

Lithium-ion Battery Fast Charging: Understanding the Effects of Transport Properties and Thermal Heterogeneity on Lithium Plating

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Abstract

Fast charging of Li-ion batteries is associated with a risk of lithium plating, a process that can lead to rapid capacity fade and safety concerns. The work presented in this thesis aims to improve the understanding of the impact of thermal conditions and cell transport properties on the lithium plating behaviour. The study focuses on two areas: the effects of the temperature and cell type on the performance of charging protocols, and the impacts of through-plane thermal gradients on the severity and distribution of plating. Following a literature review, the modelling and experimental methods are discussed. Through modelling study, it is found that the relative effectiveness of different fast charging protocols at minimising plating depends on the timescales of both solid and electrolyte phase diffusion. When these timescales are low, in power-optimised cells or at high temperatures, protocols that feature high current boost stages may reduce the amount of plating. In the latter part of the work, thermal gradients are found to increase the rate of degradation during fast charging through amplifying non-uniformity in lithium deposition. The deposits are studied through microscopy and quantified using titration gas chromatography. The plating morphology is found to affect the associated SEI layer growth and the rate of capacity fade. In colder cells, or in the colder layers of cells cycled under a thermal gradient, more dendritic morphologies and increased SEI growth are observed. In warmer cells, or warmer layers, the deposition is denser and more uniform, with little or no correlation between the amount of deposition and the amount of the SEI. Finally, cathode kinetics are found to influence the plating distribution. These findings highlight the key role of transport properties, affected by the temperature and thermal heterogeneity, in determining the plating behaviour as well as the severity of its consequences.

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Statement of Authorship and Copyright

I, Anna Iwona Tomaszewska, declare that this thesis and the work presented in it are my own. Where it has been included, the work of others has been acknowledged and is referenced appropriately.

Anna Iwona Tomaszewska (2023)

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Abbreviations

AC	Alternating Current
BMS	Battery Management System
CC-CV	Constant Current - Constant Voltage
CE	Coulombic Efficiency
CEI	Cathode-electrolyte Interphase
CP-CV	Constant Power - Constant Voltage
DC	Direct Current
DEC	Diethyl Carbonate
DFN	Doyle-Fuller-Newman
DMC	Dimethyl Carbonate
DVA	Differential Voltage Analysis
EC	Ethylene Carbonate
ECM	Equivalent Circuit Model
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EMC	Ethymethyl Carbonate
EOC	End-of-charge
EV	Electric Vehicle
FID	Flame Ionization Detector
FOM	Full Order Model
GC	Gas Chromatography
GITT	Galvanostatic Intermittent Titration Technique
HPPC	Hybrid Pulse Power Characterisation
ICA	Incremental Capacity Analysis
ICE	Internal Combustion Engine
LAM	Loss Of Active Material

LCO	Lithium Cobalt Oxide
LFP	Lithium Iron Phosphate
LLI	Loss Of Lithium Inventory
LMO	Lithium Manganese Oxide
LTO	Lithium Titanium Oxide
MCC-CV	Multistage Constant Current - Constant Voltage
MCMB	Mesocarbon Microbeads
NCA	Lithium-nickel-cobalt-aluminium Oxide
NMC	Lithium-nickel-manganese-cobalt Oxide
NMR	Nuclear Magnetic Spectroscopy
OCP	Open Circuit Potential
OCV	Open Circuit Voltage
P2D	Pseudo-Two-Dimensional
PDE	Partial Differential Equation
RMSE	Root Mean Squared Error
ROM	Reduced Order Model
SEI	Solid-electrolyte Interphase
SEM	Scanning Electron Microscopy
SOC	State-of-charge
SPM	Single Particle Model
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TGC	Titration Gas Chromatography
UVP	Universal Voltage Profile
XRD	X-Ray Diffraction

List of Symbols

α_a	Anodic charge transfer coefficient [-]
α_c	Cathodic charge transfer coefficient [-]
δ	Electrode thickness [m]
ϵ_e	Electrolyte volume fraction [-]
η_i	Overpotential of (de)intercalation (<i>int</i>) or plating (<i>lpl</i>) [V]
κ	Electrolyte conductivity [S.m ⁻¹]
κ^{eff}	Effective electrolyte conductivity [S.m ⁻¹]
ϕ_e	Electrolyte phase potential [V]
ϕ_s	Solid phase potential [V]
ρ	Density [kg.m ⁻³]
σ^{eff}	Effective electronic conductivity of the solid phase [S.m ⁻¹]
τ	Tortuosity [-]
a	Surface area to volume ratio of electrode m ⁻¹
A_c	Cross-sectional area [m ²]
c_e	Electrolyte phase concentration [[mol.m ⁻³]]
C_p	Thermal capacity [J.K ⁻¹]
c_s	Solid phase concentration [mol.m ⁻³]
$c_{s,max}$	Maximum solid phase concentration of lithium [mol.m ⁻³]

D_e	Electrolyte diffusion coefficient [$\text{m}^2.\text{s}^{-1}$]
D_e^{eff}	Effective electrolyte phase diffusion coefficient [$\text{m}^2.\text{s}^{-1}$]
D_s	Solid phase diffusion coefficient [$\text{m}^2.\text{s}^{-1}$]
E_{act}	Activation energy [$\text{J}.\text{mol}^{-1}$]
F	Faraday's constant [$96,485 \text{ s.A.mol}^{-1}$]
$i_{0,i}$	Exchange current density of (de)intercalation (<i>int</i>) or plating (<i>lpl</i>) [$\text{A}.\text{m}^{-3}$]
j	Total reaction current density [$\text{A}.\text{m}^{-2}$]
j_i	Reaction flux of (de)intercalation (<i>int</i>) or lithium plating (<i>lpl</i>) [$\text{A}.\text{m}^{-2}$]
k	Thermal conductivity [$\text{W}.\text{m}^{-1}\text{K}^{-1}$]
$k_{0,i}$	Reaction rate constant of intercalation (<i>int</i>) or plating (<i>lpl</i>) [$\text{m}.\text{s}^{-1}$]
q_e	Entropic heat source [$\text{W}.\text{m}^{-3}$]
q_{gen}	Volume-specific heat source [$\text{W}.\text{m}^{-3}$]
q_{ohm}	Ohmic heat source [$\text{W}.\text{m}^{-3}$]
$q_{r,i}$	Reaction heat source [$\text{W}.\text{m}^{-3}$]
R	Universal gas constant [$8.314 \text{ [J.mol}^{-1}\text{K}^{-1}]$]
r	Particle radius [m]
T	Temperature [K]
t^+	Lithium transport number [-]
u	Utilisation factor for the cathode
U_i	Open circuit potential of (de)intercalation (<i>int</i>) or plating (<i>lpl</i>) [V]
V_{cell}	Cell volume [m^3]

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Chapter 1

Introduction

1.1 Context and motivation

The recent years have seen a welcome recognition of the need to adjust human behaviour to avert catastrophic climate change. Among the many necessary actions, the electrification of transport is one that has consistently outperformed expectations. In 2018 - coincidentally, the year this PhD project started - Boston Consulting Group forecasted that 2% of all cars sold globally would be fully electric by 2021, and 14% by 2030 [1]. In their latest report [2], published in mid-2022, the group acknowledged the market has defied the projections to a remarkable extent, with 6% of the global light duty sales having been fully electric in 2021, further growth seen in the first half of 2022, and the 2030 projection nearly tripled to 39%. The public perception of electric vehicles (EVs) has been shifting rapidly, while governments have begun enshrining the phase-out of the internal combustion engine (ICE) into law. The UK has recently committed to end new light duty ICE sales by 2030 [3], while the European Union has set the deadline to 2035 [4]. The transition of EVs from a niche market to a global success story over the short period of a few years has surprised researchers and market experts alike.

While the market growth has been accompanied by technological advancements in both energy density and charging speeds, many challenges still remain for the full decarbonisation of transport. In the light vehicle segment, lower range and slower recharge times compared to ICE vehicles are still quoted among the main worries of prospective buyers. Range anxiety - the fear of running out of charge before reaching the destination - has long been seen as one of the most important barriers to adoption, leading to the

development of higher energy chemistries and a substantial growth in the average size of an EV battery pack in recent years. Today’s EVs can often travel 200-300 miles on a single charge, far in excess of a typical car trip [5, 6]. However, the rapid growth in deployment of Li-ion batteries has drawn increased attention to a fundamental problem: like the fossil fuels that came before them, the materials needed to make batteries are a limited resource. The recent and projected supply shortages of lithium have left some organisations questioning whether the ambitious electrification targets could be achieved. One strategy to reduce the required supply level could be to downsize light duty EV battery packs. This would offer the important additional benefit of reducing the emissions at the battery manufacturing stage, which are known to be significant [7]. However, such downsizing is likely to require a significant increase in the charging rates as well as charging infrastructure to avert the intensification of the range anxiety issue. With the increasing charging rates comes an increased risk of dangerous side reactions such as lithium plating, which can sometimes lead to battery fires. Such events, while relatively rare, are damaging to the public perception of EVs and can lead to expensive recalls. The electrification of various industry sectors is also becoming ever more important. For many industries, including mining and shipping, every minute spent charging equates to a significant financial loss, and so fast charging capability becomes not a boost but a necessity. As such, there is a growing need to understand the degradation and safety issues caused by fast charging and in particular lithium plating, which is difficult to detect and can carry severe consequences.

While improving energy densities to avert range anxiety has been studied extensively over the years, fast charging has come to the forefront of Li-ion battery research relatively recently. In 2018, the US Department of Energy announced a \$ 19 million research support package to ”enable charging in 15 minutes or less by 2028” [8]. The term ”extreme fast charging” was coined to describe this target. By that time, the industry had also realised the need for improved charging rates. The world’s first 800 V production EV, the Porsche Taycan, entered production the following year with a record-beating ability to recharge from 5 to 80% in 22.5 minutes according to the manufacturer. Since then, the limitations associated with fast charging and the strategies to overcome them have been attracting increased scientific attention, accompanied by an increase in the charging speeds of EV models coming to the market. Despite this, fast charging still has no strict definition, and

there are large differences in the terminology used by different stakeholders. For example, charging providers and OEMs usually specify charging speeds in kilowatts, researchers in C-rates, while consumer-facing media discuss them in terms of range-per-hour or charging time. Charging providers sometimes distinguish between "rapid" (typically > 50 kW) and "fast" (7 - 22 kW) chargers, to signify improvement compared to the lower power 3 kW devices. The borderlines drawn in the research literature, on the other hand, tend to be informed by the ability of today's EV-relevant Li-ion cells to withstand a given charging rate without excessive degradation. While 50 kW is equivalent to about 0.5 - 1 C and may be considered "fast" according to battery researchers, 7 kW (about C/10 or lower) is within a range that automotive Li-ion cells can comfortably support, and therefore would not be described as fast. The aforementioned term of "extreme fast charging" is also often used in the research literature. This charging rate, equivalent to about 3.2 C, is at least twice as high as most automotive-relevant Li-ion cells can safely withstand today. The DoE target also specified a minimum life requirement of 500 XFC cycles for a battery system with an energy density of at least 180 Wh/kg at pack level, but did not consider the environmental conditions. Cell temperature is a key factor that influences rate limitations, meaning a cell that can charge in 15 minutes at 30°C without significant compromise to lifetime may degrade rapidly if charged at the same rate at 0°C. In the remainder of this thesis, "fast charging" refers to charging at rates that would be expected to lead to increased degradation, which could translate to different C-rates for different cells and environmental conditions.

1.2 Research questions

The research questions explored in this thesis were shaped by the existing research gaps in the fast charging literature. The review carried out early in the project revealed that a large number of both empirical and model-based fast charging strategies have been proposed. However, for almost any type of a fast charging protocol, conflicting performance reports could be found, with several studies claiming an improved lifetime and some pointing to the opposite. The possible reasons for the discrepancies were rarely discussed. This part of the research was based on the hypothesis that different cell types (energy or power-optimised) would likely respond differently to the same charging strategy,

with the temperature being another important factor due to its effect on the diffusion rates. While the impact of the cell average temperature on the risk of plating had been investigated in many studies, the effects of thermal gradients were rarely considered and not well understood. The hypothesis that through-plane (layer-to-layer) thermal gradients would lead to an increased rate of capacity fade and cause non-uniform plating during fast charging was drawn up here. The project has set out to answer the following research questions:

- What are the reasons for the discrepancies in the performance of similar charging protocols reported in different studies?
- What are the general rules for the selection of a fast charging protocol for a given cell and temperature conditions?
- Are there significant differences in the severity of plating, depending on whether it takes place at moderate or low temperatures?
- How do through-plane thermal gradients affect the distribution and severity of plating in Li-ion cells?
- How is the overall degradation affected by the presence of a through-plane thermal gradient during fast charging?

1.3 Thesis structure

The thesis is structured as follows. Chapter 2 contains a discussion of the relevant literature, covering a background on Li-ion battery operation, physical limitations to charging rates, charging-induced degradation and fast charging protocols developed to extend battery lifetimes. Chapter 3 outlines the electrochemical-thermal model with reversible lithium plating used in this work, as well as the reasoning for the model selection. Chapter 4 describes the experimental techniques used, along with the process of experimental design. Chapter 5 presents the results of work on fast charging protocol effectiveness for different cells and at different temperatures. Chapter 6 discusses the results of the combined modelling and experimental study of the effects of through-plane thermal gradients on lithium plating severity and distribution. Finally, Chapter 7 summarises the findings

of the PhD, reiterates the limitations and recommends directions of future work to further understand lithium plating in Li-ion batteries.

Chapter 2

Literature review

This chapter contains excerpts from the paper 'Lithium-ion battery fast charging: A review', published in the journal eTransportation [9].

The research into Li-ion batteries since their inception in the 1970s has been extremely abundant, with substantial efforts being directed towards improving their energy and power density, safety and lifetime. The aim of the literature review presented here is to provide a sufficient background to the subject of the thesis, focusing on the physical limitations to charging rates, fast charging-induced degradation, charging optimisation and the interactions between the thermal conditions and electrochemical behaviour. A more general review of Li-ion battery fast charging has also been published as part of the PhD project [9].

2.1 Lithium-ion battery operation

Li-ion batteries are composed of a negative and positive electrode, a polymer separator, an organic liquid electrolyte and negative and positive current collectors. Unlike in general electrochemistry, the negative electrode is referred to as the anode while the positive is known as the cathode, irrespective of the direction of the current flow (i.e. during both the charge and discharge). The cathode material is usually a lithium transition metal oxide with a layered, spinel or olivine structure, while the anode is predominantly graphite, although other materials such as lithium titanium oxide (LTO) are used in some applications and many others are being studied. Aluminium is used as the positive current

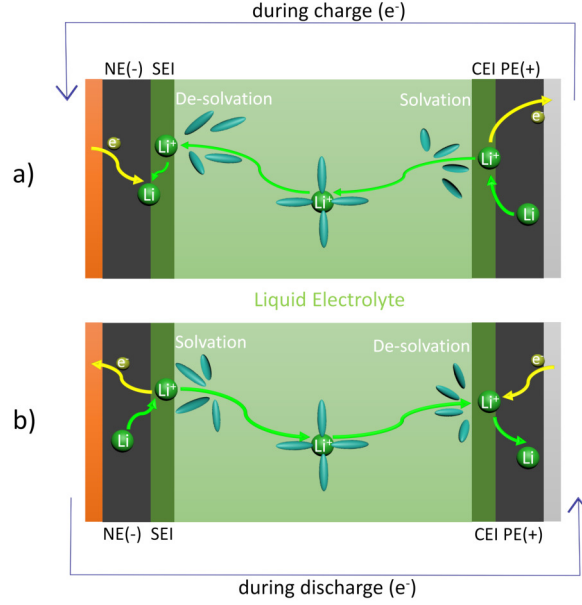


Figure 2.1: A diagram of Li^+ ion transfer during a) charge, b) discharge [9].

collector, while copper is used as the negative one due to its stability at low potentials vs Li/Li^+ . As shown in Figure 2.1, when a Li-ion cell is charged, ions move from the cathode, through the electrolyte, to the anode. The opposite happens during the discharge. The exchange of ions between the electrodes therefore relies on 1) transport processes, through both the solid electrodes and the liquid electrolyte, and 2) charge transfer reactions at the electrode/electrolyte interfaces.

2.1.1 Thermodynamics and kinetics

The open circuit voltage (OCV) of a battery is the voltage difference between its terminals when it is at equilibrium, meaning no current is flowing through it and any concentration gradients have fully relaxed. The battery OCV can be expressed using Equation 2.1, where U_{ca} stands for the cathode open circuit potential (OCP) and U_{an} represents the anode OCP. The OCP of each electrode represents its potential as a function of the lithiation fraction under no load conditions.

$$OCV = U_{\text{ca}} - U_{\text{an}} \quad (2.1)$$

The OCP is a function of material composition, lithium fraction and temperature. The cathode is the electrode with the higher OCP, while that of the anode must be lower: charge exchange between the two can only occur spontaneously from the low to

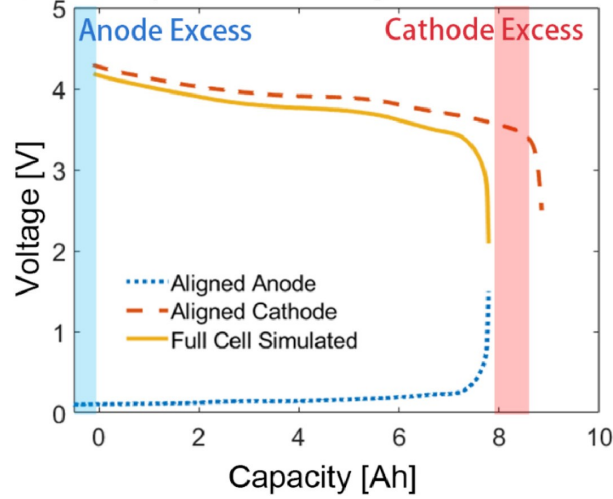


Figure 2.2: Electrode alignment and its effect on the OCV of a Li-ion cell. [10]

the high OCP, i.e. from the anode to the cathode, while energy must be supplied from an external source to cause charge exchange in the opposite direction. It is for this reason that the discharge delivers useful energy, while the charge consumes it. Typical cathode materials include layered metal oxides such as lithium cobalt oxide (LCO), lithium-nickel-cobalt-aluminium oxide (NCA) and lithium-nickel-manganese-cobalt oxide (NMC), spinel lithium manganese oxide (LMO) and olivine lithium iron phosphate (LFP). The anode is predominantly composed of either natural or synthetic graphite.

Electrode balancing at the cell design stage affects the alignment of the electrode OCPs relative to each other, and therefore has an effect on the shape of the cell OCV over the SOC range. An example of how the electrode OCPs may be aligned is shown in Figure 2.2.

As illustrated in Figure 2.2, neither electrode capacity is fully utilised in commercial cells. The graphite anode of a Li-ion cell can be delithiated to very low lithium contents without causing damage. The cathode, usually composed of a lithium transition metal oxide material, becomes structurally and chemically unstable below a certain minimum lithium content, a condition known as over-delithiation. This risks both damage to the electrode and its exothermic breakdown which could lead to a thermal runaway. Consequently, manufacturers impose a maximum voltage limit to prevent cathode over-delithiation. Neither electrode should be lithiated beyond its capacity, however overlithiation is particularly problematic for the anode since it would lead to lithium plating and a potential short circuit. It is for this reason that nearly all commercial Li-ion cells are cathode-limited, meaning they feature excess anode material. Negative-to-positive (N/P)

electrode capacity ratio is the term often used to specify the amount of the excess, with a value of 1.2 suggested to be the best compromise between maximising capacity and preventing plating [11]. In addition, each anode usually features an overhang - a small additional area beyond the footprint of the cathode - to prevent localised increased current densities at the edge of the anode resulting in local lithium plating. Despite this, plating is often observed adjacent to the overhang area in fast charged cells [12, 13, 14]. These common manufacturing decisions, while only partially effective, illustrate the importance of avoiding lithium plating for safety.

The state of thermodynamic equilibrium, represented by the OCV, implies no losses. This is naturally at odds with the battery being operated: any change in the state-of-charge (SOC) requires driving electrochemical reactions through the application of a voltage bias, tipping the system out of equilibrium. The movement of charge against a potential gradient cannot occur without losses, which manifest as overpotential in the voltage curve. The losses arise as a result of the kinetics of the physical processes taking place. The total overpotential, or polarisation, is often divided into three terms according to the physical cause: the activation overpotential, required to induce reactions, concentration overpotential, resulting from the movement of ions against a concentration gradient, and ohmic potential, which arises due to the flow of current through media of a finite resistance. While necessary for the reactions to proceed, the existence of the overpotential is the cause of heat losses and the reason why the energy efficiency of the process can never reach 100%.

The three categories of overpotential are illustrated in Figure 2.3, where subscripts c and a denote cathode and anode contributions respectively. The activation overpotential ultimately stems from the charge transfer reactions happening at both electrodes, while the concentration overpotential reflects the effects of the concentration gradients in the electrolyte and the solid electrode particles. It is worth highlighting that all sources of overpotential are sensitive to the magnitude of the current; a higher current requires a stronger driving force, and so overpotential is increased. Fast charging is therefore inherently less efficient and causes higher heat losses than slow charging.

Ohmic overpotential. Ohmic overpotential, often described as the "IR drop", results from the resistance of materials and interfaces between them to the flow of charge. This includes both the movement of electrons through the electronically conducting pathways

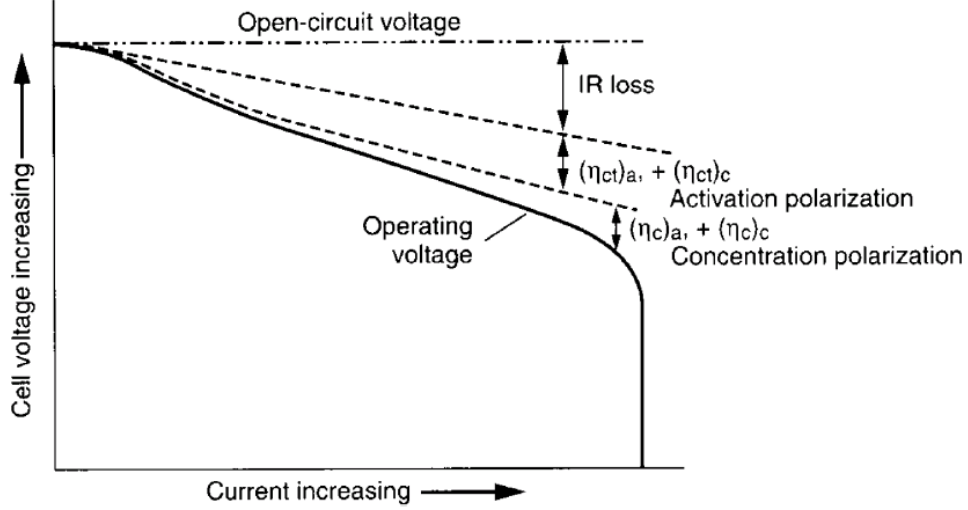


Figure 2.3: Different sources of polarisation, giving rise to overpotential. As the discharge current increases, the overpotential increases as well, dragging the voltage down from the OCV. Conversely during charge, the overpotential changes sign and the voltage is increased compared to the OCV [15].

(composite electrodes, current collectors, current collector-electrode interfaces, cell tabs, and the interface between the tabs and the external circuit) and the movement of ions through the ionically conducting electrolyte. The potential drop, or ohmic polarisation, caused by the movement of charge obeys Ohm's law according to Equation 2.2:

$$\Delta V_{\text{ohm}} = IR, \quad (2.2)$$

where $I[A]$ represents the current and R is the total internal resistance of the cell. This source of overpotential develops instantaneously due to the short timescales of electron and ion conduction. In Li-ion batteries, electron conduction is usually much faster than ion conduction, meaning the ion conduction resistance dominates the ohmic overpotential term. Consequently, the ohmic overpotential reduces with increasing temperature, as ion conduction is facilitated. This is despite the conductivity of the electronically conductive materials reducing with increasing temperatures. Electrolyte conductivity is also a function of the ion concentration, with highest conductivity typically displayed around 1 M [16]. When a high polarisation is induced by a fast charge or discharge, the local electrolyte concentration at the electrodes can deviate strongly from this value, driving increased ohmic overpotential.

Charge transfer overpotential. The intercalation reaction is a charge transfer process. The insertion of the Li^+ ions into a host requires charge transfer from the electrolyte, through the solid-electrolyte interphase (SEI), to the electrode. In order for this process to take place, a charge transfer resistance, R_{ct} , must be overcome. This resistance is also sometimes referred to as the activation resistance, and is the source of activation overpotential, also known as the charge transfer overpotential or surface overpotential. Although many models only account for the charge transfer resistance of the anode and cathode intercalation, electrochemical side reactions such as SEI growth or lithium plating also have charge transfer resistances associated with them. The mathematical definition of the charge transfer overpotential of a reaction j is given in Equation 2.3, where ϕ_s [V] is the solid phase potential, ϕ_e [V] is the electrolyte potential, U_j [V] is the OCP of the reaction, R_{SEI} [Ω] is the resistance of the SEI layer, and I [A] is the applied current.

$$\eta_{\text{ct},j} = \phi_s - \phi_e - U_j - R_{\text{SEI}}I \quad (2.3)$$

Charge transfer processes take place on a timescale of milliseconds. The overpotential associated with them therefore appears instantaneous in a voltage curve, but can be distinguished from the ohmic overpotential in high frequency measurements such as electrochemical impedance spectroscopy (EIS). Similarly to most reactions, charge transfer in Li-ion cells is facilitated at higher temperatures due to increased vibration and more frequent molecular collisions. It is also a function of SOC (albeit far weaker), with low SOC being associated with a higher charge transfer resistance in both charge and discharge directions [17]. Finally, the charge transfer overpotential is also affected by the composition of the SEI [18]. This means the electrode and electrolyte materials, as well as the formation process, can have a strong influence on the charge transfer overpotential in a fresh cell, while SEI growth with ageing typically increases this term further [19].

Concentration overpotential. The process of charging or discharging a battery requires the movement of mass - the Li^+ ions - through the solid electrodes and the electrolyte. Diffusion, driven by concentration gradients, is the main mechanism of Li^+ transport in both phases, although migration due to the potential gradients also plays a part in the electrolyte [20, 21, 22]. The concentration gradients arise as species take part in the redox reactions at the electrode/electrolyte interfaces: for instance, during charging,

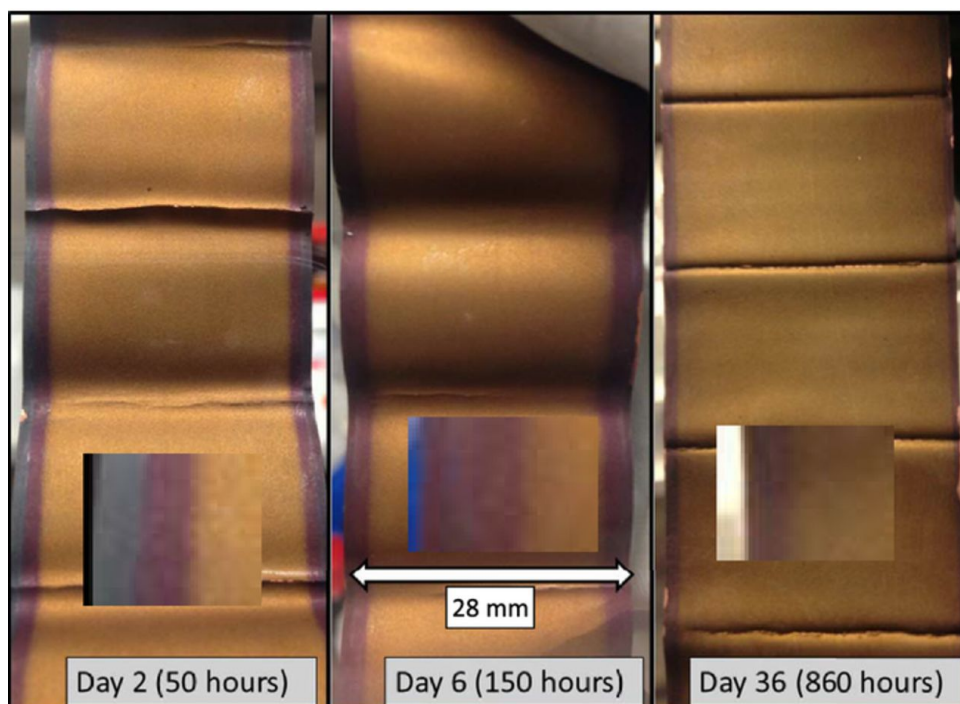


Figure 2.4: Photographs of lithiated graphite electrodes harvested from a pouch cell. The concentration gradient between the active area and the overhang gradually reduces but can still be observed after over a month in storage in an argon glovebox [23].

Li^+ ions are consumed at the anode/electrolyte interface, creating a concentration gradient in the electrolyte which acts as the driving force for the ions to diffuse from the cathode towards the anode. In the solid particle, the intercalation reaction increases the concentration of Li at the surface, driving diffusion towards the centre of the particle. The concentration polarisation produces a concentration overpotential, which varies as a function of the applied current, electrode properties (thickness, particle size, porosity, tortuosity) as well as the Li diffusion coefficient, also known as diffusivity, of the medium. The time constants of (de)intercalation are several orders of magnitude lower than those of diffusion, with solid phase diffusion being slower than the electrolyte phase diffusion. The persistence of Li concentration gradients is observed particularly easily in graphite, which exhibits distinct colour changes as it transitions through different stages of lithiation. As shown in Figure 2.4, the concentration may not fully equalise between the active area and the overhang of a graphite anode even a month after the cell is dismantled [23].

During battery operation, some concentration gradients and the associated overpotential develop nearly instantaneously as a result of the fast reactions consuming or producing species at the surface of particles which cannot be quickly replenished or redistributed due to the slower rates of diffusion. However, unlike the other sources of overpotential,

concentration overpotential continues to build up over longer timescales, and may take hours to relax once the current is removed. Temperature is one of the key factors that influence the diffusion rate, with higher temperatures leading to improved diffusion and therefore reducing the concentration overpotential. Many of Li-ion electrode materials undergo phase transitions as they are lithiated and delithiated, which have been shown to correlate with variations in the diffusion coefficient [16, 24]. This makes the concentration overpotential a non-monotonic function of the SOC. Additionally, variations in the diffusion coefficient in the charge and discharge directions have also been reported [24]. High charging or discharging currents lead to increased charge transfer at electrode/electrolyte interfaces, contributing to increased concentration gradients and overpotential as well. Finally, structural changes in the electrode materials with age, such as surface reconstruction displayed by many layered oxides, can impede diffusion pathways and cause an increase in the concentration overpotential [25].

2.1.2 Energy and power

Material aspects

Three key factors determine the energy storage capability of a Li-ion battery: the specific energy and mass loading of the electrodes, and the potential difference between them. The potential gradient between the electrodes is central to battery operation, with the cathode always having a higher potential than the anode. Cell discharge delivers useful energy since it involves moving Li^+ ions from the low to the high potential electrode, i.e. from a higher to a lower energy state. Conversely, moving the ions back from the high and to the low potential electrode, i.e. charging, requires forcing them into a higher energy state and therefore will not proceed unless energy is supplied from an external source. From the energy density perspective, the potential gap between the electrodes should be maximised, so that more energy is delivered per mole of ions transferred. However, several factors restrict the size of this gap in practice, including the poor stability of both lithium metal oxide materials and organic electrolytes at high potentials. Batteries operated to higher potentials often experience increased degradation rates [26, 27, 28]. On the anode side, lithium plating takes place when the anode potential drops below 0 V vs Li/Li^+ , meaning the minimum potential for an anode of a Li-ion battery is that of lithium. For this reason, Li metal anodes are often considered key to enabling batteries with superior

energy densities but their tendency to form lithium dendrites and consequent poor cycle life remain challenges to be resolved. Graphite has a potential very close to that of lithium, making it by far the most widely used anode material. However, this feature also makes it susceptible to undesirable lithium plating if a high overpotential, often caused by high charging rates or low temperatures, drives its potential below 0 V vs Li/Li⁺. Lithium plating, discussed in detail in Section 2.3.2, can lead to rapid capacity fade, higher risk of thermal runaway, and internal short circuits. To avoid the risk of plating, the typical graphite is sometimes replaced with higher potential materials such as LTO in high power batteries, enabling faster charging and improving safety. This reduces the potential gap between the battery electrodes, compromising the energy density. Such a solution is therefore rarely encountered in energy density-sensitive applications such as EVs.

Electrode materials also vary in their specific and volumetric energies, i.e. their lithium storage capacities per unit mass or volume. Table 2.1 lists these metrics for some of the common electrode materials. LCO was the cathode material used in the first commercial battery and remains popular today. However, the high cost of cobalt, its geographically limited supply and ethical issues considering its extraction have prompted research into chemistries that used increasing proportions of manganese and/or nickel, with high nickel formulations showing particularly high energy densities. Many of today’s cell cathodes feature all three transition metals in a formulation known as NMC. The abbreviation is often followed by three numbers denoting the ratio between the metals, e.g. NMC532 represents a ratio of 5 Ni: 3 Mn: 2 Co. The high energy density of high nickel NMC comes at the cost of reduced chemical stability, often leading to shorter lifespans and an increased risk of thermal runaway in case of abuse. LFP, the lowest energy cathode material in common use, is nonetheless often preferred for applications where long lifetime and safety are priorities thanks to its superior stability. The landscape of anode materials in commercial cells is less diverse, with most anodes being composed of either natural or synthetic graphite. While silicon can in theory offer an order of magnitude higher specific capacities, its high volume change (about 200%) on lithiation and delithiation causes increased mechanical stress which leads to fast degradation. As a result, only small quantities (< 10%) of silicon are sometimes blended with graphite anodes for improved energy density in commercial cells. Finally, LTO anodes have relatively low specific capacities but offer excellent thermal stability and are nearly immune to the growth of

passivating layers and lithium plating, resulting in long lifetimes even at high C-rates.

Table 2.1: Some of the common electrode materials for Li-ion batteries [29].

Common name	Formula	Specific capacity [mAh.g ⁻¹]	Volumetric capacity [mAh.cm ⁻³]	Potential vs. Li/Li ⁺
Cathode materials				
NMC	LiNi _x Mn _y Co _z O ₂	170-200	600-700	3.7
LCO	LiCoO ₂	145	550	3.8
LMO	LiMn ₂ O ₄	120	596	3.7
LFP	LiFePO ₄	165	589	3.4
Anode materials				
Graphite	C ₆	372	837	0.05
LTO	Li ₄ Ti ₅ O ₁₂	175	613	1.6
Silicon	Si	4,200	9,789	0.4

The power density of a battery is usually thought of purely as a measure of its ability to deliver power. It is worth noting though that it reflects the ease of mass and charge transport in general, and therefore usually correlates well with its fast charging capability as well. Power density is a function of the electrode potentials and their volumetric capacities discussed above, but also of many factors that determine the transport rates within the cell: the electrode and electrolyte diffusion coefficients, the porosity and tortuosity of each electrode, the electrode thicknesses and particle sizes, and the thickness and resistance of any surface layers such as SEI and cathode-electrolyte interphase (CEI). At the material level, a high diffusion coefficient is desirable for both the electrode materials and the electrolyte. The diffusion coefficients reported for common Li-ion battery electrolytes in the literature are relatively consistent, between $1.5 - 4.5 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ at room temperature [30, 16, 31, 32, 24]. Variations arise due to differences in solvent composition, the type of lithium salt used, and its concentration. Diffusion in the solid electrode materials is several order of magnitude slower. The reported diffusion coefficients vary between $10^{-17} - 10^{-12} \text{ m}^2.\text{s}^{-1}$ for cathode materials [33, 34, 35, 36, 37, 38], with LFP exhibiting

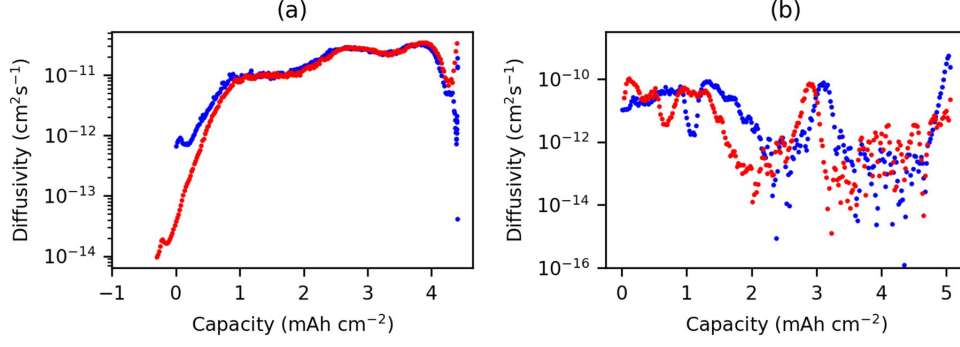


Figure 2.5: Diffusion coefficient of a) an NMC cathode, and b) a 90 wt%: 10 wt% graphite / silicon oxide anode as a function of the half cell discharge capacity (which is proportional to the lithiation fraction) [24].

lower values compared to the layered oxides such as LCO or NMC. The diffusion coefficients for carbonaceous anodes span values between $10^{-16} - 10^{-14} \text{ m}^2.\text{s}^{-1}$ [39, 40, 33] and depend on the structure, with the value being approximately an order of magnitude lower for hard carbon compared to the less ordered artificial graphite or mesocarbon microbeads (MCMB) [41]. While many modelling works still assume the solid phase diffusivities to be constant, experimental measurements have found them to vary by multiple orders of magnitude for a single material as a function of lithiation fraction. Figure 2.5 shows an example of such variation for an NMC cathode and a 90 wt% graphite/10 wt% SiO_x blend anode [24]. For the anode, characteristic spikes in diffusivity can be observed that correspond to the graphite phase transitions.

Measurement of the solid phase diffusion coefficient is, in itself, not straightforward. Common methods of measurement such as GITT or EIS require certain assumptions, including one-dimensional Fickian transport, spherical particle shape, and uniform current distribution. These assumptions generally do not apply to the porous electrode materials used in Li-ion batteries. Additionally, the measured value has been shown to depend not only on the material, but also on system properties: for instance, a higher diffusion coefficient may be measured for a thin coating compared to a thicker coating of the same electrode material. This is because the electrolyte phase transport, while typically faster than solid phase diffusion, still affects the measurement. A detailed discussion of these complications is included in Chapter 3 (Section 3.4.2).

Cell design

Since power is a measure of energy per time, it would be intuitive to assume high energy cells are also optimal for high power. In reality, the two properties are notoriously difficult to reconcile. To optimise for the energy density, the amount of active material per cell volume must be maximised. Each electrode layer should therefore be as thick as possible, ensuring fewer current collectors are needed. The high volumetric fraction of active material leaves less space for pores, impeding the electrolyte flow. Meanwhile, a cell optimised for the power or fast charging capability requires thin electrodes with a high porosity and low tortuosity to facilitate the transport of Li^+ ions through the electrolyte phase, and small particles to provide a shorter diffusion pathway through the solid electrode material (albeit at the cost of increased SEI layer growth due to the higher surface area). Indeed, cells that feature high electrode loadings and therefore high energy densities, while preferred for EVs, are particularly prone to lithium plating during fast charging due to their poor transport properties [42].

While thin electrodes have good electrolyte transport characteristics [43], when electrodes are sufficiently thick, it becomes critical to ensure sufficient Li^+ concentration at the electrode/electrolyte interface throughout the anode to keep the overpotential stable and reduce the chances of lithium plating [7, 44]. Strong heterogeneities, whether in electrode microstructures [45] or in lithium concentration gradients observed during the charging process [46], have been shown to have significant influence on lithium deposition reactions. Non-uniform SOC within graphite anodes has also been found to influence lithium plating [47], with reduced pore tortuosity highlighted as a key lever to avoid electrolyte phase transport limitations and the resulting overpotential [48, 49]. In thick anodes subjected to fast charging conditions, the lithium salt may become depleted near the current collector, leading to non-uniform electrode utilisation and an increase in the local current densities near the separator [50, 51, 48].

Cell geometrical design is another factor that can significantly affect the fast charging capability of Li-ion batteries. Cell shape and form factor influence the distribution of temperature and current, with large form factor ($> 10 \text{ Ah}$ [52]) cells being particularly prone to developing inhomogeneities [53]. Tab position within the cell, tab materials, structures, and welding methods are very important to homogenise the current distribution and limit localised heating and degradation [54, 53]. Erhard et al. [55] simulated and

measured current density distributions in large form factor single layer NMC/graphite pouch cells by placing multiple tabs at different locations along the electrodes. Current was always applied to the same pair of reference tabs, located at one side of the cell. Although the temperature differences along the cell length were negligible due to the single layer design, significant differences in local current densities were reported, highlighting the importance of tab placement. Locating the tabs at opposite sides of the cell and increasing the number of tabs [56] can reduce current and temperature gradients.

2.2 Physical limitations to charging rates

2.2.1 Rate-limiting processes

The anode receives a lot of the attention during the charging process, since multiple studies have explored the role of the cathode degradation and CEI layer growth and concluded that these processes, while important, are generally not rate-limiting for traditional Li-ion systems [47, 57, 43]. At the anode, lithium metal can begin to deposit on the surface of the graphite under certain conditions during charging. The causes for this side reaction taking place are often differentiated into the so-called solid diffusion limitation or charge transfer limitation.

In the solid diffusion-limited case, Li plating results from a lack of accessible intercalation sites within the electrode. This happens when the Li^+ ions arrive at the surface of the anode at a higher rate than the ions intercalated at the surface can diffuse further into the anode material. Understanding the site accessibility is a complex process, with studies showing that lithium diffusion into the electrode along the edge plane of graphite is significantly more likely compared to the basal plane of graphite [40, 7]. Any surplus Li^+ ions that arrive at the saturated anode surface must be plated instead, although the ions may be partially recovered through re-intercalation as the sites become available [58]. Overcharge, a condition where the cell is charged beyond the capacity of the graphite anode, is a special case of the solid diffusion limitation. The charge transfer limitation case applies when lithium plating occurs because it is thermodynamically favourable, without the need for surface saturation of the anode. This requires the anode potential to drop below the potential of Li/Li^+ . While it is possible for this condition to be met throughout the charging process, it is most likely at high SOC, when the potential of the graphite

anode is the lowest. Fast charging or charging at low temperatures increases the overpotential, thus increasing the likelihood or rate of plating. What is usually referred to as the anode potential should not be confused with the solid potential; it is in fact the solid potential at the surface reduced by the local electrolyte potential and the potential drop through the SEI. As such, negative anode potential is most likely to arise at the anode/electrolyte interface, where the electrolyte potential is highest during charging. It is worth noting that the two types of limitation are not completely separate, and the diffusion limitation may in fact be considered a case of charge transfer limitation. When the Li^+ ions accumulate in the electrolyte near the anode surface due to surface saturation, the electrolyte potential increases, pushing the anode potential below the plating potential. It is only then that plating becomes thermodynamically favourable.

Under certain circumstances, the lithium may continue to deposit preferentially where deposits already exist, forming needle-like structures known as dendrites which pose a risk of piercing the separator and causing a short circuit. As the cell is repeatedly cycled, the dendrites may also break and become electrically disconnected from the anode, reducing the amount of cyclable lithium. However, even relatively uniform lithium plating removes significantly more lithium from active availability than typical SEI layer formation on graphite, leading to dramatic capacity losses. The reactivity of lithium metal and the chemical instability of electrolyte components near the Li/Li^+ potential result in the formation of gas by-products and new SEI material, removing active materials from the system [7].

Factors that influence lithium deposition and resulting structures include lithium diffusion rates within the anode [59], limited ion transport in the electrolyte leading to concentration gradients across the anode and salt depletion at the current collector [50], and reactions at electrode/electrolyte interfaces [12]. Both materials and cell designs have been studied in detail to manage the impacts of fast charging on these phenomena [42]. Managing internal resistances, including those associated with the transport through the electrolyte and electrodes as well as charge transfer at interfaces, is important to good charging characteristics, performance, and lifetime [51], with low temperatures increasing these transport resistances and requiring more sophisticated control strategies [60]. Historically, high temperatures, such as those above 30°C were avoided for battery operation, due to the increased kinetics of SEI formation and other side reactions relative

to functional reactions. However, when batteries are subjected to fast charging, higher temperature has a beneficial effect due to the increase in the diffusion rates [42]. Recent work by Yang et al. [42] explored the dependence of the optimal cell temperature on the charging C-rate and cell energy density. The results of their modelling study showed that while both extremely low and extremely high temperatures were generally damaging, fast charging shifted the balance in favour of higher temperatures, particularly for high energy cells.

2.3 Fast charging-induced degradation

The physical limitations discussed in the previous section ultimately result in the accelerated degradation often observed in cells subjected to fast charging. Capacity fade, the most commonly used metric of degradation, describes the partial loss of a cell’s ability to store energy. Power fade, on the other hand, describes the reduction in the amount of energy a cell can deliver or accept in unit time due to an increase in resistance. The two metrics often follow different trajectories with cell ageing. The power capability of a cell is most often compromised when degradation processes lead to SEI layer growth on the anode, which can be exacerbated by high temperature operation, particle cracking which exposes fresh graphite surfaces to the electrolyte, or plated lithium reacting with the electrolyte. On the cathode side, resistance can increase not only due to the growth of passivating layers (CEI), exacerbated by high temperatures and particle cracking, but also due to the surface reconstruction of the cathode from a layered to a rock salt structure for nickel-containing materials such as NMC. Since capacity is directly related to the amount of charge that can be stored in and exchanged between a cell’s electrodes, it can degrade due to a reduction in the number of Li^+ ions available for the exchange (loss of lithium inventory (LLI)) or due to a loss of host electrode material accessible to the ions (known as loss of active material (LAM)). LLI is most often attributed to the growth of the SEI and to lithium plating, both of which remove ions from the electrolyte. LAM can take place due to multiple mechanisms, including particle cracking or pulverisation in both electrodes, electrode delamination and cathode dissolution. Local severe passivation of electrode material, for example passivation of graphite due to extensive SEI growth, can also exhibit as LAM if access to the electrode underneath is severely affected. Some

studies further distinguish between the loss of lithiated and delithiated active material. This section discusses key degradation mechanisms, their implications on cell performance and safety, as well as some of the detection and mitigation methods. In the interest of conciseness, the discussion is limited only to the mechanisms most relevant to the subject of this thesis. Many high quality reviews of Li-ion battery degradation in general are available in other publications [61, 62, 63].

2.3.1 SEI layer growth

The SEI growth at the anode/electrolyte interface is one of the main degradation mechanisms in Li-ion cells under most cycling conditions. The passive surface layer adds onto the cell impedance and diminishes the power. The lithium consumed by the SEI is not recoverable, resulting in capacity fade. While it is not a phenomenon specific to fast charging, high C-rates can affect its rate in several ways. Firstly, they increase the operating overpotential, resulting in higher heat generation. Like many reactions, SEI growth is accelerated by higher temperatures according to the Arrhenius equation. Fast charging also increases the risk of Li plating and particle pulverisation, both of which can increase the rate of SEI growth.

The electrochemical reduction of the electrolyte at the graphite anode generates a complex mixture of SEI with lithium species such as LiF, Li_2CO_3 , $(\text{CH}_2\text{OCO}_2\text{Li})_2$ [64]. The SEI layer formed initially may serve a protective function, but upon further cycling becomes unstable and grows to block pores of the electrode, which causes an impedance rise from the decrease in active surface area. At elevated temperatures (60°C or above), the dissolution and decomposition of SEI species, Li_2CO_3 for example [65], has been found to disrupt the integrity of the protective thin film to form separate islands.

Besides forming the SEI on the graphite anode, thermal decomposition of the carbonate-based electrolyte yields many other possible products, including carbon monoxide, carbon dioxide, hydrogen, ethylene, alkylfluorides, fluorophosphoric acids, etc. Gachot et al. [66] recovered lithium methyl carbonate from the separators in Li/chromium-based-oxide (Li/CBO) cells cycled at 55°C. LiPF_6 , one of the most common salts used in Li-ion cell electrolytes, is not stable at 60°C, and its dissociation into PF_5 dissolves the protective SEI and exposes fresh graphite surface [67]. The decomposition reactions are thermally activated and were observed to become significant at 85°C by comparison of Nuclear Magnetic

Spectroscopy (NMR) spectra of 1.0 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) [68]. The release of gaseous by-product during SEI formation and electrolyte decomposition also compromises the mechanical properties of the anode and the cathode.

2.3.2 Lithium plating

Lithium plating is the most concerning degradation phenomenon associated with fast charging. It is a Faradaic side reaction in which Li^+ ions that arrive at the anode during charging, rather than intercalating into it, deposit on the surface. The deposition of metallic lithium not only consumes Li^+ ions leading to capacity fade, but also poses safety risks, both due to the possibility of lithium dendrites eventually short-circuiting the cell and the effective reduction in the thermal runaway onset temperature [69, 70, 71]. As discussed in the previous section, the deposition can take place once the anode potential drops below the lithium plating potential. Since potentials in the Li-ion battery literature are usually defined with respect to Li/Li^+ , the lithium plating potential is often assumed to be 0 V. This assumption, however, ignores the variation in the plating potential with respect to temperature, which has recently been shown to be significant [72]. To correct this, the 0 V potential should be defined as that of Li/Li^+ at a specified temperature.

Lithium deposition is known to take on a range of morphologies, from uniform, through mossy, to needle-like and dendritic. Multiple factors have been shown to affect the deposition morphology. Local salt depletion at the anode has been shown to induce the formation of dendritic structures in place of the more uniform mossy deposits formed when sufficient amounts of Li are available in the electrolyte [73, 50]. The substrate surface structure [74], SEI composition [75], current density [76] and pressure [77] have all also been found to affect the plating morphology.

Fundamentally, lithium plating is a reversible reaction. However, the high reactivity of metallic lithium with the organic electrolyte results in some degree of irreversibility. In addition, the lithium deposits can become electrically disconnected from the anode, forming so-called "dead lithium". The extent of reversibility of the plating reaction is still not well understood but likely to depend on numerous factors, including the amount of lithium plated, its morphology, the operational condition that follows the plating, and temperature [78, 79, 80].

Since lithium plating is a competitive reaction to the intercalation of lithium into the anode, it is aggravated by factors that limit the rate of intercalation. Low temperatures reduce the rates of diffusion in the solid graphite particles and the electrolyte, increasing the likelihood of surface saturation of the graphite and leading to higher overpotentials. Despite the higher risk of lithium plating in cold conditions, it is worth highlighting that, similarly to other electrochemical reactions, its reaction rate and potential are also influenced by the temperature [81, 72]. The temperature sensitivity of the thermodynamics and kinetics of lithium plating has only recently drawn more attention, in light of the reports of high temperature hot spots causing plating to take place preferentially to intercalation in Li-ion cells [72], and of hot spots causing dendritic growth in lithium metal cells [82]. An in-depth discussion of the complex interactions between plating and temperature, including the recent literature and the findings of this work, can be found in Chapter 6.

In contrast to (de)intercalation, lithium plating has often been described with simpler Tafel equations in the literature [83, 42]. While this approach presumes irreversibility, it has been argued that this is sufficient for degradation modelling since only irreversible plating leads to capacity fade[42]. In the first modelling study of lithium plating in Li-ion batteries, Arora et al. [59] proposed the use of the Butler-Volmer kinetics for the reaction, but also suggested the Tafel equation could instead be used for either fully irreversible plating or for small deposits that quickly react with the electrolyte, while a linear approximation of Butler-Volmer could be suitable for conditions with high overpotential resulting in facile plating kinetics. When Butler-Volmer kinetics are used, the electrolyte concentration-dependent exchange current density is often replaced with a constant value [59, 84, 85]. The temperature dependence of the plating kinetics is nearly always ignored [83, 86, 85]. These decisions are not unjustified; since the plating exchange current density is usually fitted [83, 42], its physical meaning is often limited, leading researchers to optimise for simplicity.

It should be stressed that the kinetics, and even thermodynamics of lithium plating are still poorly understood. It is common practice to assume the plating behaviour in Li-ion batteries to be identical to that in Li/Li symmetrical cells, with the same exchange current density and activation energy, despite the substantial differences between these systems. It is well known that the plating kinetics show strong variations depending on the

electrolyte properties [87, 88, 89] as well as the dimensions and morphology of the substrate surface [90, 59, 91]. It is possible that the graphite substrate and the existence of the competing mechanism of intercalation make the plating thermodynamics and kinetics in Li-ion cells significantly different to Li metal cells, or even between different combinations of electrolytes and types of graphite. This may explain why the often quoted lithium deposition potential of 0 V vs. Li/Li⁺, based on deposition on a lithium substrate, has been contested by some researchers for Li-ion cells. Verbrugge and Koch [92] did not observe lithium plating on graphite anodes held for several minutes at a potential of - 200 mV, while Park et al. [93] reported plating at a positive anode potential of 5 mV. Typical testing methods such as OCV measurements and EIS are unable to capture the potential or the exchange current density of plating in a Li-ion system. To the best of the author’s knowledge, Ge et al. [81] remains the only study to have attempted to decouple the kinetic parameters of both intercalation and plating through the use of NMR and electrochemical modelling. This method, too, requires one to make a number of simplifying assumptions. In the absence of reliable methods to decouple the current densities, it is understandable why so many researchers rely on either fitting the plating parameters or using values measured in Li/Li cells.

Safety considerations

Dendritic growth of the metallic Li deposits is usually considered the worst-case scenario due to the prospect of the dendrite eventually reaching the cathode and short-circuiting the cell, resulting in rapid heating [94]. While this heat generation immediately melts the dendrite and breaks the short in most cases [95], it may also be sufficient to trigger further reactions such as electrolyte breakdown and cathode dissolution, leading to thermal runaway. More recently, even non-dendritic deposits have been shown to pose significant safety concerns. Reactions between lithium and the electrolyte not only contribute to the growth of the SEI layer but can also be highly exothermic and may play a part in the evolution of thermal runaway. Metallic Li is far more reactive than graphite, promoting faster SEI growth, gas generation and electrolyte decomposition [96]. It is this accelerating effect on other side reactions that is thought to result in reduced thermal runaway onset temperatures often observed in plated cells [69, 70, 97]. The thermal behaviour often returns to normal if sufficient rest time is allowed after fast charging [69, 70], which

could be explained by either the re-intercalation of the metallic lithium, its deactivation through reactions with the electrolyte to form SEI, or both. Metallic lithium has, however, been shown to persist and remain partially active at long timescales after fast charging in some cases [80, 97]. Ng et al. [97] reported a thermal runaway triggered by the reactions of metallic Li in NMC532/graphite cells as late as two weeks after fast charging. The gas generation associated with plated lithium also contributes to an increased risk of cell rupture [98]. Liu et al. [73] found the composition of the electrolyte had a strong influence on the passivation of lithium and gas generation and postulated that electrolytes containing EC could prevent plating-related gassing since EC passivates metallic Li well. This is in contrast to the observations discussed in Chapter 6 of this thesis.

2.3.3 Other degradation mechanisms

Mechanical pulverisation is another important aspect of fast charging induced degradation, and widely observed for various electrode materials including graphite [99, 100, 101], NMC [102, 103, 104], LCO [105, 106, 107], LMO [108], NCA [109], Si [110, 111] and others. Pulverisation may be observed on multiple length scales: cracks within the electrode particles [103, 106, 107], isolation of electrode particles, conductive material and binders [112], separation between active material and current collector, or delamination between electrode sheets. The main reason for these phenomena is the strain mismatch resulted from the lithium concentration gradient [102, 105, 112], which is aggravated by fast charging. Cracks propagate in both the active material particles and their surrounding passivating layers (SEI/CEI) when the energy release rate or stress intensity factor exceeds a certain threshold [105, 106]. The lattice strain along different directions varies for almost all kinds of electrode materials [108]. Primary particles are randomly oriented [102], in direct contact with adjacent primary particles. As a result, fast charging induced strain between nearby primary particles cannot be concordantly accommodated, which may cause isolation between electrode particles or conductive material and binders. The strain mismatch between electrode materials and current collector can also lead to cracks [113] or detachment [114]. Since higher C-rates induce more severe current inhomogeneity across electrode sheets, delamination may occur for cells without tight external constraints [115].

The effects of mechanical pulverisation demonstrate as LAM, LLI and impedance

growth. Cracks may lead to poor electrical conductivity and even total detachment [102], resulting in a reduction in the available electrode material. As fresh graphite surface is uncovered by the cracks, reactions with the electrolyte and SEI growth are accelerated [103, 107, 116]. Finally, consumption of the electrolyte may also reduce the wettability of electrodes and hinder ion transport [103].

The size of electrode particles has a strong influence on the magnitude of concentration gradients that can develop and, consequently, on the risk of pulverisation. Smaller particles are more resilient to cracks because of more uniform lithiation [116] and lower energy release rates [117]. However, small particles have higher specific surface areas, leading to more SEI and impedance growth. Moreover, small particles result in a lower energy density due to their lower packing density [103, 118, 116]. Thus, primary particles are sometimes packed into secondary particles. The mechanical strength of secondary particles is much lower than the intrinsic material strength of primary particles due to the weak Van der Waals interactions that hold them together [104]. Nonetheless, higher C-rates are not always reported to increase the severity of cracking in secondary particles. For NMC333 in [102], operation at 1 C did not lead to more cracks than 0.1 C. This is consistent with the results for NMC532 under 0.5 C and 2 C [104]. However, for NMC622 operated at 1 - 10 C cracks increased with C-rates, which is similar for NMC532 in [118] and NCA in [119].

While cathode degradation is usually not considered a major limitation to charging rates, it is worth highlighting some of the cathode-specific effects reported in the literature. The cathode often dominates cell polarisation, thus limiting the charge acceptance and increasing the rate of heat generation during fast charging [120, 121]. As discussed above, increased rates of cracking have been observed in some (but not all) studies for NMC cycled at high C-rates. Tanim et al. [122] found the accelerated capacity fade in NMC/graphite cells charged at up to 9 C was attributable mainly to LAM in the cathode and lithiation heterogeneity rather than to anode degradation or Li plating. Interestingly, positive effects of fast charging on the lifetime of NMC have also been reported. Quilty et al. [123] found reduced structural disordering and smaller changes in the oxidation state of Ni and Co in the cathodes of NMC/graphite cells charged at 4 C compared to those charged at 1 C, which was attributed to the lower extent of cathode delithiation achieved during fast charging. Mussa et al. [124] also noted protective effects of fast charging on NMC111.

For LFP, high C-rates have been reported to result in structural degradation and high rates of capacity fade [125, 26], although nanostructured LFP exhibits excellent high rate performance. This has been attributed to a change in the intercalation mechanism: the phase separation behaviour characteristic of bulk LFP has been shown to be replaced by a solid solution mechanism in nanostructured particles during high C-rate cycling [126, 127, 20]. Nonetheless, the low potential of LFP cathodes limits their use in high energy Li-ion cells which face the strongest limitations in charging rates.

2.3.4 Degradation diagnostics

Many diagnostic methods have been developed to identify the causes of capacity and power fade. The techniques can be divided into two categories based on the level of information they provide: degradation mode analysis methods, which differentiate only between LLI and LAM in both electrodes, and degradation mechanism identification methods, which aim to identify and/or quantify specific mechanisms such as lithium plating or particle cracking.

Differentiating between LAM and LLI

Degradation mode analysis provides relatively high level information about the causes of capacity fade. Since the shape of a cell's OCV curve depends on the balancing of the electrodes as well as the amount of available lithium, OCV-based techniques are most often used to identify LLI or LAM in either electrode. The first such method was introduced by Dubarry et al. [128], who simulated the changes in the full cell OCV as a result of each degradation mode. The OCV information was supplemented with two differential signals: the capacity change differentiated with respect to voltage (dQ/dV , or incremental capacity analysis (ICA)) and the inverse, i.e. voltage change differentiated with respect to the capacity (dV/dQ , or differential voltage analysis (DVA)). Both signals exhibit characteristic peaks and troughs which highlight the voltage plateaus associated with phase transitions in electrode materials.

The transformations of the OCV as a result of different modes of degradation are illustrated in Figure 2.6. The OCV curve of a fresh cell is shown in Figure 2.6 a), with the bars on the left illustrating the utilisation of each electrode, with the golden area representing the amount of cyclable lithium. In the following, "fully lithiated" and "fully

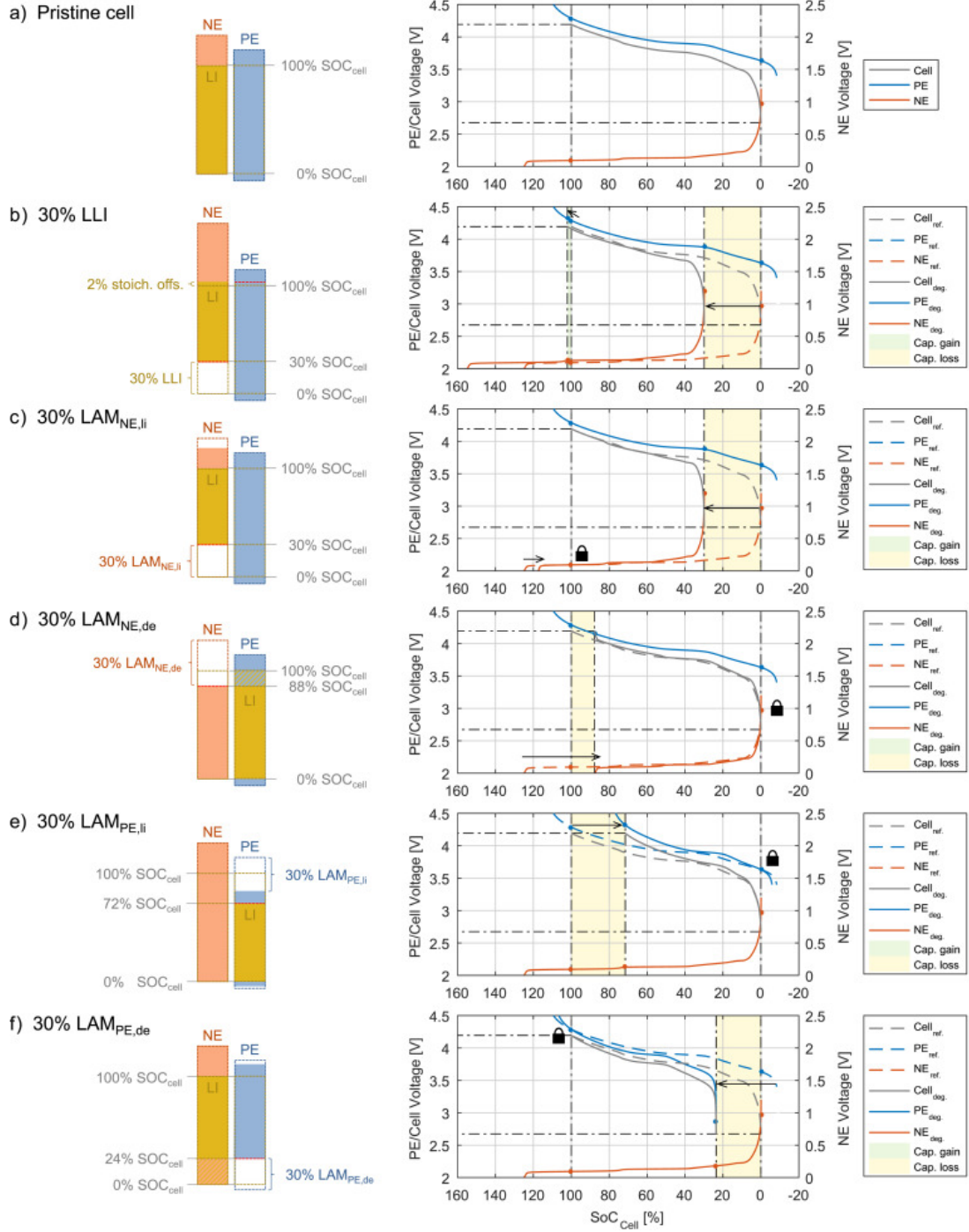


Figure 2.6: Transformations of the OCV as a result of different degradation modes. Reproduced with permission from [94]

delithiated” refers to the maximum and minimum lithiation of the electrodes in a fresh cell, rather than the absolute maximum and minimum amounts of lithium the electrode materials can hold. Figure 2.6 b) shows the changes to the OCV and electrode utilisation ranges with 30% LLI. With the decrease in the amount of cyclable lithium, the cathode can no longer be fully lithiated even when the anode is fully delithiated, resulting in the shift in the electrode alignment. Since the cathode OCP remains higher than in a fresh cell at 0% SOC, the anode needs to be delithated to a higher OCP to achieve the same full cell lower voltage limit (2.7 V in this example). Conversely, at the high SOC end (left side of the plot), the anode does not achieve as low an OCP as it would in a fresh cell when all of the cyclable lithium has been intercalated. Since the upper cut-off voltage remains the same (4.2 V here), the cathode must be delithiated to a higher OCP to reach the end-of-charge voltage. This phenomenon is known as stoichiometric shift. In extreme cases, it can cause the cathode to become over-delithiated and unstable as a result of high LLI, despite the full cell voltage limits being respected. The loss of 30% of the anode active material in the lithiated state, illustrated in Figure 2.6 c), causes a similar shift in the electrode alignment at the 0% SOC end due to a similar reduction in the amount of cyclable lithium. However, since the anode OCP shrinks as a result of loss of the electrode material, the anode reaches similar extents of lithiation at 100% SOC as it would in a fresh cell, and the cathode is not forced into over-delithiation. In case 30% of delithiated anode material is lost (illustrated in Figure 2.6 d)), the electrode alignment at the low SOC end remains the same as in a fresh cell. The anode OCP shrinks. During the charge, the anode may be lithiated to a higher extent than allowed in a fresh cell, reaching a slightly lower OCP. The maximum voltage limit is reached before the cathode is fully delithiated. This causes the shift in electrode alignment at 100% SOC. Loss of 30% of lithiated cathode material, shown in Figure 2.6 e), causes the cathode OCP to shrink and the amount of cyclable lithium to reduce. As a result, the anode can no longer be fully lithiated at 100% SOC, while the electrode alignment at 0% SOC does not change. Loss of 30% of delithiated cathode material (Figure 2.6 f)) also results in the shrinkage of the cathode OCP but without loss of lithium. As a consequence, the anode can be lithiated to the same extent as in a fresh cell (i.e. the electrode alignment at 100% SOC stays the same) but cannot be fully delithiated. The cathode must therefore be lithiated to a lower OCP than in a fresh cell to reach the same minimum voltage limit. Figure 2.6 shows

only some simple cases of each degradation mode occurring in isolation. The modes can occur concurrently with each other, while the lost electrode material may not be fully lithiated or fully delithiated. Many researchers choose to consider only three degradation modes (LLI, LAM_{NE} and LAM_{PE}), since the combination of these modes can be used to represent the loss of lithiated or partially lithiated material as well.

The shifts in the stoichiometric alignment of the electrodes and the shrinkage of electrode OCPs can often be difficult to spot in the full cell OCV. Differential techniques take advantage of the phase transitions exhibited by many electrode material, which exhibit as peaks or troughs in the incremental capacity (dQ/dV) and differential voltage (dV/dQ) signals. Each of these features can be assigned to a particular phase transition in a particular electrode [128, 129, 130]. Then, a reduction in the distance between two peaks assigned to the same electrode can be interpreted as a sign of the shrinkage of the OCP of that electrode, resulting from LAM. The absence of a particular peak at the low or high SOC end after ageing can indicate changes to the utilised portion of an electrode's OCP. A key weakness of the differential methods is their high sensitivity to the degradation heterogeneity. When each electrode layer in a cell exhibits a different level of a certain degradation mode, the phase transitions occur at slightly different times, causing differential features to become shallower and less detectable [131]. On the other hand, the information about such heterogeneities is in itself often useful.

Lithium plating detection

Irreversible lithium plating typically exhibits mainly as LLI as it result in the reduction in the amount of cyclable lithium. In some cases, lithium plating may lead to pore clogging [83, 63], which renders parts of the anode inactive and therefore exhibits as LAM_{NE}. Post-mortem, lithium plating in an anode harvested from an aged cell can be identified using NMR [132, 133, 81], optical microscopy, scanning electron microscopy (SEM) [91, 134], secondary ion mass spectrometry (SIMS), transmission electron microscopy (TEM) [135] or even simple visual inspection [14]. The oxygen in the lithium oxide, easily produced when the plated lithium is exposed to air, can also be detected using energy dispersive X-ray spectroscopy (EDS). Non-ambiguous identification of lithium plating during the cell lifetime is, however, notoriously difficult. This presents a major challenge in many applications including onboard EVs, where the unavailability of methods to detect plating

leads manufacturers to impose conservative limits on the charging rates to minimise the risk of it occurring. Even with such limitations in place, plating may occur as a result of a manufacturing defect or inaccuracies in the charging maps (look-up tables used by the BMS to determine the maximum charging current, typically as a function of temperature and SOC), leading to serious safety risks. There is therefore a clear need for methods to non-destructively identify and monitor plating, however no technique has so far been shown to be fully reliable. The methods developed to date tend to rely on detecting changes to the cell voltage curve or impedance that could suggest plating has taken place. Some of these and other techniques are summarised here.

Voltage-based methods. Lithium plating introduces a new phase that lithium can exist in a Li-ion battery. The electrochemical reaction modifies the shape of the charging voltage curve and produces a plateau, similarly to other phase transitions in electrode materials. Since plating is typically accompanied by high overpotentials which overshadow the features present in the OCV, this voltage signature is not normally detectable at the onset of plating during charging. Numerous studies have instead used the voltage plateau associated with lithium stripping or re-intercalation following a fast charge to confirm that plating had happened [42, 122, 136]. This method can detect only the reversibly plated lithium, which must be relatively extensive to produce a detectable voltage plateau [14]. Since the reversibly plated capacity is usually small compared to the cell capacity, a low discharge C-rate (about C/20) must follow the fast charge for the stripping plateau to be detected. If the fast charge is instead followed by a rest, since no voltage bias is applied to the cell, stripping cannot take place and the plateau can only arise due to re-intercalation. Similarly to the degradation mode analysis described earlier, differential signals (ICA or DVA) are often used to highlight the presence of an additional voltage plateau. An example set of DVA curves, some of which feature the inflection associated with lithium stripping, is shown in Figure 2.7 [14].

The characteristic stripping voltage plateau was first suggested as a plating identification technique by Smart et al. in early 2000's [137] but did not draw significant attention until a decade later, when it was also proposed that the length of the plateau was proportional to the amount of stripped lithium and could therefore be used as a proxy for plating quantification [138, 139]. Petzl and Danzer [140] were the first to use the differential approach, proposing that the inflection in the differential voltage curve in the

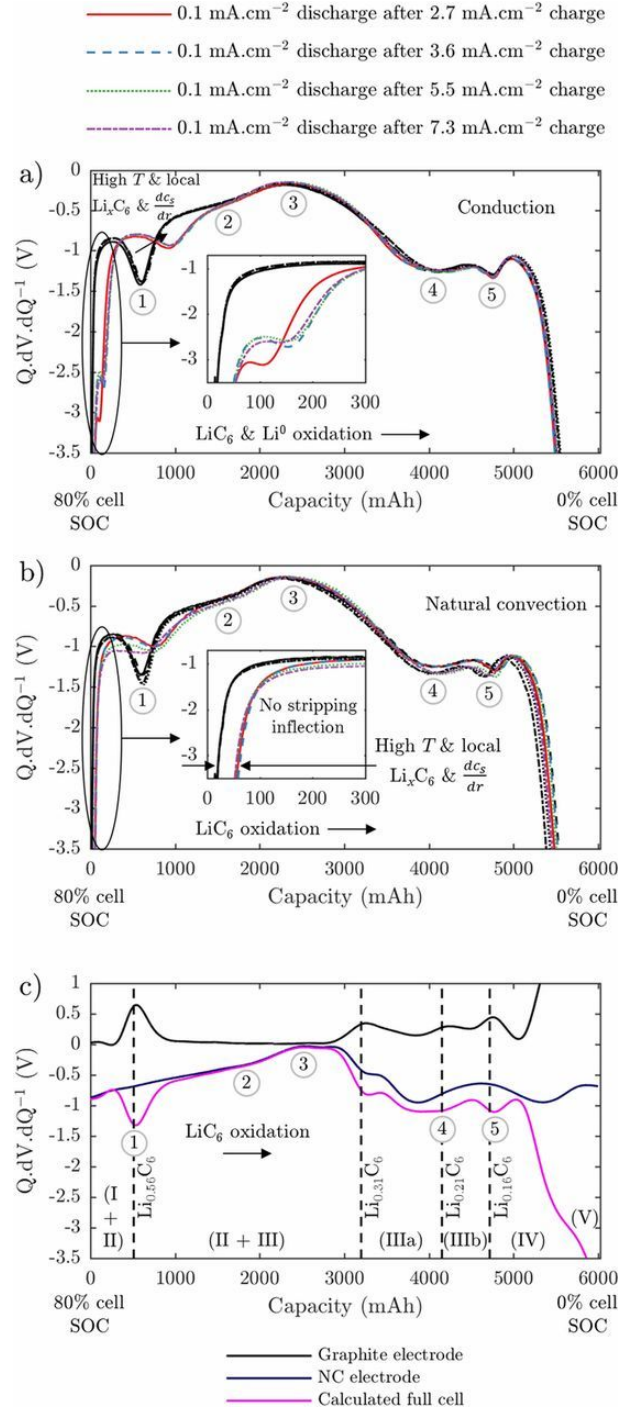


Figure 2.7: DVA curves of C/20 discharges of a Li-ion cell. Black curves represent reference discharges, i.e. discharges following a slow charge with no lithium plating expected, while the coloured curves are discharges following fast charges at different C-rates and an initial temperature of 0°C. a) Discharges for cells fast charged with a conduction thermal boundary condition. b) Discharges for cells fast charged with a natural convection boundary condition. c) DVA curves of fresh electrodes and the calculated full cell DVA. Reproduced with permission from [14].

beginning of the discharge signified the point when most of the reversibly plated lithium had been stripped. They also suggested that the capacity discharged up to that point corresponded to the stripped capacity. This theory relies on the assumption that stripping occurs preferentially to the de-intercalation of lithium from the anode, such that any current contributed by the de-intercalation is negligible until most of the plated lithium is stripped. It is unclear whether such an assumption is sufficiently justified. While the overpotential of lithium stripping is indeed higher than that of de-intercalation during the discharge due to the difference in the OCPs of these reactions, the kinetics of lithium stripping are not well understood. The localised nature of lithium deposition may also complicate the prediction of current distribution between the reactions. Even with the assumption that Butler-Volmer kinetics correctly predict both reactions, O’Kane et al. [141] has shown that the stripping inflection can only correspond to the end of stripping if the reaction rate constant for stripping is very large compared to that of de-intercalation. In other cases, the "stripping inflection" could still signify stripping, but not be directly related to the amount of stripped lithium. Instead, the modelling results suggested the presence of plated lithium could result in an earlier and more abrupt graphite phase transition, which would produce a similar voltage feature [141]. Recent experimental observations by Fear et al. [142] support this hypothesis.

While the validity of the voltage-based techniques for the quantification of plating is contested, it is clear that a voltage plateau or a characteristic DVA/ICA inflection can often point to the presence of reversibly plated lithium. The key limitation of the technique is its sensitivity; it has been shown to only be able to detect relatively extensive plating. Campbell et al. [14] investigated DVA as a plating detection method in both cells cooled via natural convection and conduction at 0°C. The technique correctly identified plating in the conduction case but failed to do so for the cells cooled via convection, despite significant amounts of plating found in the post-mortem analysis. This led them to conclude that the lack of the DVA inflection is not evidence of the absence of lithium plating.

Resistance and impedance-based methods. While a number of works explored the use of resistance and impedance signals to identify plating, the hypotheses and results have been somewhat inconsistent. One of the simplest methods proposed to distinguish lithium plating from SEI layer growth relies on the observation of both capacity fade and

resistance rise trends over time. Plating has been observed to contribute mainly to the capacity fade but have a lesser impact on the resistance compared to SEI [143] due to its high conductivity. The validity of the assumption that plating would be associated with a lower resistance rise is complicated by the interactions between the two mechanisms: since metallic lithium is highly reactive with the electrolyte, it produces an SEI of its own. The rate of this secondary SEI growth is influenced by many factors including the temperature, electrolyte composition, and the surface area of the plated lithium - the latter being substantially higher for dendritic or mossy deposits compared to more uniform plating morphologies. It is therefore likely that lithium plating can cause divergent long-term trends in resistance in different cases. Indeed, an increased rate of resistance rise has been attributed to plating in some other works [144, 145].

Some of the recent research has turned to observing the impedance behaviour during individual charges for signs of lithium plating. Under normal conditions during a charge, the cell impedance is highest at low SOC, low in the mid-SOC range, and increases again at high SOC as it becomes increasingly difficult to lithiate the nearly saturated graphite. However, if the onset of lithium plating takes place, a decrease in the charge transfer impedance may be observed [146, 147, 148]. This is because the plating reaction introduces an additional charge transfer impedance in parallel to that associated with the intercalation charge transfer impedance at the negative electrode. The effect on the overall impedance is analogous to the situation where two resistors, R_1 and R_2 , are connected in parallel: the overall resistance is reduced to $\frac{R_1 \times R_2}{R_1 + R_2}$. Koleti et al. [146] showed that this impedance reduction could be observed by interrupting a direct current (DC) charge for 3 seconds in 1% SOC increments, eliminating the need for the expensive AC equipment and improving the viability of the method for onboard detection. Interestingly, other researchers have observed an increase in both the charge transfer and the SEI impedance following the onset of lithium plating, which was attributed not to an increased amount of SEI but to the protruding lithium deposits enforcing a more tortuous lithium diffusion pathway through the layer [149]. The increased SEI impedance was also proposed as a detection technique for the onset of lithium plating. Harting et al. [150] showed that changes in the ratio between the values of the second and third harmonics of the impedance response measured by nonlinear frequency response analysis (NFRA) could also indicate plating. They, too, argued that the charge transfer resistance was increased as a result of

plating due to the lithium deposits presenting an additional barrier to the intercalation reaction. These contradictory results highlight the need for further research into the effects of lithium plating on the cell impedance spectra.

Other methods. Coulombic efficiency (CE), the ratio of the capacity recovered during a discharge to the capacity charged in the preceding charge, is one of the most commonly used metrics that could point to lithium plating [151, 152, 153]. A reduced CE suggests an increased rate of capacity loss, often observed following the onset of plating after an SEI growth-dominated ageing regime. However, the rate of capacity loss can be influenced by a number of other mechanisms, e.g. particle cracking or cathode dissolution, and it is not possible to distinguish between these based on the CE trends alone. Other promising techniques for *operando* plating detection include those based on the premise that the specific volume of mossy or dendritic lithium is significantly higher than that of lithiated graphite. As such, lithium plating may cause an increase in the cell thickness for pouch cells [154, 155, 156] or an increase in the pressure for volume-constrained cell formats, both of which can be detected with appropriate equipment. However, gas generation also leads to a volume or pressure change. Acoustic time of flight analysis has recently been demonstrated as a semi-quantitative plating detection technique [157]. The amount of plating has been shown to correlate with the degree of hysteresis in the acoustic time of flight.

2.4 Fast charging strategies

To prevent or minimise Li plating, many researchers have turned towards cell and pack level approaches which can often be implemented in real world systems in a relatively short time. Charging strategies, which determine how the current density is varied during the charging process, are an important category of such solutions and subject of a growing body of charging optimisation work. Table 2.2 contains examples of protocols proposed specifically for fast charging, followed by a discussion of each of the common types of protocols.

Table 2.2: Examples of fast charging protocols proposed in the literature. MCC-CV stands for multistage constant current-constant voltage, BC - boost charging, PC - pulse charging.

Charging protocol type	Cell information	C-rate(s)	Transition rule	Cut-off voltage [V]	Temp. [°C]	Ref.	Result
MCC-CV	NMC/Gr	0.5C followed by 1.125C	C-rate switch at 10% SOC	4.2	Room temperature	[158]	Reduced lifetime vs. 1C CC-CV
MCC-CV	High power LFP/Gr, 18650	4C followed by 1C	C-rate switch when 3.6 V reached	3.6	23	[159]	83% SOH after 4200 cycles
MCC-CV	NCA/Gr, 18650	0.5C followed by 10 s break then 0.2C; or 0.9C followed by 10 s break then 0.2C	C-rate switch at 3.9 V (determined to correspond to about 10 mV anode potential in instrumented cells)	4.2	25	[160]	15-40% faster charging and similar lifetime to 0.25C CC-CV
MCC-CV	NMC/Gr, 3.3 Ah pouch	Multiple decreasing C-rate levels from 2.4C to 0.7C	Switch C-rate when cell expands beyond a set limit	4.2	25	[156]	11% faster charge than 1C CC-CV; 20% less capacity fade at 1000 cycles, with reduced plating confirmed by teardown
BC	LCO/Gr, 18650 and unspecified chemistry prismatic	Multiple variants; most successful was 4.5C followed by 1C CC-CV	Switch C-rate after 5 min	4.3 in boost stage, then 4.2	25	[161]	30-40% improvement in charging time with comparable lifetime to 1C CC-CV
BC	High power; LMO+NMC/Gr and LFP/Gr	5 or 6 min boost stage at 4.5C, 0.9C otherwise; boost stages applied at 0, 10, or 20% SOC	C-rate switch after 5 or 6 mins	4.25 in boost stage, then 4.2 (LMO+NMC/Gr); 3.65 then 3.6 (LFP)	25	[162]	Lifetime comparable or worse than 3C CC-CV despite slower charging
PC	LCO/Gr, 18650	1C or 0.5C average	Patented pulse charging method [163]	4.2	Not given	[164]	Charging speed reduced from 3.5 h for 1C CC-CV to 1 h, similar degradation rates
MCC-CV, PC	High power LFP/Gr	Multiple protocols, C-rates up to 4C	Various	3.65	25	[165]	Similar capacity fade with CC-CV, MCC-CV and PC until 700th cycle, then increased rate of fade for CC-CV

2.4.1 Types of Charging Protocols

Standard protocols Numerous charging protocols have been proposed for Li-ion batteries. Constant Current - Constant Voltage (CC-CV) is by far the most common one. It consists of a constant current charging phase where the battery voltage increases up to a cut-off value (CC phase), followed by a constant voltage hold until the current falls to near-zero (CV phase). The CV phase allows for the concentration gradients within the electrode particles to disperse and is usually necessary to obtain high capacity utilisation without exceeding the maximum voltage. However, since the current gradually decreases during the CV phase, the charging time is significantly increased compared to CC-only charging. The simplicity and ease of implementation of CC-CV has made it the standard charging protocol in most applications. However, many other protocols have been shown to achieve reduced charging times, increased efficiencies and/or improved capacity or power retention. Figure 2.8 illustrates some of the alternative protocols proposed for fast charging.

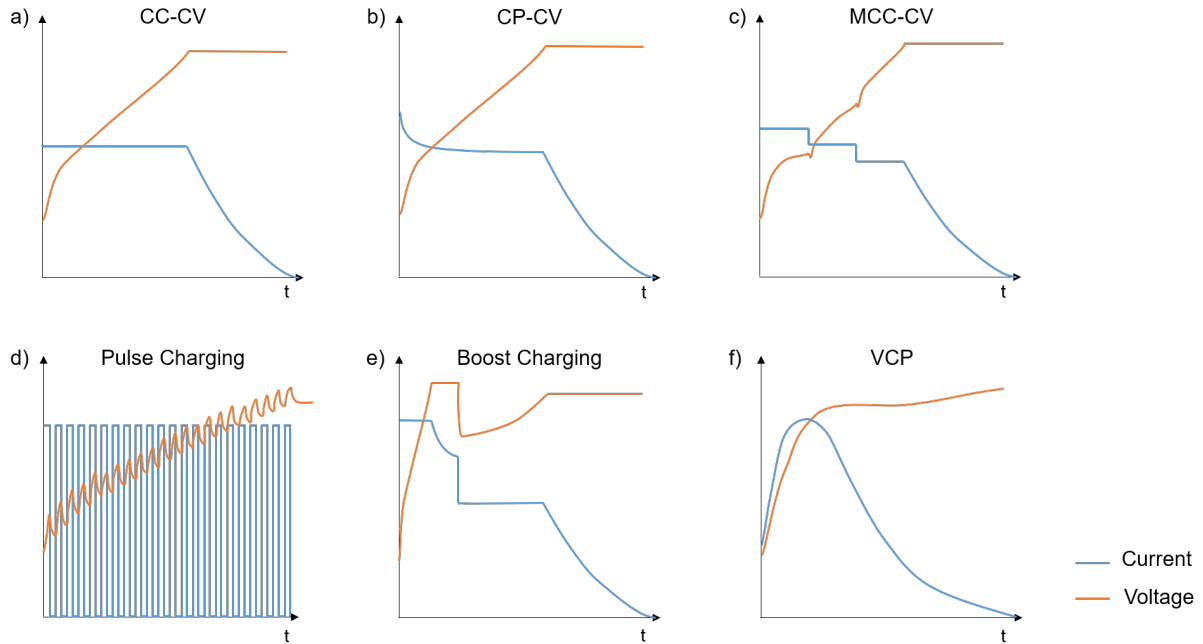


Figure 2.8: Schematic representation of common types of charging protocols proposed for fast charging. a) Constant Current - Constant Voltage (CC-CV), b) Constant Power - Constant Voltage (CP-CV), c) Multistage Constant Current - Constant Voltage (MCC-CV), d) Pulse charging, e) Boostcharging with a CC-CV-CC-CV scheme, f) Variable Current Profile (VCP), based on Ref. [75].

Zhang et al. [166] studied the effects of the CC-CV charging protocol on the reversible capacity and anode potential evolution in experimental LCO/graphite cells with embed-

ded reference electrodes as they were charged at ambient temperatures from -20°C to 10°C with C-rates between 0.16 C - 1.2 C. The results showed a positive correlation between increasing charging current in the CC phase and increasing time taken by the CV phase to complete. The authors observed that increasing the current beyond a certain value did not bring any further reduction in overall charging time due to this correlation. Both increasing the charging current and decreasing the ambient temperature was shown to result in a reduction in anode potential, with all test schemes causing the anode potential to become negative versus Li/Li^{+} at some point during charging. Negative anode potential was assumed to inevitably cause lithium plating, which was suggested as the main reason for the reduction in charged capacity at high currents and low temperatures. However, the occurrence of plating was not confirmed through other methods. Ouyang et al. [167] demonstrated that the shape of the voltage profile of large format LFP cells changed significantly with the number of cycles at 0.5 C CC-CV at -10°C , resulting in an elevated average voltage in the CC stage and longer duration of the CV stage. In comparison, the voltage profile of cells charged at 0.2 and 0.3 C at the same temperature retained a similar shape. The increased average voltage as a result of repeated cycling at higher C-rates may contribute to increased degradation rate.

Multistage Constant Current - Constant Voltage (MCC-CV) protocols Many researchers have proposed that adjusting the current levels during the charging process may limit cell degradation while reducing the charging time. Such approaches are often motivated by reducing heat generation, avoiding conditions that enable lithium plating or reducing mechanical stresses when the diffusion of Li^{+} ions is constrained. MCC-CV protocols are one of the earliest types designed specifically for fast charging. Such protocols consist of two or more constant current stages, often followed by a CV stage. Higher current levels are usually chosen for the earlier CC stages since the anode potential is less likely to become negative in the beginning of the charging process. Nevertheless, some authors have used the opposite approach with current levels increasing in later CC stages due to the lower cell resistance. Zhang [158] observed faster capacity loss in cells charged with the latter MCC-CV-CV approach compared to CC-CV and constant power - constant voltage (CP-CV) protocols with the same average C-rate of 1 C. The study concluded that CP-CV resulted in best capacity retention when the cell was fast charged (1 C), while CC-CV was less damaging for cells charged at 0.5 C. Another work [159] reported an 83%

capacity retention after 4200 cycles in an LFP cell charged with a 25-minute MCC-CV-CV protocol with two CC stages of decreasing current. Waldmann et al. [160] studied the anode potential evolution in reconstructed commercial NCA/graphite cells. Three MCC charging protocols were then tested in fresh cells of the same type. Current level was decreased just before reaching a voltage at which negative anode potential was observed in the reconstructed cells. All three protocols were faster than 0.25 C CC-CV protocol and led to a comparable rate of capacity fade. However, this protocol design method is both time consuming and expensive as it requires reconstructing the cell with a reference electrode and measuring the anode potential in the range of temperatures and currents of interest in the practical application. Spingler et al. [156] postulated that lithium deposition leads to local volume changes which can be directly measured in pouch cells *in operando* using laser triangulation, removing the need to measure the anode potential. Based on this assumption, they designed an MCC-CV protocol with multiple stages in which current level was decreased every time the maximum local expansion reached a predetermined value. Cells cycled with this protocol experienced dramatically improved capacity retention compared to a CC-CV protocol with the same average current. However, the method still requires extensive experimentation and is limited in application to pouch cells.

Pulse charging protocols Pulse charging protocols, where the charging current is periodically interrupted by short rest periods or discharge pulses, are also common in literature. The strategy aims to reduce concentration polarisation, reducing the risk of local anode potential becoming negative or reducing mechanical stresses due to uneven insertion and extraction of lithium in the solid particles. Aryanfar et al. [168] used a Monte Carlo simulation of lithium dendrite growth to show that pulse charging can also potentially inhibit dendrite propagation. One of the early studies [164] reported that a 1 C pulse charging protocol could reduce the charging time from 3.5 h for a 1 C CC-CV protocol to approximately 1 h due to the absence of the CV stage that accounted for most of the total charging time in CC-CV. Higher discharge capacities were observed for the pulse protocol relative to CC-CV which was attributed to better active material utilisation. However, since the capacities of the cells were not determined in a standard characterisation test at the beginning of life and the rate of capacity fade did not vary substantially, the discrepancy in capacities could be caused by manufacturing differences.

The same study [164] compared SEM images of both electrodes after 300 cycles, finding cracks in the cathode particles of all cells but significantly less SEI formation on the anodes of the pulse charged cells. Abdel-Monem et al. [165] monitored capacity fade and impedance changes in LFP cells cycled with eight different fast charging protocols, all belonging to CC-CV, MCC-CV or pulse charging categories. They observed comparable rates of capacity fade until the 700th cycle, when the capacity of the cell charged by CC-CV started deteriorating considerably faster. The rate of capacity fade between pulse charging and MCC-CV remained similar, however a higher rate of impedance rise was observed for the MCC-CV protocol than for pulse charging. The discrepancy in the rates of capacity fade and impedance rise was interpreted as a manifestation of different aging mechanisms occurring for each protocol. Pulse loads may lead to increased and uneven heat generation in packs connected in parallel due to the rebalancing events between pulses [169]. The implications of these effects have not been extensively studied in the context of charging protocol optimisation.

Boostcharging Boostcharging is characterised by high average current in the beginning of charge, followed by a CC-CV part with more moderate currents. The first, boostcharge stage could simply comprise a CC profile (making the protocol identical to MCC-CV-CV), a CV profile where the cell is immediately brought to a set maximum voltage by means of high initial current (CV-CC-CV), or an entire CC-CV profile (CC-CV-CC-CV) [161]. The boostcharge stage should, in any case, allow higher currents or higher maximum voltage compared to the following CC-CV part in order to reduce the overall charging time. Notten et al. [161] tested a few variations of the boostcharge protocol on both cylindrical and prismatic LCO cells with a 5 min boostcharge period. Compared to a 1 C CC-CV protocol, the charging time was reduced by about 30-40% with no noticeable acceleration in capacity fade for cylindrical cells. For prismatic cells, a smaller reduction in charging time was reported along with slightly higher rates of capacity fade. Interestingly, some of the boostcharging protocols seemed to achieve marginally better capacity utilisation at the beginning of life compared to the slower 1 C CC-CV. It is, however, unclear whether this could be due to manufacturing differences as cell capacities were not measured by a standardised test at the beginning of life. Keil and Jossen [162] arrived at contradicting conclusions after experimentally comparing cycling data from three types of 18650 cells of different chemistries charged by CC-CV, boostcharging and pulse charging protocols.

An increased rate of capacity fade was reported for boostcharging compared to CC-CV with a similar charging time, while no significant differences in capacity fade rates were observed for pulse charging. The authors concluded CC-CV was suitable for fast charging high power cells, however mentioning that MCC-CV could be useful in conditions when lithium plating is likely to occur.

Variable current profiles A number of more complex variable current profiles have also been proposed for fast charging. Sikha et al. [170] investigated a Varying Current Decay (VCD) protocol, designed to charge faster than a conventional CC-CV protocol while being less damaging than pure CV charging. The proposed protocol achieved improved capacity utilisation in the early cycles, but still resulted in a significantly higher rate of capacity fade compared to CC-CV with a similar average current. Possible overcharge of the cathode was suggested as the reason for accelerated degradation. Building on a similar idea, the Universal Voltage Profile (UVP) [75] was designed to reduce both charging time and energy losses due to heating, thus improving charging efficiency. The UVP is derived from a set of CC-CV charging curves using an optimisation algorithm for a specified charging time and target terminal voltage. A variable current profile is then calculated from the UVP and cell resistance. As the cell ages, the current profile needs to be recalculated due to changes in resistance while the voltage profile remains the same as for a fresh cell. Irrespective of the cell age, the current is always very low and rapidly increasing in the beginning of charge due to the cell resistance being highest at 0% SOC and then rapidly dropping. Maximum current is reached at relatively low SOCs, and subsequently it is gradually reduced due to the mass transport of Li becoming more constrained in increasingly lithiated graphite particles. The study demonstrated that a very high charging efficiency could be maintained even for highly aged cells. The capacity of the tested LCO/NMC cell dropped to 80% after 370 cycles with the UVP protocol compared to only 100 cycles achieved by the 2 C CC-CV protocol with a similar charging time. While the voltage profile was shown to be universal with respect to cell age, the effects of the charging conditions, most notably temperature, on the cycling performance were not investigated.

Schindler et al. [171] took the novel approach of combining previously published physically-motivated fast charging strategies. Four current-neutral current profiles were superimposed, separately and in combination, on a 1 C CC-CV protocol. The profiles are

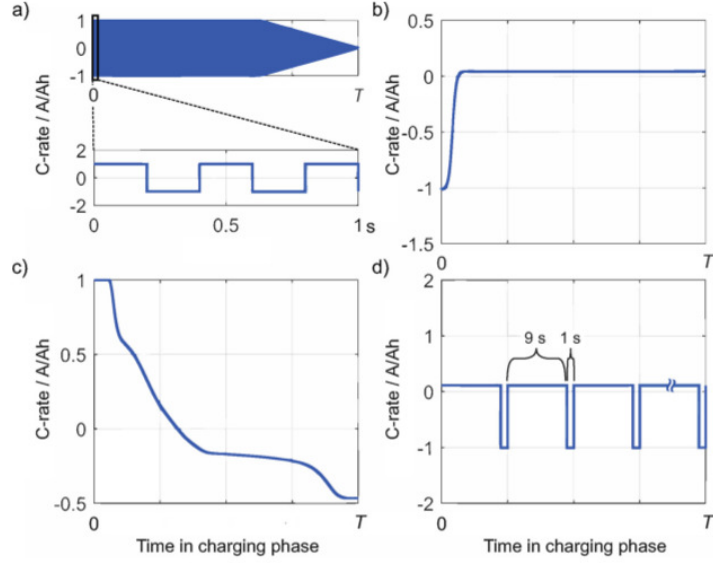


Figure 2.9: Current trajectories of superimposed profiles from Ref. [171]. a) AC pulse, b) Cold derating, c) Overpotential reserve, d) Pulse charging.

shown in Figure 2.9 and included: a) AC pulse, motivated by a decrease in cell resistance due to additional irreversible heating; b) cold derating, a profile in which a very low current is used initially due to high resistance at 0% SOC and the current is brought to a higher constant level as soon as the resistance drops; c) overpotential reserve, a profile in which the overpotential is always maintained below a certain safety limit to prevent negative anode potential, producing a gradually decreasing current profile; and d) pulse charging. Capacity fade was monitored in eighteen cells charged by different protocols, and compared to four cells charged by standard CC-CV. The best performing cell, charged by a combination of all profiles, retained 80% capacity after 800 cycles. In comparison, cells charged by CC-CV alone experienced the same capacity fade after only about 400 cycles, while the worst performing cell, charged by CC-CV combined with cold derating, completed about 330 cycles. In general, protocols that included the overpotential reserve profile resulted in best capacity retention. All tests were conducted at a temperature of 25°C and the results should not be generalised to other conditions.

2.4.2 Model-based protocol optimisation

Optimisation based on ECM type models

Some researchers have attempted to design optimal charging protocols by using Equivalent Circuit Model (ECM)-based models, which are reformulated and embedded into single-

objective or multi-objective constrained optimization problems. In these problems, ECMs are used to describe the cell behaviour, and various cost functions are set to optimise for the charging efficiency or charging time [172, 173, 174]. The heat generation and degradation caused by charging can be embedded into the basic ECM with an electro-thermal-ageing coupled model to minimise temperature rise and/or battery ageing during charging. While most such models use a lumped thermal modelling approach, some enhanced models that can distinguish the core and surface temperature or have improved fidelity at higher rates have been proposed as well [175, 176]. The ageing model is usually incorporated using an empirical equation, often in the form of an extended Arrhenius rate law with temperature, current, SOC and/or DOD dependencies [175].

ECMs can capture the electrical behaviour of the battery but fail to provide internal state information, especially for side reactions caused by charging such as SEI growth, lithium deposition, or particle cracking. Therefore, electrochemical models have drawn increasing attention.

Optimisation based on electrochemical models

Electrochemical models can be used to predict side reactions during charging due to their ability to estimate internal states such as the solid and electrolyte potentials, ion concentration, and reaction flux. Key degradation mechanisms such as Li plating, SEI layer growth or particle cracking can be explicitly incorporated into the Doyle-Fuller-Newman (DFN) model, or states such as the anode potential or surface concentration can be used to define safe operating ranges. However, it is computationally intensive to solve the partial differential equations (PDEs) in the Full Order Model (FOM). Multiple types of reduced order models (ROMs) have been proposed to improve the computational speed while retaining relatively high fidelity, allowing for onboard application. Purushothaman et al. [177] derived an analytical solution of the solid phase concentration through variable separation method. Fast charge methods of variable current pulse and nonlinear decay current were developed aiming at limiting the solid surface concentration. The model used in this case was a simplified form of the Single Particle Model (SPM) with a number of assumptions: only diffusion was modelled without considering reaction kinetics, a constant diffusion coefficient was assumed and all lithium-ion reduction was assumed to take place at the anode/separator interface. The model was not validated. The SPM can also

predict the temperature, ion concentration distribution or overpotential by extension. The extended models are embedded into optimization problems to solve for fast charging strategies with temperature or ion concentration restrictions [178, 179]. Since temperature is vital to the correct prediction of diffusion rates, SPMs are often coupled with thermal models to develop fast charging strategies applicable over wider temperature ranges [180, 181]. It is important to mention that while some of these models are validated against experimental results [180, 179], others are only validated against other models [181] or not validated at all [177, 178]. SPMs generally lose accuracy at high current densities when the concentration and potential gradients along the electrode thickness become significant [182] and thus the results of studies should be interpreted with caution unless parameterised and validated against independent experimental data sets.

Some modelling approaches have been developed that explicitly consider side reactions. Rahimian et al. [183] used an SPM that included SEI layer growth to optimise the battery cycle life through adjusting the charging C-rate as the cell aged. The simulation results suggested that cycle life could be improved if charging C-rate was increased after a certain number of cycles. The model was not validated. SEI growth models were also used to develop a MCC-CV [184] and a variable current protocol [185], but neither of these studies included full experimental validation. Lithium plating prevention has drawn increasing attention in recent years [186, 167]. The models that aim to limit lithium plating normally do so by maintaining positive anode potential. Klein et al. built a time-optimal charging problem based on a reduced-order electrochemical-thermal coupling model to predict the anode potential and temperature during fast charging [187, 188]. The model was validated against the FOM model and experimental data for a fresh cell. Han et al. proposed a novel approach to form a simplified P2D model (SP2D) while maintaining the FOM's fidelity at high rates [189, 190]. Experimental validation was not conducted. The SP2D model was then used to develop a non-destructive fast charging strategy with a variable current profile by maintaining the anode potential above a safety threshold [191]. Two cells were inspected post-mortem after five cycles using the proposed protocol and a CC-CV protocol with a comparable charging time (1.15 C), revealing visible lithium deposition on the anode of the cell charged with CC-CV but no visible deposition on the cell charged with the proposed protocol.

Recently, some physics-based ECM models have also been developed that capture

key electrochemical processes and internal states of the battery while being easier to parameterise than Pseudo-Two-Dimensional (P2D) models [192] or including additional effects such as double layer capacitance [193]. Such hybrid models vary in terms of computational demand and accuracy of prediction. While the more complex physics-informed ECMs could be useful for assessing effects in the frequency domain that standard P2D models do not capture, the simpler ones could have the advantage of being less computationally expensive or easier to parameterise than P2D with an improved fidelity and physical insight compared to standard ECMs. To the best of the author’s knowledge, these models have not yet been applied to charging protocol optimisation.

Overall, model-based charging optimisation studies often use ECM, SPM or ROM rather than FOM approaches due to their lower computational demand, which makes them potentially suitable for real-time implementation. However, this advantage often comes at the expense of accuracy, prompting the need for careful validation particularly when abuse conditions such as fast charging are being modelled. While many model-based approaches to fast charging optimisation have been proposed, relatively few of them have been fully validated against experimental results. Furthermore, validation is often conducted only against fresh cell data, which may not be sufficient for modelling studies where the main purpose is to limit long-term degradation.

2.5 Literature gaps

Fast charging and Li plating prevention have been the topic of significant research effort in the past few years. Nonetheless, many knowledge gaps still remain. The focus of this thesis is on two such gaps identified through the literature review.

The interplay between charging protocol performance and transport limitations. While many fast charging protocols have been proposed based on an array of physical motivations, most of them have only been validated at standard temperatures and for certain cell types. The severity of the transport limitations which ultimately lead to plating depends on the temperature as well as the cell design, including the diffusion properties of the electrode materials and electrolyte, electrode thicknesses, porosity and particle sizes. Since these parameters can differ substantially between cells, it is not clear whether the proposed charging protocols would be equally effective at preventing plating

when applied to other cells. Both solid and electrolyte phase diffusion, as well as the reaction kinetics, are also strongly temperature-dependent. Most charging optimisation studies only model or test proposed charging protocols at a single temperature. The variation in cell types and thermal conditions may be the reason for the contradictory claims on the performance of similar charging protocols in different studies [161, 162, 159, 194]. The first part of the work presented in this thesis investigates the relationship between the cell transport properties, temperature, and the effectiveness of charging protocols at minimising Li plating, aiming to answer the following research questions:

- What are the reasons for the discrepancies in the performance of similar charging protocols reported in different studies?
- What are the general rules for the selection of a fast charging protocol for a given cell and temperature conditions?

The influence of thermal gradients on Li plating. The effects of the cell temperature on Li plating have been studied in detail. It is generally accepted that lower temperatures lead to a higher risk of Li plating due to the reduced diffusion rates and increased overpotential. However, few studies have investigated the effect of thermal heterogeneity on Li plating in Li-ion batteries. Thermal heterogeneity introduces an additional layer of complexity, since higher temperatures reduce the local resistance and increase current densities. This has been shown to drive localised deposition at high temperature hot spots in Li metal cells [82]. In Li-ion batteries, preferential plating has been observed in the high temperature regions in the centre of fast charged cells [195, 196]. Elsewhere, Li plating was reported in the colder regions of cells fast charged under an in-plane thermal gradient [197, 78]. Through-plane thermal gradients, often encountered in EV applications due to the widespread use of surface cooling, have not been topic of much research. It is not known which regions of a cell under such a thermal gradient are most vulnerable to plating, or whether the overall plating severity is affected. These research gaps are the focus of the second part of the thesis, guided by the following questions:

- Are there significant differences in the severity of plating, depending on whether it takes place at moderate or low temperatures?

- How do through-plane thermal gradients affect the distribution and severity of plating in Li-ion cells?
- How is the overall degradation affected by the presence of a through-plane thermal gradient during fast charging?

Chapter 3

Lithium-ion battery modelling

This chapter contains excerpts from the paper, 'The effects of temperature and cell parameters on Li-ion battery fast charging protocols: a model-driven investigation', published in the Journal of the Electrochemical Society [198]. The lithium plating model presented herein is a modified version of a model developed in COMSOL by Dr Simon O'Kane. In addition, a lumped thermal model was implemented using COMSOL's functionality. The electrochemical model was also extended to a 2D multilayer geometry with fully discretised thermal coupling. Application of different charging profiles required the development of non-standard boundary conditions in COMSOL using weak formulation.

3.1 Introduction

Various models have been developed to study Li-ion batteries, ranging in complexity and accuracy depending on the application. Broadly, cell-level models are often divided into ECMs, SPMs and P2D models. ECMs approximate the cell behaviour with a model of a circuit network consisting of resistors and capacitors. Fast and easy to solve, ECMs are highly useful for online state estimation in Battery Management Systems (BMSs) on-board EVs or other battery-powered devices. However, this type of model contains little description of the physical processes taking place within the cell; rather, it replicates the observed electrical behaviour with the appropriate time constants. As a consequence, ECMs are only accurate within the range of the operational conditions they are validated for and typically lose accuracy when extreme conditions (such as high C-rate operation) are modelled, or when the behaviour of the cell is affected by its history, such as after age-

ing or in the presence of large concentration gradients. SPMs and P2Ds are two types of physics-based electrochemical models. Both directly model the physical processes (transport of species and reactions) that drive battery operation. SPMs model each electrode as a single particle, resolved in the radial (r) direction. The transport within the electrolyte is assumed to be very fast, meaning any liquid phase concentration gradients can be ignored and the electrolyte transport does not need to be explicitly modelled. This assumption is only acceptable when the rates of electrolyte diffusion are much higher than the reaction rates, i.e. at low C-rates. High C-rates increase the rate of lithium ion consumption and generation at electrode surfaces, driving higher electrolyte concentration gradients and rendering SPMs inaccurate. To address this issue, some SPM models are modified to include an additional potential drop associated with the electrolyte. Such models are known as SPM with electrolyte, or SPMe. While this does improve high C-rate accuracy, many of the interactions between the electrolyte and solid phase transport are still lost due to the single particle architecture. P2D models account for multiple particles within each electrode and also model the transport of charge and species within the electrolyte. As such, the variables are modelled as a function of the position through the depth of the cell layer (the x direction) and the position within the particle, along the pseudo-dimension of the particle radius (r). A schematic illustrating the modelling domains is shown in Figure 3.1. This structure makes P2D models well equipped to reflect the effects of the concentration gradients resulting from high C-rate operation. Naturally, this improved resolution and accuracy come at the cost of substantially increased computational complexity, slower solution times, and more difficult parameterisation. Traditional P2D models only simulate a single unit cell (one cell layer). However, the approach can be extended to multilayer geometries or along additional cell dimensions. P2D models are also known as DFN models, after the researchers who originally proposed this approach [199].

The different model types can sometimes be hybridised; for example, a number of physics-informed ECMs have been developed to combine some of the physical grounding of the more complex models with the computational efficiency of ECMs. Such models show improved accuracy compared to ECMs but often rely on additional assumptions compared to physics-based models, which restricts their ranges of validity.

The focus of this thesis is on the mechanistic understanding of the impacts of fast

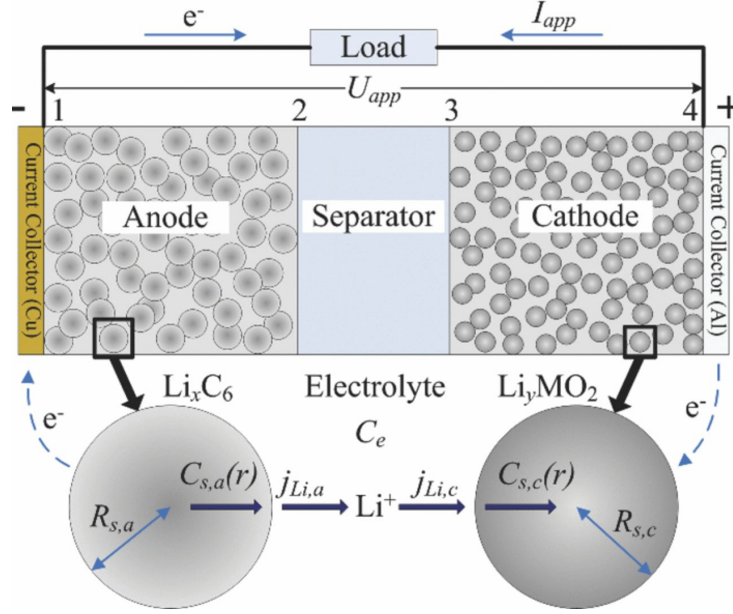


Figure 3.1: A schematic representation of the P2D or DFN model (discharge direction) [200].

charging on Li-ion battery degradation. All of the types of models described above are well proven for simulating Li-ion battery behaviour in low C-rate ranges. However, modelling fast charging and Li plating in particular presents additional challenges. Fast charging of conventional Li-ion batteries is typically a diffusion-limited process, making the correct prediction of transport limitations particularly important. As such, it is key to consider the SOC-dependency of the solid phase diffusion coefficients, which have been shown to vary by orders of magnitude as a function of the state of lithiation for typical battery materials, including graphite [16, 24]. Fast charging often drives severe concentration gradients in both the solid particles and the electrolyte, with complex interactions between both phases. The P2D or DFN model, which most accurately reflects these mass transport limitations, is therefore deemed most appropriate for the application and is discussed in further detail in this chapter. While this modelling approach cannot currently be used onboard most devices due to the high computational complexity, it provides a wealth of information about the processes that affect battery performance and lifetime. This can help guide the choice of fast charging protocols and provide understanding about the impact of thermal conditions on cell degradation. In the remainder of the thesis, the model is referred to as DFN rather than P2D to avoid confusion. This is because in parts of the work, a 2D multilayer model geometry is used. This approach is sometimes described as "P3D" in other works [201, 202] but still relies on the equations proposed by

Doyle, Fuller and Newman [199]. The following chapter introduces the model equations and discusses its assumptions and limitations, while the details of the implementation, including the geometry, are discussed in the appropriate results chapters.

3.2 Electrochemical model

The model used in this work is based on that from O’Kane et al. [141], the main difference being the inclusion of thermal coupling. That model is in turn based on the well-known DFN model [199] with the addition of lithium plating/stripping. The equations that describe the species and charge transfer in the electrode domains are drawn from the porous electrode theory as described by Newman and Tiedemann [203]. The solid electrode and liquid electrolyte phases are considered to be superimposed continua; in other words, at any node within the electrode domains of the model, the solid and liquid phases co-exist. As such, each node can be considered to represent the average behaviour of a region along the thickness of an electrode. This macroscopic formulation avoids the need to consider the complexities of the electrode microstructure, instead relying on averaged properties such as porosity and tortuosity. Additionally, the electrode particles are assumed to be spherical in shape to simplify the modelling of the solid phase diffusion. The diffusion is assumed to be one-dimensional, along the particle radius. Since battery electrolytes are typically used in concentrations of 1 M or above, the electrolyte behaviour is assumed to obey the equations of the concentrated solution theory [204, 205]. The effect of the negatively charged ions on the transport of the positively charged lithium ions is accounted for using a lithium transport number, which is a measure of the current carried by the lithium ions compared to the total current.

The model is implemented in COMSOL 5.3a, a finite element modelling software package. This solution was judged the most suitable at the time this project was started as COMSOL is designed specifically for modelling coupled phenomena and multiphysics (coupling of physical domains, e.g. electrochemical and thermal), including in multidimensional geometries. Other battery modelling environments available at the time included a MATLAB-based package Lionsimba and Python-based PyBaMM, however both were found to be significantly less stable. Solver robustness was of particular importance since the problems studied involved coupled physics as well as severe spatial and temporal

concentration and potential gradients induced by fast charging. These strengths of COM-SOL come at the price of a less intuitive interface for modifying the existing equations or implementing new ones, as weak formulations need to be used. Some of the offered functionalities are also not sufficiently stable and better replaced by custom implementations, as was found in the case of the built-in CC-CV boundary condition. The approach taken to implement these modifications is described in Section 3.5.

3.2.1 Mass transport

Two PDEs govern the conservation of mass in the solid electrode particles and the electrolyte:

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right) \quad (3.1)$$

$$\frac{\partial}{\partial t} \epsilon_e c_e = \frac{\partial}{\partial x} \left(D_e^{\text{eff}} \frac{\partial c_e}{\partial x} \right) + (1 - t^+) \frac{j}{F} \quad (3.2)$$

where c_s [mol.m⁻³] is the solid phase concentration, D_s [m².s⁻¹] is the solid phase diffusion coefficient, ϵ_e [-] is the electrolyte volume fraction, D_e^{eff} [m².s⁻¹] is the effective electrolyte phase diffusion coefficient, c_e [mol.m⁻³] is the electrolyte phase concentration, t^+ [-] is the lithium transport number, j [A.m⁻²] is the total current density and F is Faraday's constant equal to 96,485 s.A.mol⁻¹.

The effective electrolyte phase diffusion coefficient is a system property which reflects the dependence of the diffusion rate on the tortuous path Li⁺ ions take through the pores of the electrodes. It is related to the electrolyte diffusion coefficient D_e (the electrolyte solution property) according to:

$$D_e^{\text{eff}} = \frac{\epsilon_e}{\tau} D_e \quad (3.3)$$

where τ [-] is the electrode tortuosity. The diffusion coefficient D_e is a function of temperature and electrolyte concentration.

No ionic flux is allowed at the current collectors, which is expressed with two zero gradient Neumann boundary conditions:

$$\left. \frac{\partial c_e(x, t)}{\partial x} \right|_{x=0} = \left. \frac{\partial c_e(x, t)}{\partial x} \right|_{x=L} = 0 \quad (3.4)$$

3.2.2 Charge transport

The remaining two PDEs are charge balance equations for the solid and electrolyte phases:

$$\frac{\partial}{\partial x} \left(\sigma^{\text{eff}} \frac{\partial}{\partial x} \phi_s \right) - j = 0 \quad (3.5)$$

$$j + \frac{\partial}{\partial x} \left(\kappa^{\text{eff}} \frac{\partial}{\partial x} \phi_e \right) + \frac{\partial}{\partial x} \left(\kappa^{\text{eff}} T(t) \frac{2R(1-t^+)}{F} \frac{\partial}{\partial x} \ln c_e \right) = 0 \quad (3.6)$$

where σ^{eff} [S.m⁻¹] is the effective electronic conductivity of the solid phase, ϕ_s [V] is the solid phase potential, κ^{eff} [S.m⁻¹] is the effective ionic conductivity of the electrolyte, R is the universal gas constant equal to 8.314 [J.mol⁻¹K⁻¹] and ϕ_e [V] is the electrolyte phase potential. The effective conductivity κ_{eff} is related to the electrolyte conductivity κ analogously to Equation 3.3:

$$\kappa_{\text{eff}} = \frac{\epsilon_e}{\tau} \kappa \quad (3.7)$$

Two Neumann boundary conditions enforce no charge flux at the electrode/current collector interfaces:

$$\left. \frac{\partial \phi_e(x, t)}{\partial x} \right|_{x=0} = \left. \frac{\partial \phi_e(x, t)}{\partial x} \right|_{x=L} = 0 \quad (3.8)$$

3.2.3 Intercalation

A Butler-Volmer equation is used to describe the kinetics of (de)intercalation:

$$j_{\text{int}} = \frac{i_{0,\text{int}}}{F} \left[\exp \left(\frac{\alpha_{\text{a,int}} F \eta_{\text{int}}}{RT} \right) - \exp \left(-\frac{\alpha_{\text{c,int}} F \eta_{\text{int}}}{RT} \right) \right], \quad (3.9)$$

where j_{int} [A.m⁻²] is the (de)intercalation flux, T [K] is absolute temperature, and $\alpha_{\text{a,int}}$ and $\alpha_{\text{c,int}}$ are the anodic and cathodic charge transfer coefficients respectively, with both assumed to be 0.5 as is standard in the literature. The (de)intercalation exchange current density $i_{0,\text{int}}$ [A.m⁻³] is given by:

$$i_{0,\text{int}} = F k_{0,\text{int}} c_e^{1-\alpha} (c_{\text{s,max}} - c_s)^{1-\alpha} c_s^\alpha \quad (3.10)$$

where $k_{0,\text{int}}$ [m.s⁻¹] is the (de)intercalation reaction rate constant and $c_{\text{s,max}}$ [mol.m⁻³] is the maximum solid phase concentration of lithium. The intercalation overpotential η_{int}

[V] is given by

$$\eta_{\text{int}} = \phi_{\text{s}} - \phi_{\text{e}} - U_{\text{int}} \quad (3.11)$$

where U_{int} is the OCP of the intercalation reaction in the electrode, which varies with the temperature according to:

$$U_{\text{int}} = U_{\text{int,ref}} + \frac{\partial U_{\text{int}}}{\partial T}(T - T_{\text{ref}}) \quad (3.12)$$

3.2.4 Lithium plating

Lithium plating/stripping is also assumed to follow Butler-Volmer kinetics with a concentration-dependent exchange current density, in line with the current state of understanding [141, 86, 206]. Fundamentally, the reaction is reversible; however, the deposited lithium can be lost both to secondary SEI and due to the formation of dead lithium. In this thesis, modelling is used to offer a lens into single cycle plating and stripping behaviour rather than to study capacity loss over many cycles, which results from the coupling of multiple degradation mechanisms. Over a single cycle, both SEI growth and dead Li formation are assumed to be negligible. As such, plating can be approximated as fully reversible and the coupling to other degradation mechanisms can be omitted. Some researchers have proposed the anodic and cathodic charge transfer coefficients should both equal 0.5 [90, 206], resulting in a symmetrical reaction, while others have assumed the anodic coefficient to be higher at 0.6 - 0.7 with the cathodic coefficient being 0.4 - 0.3 [59, 207]. In light of this lack of agreement in the literature, the simplest form is assumed here, i.e. a symmetrical reaction. The reaction is modelled using a modified form of the expression from [141]:

$$j_{\text{pl}} = \frac{i_{0,\text{pl}}}{F} \left[\frac{c_{\text{l}}}{c_{\text{l}}^*} \cdot \exp\left(\frac{\alpha_{\text{a,pl}} F \eta_{\text{pl}}}{RT}\right) - \frac{c_{\text{Li,metal}}}{c_{\text{Li,metal}}^*} \cdot \exp\left(-\frac{\alpha_{\text{c,pl}} F \eta_{\text{pl}}}{RT}\right) \right], \quad (3.13)$$

where j_{pl} [A.m^{-2}] is the lithium plating/stripping current density, $c_{\text{Li,metal}}$ [mol.m^{-3}] is the local concentration of metallic lithium, $c_{\text{l}}^* = c_{\text{Li,metal}}^* = c_{\text{l},0}$ [mol.m^{-3}] (since the reference concentrations are arbitrary, as noted by [141]). The lithium plating exchange current density $i_{0,\text{pl}}$ [A.m^{-3}] is:

$$i_{0,\text{pl}} = F k_{0,\text{pl}} (c_{\text{Li,metal}}^*)^{\alpha_{\text{c,Li}}} (c_{\text{l}}^*)^{\alpha_{\text{a,Li}}}, \quad (3.14)$$

where $k_{0,\text{lpl}}$ [m.s^{-1}] is the lithium plating/stripping reaction rate coefficient and the lithium plating overpotential η_{lpl} [V] is:

$$\eta_{\text{lpl}} = \phi_{\text{s}} - \phi_{\text{l}} - U_{\text{lpl}} \quad (3.15)$$

If potentials are defined with respect to the potential of the Li/Li⁺ couple, then the OCP of the lithium plating/stripping reaction U_{lpl} reduces to 0 V by definition. This is, however, only true at the reference temperature T_{ref} . The potential of lithium plating varies with the temperature, similarly to that of intercalation:

$$U_{\text{lpl}} = U_{\text{lpl,ref}} + \frac{\partial U_{\text{lpl}}}{\partial T}(T - T_{\text{ref}}) \quad (3.16)$$

There is significant disagreement in the literature regarding the values used for the transfer coefficients $\alpha_{\text{a,lpl}}$ (0.3-0.5) and $\alpha_{\text{c,lpl}}$ (0.5-0.7) [59, 207, 208]. Since this work makes use of the reaction rate constant for the plating reaction as determined by [141] for the same cell, the reaction is assumed to be fully reversible and symmetrical ($\alpha_{\text{a,lpl}} = \alpha_{\text{c,lpl}} = 0.5$) as in that study, despite some degree of irreversibility observed in practice. It is worth highlighting that the rate of lithium plating according to the above equations is both overpotential and ion concentration dependent, which is important for modelling fast charging due to the ion concentration gradients that develop across the anode.

The total current density is the sum of the current densities of the two component reactions, i.e.:

$$j = j_{\text{int}} + j_{\text{lpl}}, \quad (3.17)$$

When modelling long-term degradation, the current density of the SEI layer growth should also be included. However, the interactions between Li plating and SEI are still poorly understood. In this thesis, the

3.2.5 Temperature sensitivity

Solid phase diffusion coefficients, electrolyte conductivity (and diffusivity - since the two are coupled by the Einstein relation, as explained later in Section 3.4.1) and charge transfer

reaction rates vary with the temperature according to the general Arrhenius rate law:

$$\Psi = \Psi_{\text{ref}} \exp \left[\frac{E_{\text{act}}^{\Psi}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \quad (3.18)$$

Where Ψ is the temperature-dependent property, Ψ_{ref} is the value of that property at the reference temperature T_{ref} [K], and E_{act}^{Ψ} [J.mol⁻¹] is the activation energy.

3.3 Thermal model

Two different types of thermal model are used in this thesis. The first, used to study the effects of charging protocols on lithium plating propensity in Chapter 5, is a 1D thermal model, however only the average temperature is fed back to the electrochemical model instead of full node-by-node coupling. This semi-lumped thermal modelling framework reflects the effect of uneven heat generation and rejection through the cell layer (i.e. the majority of heat being generated in the active materials and then rejected via both the active material and the current collectors) on the average temperature rise, but does not feed information about temperature heterogeneity back to the electrochemical model. This is considered sufficient since thermal gradients are not considered in that part of the work. Chapter 6, on the other hand, focuses on the effects of through-plane thermal gradients on fast charging-induced degradation. As such, a 2D thermal model is required, with the two dimensions representing the cell thickness (accounting for the multiple layers) and cell length. The third dimension of cell width is not modelled, since the behavior is expected to be analogous to the length dimension. This section outlines the model equations applicable to both these models, with details of each implementation discussed in the appropriate chapters.

Within the thermal model, each component layer is assumed to have a constant heat capacity, density and thermal conductivity. Unsteady heat equation (Equation 3.19) is applied to compute the change in temperature, ensuring the conservation of energy.

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + q_{\text{gen}} \quad (3.19)$$

where ρ [kg.m⁻³] is the density, C_p [J.K⁻¹] is the thermal capacity, k [W.m⁻¹K⁻¹] is the thermal conductivity of the component layer and q_{gen} [W.m⁻³] is the total volume-specific

heat source.

The heat generation in a Li-ion battery stems from several processes, resulting in multiple component heat source terms. The first component, reaction heat q_r , results from the overpotential required to drive the electrochemical reactions. It is calculated as the product of the local overpotential and current density, and then integrated over the domain. Reaction heat is produced in both electrodes but not the separator, since the latter does not take part in the reactions. As both (de)intercalation and lithium plating are modelled, both reactions produce heat.

$$q_{r,i} = \frac{A_c}{V_{\text{cell}}} \int_x^{x+dx} j_i(\phi_s - \phi_e - U_i) dx \quad (3.20)$$

where A_c [m²] is the cross-sectional area, V_{cell} [m³] is the cell volume and subscript $i \in (\text{int}, \text{lpl})$ signifies one of the reactions, either (de)intercalation or plating.

Heat is also produced as a result of the movement of charge against the resistance of each phase (electrodes, electrolyte, and current collectors). This component term, known as ohmic heating q_{ohm} , can be calculated from the potential gradients computed in the electrochemical model and the resistance of the current collectors:

$$q_{\text{ohm}} = \frac{A_c}{V_{\text{cell}}} \left(\int_x^{x+dx} \left(\sigma^{\text{eff}} \frac{\partial}{\partial x} \phi_s + \frac{\partial}{\partial x} \left(\kappa^{\text{eff}} \frac{\partial}{\partial x} \phi_e \right) + \frac{\partial}{\partial x} \left(\kappa^{\text{eff}} T(t) \frac{2R(1-t^+)}{F} \frac{\partial}{\partial x} \ln c_e \right) dx \right) + \frac{R_{\text{cc}}}{A_c} \times I^2 \right) \quad (3.21)$$

where R_{cc} [Ω] is the resistance of the current collectors, and I [A] is the current applied. Some terms of Equation 3.21 reduce to zero in each domain: in the electrodes and the separator, the last term is equal to zero, whereas in the current collectors it is the integral term. The contact resistance of the tabs is omitted.

Finally, the phase transitions in the electrode materials on lithiation and delithiation lead to entropic changes which can either generate or consume heat. This is the only source of reversible heat generation considered, and is related to the temperature dependency of the potential of each electrode:

$$q_e = \frac{a_j T}{V_{\text{cell}}} \frac{\partial U}{\partial T} \quad (3.22)$$

The total volume-specific heat source is then computed as the sum of component heat

sources:

$$q_{\text{gen}} = q_{\text{r,int}} + q_{\text{r,lpl}} + q_{\text{ohm}} + q_{\text{e}} \quad (3.23)$$

3.4 Parameterisation and parameter uncertainty

3.4.1 Parameterisation

Electrochemical model parameters The model is parameterised for a 7.5 Ah Kokam pouch cell (model number SLPB75106100). The cell is characterised by high manufacturing consistency and was studied by Ecker et al. in two complementary papers, one focused on experimental parameterisation [16] and the other on model validation [209]. While the papers are some of the most thorough parameterisation works in the Li-ion modelling literature, the resulting parameter set was still found to be inaccurate for charging simulations. The details of this inaccuracy are discussed in Chapter 5. To mitigate the impacts of incorrect parameters as well as to ensure the generality of the conclusions, all the results presented in this thesis are confirmed through parameter sensitivity studies and/or experimental validation.

The parameters of the electrochemical model are detailed in Table 3.1 along with the sources. Most of the values come from the aforementioned Ecker et al. [209]. That work did not consider lithium plating and therefore did not report the rate constant k_{Li} for the plating reaction. O’Kane et al. [141] studied the differential voltage minima induced by lithium stripping using the DFN model with Ecker et al.’s parameter set [209] backed by the experimental data measured on the same cell by Campbell et al. [14]. The simulations suggested a k_{Li} value of $1 \times 10^{-10} \text{ m.s}^{-1}$ best fitted the experimental data. The same value is used in the current paper, although it must be stressed that the values for k_{Li} are typically fitted due to the difficulty of measurement and are therefore highly uncertain.

The values for the maximum concentration of Li in the electrodes are modified to account for the fact that not all electrode volume is active due to the electrode porosity as well as the binder and conductive additive content. From Ecker et al. [209], the volumetric fraction of the active material is 0.555 for the anode and 0.580 for the cathode, while the maximum Li concentrations for the pure active materials are 31920 mol.m^{-3} and 48580 mol.m^{-3} , respectively. The values given in Table 3.1 are simply the product of the active

material fraction and the maximum Li concentration for the pure active material.

Table 3.1: Parameters used for the electrochemical model.

Symbol	Description	Value			Ref.
		Anode	Cathode	Separator	
δ	Electrode/separator thickness, m	73.7×10^{-6}	54.5×10^{-6}	19×10^{-6}	[16]
r	Solid particle radius, m	13.7×10^{-6}	6.5×10^{-6}	-	[209]
ϵ	Electrolyte volume fraction	0.329	0.296	0.5	[209]
τ	Tortuosity	2.03	1.94	1.67	[209]
$c_{\max}$	Maximum concentration of Li in the electrode, mol.m^{-3}	17715.6	28176.4	-	[209]
σ	Electrode conductivity, S.m^{-1}	14	68.1	-	[209]
u	Utilization fraction for positive electrode (to account for the cathode end-of-charge SOC being non-zero - for details please refer to [16])	-	0.74	-	[209]
C_{SEI}	Fraction of positive electrode capacity lost to the SEI	-	0.104	-	[141]
k_{int}	Intercalation reaction rate constant at 296K, m.s^{-1}	1.99×10^{-10}	5.19×10^{-11}	-	[16]
k_{Li}	Li plating reaction rate constant, m.s^{-1}	1×10^{-10}	-	-	[141]
E_{D}	Activation energy of Li diffusion in the solid electrode, J.mol^{-1}	30300	80600	-	[209]
$E_{\text{k,int}}$	Activation energy of the (de)intercalation reaction rate constant, J.mol^{-1}	53400	43600	-	[209]
L_{cc}	Current collector thickness, m	14.7×10^{-6}	15.11×10^{-6}	-	[16]
A_{c}	Electrode cross-sectional area, m^2	8.585×10^{-3}			[16]
n	Number of cell layers	48			[16]
t^+	Lithium transport number	0.26			[16]
$c_{\text{l},0}$	Initial electrolyte salt concentration, mol.m^{-3}	1000			[16]
E_{κ}	Activation energy of electrolyte conductivity, J.mol^{-1}	17100			[209]
F	Faraday's number, C.mol^{-1}	96485			-
R	Universal gas constant, $\text{J.mol}^{-1}.\text{K}^{-1}$	8.3145			-
M_{Li}	Molar mass of Li, kg.mol^{-1}	6.94×10^{-3}			[141]
ρ_{Li}	Density of metallic Li, kg.m^{-3}	534			[141]

The OCPs of the electrodes as a function of the degree of lithiation are shown in Figure 3.2.

In addition to the electrode OCPs, the diffusion coefficients also vary with the lithium content, while the electrolyte conductivity varies with the electrolyte salt concentration. The solid phase diffusion coefficients were calculated from 150 s GITT discharge pulses

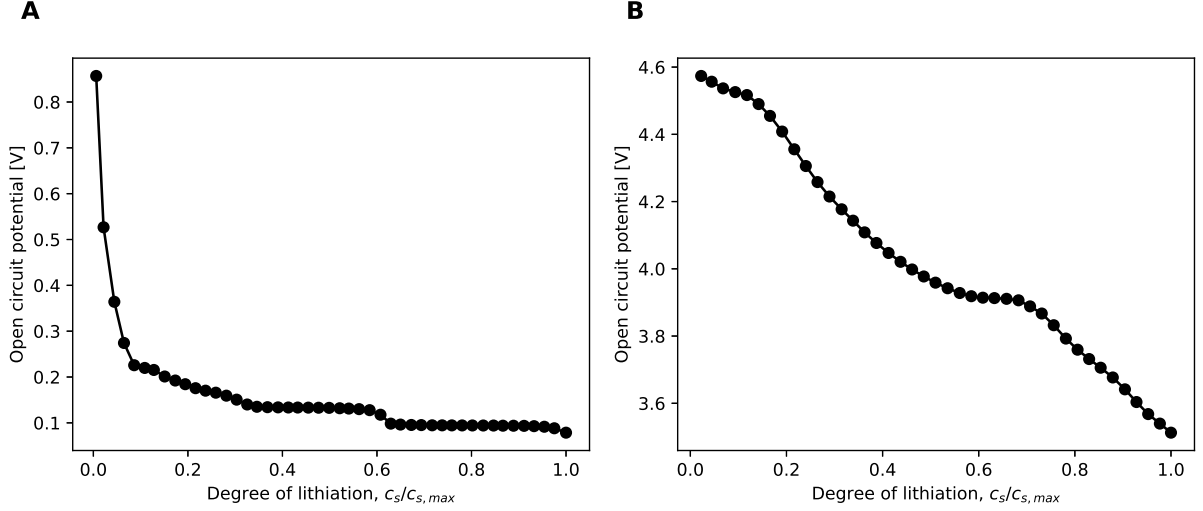


Figure 3.2: Open circuit potential curves of a) the anode, b) the cathode [16].

of 0.05 C for the anode and 0.1 C for the cathode. The functions, as measured by Ecker et al. [16] at 23°C, are shown in Figure 3.3.

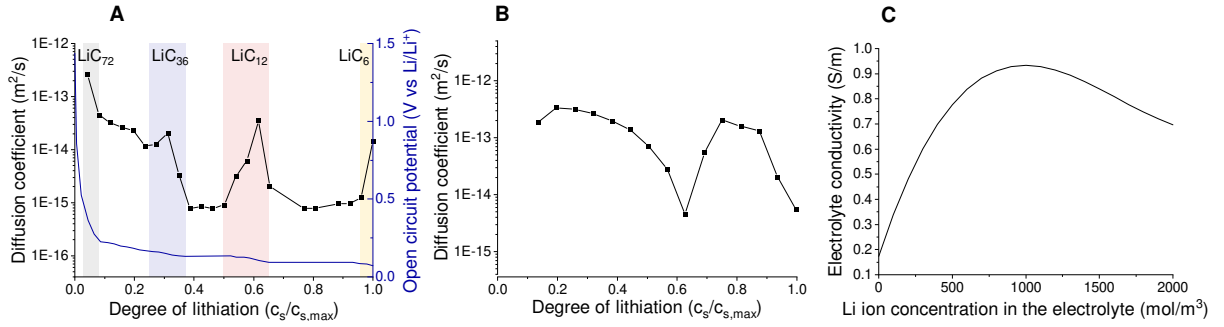


Figure 3.3: Transport properties. a) Diffusion coefficient in the anode, b) Diffusion coefficient in the cathode, c) Electrolyte conductivity. Re-plotted using data from [16]

The electrolyte conductivity is a polynomial as fitted to experimental data by [16]:

$$\kappa(c_e, T) = 2.667 \times 10^{-10} c_e^3 - 1.2983 \times 10^{-6} c_e^2 + 1.7917 \times 10^{-3} c_e + 0.1726 \quad (3.24)$$

Similarly to [141] and [16], it is assumed the electrolyte diffusivity can be computed from its conductivity using the Einstein relation:

$$D_e(c_e, T) = \frac{RT}{F^2 c_e} \kappa(c_e, T) \quad (3.25)$$

Einstein relation only holds for dilute solutions, where the ion-ion interactions can be

ignored. However, the value calculated by Ecker et al. [16] for 1 molar electrolyte at 23°C ($2.44 \times 10^{-10} \text{m}^2 \text{s}^{-1}$) is similar to that measured for the same electrolyte composition using NMR by Capiglia et al. ($2.25 \times 10^{-10} \text{m}^2 \text{s}^{-1}$) [30] and through a galvanostatic polarisation experiment by Nyman et al. ($3.7 \times 10^{-10} \text{m}^2 \text{s}^{-1}$) [210]. As such, it can be considered a good approximation.

Thermal model parameters The parameters for the thermal model used in Chapter 5 were taken from Taheri et al. [211] and are summarised in Table 3.2. Since thermal gradients are not considered in this part of the work, the contact resistances between cell components are ignored.

Table 3.2: Parameters used for the thermal model.

Symbol	Description	Value					Ref.
		Neg. CC	Anode	Separator	Cathode	Pos. CC	
δ	Thickness, μm	14.7	73.7	19	54.5	15.11	[16]
k	Thermal conductivity, $\text{W.m}^{-1}.\text{K}^{-1}$	398	1.04	0.34	1.58	238	[211]
ρ	Density, kg.m^{-3}	8933	1555	1017	2895	2702	[211]
C_p	Heat capacity, $\text{J.kg}^{-1}.\text{K}^{-1}$	385	1437	1978	1270	903	[211]
h_{conv}	Convective heat transfer coefficient, $\text{W.m}^{-2}.\text{K}^{-1}$	8					-

3.4.2 Key parameter uncertainties

As mentioned in the preceding section, many of the DFN model parameters are difficult to measure accurately and therefore carry significant uncertainties. Not all of these uncertainties are equally detrimental to the accuracy of the results. Li et al. [212] have shown

that in the DFN model, the simulated terminal voltage curves are most sensitive to the parameters that describe the transport in the solid electrodes and their ability to store charge, including the electrode thicknesses, particle sizes, active material fractions, reaction rate coefficients and solid phase diffusion coefficients. By comparison, the electrolyte properties have little effect on terminal voltage but do affect other internal states of the battery, such as local overpotential and current distribution. The parameter sensitivities of interest may vary depending on the phenomenon being studied. At high C-rates, when the reaction rates are fast, transport of species usually becomes the bottleneck. Hence, lithium plating propensity is particularly sensitive to the rate of lithium diffusion in the graphite particles. While the diffusion of lithium ions within the electrolyte is orders of magnitude faster, it does affect the current distribution along the thickness of the anode and is considered to be the main reason behind the tendency of lithium plating to be most severe at the anode/separator interface. The kinetics of the plating reaction are also important to the severity of plating. When studying plating at different temperatures as in this thesis, the uncertainties associated with the measurement of the activation energies of these processes need to be appreciated. The key parameter uncertainties that could affect the validity of the results of this work are discussed in the following.

Lithium diffusion in the solid electrodes. Compared to the electrochemical reactions and the ion transport through the electrolyte, solid-state diffusion of lithium is orders of magnitude slower and therefore often acts as a limiting factor in the context of fast charging. The solid phase diffusivities of the electrode materials affect the local overpotential and terminal voltage, and control the (de)intercalation reaction rate when the particle surfaces are either saturated or depleted, which impacts on the rates of competing reactions such as lithium plating. Among the techniques to measure the solid phase diffusion coefficients, galvanostatic intermittent titration technique (GITT) and EIS are the most common. GITT is a technique where a short current pulse is applied to a cell at its equilibrium state. Any voltage change after subtracting the iR drop is assumed to be due to the build-up of a solid phase concentration gradient, neglecting the electrolyte transport and reaction kinetic effects. The use of half cells allows for the independent measurement of the anode and cathode diffusivities. The following assumptions are typically made:

- the diffusion is one-dimensional and follows the Fickian model ($U \propto t^{1/2}$),
- the particles are spherical and of a uniform size (no size distribution),
- the particle surface area is the same as the effective surface area for intercalation,
- the current is uniformly distributed in the composite electrode.

The effective diffusion coefficient can then be calculated according to:

$$D_s = \left[\frac{4 \times r^2}{\pi \times t} \right] \times \left[\frac{\Delta E_s}{\Delta E_t - iR} \right]^2 \text{ when } t \ll \left(\frac{r^2}{D_s} \right), \quad (3.26)$$

where t [s] is the pulse duration, ΔE_s [V] is the change in the equilibrium potential and ΔE_t [V] is the voltage change during the current pulse. The measurement of these quantities is illustrated in Figure 3.4.

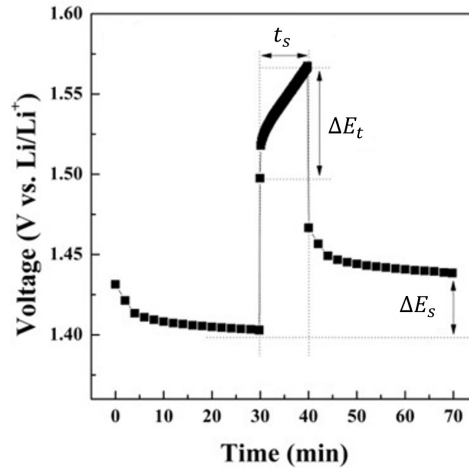


Figure 3.4: An example of the GITT diffusion coefficient measurement [213].

Undisputably, many of these assumptions are oversimplifications when applied to a porous Li-ion battery electrode. Firstly, the sluggish transport of Li⁺ ions in conjunction with the much faster transport of electrons makes the current distribution through the electrode inherently non-uniform. The particle shape assumption is also not realistic: while the particles can be nearly spherical for some materials (e.g. NMC), most common anodes are made of natural, flaky graphite, while both the anode and cathode particles often display size distributions. The applicability of the Fickian diffusion model has been questioned, particularly for the electrode materials that undergo phase transformations during the charge and/or discharge such as graphite and LFP [214]. The diffusion is also

not one-dimensional from the surface of the particle towards the centre. The path of diffusion depends on the crystal structure and orientation; for instance, graphite exhibits a diffusivity about 4-5 orders of magnitude higher along the graphene plane compared to along the grain boundaries [40]. For all these reasons, while GITT is the most common method to measure the solid phase diffusion coefficients of battery electrode materials, it can hardly be regarded as accurate. The measured values often require some adjustment to fit experimental voltage curves. Dees et al. [215] studied the diffusion coefficients of NCA obtained using GITT and by fitting an electrochemical model based on the concentrated solution porous electrode theory to experimental data. The GITT values were consistently lower than the fitted ones but both followed similar trends as a function of SOC, leading the authors to conclude that GITT was not accurate for model parameterisation but did capture the variation in diffusivity with the degree of lithiation. Geng et al. [216] performed a similar comparison, concluding that GITT could yield a value close to that which fit the DFN model. Differences in the experiment design and fitting procedures may have contributed to this disagreement.

Alternatively, the solid phase diffusion coefficients can be determined by fitting the EIS spectrum. The solid phase diffusion is typically represented by a Warburg diffusion element, which exhibits as a low frequency 'tail' in the Nyquist plot. The measurements can be carried out on half-cells or in full cells with reference electrodes to distinguish between the diffusion in the anode and the cathode. This method is also not free from ambiguity. Depending on the starting parameters, different values may be fitted for each element of the circuit and, consequently, for the diffusion coefficient. This is likely the reason for the lower popularity of EIS compared to GITT for determining diffusion coefficients. Additionally, EIS involves the application of a sinusoidal current or voltage signal and requires the cell to remain in the linear response region, enforcing low polarisation and therefore low current densities. These conditions are not representative of DC fast charging. Ecker et al. [16] arrived at significantly different values of the solid diffusion coefficients when using GITT and EIS. Deng et al. [217] has recently shown that both methods should yield consistent results, provided the experiments are designed such that only a thin surface layer of the electrode is taking part in the (de)intercalation. This was not the case in Ecker et al.'s [16] paper.

The low current densities required by both GITT and EIS may be a key culprit

behind the poor fit of the measured diffusion coefficients to experimental data noted by multiple researchers [24, 215]. The issues associated with this requirement are not the only ones that complicate the use of experimentally measured diffusion coefficients as model parameters. Solid phase diffusivity has been shown to increase with higher applied currents [218, 216], thinner electrodes or higher electrolyte diffusion coefficients [216] as well as to vary between the lithiation and delithiation [24]. Increased mechanical stress, influenced by both the particle size and C-rate, has also recently been reported to enhance diffusion rates [219]. These effects are likely to cause a particularly strong divergence between the measured and operational diffusion coefficients during fast charging, but are typically not accounted for in electrochemical models.

Lithium diffusion in the electrolyte According to the material safety data sheet provided by the manufacturer, the simulated cell uses a mixture of EC and ethymethyl carbonate (EMC) with LiPF_6 salt as the electrolyte. The composition percentages or the molarity of the salt are not reported. Since it was not possible to extract the electrolyte from the cell, Ecker et al. [16] measured the conductivity of LP50 by BASF, an electrolyte containing EC and EMC in equal proportions along with 1 M LiPF_6 , and correlated it to the diffusivity using the Einstein relation. Both properties are likely to differ to some extent from the mixture used by Kokam, which may also include unreported additives. Electrolyte properties have a relatively weak effect on the terminal voltage simulated in the DFN model [212, 220] but are critical in determining the current distribution through the depth of the electrodes, and therefore have a strong impact on the plating distribution. The model assumes the initial electrolyte concentration to be 1 M since LP50 displays the highest conductivity at this concentration [221], making it a likely configuration to be chosen by the cell manufacturer.

Intercalation and plating reaction kinetics The kinetics of both the (de)intercalation and plating reactions are described with Butler-Volmer equations in the model. Although it does not account for the complex phase separation phenomena exhibited by certain materials including LFP [214, 222] and graphite [223], the Butler-Volmer equation has repeatedly been shown to provide a useful and simple approximation, making it by far the most popular model of the intercalation reaction kinetics in the continuum level modelling literature. The parameterisation of the equation requires the measurement of the

exchange current density for both electrodes, usually done using EIS. As discussed above, fitting EIS spectra is non-trivial and likely to introduce a significant error. Ecker et al. [16] found it necessary to increase the experimentally measured exchange current density of the anode by an order of magnitude (from 7.05×10^{-5} to $5.39 \times 10^{-4} \text{A.cm}^{-2}$ at 50% SOC) to fit the measured discharge voltage curves. Smart et al. [139] found that the percentage of the solvent components in an LiPF_6 electrolyte could affect the anode exchange current density by a factor of 7, while having a negligible impact on the cathode exchange current density. This points to the strong influence of the SEI on the charge transfer kinetics at the anode. Since the half cells used by Ecker for the EIS measurements contained the LP50 electrolyte which could have had a different composition to that used in the commercial cells, while the formation procedure was probably different from that used by the manufacturer, the measured anode exchange current density is likely to need adjustment. Recognizing the limitations of the experimental measurement, the value fitted by Ecker et al. [209] was used as a starting point in this work but later re-fitted to measured charging voltage curves, which resulted in a value closer to the experimental one. The details of this adjustment are discussed in Chapter 5.

In this work, lithium plating is considered to depend on both the electrolyte concentration and temperature. There are few studies in the literature that attempted the measurement of the exchange current density of lithium plating [87, 90, 84], and fewer still that did so in a Li-ion system [81]. The reported values vary by at least four orders of magnitude. In light of these discrepancies, it was considered best in this work to use a value of the reaction rate constant as fitted by O’Kane et al. [141] to the voltage relaxation data reported by Campbell et al. [14] for the same cell model as used here. Since O’Kane et al. did not consider the temperature sensitivity of the plating reaction kinetics, the activation energy was taken from the only work known to the author that has measured it experimentally in a Li-ion cell [81]. Both the reaction rate coefficient and the activation energy are likely to exhibit large inaccuracies, the impacts of which are mitigated using sensitivity studies and/or experimental validation.

Activation energies The difficulty of measuring the temperature-dependent properties, such as reaction rate constants and diffusivities, inevitably leads to variations in the measured activation energies for these properties as well. The uncertainty associated with the measurement of the activation energy of solid phase diffusion is illustrated starkly in

the results reported for the positive electrode in Ecker et al. [16], the source of most parameters used in the current work. While the diffusivity measured using GITT at different temperatures exhibited an activation energy of 31.7 kJ.mol^{-1} , the same property measured with EIS had an activation energy of 80.6 kJ.mol^{-1} , amounting to an increase of about 150%. Ecker et al. [209] selected the latter value as it provided a better fit to their validation data. In contrast, the data collected in this work using the same cells suggests the lower measurement may be closer to the correct value. This is discussed in detail in Chapter 6. The activation energy of the plating reaction may carry an even higher uncertainty. To the best of the author’s knowledge, the only study that has attempted to quantify it in a Li-ion battery system was Ge et al. [81], who arrived at the value of 35 kJ.mol^{-1} using NMR in conjunction with DFN modelling. Ecker et al. [224] and Berliner et al. [225] also measured the activation energy of lithium plating, getting similar values of 65 and 70-75 kJ.mol^{-1} respectively, but both used Li/Li symmetrical cells. There is no clear reason to assume that the kinetics of plating are the same on lithium metal and lithiated graphite substrates. Consequently, the current work uses the value reported by Ge et al. [81], despite the high uncertainty stemming from the lack of comparable data reported elsewhere in the literature. The strong temperature sensitivity of the processes key to battery operation means that the uncertainties associated with the measurement of activation energies may translate to very significant errors in simulation results. This is particularly important when studying the effects of thermal heterogeneities, or when extrapolating the results of a model outside of the temperature bounds within which it was parameterised.

3.5 Formulation of charging profile boundary conditions

The model was implemented in the finite element simulation software COMSOL Multiphysics version 5.3a with a Batteries and Fuel Cells module. The software includes a default constant current charging/discharging node as well as a built-in CC-CV boundary condition, however the latter was found to cause numerical instabilities in many of the simulations, while other charging modes could not be implemented using the built-in functions. The cause of the instability is difficult to determine given the grey-box nature

of some of COMSOL's functionalities. As such, custom boundary conditions were formulated. COMSOL solves PDEs by approximating them with a weak formulation, i.e. each PDE is approximated by repeatedly integrating it over a very narrow range Ω over the domain in which it holds. Consider a function $g(x)$ that is defined by the gradient of the function $f(x)$, i.e.

$$g(x) = -\partial_x f(x) \quad (3.27)$$

The function $g(x)$ is in the form of a diffusion equation which can be applied to many physical systems (e.g. diffusion of particles, heat flux, movement of charge, etc.) The problem to solve is:

$$\partial_x g(x) = 0 \quad (3.28)$$

In a mathematical model, this corresponds to imposing a constraint on the system. The problem can be approximated through integration over a narrow range Ω :

$$\int_{\Omega} \partial_x g(x) dx = 0 \quad (3.29)$$

Equation 3.29 relaxes the original constraint, imposing that the average value of $\partial_x g(x)$ is zero over the range Ω rather than requiring that $\partial_x g(x)$ is zero at every point within the domain (hence the name "weak formulation"). Using a narrower range leads to a more accurate result. In the limit as Ω approaches zero, the original differential is recovered.

To sample the value of $\partial_x g(x)$ over the narrow range Ω , the integrand can be multiplied by a weight function $\tilde{f}(x)$ that is non-trivial only over a narrow range. The function $\tilde{f}(x)$ is known as a test function. The process is repeated in every narrow range in the domain over which the original PDE is defined, adjusting the test function so that it is non-trivial only in the proximity of that range. In finite element software, the narrow ranges correspond to the elements defined by the mesh, while the test functions are defined by polynomials that are non-trivial only for a small group of neighbouring elements. If a function $f(x)$ is a solution for a sufficient number of test functions $\tilde{f}(x)$ within the domain, it is likely to be a solution of the original PDE defined over that domain.

$$\int_a^b \partial_x g(x) \cdot \tilde{f}(x) = \int_a^b \partial_x^2 f(x) \cdot \tilde{f}(x) = 0 \quad (3.30)$$

In Equation 3.30, $\tilde{f}(x)$ represents a set of test functions over the domain rather than

a single function. To reduce the order of differentiation, Gaussian divergence theorem (integration by parts) is then employed:

$$g(x=b)\tilde{f}(x=b) - g(x=a)\tilde{f}(x=a) - \int_a^b g(x) \cdot \partial_x \tilde{f}(x) dx = 0 \quad (3.31)$$

Or, recalling the definition of $g(x)$ (Equation 3.27):

$$\partial_x f(x=b)\tilde{f}(x=b) - \partial_x f(x=a)\tilde{f}(x=a) - \int_a^b \partial_x f(x) \cdot \partial_x \tilde{f}(x) dx = 0 \quad (3.32)$$

Equations 3.31 and 3.32 introduce the first derivative of the test function. However, since the test function is merely a tool to obtain a solution, i.e. it is arbitrary as long as it is non-trivial only over a narrow range, an easily differentiable function can be chosen. Equation 3.32 is the final form of a boundary condition expressed in its weak form: the integral term relates the test function to the solution, while the first two terms on the left hand side specify the gradients at the boundaries of the domain.

Custom charging profiles, or other non-standard boundary conditions, can therefore be implemented using a weak contribution node. For example, a CP-CV charging profile can be implemented by applying the following weak contributions at the positive current collector:

$$\int \tilde{i}_{\text{app}} [(CV_{\text{on}} == 0) (i_{\text{app}}\phi_s - P_{\text{charge}}) + (CV_{\text{on}} == 1) (\phi_s - V_{\text{max}})] dV = 0 \quad (3.33)$$

$$\int i_{\text{app}} \tilde{\phi}_s dV = 0 \quad (3.34)$$

Where i_{app} is the applied current, P_{charge} is the constant power in the CP phase, V_{max} is the maximum voltage and CV_{on} is a binary variable that is false in the CP phase and true in the CV phase, after V_{max} has been reached. Here, Equation 3.34 relates the gradient of the potential (i.e. current, i_{app}) to the test function $\tilde{\phi}_s$, while Equation 3.33 specifies the value of the gradient at the positive current collector, effectively imposing a Neumann boundary condition.

Chapter 4

Experimental methods

This chapter describes the experimental methodology and equipment used to achieve the objectives of the thesis. The original contributions include the design of experiments, development of the titration gas chromatography as a method for quantifying Li plating on graphite, and the study of gas chromatography results for different levels of graphite lithiation. The rig used in the experiments that required thermal control with Peltier elements was based on a previous design developed by Dr Teddy Szemberg O'Connor, who kindly shared the basic design files. The main modifications implemented here included changing the design of the cell holder, upgrading the enclosure to a steel one for safety reasons, and replacing the cooling water system with a more powerful chiller-based system to enable lower temperature, high C-rate experiments. The Peltier control system and the accompanying software were developed by Gavin White and Dr Felix Russell. The DVA analysis was carried out using a modified version of the code developed by Dr Jingyi Chen and Dr Max Naylor-Marlow, which itself was based on the works of Birkel et al. [94] and Feng et al. [226]. The sequence and timing of steps used for titration gas chromatography experiments was defined and calibrated in collaboration with Dr Bethan Davies based on the dead lithium quantification technique for lithium metal batteries first reported in [227].

4.1 Introduction

Lithium plating in Li-ion batteries is notoriously challenging to identify, monitor or quantify. While the work presented in this thesis was originally model-led, the design of

experiments to validate and extend the findings of the simulations was at least as important as the modelling effort. Two sets of experiments were performed: one attempting to investigate the Li plating patterns in the presence of a thermal gradient over a single fast charge, the other focusing on longer-term degradation. The techniques used to study Li plating ranged from capacity fade trend observations, online methods such as ICA and DVA, through to post-mortem examination, SEM imaging and titration gas chromatography (TGC).

This chapter outlines the methods used, provides the reasoning behind the design of the experiments, and discusses some of the key limitations.

4.2 Cell selection

The cell selected for the experiments was a 7.5 Ah pouch cell manufactured by Kokam (model no. SLPB75106100). According to the manufacturer, the cell can be cycled between 2.7-4.2 V. A maximum C-rate of 1 C in the temperature range of 0 - 40°C is recommended for charging, while discharging is allowed with a C-rate of 5 C in the temperature range of -20 - 60°C. The manufacturer claims the anode is composed of carbon whereas the cathode is NMC in unspecified proportions; however, induced coupled plasma (ICP) spectroscopy experiments conducted by Ecker et al. [16] detected no manganese in the cathode, instead identifying the material as $\text{LiNi}_{0.4}\text{Co}_{0.6}\text{O}_2$. Manganese was also not found in the EDS spectra collected as part of this work. Despite the relatively low maximum charging C-rate, the cell can be considered a hybrid energy/power type, with electrode thicknesses of about 75 μm , an energy density of 173 Wh.kg^{-1} and a specified resistance of 3 $\text{m}\Omega$. The cell was selected for two reasons. Firstly, it had been thoroughly parameterised in two papers by Ecker et al. [16, 209]. With this major part of work already done, more effort could be directed towards answering the research questions. Secondly, the cell had proven to be manufactured to a high standard in previous tests conducted by the Electrochemical Science and Engineering Group [14, 130], with little deviation in performance between individual cells. The high manufacturing consistency was confirmed by measuring the capacity and resistance (using hybrid pulse power characterisation (HPPC)) of all cells used in this work prior to further testing.

4.3 Test protocols

Two sets of experiments were performed, each employing a number of techniques to investigate the distribution and severity of lithium plating:

1. **Single fast charge tests on two cells connected in parallel.** As discussed in Chapter 2, DVA is a popular technique used to detect, and often to attempt to quantify, reversible plating. To this end, a cell is subjected to a slow discharge soon after fast charging. The amount of stripped lithium is inferred from the charge throughput up until a characteristic voltage plateau is reached during the discharge. The method cannot provide any information about the spatial variation in Li plating patterns since any voltage measurement on the full cell conflates information from all its layers. The layered construction and thin casing of pouch cells can, however, be leveraged to design an experiment on a multi-cell system that approximates the behaviour of a single thicker cell during a fast charge, while enabling the measurement of multiple voltages corresponding to different sections of this "multi-cell" during the subsequent discharge. After fast charging, the cells can be disconnected to investigate the amount of Li stripped in each cell separately.

In the tests conducted here, two cells were individually discharged to 2.7 V at a rate of C/10 following initial characterisation. Subsequently, the cells were connected in parallel, held together with two 0.5 mm thick thermal interface pads (t-Global Technology, thermal conductivity of $12.5 \text{ W.m}^{-1}\text{K}^{-1}$), and placed in a test rig capable of independently controlling the temperature of the outer surface of each cell. Two channels of a Basytec 40 A XCTS cycler were used in parallel for each experiment. The tabs of the cells were clamped between two brass blocks with a block of polypropylene separating the tabs of each cell from each other. The bolts used to hold the assembly together were also made of polypropylene. Another brass block was bolted onto the two terminal blocks using steel bolts to ensure electrical connection which could be quickly removed (see Figure 4.1c)). The ring terminal of each cycler channel was clamped on opposite sides of the tab assembly. This was done to minimise the differences in the current distributions between the cells (other than those caused by the thermal gradient) by ensuring symmetrical connections between the channel terminals and the tabs of each cell, as well as to enable

fast disconnection. The two cells were selected from the set of 12 cells following initial characterisation in such a way as to ensure their capacities and resistances were as similar as possible. Perfect matching of these characteristics was, however, not possible. To avoid magnifying the differences in current distribution beyond what would be induced by the imposed thermal gradient, the cell with the higher measured resistance out of each pair was selected as the warmer cell during the experiment. The connected cells were allowed to balance for 24 hours with the same temperature setpoint (equal to the mean temperature T_{mean} for the test) applied to the outer face of each cell. For all tests, a gradient of 10°C was then maintained across the cell assembly during the fast charge, i.e. the outer surface of one cell was maintained at the temperature of $(T_{\text{mean}} + 5^{\circ}\text{C})$ while the outer surface of the other cell was maintained at $(T_{\text{mean}} - 5^{\circ}\text{C})$, with T_{mean} equal to 0°C or 25°C . After allowing an hour for thermal equilibration at the set thermal gradient, the cells were fast charged with a current of 30 A (2 C for the parallel module) up to 4.2 V, and then CV charged up to 80% rated SOC (12 Ah). The temperature setpoints were then changed to the same value T_{mean} for both cells and the cells were quickly disconnected by removing the interconnecting brass block. The setpoint change and disconnection took a maximum of 20 s. The rest period was continued up to a total of 6 minutes, which was determined to be sufficient for the thermistor placed between the cells to reach the new setpoint, indicating the cells were likely to have reached similar internal temperatures, too. While a longer rest time would normally be preferred to achieve thermal equilibration, the observation of the stripping minimum in the DVA spectrum of the subsequent discharge was important for these tests. A longer rest would have increased the probability of the plated lithium reintercalating before the discharge commenced. Following the rest, the cells were individually discharged with a current of 0.375 A (C/20) to 2.7 V. The collected discharge data was then analysed to investigate the presence and location of the stripping minimum in the DVA spectrum, as well as the SOC distribution between the cells.

2. Long-term cycling of individual cells with or without a thermal gradient.

Following initial characterisation, cells were installed in the test rig and the temperature was set to the desired setpoint. Tests involved cells being cycled with a

temperature of 0 or 25°C imposed on each cell surface, as well as tests with the same average temperature but with a constant thermal gradient of 5°C across the cell. In other words, in the uniform temperature experiments both cell surfaces were held at T_{mean} , while in the thermal gradient experiments one cell surface was held at $(T_{\text{mean}} - 2.5^\circ\text{C})$, while the other was held at $(T_{\text{mean}} + 2.5^\circ\text{C})$. These boundary conditions were maintained throughout the tests, except during the characterisation cycles when T_{mean} was always imposed on both cell surfaces. For most tests, the thermal gradient was not removed for the discharge steps as it was found a higher number of temperature setpoint changes increased the probability of errors due to the Peltier control software missing a message from the cycler software. The time available for the completion of the tests was not sufficient to resolve such synchronisation issues. This may also be considered more representative of real life conditions, as surface cooling leads to thermal gradients during both charge and discharge steps in battery packs. However, one cell was cycled at a temperature of 0°C with a 5°C thermal gradient which was maintained only during the fast charge steps and removed for the discharge steps as well as for the characterisation. The results, discussed in Chapter 6, were used to assess the influence of the presence of the thermal gradient during discharge on the rate of capacity fade. The cells tested with $T_{\text{mean}} = 0^\circ\text{C}$ were fast charged with a current of 15 A (2 C), which was increased to 30 A (4 C) the cells with $T_{\text{mean}} = 25^\circ\text{C}$ after it was found that the rate of capacity fade was low at 2 C with a reduced probability of Li plating due to the significantly better diffusion kinetics at higher temperatures. During cycling, all cells were discharged with a current of 7.5 A (1 C). The characterisation, performed every 10 cycles, consisted of a fast charge at the same C-rate as during cycling, followed by a 15 min rest and then a C/10 discharge at T_{mean} . The rest was introduced after the fast charge to investigate whether Li plating would lead to an increase in the resting voltage as reported by Tanim et al. [228]. The data collected was analysed for capacity and DVA/ICA trends. At the end of the cycling, most cells were disassembled for post-mortem analysis, including visual inspection, SEM, EDS and plated lithium quantification using TGC.

It should be clarified that the T_{mean} referred to above is only an approximation of the average cell temperature. Due to the heat generation within the cells and the high C-rates

involved, the real average temperature is expected to be slightly higher than the mean of the surface temperatures imposed during cycling. Such heating effect would have affected tests both with and without a thermal gradient. Similarly, the cells that had the same temperature imposed on both cell faces are referred to as "thermally uniform" for the remainder of this thesis for conciseness, despite the fact that their internal temperature would have been slightly higher than the controlled surface temperature.

4.4 Experimental setup

Both the single fast charge and cycling tests were conducted in the rig pictured in Figure 4.1. Diagrams of the experimental set up are shown in Figure 4.2. The rig used two Peltier elements on each side to independently control the temperature of both cell surfaces. Thermal interface pads (t-Global Technology) with a thickness of 1 mm and a thermal conductivity of $12.5 \text{ W.m}^{-1}\text{K}^{-1}$ were used to ensure good thermal contact at all interfaces between the cell, the copper heat transfer plates, the Peltier elements, and the cooling water blocks. The water used to remove the heat generated by the Peltier elements was pumped from a chiller, which controlled its temperature to 10°C . The rig was designed to hold the cells upright with the tabs facing up, to ensure safety in case of significant condensation or a water leak from the cooling system. The temperature on both faces of the cell was measured by six thermistors (one per Peltier element plus another in the middle of each cell side), with an additional thermocouple connected to the battery cycler in order to trigger channel shutdown if the temperature cut-off of 60°C was reached. Each Peltier element was connected to a thermal fuse rated to 73°C , which would cut off the current to that Peltier in case this temperature threshold was breached. The control software was programmed to shut down all the Peltier elements if the temperature reading of any of the thermistors exceeded 40°C . The temperature control software, developed by Gavin White and Felix Russell at the Electrochemical Science and Engineering Group, used a Proportional Integral Derivative (PID) controller with separate PID parameters for each of the Peltier elements, all estimated using the Ziegler-Nichols method. The test rig was enclosed in a steel container throughout the duration of the experiments to minimise the impact in the event of a short circuit, fire or cell rupture. The cooling water pipes as well as the cycler channel and Peltier element cables were fed through four holes

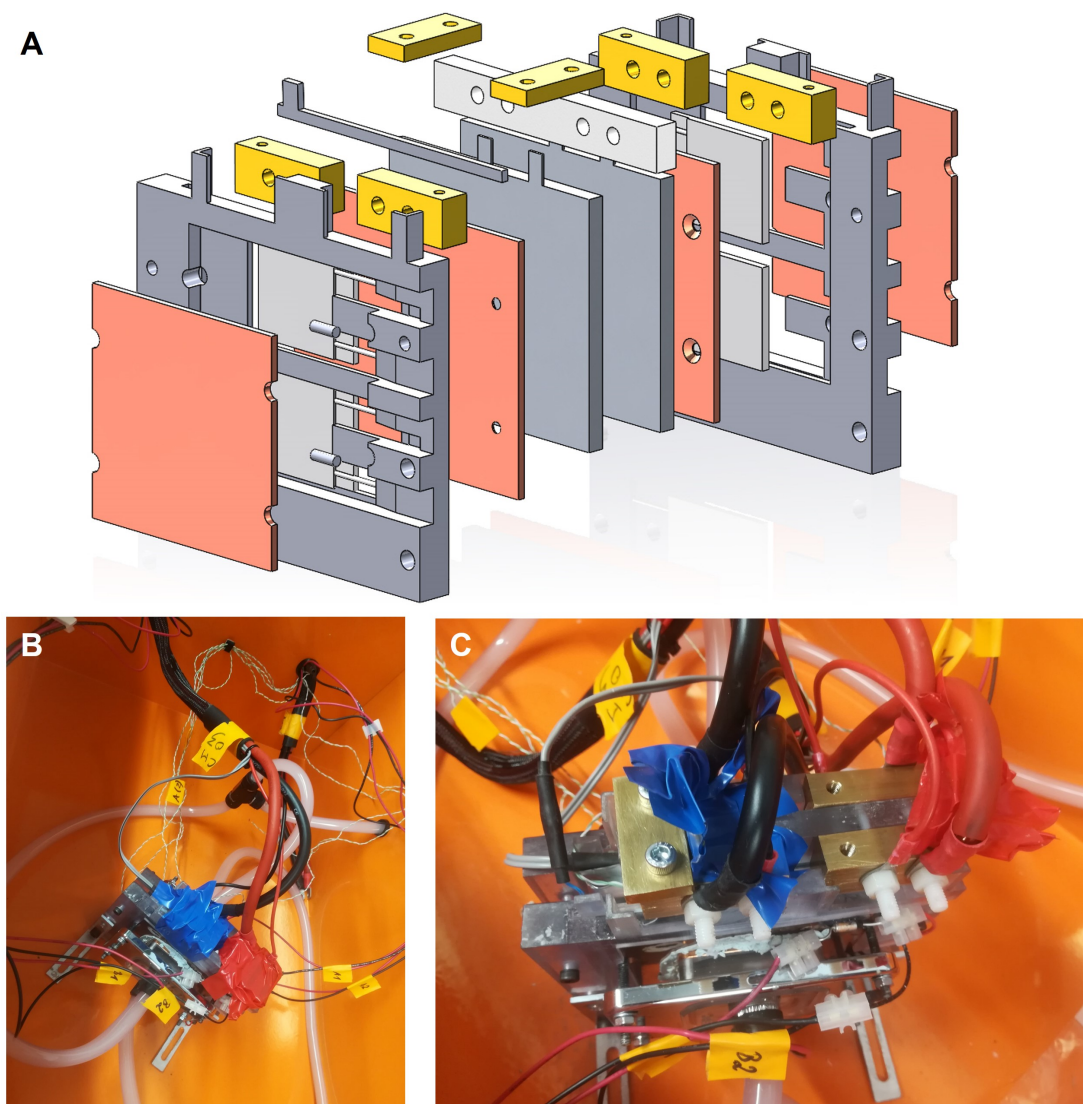


Figure 4.1: Test rig set up. a) Exploded CAD rendering showing the set up with two cells in parallel. Note the thermal interface pads, water blocks and pipes are omitted here. b) Photograph of the set up with a single cell installed, c) Photograph showing the removable connection between terminal blocks used for the single fast charge tests on two cells in parallel.

drilled in the walls of the container. Lights were installed within the container and a web camera was used to monitor the experiment. Prior to the commencement of experiments, the performance of the temperature control rig was verified on cells that were not being cycled. The temperature setpoints were changed repeatedly within a -9°C to 35°C range, and PID parameters were tuned to ensure the new setpoint was always reached within 20 s for a change of 5°C and within 30 s for a change of 10°C . It was also verified that 6 minutes was a sufficient amount of time for a thermistor placed between two temperature-

controlled cells to reach a new setpoint after a 10°C setpoint change. The same tests were then repeated with cells undergoing a 2C fast charge at 15 and 25°C and a 1C fast charge at 10°C. The ability of the rig to maintain a near-constant temperature difference between the outer surfaces of two cells fast charged in parallel was also verified.

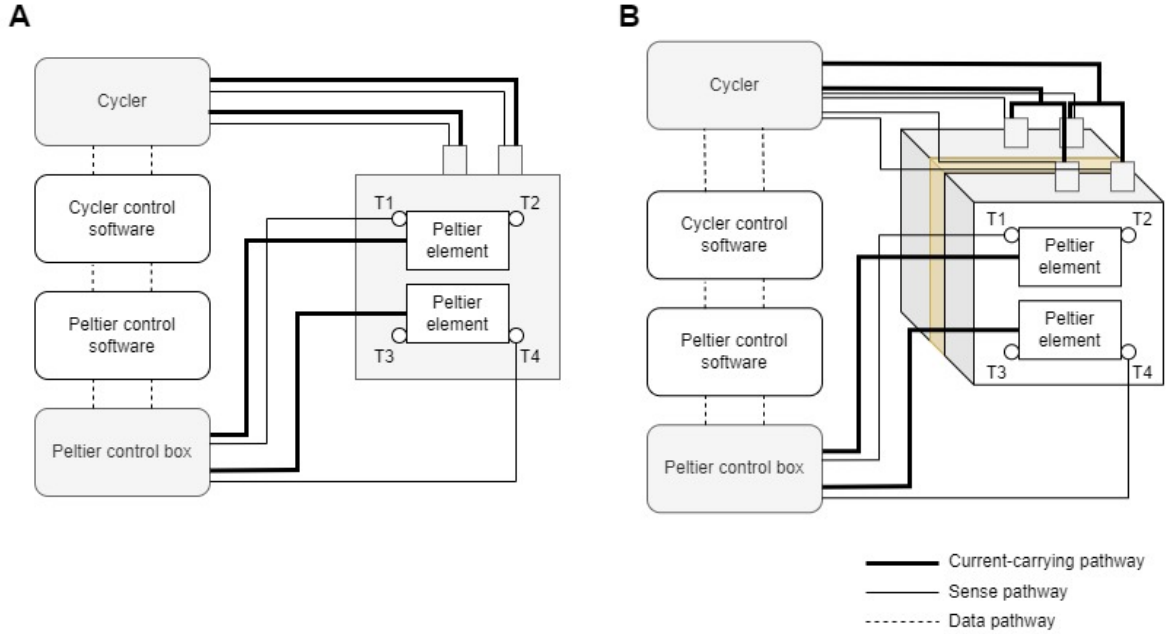


Figure 4.2: Diagrams of the experimental set up: a) single cell experiment, b) two-cell experiment. To maintain clarity, connections are shown only for the visible measurement and control points, and the cooling water circuit is omitted. T1-T5 are thermistor locations. Note an additional thermistor T0 (not shown) is located between the two cells, in the centre.

4.5 Differential Voltage and Incremental Capacity Analysis

In this work, DVA was used for two purposes: to attempt to identify Li stripping following a fast charge in the single cycle experiments on parallel-connected cells, and to monitor degradation modes and ageing heterogeneity during cycling experiments. For the latter, a C-rate of C/10 was deemed sufficiently low. For the single fast charge experiments, a lower C-rate of C/20 was used to improve the identifiability of the stripping voltage plateau.

The ICA and DVA curves were extracted from the slow discharge voltage curves. To ensure repeatability, the differentiation was carried out using the LEAN algorithm

[226]. Rather than smoothing the voltage data before differentiating, which can introduce significant variations depending on the employed smoothing and differentiation methods, this technique involves counting the instances of values in each voltage 'bucket'. In this work, a bucket range of 2 mV - double the precision of the cycler - was used. Assuming the discharge current and the data collection rate are constant and the voltage is strictly non-increasing over time, the voltage curve can be reconstructed from this histogram data. The value of $dQ.dV^{-1}$ is then computed by multiplying the number of values in each voltage bucket by the bucket range and dividing by the total number of voltage readings in the full discharge curve. The $dV.dQ^{-1}$ is calculated simply as the inverse of $dQ.dV^{-1}$.

The core code used for the differentiation using the LEAN algorithm and peak tracking was based on a code developed in MATLAB by Dr Jingyi Chen and Dr Max Naylor-Marlow [10, 130] and implemented in Python 3. Some smoothing of the resulting $dQ.dV^{-1}$ and $dV.dQ^{-1}$ curves was still required to produce interpretable results. This was achieved through convolution of the curves with a Gaussian probability distribution function with a mean value of 0 and a standard deviation of 3. These values were found to result in the features associated with the phase transitions in both electrodes being preserved, while rejecting measurement noise.

4.6 Electrode harvesting and testing

Following the longer term degradation tests, most cells were disassembled in an argon atmosphere in a glovebox. The cells were cut open using ceramic scissors. Then, the separator and the electrodes were carefully peeled off layer-by-layer and arranged in the same order as in the cell while keeping the cathodes and anodes separate.

When collecting electrode samples for SEM or for further testing, it is common practice to wash them in DMC or another organic solvent to remove any salt deposits. However, when studying the products of side reactions such as SEI or plated lithium, this process can easily affect the results. Somerville et al. [229] studied washed and unwashed electrodes and found that in most cases, washing at least partially dissolved the SEI. Metallic lithium also reacts with organic solvents. While Li-ion batteries use mixtures of similar solvents as electrolytes, the electrode harvesting and washing procedures can disturb the passivating

layers on the electrode, causing further reactions and leading to a side product profile that is different from the one present in the battery prior to disassembly. As such, the electrodes were not washed for any of the tests in this work. Salt deposits were found not to be extensive enough to interfere with SEM imaging, while half cells built using either washed or unwashed electrodes showed similar performance.

4.6.1 Coin cell preparation and testing

Both anode half cells and full cells were constructed using some of the harvested electrodes. First, one side of the electrodes was gently removed using N-Methyl-2-pyrrolidone (NMP) and a toothbrush. The electrodes were punched out using a manual punch. The two configurations used were:

- **Anode half cells** composed of lithium and anode disks, each with a 16 mm diameter, separated with a polypropylene (PP) separator (Celgard 2400, 25 μm thick, 18 mm dia.) and encased in a standard 2032 coin cell case. One 1 mm stainless steel spacer and a spring was used on the lithium (negative) side. 80 μL of 1 M LiPF_6 in 50:50 EC/EMC was added to each cell, with about a quarter of this amount dripped onto the graphite electrode prior to assembly and the rest dripped onto the separator.
- **Full cells** were built in the commercially available PAT-cell testing rigs manufactured by EL-Cell. The electrodes were punched out to a diameter of 18 mm as required by the rigs. Each cell contained an insulation sleeve which comprised of a 220 μm separator and a ring Li reference electrode, also supplied by EL-Cell. 100 μL of the same 1 M LiPF_6 in 50:50 EC/EMC electrolyte was added, with about a quarter dripped onto the anode, quarter onto the cathode and the rest onto the separator. The PAT-cell configuration not only ensured improved reproducibility compared to standard coin cells due to the well-controlled electrode alignment but also allowed for the measurement of the anode potential in a full cell.

All the constructed cells were rested for at least 12 hours before any cycling to allow time for wetting. The cells then underwent three 0.03 C charge/discharge cycles at room temperature to allow for the re-formation of the SEI. Another C/20 cycle followed, which was used to evaluate the quality of the coin cell. If the capacity of either charge or

discharge in this cycle deviated from the expected value by more than 3%, the cell was rejected. This qualification process had to be introduced due to the high variability in the quality of the cells. About 50% of all constructed cells met the criterion. This limits, but does not eliminate, the random error in the test results. Random error would ideally be eliminated with a large enough sample size; however, due to the limited time available for the experiments, only one cell per test condition was used in this work.

4.6.2 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

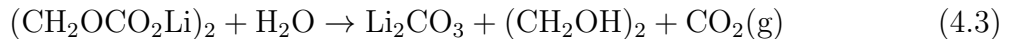
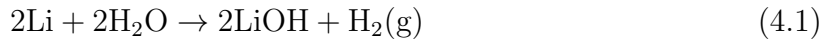
Following the cycling experiments, some electrode samples were imaged using SEM and/or EDS with a JEOL 6010LA microscope. Unless otherwise stated, an acceleration voltage of 10 kV and a spot size of 45 was used as these parameters were found to provide good quality images of the surface structure. For the EDS analysis, the spot size had to be increased to 60-65 to obtain sufficient signal. During the transfer from the glovebox to the microscope, the samples were exposed to air. While Li metal is not detectable using EDS, it reacts with oxygen in the air to form lithium oxide. The oxygen atoms in the lithium oxide can then be detected. It should be noted that EDS is not a surface characterisation technique as the X-ray interaction volume (the region of X-ray excitation) lies below the surface. As such, the results yield information about the composition of a surface layer, usually a few micrometers thick, rather than the surface itself. For SEM imaging, a secondary electron detector was used. The interaction volume for the secondary electrons varies with the acceleration voltage and the atomic number of the material but is significantly smaller than for X-rays, typically extending on the scale of nanometers below the surface [230].

4.7 Titration gas chromatography for quantifying lithium plating

One of the key challenges of this work was quantifying the differences in plating among different layers of a single cell. To this end, a technique of titration gas chromatography was validated and used for local plating quantification. The technique is based on a recent

paper by Fang et al. [227], where it was used to quantify dead lithium in cycled lithium metal cells. Additionally, some of the SEI species can be detected and quantified.

While the reactivity of lithium is often a challenge in post-mortem analysis, it can also be leveraged for the purposes of quantification. In the presence of water, lithium is known to react easily and violently to form lithium hydroxide and hydrogen. Rather than quantifying lithium directly, hydrogen can be quantified and used to infer the amount of lithium. Similarly, some of the organic SEI species are known to react with water, producing carbon dioxide. The following reactions can be expected to take place when anode material is titrated with water [231]:



In the above, the letter 'R' represents the rest of the molecule (a group of carbon and hydrogen atoms). In theory, the reaction of lithium hydride (LiH) with water can also produce hydrogen, skewing the results of lithium quantification. However, Fang et al. [227] confirmed there was no appreciable amount of LiH deposited on their lithium metal electrodes. Gong et al. [231] used heavy water (deuterium oxide, D_2O) instead of regular water in the titration to distinguish between the deuterium (hydrogen isotope with one neutron, as opposed to the more common isotope, protium, with no neutrons) in the D_2 form produced by the reaction of lithium and the deuterium hydride (DH) produced by the reaction of LiH. They too found the latter to only be present in negligible amounts. As such, it was assumed here that LiH was unlikely to contribute significantly to the amount of hydrogen detected.

While previous works used TGC to quantify the total lithium content on copper current collectors [227] or in silicon electrodes [232], here the aim is to quantify metallic lithium deposited on graphite electrodes. This introduces an additional complication as lithiated graphite is a strong reducing agent and, similarly to metallic lithium, produces hydrogen on contact with water. As such, the measured amount of hydrogen depends on

both the amount of the deposited metallic lithium and the amount of lithium remaining in the graphite particles. All batteries in this work were discharged at a low rate of C/10 and held at the minimum voltage of 2.7 V for 3 hours prior to disassembly. Lower voltages were not used due to the possibility of copper dissolution and/or SEI breakdown, which could affect the chemical composition of the electrode. Delithiated in this way, the graphite is likely to still contain some lithium, both due to the minimum voltage constraint and the possibility of some of the anode material having become electrically disconnected through fracture and pulverisation during cycling. Sacci et al. [233] studied the reactivity of graphite electrodes in a dry room environment using NMR and X-Ray Diffraction (XRD), finding that any phases containing more lithium than LiC_{24} were unstable even at the low humidity of <1%. It is reasonable to expect that in contact with liquid water, partially lithiated graphite would be at least as unstable as in a dry room environment. The magnitude of this contribution to the total amount of hydrogen detected was therefore also evaluated in Chapter 6.

4.7.1 Equipment and procedure

The samples to be tested were collected in an argon glovebox and sealed in 40 mL glass vials. The vials were a standard type used for headspace gas chromatography (GC) experiments, with airtight caps fitted with polypropylene septa. When introduced into the GC, the septa are pierced to draw the gas out of the vials. The vials were additionally wrapped in parafilm to further minimise any exchange between the contents and the air. For the tests involving calibration gas, a vial was first filled from a continuous supply and then 2 mL of the gas was transferred to another vial containing only argon using a syringe. For any tests performed on lithium or the graphite anode samples, 1-2 mL of deionised water was introduced into the vials using a syringe and mixed with the contents, before proceeding to the GC.

The GC experiments were conducted using the Multiple Gas Analyzer #5 (MG#5) system by SRI Instruments, equipped with a 2-metre, 1.8" dia HayeSep D separation column. HayeSep D is a porous polymer, particularly useful for separating light gases. The system was used in the headspace configuration, meaning the gas to be tested was sampled from vials rather than from a continuous supply. Argon was used as the carrier gas. Hydrogen was also supplied from an electrolyser for one of the detectors.

The gas species were identified using a thermal conductivity detector (TCD) and a flame ionization detector (FID) preceded by a methaniser. The TCD differentiates between gases that differ in thermal conductivity. Hydrogen has a very high thermal conductivity compared to other gases, hence it can be easily detected against the argon carrier. Carbon dioxide, however, has a thermal conductivity similar to that of argon and does not normally produce a peak in the spectra recorded by the TCD unless a different carrier gas is used, necessitating the use of another detector. FID is the most commonly used gas detection method in GC. As the analyte-containing carrier gas leaves the separation column and enters the FID, it is mixed with hydrogen. The mixture is then burned in air under a negative polarising voltage, ionising the carbon atoms in the analyte. A current is produced as the detector collects the ions, allowing for the detection and quantification of the carbon-containing species. While the FID can only detect organic compounds that burn in air, carbon dioxide can be converted into methane in a methaniser immediately before entering the detector. This solution is simple and cost-effective, making it very popular for carbon dioxide quantification in GC.

The separation of gas species present in the analyte relies on the differences in their molecular weight and affinity to the adsorbant. Hydrogen, being the lightest element, can flow through the column quickly and is often difficult to separate from air and other light gases. One solution would be to use a molecular sieve column in place of the HayeSep D. However, water easily clogs the adsorption sites of such columns and can only be desorbed at high temperatures. To include a high temperature desorption step between each test would unreasonably extend the duration of the experiments and could lead to inaccurate results if the water was not removed completely. Instead, the HayeSep D column was used in combination with a temperature of 40°C, the lowest possible with the equipment. The low temperature was found to be sufficient to separate hydrogen from other light gases, at the expense of an extended experiment duration.

The design of the GC procedure typically requires a trial and error approach. Unlike with some other analytical chemistry techniques, there is no standard response that a given species is expected to produce in the spectrum. Instead, the response depends on the system set-up, the environmental conditions, and the timing of the opening and closing of the valves that control the flow of the carrier gas and the analyte through the system. In this work, the procedure was optimised through tests on a calibration gas

containing hydrogen and carbon monoxide in an argon balance. The finalised headspace GC procedure, followed in all tests presented here, consisted of the following steps:

1. Start the carrier gas flow (0 s)
2. Open inlet valve [Relay E] to the vial (6 s) to allow the argon carrier gas to flow in. Wait for the pressure to build up in the vial.
3. Close the inlet valve [Relay E] (12 s).
4. Open the loading valve [Valve #3] between the vial and the sampling loop. The pressure gradient will then cause the mixture of the carrier gas and analyte to load onto the loop (18 s).
5. Close the loading valve [Valve #3] (24 s).
6. Open the valve between the sampling loop and the HayeSep D column [Valve #2] to allow the carrier gas and analyte mix to flow through (60 s).
7. Once the sample leaves the column, close Valve #2 and finish the experiment (600-1080 s).

The valve numbers in the procedure refer to the designations in the manufacturer's system diagram as provided with the equipment, shown in Figure 4.3.

The final step varied in length depending on the sample tested. It was found that while 10 minutes was enough for the calibration gas or the gases produced by the reactions between weighed lithium and water to exit the column, any samples that contained traces of electrolyte produced heavier organic gases which took a longer time to leave the column. While these gases were not of interest in this work, they would have interfered with the results of the following test if not allowed time to fully clear. The tests were controlled using open source software PeakSimple v4.53 from SRI Instruments.

Headspace GC is particularly useful when only a small amount of analyte gas is available which cannot be supplied continuously, as was the case for the experiments performed here. The key drawback is that repeated sampling from the same vial produces different results, as the analyte is diluted with the carrier gas every time it is sampled. As such, the discussion in this thesis is based on the results produced by the first instance of every test. While repeats were performed for many of the tests, this was only to increase the

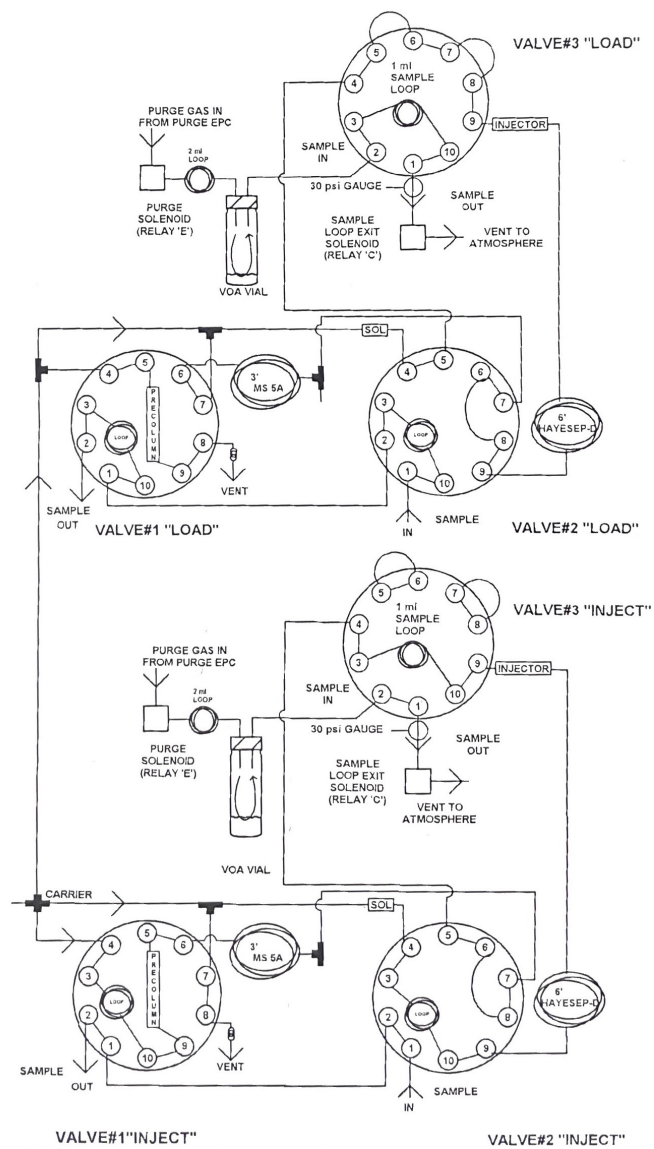


Figure 4.3: Diagram of the headspace GC system MG#5 as provided by the manufacturer, SRI Instruments.

confidence in the previous result by confirming that the ratio of the component species remained unchanged. At the start of every day of testing, the test was performed 5 times with pure argon before proceeding to any other samples. This was done to ensure that any trace contaminants from tests performed by other lab users, some of which involved heavy hydrocarbons which can linger in the column, were no longer present. Measurements conducted on multiple vials containing calibration gas of the same composition produced very similar results (see Figure 4.4), which suggests the experiment is highly repeatable where multiple samples of the same composition are available, provided the procedure outlined here is followed.

The collected data was analysed using a Python 3 code adapted from [234]. The code computes the areas of n individual peaks by fitting a superposition of n Gaussian distribution functions. Both symmetrical and skewed peaks can be fitted.

4.7.2 Validation against a calibration gas

The first set of tests was performed on a calibration gas containing 1 % hydrogen and 1% carbon monoxide in an argon balance. While carbon monoxide is not of interest to the subject of this thesis, its properties (weight and affinity to the adsorbant) were deemed sufficiently similar to carbon dioxide, which was not available for calibration. The identification of the carbon dioxide peak, based on both the observations from the calibration gas experiments and other information, is discussed and justified in Section 4.7.4.

There are two reasons for conducting validation experiments with a calibration gas before proceeding to sample testing. Firstly, it is necessary to establish how long hydrogen takes to travel through the column at the conditions used in the procedure, giving confidence of the hydrogen peak assignment in the later experiments. Calibration gas tests are also necessary to select the experimental conditions and to time the steps of the procedure appropriately to allow for both the observation of the hydrogen peak and for its separation from the peaks produced by other species, including water vapour, air, and hydrocarbons. It is at this point that the GC procedure is calibrated. While these tests could also be used to produce a calibration curve relating the amount of hydrogen to the detected peak area, in practice the collection of the gas using a syringe and its transfer to another vial can introduce large errors in the gas quantity. As such, this calibration was

not conducted, and tests on lithium titrated with deionised water were used to produce the calibration curves instead.

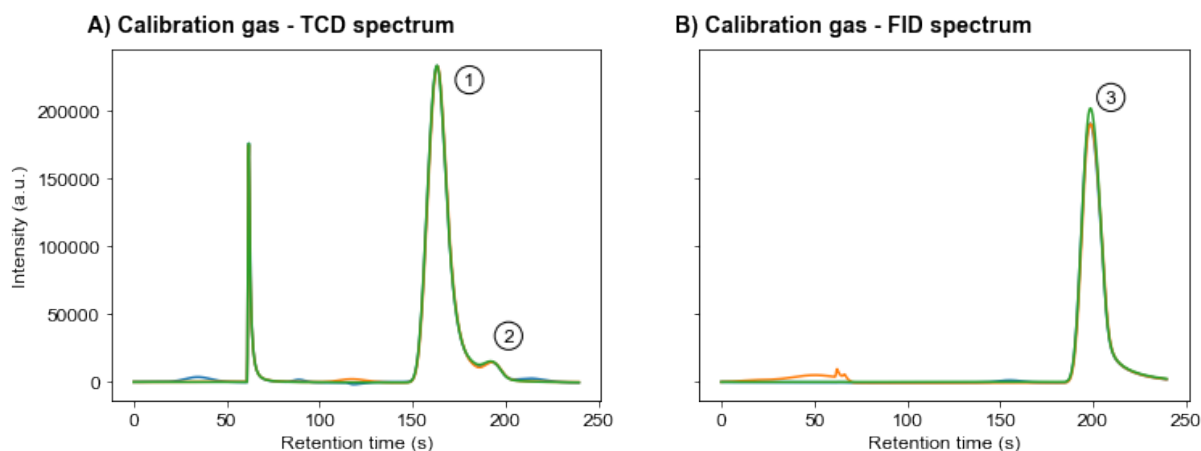


Figure 4.4: Example chromatographs obtained from the validation testing of the GC procedure with 3 different samples of the calibration gas containing 1% H_2 and 1% CO in Ar balance.

Figure 4.4 shows the chromatographs obtained for three samples of the H_2/CO calibration gas, using the finalised experimental procedure. It is clear that the hydrogen peak is consistently detected at about 160 s in the TCD spectrum, followed by the carbon monoxide peak appearing in the FID spectrum at 200 s. Two additional features are visible in the TCD spectrum: the first, non-Gaussian peak at 60 s is caused not by a chemical species, but by the instantaneous pressure change caused by the opening of Valve #2, which controls the flow of gas between the sampling loop and the column. The second Gaussian peak in the spectrum at 190 s partially overlaps with the larger hydrogen peak. The most likely origin of this peak is air and/or water vapour introduced into the vial during the injection of the calibration gas. The peak was present with varying intensities in nearly all samples tested. Further reasoning behind this peak assignment is discussed in Section 4.7.4. While this peak is much smaller compared to the hydrogen one in Figure 4.4, in the later experiments the hydrogen content was significantly lower while water was purposefully introduced into the vials, increasing the intensity of the air/water peak. Some overlap between the two peaks was found to be unavoidable with this experimental set-up. Nonetheless, the peaks could still be reliably separated and analysed individually by fitting a sum of Gaussian curves to the data.

4.7.3 Calibration against known amounts of lithium

To be used for quantification purposes, the TGC method was first calibrated with known amounts of lithium. The sample weights were limited to between 0.01 - 1.25 mg, both for safety reasons and to investigate the sensitivity of the technique. Some samples were obtained by cutting off small pieces from a solid lithium chip inside an argon glovebox with a scalpel. This method, while simple, was found to be prone to large measurement errors due to the small weights being measured. Smaller samples of lithium were therefore plated. Copper/lithium coin cells with a 1 M LiPF_6 in 50:50 EC/EMC electrolyte were constructed in order to do this. The lithium was plated onto copper using a current of 1 mA, equivalent to about $0.5 \text{ mA}\cdot\text{cm}^{-2}$. The cells were then disassembled in a glovebox and the copper with plated lithium was placed in vials along with the separator. The separator was included since it is common for the deposited lithium to grow into the separator pores, which makes it likely for metallic lithium residues to remain there following disassembly.

Both the weighed and plated lithium samples were then titrated with 1 mL of deionised water using a syringe in airtight 40 mL vials with flexible polypropylene caps. The samples were mounted onto the headspace sampling system of the GC and tested according to the procedure described in Section 4.7.1. Figure 4.5 shows the calibration curves obtained for both sets of samples.

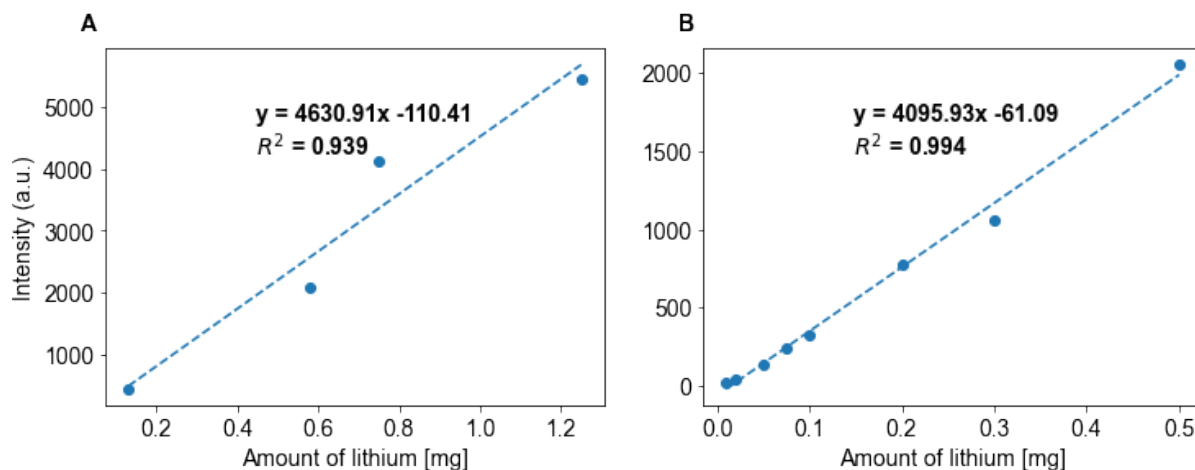


Figure 4.5: Calibration curves obtained from GC experiments on known amounts of lithium titrated with 1 mL of deionised water. a) Lithium weighed using an analytical laboratory scale with a resolution of 1×10^{-5} g. b) Lithium plated onto copper current collectors.

The curves verify that the amount of hydrogen detected is directly proportional to the amount of lithium in the vial. While there is a small difference in the slope between the

two sets of data, this can be attributed to the uncertainties involved in the measurements. For the weighed lithium, the sample weights ranged between 0.13 - 1.25 mg. Although the resolution of the scale was 1×10^{-5} g, measurements of such small amounts can be affected by factors such as movements of the operator, vibrations, or other lab users passing by in proximity to the glovebox. The random error is therefore significant. In case of the plated lithium, a 100% plating efficiency is assumed for the quantification. In reality, the efficiency is likely lower. Some of the lithium is consumed to form SEI due to the presence of the electrolyte in the coin cell. In light of these known errors, the slopes of the calibration curves are deemed sufficiently similar. Since the tests done using plated lithium produced more precise results and due to the high error associated with weighing small samples, the plated lithium calibration curve was used for lithium quantification in the later experiments. The root mean squared error (RMSE) of this calibration curve is 0.01 mg.

4.7.4 Identification of other peaks

While the hydrogen peak could be identified simply through comparison to the calibration gas, the assignment of other peaks required further analysis. The peaks are numbered in Figure 4.6, while Table 4.1 summarises the retention time ranges of each peak. The reasons for the assignments are discussed below.

Table 4.1: Retention time ranges of each peak identified in the GC spectra in various experiments. The peak numbers correspond to Figure 4.6

Peak no.	Species	Formula	Detector	Retention time range [s]	Notes
1	Hydrogen	H ₂	TCD	162-177	-
2	Air/water vapour	N ₂ /O ₂ /H ₂ O	TCD	189-205	A mixture of gases present in air
3	Carbon dioxide	CO ₂	FID	265-284	-
N/a	Carbon monoxide	CO	FID	194-206	Only present in the calibration gas
4 and 5	Hydrocarbons	Various possible	FID	504-525 and 955-990	Present in some of the electrolyte-contaminated samples

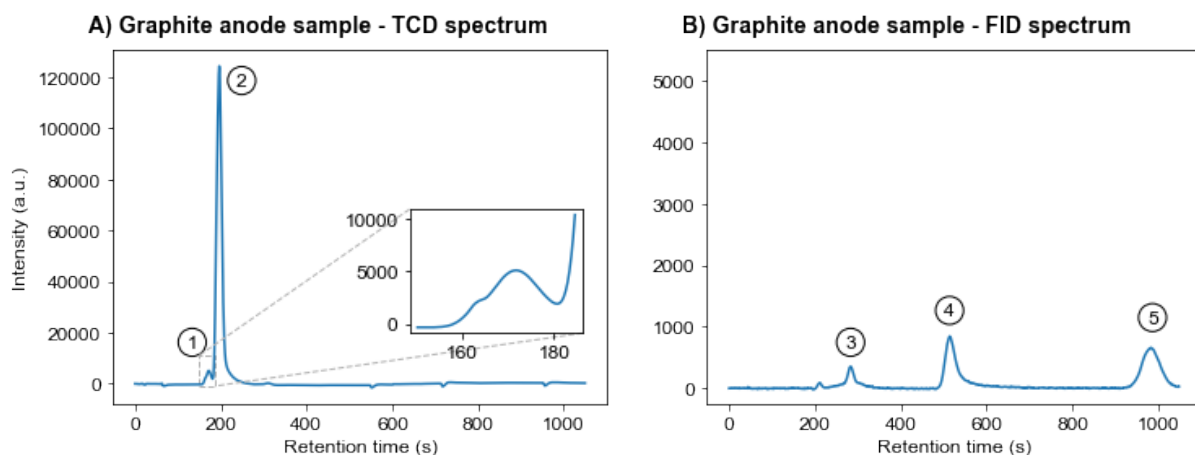


Figure 4.6: Example chromatographs collected from a sample of graphite titrated with 1 mL of deionised water. The identified peaks are highlighted. Note the different ranges of the y-axes: the signal obtained with the TCD was significantly stronger than with the FID.

Peak 2: Water vapour/air The large peak which appears in the TCD spectrum immediately after hydrogen is assumed to be produced by water vapour and a mix of light gases present in the air, such as oxygen and nitrogen. The GC setup used in this work could not separate these gases due to their similar physical properties. The peak appears in all tested samples, including control samples containing only deionised water or only air in argon balance. While in theory, the tested vials should not contain air, it is likely that some oxygen and/or nitrogen is present in the water injected into the vials. The peak area was not found to be proportional to the amount of material tested, but the peak was more pronounced for samples containing added water. Both oxygen and nitrogen react with lithium and could have some impact on the results. However, the consistent relationship between the mass of lithium samples tested and the area of the hydrogen peak suggests that the amount of lithium lost to these reactions is either insignificant compared to the amount reacting with the water, or that it is consistent between different samples. Either of these possibilities introduce an error in the amount of lithium quantified but are not likely to affect the relative amounts detected between different samples. As such, the method remains suitable for quantifying the distributions of lithium across the cell caused by fast charging with a thermal gradient.

Peak 3: Carbon dioxide The area of the peak produced by carbon dioxide should be directly proportional to the amount of SEI present in the sample, assuming the com-

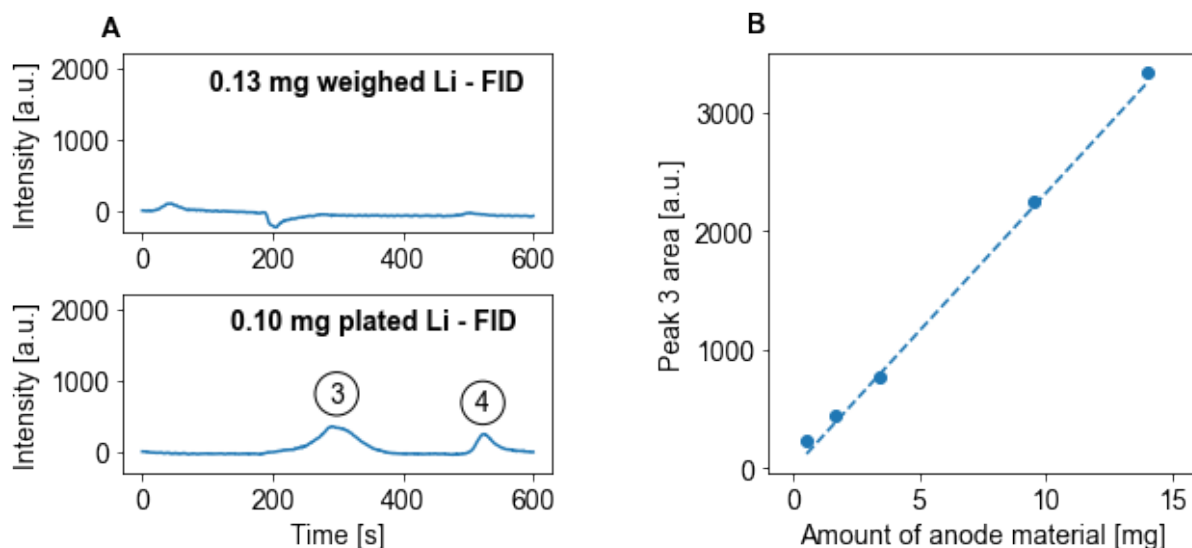


Figure 4.7: Identification of the carbon dioxide peak. a) Peak 3 is detected in plated lithium samples, but not in weighed lithium samples. This suggests the peak originates from the presence of SEI in the plated samples. b) The area of Peak 3 is roughly proportional to the mass of the aged anode material sampled from a single anode. Both these facts confirm the peak corresponds to the carbon dioxide produced in the reactions of SEI with water.

position of the SEI is similar for all samples. As discussed previously, carbon dioxide is unlikely to produce a noticeable response in the TCD spectrum as its thermal conductivity is similar to that of argon, however should be detected by the FID. Since in this work carbon dioxide is expected to be produced by the reactions between the SEI and water, the peak should appear for both the graphite anode and plated lithium samples (since both had been in contact with an electrolyte) but be absent in the weighed lithium spectra. The confirmation of this hypothesis is shown in Figure 4.7a). Carbon dioxide molecules are also lighter and smaller than most carbohydrate gases that are detected by the FID and so can be expected to appear as a relatively early peak in that spectrum. Finally, the amount of carbon dioxide detected should be roughly proportional to the weight of the plated lithium or graphite sample, assuming different areas of the electrode feature SEI of a similar composition and thickness. As shown in Figure 4.7b), the area of Peak 3 was indeed roughly proportional to the amount of graphite tested, with some deviations that can be explained by the small local variations in the SEI. Consequently, Peak 3 can be confidently assigned to carbon dioxide.

Peaks 4 and 5: Electrolyte carbohydrates The final two peaks observed in the FID spectra are both assigned to organic compounds of different molecular weights. The peaks appear only for those samples that had been in contact with an electrolyte. The composition of the electrolyte used in the Kokam cells is not known, except that the solvent is a mixture of EC and EMC and the salt is LiPF_6 . An EC/EMC solvent with 1 M LiPF_6 was also used in the copper/lithium coin cells. As such, Peak 4 could be produced by ethylene, while Peak 5 may be due to a heavier carbohydrate. The areas of both peaks are not proportional to the amount of material tested, but do seem to be affected by the length of time elapsed between the cell disassembly and the sample being enclosed in a vial. For the anodes that were stored in the glovebox for over 3 days, peaks 4 and 5 were not observed. Such long times likely allow for the electrolyte to completely evaporate. These peaks were not deemed of interest to this work, hence no further analysis was done to assign them to specific compounds.

Chapter 5

The effects of cell parameters and temperature on the performance of charging protocols

This chapter contains a modified form of the paper, 'The effects of temperature and cell parameters on Li-ion battery fast charging protocols: a model-driven investigation', published in the Journal of the Electrochemical Society [198].

5.1 Introduction

Charging protocol optimisation is one of the often proposed strategies to reduce or prevent lithium plating. Protocols such as boost charging, MCC-CV, pulse charging and others have been shown to extend the lifetime of fast charged cells in some circumstances but the underlying mechanisms are poorly understood and negative impacts on lifetime have also been reported [9]. The work presented in this chapter aims to answer the following research questions:

- What are the reasons for the discrepancies in the performance of similar charging protocols reported in different studies?
- What are the general rules for the selection of a fast charging protocol for a given cell and temperature conditions?

5.2 Literature review

During charging, the inclusion of a constant voltage stage once the maximum cell voltage is reached is often necessary to maximise the charged capacity, albeit at the cost of increasing the charging time. With higher C-rates in the constant current stage, the overpotential increases, resulting in an earlier switch to the constant voltage stage. It is for this reason that increasing the C-rate in CC-CV beyond a certain point, dependent on both the cell and the operating temperature, offers diminishing returns in terms of the charging speed. A number of both model-based and experimental studies have proposed to maximise the charging speed by increasing the current level at the beginning of the charging process, arguing that such a strategy would not cause accelerated degradation due to the lower risk of lithium plating at low SOC. As the SOC increases and the surface of the graphite anode becomes saturated, the current is reduced to allow for the concentration gradients to relax and the overpotential to decrease. The decaying current strategy has been shown to achieve significantly better lifetime compared to the fast charging methods where the current level is increased at higher SOC [166].

This work investigates a type of current decay protocol known as boost charging, first proposed by Notten et al. [161]. Boost charging begins with a short (typically 5-minute) boost period where the current, and often also the voltage, is raised beyond the manufacturer-recommended limit. This stage may consist of a single constant current step, a constant voltage step, or both. The boost stage is followed by a regular CC-CV stage with a reduced C-rate. The original study [161] reported no significant impacts on lifetime compared to standard CC-CV, even when the maximum voltage in the boost stage was raised to 4.4 V instead of the manufacturer-recommended 4.2 V. As much as 50% capacity could be charged in less than 10 minutes compared to about 17% with CC-CV, although the difference would be reduced for higher charged capacities since, in the last CV stage, boost charging follows a similar current profile to CC-CV. The consequences of this type of protocol may vary depending on the dominant degradation mechanism: while the risk of lithium plating is indeed reduced at low SOC, other mechanisms may be exacerbated by the boost stage. In particular, exceeding the manufacturer-recommended voltage may cause cathode and electrolyte instability, while the increased heat generation due to the combination of high current and high resistance at low SOC may accelerate SEI growth. Exceeding manufacturer's operational limits would also be considered an

abuse condition, usually voiding cell warranty and potentially compromising safety. A boost charge protocol is therefore unlikely to be pursued by OEMs unless accepted by the cell manufacturer and proven to be safe.

Keil and Jossen [162] investigated boost charging on two different cells. In contrast to the previous work, they found boost charging protocols caused accelerated degradation compared to CC-CV with the same charging time. All experiments in both studies were conducted at an ambient temperature of 25 °C. While Notten et al. [161] did not discuss the type of cells used beyond the form factor (one cylindrical and one prismatic model), Keil and Jossen [162] specified that both their batteries were power-optimised 18650-type cells. Kremzow-Tennie et al. [235] reported a 7% improvement in the charging speed with no significant change in the maximum cell temperature for boost charging compared to CC-CV but did not investigate the lifetime effects. A number of other works have assessed MCC-CV type protocols that resembled the decaying current profile of boost charging, reporting mixed effects on lifetime [159, 236, 194].

The charging protocols that aim to avoid negative anode potentials, often proposed in model-based studies [237, 238, 239], also feature decaying current profiles but avoid or limit the use of arbitrary parameters. They are, however, often difficult to parameterise, implement, or update as the cell ages. Some rely on the operando measurement of anode potential, which would be difficult to implement in commercial cells due to the complexity of integrating a reference electrode [238]. Adam et al. [239] cycled cells with various anode potential-tracking protocols designed using a P2D model of a fresh cell and confirmed plating in most of the cells after a number of cycles. Mai et al. [237] proposed charging protocols that approximated an anode potential-tracking protocol without requiring the anode potential measurement, but the study did not include experimental validation. The implementation of such protocols would still require thorough parameterisation.

The testing conditions in previous studies were often limited to room temperature. Additionally, many did not discuss the type of cell used in the experiments, and no clear reasons have been identified for the discrepancies between the findings of different papers. Both the temperature and cell type have substantial impacts on fast charging behaviour. High temperatures increase the rate of side reactions such as SEI layer growth and have traditionally been avoided. However, low temperatures reduce the rates of mass transport in both the electrode particles and the electrolyte, resulting in more severe concentration

gradients, higher overpotentials and increased risk of lithium plating during charging.

Waldmann et al. [240] investigated the balance between these two effects, finding the optimal charging temperature for their high power cell to be around 25 °C. This value should not be misinterpreted as the optimum for any cell or any charging C-rate. The interplay between the cell type, temperature, charging C-rate and Li plating and SEI growth rates was not studied in that work. The general trends can, however, be predicted based on the well-established Fickian diffusion model and knowledge of the effects of temperature on diffusion rates. Increasing the energy density of the cell is usually achieved by using thicker electrodes, resulting in an increase in the length of the ion diffusion pathway. The higher concentration gradients through the electrodes that consequently arise lead to an increase in overpotential, creating more favourable conditions for plating. As an effect, the optimum cell temperature for high energy cells shifts towards higher values as the diffusion rates have to be improved to offset the increase in the diffusion distance. Increasing the C-rate, on the other hand, results in more lithium ions arriving at the surface of the graphite particles per unit time. If the rate at which the ions are supplied is higher than the rate at which the intercalated lithium can diffuse from the surface further into the particles, then again severe concentration gradients can arise both in the solid particles and the electrolyte. This leads to an increase in overpotential and saturation of the intercalation sites, favouring plating. In this situation as well, the optimal temperature increases since improved diffusion rates are needed. Yang and Wang illustrated these effects using an electrochemical-thermal model [42]. and later claimed temperatures as high as 60°C to be optimal for 6 C charging [241, 242]. It should be highlighted, however, that these results were based on simulations which only accounted for Li plating and SEI layer growth and did not consider other degradation mechanisms. Not only are the models and parameters used to account for these phenomena associated with large uncertainties, but a risk of thermal runaway may exist for some cells at these temperatures. Finally, energy cells generally generate more heat than power cells for a given C-rate due to the increased transport losses. This temperature rise also needs to be taken into account when determining the optimal initial cell temperature for fast charging, ensuring that safety thresholds are not exceeded at any point during the charging process.

For any alternative charging protocol to become commercially viable, its effects on degradation mechanisms, and lithium plating in particular, must be understood for all

possible use cases. Despite this fact, many studies on fast charging optimisation make no attempt at testing or simulating their charging strategies on multiple cell types or in colder climates. This work aims to evaluate the effects of both the environmental conditions and cell parameters on the performance of boost charging protocols and provide insights on the underlying mechanisms. An electrochemical-thermal model with thermal coupling is used for this purpose. This enables the study of the trends in the Li plating behaviour for different cell types and temperatures. Section 5.3 outlines the modeling approach used in this study. A 1D Doyle-Fuller-Newman type model, with additional lithium plating/stripping equations, is coupled to a thermal model to simulate the temperature and lithium concentration profiles. Section 5.4 contains the discussion of the modeling results, including sensitivity studies to assess the effects of key cell parameters and temperature on the plating propensity of the fast charging protocols. Overall, the results show that the choice of charging protocol should depend on both the cell to be fast charged and the temperature, in particular on the solid and electrolyte phase diffusion timescales. This work highlights the need for more comprehensive evaluation of charging protocols, accounting for the full scale of expected charging conditions.

5.3 Model implementation

A 1D DFN model was used in this study. Since the details of the model have already been discussed in Chapter 3, only the key features and details of implementation are summarised here. The plating reaction was assumed to be fully reversible and symmetrical, with cathodic and anodic charge transfer coefficients $\alpha_c = \alpha_a = 0.5$. As explained in Chapter 3, there is little agreement between different studies on what the values of the charge transfer coefficients should be. As such, the value of 0.5 is chosen here both for convenience and agreement with a previous study conducted on the same cell, from which the kinetic parameters of plating were also taken [141]. Since fast charging in Li-ion cells is typically diffusion-limited [243], the modelling of the transport properties is particularly important. The diffusion was modelled as nonlinear, i.e. with lithium concentration-dependent diffusion coefficients in both electrodes. As discussed in Chapter 3, the diffusion coefficients are very difficult to measure accurately. However, while the value of the average diffusion coefficient for the same materials measured in different

studies can vary by orders of magnitude, the trends in values with respect to lithium concentration are relatively consistent. For instance, many researchers have reported reduced diffusion coefficients for graphite in the regions corresponding to the phase transitions (i.e. potential plateau regions) [16, 24]. This concentration-dependent behaviour was deemed important to simulate as it translates into hindered solid phase transport in the SOC ranges where phase transitions occur, which may affect plating propensity when different current profiles are applied. The electrolyte conductivity also varies with the local ionic concentration.

The physical processes taking place in a battery, including lithium plating, are sensitive to temperature. To account for these effects, the electrochemical model is coupled to a thermal model. The thermal model includes the copper and aluminium current collectors in addition to the active material components (electrodes and electrolyte) and the separator. The current collectors were included to account for their impact on the heat transfer between the cell and the surroundings, although this was found to be negligible in this study. The same architecture was later used to build the 2D multilayer model, where the inclusion of the current collectors was more important as the heat transfer was modelled in both in-plane and through-plane directions. The local irreversible heat generation rate, consisting of polarisation and ohmic heat contributions, is calculated at each node in the electrochemical model. The entropic heat generation is not taken into account since the polarisation heat is expected to dominate heat generation due to the high currents used during fast charging [244, 245]. The local heat generation rates computed in the electrochemical model are averaged over the entire cell and the average value is used as the heat source in the thermal model (see Figure 5.1). The semi-lumped thermal modeling approach is applied here since no significant thermal gradients are expected within the single cell layer simulated in the P2D electrochemical model. In reality, thermal gradients would develop due to the heterogeneous current distribution and the inherent differences in the thermal boundary conditions between cell layers. The effects of such gradients are outside the scope of this study but investigated in Chapter 6.

Natural convection is assumed to be the only heat loss mechanism, according to:

$$q_{\text{loss}} = h_{\text{conv}} A_{\text{surf}} (T_{\text{surf}} - T_{\text{amb}}) \quad (5.1)$$

where h_{conv} [$\text{W.m}^{-2}.\text{K}^{-1}$] is the convection coefficient, T_{surf} [K] is the surface tempera-

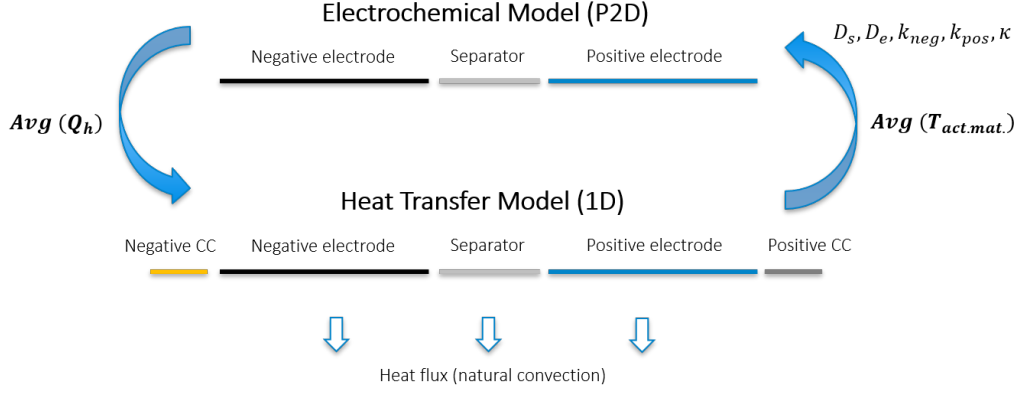


Figure 5.1: A diagram illustrating the coupling between the electrochemical and thermal models.

ture and T_{amb} [K] is the ambient temperature. Equation 5.1 is applied as the boundary condition on the external surfaces of the cell.

The local temperature computed in the thermal model is then averaged over the active material of the cell and the internal temperature in the electrochemical model is updated accordingly. Solid phase diffusion coefficients, electrolyte conductivity and charge transfer reaction rates vary with the temperature according to the general Arrhenius rate law. The electrolyte diffusivity is also temperature-dependent, since it is coupled to the conductivity via the Einstein relation, as explained in Chapter 3.

5.3.1 Implementation of charging protocols

The implementation of the charging protocols in the model is achieved through modifying the boundary condition at the positive current collector. Charging is always simulated up to 80% SOC based on the nominal cell capacity, in line with the standard for fast charging in the literature [14].

CC-CV The CC-CV charging is simulated with a rate of 2C, equivalent to 36.4 Am^{-2} for the cell in this study. The C-rate is defined with respect to the initial nominal capacity, i.e. a given C-rate corresponds to the same current density irrespective of the temperature and cell SOH. While 2C falls short of achieving the often quoted target of 10-15 minute recharge [246, 247, 238], it was deemed to be the maximum reasonable C-rate for this cell. The manufacturer's recommendation for maximum charging C-rate is 1C, while simulations have shown that increasing the C-rate beyond 2C did not significantly improve

the charging speed especially at lower temperatures due to the increased overpotential and early switch to the constant voltage charging mode.

Boost charging Boost charging is implemented with a 5-minute boost period, where the current is increased to I_{boost} and the voltage limit is increased to 4.3 V. The current is then lowered to I_{low} , followed by a constant voltage charge at the standard 4.2 V. The value of I_{boost} and I_{low} varies depending on the initial temperature, in order to match the charging time to that of 2 C CC-CV at that temperature. At each temperature, the CC-CV charging time to 80% SOC is first determined through simulation. Then, the boost charging C-rates are manually adjusted to match the same charging time. A value of I_{boost} is chosen such that immediately after the boost stage, the voltage relaxes sufficiently to allow for another, lower current CC stage of a duration at least twice as long as the boost stage, before the final voltage limit is reached. With decreasing temperatures, the boost stage current is reduced to ensure at least half of the time spent in the boost stage is at constant current. The values used at each temperature are given in Table 5.1.

5.3.2 Charging Parameters

All CC-CV charging is simulated at 2C, with a CV phase at the manufacturer-recommended 4.2 V until the SOC of 80% is reached. The limit of 80% SOC was selected for consistency with other studies [14, 248] as well as the current Society of Automotive Engineers (SAE) Level 3 fast charging standard [249]. Beyond this point, automotive-relevant cells usually approach the upper voltage cut-off during fast charging, causing the charging rate to slow down considerably. Boost charging parameters have to be adjusted at different temperatures to match the average charging rate of CC-CV at that temperature. In all cases, boost charging is allowed to reach a higher voltage in the low-SOC boost stage (4.3 V) than in the subsequent high SOC, low current stage (4.2 V).

Table 5.1: Parameters used to simulate CC-CV and boost charging.

Symbol	Description	Value		
		25°C	0°C	-15°C
I_{boost}	Current density in the CC boost stage of boost charging	$3.8 \times i_{1C}$	$3.2 \times i_{1C}$	$2.3 \times i_{1C}$
I_{low}	Current density in the low current stage of boost charging	$1.4 \times i_{1C}$	$1.4 \times i_{1C}$	$1.1 \times i_{1C}$
i_{1C}	1C electrode current density, $A.m^{-2}$	18.2		
I_{CC}	Current density in CC stage of CC-CV	$2 \times i_{1C}$		
V_{min}	Lower voltage limit, V	2.7		
V_{max}	Upper voltage limit for CC-CV and the final CV stage of boost charging, V	4.2		
V_{boost}	Raised upper voltage limit for the boost stage of boost charging, V	4.3		

5.4 Results & discussion

5.4.1 Effects of temperature on the current and voltage profiles

Figure 5.2 shows the current and voltage profiles for the two charging protocols at different temperatures. As the initial cell and ambient temperature drops, the overpotential increases due to the slower kinetics; consequently, the maximum voltage limits are reached sooner, making the constant current steps shorter and the constant voltage steps longer. This results in a reduced average charging speed. The 2C CC-CV charging protocol takes about 1700 s to charge the cell to 80% SOC at 25°C, but the charging time increases to 2100 s at 0°C and over 4000 s at -15°C.

Consequently, the boost charging protocol parameters are adjusted to match the charging speed of 2C CC-CV at each temperature. The current and voltage profiles of the two protocols become more similar as the temperature drops due to the earlier onset of the final constant voltage stage. The jagged appearance of some of these profiles, particularly in the constant voltage stages, arises from the nonlinear diffusion coefficients used in the model. Since the model is one-dimensional, it does not capture the lithiation heterogeneity across the cell layers or within individual electrodes, other than in the electrode thickness direction. Sharp rises or falls in the diffusion coefficient cause spikes in the overpotential, which manifest as abrupt changes in the current density in order to satisfy the constant voltage boundary condition. This behaviour is observed when the solid-phase diffusion is very slow compared to the reaction rate, i.e. at low temperatures or at high C-rates,

and in the lithiation regions where abrupt spikes in Li diffusivity is observed. For the cell studied here such spikes are observed around 40% SOC for the cathode as well as 60% and 95-100% SOC for the anode. The overpotential spikes are particularly pronounced once the graphite surface is saturated during fast charging due to the coupling between the severely reduced intercalation rate, increased local electrolyte concentration and increased electrolyte potential. In a real cell, the degree of lithiation among individual electrode particles is far more heterogeneous, resulting in a smooth current and voltage profile. This shortcoming is unlikely to affect the predicted relative performance of the charging protocols, particularly as the current fluctuations are mostly seen in the high SOC ranges after the boost stage, when the current density becomes similar between CC-CV and boost charging.

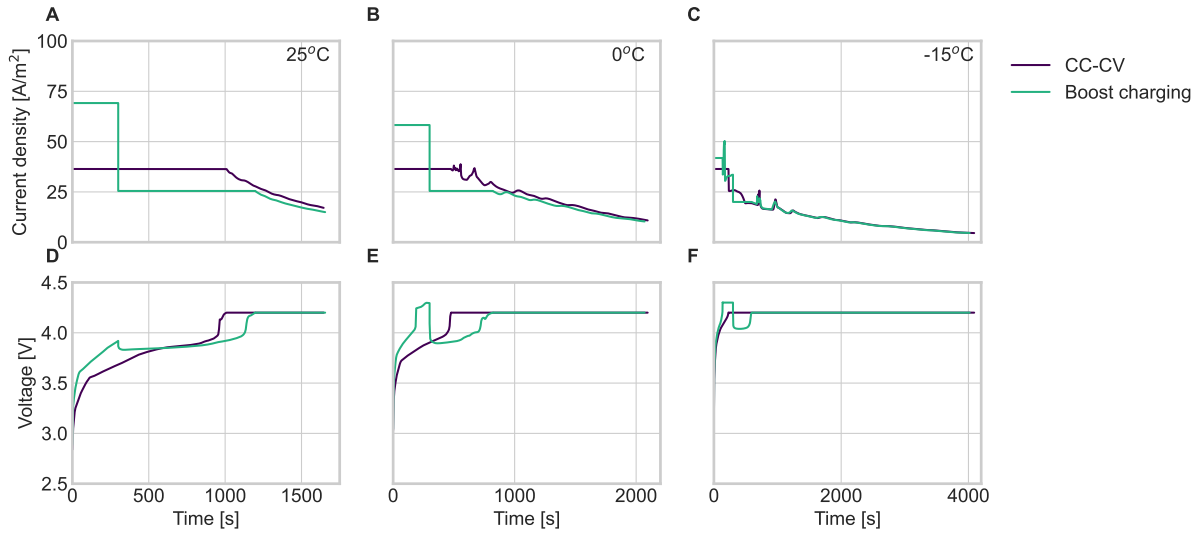


Figure 5.2: Model-predicted current profiles of the charging protocols at the initial charging temperature of a) 25°C, b) 0°C, c) -15°C. Voltage profiles at the initial charging temperature of d) 25°C, b) 0°C, c) -15°C.

Figure 5.3 shows the evolution of the total amount of plated lithium, local concentration of metallic lithium at the anode/separator and the anode/current collector interfaces, and cell temperature for the two charging protocols starting from different initial temperatures. When the cell is charged from 25°C, the advantages of boost charging over CC-CV are clearly noticeable. The onset of plating is delayed and the rate of plating is reduced, leading to a reduction in the total plating amount of 40% compared to CC-CV at the end of charge. Counter-intuitively, boost charging also reduces the maximum temperature rise. While boost charging initially subjects the cell to a high C-rate, increasing the heat generation, the C-rate in the later stages of charging is lower than that of CC-CV, leading

to a reduced heat generation at this stage and a lower temperature rise overall. However, the relative performance of the protocols changes as the initial temperature drops. When charging from 0°C, the overall plating propensity becomes comparable between the two protocols. While boost charging does slightly reduce the amount of plated lithium at the end of charge, the onset of plating is triggered about 300 s earlier and the plating rate is initially significantly higher compared to CC-CV.

In this work, lithium plating is assumed to be fully reversible; if in reality some proportion of lithium is plated irreversibly, the difference between the plated amount at the end-of-charge for both protocols would reduce. The plating distribution varies significantly: boost charging leads to more heterogeneous plating along the anode depth compared to CC-CV, with the concentration of lithium near the separator being twice as high as that near the current collector at the end of charge. The temperature rise is comparable for both protocols: while the maximum cell temperature reached during charging is slightly higher for CC-CV, the boost charged cell spends a longer time at elevated temperatures due to the high heat generation rate during the boost stage. When the initial temperature is reduced further to -15°C, CC-CV leads to slightly less plating overall and substantially more uniform plating distribution than boost charging. While the difference in the total amount plated between the two protocols is marginal, the local plating rate at the anode/separator interface is significantly higher for boost charging than for CC-CV. This localised plating during boost charging may increase the probability of dendritic growth and/or pore clogging [250, 83]. The temperature profiles for both protocols converge except for the first 300 s, where the boost stage of the boost charging protocol causes an increased heat generation rate.

A clear trend emerges from the data shown in Figure 5.3: while boost charging is beneficial compared to CC-CV in terms of both limiting the plating propensity and temperature rise for this cell when fast charged from room temperature, the advantages reduce with a drop in the initial cell temperature. Finally, at -15°C, CC-CV slightly outperforms boost charging at limiting the overall plating amount, while also leading to significantly more uniform plating across the anode thickness. The relatively small difference in the overall plating amount between these two protocols at low temperatures is to be expected: since the 4.2 V voltage limit is reached sooner, the current and voltage profiles of both protocols become similar over most of the SOC range, with differences only at low SOC.

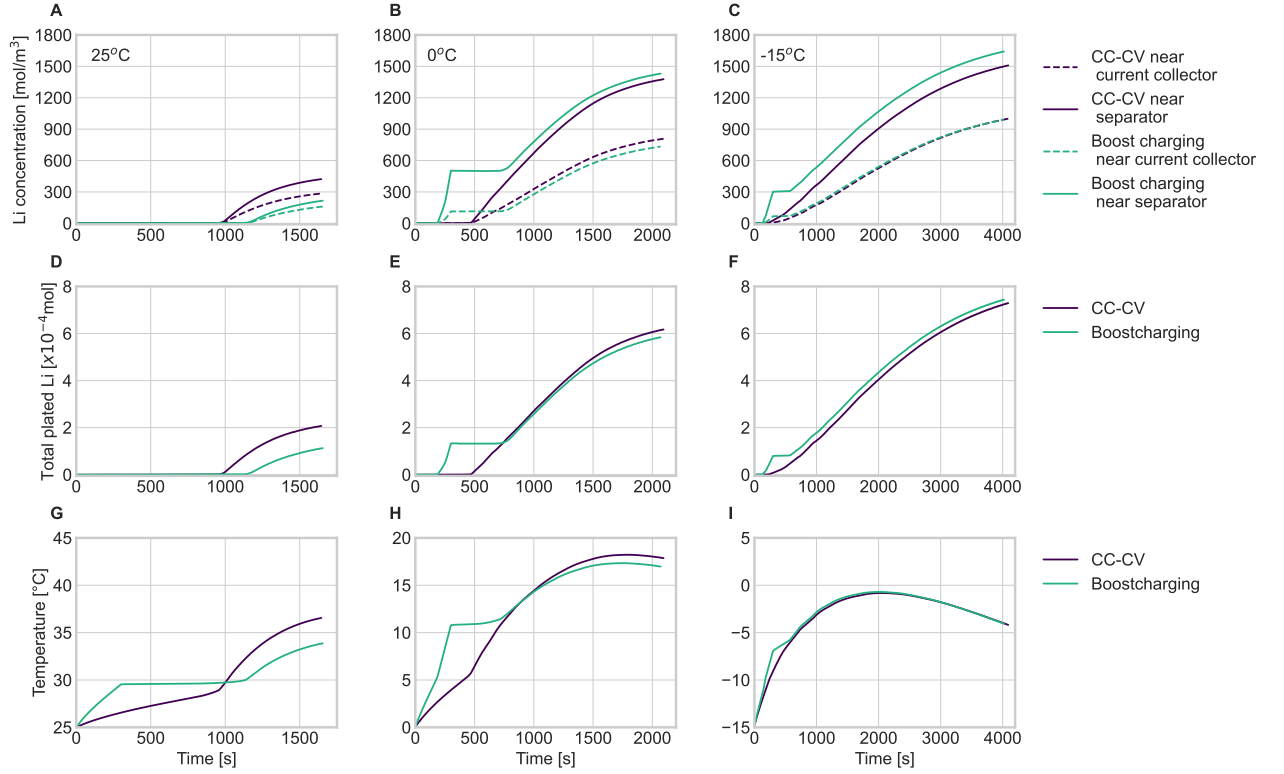


Figure 5.3: Local concentration of plated lithium at the anode/seperator and anode/current collector interfaces at different temperatures (a-c), corresponding total amounts of plated lithium (d-f) and cell temperature profiles (g-i). All profiles are model-predicted.

5.4.2 Ion transport limitations

Plating heterogeneity across the anode thickness gives an indication of the underlying mass transport limitations. Gradients in plated lithium concentration along the anode depth, with substantially higher amounts of plating near the current collector-separator interface, have previously been predicted through modelling [42] and observed using in-situ XRD [223, 251]. While the ion diffusivity through the electrolyte in Li-ion cells is several (2-6) orders of magnitude higher than in the solid electrode materials, the length scale is considerably larger, with the anode thickness typically being an order of magnitude higher than the particle radius. The timescale of diffusion is directly proportional to the square of the diffusion length scale and inversely proportional to the diffusion coefficient - as such, increasing the length scale by a factor of 10 has a similar effect as reducing the diffusion coefficient by a factor of 100. Consequently, the ion transport can in some cases limit cell performance, while the build-up of concentration gradients in the electrolyte often results in non-uniform lithiation. It is well known that lithium plating is most likely to

start at the anode/separator interface before propagating further into the anode [42, 12]. This is primarily due to the limited rates of ion transport in the electrolyte: since an ion concentration gradient arises through the anode depth, there are more ions available for reaction near the separator than near the current collector. The electrochemical model used in this work accounts for the concentration dependence of both the intercalation and the plating reactions. As a consequence, the increased ion concentration near the separator results in an increased rate of lithiation and, once the local anode potential drops below 0 V vs. Li/Li^+ , an increased rate of plating. Ion concentration is also coupled to the electrolyte potential, which in turn contributes to the anode potential.

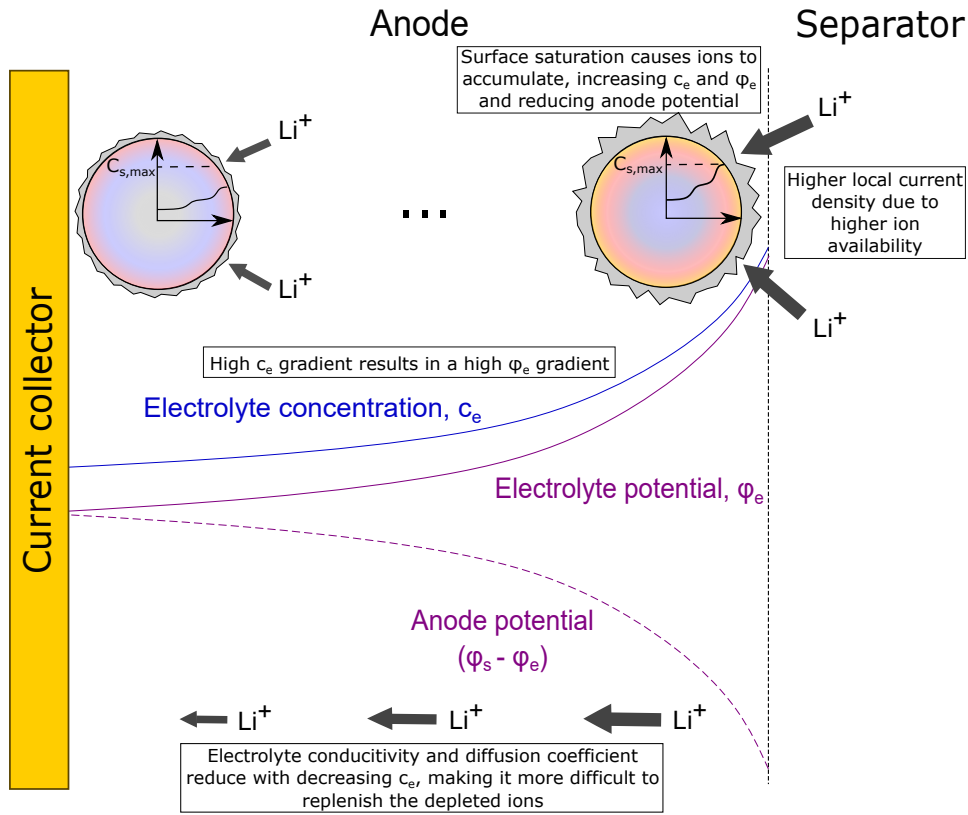


Figure 5.4: A diagrammatic representation of the effects of the transport limitations on the local plating propensity.

Careful inspection of Equation 3.6, which defines the electrolyte potential in the DFN model, reveals a number of effects that the ion concentration has on the electrolyte potential as illustrated in Figure 5.4. First, a higher gradient in the electrolyte concentration should result in a higher gradient in the electrolyte potential. Second, the local reaction current density j , composed of both the intercalation and the plating current densities, increases with increased electrolyte concentration due to the higher availability of the lithium ions for the reactions. A higher reaction current density then leads to an increase

in the local electrolyte potential. Finally, the electrolyte conductivity κ is concentration-dependent and highest at around 1 M (see Figure 3.3). At the point of maximum electrolyte depletion, the local electrolyte concentration for the boost charging protocol at -15°C falls to as little as 0.35 M near the current collector (see Figure 5.5b), reducing the conductivity by about 30%. A reduction in conductivity leads to an increase in the electrolyte potential. The combined result of these concentration-driven effects is that severe gradients in the electrolyte concentration across the anode lead to an increase in the electrolyte potential, with the highest electrolyte potential observed near the separator and lowest near the current collector. The overpotential for the plating reaction is defined as $\eta_{\text{Li}} = \phi_s - \phi_e - U_{\text{Li}}$, which reduces to $\phi_s - \phi_e$ (also known as the anode potential) if the potential is defined against the Li/Li^+ couple. Consequently, an increased electrolyte potential results in a reduced anode potential and increases the driving force for plating, particularly near the separator.

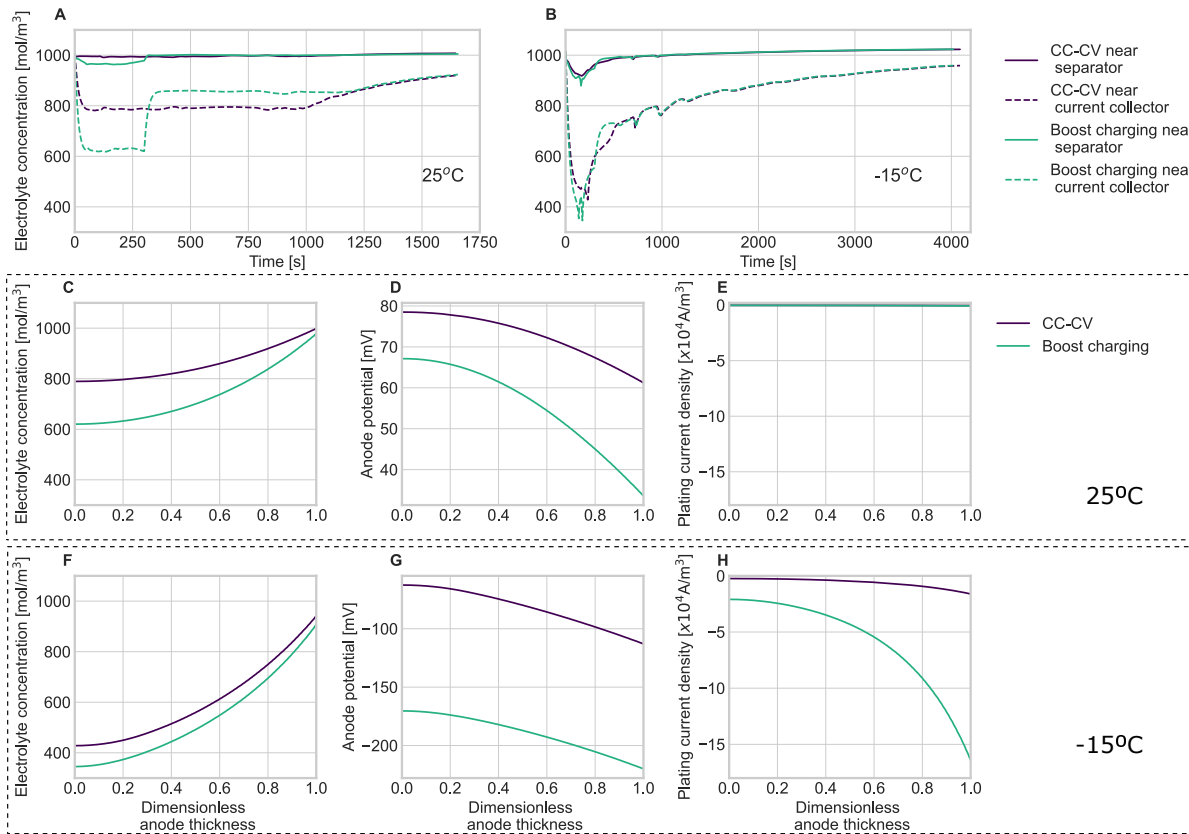


Figure 5.5: Effects of the ion transport limitations on the plating propensity at 25°C and -15°C . Electrolyte concentration at the anode/separator and anode/current collector interfaces at a) 25°C and b) -15°C . Local electrolyte concentration, anode potential and plating current density profiles along the anode depth at the time of maximum electrolyte depletion at 25°C ($t = 290$ s) (c-e) and -15°C ($t = 185$ s) (f-h).

Figure 5.5 demonstrates the effects of the ion concentration gradients on the anode potential and local plating current density through the anode depth. The variations in the current profiles among the charging protocols lead to a variation in the severity of the concentration gradients they induce: since the peak current of boost charging is higher than the flat maximum current of CC-CV, boost charging may lead to increased concentration gradients if the rate of ion transport through the electrolyte is not fast enough to accommodate the increased current. As can be seen in Figure 5.5a-b, boost charging drives higher ion concentration gradients at low SOC's at both 25°C and -15°C. However, for the ion concentration gradients to affect the lithium plating rates, the thermodynamic condition of the anode potential falling below 0 V vs Li/Li⁺ must be met.

Figure 5.5c-e shows the maximum ion concentration gradients induced by both protocols along with the corresponding anode potential gradients and lithium plating current densities for charging from 25°C. While the boost stage of boost charging does induce a higher concentration and anode potential gradient than CC-CV, this does not translate to increased plating rates since the thermodynamic condition for plating is not met at low SOC's at this temperature. However, the reduced diffusion rates and increased overpotential at lower temperatures enable plating at much lower SOC's. Figure 5.5f-h demonstrates the effects of the ion concentration and potential gradients on the local plating current density at -15°C. The high boost current of boost charging once again induces more severe ion concentration and anode potential gradients than CC-CV. The anode potential, affected by both the ion concentration and the total current density, is also about 150 mV lower throughout the anode compared to CC-CV. Crucially, at this temperature, the anode potential drops below 0 V vs Li/Li⁺ already during the boost stage, satisfying the thermodynamic condition for plating. The effects of the increased ion concentration gradient and the lower anode potential combine to induce increased plating current densities compared to CC-CV throughout the anode as shown in Figure 5.5h. A strong gradient in the plating current density can be observed as well: the low anode potential and high ion availability cause the plating rate near the separator to reach values eight times higher than near the current collector. This strong plating heterogeneity along the anode depth would be concerning, as Li dendrites forming at the anode/separator interface could grow through the separator and eventually reach the cathode, causing an internal short circuit. The ion concentration gradients reduce after the boost stage and match those caused by

CC-CV as shown in Figure 5.5b. However, since the anode potential remains negative, the lithium plated during the boost stage is not stripped and the concentration of the plated lithium remains heterogeneous across the anode.

5.4.3 Solid transport limitations

The division of the total current between the plating and intercalation reactions is affected not only by the ion transport limitations, but also by the availability of intercalation sites. If the surface of a graphite particle becomes saturated and the diffusion rate of the intercalated lithium through the particle is insufficient, lithium-ions will accumulate at the surface. This increases both the local ion concentration and electrolyte potential, making the anode potential more likely to drop below 0 V vs Li/Li⁺ and thus enabling, or accelerating, the plating reaction. To compare the solid phase concentration gradients between the charging protocols, the surface-to-center concentration ratio can be defined:

$$c^* = \frac{c_{s,\text{surface}}}{c_{s,\text{center}}} \quad (5.2)$$

High values of c^* indicate high surface saturation and poor utilisation of the active material in the center of the particles. Since the solid and electrolyte phase transport are coupled, the value of c^* varies along the depth of the anode, with highest values expected near the separator. Figure 5.6 shows the evolution of the concentration ratio c^* at the anode/separator and the anode/current collector interfaces for the two protocols at 25°C and -15°C. Temperature has a dramatic effect on the solid concentration gradients, with the c^* values at -15°C being nearly an order of magnitude higher than at 25°C. The solid phase concentration gradients induced during the boost stage of boost charging are higher than those induced by CC-CV at both conditions. However, a relaxation of the concentration gradients can be observed during the low current stage following the boost stage at 25°C. Boost charging therefore only drives higher concentration gradients than CC-CV at low SOC, before the thermodynamic condition for lithium plating is met. At high SOC, CC-CV induces stronger concentration gradients than boost charging, which favours lithium plating. Both protocols exhibit markedly higher c^* values near the separator than near the current collector. At -15°C, the boost stage of boost charging induces very steep concentration gradients, with surface concentration being nearly 100 times

higher than the concentration at the center of the particles. Interestingly, the c^* values are almost as high near the current collector as near the separator, indicating that the solid phase transport acts as the primary rate limiting factor throughout the anode. For CC-CV, c^* remains about 50% higher near the separator than near the current collector. At this temperature, the reduced diffusion rates drive the anode potential below 0 V vs Li/Li⁺ already at low SOC. The increased concentration gradients induced by the high current of the boost stage lead to an increased plating rate compared to CC-CV. Following the boost stage, the c^* values of boost charging only reduce below those of CC-CV for a short time, before the values of both protocols converge as they enter the final constant voltage stages. The plating rates also become similar at high SOC (see Figure 5.3f).

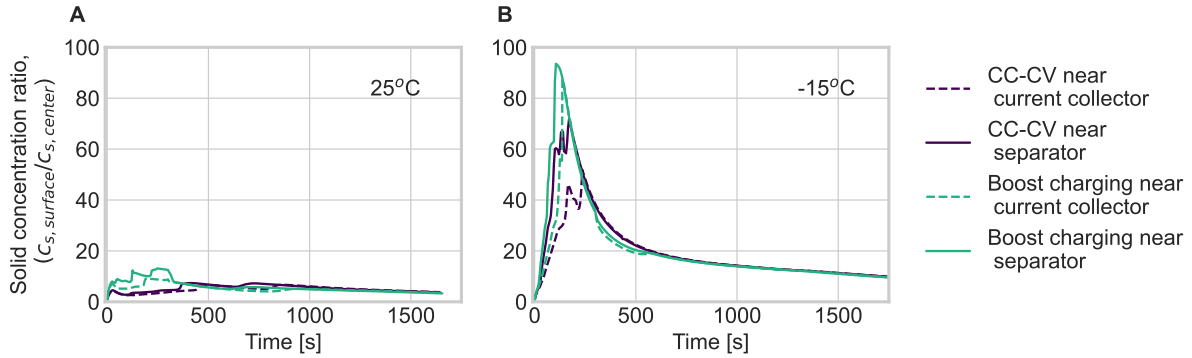


Figure 5.6: Surface-to-center solid particle lithium concentration ratios at the anode/separator and the anode/current collector interfaces at a) 25°C and b) -15°C. Note that only the first 1750 s is shown in b) to better showcase the differences in the solid concentration gradients at low SOC.

Both the ion and solid phase transport limitations impact the relative performance of the charging protocols. While the high current during the boost stage of boost charging does induce stronger concentration gradients than CC-CV at all temperatures, this will only lead to increased lithium plating rates if the transport limitations are so severe that the thermodynamic condition for plating is met. For the cell simulated in this study, the diffusion rates in both phases at 25°C are fast enough to avoid causing the anode potential to become negative during the boost stage. Therefore, the high boost current at low SOC does not increase the amount of plated lithium, in line with the findings of the original experimental study [161]. In fact, since after the boost stage the current is reduced compared to a CC-CV protocol with the same charging speed, reduced lithium plating rates are observed with boost charging. However, the same advantage cannot be realised at low temperatures, where the reduced diffusion rates drive severe concentration gradients

in the electrolyte and the solid particles, causing the anode potential to drop below 0 V already during the boost stage and substantially increasing the plating rate. While the concentration gradients do reduce in the later stages of charging, the anode potential remains negative and the plated lithium cannot be stripped during this operational phase.

5.4.4 Extension to other cells

The cell investigated in this study is a relatively high energy type, with an anode thickness of $73.6\ \mu\text{m}$, anode particle size of $13.7\ \mu\text{m}$ and a maximum manufacturer-recommended charging C-rate of 1C. To investigate how the same charging protocols would perform on a more power-optimised cell, the cell parameters were altered in the model. The electrode thickness and particle size affect the electrolyte and solid phase transport respectively. These effects are studied separately by first simulating a cell with halved electrode thicknesses and then a cell with a halved anode particle size. While changing the particle size does not affect the amount of the active material in the model, halving the electrode thicknesses produces a cell layer with half the active material and about half the capacity. The number of cell layers was therefore doubled in the model to maintain the same cell capacity. Figure 5.7 shows the lithium plating results of the same charging protocols on the two simulated power cells. For a cell with halved electrode thicknesses (Figure 5.7a-f), the plating rates become more homogeneous across the anode thickness compared to the original cell for all protocols and conditions. This is in line with the expectations: since the lithium ions have a shorter distance to travel across the electrode, the ion concentration is more uniform, promoting more homogeneous lithiation and plating. Similar trends can be observed as for the original cell: while boost charging results in reduced rates of plating compared to CC-CV at moderate temperatures, at sub-zero temperatures the relative performance changes, with marginally more plating caused by boost charging. No significant differences in the plating homogeneity can be observed between the charging protocols, suggesting that halving the electrode thicknesses facilitates the ion transport sufficiently to accommodate the high currents of boost charging.

The lithium plating profiles for a cell with a reduced anode particle size are shown in Figure 5.7g-l. Note the upper y-axis limits are much lower compared to 5.7a-f. The plating rates are reduced dramatically for all charging conditions due to the reduced solid phase diffusion distance and more uniform particle lithiation. At 25°C , very little lithium

plating can be observed with either protocol. At 0°C, the amount of plated lithium at the end of charge is about five times higher for CC-CV than for boost charging. CC-CV also causes more heterogeneous plating, which can be attributed to the fact that the plating onset is shifted to a high SOC, when the charging current of CC-CV is higher than the low current stage of boost charging. At -15°C, boost charging still leads to a reduced plating propensity relative to CC-CV, although the difference between the protocols is reduced compared to the 0°C case. This suggests that the improved solid phase transport shifts the balance between the performance of the two protocols in favour of boost charging, as the lithium intercalated at the surface can more easily diffuse through the particles even during the boost stage.

The electrode thickness and particle size are not the only parameters that affect diffusion in the two phases. To investigate the effect of transport rates more broadly, it is useful to consider diffusion timescales. The solid phase diffusion timescale τ_s can be estimated according to the equation:

$$\tau_s = \frac{r_{p,neg}^2}{D_{s,neg}}, \quad (5.3)$$

where $r_{p,neg}$ [m] is the anode particle radius and $D_{s,neg}$ [m².s⁻¹] is the diffusion coefficient of the intercalated lithium in the anode. A similar equation can be used to define the ion diffusion timescale through the electrolyte:

$$\tau_e = \frac{L_{neg}^2}{\left(\frac{\epsilon_e}{\tau}\right)D_e}, \quad (5.4)$$

where L_{neg} [m] is the anode thickness, ϵ_e [-] is the electrolyte volume fraction in the anode, τ [-] is the anode tortuosity and D_e [m².s⁻¹] is the ion diffusion coefficient through the electrolyte. The term in the denominator is often termed the effective ion diffusion coefficient as it accounts for the tortuous diffusion pathway through the pores of the electrode. Figure 5.8 illustrates the performance of boost charging relative to CC-CV, mapped against the ion and solid phase diffusion timescales. The size of the data points is proportional to the amount of plated lithium at the end-of-charge, while the colour represents the percentage difference in the plated amount for boost charging compared to CC-CV. The presented data are the results of simulations where the parameters of Equations 5.3 and 5.4 were varied one at a time.

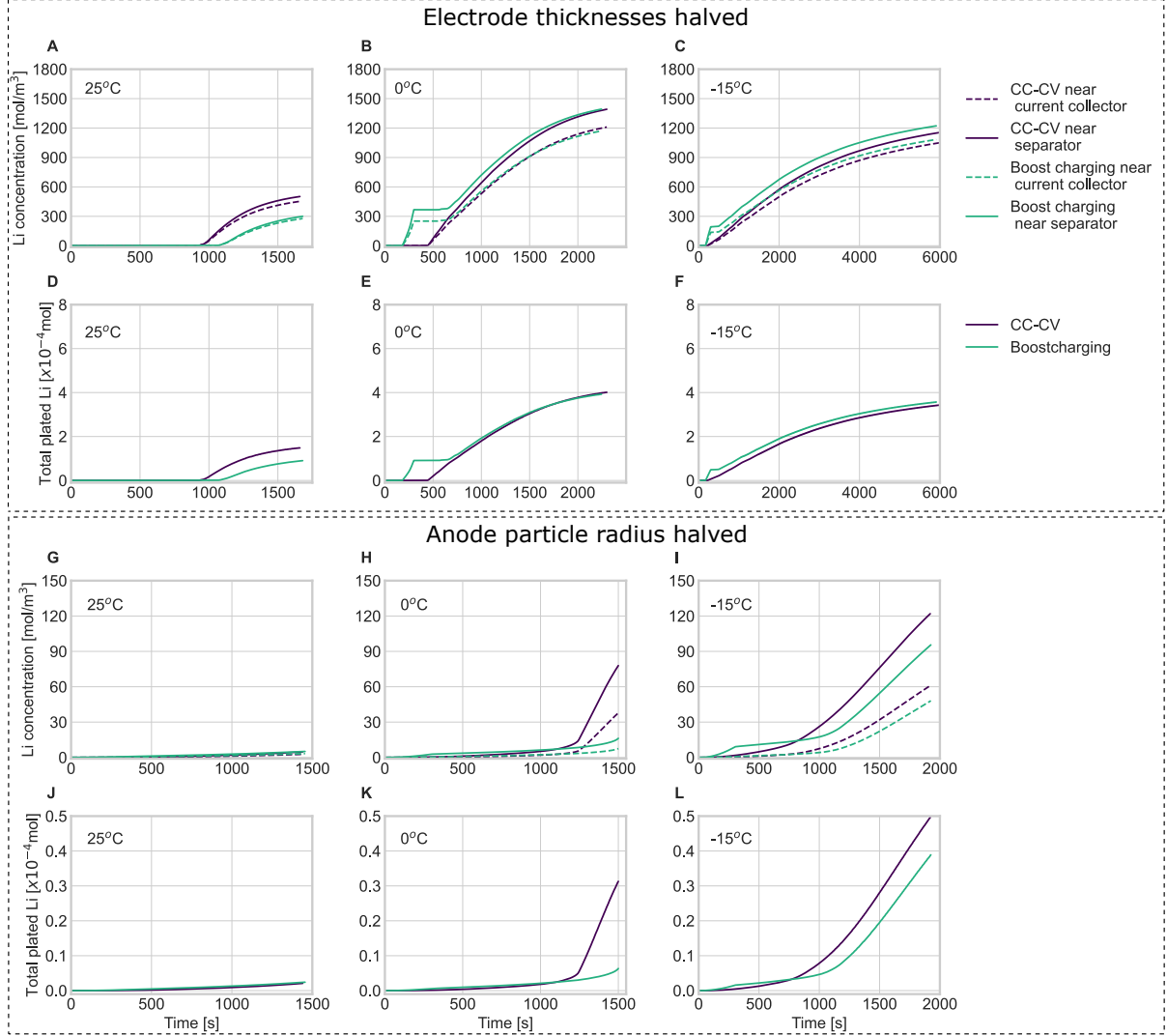


Figure 5.7: Model-predicted lithium plating propensity with CC-CV and boost charging for two different types of a "power cell". Local lithium concentration at the anode/separators and the anode/current collector interfaces for a cell with halved electrode thicknesses at different temperatures (a-c) and the corresponding total plated lithium profiles (d-f). Local lithium concentration for a cell with a halved anode particle size (g-i) and the corresponding total plated lithium profiles (j-l).

In the model, the solid and electrolyte phase diffusion coefficients vary as a function of lithiation and ion concentration respectively, and both are also temperature-dependent. As a result, the diffusion timescales vary in time and space during the charging process. For simplicity, the solid diffusion timescales plotted in Figure 5.8 are evaluated using the average values for the anode diffusion coefficient at the initial cell temperature, while the ion diffusion timescales are evaluated using the electrolyte diffusion coefficient at the average concentration of 1 M at the initial cell temperature. The solid phase diffusion timescale is two orders of magnitude slower than the ion diffusion timescale, and con-

sequently has a stronger impact on the overall amount of plating. The overall plating amount tends to increase as the solid diffusion timescale increases, until it plateaus above τ_s values of about 10 hours. The plateau in the plating propensity is caused by the decrease in the effective charging rate. As the solid phase mass transport rates become increasingly limited, the voltage limits are reached earlier, reducing the average charging speed. This phenomenon, in turn, has a limiting effect on the rate of lithium plating.

The solid phase diffusion timescale also has a stronger impact on the relative performance between the protocols, while the ion diffusion timescale affects it to a smaller extent. Boost charging is clearly beneficial in terms of reducing the lithium plating amount when both diffusion timescales are sufficiently short. This is because fast transport makes it possible for the anode to accommodate the high boost current without inducing severe concentration gradients that would cause the anode potential to become negative during the boost stage. With very high solid diffusion timescales (> 20 h), boost charging causes a slight increase in plating compared to CC-CV at the same conditions. The difference between the protocols is not large since at these conditions the final voltage limit is reached relatively quickly and both protocols follow similar voltage and current profiles except at low SOC. When the solid phase diffusion is fast (< 5 h), the effects of the ion diffusion become more apparent: boost charging best limits plating when the ion diffusion is fast, but the balance shifts in favour of CC-CV as the ion diffusion timescale increases. Slow ion diffusion also leads to higher plating heterogeneity with boost charging compared to CC-CV which is not accounted for in Figure 5.8.

Overall, the simulation results indicate that boost charging can effectively reduce the degradation rate due to lithium plating in power cells, as well as in higher energy cells at moderate to high temperatures. If the diffusion rates are sufficiently fast to prevent the onset of plating in the boost stage, boost charging is likely to cause less plating than CC-CV with the same charging time since it features lower currents at high SOC. However, there are some caveats to this conclusion. The underlying assumption in this work is that the charging rate is limited by lithium plating on the anode. While this is known to often be the case, the charging rates of some cells can be limited by the mechanical degradation of either electrode [122, 252, 102]. Boost charging protocols that feature higher than manufacturer-recommended voltage limits in the boost stage may also cause increased degradation due to the cathode or electrolyte stability issues, even where they

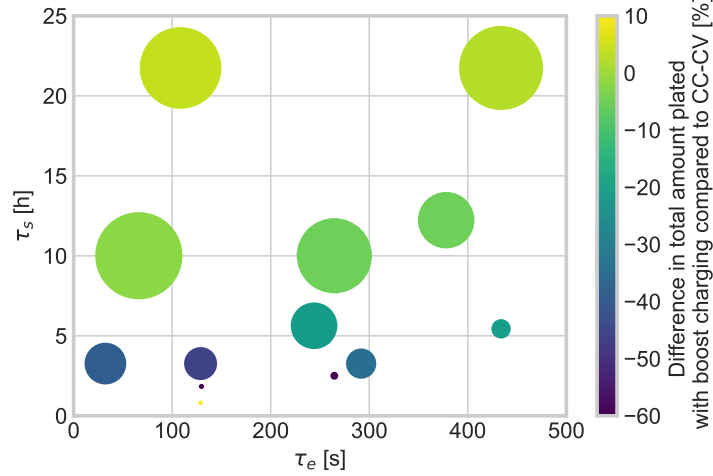


Figure 5.8: Plating propensity of boost charging compared to CC-CV mapped against the solid and ion diffusion timescales. The colour of the data points represents the percentage difference in the end-of-charge lithium plating amount relative to CC-CV at the same conditions, while the size is proportional to the absolute amount of lithium plated. Note that the data points are only visible for the simulations where the amount of plating was non-negligible.

do not trigger lithium plating. The model also assumes a uniform temperature throughout the cell, which is reasonable for a single cell layer but not true for a cell in a module or pack. The magnitude of the thermal gradients depends on the cell geometry, form factor, pack architecture and the thermal management strategy. For those systems that exhibit significant temperature or current heterogeneities, the high peak currents of the boost stage may amplify them [253, 254]. This effect is exemplified by the power cell versus energy cell simulations, where boost charging leads to increased plating heterogeneity in the energy-optimised cell. The influence of thermal gradients on the lithium plating behaviour was out of the scope of this study but will be subject of a future work.

5.4.5 Validity of the model predictions: simulating fast charging with parameters validated against discharge data

This study is based on the results of numerical simulations using parameters measured in other works [16, 209, 211, 141]. As such, it is important to establish to what extent the conclusions rely on the accuracy of the model parameters, many of which carry significant uncertainties. The parameter studies carried out in Section 5.4.4 show that varying the transport-related parameters does not invalidate the conclusions, with boost charging generally causing less plating when lithium diffusion is faster but with reduced or no

benefits when diffusion timescales are long. To further investigate the validity of the modeling results, the simulated voltage, current and temperature curves were compared to experimentally measured ones for both CC discharge and CC-CV charge. While the simulations matched the experiments reasonably well in the discharge direction, the same parameters did not produce accurate results for the charge curves. As shown in Figure 5.9, the simulations tended to underestimate the overpotential at low SOC and overestimate it at high SOC.

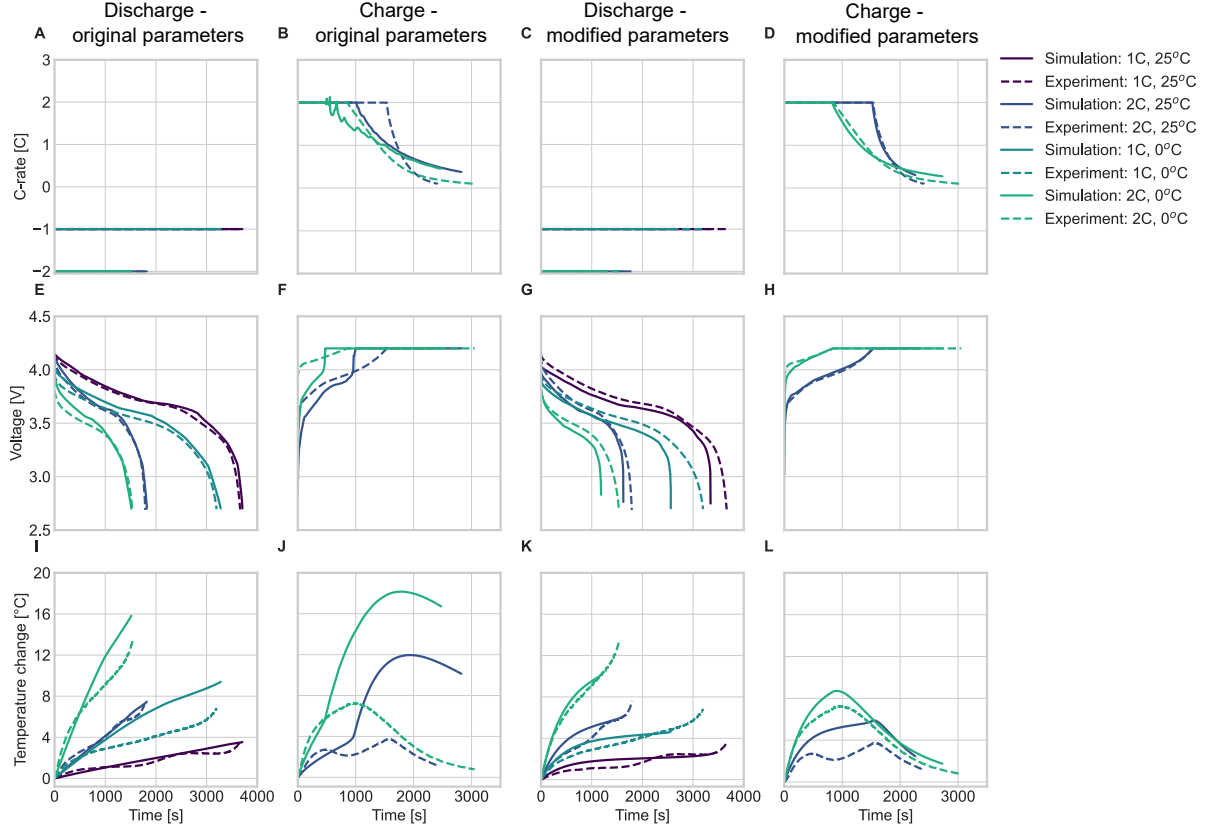


Figure 5.9: Comparison of simulated and experimentally measured C-rate (a-c), voltage (d-f) and temperature change (g-i) curves. The simulations shown in the first two columns from the left use the original parameter set from Ecker et al. [209]. The simulations shown in the last column use a modified parameter set which better matches the experimental data. All charge data is shown for 2C CC-CV up to the charged capacity of 6.41 Ah for 0°C and 7.47 Ah for 25°C.

Battery models are often validated using mainly experimental discharge data [209, 24]. The electrochemical model parameter set used in this work was validated thoroughly on discharge voltage curves at different C-rates and temperatures, as well as on some charge/discharge pulse data [209]. However, a comparison of the simulated and experimental full charge curves was only presented for a 1C charge at 25°C and displayed a noticeable discrepancy. In reality, the overpotentials observed in the charge and discharge

directions are not equal, and can exhibit different variations as a function of SOC [255, 24]. Such differences in overpotentials can be caused by variations in a number of parameters. Li et al. [212] have shown that in the DFN model, the simulated terminal voltage curves are most sensitive to the parameters that describe the transport in the solid electrodes and their ability to store charge, including the electrode thicknesses, particle sizes, active material fractions, reaction rate coefficients and solid phase diffusion coefficients. The diffusion coefficients in particular are difficult to measure accurately, and have been shown to vary with the applied current [218] as well as between the lithiation and delithiation [24]. The activation energies of the solid phase diffusion measured by Ecker et al. [16] using EIS and GITT varied considerably as well. The authors also found they had to fit a different value of the anode exchange current density to the one measured experimentally in order to better match the measured discharge voltage [209]. Since these parameters can be considered to have the highest uncertainty, they are adjusted in this work to improve the fit to the measured charge curves. The parameter modifications are summarised in Table 5.2.

Table 5.2: Parameters modified to fit the experimental charging data. Note the changes to the diffusion coefficients are not included here and instead shown in Figure 5.10.

Symbol	Value		
	Original	Modified	Percentage change
$E_{D,s,neg}$	30300 J.mol ⁻¹	42420 J.mol ⁻¹	+40%
$E_{D,s,pos}$	80600 J.mol ⁻¹	56420 J.mol ⁻¹	-30%
$k_{int,neg}$	$1.99 \times 10^{-10} \text{ m.s}^{-1}$	$1 \times 10^{-11} \text{ m.s}^{-1}$	-95%
h_{conv}	$8 \text{ W.m}^{-2} \text{ K}^{-1}$	$40 \text{ W.m}^{-2} \text{ K}^{-1}$	+400%

The modified parameters should not be misinterpreted as 'correct' - the adjustments are made only to demonstrate that the key conclusions of this work do not change with a parameter set that better fits the experimental data. A thorough parameterisation with additional validation experiments would be necessary to establish which parameters do in fact differ between the charge and discharge processes and to what extent. Nevertheless, it was important not to modify the experimentally measured parameters in a random manner. In all cases, the parameters are adjusted within the range of values found in the literature. The following explains the reasoning behind each of the applied changes.

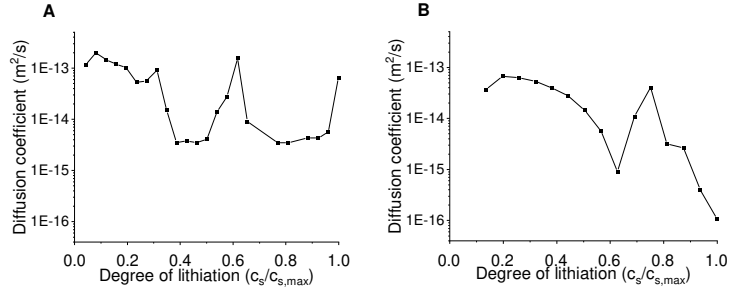


Figure 5.10: Modified solid phase diffusion coefficients for the a) anode, b) cathode.

Diffusion coefficients and their activation energies Diffusion coefficients of porous electrode materials are notoriously difficult to measure. Two common methods of measurement are EIS and GITT, both of which rely on the use of low currents. Recent research has shown diffusivity increases with higher C-rates [218]. Diffusion coefficients have also been shown to vary between the lithiation and delithiation [24]. The values reported in the literature span multiple orders of magnitude [16, 212], while researchers still commonly use either constant or nonlinear (SOC-dependent) diffusion coefficients. The GITT and EIS results reported by Ecker et al. [16] varied slightly at 23°C, and more significantly at other temperatures. Since the EIS results featured more data points, they were used both in their follow-up validation paper [209] and in the current work. Due to the uncertainties associated with the measurement technique, it is the diffusion coefficients that the most significant modifications were applied to. The key difference between the measured and simulated charging voltage curves was that the overpotential was underestimated at low battery SOC and overestimated at high SOC. Sensitivity studies revealed that the high SOC region of the voltage curve was more sensitive to the anode diffusion coefficient, while the low SOC region was more sensitive to the cathode diffusion coefficient. As such, the cathode diffusion coefficient was reduced by a factor of 5 while the anode diffusion coefficient was increased by a factor of 4.5. Following these changes, the model fit was improved over most of the voltage range, but a significant discrepancy remained at the low SOC end (<15%). To better match this voltage region, the shapes of the diffusion coefficient curves were also modified. For the cathode, the four highest lithiation data points measured by Ecker et al. [16] were reduced by a factor of 10. For the anode, the lowest lithiation data points were increased by a factor of 10. The modified diffusion coefficient curves are shown in Figure 5.10.

These modifications produced a good fit at 25°C but not at 0°C, where the overpoten-

tial was still overestimated at low SOC's and underestimated at high SOC's. The activation energies of the diffusion coefficients were therefore also adjusted. The activation energy of the cathode diffusivity used originally was relatively high at $80,600 \text{ J.mol}^{-1}$. This value was obtained using EIS measurements, whereas GITT results showed a much lower degree of temperature sensitivity at $31,700 \text{ J.mol}^{-1}$ [16]. A value of $56,400 \text{ J.mol}^{-1}$, which lies about halfway between the two measured values, best fitted the experimental data. The activation energy of the anode diffusivity used in the original simulations was fitted since the experimentally measured values produced a poor fit to the discharge data in Ecker et al.'s validation paper [209]. Here, the fitted value was increased by 30% from $30,300 \text{ J.mol}^{-1}$ to $42,400 \text{ J.mol}^{-1}$, which also falls between the values measured using EIS and GITT ($40,800\text{-}48,900 \text{ J.mol}^{-1}$) [16].

Intercalation reaction rate constant for the anode Another parameter that had to be fitted in the said validation paper [209] was the exchange current density for (de)intercalation in the anode. The experimentally measured value of $7.05 \times 10^{-5} \text{ A.cm}^{-2}$ had to be increased by nearly an order of magnitude to $5.39 \times 10^{-4} \text{ A.cm}^{-2}$ which corresponds to a (de)intercalation reaction rate constant of $1.99 \times 10^{-10} \text{ m.s}^{-1}$ in the model used here. Reducing the rate constant to $1 \times 10^{-11} \text{ m.s}^{-1}$ (corresponding to 40% of the experimentally measured value) best fitted the charging data.

Convective heat transfer coefficient The modifications discussed above produced a good fit to the charging voltage and current curves but still overestimated the temperature rise. Since diffusion and reaction rates are highly temperature-dependent, it is important that the simulated temperature rise is not unrealistic. To better fit the temperature rise, the convective heat transfer coefficient was increased to $40 \text{ W.m}^{-2}\text{K}^{-1}$. While this value is at the upper end of the typical range for free convection in air, there is no physical reason why it should vary between the charge and discharge directions given the same thermal boundary conditions. In reality, the differences in the temperature rise could be caused by differences in the entropic heat generation, charge transfer impedance, current distribution or other factors. Since finding the most accurate parameters was not the focus of this work, the simplest adjustment was made by varying the convective heat transfer coefficient. A detailed parameterisation study would be required to find the parameters that do in fact vary between the charge and discharge.

The fit of the model with the modified parameter set against the experimental charge data is shown in Figure 5.9(d,h,l). The fit is improved substantially, with a voltage RMSE of 22 and 30 mV at 25°C and 0°C, respectively, compared to 111 and 116 mV with the original parameters, and a C-rate RMSE of 0.06 and 0.10 C compared to 0.36 and 0.24 C originally. The simulated temperature change is still higher than the measured surface temperature change, although part of this difference could be attributed to the fact that the model simulates the temperature in the active material rather than the cell surface. The temperature RMSE with the modified parameter set is 1.3 and 0.4 °C at 25°C and 0°C, respectively, compared to 5.7 and 9.8°C originally. There is also some discrepancy between the model-predicted and measured voltage curves at low SOC at 0°C, which may stem from the assumption that a single activation energy value describes the temperature dependence of the diffusion coefficients over the entire SOC range. It is possible that this temperature sensitivity varies with the SOC [16]. The fit of the same modified parameter set against discharge data, shown in Figure 5.9(c,g,k), is compromised to improve the charge data fit. With the modified parameter set, the discharge behaviour predicted by the model deviates from experimental measurements particularly at low SOC, where the overpotential is overestimated. This is likely due to the shape of the cathode diffusion coefficient, which was modified to address the underestimation of the charge overpotential in this SOC region with the original parameter set. It is not clear whether the discrepancy in the charge and discharge overpotentials at low SOC stems from the diffusion coefficients being different for lithiation and delithiation in this region, or whether a more consistent fit could be produced with another parameter set. In the discharge direction, the voltage RMSE with the original parameter set amounts to 57 mV. With the parameter set optimised for the charge data, the RMSE increases to 83 mV. Note the RMSE does not quantify the error at very low SOC, where the voltage with the modified parameter set is undefined due to the reduced predicted accessible capacity. For the purpose of this study, this fit is acceptable, as the conclusions rely primarily on the outcomes of the parametric studies presented in the Section 5.4.4.

As shown in Figure 5.11, the plating rates are strongly affected by the parameter modification but still follow similar trends for the two charging protocols. Note that the first column shows the results at 10°C rather than 25°C since the plating rate was found to be negligible at 25°C with both protocols when using the modified parameter set. The

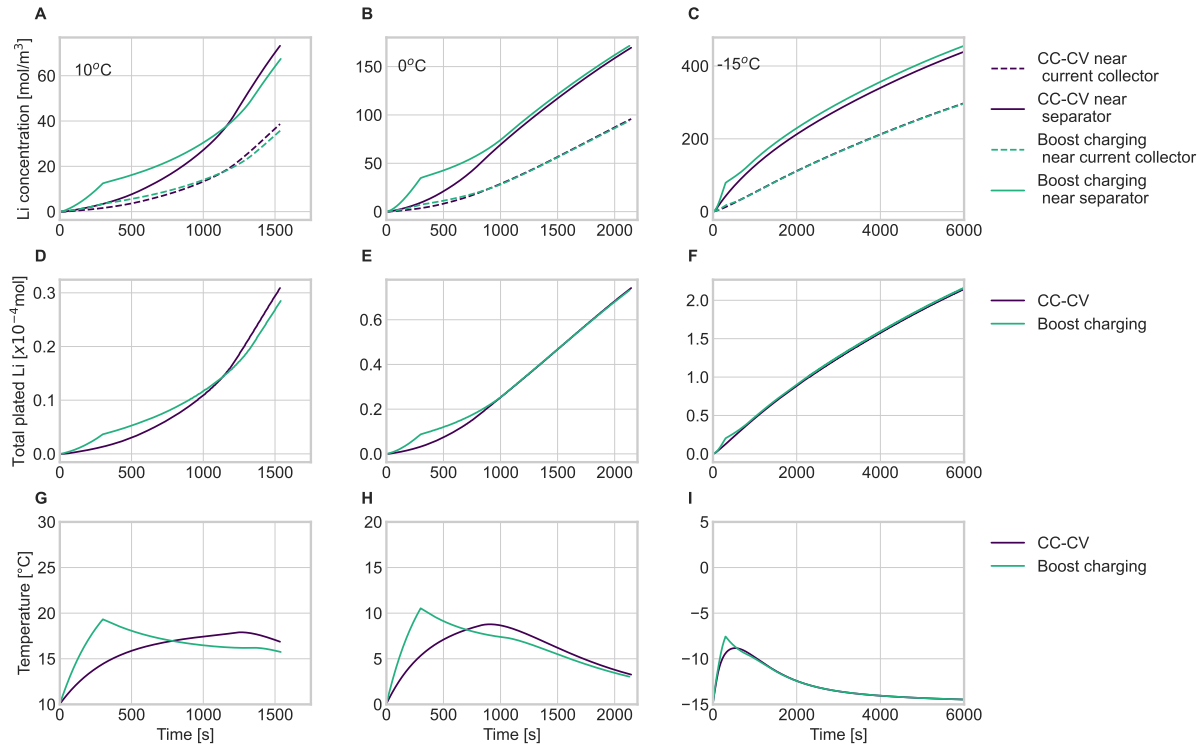


Figure 5.11: Local concentration of plated lithium at the anode/separator and anode/current collector interfaces at different temperatures (a-c), corresponding total amounts of plated lithium (d-f) and cell temperature profiles (g-i) with a starting temperature of 10°C (a,d,g), 0°C (b,e,h) and -15°C (c,f,i). All profiles are model-predicted.

y-axis ranges differ between different starting temperatures due to the larger differences in the simulated plating rates. The overall effect of the modifications is that the simulated cell is now better suited to fast charging with a shorter solid phase diffusion timescale (due to the higher diffusion coefficients) than with the original parameter set. The amount of plating is reduced for both protocols at all conditions. However, boost charging still reduces the total amount of plating compared to CC-CV at above-zero temperatures. At sub-zero temperatures, the plated amounts at the end of charge are very similar for both protocols, with boost charging producing only a marginally higher total amount but with a more heterogeneous distribution. A major difference compared to the original simulations is that boost charging does trigger plating during the boost stage even at relatively high temperatures, before the plating rate decreases during the following low current stage. It also causes a significantly higher temperature rise during the boost stage. These observations can be attributed to the higher overpotential at low SOC with the modified parameter set, which favours an earlier onset of plating as well as higher heat generation. The higher overpotential was achieved through reducing the anode diffusion

coefficient at very low lithiation and reducing the cathode diffusion coefficient at high lithiation. These changes do tip the balance in favour of CC-CV at low SOC's since the lithium diffusion is effectively slower in both electrodes during the boost stage of boost charging. However, for high enough temperatures, the plating rate caused by CC-CV at higher SOC's still outpaces that caused by the lower current stage of boost charging, resulting in CC-CV producing more plating at the end of charge. The lower diffusion coefficients at low SOC's also reduce the overall differences between the plating rates caused by boost charging and CC-CV across all the studied conditions. The advantages of boost charging are therefore dependent on the variation of the anode diffusion coefficient with the intercalation fraction; however, previous studies have consistently found it to be relatively high at low states of lithiation [24, 256, 257].

These results demonstrate that the conclusions of the present work, based largely on parametric studies, are valid for various parameter sets. Additionally, the relative differences between the plating rates caused by CC-CV and boost charging are found to depend on the variation of the graphite diffusion coefficient with the state of lithiation. However, the large discrepancies between the measured and simulated charge curves with the original parameter set highlight the need to validate models thoroughly against experimental data in both the discharge and charge directions. Some parameters may differ between the lithiation and delithiation processes, significantly affecting the results of model-based studies.

5.5 Summary

Charging protocol optimisation is a promising strategy to reduce or prevent lithium plating in lithium-ion cells while maximising the charging speed. However, for any alternative charging protocol to be deployed in practice, its effects on different cells must be understood throughout the temperature range of interest to the application. Many previous studies have only assessed the performance of charging protocols at room temperature and on only one cell model, often leading to disagreement between the results of different studies.

In this work, an electrochemical-thermal model is used to investigate the performance of CC-CV and boost charging at temperatures ranging from -15 to 25°C and with varying

cell parameters. In order to study the effects of each charging protocol on the plating severity as well as heterogeneity, lithium plating is modelled explicitly. This is in contrast to some other studies which assume the extent of plating to be proportional to the amount of time spent at negative anode potentials, ignoring the differences in local plating rates as a result of gradients in overpotentials and electrolyte concentrations along the anode depth. It is shown that the relative performance of the charging protocols ultimately depends on the solid phase and ion diffusion timescales. Boost charging is found to be most suitable for power-optimised cells with better electrolyte and solid phase transport characteristics, while its use for energy cells only limits lithium plating at moderate or higher temperatures. For the original, relatively high energy cell at subzero temperatures, boost charging is found to cause a slight increase in the lithium plating propensity compared to CC-CV, along with significantly more heterogeneous plating rates along the anode depth and substantially higher concentrations of plated lithium at the anode/separator interface. This behaviour is found to be caused by the concentration gradients induced by boost charging, which are severe enough at subzero temperatures to push the anode potential below 0 V vs Li/Li⁺ and enable lithium plating at very low SOC. The severe concentration gradients in the electrolyte not only increase the overpotential throughout the anode, but also favour heterogeneous deposition due to the concentration and overpotential dependence of plating. At 25°C, the diffusion rates in both the electrolyte and solid phases are fast enough to accommodate the boost current without triggering plating.

Solid phase diffusion is found to have the dominant effect on the overall lithium plating propensity. When the diffusion in the anode particles is very slow (solid diffusion timescales > 20 h), boost charging tends to cause slightly increased plating rates compared to CC-CV. This means that boost charging may not offer significant lifetime advantages in conditions most favourable to plating, such as very low temperatures or in cells with large anode particles. An additional factor in the performance of boost charging relative to CC-CV is the SOC dependency of the anode diffusion coefficient. Boost charging is likely to particularly benefit the cells with anodes that exhibit a higher diffusivity at low lithiation, as has been found to be the case with many graphite anodes in the literature. The ion diffusion timescales are two orders of magnitude shorter than the solid diffusion, and as such affect the relative performance to a lesser extent. Slow ion diffusion does, however, promote more heterogeneous plating through the anode.

The findings of this study highlight the need for more comprehensive evaluation of fast charging protocols under a variety of thermal conditions and on different cells. The ability of a charging protocol to limit or prevent lithium plating depends on the interaction between its current profile and the transport rates within the cell. As such, the results of a charging optimisation study conducted on one cell at a single temperature point cannot be extrapolated to other cells or different climates.

Chapter 6

Lithium plating under thermal gradients

6.1 Introduction

Understanding the effects of temperature and thermal heterogeneity on the Li plating behaviour and the associated degradation was a key objective of this PhD project. The work presented in the following chapter focuses on through-plane thermal gradients in pouch cells. During fast charging in applications such as EVs, pouch cells are often aggressively surface cooled to reduce their absolute temperature and prevent overheating. Due to the poor through-plane thermal conductivity of Li-ion cells, such cooling can introduce significant thermal gradients across individual cells. This study attempts to answer the following questions:

- Are there significant differences in the severity of plating, depending on whether it takes place at moderate or low temperatures?
- In a cell fast charged under a thermal gradient, which region is the most susceptible to plating?
- What is the effect of thermal gradients on the local and global degradation?

Section 6.2 discusses the key recent literature on the effects of thermal heterogeneities on plating and degradation. The modelling and experimental design aspects are summarised briefly in Sections 6.3 and 6.4, respectively, with further detail available in Chapters 3 and 4. The results are discussed in Section 6.5.

6.2 Literature review

The relationship between the absolute cell temperature and the risk of Li plating has been studied extensively as discussed in previous chapters. The fact that increased current densities are more likely to lead to plating is similarly well established. Only a few recent works, however, have attempted to study the impact of thermal gradients on the plating risk or distribution within a cell. In theory, plating in this case should be affected primarily by two factors: the reduced rate of diffusion in the colder layers of the cell, and the temperature-dependent current distribution.

While most previous literature has only considered the effects of the average temperature, the recent few years have seen a surge of interest in the interactions between temperature non-uniformities and degradation. In particular, a number of studies in the Li metal battery literature have investigated the effect of high temperature hot spots on the deposition behaviour. Zhu et al. [82] observed fast, dendritic growth and short circuit at a high temperature hot spot induced using a laser. The rate of growth increased with higher hot spot temperatures, while the deposits became more localised. The effect was attributed to the strongly increased current density caused by the low local impedance. Vishnugopi et al. [258] used coarse-grained kinetic Monte Carlo simulations to show that while a uniform temperature of 75°C could suppress dendrite formation in Li metal cells, temperature non-uniformity between the Li electrode and the electrolyte encourages dendritic growth and is therefore detrimental to the cell's lifetime. The model was designed to simulate a heated electrode, i.e. the Li metal was simulated at higher temperatures than the adjacent electrolyte. The results point to the key role of the electrolyte phase transport in determining the deposition morphology.

The influence of thermal heterogeneity on degradation is also increasingly being addressed in the conventional Li-ion literature. McCleary et al. [259] modelled the temperature, current and voltage heterogeneities that naturally develop in spirally wound (cylindrical and prismatic) cells during operation. Their results suggested that Li plating was most likely in the proximity of the tabs. Since their model assumed the tabs were placed in the center of the cell - the highest temperature region during cycling - it is unclear whether the geometry or the temperature distribution had the dominant effect in determining the current density and plating distributions. Sturm et al. [260] recently studied the effect of multitab cylindrical cell designs on the utilisation homogeneity and Li

plating during fast charging. Their modelling results showed that increasing the number of uniformly spaced tabs homogenised the current density distribution over the electrode area and, improved electrode utilisation and increased the charge capacity, but increased the risk of plating. This was attributed to the higher SOC at the end of charge. A follow-up work [261] also investigated the effects of cooling, finding that the cold spots induced near the surface of the simulated cylindrical cell were at an increased risk of plating. Another study [262] used a 3D electrochemical-thermal model to study fast charging in a pouch cell under natural convection conditions. In the modelled cell, plating only became likely in extreme conditions (4C at 0°C). The plating risk distribution was found to be determined mainly by the in-plane anode potential distribution, again leading to a higher risk near the tabs, although the through-plane maximum thermal gradient of 0.3°C in the simulations was probably too small to significantly affect plating. Sieg et al. [195] in their study on diagnosing heterogeneous degradation using DVA reported localised Li plating in the centre of a stacked pouch cell, which they attributed to the high local current density caused by the higher temperature of that region. Paarman et al. [197] recently studied the effects of large (up to 50°C) in-plane thermal gradients in pouch cells, finding the global rate of capacity fade to be similar irrespective of the presence of the thermal gradient. This result was particularly surprising as the post-mortem analysis (visual inspection, SEM and specific weight measurements) showed a strong correlation between the local temperature and amount of plated lithium, with cold regions experiencing more plating. The specific weight of the anodes of cells cycled at low temperatures under a thermal gradient was also found to be higher than that of the thermally uniform cells with the same average cycling temperature, which was found to correlate with a higher overall plating amount. The authors did not explain why these differences in plating trends did not affect the capacity fade. Storch et al. [196] recently investigated the degradation patterns in a large format 39 Ah pouch cell charged with a current profile designed to avoid negative anode potentials. Despite the use of this current profile, they reported significant plating in the centre of the cell, which was attributed to the coupled effects of the temperature gradient. The authors argued that the higher temperature in the centre of the cell caused an increase in the local current density, which in turn led to lateral diffusion in the electrolyte to replace the consumed Li ions. This then resulted in a higher local electrolyte potential, lower anode potential and localised overcharging, thus enabling lithium plating

despite the global anode potential remaining positive. In an experimental study on coin cells, Carter et al. [263] highlighted the importance of the balance between the anode and cathode diffusion kinetics. The results showed that imposing a higher temperature on the anode side of the cell reduced the risk of plating by improving transport rates in the anode. Conversely, imposing a higher temperature on the cathode side increased the risk of plating by introducing a mismatch between the rates of faster cathode and slower anode diffusion. The authors did acknowledge that in most practical applications where the electrodes are typically double-sided, the directionality of the thermal gradient varies from one layer to the next. Fear et al. [78], of the same research group, modelled both the inter-electrode thermal gradients in coin cells and in-plane gradients in pouch cells, confirming that the inter-electrode gradients could alter the plating severity depending on their direction. In contrast, the in-plane thermal gradients were found to affect the plating distribution, but not the plating severity.

The effects of through-plane thermal gradients on Li plating in pouch cells have not been studied in detail. Unlike cylindrical and prismatic cells which normally use wound electrodes, pouch cells usually feature stacked architectures, leading to differences in the interplay between the thermal environment and current distributions. At the same time, the pouch cell design combined with surface cooling remains popular with EV manufacturers. Among the studies that have investigated thermal gradients in pouch cells, most have focused on in-plane temperature heterogeneity. Many have also been model-based with no or little validation experimental validation. As such, a knowledge gap remains around the effect of through-plane thermal gradients on the plating behaviour in commercial pouch cells. It is not clear whether the presence of such gradients during fast charging leads to more severe plating or more severe cell degradation in general, or if it has no global effect. Given the complex interplay between temperature, diffusion kinetics and current distribution, it is also not known whether it is the warmer or colder areas within the cell that are more susceptible to plating. The following work attempts to fill this gap.

6.3 Modelling framework

The equations of the model used in this study are the same as outlined in Chapter 3, with the model geometry extended into 2D with multiple layers, modelling the cell thickness and length. The 7.5 Ah Kokam cell is composed of 48 layers, with each current collector coated on both sides, except for the outermost cathode layers which are single-sided. This construction was reflected in the model, albeit with a reduction from 48 layers to 12 to improve the speed of computation. As such, any simulated layer can be thought of as an average of 4 layers of the real cell.

The multilayer geometry was built in COMSOL 5.3a, using the geometrical dimensions of the components as measured by Ecker et al. [16]. The architecture is illustrated in Figure 6.1. Due to the 2D geometry of the model, the current collectors had to be joined on opposing sides rather than close to each other as in the real Kokam SLPB75106100 cell (see Figure 6.1). This may lead to a more homogeneous current distribution along the layers compared to the real cell. Such lateral current distributions have previously been shown to affect the distribution of plating, but not its severity [78]. The focus of this study is primarily on the effect of through-plane thermal gradients, so this simplification is deemed acceptable. Nonetheless, in-plane distributions are investigated through experimental means.

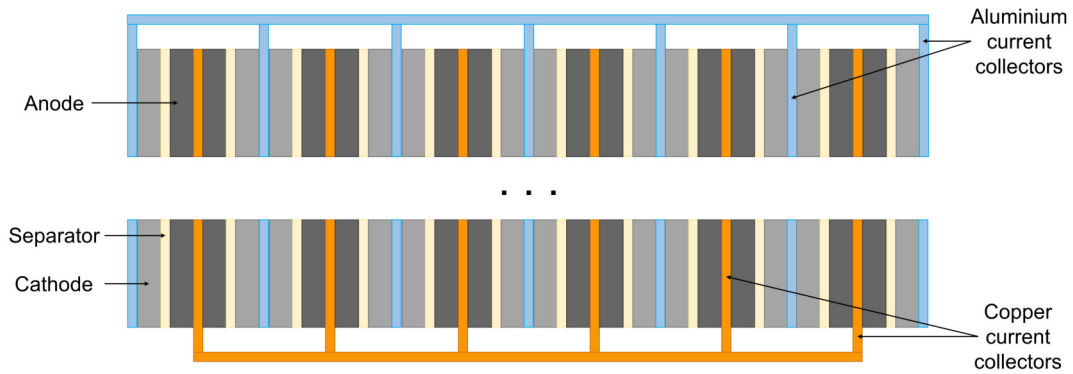


Figure 6.1: An illustration of the multilayer model geometry as implemented in COMSOL 5.3a.

6.3.1 Model parameters

The modified parameter set presented in Chapter 5 was used for the electrochemical model in this study. In addition, a temperature dependency was introduced for the

plating reaction exchange current density. Only one work could be found that measured the activation energy to be 35,300 J.mol⁻¹ in a Li-ion system, using NMR experiments combined with electrochemical modelling. This value is adopted here as well, although the high uncertainty associated with it should be recognised as discussed in Chapter 3.

6.4 Experimental

6.4.1 Test protocols

Cell screening and preconditioning.

For the results of the experiments to be determined primarily by the thermal conditions, it is imperative that the electrochemical performance of the cells should be as similar as possible. Manufacturing variations can be significant within the same cell model, particularly if the cells are manufactured in different batches or if the cell model has only recently been introduced [264]. For this reason, the well established and consistently manufactured Kokam SLPB75106100 lends itself well to the study. In addition to being drawn from the same batch, all cells used in this work were subjected to a characterisation procedure, consisting of a C/10 discharge capacity check and a HPPC resistance measurement at 10% SOC intervals. A current pulse of 1C for 10 s was used for the pulses, with C/10 discharge C-rate used to transition between the SOC points and a 1 hour rest after each pulse or SOC change.

Single fast charge tests on cells connected in parallel

Each multilayer Li-ion cell is a network of layers connected in parallel. While various types of internal electrochemical sensors are being developed, instrumenting individual layers to measure the current and Li plating distributions between them has not yet been demonstrated and is beyond the scope of this work. Instead, the experiments conducted here make use of the similarity between the parallel network of layers within an individual cell and two cells connected in parallel. It is assumed that differences in the plating behaviour between the two cells approximate the differences that would be seen in two halves of a single cell fast charged under a thermal gradient applied across its two faces. Pouch cells lend themselves well to such a study due to their shape and the soft casing.

When pressed together, the electrode layers of two cells are separated by two layers of the aluminium pouch material and several layers of the separator which do introduce an additional thermal resistance, but nonetheless resemble an individual cell more closely than similar configurations of hard-cased cell formats. In the single fast charge experiments, two cells were pressed together with a 1 mm thick thermal interface pad (t-Global Technology, thermal conductivity of $12.5 \text{ W.m}^{-1}\text{K}^{-1}$) and a flat thermistor between them, in the centre of each cell. The thermistor was used to establish the time taken for the cells to reach thermal equilibrium following a change in the temperature setpoints, as well as to monitor the temperature between them during the experiments. The cells were then placed in the rig described in Chapter 4. The cells were fast charged at a rate of 2C for the test with a mean temperature of 0°C or 15°C and 4C for 25°C , with a 10°C thermal gradient imposed in all cases. Following the fast charge, the cells were immediately disconnected, the temperature setpoint was changed to the mean test temperature for both cells and a total time of 6 minutes was allowed for thermal equilibration. This amount of time was found to be sufficient for the thermistor placed between the cells to reach the new temperature setpoint under all tested conditions. The cells were then individually discharged at a rate of C/20 with the aim of detecting and analysing the stripping voltage plateau.

Degradation tests on individual cells

The longer term degradation tests were conducted on individual cells, with a mean cell temperature of either 0°C or 25°C . The 0°C tests were conducted with a fast charging C-rate of 2C, while the 25°C tests used a C-rate of 4C since initial testing indicated very low rates of capacity fade at 2C. The cells were discharged at 1C in all cases. For each mean temperature, one cell was cycled with the same temperature imposed on both cell faces and another was cycled with a constant thermal gradient of 5°C , meaning one cell face was held at $T_{\text{ave}}+2.5^\circ\text{C}$ and the other at $T_{\text{ave}}-2.5^\circ\text{C}$. Every 10 cycles, a characterisation routine consisting of a fast charge and a C/10 discharge was performed, during which both cell faces were held at the mean test temperature. Due to the limitations in lab access as a result of the COVID-19 pandemic, only one cell could be tested per cycling condition.

6.4.2 Post-mortem analysis

Following the long term cycling experiments, the cells were disassembled in an Ar-filled glovebox according to the procedure described in Chapter 4. The post-mortem analysis included visual inspection, SEM on fragments of the electrode samples, and TGC on samples of anode material. Due to the lack of a transfer stage, the samples were exposed to air before being studied under the SEM. Li reacts with oxygen in the air, and it is the oxygen atoms in the resultant LiO_2 that can then be detected using EDS and indicate plating [14]. Details of the procedures can be found in Chapter 4.

6.5 Results & discussion

6.5.1 Cell screening

The measured capacities and 10 s DC resistances at 50% SOC of all cells used in this work are listed in Table 6.1. The resistance vs SOC profiles collected in the HPPC tests are shown in Figure 6.2. The discharge resistance is consistently slightly higher than the charge resistance for each cell. The same trend has been found by other researchers [265, 266] and attributed to the fact that discharging requires the removal of Li ions from a high energy state in the anode and insertion into a low energy configuration in the cathode, which is harder than the reverse process [265].

The cells are characterised by good manufacturing consistency, exhibiting a mean capacity of 7.67 Ah with a standard deviation of 0.02 Ah) and a mean 50% SOC resistance of 6.86 m Ω with a standard deviation of 0.26 m Ω . While some variations are inevitable, the cells were matched to experiments in such a way as to ensure a minimum difference in the capacity and resistance between any pair of cells connected in parallel in the single fast charge experiments or cycled at the same conditions with and without a thermal gradient. The test assignment is specified in Table 6.1. For clarity, the cells are numbered after the temperature they were tested at. The letters that follow the number stand for: W - warmer cell, C - colder cell, U - thermally uniform, and G - thermal gradient. The W and C designations are used for single cycle tests in parallel connection while U and G are used for longer term capacity fade tests.

Table 6.1: Measured initial capacities and 10 s DC resistances at 50% SOC for each cell used in the experiments. All values measured at 25°C.

Test (S = single cycle, L = long term)	Temperature [°C]	Thermal gradient [°C]	C-rate [C]	Cell no.	Measured initial capacity [Ah]	Initial charge resistance at 50% SOC [mΩ]
S	25	10	4	25W	7.664	6.89
S	25	10	4	25C	7.674	6.88
S	15	10	2	15W	7.670	6.62
S	15	10	2	15C	7.668	6.57
S	0	10	2	0W	7.683	6.86
S	0	10	2	0C	7.669	6.78
L	25	0	4	25U	7.674	6.68
L	25	5	4	25G	7.674	7.03
L	0	0	2	0U	7.713	6.65
L	0	5	2	0G	7.704	6.26

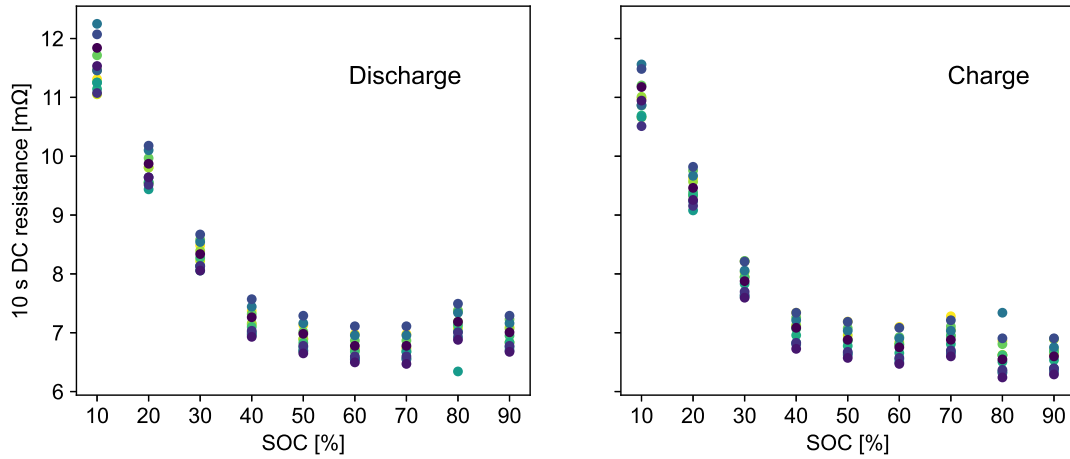


Figure 6.2: 10 s DC resistances as a function of SOC and charge/discharge direction measured for each cell in the HPPC tests.

6.5.2 SOC divergence and reversible Li plating in cells under a thermal gradient

The local current density is a key factor influencing the Li plating propensity. While the current distributions were not directly measured in the experiments on parallel-connected cells in this study, the SOC difference after the fast charge can be determined from the individual discharge curves. Figure 6.3 shows the voltage curves obtained from the individual discharge of the cells following a fast charge in parallel connection. It is clear that the cells that were warmer during the fast charge were charged to substantially higher SOC, with the difference increasing from 6.9% at the mean temperature of 25°C to 9.2% at 0°C.

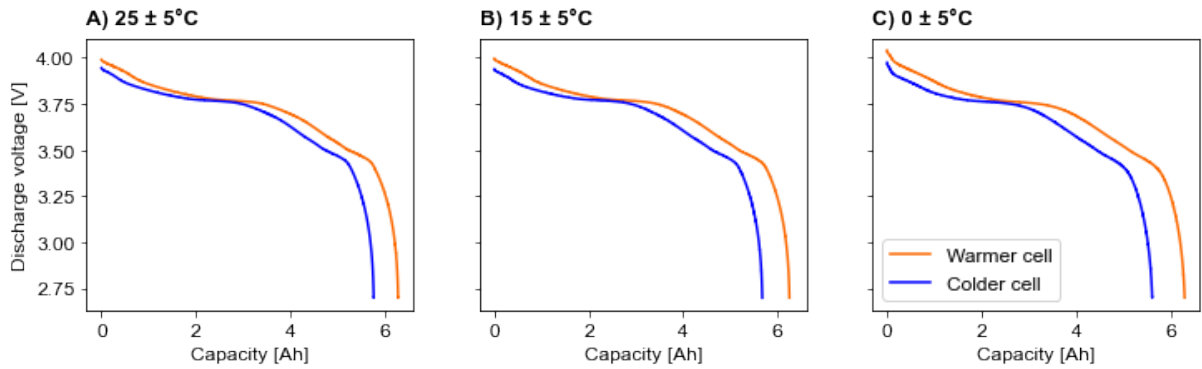


Figure 6.3: Discharge voltage curves of the cells discharged individually following a fast charge in parallel connection.

Table 6.2: Measured SOC differences between cells fast charged with a 10°C thermal gradient.

Mean temperature [°C]	Colder cell discharge capacity [Ah]	Warmer cell discharge capacity [Ah]	SOC difference [%]
25	5.766	6.282	6.9
15	5.676	6.252	7.7
0	5.615	6.302	9.2

Current distribution in parallel-connected Li-ion battery modules has been studied in some detail. It is a common finding that while the current density initially tends to be higher in the warmer (lower resistance) cells, the OCV gradient eventually becomes high enough to drive the redistribution of the current towards the colder cells due to the fact that parallel-connected branches must maintain the same voltage. While this behaviour is

certainly typical of many Li-ion systems, one should bear in mind that the voltage of the parallel branches is determined by both their OCVs and their overpotentials. Few studies on current distribution in parallel-connected modules have considered fast charging conditions, where the high currents substantially elevate the magnitude of the overpotential. This can limit [267, 268] or entirely prevent the redistribution of current towards the colder (or higher resistance) branches towards the end of a fast charge. Additionally, the set-up of the experiments in this work ensures that a nearly constant 10°C thermal gradient is maintained across the cells, causing a large resistance gradient as well. An existence of a thermal gradient with a fixed direction is typical in practice due to the design of battery surface cooling systems, although its magnitude would be smaller than in the experiments presented here. The large SOC differences observed demonstrate the tendency of fast charging to magnify heterogeneity. Indeed, modelling the same experiment (see Figure 6.4) shows that the current distributions converge to an extent only towards the end of charge, driven by the lower overpotential and high SOC difference. The coldest layers only see a higher local current density compared to the warmest ones when the total current density reduces to very small values in the CV phase. The absolute difference in local current densities at this point is too small to cause the SOC of the colder and warmer layers to equalise. While the uncertainties of the model parameters are too high to confirm that no SOC convergence happens in the experiments, it is clear from the experimental results in Figure 6.3 that the SOC distribution remains heterogeneous up till the end of the fast charges.

The SOC heterogeneity highlights the fact that the prediction of the cell most vulnerable to plating under a thermal gradient is not straightforward. While the diffusion is severely impeded in the colder cell, the warmer one experiences a higher average current density and is charged to a higher SOC. All of these are risk factors for Li plating.

As described previously, ICA and/or DVA may be used to identify reversible plating, while some researchers have pursued these methods for the purpose of quantification as well. Both the $dV.dQ^{-1}$ and $dQ.dV^{-1}$ curves obtained from the individual discharge of the cells fast charged in parallel are presented in Figure 6.5.

Multiple studies have previously shown that ICA/DVA is not infallible at diagnosing plating, particularly when it is not severe over a single cycle. The curves in Figure 6.5 only feature the characteristic stripping extrema for the cells charged at an average temperature

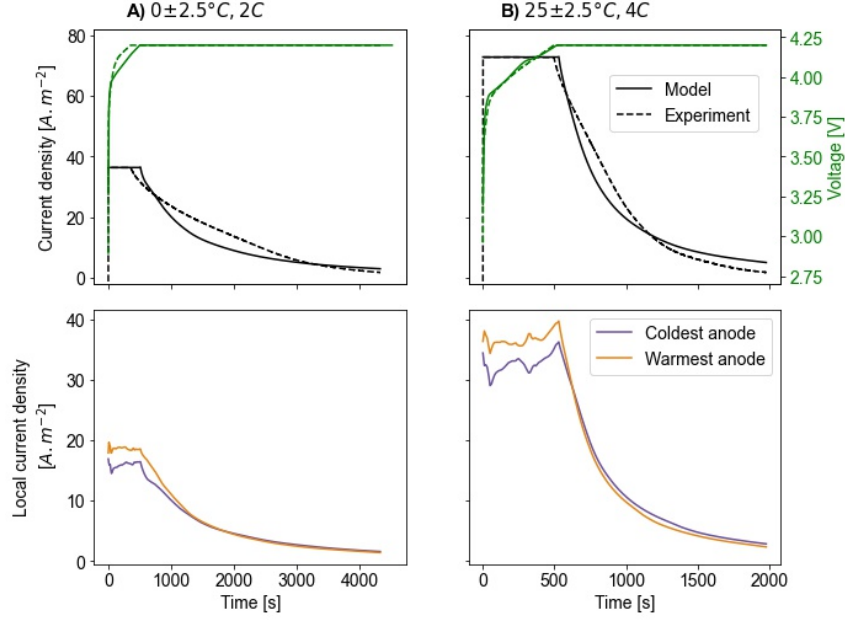


Figure 6.4: Modelled current distributions between cell layers for the conducted experiments.

of 0°C. While this does point to a significant extent of plating at this condition, the absence of the feature at other temperatures does not disprove the occurrence of plating [14].

According to some researchers, the amount of charge passed during the discharge up until the stripping inflection is roughly equal to the charge of the stripped lithium. As discussed previously, the implied assumption that no deintercalation from graphite takes place in that time has not been proven. Recently, Fear et al. [142] proposed a different method to quantify reversible plating based on DVA, which they showed better correlated to the amount of lithium plated as indicated by CE measurements. It should be noted here that these measurements do not necessarily reflect the amount of lithium plated: one reason is that DVA can only detect reversible plating whereas CE is affected only by irreversible plating, as well as many other side reactions. The need to validate with a more accurate lithium quantification technique was acknowledged by the authors [142]. The proposed empirical method relies on a metric they called 'S-factor', defined by the following expression:

$$S = \frac{dV}{dt_s} \times t_s, \quad (6.1)$$

where $\frac{dV}{dt_s}$ is the magnitude of the stripping DVA peak and t_s is the time period between the start of discharge and the peak occurring. The S-factor cannot measure the absolute amount of lithium stripped but was found to be proportional to the coulombic inefficiency

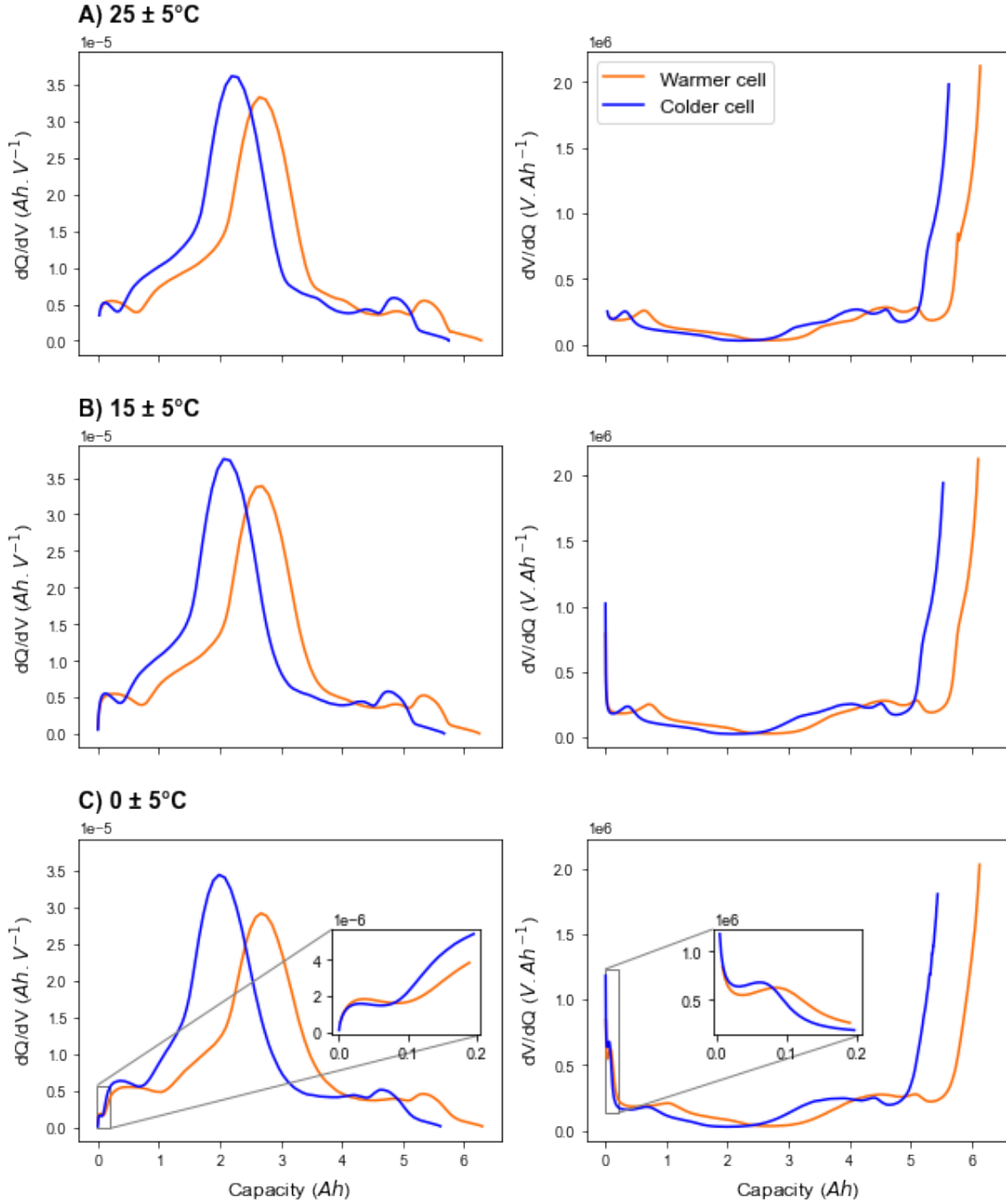


Figure 6.5: IC and DV ($dQ \cdot dV^{-1}$ and $dV \cdot dQ^{-1}$) curves obtained by differentiating the individual discharge voltage curves of cells fast charged in parallel with a thermal gradient of 10°C with a mean temperature of a) 25°C , b) 15°C , c) 0°C .

and correlated well with the plated area observed using optical microscopy, indicating it is possibly also proportional to the stripped amount.

Table 6.3: Estimated amounts (absolute or relative) of lithium stripped following fast charging in parallel in the cells charged at an average temperature of 0°C, quantified using the time period and S-factor methods. Note the accuracy of these techniques has not been comprehensively studied, and the many limitations are discussed below.

Cell	Stripping peak location [mAh]	Stripping peak height [V.Ah ⁻¹]	Absolute amount of Li stripped based on plateau length [mAh]	Relative amount of Li stripped according to the S-factor method [a.u.]
0W	85.7	6.24×10^5	85.7	5.35×10^7
0C	62.6	6.78×10^5	62.6	4.24×10^7

Table 6.3 shows the amounts of stripped lithium in the cells fast charged at 0°C as quantified using both methods. According to the time period method, the amount of Li stripped is 37% higher in the warmer cell than in the colder one. While the distribution indicated by the S-factor method is slightly less heterogeneous with a 26% difference, both methods suggest the warmer cell experienced significantly more Li plating. The caveats to this conclusion are numerous, however. Firstly, DVA can indicate only reversible plating: if the extent of reversibility differs between the cells, the result may not reflect the difference in the total amounts plated. The stripping period is also affected by the stripping rate, which is likely not equal. The standard time period method ignores this fact by assuming all current can be attributed to stripping up until the stripping inflection. While the stripping rates under discharge have not been thoroughly studied, Yang et al. have shown that during rest the rates of stripping and reintercalation are limited by the rate of diffusion in the underlying graphite [86] which is about an order of magnitude faster for dilute stages compared to the highly lithiated stages. Fear et al. [142] have argued that, as a consequence, the conditions that lead to more heterogeneous lithiation, such as charging at high C-rates and/or lower temperatures, should lead to a higher stripping rate and therefore an earlier occurrence of the stripping inflection. The S-factor method attempts to solve this problem by taking into account the height of the peak but it remains an approximate empirical correlation which requires further validation. Finally, measurement error could not be avoided in the design of the experiment: since the thermal gradient must be removed between the fast charge and the discharge, a

thermal equilibration time of 6 minutes was allowed. During that time, part of the plated lithium may have reintercalated into the graphite. Taking these facts into account, DVA may not be accurate as a quantification technique.

6.5.3 Diagnosing degradation and degradation heterogeneity

Degradation trends

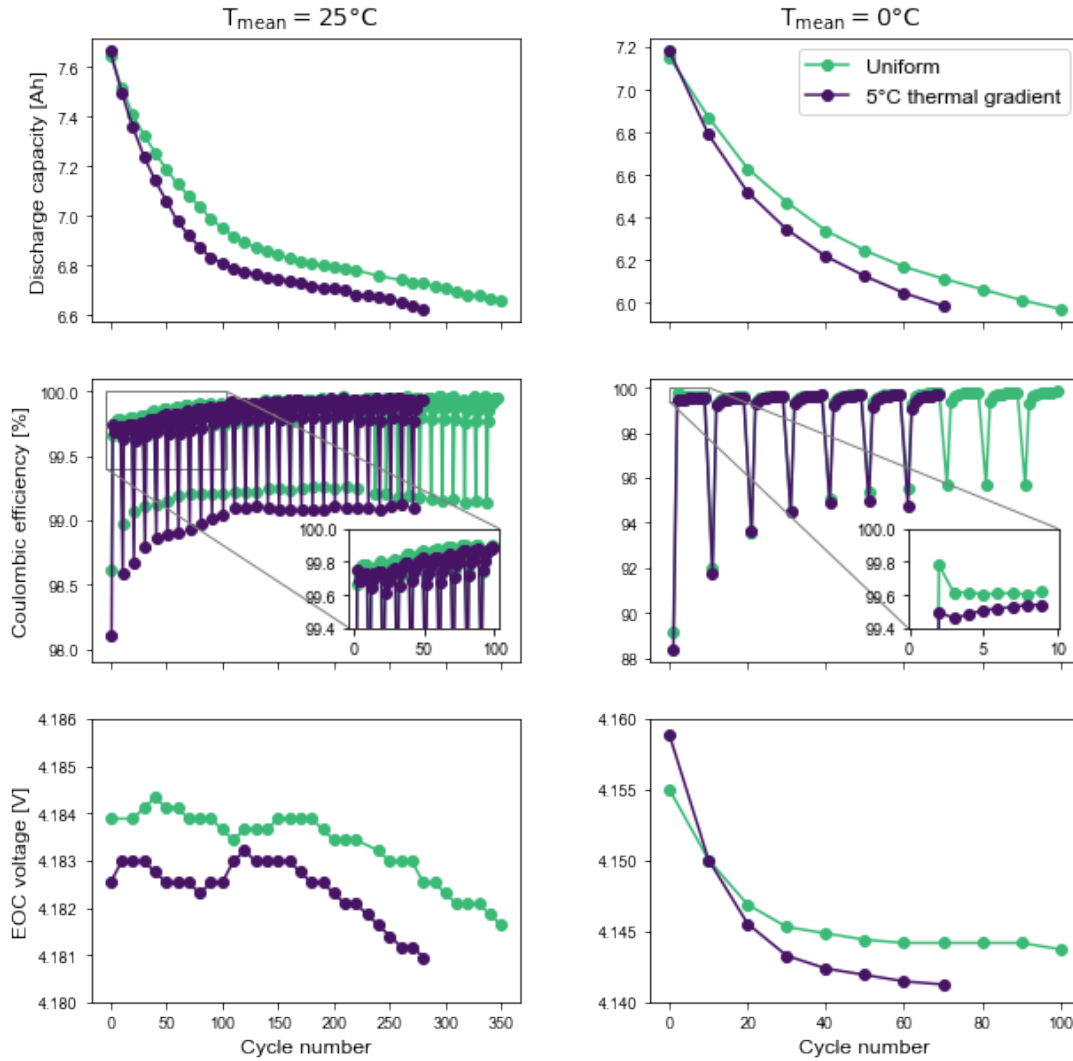


Figure 6.6: Results of long-term cycling experiments with different mean cell temperatures. a-b) Capacity fade, c-d) Coulombic efficiency, e-f) End-of-charge voltage.

The second set of experiments, involving longer-term cycling of individual cells, allows for further investigation of the effect of thermal gradients on both Li plating and capacity fade. Figure 6.6 shows the capacity fade, Coulombic efficiency and end-of-charge (EOC) voltage trends for the cells cycled with a mean temperature of 0°C and 25°C with or

without a 5°C through-plane thermal gradient. The EOC voltage is the voltage measurements taken 15 minutes after a fast charge. Tanim et al. [228] has recently proposed this as a simplified metric capturing the high voltage plateau associated with Li stripping. Other works suggest Li plating may reduce cell impedance, which could also be captured through a higher rest voltage[146, 147]. The EOC voltage measurement should not be relied on to identify plating on its own: after 15 minutes, both thermal and concentration gradients may still be present within the cell, either of which could also give rise to a higher voltage measurement [14]. On the other hand, a resting period long enough for these gradients to relax may also allow for all reversibly plated Li to intercalate, at which point the raised voltage would no longer be observed. In this work, a combination of signals including CE, EOC voltage, capacity fade trends and discharge voltage curves are analysed to improve identification reliability. While both cells tested at 0°C were cycled to the end of life, defined as 80% rated capacity retention, the 25°C tests were terminated before this point due to the slow rate of capacity fade.

Notably, the presence of a thermal gradient leads to increased capacity fade at both mean temperatures. For the cells cycled at 25°C, two degradation regimes can be observed: up to about 120 cycles for the thermally uniform case and 100 cycles for the thermal gradient case, the capacity fade proceeds relatively quickly, while the CE edges slowly increases with cycling. Note that the drop in the CE values every 10 cycles is caused by the higher capacity charged in the preceding characterisation cycle. During this cycling period, the EOC voltage remains stable. In the later cycling period, a marked decrease in the rate of capacity fade is observed as the CE stabilises at relatively high values of over 99.8%. The EOC voltage starts decreasing with every characterisation cycle, however the magnitude of the decrease is close to the 1 mV precision limit of the cycler. In this period, the rate of capacity fade and the CE become similar irrespective of the presence of a thermal gradient. The observed rates of capacity fade and CE values, when compared with the literature, suggest relatively slow degradation with no clear sign of Li plating. The cells retain about 88% of rated capacity after 290 cycles when aged with a thermal gradient, or 350 cycles without. The EOC voltage does not rise with cycling as observed in plated cells by Tanim et al. [228], although it's worth noting that this value would not be expected to increase if plating takes place from the very early cycles. Nonetheless, the existence of two distinct capacity fade regimes suggests a likely change

in the dominant degradation mechanism. The latter, slower degradation regime is likely dominated by SEI growth: in addition to the mild capacity fade, the reduction in the EOC voltage with cycling can be attributed to an increase in the internal resistance. The faster fade in the earlier cycles could be caused by plating or particle cracking. Both these mechanisms could be counteracting the SEI-caused drop in the EOC voltage, either due to Li stripping or a reduction in the effective particle size. The latter seems less likely as any newly exposed electrode surfaces should soon be passivated, leading to an increase in resistance and a lower EOC voltage. During this early period of cycling, the capacity fade of the cell cycled under a thermal gradient is markedly faster compared to the uniform cell.

The cells cycled at the mean temperature of 0°C lose capacity at a much higher rate, despite the lower charging rate of 2C. The rate of fade is higher for the cell cycled under a thermal gradient, which reaches 20% fade after only 70 cycles compared to 100 cycles for the thermally uniform cell. It should be noted that these capacities, measured at the cycling temperature of 0°C, are not directly comparable to the 25°C results. The CE is slightly higher for the uniform cell in the early cycles, before both cells stabilise at about 99.6% (ignoring the lower CE values immediately after each characterisation cycle). The EOC voltage decreases in the first 30 cycles and then stabilises for the uniform cell while the rate of the decrease reduces for the cell cycled under a gradient. At this temperature, the higher rate of fade may be indicative of Li plating.

The EOC voltage is measured at a single point in time - in this case 15 minutes after a fast charge - and may not capture the effect of the reintercalation of plated Li if the voltage plateau associated with this process ends earlier. The cell voltages throughout the entire 15 minute rest period after each characterisation cycle fast charge are therefore also evaluated in Figure 6.7. The voltage drop during this period is slightly larger for cell 25G than for cell 25U. It is also larger for cell 0G than for 0U, except for the first cycle. This could be either due to the higher resistance of the cells cycled under a thermal gradient, or due to their lower capacity utilisation. No voltage plateau is observed for any of the cells. If reintercalation does take place, its rate appears too small to be detected.

As mentioned previously, the thermal gradient was not removed during discharge steps for cells 25G and 0G. To confirm that the increased degradation is indeed driven by the presence of the thermal gradient during charge and not discharge, the 0°C thermal gradient

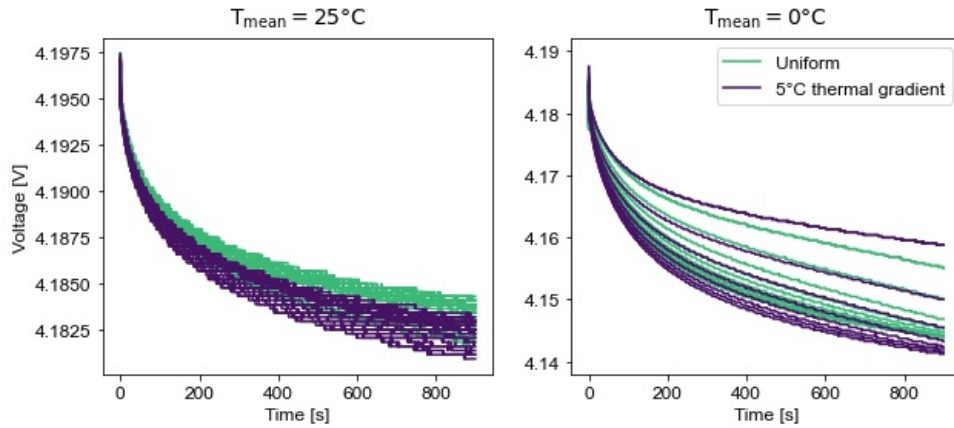


Figure 6.7: Cell voltages during the 15 minute rest after each characterisation cycle fast charge (every 10th cycle). No voltage plateaus indicative of Li reintercalation can be observed.

experiment was repeated with the gradient applied only during the fast charge steps. Additional 5 minute rest periods were introduced between each charge and discharge for this test to allow time for thermal equilibration. A comparison of the capacity fade trend for the three testing conditions (thermally uniform, 5°C thermal gradient during both charge and discharge, and 5°C gradient only during charge) is shown in Figure 6.8.

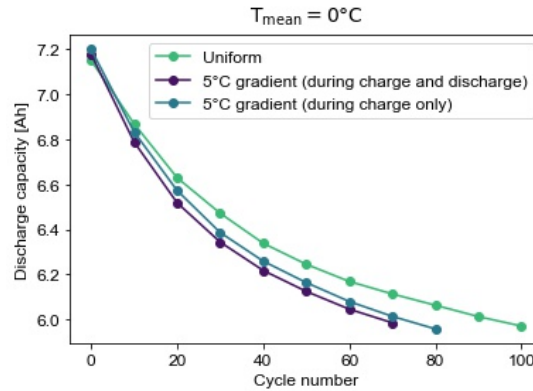


Figure 6.8: The capacity fade in the cells cycled at the mean temperature of 0°C. The presence of the thermal gradient during the discharge seems to have a minor effect compared to its presence during the fast charge.

The cell cycled with a thermal gradient imposed only during the charging steps did show a slightly lower rate of capacity fade compared to cell 0G, but still significantly higher compared to cell 0U. The difference between the two cells cycled with a thermal gradient is small, and may be due to both the absence of the gradient during discharge and the additional rest steps after each fast charge allowing more of the plated lithium to intercalate into the anode. Despite these additional rest periods, the capacity fade is still

clearly accelerated compared to the thermally uniform case. This supports the hypothesis that most of the increased degradation is caused by the presence of the thermal gradient during the charge rather than during the discharge.

DV and IC analysis

The evolution of $dQ.dV^{-1}$ and $dV.dQ^{-1}$ curves, shown in Figure 6.9, provides further information about the dominant degradation mechanisms in each case. Note that the curves are plotted only for every other characterisation cycle in case of the 25°C cells to avoid overcrowding the plots. The data for some of the characterisation cycles (cycles 230 and 240 for cell 25U and cycle 60 for cell 0U) was lost due to a data corruption issue. The first 5 data points (0.5 s) and last 10 points (1 s) of the data is truncated for the $dV.dQ^{-1}$ curves at 25°C; in case of the 0°C cells, the first 15 data points (1.5 s) and the last 10 points (1 s) are truncated. This is to improve the visibility of the features in the middle portion of the curves as well as to avoid computation errors. The $dV.dQ^{-1}$ curve is the inverse of the $dQ.dV^{-1}$; as the latter approaches zero at the beginning and end of discharge, the former approaches infinity. The peaks were ascribed to the individual electrodes (A - anode, C - cathode) based on the half-cell curves available from [130].

There is a stark difference between the curves obtained at 25°C and 0°C: while in the former case, most peaks are relatively sharp, in the latter the peaks are less numerous, wider and shallower. For the cells cycled at 25°C, the change in the rates of capacity fade is clearly reflected in the $dQ.dV^{-1}$ and $dV.dQ^{-1}$, with the majority of the change seen in the first 100-120 cycles. For the later cycles, the curves nearly overlap. The degradation for both cell 25U and 25G appears LLI-dominated, with the endpoints of the curves progressing towards lower capacities with little change in the location of the peaks relative to each other. Peak C2 moves slightly closer to peak C1 over the cell lifetimes, indicating some LAM in the cathode. Estimation of LAM in the anode is not possible, as peak A1 quickly reduces in size and becomes unidentifiable, while peaks A2 and A3 disappear as a result of LLI. As the cells age, an additional shoulder is revealed to the right hand side of peak C2 due to the shift in its position. Overall, the peaks become broader and shallower, which may indicate heterogeneous degradation. This behaviour is observed for both cells; no difference in the degradation heterogeneity is evident from either the $dQ.dV^{-1}$ or $dV.dQ^{-1}$ curves.

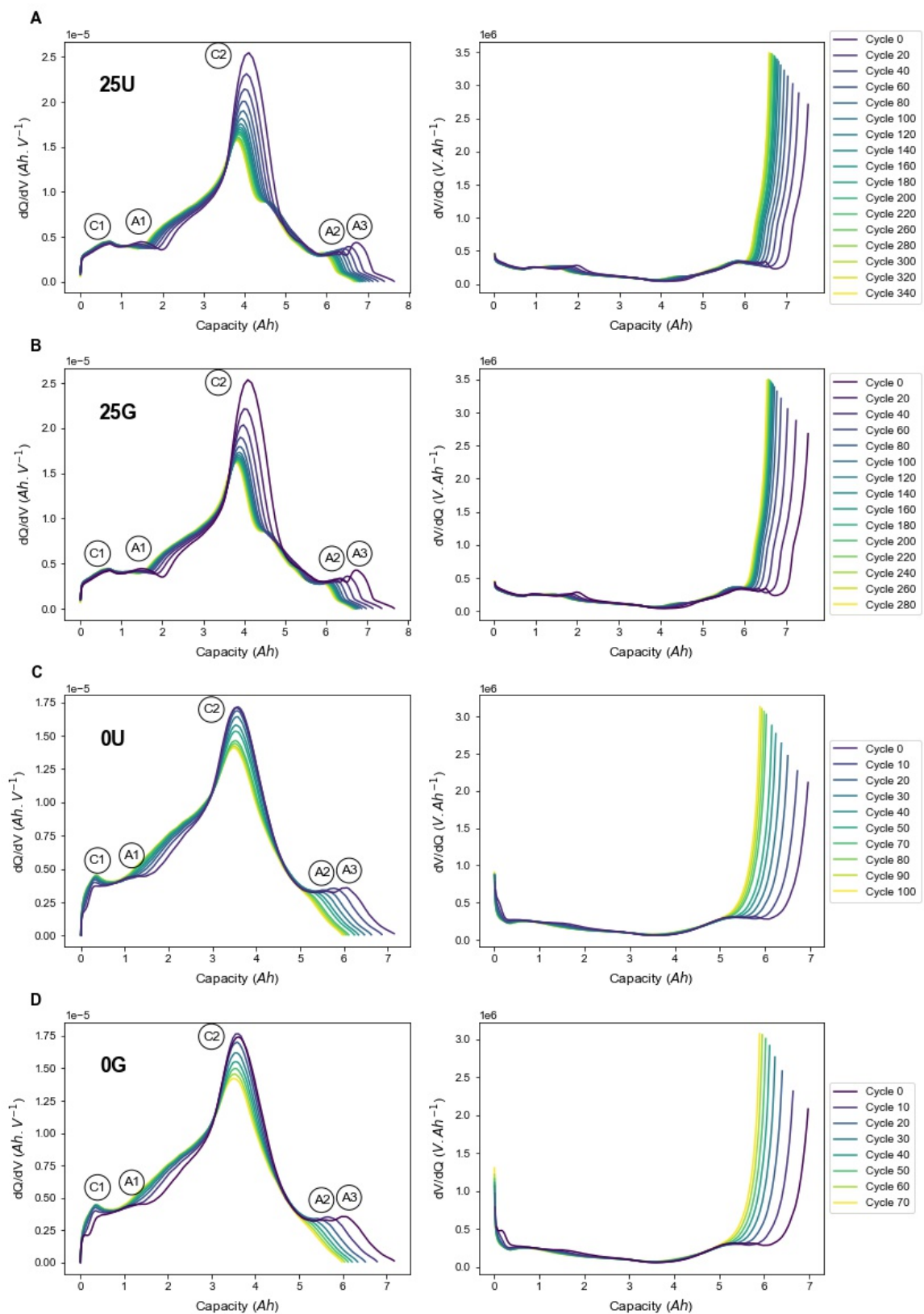


Figure 6.9: IC and DV ($dQ.dV^{-1}$ and $dV.dQ^{-1}$) discharge curves for the cycled cells. a) Cell 25U, b) Cell 25G, c) Cell 0U, d) Cell 0G.

Both cells cycled at 0°C exhibit flattened, wide $dQ.dV^{-1}$ peaks from early in life. This is likely due to both the lower measurement temperature, and the high concentration gradients caused by the fast charge preceding the slow discharge. Interestingly, despite the higher C/10 discharge rate, the voltage plateau associated with Li stripping can be observed as an IC/DV inflection in cycle 0 (initial characterisation after a single fast charge) and cycle 10 in both cases. Only in cycle 0 of test 0G is the effect strong enough to exhibit as a $dV.dQ^{-1}$ peak, however. While it seems plausible that cell 0G is experiencing more plating than cell 0U due to the stronger effect on the former’s voltage curve, in the absence of the DVA peak for cell 0U it is not possible to quantify the difference. The inflection becomes less pronounced from cycle 0 to cycle 10, and completely disappears in the later cycles for both cells. The degradation at this temperature also appears to be LLI-dominated. The location of peaks C1 and C2 relative to each other remains stable over the cells’ lifetimes, indicating very little or no LAM in the cathode. LAM in the anode cannot be diagnosed, as the broadening of peak C2 leads to the disappearance of peak A1 after cycle 0. Peaks A2 and A3 also become unidentifiable after cycle 0 and 30, respectively, due to the progression of LLI and the resulting reduction in the discharge capacity. For both cells 0G and 0U, the peaks gradually become shallower, indicating degradation heterogeneity; once again, no clear difference in the degradation heterogeneity is indicated by the DV or IC analysis.

Post-mortem examination

Following the cycling experiments, cells 0G, 25G and 25U were disassembled in a glovebox for further examination. The exception was cell 0U. After two weeks of storage in a thermal chamber at 25°C, the cell unexpectedly swelled. Transfer into the glovebox was at this stage deemed unsafe and the cell had to be disposed of. The spontaneous gas generation during rest may have been caused by the plated Li. A delayed onset of gassing and thermal runaway within a similar timeframe has been reported in plated cells [97].

Figure 6.10 shows the anodes collected from the cycled cells, arranged in order. The coldest and warmest anodes of each cell are shown in more detail in Figure 6.11. The appearance of the anodes cycled at 0°C and 25°C is markedly different. The anode of the low temperature cell appears golden in Figure 6.10, which suggests high lithiation near the surface despite the cell having been discharged and held at 2.7 V for three hours

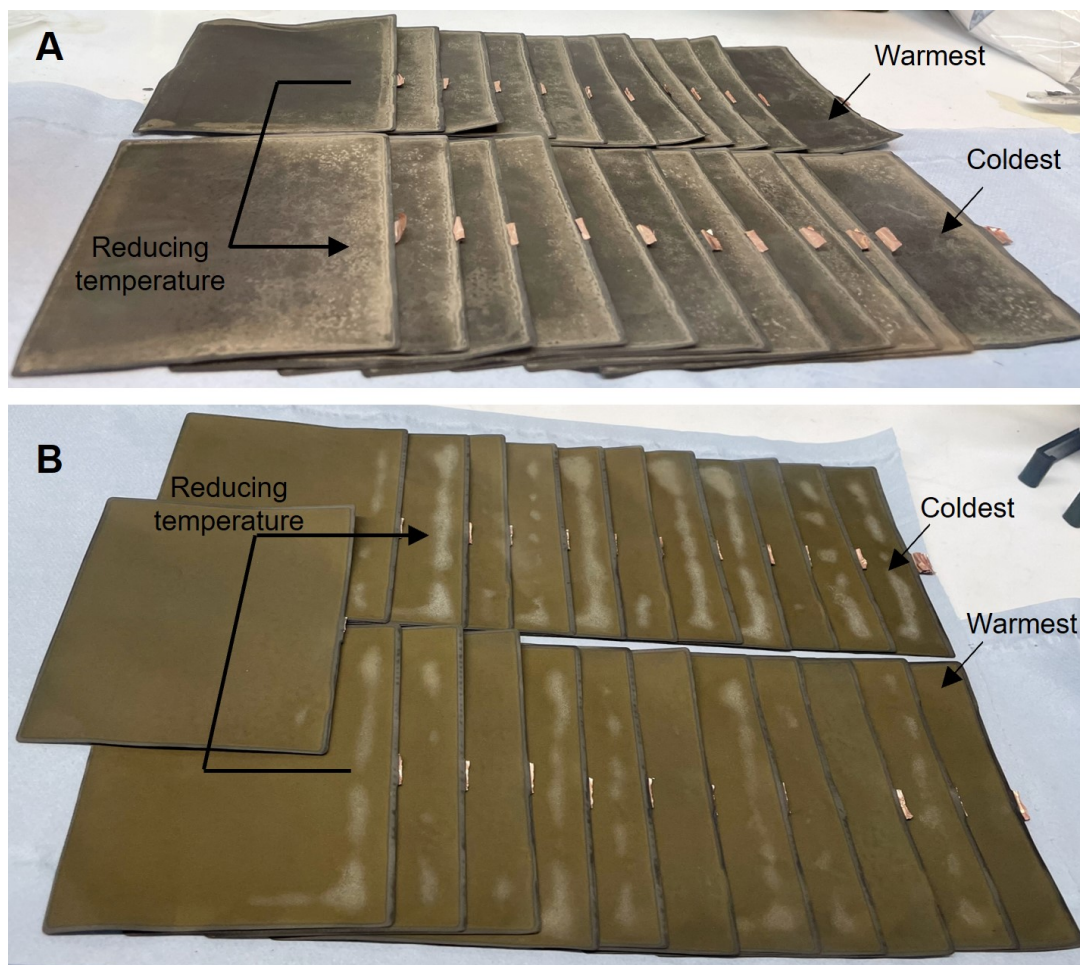


Figure 6.10: Anodes harvested from the cycled cells: a) cell 25G, b) cell 0G

before disassembly. Under most circumstances, the anode surface would be expected to have the lowest state of lithiation immediately after a discharge, making this observation rather surprising. Interestingly, recent XRD experiments by Finegan et al. [223] have revealed that the presence of plated lithium may lead the surrounding graphite to remain in Stage I (LiC_6) even after a complete discharge. The golden colour partially subsided after 10 days in storage in the glovebox (see Figure 6.11). The controlled atmosphere of the glovebox should largely prevent oxidation; as such, the change of colour may be due to the concentration-driven redistribution of lithium from the surface towards the bulk of the anode. Near the cell tabs, regions of white hue are visible to the naked eye. The layers of the cell were held together by four glue spots: these inactive regions are seen as black circles near the corners of one side of each anode in Figure 6.11. The glue spots are also encircled with white-coloured deposits. The encircling was seen throughout each cell, but was generally fainter for the glue spots further from the tabs. Across the cell layers, the

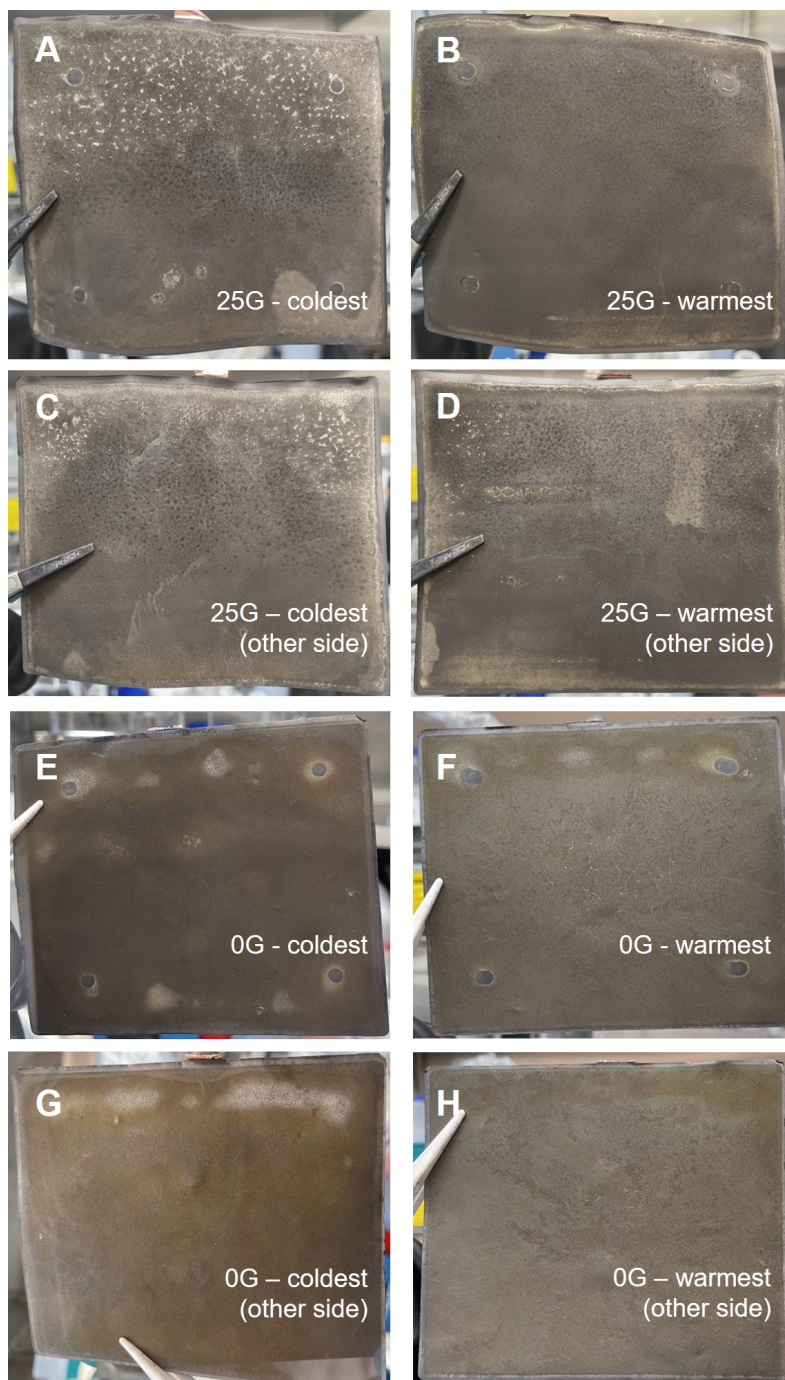


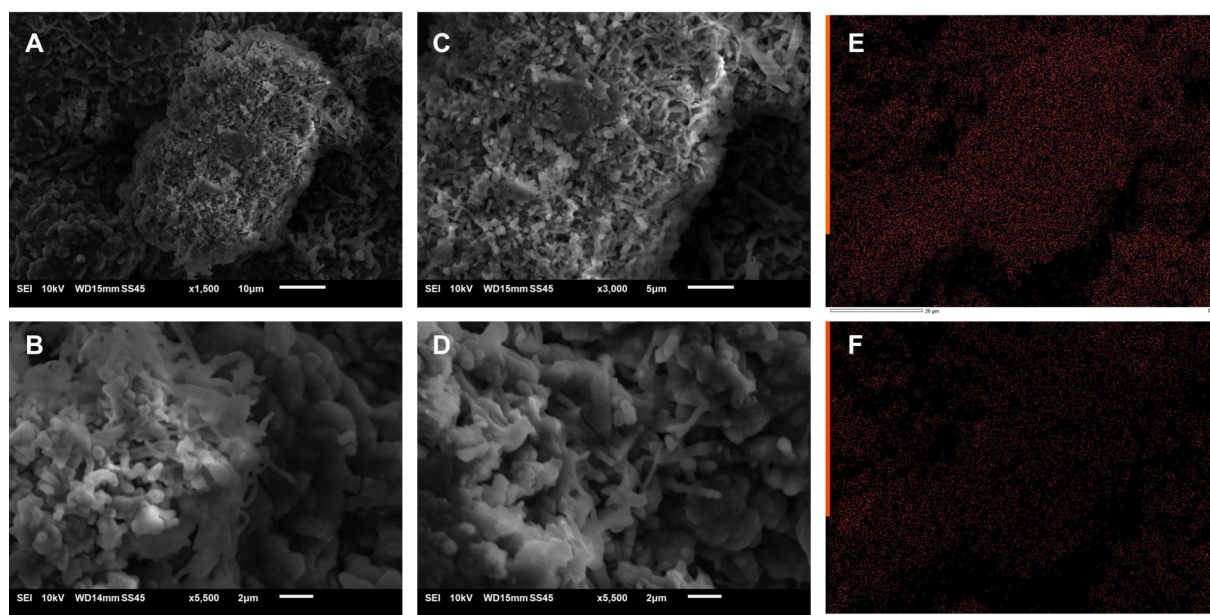
Figure 6.11: Close-up photos of both sides of coldest and warmest anode sheets of each cell.

areal coverage of the deposits appears to increase in the direction opposite to the thermal gradient, i.e. from the warmer to the colder layers. The colouring of the anodes harvested from both 25°C cells is more varied: most of the area appears dark grey, as expected of delithiated graphite. A silver border is seen along much of the overhang of most anodes. Deposition at this location is typical of Li plating. Numerous silver spots can also be seen over about one to two-thirds of the area of most anodes. The areas far from both the tabs

and the overhang appear less affected by the deposits. In addition, numerous darker spots are also noticeable. Again, the areal coverage of the deposits appears to increase from the warmer to the colder cell layers. Both the white hue observed on the anodes of the the 0°C cell and the silver deposits in the 25°C cell are indicative of plating. To confirm this, as well as to investigate the reason for the difference in the macroscopic appearance, samples of the affected regions were collected and studied using SEM.

The SEM images obtained from the visibly plated regions near the tabs of each cell cycled under a thermal gradient (cells 0G and 25G) are shown in Figures 6.12 and 6.13. The images reveal substantial variations in the plating morphology, both between the cells and within each cell. In the 0°C cell, dendritic deposits were found throughout the tested samples, albeit their structure differed between the layers. The coldest layer featured predominantly bean-shaped bundles of densely entangled, elongated deposits, a few tens of microns across. This suggests localised deposition, where lithium continued to plate preferentially on top of the nucleates that formed early on in the cycling. On the warmest anode, similar collections of dendrites were not observed. Instead, many of the deposits assumed a flake shape, with some long thin needles dispersed elsewhere. Of course, given the localised nature of SEM examination, it is possible that such deposits existed in areas that were not tested. However, the differences may be caused by the lower diffusion rates in the colder layers favouring a more dendritic, localised deposition, while the better transport rates in the warmer layers enable a more uniform, dispersed nucleation. Cell 25G provides further, and perhaps stronger, support for this explanation. At the low magnification of 150x-300x, a cracked surface can be seen for both the warmest and the coldest anode. However, the surface of the warmest anode appears smoother and more even, while the coldest one features numerous protrusions. At higher magnifications, the difference becomes clearer. The coldest anode features numerous flake-like deposits, interconnected with needles, with some smoother surfaces. The warmest anode, on the contrary, presents predominantly a smooth, even plate of dense deposition, with some bead-shaped protrusions. In places, more ragged deposits can also be seen. Overall, the deposition appears far more uniform on the warmer anode. The SEM images reveal substantial deposition in both cells, both in the warmest and coldest anodes. While the differences in the deposition morphology are noticeable, it is not clear whether the plating is more concentrated in some samples than others. Away from the tabs, in the regions

Cell 0G – coldest anode



Cell 0G – warmest anode

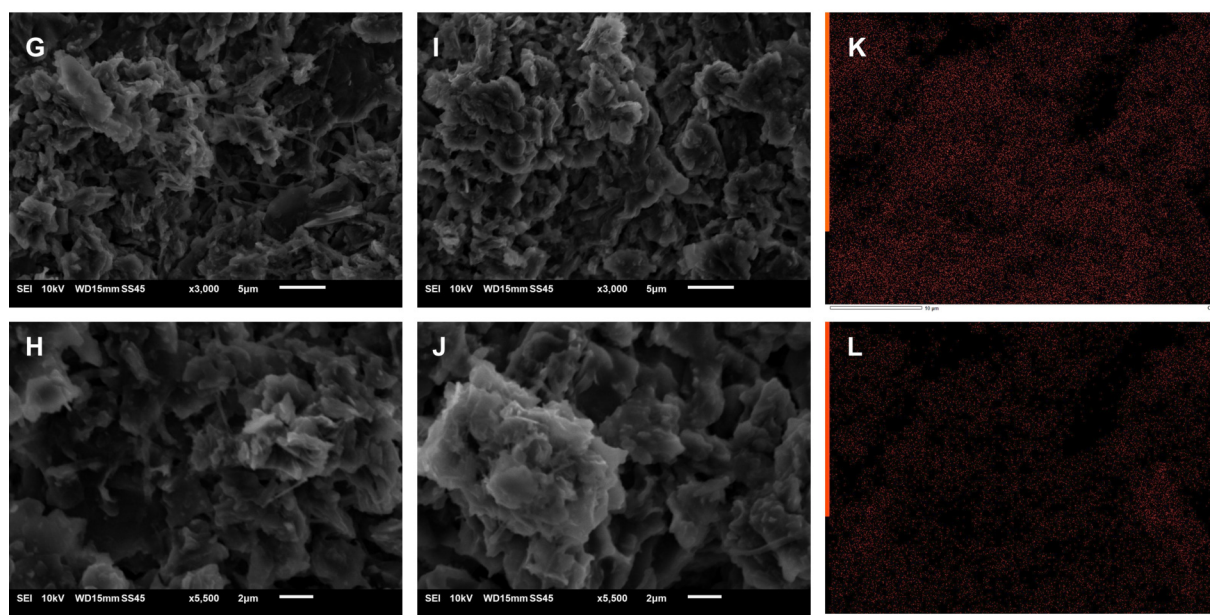
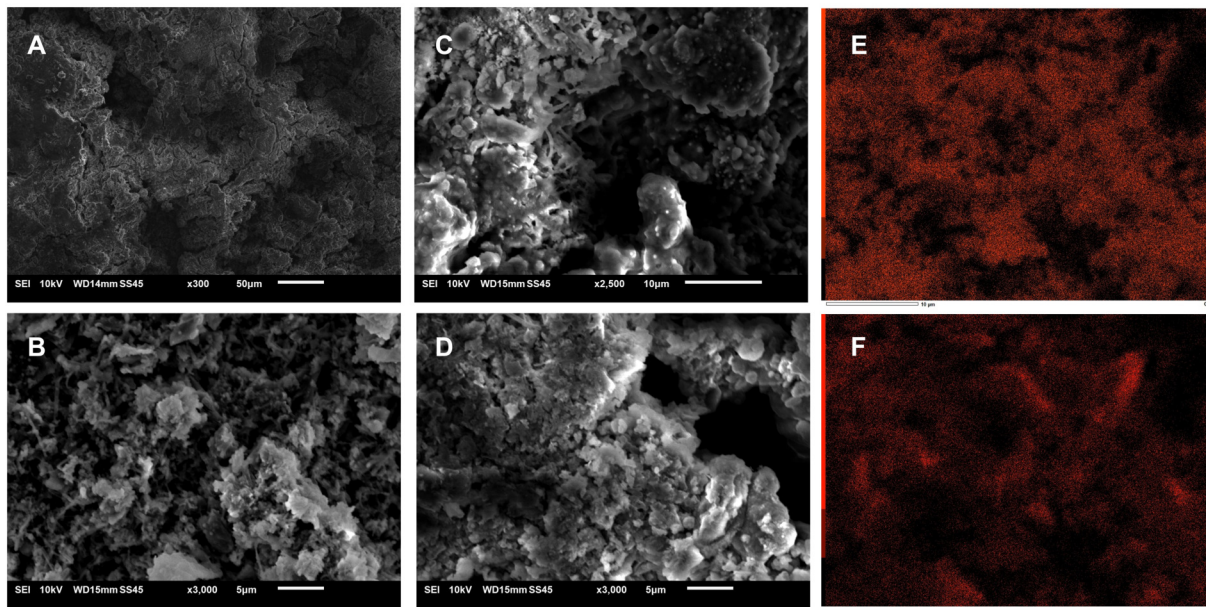


Figure 6.12: SEM images of the the visibly plated regions of the anodes collected from cell 0G. a-d) Dendritic deposits from different regions of the colder anode sample. e) EDS image of the oxygen distribution, which typically indicates oxidised Li. f) EDS image of the carbon distribution. g-j) Dendritic deposits are also present, but more dispersed, on the warmer anode sample. e) EDS image of the oxygen distribution. f) EDS image of the carbon distribution. Note the settings for the EDS were different here compared to the later figures (spot size of 60 rather than 45), which resulted in a lower signal intensity.

Cell 25G – coldest anode



Cell 25G – warmest anode

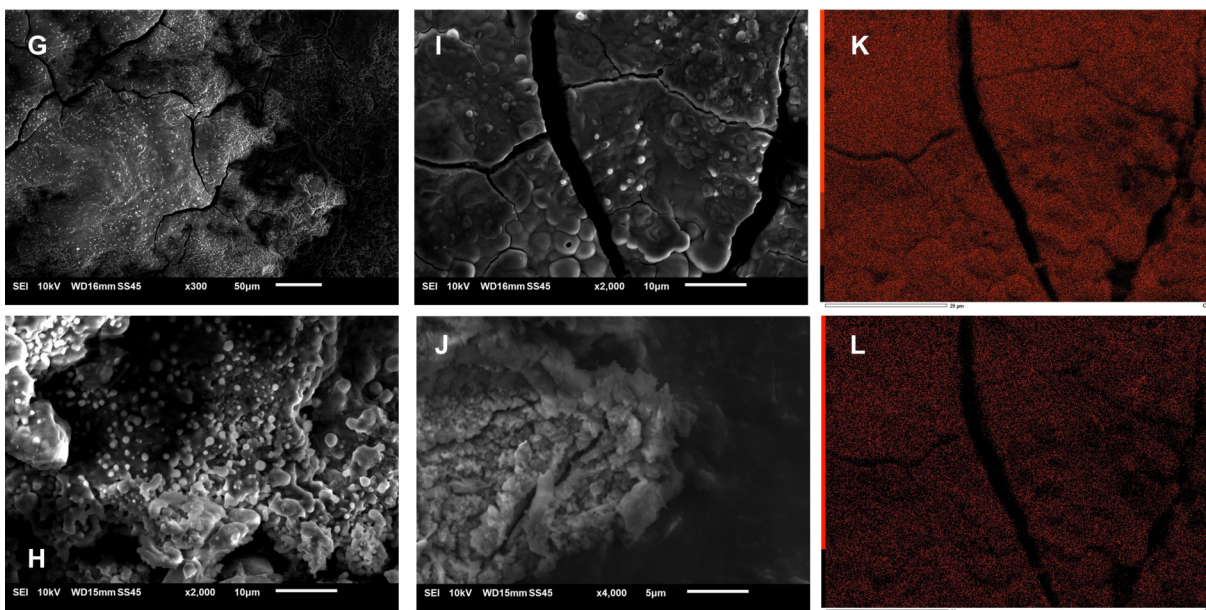


Figure 6.13: SEM images of the the visibly plated regions of the anodes collected from cell 25G. a-d) Flake-like and dendritic deposits from different regions of the colder anode sample. e) EDS image of the oxygen distribution. f) EDS image of the carbon distribution. g-j) On the warmer anode sample, smooth, uniform deposits dominate. e) EDS image of the oxygen distribution. f) EDS image of the carbon distribution.

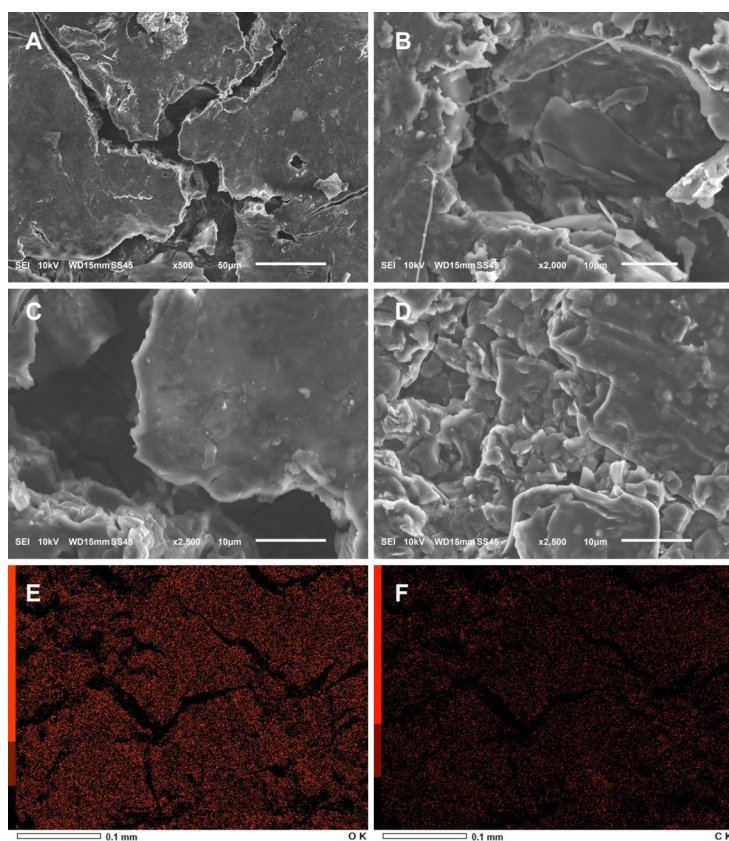


Figure 6.14: SEM images of the the visibly plated regions of the anodes collected from cell 25U. a-d) The anode is covered mostly with smooth, uniform deposition layers, many of which have cracks. e) EDS image of the oxygen distribution. f) EDS image of the carbon distribution.

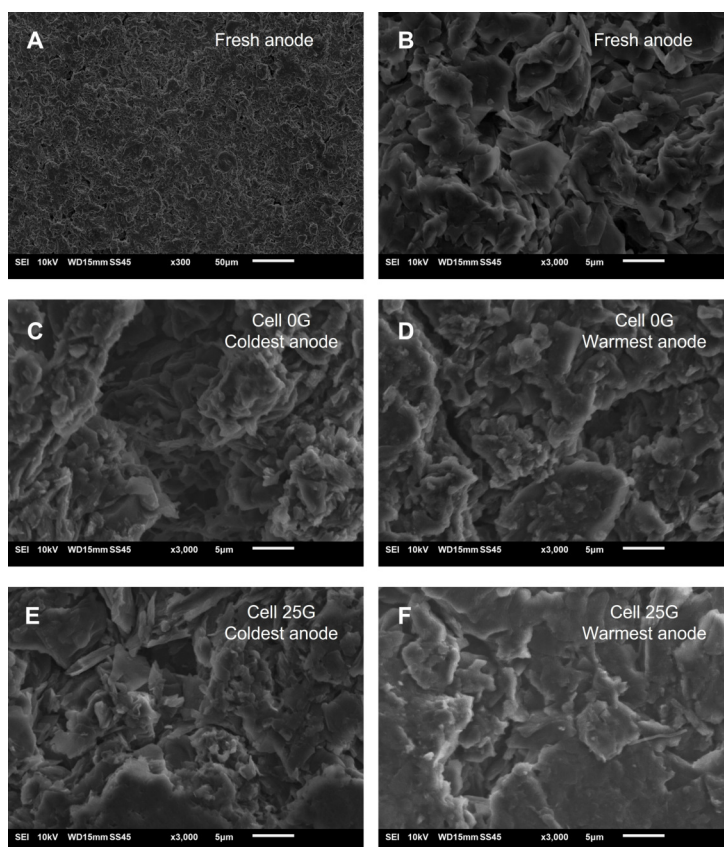


Figure 6.15: SEM images of a fresh anode and the regions of the anodes of cells 0G and 25G that did not appear plated to the naked eye. a-b) Fresh anode, c-d) cell 0G, e-f) cell 25G.

that did not appear plated on visual inspection, the microscopic signs of plating are also not as obvious (see Figure 6.15). Compared to a fresh anode sample, it is clear the anodes of both cells are covered with thicker layers of SEI. Some smooth, uniform plating can be seen on the warmest anode of cell 25G, however it appears Li deposition is relatively scarce compared to the regions closer to the tabs.

Figure 6.14 shows the SEM images collected from the region near the tabs of an outermost anode of the thermally uniform cell 25U (as mentioned previously, cell 0U could not be disassembled). The plating morphology appears similar to that of the warmer side of cell 25G, with uniform, smooth deposition layers with many cracks. Some needle-shaped structures can be noticed in Figure 6.14b). Looking closely at Figure 6.14a) and c), further smooth deposition layers are also visible in between the cracks of the top layer. In this cell, too, the areal coverage of Li plating is substantial, but it is not possible to compare the amount to that seen in cell 25G based on the images alone.

6.5.4 Quantifying local plating with gas chromatography

Contributions from partially lithiated graphite

Similarly to metallic Li, lithiated graphite is a strong reducing agent. As a consequence, its reaction with water also produces hydrogen. The contributions to the hydrogen peak from the partially lithiated graphite must therefore be assessed. Figure 6.16 shows the relationship between the extent of lithiation of the graphite and the hydrogen peak area measured in the TGC experiments. The detected Li concentration was computed based on the calibration curve obtained in Chapter 4 (Figure 4.5).

TGC of the fully lithiated anode sample results in a hydrogen peak of 223 a.u./mg, corresponding to a lithium content of 57.1 μg per 1 mg of the anode material. Pure LiC_6 contains up to 88.6 μg of lithium per milligram. The volumetric fraction of the active material in the anode of the Kokam SLPB75106100 was quantified by Ecker et al. [16] to be 0.555, however the mass fraction is not known. The TGC result seems reasonable in comparison to these numbers. Such a high number, in combination with the linear relationship between the graphite SOC and the peak area, also indicates that nearly all lithium is removed from the graphite on contact with water. There is some indication that the graphite may become stable in water at states of lithiation below 5%, as the hydrogen peak produced by the 0% and 5% samples has nearly the same area. However,

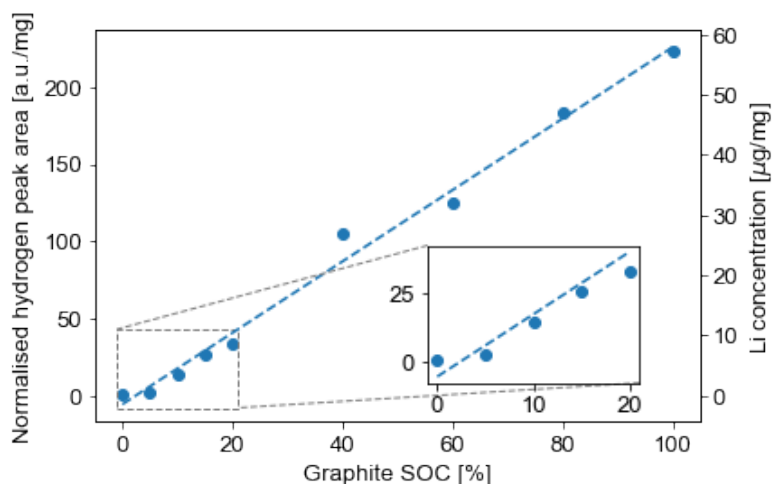


Figure 6.16: Hydrogen peak area (normalised to the sample weight) is nearly directly proportional to the extent of lithiation of the graphite.

further testing would be needed to verify this.

DV and IC analysis of the cell used in the experiments presented here previously revealed that the anode is nearly fully delithiated at 0% fresh full-cell SOC [130]. However, an aged anode is likely to contain some lithium in the graphite particles that became electrically disconnected due to the repeated swelling and contraction during cycling. Unfortunately, the poor identifiability of the anode peaks in the IC and DV spectra of the cells has made quantitative diagnosis of anode LAM impossible for the cells studied here. The SEM images presented in Figures 6.12 and 6.13 indicate cracking in the deposition layers, with the anode particles largely invisible beneath them. The golden appearance of cell 0G (see Figure 6.10) immediately after disassembly indicates high states of lithiation close to the surface, but the concentration gradient appeared to have dispersed during storage in the glovebox (Figure 6.11), indicating the state of lithiation of the bulk of the anode was much lower. It is nonetheless clear that the amount of Li quantified in the TGC experiments contains some contributions from incompletely delithated graphite. To further differentiate between the metallic Li and partially lithiated graphite, an additional analysis method that can distinguish between lithium phases, such as NMR, would be required. Such a method was unfortunately not available for this study.

Plating distribution in cycled cells

The cells cycled under a thermal gradient (cells 0G and 25G) were tested for Li plating distribution using TGC. The method is suitable only for small samples, in the range of

a few milligrams of the anode material, while each run of the test is time-consuming at about 18 minutes. As such, the testing was limited to 16 samples per cell. Four samples were collected by scraping off a 2.5 cm x 2.5 cm area from each corner of the coldest and warmest anodes, as well as from the third coldest and the third warmest anode. In each case, the side of the anode without the glue spots was used to avoid introducing additional chemical species.

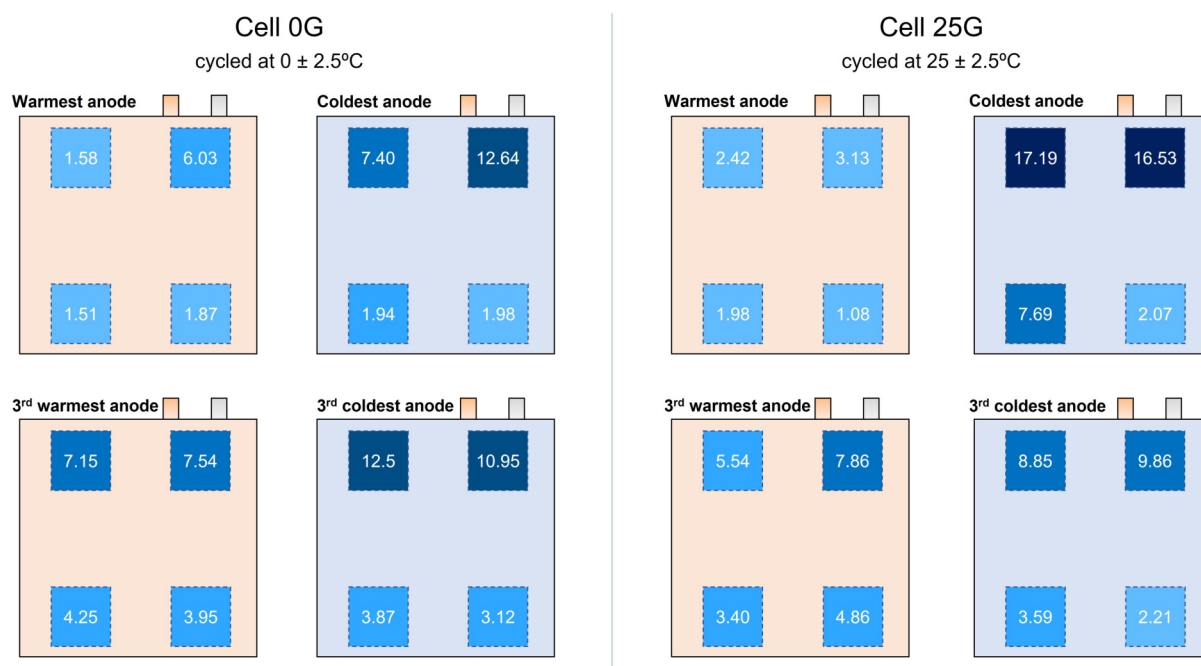


Figure 6.17: Results of the TGC measurements on samples of anode material harvested from the cells cycled under a thermal gradient.

Figure 6.17 shows the results of the TGC experiments. The concentrations of plating detected largely confirm the earlier macroscopic observations. The colder layers of each cell are confirmed to contain significantly more Li, with a particularly high concentration near the current collector tabs. The plating is more heterogeneous in cell 25G, with about $17 \mu\text{g}$ of Li detected per 1 mg of the tested material near the tabs in the coldest layer, and only about $3 \mu\text{g}$ in the warmest layer. In comparison, about $7\text{--}13 \mu\text{g}/\text{mg}$ were found near the tabs of the coldest anode of cell 0G, with $2\text{--}6 \mu\text{g}/\text{mg}$ near the tabs of the warmest layer. The calibration curve used to calculate the amount of plated Li, presented in Chapter 4, displayed an RMSE of $10 \mu\text{g}$ of Li for pure Li samples of up to 0.5 mg, that is about 2% in relative terms. As such, the differences in the amounts of plating detected in different samples are clearly significant with respect to error. The amount of lithium plated is confirmed to decrease with increasing layer temperature within each cell.

Surprisingly, the average concentration of Li detected in cell 25G is slightly higher at 6.14 $\mu\text{g}/\text{mg}$ compared to 5.52 $\mu\text{g}/\text{mg}$ detected in cell 0G, despite the much slower capacity fade exhibited by the former during the cycling tests. However, this result may be partly due to the small sample size compared to the size of the cells. Overall, the average plating severity appears comparable in both cells, with a higher plating heterogeneity observed in cell 25G.

SEI distribution trends

For the vast majority of Li-ion cells that use low potential anodes, capacity fade is inextricably linked to SEI growth under most circumstances. As explained earlier, TGC offers a useful lens into the SEI distribution, albeit with some caveats. Firstly, the SEI is a complex composite, made up of a variety of both organic and inorganic species. Only the organic compounds that produce CO_2 on contact with water can be identified using TGC. Secondly, the experiments conducted here revealed that the intensity of the carbon dioxide peak was substantially smaller compared to the hydrogen one. As such, the quantification of the SEI is subject to a larger error. Bearing these limitations in mind, the correlation between the area of the H_2 and CO_2 peaks was analysed and is presented in Figure 6.18. For each cell, the data was split into the "colder side" (combining the coldest and third coldest anodes) and "warmer side" (combining the warmest and third warmest anode). Pearson's correlation coefficient was computed according to Equation 6.2 for each dataset in order to examine any correlation.

$$r_{\text{Pearson}} = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}} \quad (6.2)$$

In the equation above, x_i represents the values of the x variable in the sample, $\bar{x}$ is the mean of those values, y_i represents the values of the y variable, and $\bar{y}$ is the mean of the y values. Pearson's coefficient can vary between -1 to 1, with higher positive values signifying a stronger positive correlation, lower negative values indicating a stronger negative correlation, and values close to 0 indicating a lack of correlation. In all cases, the R^2 values are lower than those of Pearson's coefficient. This can be largely attributed to the relatively low measurement precision caused by the low intensity of the CO_2 peak. The strongest correlation, with a relatively high Pearson's coefficient of 0.851, was exhibited by the cold side of cell 0G, with the warm side having a slightly lower coefficient of 0.757.

A yet weaker but not insignificant correlation with a Pearson's coefficient of 0.626 existed for the cold side of cell 25G. The warm side of that cell showed no correlation, with a coefficient of -0.054. These results have interesting implications in the context of the morphological differences discussed in Section 6.5.3. Generally, it would be reasonable to expect the presence of plating to lead to an increase in the amount of SEI due to the metallic Li reacting with the electrolyte. However, the correlation between the amount of SEI and the amount of plated Li would hold only if the surface area of the metallic Li in contact with the electrolyte increases proportionally to the amount of Li plated. For both sides of cell 0G and the cold side of cell 25G, this seems to be the case. The deposits observed on the cold side of cell 0G were predominantly dendritic, while those on the warm side mostly resembled flakes, with some needle-shaped deposits. The deposition on the cold side of cell 25G had a predominantly flake-like morphology, with some smoother plating also observed. Dendritic Li is likely to have the highest surface area, followed by flake-like deposits and then smooth, uniform deposition. Pearson's coefficient between the plated Li and SEI then appears to decrease with more uniform deposition, as does the slope of the correlation. Finally, for the warm side of cell 25G, where the SEM images showed very smooth plating, the correlation is completely absent. This suggests that the uniform deposition on the warmer side of the cell, while clearly abundant, is less detrimental to the cell performance and lifetime as it does not result in an increased rate of SEI growth. The majority of the plating-caused capacity fade must in this case come from the electrical isolation of the deposits from the anode, i.e. the formation of "dead Li". This mechanism should also be reduced compared to the case of more dendritic deposits, which have been shown to be prone to base dissolution. The uniform deposition may then explain why, despite the amount of the Li plated being comparable to cell 0G and significant enough to be observable with the naked eye, cells 25G and 25U displayed surprisingly slow capacity fade.

The TGC results for cell 25U are shown in Figure 6.19. Since the cell was cycled with the same temperature imposed on both faces, one of the outermost and one of the middle anodes were selected for testing. Both the plating distribution and the correlation between the CO₂ and H₂ peaks look very similar to the warmer side of cell 25G. Pearson's coefficient is very low at -0.119, indicating no correlation. Another similarity is the plating morphology - the SEM images in Figure 6.14 show smooth, uniform deposition. For this

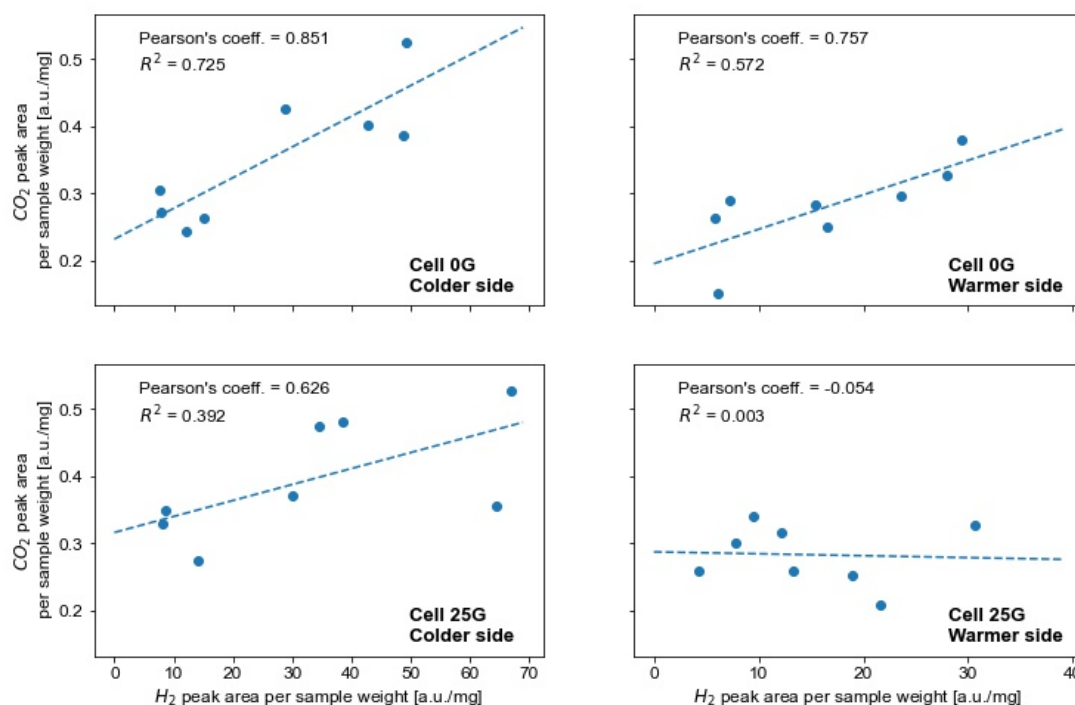


Figure 6.18: The area of the CO_2 peak shows a correlation with the amount of Li detected for the anodes that displayed dendritic or flake-like deposits, but not for the uniformly plated ones.

cell too, it seems the extensive but seemingly uniform plating does not cause an increase in the amount of SEI, resulting in a relatively low rate of capacity fade despite significant plating. The assessment of the plating uniformity is, however, based on the inspection of a limited number of samples with SEM. A more thorough study of the thickness and density of the plated layer would be necessary to confirm that plating is definitely uniform. There is some heterogeneity to the distribution of the plated Li measured with TGC (Figure 6.19), with the outer layer showing slightly more deposition compared to the middle layer. This could be attributed to its marginally lower temperature during cycling due to the proximity to the Peltier elements. The typical lateral distribution, with higher concentrations of lithium near the tabs, is also seen. Li plating is by nature a localised degradation mechanism, so these variations are not surprising; nonetheless, the plating distribution is confirmed to be more uniform compared to cell 25G. The average concentration of Li detected is also lower at $4.10 \mu\text{g}/\text{mg}$, compared to $6.14 \mu\text{g}/\text{mg}$.

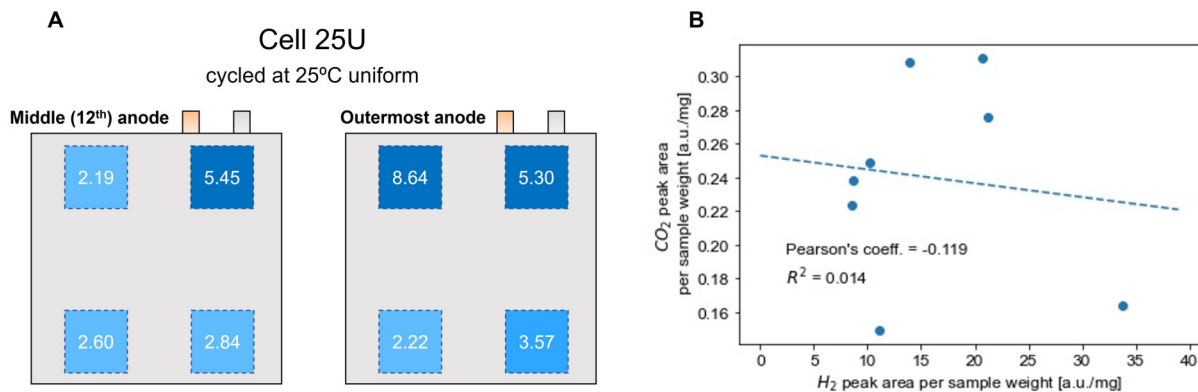


Figure 6.19: TGC results for cell 25U. a) Concentration of Li detected [$\mu\text{g}/\text{mg}$ anode], b) The CO₂ and H₂ peak areas show no correlation.

6.5.5 Cell as a system: how diffusion in the cathode affects lithium plating

As mentioned previously, this work was originally modelled. However, most of the discussion so far has been centred around the experimental results. There are two reasons for this: firstly, the experiments revealed complexities that affect the severity and distribution of plating that are not captured by the DFN-based plating model, such as the morphological differences and possible variations in the reversibility of the deposition. Secondly, the results of the original simulations for cell 0G were quickly proven wrong once the disassembled cell was examined. The original simulation indicated plating would be more severe in the warmer cell layers, contrary to the experimental findings. The reason for the discrepancy was studied, once again revealing the importance of accurate parameter estimation. For cell 25G, the simulation and experimental results were in agreement, concluding that the colder layers were more prone to plating at higher average cell temperatures.

The plating distributions predicted by the multilayer DFN model depend primarily on the activation energies of physical processes such as diffusion, intercalation and plating, as it is these values that determine the differences in the current density and transport properties between the colder and warmer layers. The activation energy values were therefore varied one at a time to identify the reason for the discrepancy between the model and experiments. The intuitive approach is to start by addressing the activation energies associated with the solid phase diffusion in the anode, Li plating and intercalation. However, varying these values within reasonable ranges failed to reproduce the experimental result. Interestingly, the parameter most likely to have caused the incorrect simulation results

was identified not on the anode, but on the cathode side - the activation energy of the solid phase diffusion in the cathode.

As mentioned previously, Ecker et al. [16] used two methods to determine the solid phase diffusion coefficients at a range of temperatures: EIS and GITT. Unlike for the anode where both methods gave similar and reasonable results, on the cathode sides the two values were vastly different at $31,700 \text{ kJ.mol}^{-1}$ (GITT) and $80,600 \text{ kJ.mol}^{-1}$ (EIS). The final parameter set validated on discharge data in the follow-up paper [209] contained the EIS-measured value, despite a GITT measurement being used for the baseline 23°C diffusivity. It was already discussed in Section 5 that this high activation energy did not appear consistent with the experimental charging curves recorded at 0°C and 25°C . The likely error in this parameter has implications for the plating distribution predicted in the current study as well. Figure 6.20 illustrates this point. The first column of plots represents the simulation results at $0 \pm 2.5^\circ\text{C}$ for the modified parameter set which was based on Ecker et al.'s measurements and re-fitted to the experimental charging data in Chapter 5. The second column uses the same parameter set, except the activation energy of solid diffusion in the cathode is replaced with the EIS-measured value from [16]. The third column shows the model results when the lower, GITT-measured value is used. While in all cases the plating at first proceeds faster in the warmest layer of the cell, the latter stages of charging differ substantially. With a $E_{a,\text{Dspos}}$ value, the plating current remains higher in the warmest layer for the majority of the charge, falling below the coldest layer only towards the end. As the value is reduced, the crossover point happens sooner in the charge, causing the concentrations of metallic Li in the coldest and warmest layers to converge. When the $E_{a,\text{Dspos}}$ value is equal to that measured in the GITT experiments, the crossover takes place early enough to cause the plating concentration in the coldest layer to overtake the warmest layer towards the end of charge, making the plating distribution result qualitatively consistent with the experimental results presented earlier in this chapter. For fast charging at $25 \pm 2.5^\circ\text{C}$ (see Figure 6.21), smaller differences exist between the different parameter sets since the cell temperature is closer to that of the reference temperature for the cathode diffusion coefficient. All three parameter sets give results consistent with the experiments, with the colder cell layers experiencing more severe plating.

This simulation result does not necessarily prove that the GITT-measured value of

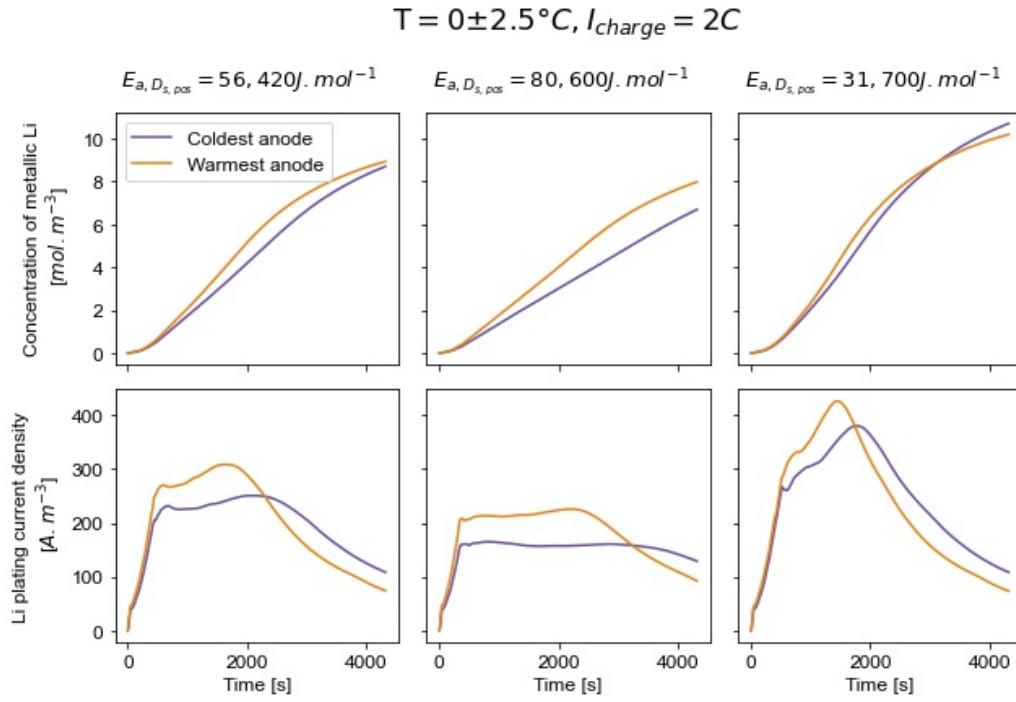


Figure 6.20: Simulated plating distributions between the coldest and warmest cell layers as a function of the activation energy of solid phase diffusion in the cathode at 0°C . Cathode diffusion kinetics clearly affect the plating distribution.

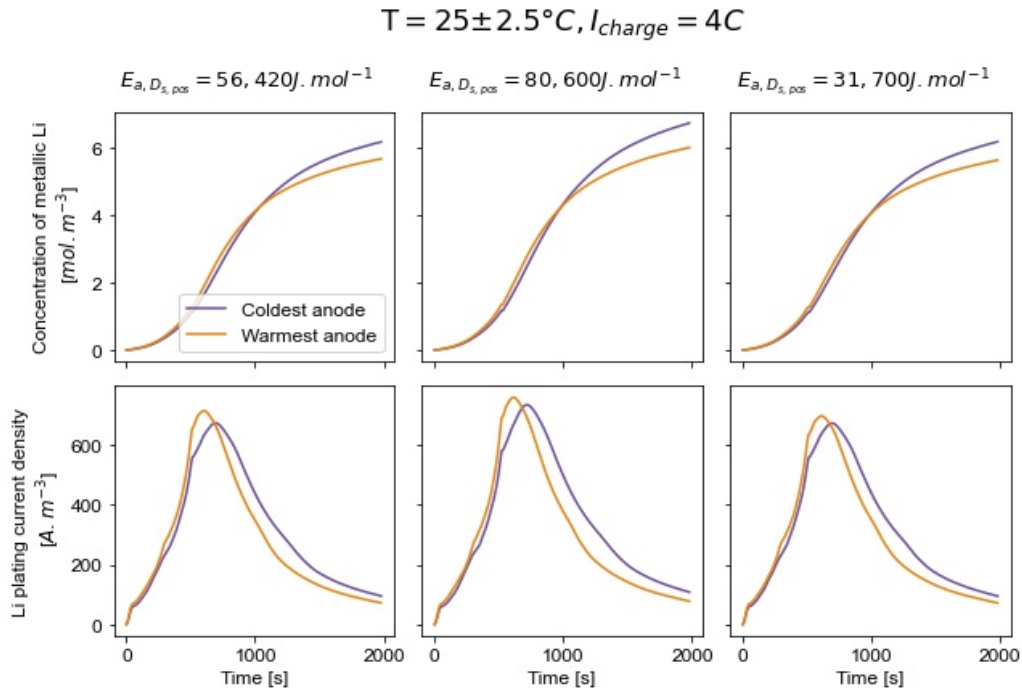


Figure 6.21: Simulated plating distributions between the coldest and warmest cell layers as a function of the activation energy of solid phase diffusion in the cathode at 25°C .

$E_{a,D_{spos}}$ is correct or that the EIS-measured one is incorrect: the cell is a complex system, and it is possible that different combinations of the activation energies of the other processes would produce a similar result. Nonetheless, it does highlight the importance of the diffusion kinetics in the cathode in determining plating behaviour. During fast charging, the reaction rates in both the anode and the cathode typically become diffusion-limited. As such, cathode diffusivity plays a crucial role in determining the current distribution throughout the cell. A higher value of $E_{a,D_{spos}}$ means that the warmest cell layers attract significantly higher current densities. As a result, plating in those layers becomes more likely or more severe. On the contrary, lower values result in more homogeneous current distributions. In this case, the colder layers eventually experience more plating due to the more limited ability of their anodes to accommodate current. In addition, these simulation results reveal the the plating distributions observed in the cell studied here may not be replicated in all other cells. Since the plating distribution ultimately depends on the balance between the rates of multiple physical processes, it is entirely possible that other cells, using different electrode materials, could exhibit different plating distribution trends.

6.6 Summary

In this chapter, the effects of through-plane thermal gradients during fast charging were studied to understand how temperature heterogeneities affect both the distribution and the severity of plating.

Thermal gradients were found to affect the capacity retention, reducing the cell life-time compared to thermally uniform cases. While cells cycled at 2C with the mean temperature of 0°C degraded quickly, the capacity fade in the cells cycled at 4C with the mean temperature of 25°C was surprisingly slow. The post-mortem examination results revealed a complex picture of the interactions between non-uniform temperatures and Li plating. All the tested cells were found to have experienced severe plating, with deposits visible with the naked eye on cell disassembly and confirmed using both SEM and TGC. As expected, the cells cycled with a through-plane thermal gradient exhibited high heterogeneity between the cell layers. The examined thermally uniform cell, cycled with the same temperature imposed on both cell faces, showed more uniform plating in comparison

- although the localised nature of this degradation mechanism still meant higher levels of deposition near the current collector tabs and some variations between the layers. The imposition of the thermal gradient also seemed to result in an increase in the average plating concentration based on the TGC results. Substantial differences in the plating morphology were found to be the likely reason for the differences in the capacity fade between cells cycled at 0°C and 25°C, with the former exhibiting more localised, dendritic Li deposition. The colder layers of cells cycled under thermal gradients were also found prone to more dendritic plating, while the warmer layers exhibited a more uniform plating morphology similar to that of a thermally uniform cell. A correlation was found between the concentrations of the plated Li and SEI detected using TGC for those electrodes that featured dendritic or flake-like deposits with high surface areas. For the more uniformly plated electrodes, this correlation was absent. This finding suggests that Li plating is not always equally detrimental: while dendritic deposition increases the rate of SEI growth due to its surface area, uniform plating may not, explaining the low rate of capacity fade observed in the cells fast charged at higher temperatures. Moreover, the DVA results for two cells fast charged in parallel at 0°C with a thermal gradient of 10°C indicated that more Li was stripped from the warmer cell, which could be caused by a higher reversibility of plating. However, the stripping peak could not be detected for cells fast charged at 15 or 25°C while DVA is still not fully validated as a quantification technique, limiting the reliability of this finding. Finally, the results of simulations with a 2D multilayer electrochemical-thermal model highlight the importance of the cathode diffusion kinetics for determining the current density distribution, and therefore the plating distribution, in Li-ion cells. This finding highlights the need to consider the cell as a system, rather than assuming the more common approach of ignoring the cathode-anode interactions.

Chapter 7

Conclusions

The aim of this thesis was to develop a better understanding of fast charging-induced degradation, providing answers to the research questions set out in Chapter 1. Since lithium plating has often been shown to be a key mechanism of degradation and a safety concern during fast charging, it was the focus of the work presented here, with less attention paid to other mechanisms that can be important, such as SEI layer growth, electrolyte oxidation at the cathode or mechanical degradation. Rather than proposing charging protocols that could prevent plating in a specific set of circumstances, the focus has been on understanding both the performance of charging protocols and the effects of thermal conditions more broadly.

The literature research conducted at the beginning of the project highlighted a number of gaps in the understanding of lithium plating during fast charging. Firstly, it was found that while many fast charging protocols have been proposed, most were shown to be beneficial for some cells but not for others, and the reasons for these discrepancies were not well understood. This gap was addressed through a modelling study, which showed that the ability of a fast charging protocol to minimise plating is determined by the transport properties - in particular the solid phase and electrolyte diffusion timescales - and the initial cell temperature. This finding can inform the selection of suitable charging protocols for a given cell and environmental conditions. It was also found that despite through-plane thermal gradients being common in battery packs, previous studies had not characterised their effects on the severity and distribution of Li plating. The experimental and modelling work reported in this thesis led to the conclusion that thermal gradients during fast charging increased plating heterogeneity and reduced cell lifetime.

The local temperature was also found to impact the plating morphology, with indications of increased SEI growth on the dendritic Li deposited at lower temperatures. Warmer local temperatures were found to lead to more uniform deposition, which did not seem to correlate to increased SEI growth. This highlights the complexity of the interactions between different degradation mechanisms, adding to the existing body of knowledge on the positive feedback between Li deposition and secondary SEI growth but also suggesting that in some cases such positive feedback may not exist. The understanding of the accuracy of titration gas chromatography in quantifying Li plating was advanced in this thesis by demonstrating that the Li intercalated within the graphite anode contributes to the TGC results even at very low states of lithiation. While this highlights the limitations of the technique in the quantification of plating, it also underscores its potential usefulness in the post-mortem quantification of the local state of lithiation in graphite electrodes. Finally, the results presented here add to the growing body of evidence that Li plating is affected not only by the properties of the anode, but also those of the cathode. The understanding of this crosstalk, identified also in several recent studies, is expanded through a model-based demonstration of the effect of the activation energy of solid phase diffusion in the cathode on the spatial distribution of Li plating. The following sections discuss individual results of this thesis in more detail.

7.1 Effects of temperature and cell type on fast charging protocol performance

The first part of this project aimed to answer the following research questions:

- What are the reasons for the discrepancies in the performance of similar charging protocols reported in different studies?
- What are the general rules for the selection of a fast charging protocol for a given cell and temperature conditions?

To address these, the performance of fast charging protocols in energy and power-optimised cells was investigated at a range of temperatures. Boost charging and the traditional CC-CV protocol were selected for comparison. Boost charging is guided by the same principle as many other fast charging protocols which feature highest current at

low SOC to take advantage of the lower risk of lithium plating, gradually tapering the current as this risk increases. The modelling results showed that the conflicting reports on the impacts of boost charging on cell lifetime in the literature are likely to stem from the differences in the transport properties (energy versus power-optimised design) of the cells used in various studies. The ambient temperature (or, more correctly, the initial temperature of the cell) was also found to strongly impact the relative effectiveness of each charging protocol at minimising Li plating. It was found that the solid phase and electrolyte diffusion timescales at the relevant temperature could be used to guide the selection of the fast charging protocol. Boost charging was found to lead to a reduced average plating rate when the solid diffusion timescale was low. Increasing solid phase diffusion timescales reduced this advantage, with boost charging leading to a slightly increased plating rate for high energy cells at low temperatures. High electrolyte diffusion timescales had a weak effect on the average plating rate but led to more heterogeneous plating along the anode thickness, particularly for boost charging.

7.1.1 The significance of diffusion timescales

Overall, it was shown that the relative performance of boost charging and CC-CV ultimately depended on the diffusion timescales, affected both by the design of the cell (the chosen materials and their diffusion coefficients, particle sizes, anode thickness, porosity and tortuosity) and the temperature. With lower diffusion timescales, i.e. at higher temperatures or in more power-optimised cells, boost charging was found to outperform CC-CV in terms of minimising Li plating due to the ability of the cells to accept high charging rates in the beginning of the charge without triggering plating, or the ability to intercalate the plated Li later in the fast charge. Two diffusion timescales were defined, one for the ionic transport in the electrolyte phase and one for the solid phase transport. While the solid phase diffusion timescale was found to have a dominant effect on the absolute amount of plating as well as the relative ability of the charging protocols to minimise it, the electrolyte phase diffusion timescale strongly affected the distribution of plating through the anode thickness. The distribution of the deposits is significant, since localised plating is more likely to be dendritic and therefore lead to dangerous short circuits or dead lithium formation. These findings are, of course, subject to the limitations of the modelling approach. The DFN model used in this study assumes Fickian

diffusion and Butler-Volmer reaction kinetics, both of which are coupled at the particle surface. At high current densities, the reaction rate is always predicted to increase, meaning diffusion must be the limiting process. While the DFN is the most widely used and accepted electrochemical model for Li-ion batteries, this view of battery kinetics has been contested [222, 269], particularly for phase-changing materials such as graphite. It is possible that future electrochemical models identify reaction kinetics rather than diffusion as the limiting process in some circumstances, in which case the timescales associated with the reaction kinetics may be found to be more significant than the diffusion limitations in determining the plating behaviour.

7.1.2 Nonlinear diffusion affects the performance of fast charging protocols

The variation in the solid phase diffusivity of graphite as a function of the lithiation fraction was shown to affect the extent of plating caused by the boost stage of boost charging, and therefore the relative performance of the charging protocols. This result was based on simulations featuring the diffusion coefficient curve as measured by [16] versus simulations using a modified curve that better fitted experimental charge data. In particular, the magnitude of the diffusion coefficient at low graphite lithiation (i.e. low cell SOC) affected whether or not the boost stage of boost charging induced plating. The diffusion coefficient has been shown to be relatively high at low states of lithiation [16, 24, 257] but nonetheless, the values reported in the literature vary by orders of magnitude. Boost charging is best able to minimise the amount of plating if the graphite diffusion coefficient is high at low SOC, when the boost current is applied. The lower the diffusion coefficient at low SOC, the lesser the advantage of using high charging currents at this stage. Consequently, the amount of plating induced by boost charging becomes more similar to that induced by CC-CV. In cases where the simulated difference between the plating induced by boost charging and CC-CV are small, boost charging should likely be avoided as the increased C-rate and sometimes voltage in the boost stage may increase the likelihood of degradation mechanisms which were not modelled here, such as cathode surface degradation, electrolyte oxidation, or particle cracking, without providing the benefit of curtailed Li plating. Additional research is needed on the effects of boost charging and similar protocols on these degradation mechanisms. The variation

of the diffusion coefficient as a function of lithiation is likely to affect the performance of other fast charging protocols, many of which are developed on the premise of applying increased currents at low SOC's due to the reduced risk of plating. Depending on the value of the diffusion coefficient in this range, plating may not always be avoided.

7.1.3 The importance of model validation in the relevant operational modes

The modelling work presented here initially made use of one of the most thorough parameterisation papers on Li-ion batteries [16], which however focused the validation and tuning of the parameters on experimental discharge data. While this parameter set did indeed reflect the discharge voltage well, this was not true for the charging voltage or current in the constant voltage stage. Further parameter tuning was performed to ensure the parameterisation errors did not invalidate the findings of this work. This learning does, however, highlight the need to parameterise electrochemical models on both charge and discharge data, or at least in the operational mode of interest to a particular work. Parameter sets validated on discharge data cannot be used to model charging without further validation. The reason for this is two-fold. Firstly, there are many parameter sets that can provide a similarly good fit to a set of discharge curves. Many of the parameters, even if measurable, are associated with high measurement errors and often have to be adjusted when applied in a model. However, fitting can only arrive at an improved parameter value if sufficient data is available. Augmenting the experimental dataset with charging data reduces the number of degrees of freedom - although it does not eradicate the problem, as it is still likely multiple equally good parameter sets can be found. It is also possible that no parameter set can fully fit the data if the model does not include all the necessary physics to reflect the observed cell behaviour. Secondly, some of the properties may be altered at different conditions. Diffusion coefficients are a good example of such a property, as they have been shown to vary between the lithiation and delithiation [24] as well as increase with higher current densities [218, 216] and increased mechanical stress [219]. In both common measurement techniques, GITT and EIS, low current densities are usually employed. In case of EIS, this is to ensure linear behaviour, while simplifying assumptions applicable only at low currents are often made in the analysis of GITT data. Additionally, the values of the diffusion coefficient measured in experiments

are affected by the electrode thickness and the electrolyte diffusivity [216]. More research is needed to understand how the variations of the diffusion coefficient as a function of these variables should be treated in electrochemical models. It should also be highlighted that the model used in this work is still only an approximation. Continuum level models do not account for local heterogeneities, which have often been found to strongly affect plating. Both macro- and microscale plating heterogeneity is evident in teardown, SEM and TGC data presented in this thesis, yet ignored in the DFN modelling framework. The 1D DFN implementation also assumes uniformity within the cell: only a single cell layer is explicitly modelled, with all remaining layers assumed to behave identically. This approximation may be acceptable for small cells, but is likely to misrepresent a large (> 10 Ah) form factor cell which would be subject to larger temperature and current density variations. In such a cell, the risk of local overcharge is increased, and so the effects of either charging protocol could vary significantly from this study. The equations used to model reaction kinetics are also empirical approximations, and plating kinetics in particular are still not well understood. While the findings of such models can be useful in predicting or understanding patterns, they should not be trusted to capture all physics that affect degradation.

7.2 Lithium plating under thermal gradients

The latter part of the project focused on better understanding how thermal conditions, in particular thermal gradients, affected lithium plating behaviour and overall degradation in fast charged cells. The following research questions were addressed:

- Are there significant differences in the severity of plating, depending on whether it takes place at moderate or low temperatures?
- How do through-plane thermal gradients affect the distribution and severity of plating in Li-ion cells?
- How is the overall degradation affected by the presence of a through-plane thermal gradient during fast charging?

Through experiments on mid-energy NMC/Gr pouch cells, it was shown that the amount of irreversibly plated lithium was not directly proportional to observed capacity fade. The

more dendritic plating found in cells cycled at lower temperatures was found to correlate to more severe fade. Cells cycled at a moderate temperature (25°C) exhibited only limited losses of capacity, despite containing similar amounts of plated lithium as quantified through titration gas chromatography. Irrespective of the mean cell temperature, cells fast charged under through-plane thermal gradients were found to degrade at a higher rate compared to thermally uniform cells. The amount of plated lithium was found to generally increase with lower cell layer temperatures. Colder anodes within individual cells were also found to display more dendritic deposits and higher amounts of the SEI species identifiable through TGC. While these findings offer partial answers to the research questions enumerated above, the results should in the future be confirmed on other cells and through more sensitive lithium and SEI quantification techniques.

7.2.1 Thermal gradients and global degradation rates

Thermal gradients have previously been shown to increase global capacity fade rates at moderate cycling conditions [270, 253]. This work confirms that the increased degradation rate is observed also during fast charging, irrespective of whether the mean temperature is low (0°C) or moderate (25°C). It was shown that the increased capacity fade stems primarily from the presence of the thermal gradient during the fast charging step, rather than during the lower rate discharge. While this work has focused on lithium plating, it is possible other degradation mechanisms are also affected by the thermal heterogeneity.

7.2.2 Distribution of lithium plating

The plated Li was found to be distributed unevenly through the cell layers, in addition to the heterogeneity in the lateral (along the layer) direction for the cells cycled under a through-plane thermal gradient. Plating is by nature a localised degradation mechanism, and so localised deposits near the tabs and along the overhang areas were found for all cells. However, the cells cycled under a thermal gradient showed increased plating heterogeneity. In case of the cell studied here, the deposition was increased in the colder cell layers and reduced in the warmer ones. Interestingly, the plating distribution was more uneven in the cell cycled at 25°C with a charging rate of 4 C than in the cell cycled at 0°C with a charging rate of 2 C. Parametric studies on the impact of the activation energies of key processes (Li plating, intercalation, and solid phase diffusion in both the

anode and the cathode) on plating distribution showed why this might be the case. In general, lower values of these parameters indicate a lower temperature sensitivity and lead to a more homogeneous current and plating distribution under a thermal gradient, while high values promote non-uniformity in both the current distribution and the resulting plating patterns. For the parameter set studied here, increased values of the activation energy of the cathode diffusion coefficient increased the amount of plating in the warmer layers, but at low temperatures the opposite effect was observed, with preferential plating in the colder layers. The activation energies of other key processes - diffusion in the anode, intercalation, and plating itself - also have an effect on the plating distribution when the cell temperature is not uniform. It is the interplay of these parameters that determines the plating distribution and the extent of heterogeneity, rather than any one parameter itself. Since the activation energies of each process are not equal, a change in temperature shifts the balance between their rates. As such, it is not straightforward to predict whether a 10°C gradient with a mean temperature of 0°C would cause more or less plating heterogeneity than with a mean temperature of 25°C. The cell studied here showed increased heterogeneity with a higher mean temperature, however the same pattern cannot be expected of other cells unless the activation energies associated with these key processes are the same. Since various electrode materials are used in Li-ion batteries, it is possible that other cells could show different plating distributions. Similarly, the activation energy of the plating reaction may vary in different Li-ion systems, affecting the extent of plating heterogeneity as well as its local severity.

7.2.3 Lithium plating severity

Some of the most interesting findings were those pertaining to the severity of plating. The intuitive way to define severity is by linking it to the total amount of the Li plated. This work, however, highlights that the two are not necessarily equivalent if it is the overall impact on degradation that is of interest. The cells cycled under a thermal gradient with a mean temperature of 0°C for 70 cycles and 25°C for 280 cycles were found to have experienced similar average amounts of plating, quantified using TGC. However, in the low temperature cell this was accompanied by rapid capacity fade, resulting in the end-of-life condition of 80% rated capacity retention being met after 70 cycles. This was not the case for the moderate temperature cell, which retained 88% rated capacity after 280 fast

charge cycles and had transitioned into a regime of slow capacity fade. Differences were also found in the morphology of the lithium deposits, which may have contributed to the different trends in the capacity fade. At 25°C, the deposition was found to be relatively dense and uniform, with a low surface area. The amount of the SEI detected was found not to correlate with the amount of Li in case of such uniform plating. Conversely, at 0°C the deposits were found to take on flake-like or dendritic morphologies, with high surface areas. In this case, the amount of the SEI did show a positive correlation with the amount of Li. Such differences were found also within each cell. The colder layers were found to feature more flake-like or dendritic Li deposits with increased SEI growth, while the warmer layers featured less plating, more uniform morphologies and a lesser or no correlation between the amounts of Li and SEI detected. This indicates that uniform plating regimes are less detrimental to cell lifetimes not only because of their better structural integrity compared to dendrites, but also due to reduced Li/electrolyte reactions. As such, plating can be considered more severe at lower mean temperatures, or in the colder layers of cells fast charged under a thermal gradient, since it is more likely to lead to increased rates of capacity fade. The overall amount of plating contributes to the degradation severity, but is clearly not the only factor. It should be stressed, however, that the differences in the capacity fade between cells cycled with or without a thermal gradient cannot be conclusively attributed to differences in plating patterns only. Other degradation mechanisms may also be sensitive to the presence of the thermal gradient. Unfortunately, the large ageing heterogeneity and consequent disappearance of peaks in the $\frac{dV}{dQ}$ and $\frac{dQ}{dV}$ spectra prevented quantification of LLI and LAM for each cell, which could provide information about other degradation mechanisms.

7.2.4 Cathode kinetics affect lithium plating

Cathode kinetics are rarely considered in the studies that investigate Li plating. While the importance of anode diffusion and reaction rates is obvious, Li-ion cells are complex systems with a multitude of physical interactions between cell components. In this work, it was found that an error in the activation energy of the cathode solid phase diffusion led to an incorrect prediction of Li plating distribution in cells cycled under a thermal gradient using a multilayer DFN model. This is because the cathode kinetics are a contributing factor in determining the current distribution through the cell. A similar point on the

importance of cathode diffusivity in determining the severity of plating was recently made for coin cells cycled with a thermal gradient [263]. These findings suggest that the same anode paired with different cathodes may display significantly different plating behaviours.

7.2.5 Titration gas chromatography for post-mortem quantification of lithium plating

The novel technique of titration gas chromatography, recently developed for quantifying dead Li in Li metal cells, was studied and validated here for the quantification of Li plating in Li-ion systems. It was found that the contributions of partially lithiated graphite to the detected amount of hydrogen could not be fully decoupled from the contributions of metallic lithium. This is because both species are strong reducing agents. It is therefore important that this technique is only used for plating quantification in cells that had been discharged prior to disassembly, and that the graphite contributions are taken into consideration when analysing the results. The technique has also been found to be promising for accurate estimation of the local graphite lithiation in post-mortem analysis, as the area of the hydrogen peak detected varies linearly with the extent of lithiation.

7.3 Future work

A curious property of research is that with every question answered, more questions tend to arise. The limitations of this work should be appreciated and addressed, while the findings also bring to mind new topics to be studied. The following are just some research directions that could further validate and expand the work presented in this thesis.

- The kinetics and thermodynamics of Li plating in Li-ion systems are still poorly understood. Researchers often borrow plating behaviours, thermodynamic limits and kinetic constants from the Li metal cell literature, without sufficient evidence that such transfer is justified. For example, only one work was found to measure both the reaction rate constant and activation energy of lithium plating in a Li-ion system [81]. More such studies are needed to understand how the plating kinetics differ between Li-ion and Li metal batteries, or on different graphite substrates.
- Diffusion timescales in both the solid and liquid electrolyte transport were found to

affect the effectiveness of boost charging at minimising Li plating. This finding is expected to affect many other fast charging protocols that feature increased C-rates in the early charging stages, which should be confirmed through further study. The findings would also benefit from experimental validation, which could not be carried out within the timescale of this project.

- The work on the relative performance of charging protocols presented here was focused only on Li plating, without considering SEI layer growth, particle cracking or cathode degradation. The findings presented later showed that the amount of plating is not always a good predictor of capacity fade. As such, further study is needed to establish whether the reductions in Li plating rates that can be achieved with boost charging in some circumstances lead to a reduced overall rate of capacity fade.
- The effects of thermal gradients on the reversibility and severity of plating reported in this work require further study. Here, only constant thermal gradients of specific magnitudes have been investigated. It would be worthwhile to extend the study into other thermal conditions, particularly those with temporal changes in the temperature as encountered in EV battery packs.
- The extent of correlation between Li plating and SEI growth for different deposition morphologies should be investigated further. Here, TGC was the only quantification method available. While promising, TGC is limited in the type of SEI species that can be detected, as only some organic species produce carbon dioxide on contact with water. The findings presented here should be validated with more established quantification methods that can detect additional SEI species, for example XRD or NMR.
- In the thermal gradients work, lithium plating was found to be more uniform and likely to be more reversible in the warmer regions of the cell, as well as in cells cycled at higher mean temperatures. Increased Li plating in these morphological regimes was found not to be associated with increased SEI growth, implying it led to reduced reactions with the electrolyte in comparison to localised, dendritic deposition. According to the current literature [69, 70, 97], the increased risk of thermal runaway in cells that experience plating is likely driven by the reactivity

of the plated Li with the electrolyte. It is possible that in addition to a reduced risk of a short circuit, uniform plating regimes also do not compromise the thermal runaway onset temperatures to the same extent as dendritic deposits. The findings on the lack of correlation between uniform plating and SEI growth should be further validated in other cells, with an extension to investigate the implications on the thermal runaway behaviour.

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