users could also benefit from considering stack pressure when developing control systems and working on developing lifetime models for lithium-ion pouch cells.

4.1 Further Work

This thesis could be expanded through further experimental testing. First, it is recommended that all testing be repeated on additional samples to attain statistical relevance and enable an uncertainty analysis on the observed pressure effects. It is also recommended to expand the pressure design space and investigate higher pressures on both cell models to confirm the behaviour across a larger design space. In addition to this, it is recommended to continue life cycle testing to the end of life. Finally, it is recommended to include environmental temperature considerations as it is hypothesized that the temperature will not only affect the performance of the cell but also the expansion and contraction during operation. This will be highly dependent on the materials used in within the manufacturing of the cell, environmental temperature, and heat generation of the experimental protocol.

Further model development would benefit from incorporating pressure and temperature dependencies in a more robust methodology that could be deployed into a control system. In addition, model refinement would provide the opportunity to speed up the fitting process and allow for more usability across larger design spaces.

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Appendix A

Datasheet for Melasta SLPB7336128HV

The full datasheet for the high-voltage cell used in the experimental testing can be found in this appendix.

Product Specification

Polymer Li-Ion Cell

3.8V 3700mAh 15C

(Model No.: SLPB7336128HV)



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MELASTA

锂聚合物电池 LIPO BATTERIES

Dec 18th,2020

This information is generally descriptive only and is not intended to make or imply any representation, guarantee or warranty with respect to any cells and batteries. Cell and battery designs/specifications are subject to modification without notice. Contact MELASTA for the latest information.

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1. 序言 PREFACE

此规格书适用于深圳市风云电池有限公司的锂聚合物可充电电池产品

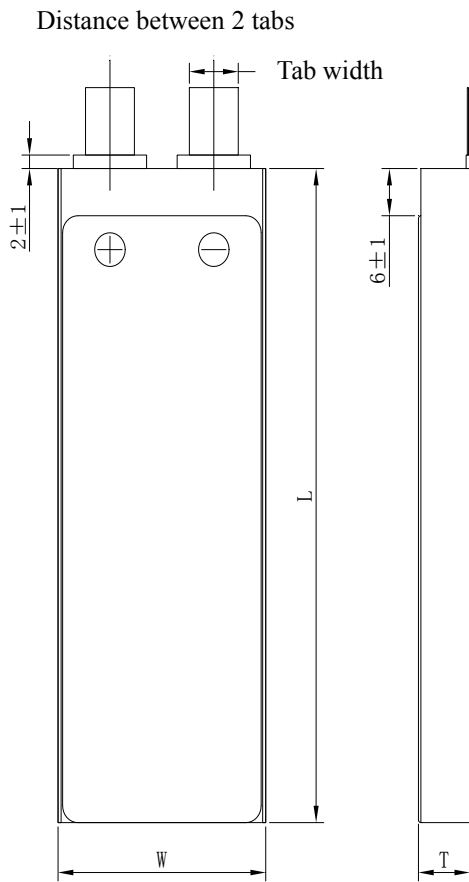
The specification is suitable for the performance of Lithium-Polymer (LIP) rechargeable battery produced by the SHENZHEN MELASTA BATTERY CO., LTD.

2. 型号 MODEL

SLPB7336128HV 3700mAh 15C 3.8V

3. 产品规格 SPECIFICATION

单颗电池规格 Specifications of single cell



◆电芯正极材料 Cell Cathode Material		LiCoO2
◆标称容量 Typical Capacity①		3700mAh
◆标称电压 Nominal Voltage		3.8V
◆ 充电条件 Charge Condition	最大电流 Max. Continuous charge Current	7.4A
	峰值充电 Peak charge current	12A(≤3sec)
	电压 Voltage	4.35V±0.03V
◆ 放电条件 Discharge Condition	Max Continuous Discharge Current	55A
	Peak Discharge Current	80A(≤3sec)
	Cut-off Voltage	3.0V
◆交流内阻 AC Impedance(mΩ)		<2.6
◆循环寿命【充电:0.5C,放电:15C】 Cycle Life【CHA:0.5C,DCH:15C】		>100cycles
◆使用温度 Operating Temp.	充电 Charge	0℃~45℃
	放电 Discharge	-20℃~60℃
◆ 电芯尺寸 Cell Dimensions	厚度 Thickness(T)	7.0±0.3mm
	宽度 Width(W)	36.0±0.5mm
	长度 Length(L)	128.0±0.5mm
	极耳间距 Distance between 2 tabs	15±1mm
◆ 极耳尺寸 Dimensions of Cell tabs	极耳材料 Tab Material	Nickel-plated Copper
	极耳宽度 Tab Width	8mm
	极耳厚度 Tab Thickness	0.2mm
	极耳长度 Tab Length	10.0±1.0mm
◆重量 Weight(g)		69±2g
①标称容量： 0.2C,4.35V~3.0V@23℃±2℃ Typical Capacity:0.2C,4.35V~3.0V@23℃±2℃		

4. 电芯性能检查及测试 BATTERY CELL PERFORMANCE CRITERIA

在进行下列各项测试前每颗电池应用 0.5C 放至 3.0V。如果没有特别规定，测试应在电池交付 1 个月内按以下各项条件进行：

Before proceed the following tests, the cells should be discharged at 0.5C to 3.0V cut off. Unless otherwise stated, tests should be done within one month of delivery under the following conditions:

环境温度 Ambient temperature: $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$

相对湿度 Relative Humidity: $65 \pm 20\% \text{RH}$

注意标准充放电为 Note Standard Charge/Discharge Conditions:

充电 Charge: 以 0.5C 电流恒流充电至限制电压 4.35V 时,改为恒压充电,直到截止电流为 0.05C 时停止充电;The battery will be charged to 4.35V with 0.5C from constant current to constant voltage, when the current is 0.05C, stop to charge.;

放电 Discharge: 0.5C to 3.0V/cell

测试项目 Test	单位 Unit	规格 Specification	条件 Condition	备注 Remarks
容量 Capacity	mAh	≥ 3700	标准充放电 Standard Charge / Discharge	允许循环 3 次 Up to 3 cycles are allowed
开路电压 Open Circuit Voltage (OCV)	V	≥ 4.20	标准充电后 1 个小时内 Within 1 hr after standard charge	单位颗 Unit cell
内阻 Internal Impedance (IR)	m Ω	≤ 2.6	充满电后用 1kHz 测试 Upon fully charge at 1kHz	*
高倍率放电 High Rate Discharge (15C)	min	≥ 3.6	标准充电/休息 5 分钟 用 15C 放电至 3.0V Standard Charge/rest 5min discharge at 15C to 3.0V	允许循环 3 次 Up to 3 cycles are allowed
低温放电 Low Temperature Discharge	min	≥ 210	标准充电后贮藏在 $-20 \pm 2^{\circ}\text{C}$ 环境中 2 小时 然后用 0.2C 放电 Standard Charge, Storage: 2hrs at $-20 \pm 2^{\circ}\text{C}$ 0.2C discharge at $0 \pm 2^{\circ}\text{C}$	3.0V/cell Cut-off
自放电 Charge Reserve	min	$\geq 85\%$ (初始容量 First Capacity)	标准充满电后 20 度贮藏 30 天, 标准 0.5C 放电 Standard charge Storage at 20 degree: 30days Standard discharge (0.5C)	3.0V/cell Cut-off
寿命测试 Cycle Life Test	Cycle times	≥ 100	充电: 0.5C 充电至 4.35V, 放电, 15C 放电至 3.0V, 当放电容量降至初始容量的 80% 时, 所完成的循环次数定义为该电芯的循环寿命 Charge: 0.5C to 4.35V, Discharge: 15C to 3.0V, 80% or more of 1 st cycle capacity at 15C discharge of Operation	Retention capacity 容量保持 $\geq 80\%$ of initial capacity

短路测试 External Short Circuit	N/A	不着火不爆炸 No Fire and No Explosion	标准充电后, 在 20℃±5 环境中用超过 0.75mm ² 金属丝将单颗电池短路至电池恢复到常温。 After standard charge, short-circuit the cell at 20℃±5℃ until the cell temperature returns to ambient temperature.(cross section of the wire or connector should be more than 0.75mm ²)	*
自由跌落测试 Free Falling(drop)	N/A	不着火不爆炸 No Fire and No Explosion	跌标准充电后, 搁置 2 小时。从 1.2M 高任意方向自由跌落 30MM 厚木板 3 次 Standard Charge, and then leave for 2hrs, check battery before / after drop Height: 1.2m Thickness of wooden board: 30mm Direction is not specified Test for 3 times	*

5. 贮存及其它事项 STORAGE AND OTHERS

5.1 环境温度 Ambient temperature: 20℃±5℃

相对湿度 Relative Humidity: 65±20%RH

5.2 请每隔 3 个月按下面方法激活电池一次:

Please activate the battery once every 3 months according to the following method:

0.2C 充电至 4.35V, 休息 5 分钟, 然后用 0.2C 放电至每颗电池 3.0V, 休息 5 分钟, 0.2C 充电 3.9V。

Charge at 0.2C to 4.35V, rest 5 min, then discharge with 0.2C to 3.0V/cell, rest 5 min, then charge at 0.2C to 3.9V.

6. 聚合物锂离子充电电芯操作指示及注意事项 HANDLING PRECAUTIONS AND GUIDLINE

声明一:

客户若需要将电芯用于超出文件规定以外的设备, 或在文件规定以外的使用条件下使用电芯, 应事先联系风云公司, 因为需要进行特定的实验测试以核实电芯在该使用条件下的性能及安全性。

Note(1):

The customer is requested to contact MELASTA in advance, if and when the customer needs other applications or operating conditions than those described in this document. Additional experimentation may be required to verify performance and safety under such conditions.

声明二:

对于在超出文件规定以外的条件下使用电芯而造成的任何意外事故, 风云公司概不负责

Note (2):

MELASTA will take no responsibility for any accident when the cell is used under other conditions than those described in this Document.

声明三:

如有必要, 风云公司会以书面形式告之客户有关正确操作使用电芯的改进措施。

MELASTA will inform, in a written form, the customer of improvement(s) regarding proper use and handing of the cell, if it is deemed necessary.

6.1. 充电 Charging

6.1.1 充电电流 Charging current:

充电电流不得超过本标准书中规定的最大充电电流。使用高于推荐值电流充电将可能引起电芯的充放电性能、机械性能和安全性能的问题, 并可能会导致发热或泄漏。

Charging current should be less than maximum charge current specified in the Product Specification.

Charging with higher current than recommended value may cause damage to cell electrical, mechanical and safety performance and could lead to heat generation or leakage.

6.1.2. 充电电压 Charging voltage:

充电电压不得超过本标准书中规定的额定电压 (4.35V/电芯)。4.38V 为充电电压最高极限, 充电器的设计应满足此条件; 电芯电压高于额定电压值时, 将可能引起电芯的充放电性能、机械性能和安全性能的问题, 可能会导致发热或泄漏。

Charging shall be done by voltage less than that specified in the Product Specification (4.35V/cell).

Charging beyond 4.38V, which is the absolute maximum voltage, must be strictly prohibited. The charger shall be designed to comply with this condition. It is very dangerous that charging with higher voltage than maximum voltage may cause damage to the cell electrical, mechanical safety performance and could lead to heat generation or leakage.

6.1.3. 充电温度 Charging temperature:

电芯必须在 0℃~45℃的环境温度范围内进行充电

The cell shall be charged within 0℃~45℃ range in the Product Specification.

6.1.4. 禁止反向充电 Prohibition of reverse charging:

正确连接电池的正负极, 严禁反向充电。若电池正负极接反, 将无法对电芯进行充电。同时, 反向充电会降低电芯的充放电性能、安全性, 并会导致发热、泄漏。

Reverse charging is prohibited. The cell shall be connected correctly. The polarity has to be confirmed before wiring. In case of the cell is connected improperly, the cell cannot be charged. Simultaneously, the reverse charging may cause damaging to the cell which may lead to degradation of cell performance and damage the cell safety, and could cause heat generation or leakage.

6.2. 放电 Discharging

6.2.1. 放电电流 Discharging current

放电电流不得超过本标准书规定的最大放电电流, 大电流放电会导致电芯容量剧减并导致过热。

The cell shall be discharged at less than the maximum discharge current specified in the Product Specification. High discharging current may reduce the discharging capacity significantly or cause over-heat.

6.2.2. 放电温度 Discharging temperature

电芯必须在-20℃~60℃的环境温度范围内进行放电。

The cell shall be discharged within -20℃~60℃ range specified in the Product Specification.

6.2.3. 过放电 Over-discharging:

需要注意的是, 在电芯长期未使用期间, 它可能会用其它自放电特性而处于某种过放电状态。为防止放电的发生, 电芯应定期充电, 将其电压维持在 3.6V 至 3.9V 之间。

过放电会导致电芯性能、电池功能的丧失。

充电器应有装置来防止电池放电至低于本标准书规定的截止电压。此外, 充电器还应有装置以防止重复充电, 步骤如下:

电池在快速充电之前, 应先以一小电流 (0.01C) 预充电 15~30 分钟, 以使 (每个) 电芯的电压达到 3V 以上, 再进行快速充电。可用一计时器来实现该预充电步骤。如果在预充电规定时间内, (个别) 电芯的电压仍未升到 3.0V 以上, 充电器应能够停止下一步快速充电, 并显示该电芯/电池正处于非正常状态。

It should be noted that the cell would be at over-discharged state by its self-discharge characteristics in case the cell is not used for long time. In order to prevent over-discharging, the cell shall be charged periodically to maintain between 3.6V and 3.9V.

Over-discharging may causes loss of cell performance, characteristics, or battery functions.

The charger shall be equipped with a device to prevent further discharging exceeding a cut-off voltage specified in the Product Specification. Also the charger shall be equipped with a device to control the recharging procedures as follows:

The cell battery pack shall start with a low current (0.01C) for 15-30 minutes, i.e.-charging, before rapid charging starts. The rapid charging shall be started after the (individual) cell voltage has been reached above 3V within 15-30 minutes that can be determined with the use of an appropriate timer for pre-charging. In case the (individual) cell voltage does not rise to 3V within the pre-charging time, then the charger shall have functions to stop further charging and display the cell/pack is at abnormal state.

6.3. 贮存 Storage:

电芯储存温度必须在 $-10^{\circ}\text{C}\sim 45^{\circ}\text{C}$ 的范围内,长期存储电池(超过3个月)须置于温度为 $23\pm 5^{\circ}\text{C}$ 、湿度为 $65\pm 20\%\text{RH}$ 的环境中,贮存电压为3.6V~3.9V

The cell shall be stored within $-10^{\circ}\text{C}\sim 45^{\circ}\text{C}$ range environmental condition, If the cell has to be stored for a long time (Over 3 months), the environmental condition should be; Temperature: $23\pm 5^{\circ}\text{C}$

Humidity: $65\pm 20\%\text{RH}$, The voltage for a long time storage shall be 3.6V~3.9V range.

6.4. 电芯操作注意事项 Handling of Cells:

由于电芯属于软包装,为保证电芯的性能不受损害,必须小心对电芯进行操作。

Since the battery is packed in soft package, to ensure its better performance, it's very important to carefully handle the battery;

6.4.1. 铝箔包装材料易被尖锐部件损伤, 诸如镍片, 尖针。

The soft aluminum packing foil is very easily damaged by sharp edge parts such as Ni-tabs, pins and needles.

·禁止用尖锐部件碰撞电池;

Don't strike battery with any sharp edge parts;

·取放电芯时, 请修短指甲或戴上手套;

Trim your nail or wear glove before taking battery;

·应清洁工作环境, 避免有尖锐物体存在;

Clean work table to make sure no any sharp particle;

6.4.2. 禁止弯折顶封边;

Don't bend or fold sealing edge;

6.4.3. 禁止打开或破坏折边;

Don't open or deform folding edge;

6.4.4. 禁止弯折极片;

Don't bend tab ;

6.4.5. 禁止坠落、冲击、弯折电芯;

Don't Fall, hit, bend battery body;

6.4.6. 任何时候禁止短路电芯, 它会导致电芯严重损坏;

Short circuit terminals of battery is strictly prohibited, it may damage battery;

6.5. 电池外壳设计 Notice Designing Battery Pack;

·电池外壳应有足够的机械强度以保证其内部电芯免受机械撞击;

Battery pack should have sufficient strength and battery should be protected from mechanical shock;

制造商保留在没有预先通知的情况下改变和修正设计及规格说明书的权力

Melasta reserves the right to alter or amend the design, model and specification without prior notice

·外壳内安装电芯的部位不应有锋利的边角;

No Sharp edge components should be inside the pack containing the battery;

6.6. 电芯与外壳组装注意事项 Notice for Assembling Battery Pack

6.6.1. 电芯的连接 Tab connection

建议使用超声波焊接或点焊技术来连接电芯与保护电路模块或其它部分。如使用手工锡焊, 须注意以下事项, 以保证电芯的功能:

Ultrasonic welding or spot welding is recommended to connect battery with PCM or other parts. If apply manual solder method to connect tab with PCM, below notice is very important to ensure battery performance.

a) 烙铁的温度可控能防静电;

The solder iron should be temperature controlled and ESD safe

b) 烙铁温度不能超过 350℃

Soldering temperature should not exceed 350℃

c) 锡焊时间不能超过 3 秒;

Soldering time should not be longer than 3s

d) 锡焊次数不能超过 5 次;

Soldering time should not exceed 5 times Keep battery tab cold down before next time soldering

e) 必须在极片冷却后再进行二次焊接; 禁止直接加热电芯, 高于 100℃会导致电芯损坏。

Directly heat cell body is strictly prohibited, Battery may be damaged by heat above approx. 100℃

6.6.2. 电芯的安装 Cell fixing

·应将电芯的宽面安装在外壳内;

The battery should be fixed to the battery pack by its large surface area

·电芯不得在壳内活动。

No cell movement in the battery pack should be allowed

7. 其它事项 OTHERS

7.1. 防止电池内短路 Prevention of short circuit within a battery pack

使用足够的绝缘材料对线路进行保护

Enough insulation layers between wiring and the cells shall be used to maintain extra safety protection.

7.2. 严禁拆卸电芯 Prohibition of disassembly

7.2.1. 拆卸电芯可能会导致内部短路, 进而引起鼓气、着火及其它问题

The disassembling may generate internal short circuit in the cell, which may cause gassing, firing, or other problems.

7.2.2. 聚合物锂电池理论上不存在流动的电解液, 但万一有电解液泄漏而接触到皮肤、眼睛或身体其它部位, 应立即用清水冲洗电解液并就医

LIP battery should not have liquid from electrolyte flowing, but in case the electrolyte come into contact with the skin, or eyes, physicians shall flush the electrolyte immediately with fresh water and medical advice is to be sought.

7.3. 在任何情况下, 不得燃烧电芯或将电芯投入火中, 否则会引起电芯燃烧, 这是非常危险的, 应绝对禁止

Never incinerate nor dispose the cells in fire. These may cause firing of the cells, which is very dangerous and is prohibited.

7.4 不得将电芯浸泡液体，如淡水、海水、饮料(果汁、咖啡)等

The cells shall never be soaked with liquids such as water, seawater drinks such as soft drinks, juices coffee or others.

7.5 更换电芯应由电芯供应商或设备供应商完成，用户不得自行更换

The battery replacement shall be done only by either cells supplier or device supplier and never be done by the user.

7.6 禁止使用已损坏的电芯 Prohibition of use of damaged cells

电芯在运输过程中可能因撞击等原因而损坏，若发现电芯有任何异常特征，如电芯塑料封边损坏，外壳破损，闻到电解液气体，电解液泄漏等，该电芯不得使用。

有电解液泄漏或散发电解液气味的电池应远离火源以避免着火。

The cells might be damaged during shipping by shock. If any abnormal features of the cells are found such as damages in a plastic envelop of the cell, deformation of the cell package, smelling of electrolyte, electrolyte leakage and others, the cells shall never be used any more.

The cells with a smell of the electrolyte or a leakage shall be placed away from fire to avoid firing.

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Appendix B

Datasheet for Melasta SLPBA442124

The full datasheet for the conventional cell used in the experimental testing can be found in this appendix.

Product Specification

Polymer Li-Ion Cell

3.7V 5500mAh 20C

(Model No.:SLPBA442124)



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MELASTA

聚合物锂电池 LIPO BATTERIES

Apr 30th,2019

This information is generally descriptive only and is not intended to make or imply any representation, guarantee or warranty with respect to any cells and batteries. Cell and battery designs/specifications are subject to modification without notice. Contact MELASTA for the latest information.

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1. 序言 PREFACE

此规格书适用于深圳市风云电池有限公司的锂聚合物可充电电池产品

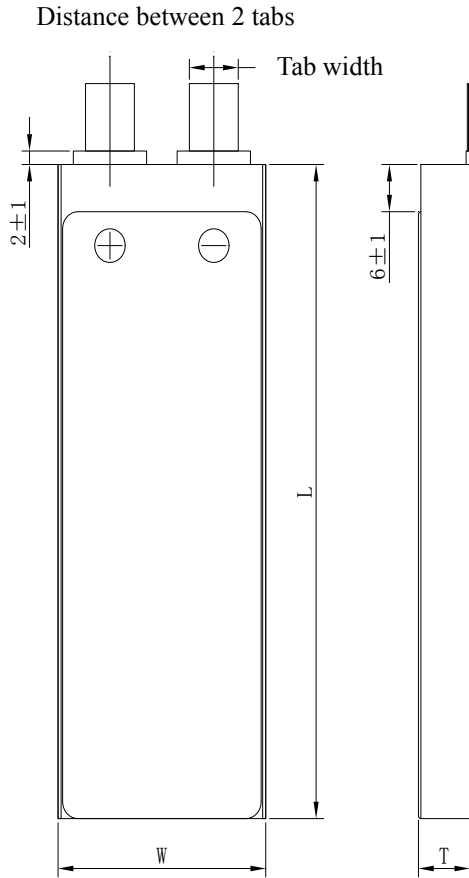
The specification is suitable for the performance of Lithium-Polymer (LIP) rechargeable battery produced by the SHENZHEN MELASTA BATTERY CO., LTD.

2. 型号 MODEL

SLPBA442124 5500mAh 20C 3.7V

3. 产品规格 SPECIFICATION

单颗电池规格 Specifications of single cell



◆电芯正极材料 Cell Cathode Material		LiCoO2
◆标称容量 Typical Capacity①		5500mAh
◆标称电压 Nominal Voltage		3.7V
◆ 充电条件 Charge Condition	最大电流 Max. Continuous charge Current	11A
	峰值充电 Peak charge current	16.5A(≤3sec)
	电压 Voltage	4.2V±0.03V
◆ 放电条件 Discharge Condition	Max Continuous Discharge Current	110A
	Peak Discharge Current	137.5A(≤3sec)
	Cut-off Voltage	3.0V
◆交流内阻 AC Impedance(mOHM)		<2.0
◆循环寿命【充电:0.5C,放电:20C】 Cycle Life【CHA:0.5C,DCH:20C】		>100cycles
◆使用温度 Operating Temp.	充电 Charge	10℃~45℃
	放电 Discharge	-20℃~60℃
◆ 电芯尺寸 Cell Dimensions	厚度 Thickness(T)	9.9±0.3mm
	宽度 Width(W)	41.8±0.5mm
	长度 Length(L)	125.5±0.5mm
	极耳间距 Distance between 2 tabs	21±1.0mm
◆ 极耳尺寸 Dimensions of Cell tabs	极耳材料 Tab Material	Nickel-plated Copper
	极耳宽度 Tab Width	12mm
	极耳厚度 Tab Thickness	0.2mm
	极耳长度 Tab Length	30±1.5mm
◆重量 Weight(g)		116.5±2.5g
①标称容量: 0.2C,4.2V~3.0V@23℃±2℃ Typical Capacity:0.2C,4.2V~3.0V@23℃±2℃		

4. 电芯性能检查及测试 BATTERY CELL PERFORMANCE CRITERIA

在进行下列各项测试前每颗电池应用 0.5C 放至 3.0V。如果没有特别规定，测试应在电池交付 1 个月内按以下各项条件进行：

Before proceed the following tests, the cells should be discharged at 0.2C to 3.0V cut off. Unless otherwise stated, tests should be done within one month of delivery under the following conditions:

环境温度 Ambient temperature: $20^{\circ}\text{C} \pm 5^{\circ}\text{C}$

相对湿度 Relative Humidity: $65 \pm 20\% \text{RH}$

注意标准充放电为 Note Standard Charge/Discharge Conditions:

充电 Charge: 以 0.5C 电流恒流充电至限制电压 4.2V 时,改为恒压充电,直到截止电流为 0.05C 时停止充电;The battery will be charged to 4.2V with 0.5C from constant current to constant voltage, when the current is 0.05C, stop to charge.;

放电 Discharge: 0.5C to 3.0V/cell

测试项目 Test	单位 Unit	规格 Specification	条件 Condition	备注 Remarks
容量 Capacity	mAh	≥ 5500	标准充放电 Standard Charge / Discharge	允许循环 3 次 Up to 3 cycles are allowed
开路电压 Open Circuit Voltage (OCV)	V	≥ 4.15	标准充电后 1 个小时内 Within 1 hr after standard charge	单位颗 Unit cell
内阻 Internal Impedance (IR)	m Ω	≤ 2.0	充满电后用 1kHz 测试 Upon fully charge at 1kHz	*
高倍率放电 High Rate Discharge (20C)	min	≥ 2.7	标准充电/休息 5 分钟 用 20C 放电至 3.0V Standard Charge/rest 5min discharge at 20C to 3.0V	允许循环 3 次 Up to 3 cycles are allowed
低温放电 Low Temperature Discharge	min	≥ 210	标准充电后贮藏在 $-20 \pm 2^{\circ}\text{C}$ 环境中 2 小时 然后用 0.2C 放电 Standard Charge, Storage: 2hrs at $-20 \pm 2^{\circ}\text{C}$ 0.2C discharge at $0 \pm 2^{\circ}\text{C}$	3.0V/cell Cut-off
自放电 Charge Reserve	min	$\geq 85\%$ (初始容量 First Capacity)	标准充满电后 20 度贮藏 30 天, 标准 0.5C 放电 Standard charge Storage at 20 degree: 30days Standard discharge (0.5C)	3.0V/cell Cut-off
寿命测试 Cycle Life Test	Cycle times	≥ 100	充电: 0.5C 充电至 4.2V, 放电, 20C 放电至 3.0V, 当放电容量降至初始容量的 80% 时, 所完成的 循环次数定义为该电芯的循环寿命 Charge: 0.5C to 4.2V, Discharge: 20C to 3.0V, 80% or more of 1 st cycle capacity at 20C discharge of Operation	Retention capacity 容量保持 $\geq 80\%$ of initial capacity

短路测试 External Short Circuit	N/A	不着火不爆炸 No Fire and No Explosion	标准充电后, 在 20℃±5 环境中用超过 0.75mm ² 金属丝将单颗电池短路至电池恢复到常温。 After standard charge, short-circuit the cell at 20℃±5℃ until the cell temperature returns to ambient temperature.(cross section of the wire or connector should be more than 0.75mm ²)	*
自由跌落测试 Free Falling(drop)	N/A	不着火不爆炸 No Fire and No Explosion	跌标准充电后, 搁置 2 小时。从 1.2M 高任意方向自由跌落 30MM 厚木板 3 次 Standard Charge,and then leave for 2hrs,check battery before / after drop Height: 1.2m Thickness of wooden board: 30mm Direction is not specified Test for 3 times	*

5. 贮存及其它事项 STORAGE AND OTHERS

5.1 环境温度 Ambient temperature: 20℃±5℃

相对湿度 Relative Humidity: 65±20%RH

5.2 请每隔 3 个月按下面方法激活电池一次:

Please activate the battery once every 3 months according to the following method:

0.2C 充电至 4.2V, 休息 5 分钟, 然后用 0.2C 放电至每颗电池 3.0V, 休息 5 分钟, 0.2C 充电 3.9V。

Charge at 0.2C to 4.2V, rest 5 min, then discharge with 0.2C to 3.0V/cell,rest 5 min, then charge at 0.2C to 3.9V.

6. 聚合物锂离子充电电芯操作指示及注意事项 HANDLING PRECAUTIONS AND GUIDLINE

声明一:

客户若需要将电芯用于超出文件规定以外的设备, 或在文件规定以外的使用条件下使用电芯, 应事先联系风云公司, 因为需要进行特定的实验测试以核实电芯在该使用条件下的性能及安全性。

Note(1):

The customer is requested to contact MELASTA in advance, if and when the customer needs other applications or operating conditions than those described in this document. Additional experimentation may be required to verify performance and safety under such conditions.

声明二:

对于在超出文件规定以外的条件下使用电芯而造成的任何意外事故, 风云公司概不负责

Note (2):

MELASTA will take no responsibility for any accident when the cell is used under other conditions than those described in this Document.

声明三:

如有必要, 风云公司会以书面形式告之客户有关正确操作使用电芯的改进措施。

MELASTA will inform, in a written form, the customer of improvement(s) regarding proper use and handing of the cell, if it is deemed necessary.

6.1. 充电 Charging

6.1.1 充电电流 Charging current:

充电电流不得超过本标准书中规定的最大充电电流。使用高于推荐值电流充电将可能引起电芯的充放电性能、机械性能和安全性能的问题, 并可能会导致发热或泄漏。

Charging current should be less than maximum charge current specified in the Product Specification.

Charging with higher current than recommended value may cause damage to cell electrical, mechanical and safety performance and could lead to heat generation or leakage.

6.1.2. 充电电压 Charging voltage:

充电电压不得超过本标准书中规定的额定电压 (4.2V/电芯)。4.25V 为充电电压最高极限, 充电器的设计应满足此条件; 电芯电压高于额定电压值时, 将可能引起电芯的充放电性能、机械性能和安全性能的问题, 可能会导致发热或泄漏。

Charging shall be done by voltage less than that specified in the Product Specification (4.2V/cell).

Charging beyond 4.25V, which is the absolute maximum voltage, must be strictly prohibited. The charger shall be designed to comply with this condition. It is very dangerous that charging with higher voltage than maximum voltage may cause damage to the cell electrical, mechanical safety performance and could lead to heat generation or leakage.

6.1.3. 充电温度 Charging temperature:

电芯必须在 0℃~45℃的环境温度范围内进行充电

The cell shall be charged within 0℃~45℃ range in the Product Specification.

6.1.4. 禁止反向充电 Prohibition of reverse charging:

正确连接电池的正负极, 严禁反向充电。若电池正负极接反, 将无法对电芯进行充电。同时, 反向充电会降低电芯的充放电性能、安全性, 并会导致发热、泄漏。

Reverse charging is prohibited. The cell shall be connected correctly. The polarity has to be confirmed before wiring. In case of the cell is connected improperly, the cell cannot be charged. Simultaneously, the reverse charging may cause damaging to the cell which may lead to degradation of cell performance and damage the cell safety, and could cause heat generation or leakage.

6.2. 放电 Discharging

6.2.1. 放电电流 Discharging current

放电电流不得超过本标准书规定的最大放电电流, 大电流放电会导致电芯容量剧减并导致过热。

The cell shall be discharged at less than the maximum discharge current specified in the Product Specification. High discharging current may reduce the discharging capacity significantly or cause over-heat.

6.2.2. 放电温度 Discharging temperature

电芯必须在-20℃~60℃的环境温度范围内进行放电。

The cell shall be discharged within -20℃~60℃ range specified in the Product Specification.

6.2.3. 过放电 Over-discharging:

需要注意的是, 在电芯长期未使用期间, 它可能会用其它自放电特性而处于某种过放电状态。为防止放电的发生, 电芯应定期充电, 将其电压维持在 3.6V 至 3.9V 之间。

过放电会导致电芯性能、电池功能的丧失。

充电器应有装置来防止电池放电至低于本标准书规定的截止电压。此外, 充电器还应有装置以防止重复充电, 步骤如下:

电池在快速充电之前, 应先以一小电流 (0.01C) 预充电 15~30 分钟, 以使 (每个) 电芯的电压达到 3V 以上, 再进行快速充电。可用一计时器来实现该预充电步骤。如果在预充电规定时间内, (个别) 电芯的电压仍未升到 3.0V 以上, 充电器应能够停止下一步快速充电, 并显示该电芯/电池正处于非正常状态。

It should be noted that the cell would be at over-discharged state by its self-discharge characteristics in case the cell is not used for long time. In order to prevent over-discharging, the cell shall be charged periodically to maintain between 3.6V and 3.9V.

Over-discharging may causes loss of cell performance, characteristics, or battery functions.

The charger shall be equipped with a device to prevent further discharging exceeding a cut-off voltage specified in the Product Specification. Also the charger shall be equipped with a device to control the recharging procedures as follows:

The cell battery pack shall start with a low current (0.01C) for 15-30 minutes, i.e.-charging, before rapid charging starts. The rapid charging shall be started after the (individual) cell voltage has been reached above 3V within 15-30 minutes that can be determined with the use of an appropriate timer for pre-charging. In case the (individual) cell voltage does not rise to 3V within the pre-charging time, then the charger shall have functions to stop further charging and display the cell/pack is at abnormal state.

6.3. 贮存 Storage:

电芯储存温度必须在 $-10^{\circ}\text{C}\sim 45^{\circ}\text{C}$ 的范围内,长期存储电池(超过3个月)须置于温度为 $23\pm 5^{\circ}\text{C}$ 、湿度为 $65\pm 20\%\text{RH}$ 的环境中,贮存电压为3.6V~3.9V

The cell shall be stored within $-10^{\circ}\text{C}\sim 45^{\circ}\text{C}$ range environmental condition, If the cell has to be stored for a long time (Over 3 months), the environmental condition should be; Temperature: $23\pm 5^{\circ}\text{C}$

Humidity: $65\pm 20\%\text{RH}$, The voltage for a long time storage shall be 3.6V~3.9V range.

6.4. 电芯操作注意事项 Handling of Cells:

由于电芯属于软包装,为保证电芯的性能不受损害,必须小心对电芯进行操作。

Since the battery is packed in soft package, to ensure its better performance, it's very important to carefully handle the battery;

6.4.1. 铝箔包装材料易被尖锐部件损伤, 诸如镍片, 尖针。

The soft aluminum packing foil is very easily damaged by sharp edge parts such as Ni-tabs, pins and needles.

·禁止用尖锐部件碰撞电池;

Don't strike battery with any sharp edge parts;

·取放电芯时, 请修短指甲或戴上手套;

Trim your nail or wear glove before taking battery;

·应清洁工作环境, 避免有尖锐物体存在;

Clean work table to make sure no any sharp particle;

6.4.2. 禁止弯折顶封边;

Don't bend or fold sealing edge;

6.4.3. 禁止打开或破坏折边;

Don't open or deform folding edge;

6.4.4. 禁止弯折极片;

Don't bend tab ;

6.4.5. 禁止坠落、冲击、弯折电芯;

Don't Fall, hit, bend battery body;

6.4.6. 任何时候禁止短路电芯, 它会导致电芯严重损坏;

Short circuit terminals of battery is strictly prohibited, it may damage battery;

6.5. 电池外壳设计 Notice Designing Battery Pack;

·电池外壳应有足够的机械强度以保证其内部电芯免受机械撞击;

Battery pack should have sufficient strength and battery should be protected from mechanical shock;

·外壳内安装电芯的部位不应有锋利的边角;

No Sharp edge components should be inside the pack containing the battery;

6.6. 电芯与外壳组装注意事项 Notice for Assembling Battery Pack

6.6.1. 电芯的连接 Tab connection

建议使用超声波焊接或点焊技术来连接电芯与保护电路模块或其它部分。如使用手工锡焊, 须注意以下事项, 以保证电芯的功能:

Ultrasonic welding or spot welding is recommended to connect battery with PCM or other parts. If apply manual solder method to connect tab with PCM, below notice is very important to ensure battery performance.

a) 烙铁的温度可控能防静电;

The solder iron should be temperature controlled and ESD safe

b) 烙铁温度不能超过 350℃

Soldering temperature should not exceed 350℃

c) 锡焊时间不能超过 3 秒;

Soldering time should not be longer than 3s

d) 锡焊次数不能超过 5 次;

Soldering time should not exceed 5 times Keep battery tab cold down before next time soldering

e) 必须在极片冷却后再进行二次焊接; 禁止直接加热电芯, 高于 100℃会导致电芯损坏。

Directly heat cell body is strictly prohibited, Battery may be damaged by heat above approx. 100℃

6.6.2. 电芯的安装 Cell fixing

·应将电芯的宽面安装在外壳内;

The battery should be fixed to the battery pack by its large surface area

·电芯不得在壳内活动。

No cell movement in the battery pack should be allowed

7. 其它事项 OTHERS

7.1. 防止电池内短路 Prevention of short circuit within a battery pack

使用足够的绝缘材料对线路进行保护

Enough insulation layers between wiring and the cells shall be used to maintain extra safety protection.

7.2. 严禁拆卸电芯 Prohibition of disassemble

7.2.1. 拆卸电芯可能会导致内部短路, 进而引起鼓气、着火及其它问题

The disassembling may generate internal short circuit in the cell, which may cause gassing, firing, or other problems.

7.2.2. 聚合物锂电池理论上不存在流动的电解液, 但万一有电解液泄漏而接触到皮肤、眼睛或身体其它部位, 应立即用清水冲洗电解液并就医

LIP battery should not have liquid from electrolyte flowing, but in case the electrolyte come into contact with the skin, or eyes, physicians shall flush the electrolyte immediately with fresh water and medical advice is to be sought.

7.3. 在任何情况下, 不得燃烧电芯或将电芯投入火中, 否则会引起电芯燃烧, 这是非常危险的, 应绝对禁止

Never incinerate nor dispose the cells in fire. These may cause firing of the cells, which is very dangerous and is prohibited.

7.4 不得将电芯浸泡液体，如淡水、海水、饮料(果汁、咖啡)等

The cells shall never be soaked with liquids such as water, seawater drinks such as soft drinks, juices coffee or others.

7.5 更换电芯应由电芯供应商或设备供应商完成，用户不得自行更换

The battery replacement shall be done only by either cells supplier or device supplier and never be done by the user.

7.6 禁止使用已损坏的电芯 Prohibition of use of damaged cells

电芯在运输过程中可能因撞击等原因而损坏，若发现电芯有任何异常特征，如电芯塑料封边损坏，外壳破损，闻到电解液气体，电解液泄漏等，该电芯不得使用。

有电解液泄漏或散发电解液气味的电池应远离火源以避免着火。

The cells might be damaged during shipping by shock. If any abnormal features of the cells are found such as damages in a plastic envelop of the cell, deformation of the cell package, smelling of electrolyte, electrolyte leakage and others, the cells shall never be used any more.

The cells with a smell of the electrolyte or a leakage shall be placed away from fire to avoid firing.

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Appendix C

MBPF Teensy & TE FX29 Implementation

The following code was utilised for pressure data collection with the Modular Battery Pressure Fixture [68]. This code was developed from the code used by Leonard et al. [38]

```
1 //For use with FX29 load cell and Teensy 4.1
2
3 #include <Wire.h>
4
5 float Offset = -0.0;    //Offsets for load cells in Newtons
6 float Offset1 = -0;
7
8 // Load Cell
9 int wire_in = 40; //I2C address for FX29 Load Cell
10 uint8_t bridge_data[3] = {0}; //2 bytes to pull data from sensor
11 uint8_t bridge_data1[3] = {0}; //2 bytes to pull data from
    sensor
12
13 bool force_flag = false;
14 int force_counts = 0;
15 int force_counts1 = 0;
16
17
18 float error = 0; // offset to zero load cell
19
20 float forceConvert(int counts) {                                //converts
    counts to force
21     float force = (counts - 1000.0) * 100.0 / 14000.0;
22     return force = force * 4.4482216;                            //
    lbf to N
```

```

23 }
24
25 // Teensy4.1 pins 19 SCL (Y), 18 SDA (W) [first load cell] //
    16 SCL1 (Y), 17 SDA1 (W) [second load cell] //
26
27 // Teensy4.1 requires external pullup resistors ~4.7kOhm
28 // FX29 Red (V+), Black (V-), Yellow (SCL) (19), White (SDA)
    (18)
29
30 // Timer to call function at specific frequency
31 IntervalTimer forceDataTimer;
32
33 // RawHID Print Buffer:
34 byte print_buffer[64];
35 int buffer_count = 0;
36 byte f_data = 0x46; //'F'
37
38 void setup() {
39     pinMode(LED_BUILTIN, OUTPUT);
40     delay(100);
41     //I2C Interface: Load cell
42     Wire.begin(); //initializes I2C
43     Wire1.begin();
44     Serial.begin(9600); //initiliazes serial monitor
45     Wire.beginTransaction(wire_in); //get ready to tell sensor we
        want data
46     Wire.write(0); //tell sensor we want data
47     Wire.endTransmission(); //end transmission to sensor
48     Wire1.beginTransaction(wire_in);
49     Wire1.write(0);
50     Wire1.endTransmission();
51     delay(1000);
52
53     //Get force data interupt
54     forceDataTimer.begin(getForceISR, 10000); //10,000us = 100hz
        //frequency of getForceISR
55 }
56
57 void loop() {
58     // Load Cell Main Loop
59     if (force_flag) {
60         print_buffer[buffer_count] = f_data;
61         print_buffer[buffer_count + 1] = bridge_data[0];
62         print_buffer[buffer_count + 2] = bridge_data[1] & 0x3f;
63         buffer_count += 3;
            //increases buffer count

```

```

64     force_counts = (bridge_data[0] << 8 | bridge_data[1]) & 0
        x3fff;           //determines force counts
65     force_counts1 = (bridge_data1[0] << 8 | bridge_data1[1]) & 0
        x3fff;
66     force_flag = false;
        //triggers "getForceISR()"
67
68     delay(20);
69
70 }
71 if (buffer_count >= 61) {                               //if buffer
        has gone on for long enough
72     for (int i = buffer_count + 1; i < 63; i++) { //loop to
        clear print buffer
73         print_buffer[i] = 0;
74     }
75
76     float force1 = forceConvert(force_counts)+Offset;
77     float force2 = forceConvert(force_counts1)+Offset1;
78     float force3 = force1 + force2;
79     Serial.print(force1);
80     Serial.print(" ");
81     Serial.print(force2);
82     Serial.print(" ");
83     Serial.println(force3);
84     buffer_count = 0;
85 }
86
87 }
88
89 // Force I2C interrupt routine
90 void getForceISR() {
91     if (!force_flag) {
92         digitalWrite(LED_BUILTIN, HIGH);
93         int ec = Wire.requestFrom(wire_in, 2); //request two bytes
        of data from load cell
94         int ec1 = Wire1.requestFrom(wire_in, 2);
95         if (ec == 0 ) {
96             Serial.println("1st Device not responding"); //if no
        response
97         }
98         if (ec1 == 0) {
99             Serial.println("2nd Device not responding"); //if no
        response
100         }
101

```

```
102     bridge_data[0] = Wire.read();           //assign the bytes read
103     bridge_data[1] = Wire.read();           from the 1st load cell to "bridge_data"
104     bridge_data[2] = Wire.read();
105
106     bridge_data1[0] = Wire1.read();          //assign the bytes
107     bridge_data1[1] = Wire1.read();          read from the 2nd load cell to "bridge_data"
108     bridge_data1[2] = Wire1.read();
109
110     force_flag = true;                      //triggers first if
111     digitalWrite(LED_BUILTIN, LOW);          statement
112 }
113 }
```

Appendix D

Equivalent Circuit Model Discretisation

This appendix contains the full discretisation for the presented equivalent circuit model. Throughout the discretisation, the assumption is made that the system is being sampled at Δt where $t_0 = k\Delta t$ and $t = (k + 1)\Delta t$. To simplify the presentation, square brackets $[*]$ are utilized to represent Δt and thus $t_0 = k\Delta t$ becomes $[k]$ and $t = (k + 1)\Delta t$ becomes $[k + 1]$. First, equation 3.2 becomes the following:

$$z[k + 1] = z[k] - \frac{\Delta t}{Q}\eta[k]i[k] \quad (\text{D.1})$$

where $z[k]$ is the state-of-charge at time k . To discretise equation 3.10, the form of the differential equation presented in D.2 is utilized:

$$\dot{x}(t) = ax(t) + bu(t) \quad (\text{D.2})$$

where $i_{R_n}(t)$ as $x(t)$ and $i(t)$ as $u(t)$ is evaluated. To simplify the discretisation, the following are used: $a = -\frac{1}{R_n C_n}$ and $b = \frac{1}{R_n C_n}$. This then results in the following equation in the form of equation D.2:

$$\frac{di_{R_n}}{dt} = ai_{R_n}(t) + bi(t) \quad (\text{D.3})$$

Moving the $i_{R_n}(t)$ term to the left-hand side and multiplying both sides by e^{-at} provides the following:

$$e^{-at} \left(\frac{di_{R_n}}{dt} - ai_{R_n}(t) \right) = e^{-at} bi(t) \quad (\text{D.4})$$

The left-hand side of equation D.4 can then be simplified to the following:

$$\frac{d}{dt}(e^{-at}i_{R_n}(t)) \quad (\text{D.5})$$

resulting in D.4 becoming the following:

$$\frac{d}{dt}(e^{-at}i_{R_n}(t)) = e^{-at}bi(t) \quad (\text{D.6})$$

Both sides of the equation can now be integrated over the time interval of 0 to t , rewriting the equation in terms of τ .

$$\int_0^t \frac{d}{d\tau} [e^{-a\tau}i_{R_n}(\tau)] d\tau = \int_0^t e^{-a\tau}bi(\tau)d\tau \quad (\text{D.7})$$

Completing the integration on the left-hand side of the equation can be simplified to

$$e^{-a\tau}i_{R_n}(t) - i_{R_n}(0) \quad (\text{D.8})$$

Rearranging the right-hand side of the equation results in the following:

$$e^{-a\tau}i_{R_n}(t) = i_{R_n}(0) + \int_0^t e^{-a\tau}bi(\tau)d\tau \quad (\text{D.9})$$

Multiplying both side by e^{at} to isolate i_{R_n} results in the following:

$$i_{R_n}(t) = e^{at}i_{R_n}(0) + \int_0^t e^{a(t-\tau)}bi(\tau)d\tau \quad (\text{D.10})$$

The discretisation process can now begin with substituting t for $(k+1)\Delta t$. This results in the following:

$$i_{R_n}((k+1)\Delta t) = e^{a(k+1)\Delta t} i_{R_n}(0) + \int_0^{(k+1)\Delta t} e^{a((k+1)\Delta t - \tau)} bi(\tau) d\tau \quad (\text{D.11})$$

Separating the integral into two parts: $[0, k\Delta t]$ and $[k\Delta t, (k+1)\Delta t]$, results in the following:

$$i_{R_n}((k+1)\Delta t) = e^{a(k+1)\Delta t} i_{R_n}(0) + \int_0^{k\Delta t} e^{a((k+1)\Delta t - \tau)} bi(\tau) d\tau + \int_{k\Delta t}^{(k+1)\Delta t} e^{a((k+1)\Delta t - \tau)} bi(\tau) d\tau \quad (\text{D.12})$$

The $e^{a\Delta t}$ term can be removed from the first two terms of the right-hand side of the equations providing us with the following:

$$i_{R_n}((k+1)\Delta t) = e^{a\Delta t} e^{ak\Delta t} i_{R_n}(0) + e^{a\Delta t} \int_0^{k\Delta t} e^{a(k\Delta t - \tau)} bi(\tau) d\tau + \int_{k\Delta t}^{(k+1)\Delta t} e^{a((k+1)\Delta t - \tau)} bi(\tau) d\tau \quad (\text{D.13})$$

The first two terms of the right-hand side can now be simplified as follows:

$$e^{a\Delta t} \left[\int_0^{k\Delta t} e^{a(k\Delta t - \tau)} bi_{R_n}(\tau) d\tau + e^{ak\Delta t} i_{R_n}(0) \right] = i_{R_n}(k\Delta t) \quad (\text{D.14})$$

Substituting this into equation D.13 results in the following:

$$i_{R_n}((k+1)\Delta t) = e^{a\Delta t} i_{R_n}(k\Delta t) + \int_{k\Delta t}^{(k+1)\Delta t} e^{a((k+1)\Delta t - \tau)} bi(\tau) d\tau \quad (\text{D.15})$$

Factoring the integral results in the following:

$$i_{R_n}((k+1)\Delta t) = e^{a\Delta t} i_{R_n}(k\Delta t) + e^{a(k+1)\Delta t} \int_{k\Delta t}^{(k+1)\Delta t} e^{-a\tau} bi(\tau) d\tau \quad (\text{D.16})$$

It is now assumed that $i(\tau)$ is constant over the interval $[k\Delta t, (k+1)\Delta t]$ and can be approximated by $i(k\Delta t)$.

$$i_{R_n}((k+1)\Delta t) = e^{a\Delta t}i_{R_n}(k\Delta t) + e^{a(k+1)\Delta t}bi(k\Delta t) \int_{k\Delta t}^{(k+1)\Delta t} e^{-a\tau} d\tau \quad (D.17)$$

The final integration can now be solved as follows:

$$\begin{aligned} i_{R_n}((k+1)\Delta t) &= e^{a\Delta t}i_{R_n}(k\Delta t) + e^{a(k+1)\Delta t}bi(k\Delta t) \left[-\frac{1}{a}e^{-a\tau} \right]_{k\Delta t}^{(k+1)\Delta t} \\ &= e^{a\Delta t}i_{R_n}(k\Delta t) + e^{a(k+1)\Delta t}bi(k\Delta t) \frac{1}{a} \left[e^{-ak\Delta t} - e^{-a(k+1)\Delta t} \right] \\ &= e^{a\Delta t}i_{R_n}(k\Delta t) - bi(k\Delta t) \frac{1}{a} \left[e^{a\Delta t} - 1 \right] \end{aligned} \quad (D.18)$$

As was done previously, $[k+1]$ is now substituted for $(k+1)\Delta t$ and $[k]$ for $k\Delta t$ as well as reintroducing the terms a and b resulting in the following:

$$i_{R_n}[k+1] = e^{-\frac{\Delta t}{R_n C_n}} i_{R_n}[k] + \left[e^{\frac{\Delta t}{R_n C_n}} - 1 \right] i[k] \quad (D.19)$$

Finally, equation 3.5 can be discretised through the same procedure providing equation D.20.

$$v[k] = V_{OCP}(z[k]) + i[k]R_0 + \sum_n i_{R_n}[k]R_n \quad (D.20)$$

Combining this with equations D.19 and D.1 provides the final three equations for implementation which will be covered in the following section.