Dynamic Battery Usage and its Effect on Degradation

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Dynamic Battery Usage and its Effect on Degradation KRISTIAN FRENANDER Department of Electrical Engineering Chalmers University of Technology

Abstract

The urgent need for decarbonisation has placed significant pressure on the transportation sector to transition away from fossil fuels, with lithium-ion batteries (LIBs) emerging as the leading alternative for clean transportation. However, despite rapid advancements in LIBs, the mechanisms of battery degradation – particularly under the dynamic usage conditions typical of vehicle applications – remain insufficiently understood.

This thesis contributes to the understanding of how usage conditions influence battery degradation, with a particular focus on operating conditions relevant to vehicle applications. Key factors investigated include variations in the state of charge window, dynamic cycling during charge and discharge, and temperature effects. The compiled studies present findings from battery ageing experiments on energy-optimised LIBs, addressing three main aspects of degradation:

- State of charge dependence: Doping with SiO_x in the graphite negative electrode is shown to dominate battery degradation.
- Charge and discharge dynamics: Ageing studies reveal that dynamic cycling significantly improves durability, particularly when charging the battery.
- Cell-to-cell variance: Statistical analysis indicates that a minimum of four replicates per test condition is required to ensure robust ageing assessments.

Beyond these main findings, this thesis also presents electrochemical analysis methods for determining the degradation of individual materials in mixedmaterial electrodes, statistical methods for analysing high-variance degradation data, and novel approaches for parameterisable dynamic life cycle testing of LIBs. Collectively, these contributions provide data and analytical tools for understanding battery degradation in dynamic usage conditions and its underlying causes.

Keywords: Lithium-ion Battery, Battery Degradation, Electrochemistry.

List of Publications

This thesis is based on the following publications:

[A] **Kristian Frenander**, Torbjörn Thiringer, "Low Frequency Influence on Degradation of Commercial Li-ion Battery". Low Frequency.

[B] N. Roy Chowdhury, A.J. Smith, **K. Frenander**, A. Mikheenkova, R. Wreland Lindström, T. Thiringer, "The state of charge dependence of degradation in lithium-ion cells from a Tesla model 3". Small SOC window.

[C] A. Mikheenkova, A.J. Smith, **K. Frenander**, Y. Tesfamhret, N. Roy Chowdhury, Cheuk-Wai Tai, T. Thiringer, R. Wreland Lindström, M. Hahlin, M.J. Lacey, "Ageing of High Energy Density Automotive Li-ion Batteries: The Effect of Temperature and State-of-Charge". Large SOC window.

[D] **K. Frenander**, T. Thiringer, "Analysis of the number of replicates required for Li-ion battery degradation testing". Number of Replicates.

[E] **K. Frenander**, D. Jutsell Nilsson, T. Thiringer, "Extending Battery Lifetime by Pulse Charging".

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Acronyms

ANOVA:	Analysis of Variance
BEV:	Battery Electric Vehicle
BoL:	Beginning of Life
CC:	Constant Current
CCCV:	Constant Current, Constant Voltage
DEC:	Diethyl Carbonate
DFN:	Doyle-Fuller-Newman
DMC:	Dimethyl Carbonate
DVA:	Differential Voltage Analysis
EC:	Ethylene Carbonate
EDS:	Energy-Dispersive X-ray Spectroscopy
EIS:	Electrochemical Impedance Spectroscopy
EMC:	Ethyl Methyl Carbonate
EoL:	End of Life
EV:	Electric Vehicle
FCE:	Full Cycle Equivalent
ICA:	Incremental Capacity Analysis
ICI:	Intermittent Current Interruption
ICP-OES:	Inductively Coupled Plasma–Optical Emission Spectroscopy
LAM:	Loss of Active Material
LFP:	Lithium Ferrophosphate

LIB:	Lithium-Ion Battery
LLI:	Loss of Lithium Inventory
LMO:	Lithium Manganese Oxide
Lrg. Δ SOC:	Large Δ SOC Study
LTO:	Lithium Titanium Oxide
NCA:	Lithium Nickel Cobalt Aluminium Oxide
NE:	Negative Electrode
NMC:	Lithium Nickel Manganese Cobalt Oxide
OCV:	Open Circuit Voltage
PE:	Positive Electrode
RPT:	Reference Performance Test
SEI:	Solid-Electrolyte Interphase
SEM:	Scanning Electron Microscopy
Sm. Δ SOC:	Small Δ SOC Study
SoC:	State of Charge
SoH:	State of Health
TEM:	Transmission Electron Microscopy
TMO:	Transition Metal Oxide
XRD:	X-ray Diffraction

Mathematical symbols

Symbols

α	Transfer coefficient
β	Bruggeman coefficient
ϵ	Volume fraction
η	Overpotential in redox reaction, V
σ	Conductivity, $\mathrm{S}\mathrm{m}^{-1}$
ϕ	Electrochemical potential, V
a	Area, m^2
с	Lithium ion concentration, $mol m^{-3}$
D	Diffusion coefficient, $m^2 s^{-1}$
E	Voltage, V
F	Faraday constant, $96485\mathrm{As/mol}$
$f_{\rm A}$	Activity coefficient of salt in electrolyte
i	Current density, $A m^{-2}$
Ι	Full cell current, A
i_0	Exchange current density, ${\rm Am^{-2}}$
k	Reaction rate constant, ${\rm ms^{-1}}$
n	Number of electrons in redox reaction
Q	Cumulative capacity, Ah
R	Gas constant, $8.314 \mathrm{J}\mathrm{mol}^{-1}\mathrm{K}$
r	Radial distance in particle, m

- $R_{\rm p}$ Particle radius, m
- T Temperature, K
- t Time, s
- t^0_+ Lithium ion transference number
- U Voltage, V

Symbols

α Variance between su	$_{\rm absets}$
------------------------------	-----------------

- ϵ Noise estimation
- μ Mean value
- df Degrees of Freedom
- E Expected value
- H Statistical hypothesis
- MS Mean Squares
- SS Sum of Squares

Subscripts

a	Anodic
с	Cathodic
cell	Cell
ct	Charge transfer
eff	Effective
eq	Equilibrium
1	Liquid electrolyte phase

- Li Plated lithium
- neg Negative electrode
- pos Positive electrode
- ref Reference
- s Solid phase
- surf Particle surface

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Part I

Overview

CHAPTER 1

Introduction

This chapter introduces the background, motivation, and overall scope of the research presented in this thesis.

1.1 Background

With increasing awareness of the urgent need to de-carbonise the global economy – particularly the transportation and power sectors – lithium-ion batteries (LIBs) have become a crucial technology for reducing carbon emissions.

The transport sector accounts for 23% of global anthropogenic CO_2 emissions [1], with road transport responsible for 74.5% of that total [2]. Thus, the potential to reduce CO_2 emissions through vehicle electrification is substantial.

Having emerged as the dominant energy storage technology chosen by the vehicle industry when shifting to electric propulsion, LIBs are seen as a key technology for a green economy. This has led to large investments into LIB technology in recent years. This has, among other things, led to a 70% cost reduction in the decade between 2010 and 2020 [3]. Yet the battery remains the most expensive component in an electric vehicle (EV) [4] making it a

key component in making EVs more affordable, to continue increasing market penetration and reduce tailpipe emissions.

Furthermore, batteries are heavy and have a significant environmental footprint, particularly when manufactured from virgin materials [5]. Their size and weight also make them expensive and inconvenient to replace, reinforcing the importance of durability as a key factor in reducing both lifecycle costs and the environmental impact of LIBs.

To improve the lifetime of LIBs both the ageing mechanisms and the usage conditions that trigger them need to be better understood. To achieve this requires both better modelling abilities as well as better and more efficient testing procedures, which is what this thesis seeks to contribute to.

1.2 Previous Work

The increasing market penetration of LIBs has made understanding their ageing mechanisms a field of major interest. Numerous studies have examined the influence of static parameters such as C-rate [6], [7], state of charge (SoC) levels [8], [9], temperature [10]–[12] or combinations thereof [13]–[15]. However, relatively limited research has been conducted on the impact of dynamic usage, despite its relevance as the primary mode of operation in electric vehicles (EVs). Dynamic cycles derived from driving patterns have been investigated in [15]–[19] while duty cycles from other dynamic applications have been utilised in [20], [21]. Among the studies focusing on dynamic ageing, only a few had a reference test of similar current, making direct comparisons challenging. The reported influence of dynamic cycling varies significantly: some studies, such as [15], [19], report a strong impact, whereas others, such as [16], suggest only minor effects – except at low temperatures.

Similarly, research on dynamic current charging and its effects on battery durability, the results reported in literature have been non-conclusive. While some researchers report little to no impact, or even negative effects [22]–[24], other researchers have found significant positive effects from dynamic charging [25]–[27]. Notably, more recent studies, including the comprehensive work by Geslin et al. [19], consistently report positive effects of dynamic usage on battery durability, particularly in the context of dynamic charging.

While these works provide valuable insights, the inherent variability in realworld battery operation and the strong dependence of ageing processes on battery chemistry [13] underscore the need for further research. A deeper understanding of how specific usage parameters affect ageing is essential for optimizing lifetime testing protocols and improving battery management strategies.

The large-scale testing required to isolate the effects of individual usage parameters presents inherent challenges. Extensive experimental matrices are costly and require long test durations to obtain conclusive results. Given these constraints it is highly important to understand cell-to-cell variance and it impact on the sample size required for robust statistical analysis. Cell-tocell variance primarily arises from manufacturing tolerances, which lead to minor differences in electrode morphology, coating homogeneity and internal design. These small variations can become amplified during ageing, ultimately resulting in significant differences in degradation rates across cells [28], [29].

Despite its importance, intrinsic variability in LIB ageing has received limited attention in the literature. A notable exception is the work of Dechent et al. [30], who analysed multiple datasets using sophisticated statistical methods to estimate the number of replicates required for reliable ageing studies. Their findings indicate that a sample size of approximately 10 is required. Strange et al. [31] further refined this methodology, providing a more general recommendation of a minimum sample size of 9 for robust results. This is significantly higher than the sample sizes typically used in earlier studies and would substantially increase the cost of durability testing.

Additional studies have examined the impact of cell-to-cell variance at the module and pack level, highlighting how these variations affect overall system performance [32]–[34]. Moreover, several works have proposed methods for identifying and filtering out outliers to improve dataset reliability [35], [36].

Given the constraints introduced by testing – combined with the great value of being able to simulate various usage profiles and reduce time to results – interest in modelling degradation of LIBs has surged. Broadly, these modelling approaches can be categorized into:

- Empirical modelling
- Physical modelling

where the empirical model approach uses data from a test matrix to fit parameters in a model directly correlating usage to degradation, without attributing it to specific chemical processes. Examples of such models can be found in [37]–[40]. Furthermore some authors have attempted to correlate the statistical model to the ageing processes in the battery, see [41], [42].

Lately however, the development of physics-based models and an increasing understanding of the parameters required, particularly for the Doyle-Fuller-Newman (DFN) model, have led to a growing shift in interest toward physical modelling. In this context, physical models extend idealised representations of battery behaviour by explicitly incorporating side reactions in addition to the desired redox reactions associated with normal battery operation. The DFN model is commonly used as the foundation for such extensions.

This was pioneered by Arora *et al.* [43] who focused on Li plating and has since then been complemented by advances in solid-electrolyte interphase (SEI) models [15], [44]–[46], refined Li plating models [47]–[50], and particle stress and crack propagation models [51]–[53]. More recent developments have introduced coupled reaction models, which explicitly account for interactions between degradation mechanisms, including SEI reformation at crack surfaces and ageing effects in mixed-electrode systems [54], [55].

Although calibration and validation of these models still require substantial experimental data, recent advances in parameter estimation techniques and the availability of public datasets – such as LiionDB [56] – are expected to improve prediction accuracy without significantly increasing experimental effort. As these modelling approaches continue to develop, contributions to both model refinement and parameter validation remain crucial for improving predictive capabilities and accelerating battery lifetime optimization.

1.3 Purpose

The purpose of this thesis is to further the understanding of ageing of LIBs, both by investigating influence of cycling conditions, and by investigating the ageing processes that occur during cycling by both non-invasive and postmortem techniques. The knowledge generated should also help the development of ageing models, both empirical and physical.

Specifically this thesis focuses on investigating the influence of dynamic usage, as compared to constant current testing conditions, with the purpose of showing efficient and manageable ways to include this in lifetime assessment of commercial batteries. Utilising this kind of test methodology could possibly save test time and resources needed for comprehensive investigation of ageing behaviour.

1.4 Contributions to State of the Art

The main project contributions found in this thesis are:

- Developed and demonstrated test methods that take account for dynamic usage with minimal governing parameters.
- Established that not taking dynamics into account in lifetime cycle testing, will affect the results, and can lead to erroneous conclusions.
- Proved that electrodes with an SiO_x -graphite blend exhibit strong SoC dependence, with rapid initial capacity fade when cycled at low SoC.
- Demonstrated that non-invasive characterisation methods can effectively reveal heterogeneity in the ageing of individual materials within mixed-material electrodes.
- Development of hysteresis analysis as tool for qualitatively assessing the individual ageing of SiO_x and graphite in mixed negative electrode.
- Proposed and validated a novel method for determining the number of replicates required for robust conclusions in LIB degradation studies.
- Showed that dynamic pulse charging is likely to contribute less to Li plating and SEI re-formation than constant current (CC) charging.

1.5 Thesis Outline

This thesis is arranged in the following way: Chapters 2 to 4 contain the studies presented in the appended papers, presenting theory for LIBs, ageing processes, and details on the experimental techniques utilised in the study. Moreover the key results from the studies investigating how the SoC levels and dynamic discharge currents affect the ageing of LIBs are presented together with the main findings from the study investigating dynamic charging and its effect on LIB degradation. Finally, Chapter 4 also includes a summary of the findings from the study on number of replicates required for reliable conclusions from LIB ageing studies in laboratory environment. Chapter 5 and 6 present the conclusions of the study and suggested future work.

CHAPTER 2

Theory

This chapter outlines the theoretical framework and key models that underpin the analysis and interpretation of the results.

2.1 Lithium-ion Battery

Batteries, and electrochemical cells in general, are composed of two electrodes, one positive with higher potential and one negative with lower potential. One part of the redox (reduction/oxidation) reaction of the full cell will happen at each electrode, meaning that electrons are yielded at one electrode and consumed at the other. In a battery, by electrically insulating the electrodes while maintaining ionic connection through an electrolyte, the electrons involved in the redox reaction are forced to travel through an external circuit and thus produce electrical work in an external system. Thus the battery can work as an energy source for applications such as electric vehicles, consumer electronics, power tools etc.

The term *lithium-ion battery* specifically denotes electrode material pairings that operate with Li^+ as the positive mobile ionic species, meaning that Li^+ is the positive ion carrying current through the electrolyte to maintain charge

balance while electrons carry the current in the external circuit. Nearly all currently available commercial LIBs are of insertion type, where the Li is inserted into a host structure where it diffuses into free sites and is stored until next cycle, but metallic electrodes also exist. The host structure enables reversibility of the process as Li^+ can be inserted and removed repeatedly making the battery rechargeable. The ion transfer between electrodes can happen either spontaneously from negative to positive electrode (discharge) or driven by an external electrical voltage from positive to negative electrode (charge).

In Fig. 2.1 a cross-section of the battery is schematically represented with its most important components and the electron and Li⁺ flow during discharge. The main components are:

- 1. Positive current collector. Typically manufactured from aluminium.
- 2. Positive electrode (PE). Commonly a transition metal oxide, often with high Nickel content, such as $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Al}_{0.05}\text{O}_2$ (NCA) or $\text{LiNi}_a\text{Co}_b\text{Mn}_c\text{O}_2$ (NMC) where a+b+c=1 and commonly $a \approx 0.85$ for high energy density applications such as EVs. Other common materials include LiFePO₄ (LFP) and LiMnO₂ (LMO) [5].
- 3. Separator. Ensures electrical insulation while permitting ionic transport, typically this is achieved with a polymer soaked in electrolyte [57].
- 4. Negative electrode (NE). Until recently pure graphite was dominant as negative electrode material, but in recent years blended electrodes with graphite and silicon oxides SiO_x have reached the market. For this study the focus will be solely on blended negative electrodes. Lithium titanium oxide (LTO) can also be found in some commercial applications.
- 5. Negative current collector. Nearly exclusively made of copper in commercial applications.

To facilitate ion and mass transfer, the entire separator-electrode stack is soaked in an electrolyte. For almost all of the commercially available LIBs today the electrolyte is in liquid form, and while some examples of solid electrolytes exist they are outside the scope of this study. The liquid electrolytes are typically designed using a Li salt, normally LiPF₆, in solution in a mixture of different carbonates. Some of the most commonly used are dimethyl



Figure 2.1: Graphic summary of physical processes in battery during discharge and their connection to the DFN model. Li⁺ ions are released from the negative electrode, in pairs with electrons, in a charge transfer reaction. They are then separated and electrons transported through external circuit while Li⁺ transport happens through the liquid electrolyte as mass transfer. Li⁺ and electrons then combine in charge transfer reaction on positive electrode surface and diffuse to a free site in the porous electrode via solid state mass transfer.

carbonate (DMC), ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) but further compounds are also common. The carbonates are combined in different ratios to design electrolytes with different properties. Other chemical additives are also added to improve the performance of the battery [58].

Furthermore the electrolyte needs to be stable over a wide potential range, due to significant potential differences between the positive and negative electrodes. As the electrolyte is in direct contact with the electrodes it must withstand the reductive and oxidative potential of the electrodes [59].

When Li⁺ shuttles back and forth between electrodes during operation of the battery, the concentration of Li in the respective electrode changes, changing the available energy in the battery. To track the amount of charge available to the user of the battery the quantity state of charge is defined. It is indicating how much capacity is available to discharge from the battery, ideally correlating to the amount of Li stored in each electrode. As the actual concentration in the host structures is not measurable in an operational battery it is typically tracked via the open circuit voltage (OCV), the voltage of the battery when there is no current flowing. The SoC is defined between 0% and 100% based on the OCV interval that the battery can be operated in. The correlation between SoC and OCV is graphically represented in Fig. 2.2.

2.2 Modelling of Li-ion Batteries

Doyle Fuller Newman Model

The most established model for calculating and describing the internal behaviour of Li Ion Batteries is the Doyle-Fuller-Newman (DFN) model, proposed by the three researchers the model is named after in a series of papers in the early nineties [60]–[62]. The equations used in the model are summarised in Table 2.1, with the different processes occurring in the battery shown in Fig. 2.1.

In the DFN model, solid-state diffusion within the electrode particles is described by Fick's law, see Equation 2.1. Mass transport and concentration dynamics in the electrolyte are captured using concentrated electrolyte theory, as shown in Equation 2.2 and Equation 2.3. The influence of electrode porosity on transport properties is accounted for through porous electrode



Figure 2.2: Open circuit voltages of full cell, positive electrode and negative electrode plotted versus SoC for the full cell. Note that unused capacity of electrodes extend outside 0 and 100% full cell SoC.

theory, employing the Bruggeman correction, see Equation 2.4, where the correction factor β typically takes a value around 1.5 but may vary depending on morphology. The interfacial charge transfer reaction at the electrode surface is modelled using the Butler–Volmer equation, see Equation 2.5, with the exchange current density defined by Equation 2.6.

The DFN model can also be augmented to include non-ideal behaviour and side reactions [54], making it a popular choice for researchers focusing on battery ageing.

Process	Equation	
Solid state mass	$\frac{\partial c_{\rm s}}{\partial t} = \frac{D_{\rm s,eff}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right)$	(2.1)
transfer	$\frac{\partial c}{\partial r}\bigg _{r=0} = 0 \qquad D_{\rm s} \left. \frac{\partial c_{\rm s}}{\partial r} \right _{r=R_{\rm p}} = \frac{i}{Fa_{\rm s}}$	
	$\epsilon \frac{\partial c_1}{\partial t} = \nabla \cdot D_{1,\text{eff}} \nabla c - \frac{i_1 t_+^0}{F}$	(2.2)
Mass transfer in electrolyte	$\mathbf{i}_{\mathrm{l}} = -\sigma_{\mathrm{l,eff}} \nabla \phi_{\mathrm{l}} + \left(\frac{2\sigma_{\mathrm{l,eff}} RT}{F}\right) \left(1 + \frac{\partial \ln f_{\mathrm{A}}}{\partial \ln c_{\mathrm{l}}}\right) \left(1 - t_{+}^{0}\right) \nabla \mathbf{f}_{\mathrm{H}}$	$\ln c_1$ (2.3)
	$\sigma_{l,eff} = \sigma_l \epsilon_l^{\beta}$ $D_{l,eff} = D_l \epsilon_l^{\beta}$	(2.4)
	$i = i_0 \left(\exp\left(\frac{\alpha_a nF}{RT} \eta\right) - \exp\left(-\frac{\alpha_c nF}{RT} \eta\right) \right)$	(2.5)
Charge transfer reaction	$i_{0} = Fk_{\rm ct} \left(c_{\rm s,max} - c_{\rm s,surf} \right)^{\alpha \rm a} c_{\rm l}^{\alpha \rm a} c_{\rm s,surf}^{\alpha \rm c}$	(2.6)
	$\eta = E_{ m ct} - E_{ m eq}$	

Table 2.1: Summary of equations as used in the DFN model.

2.3 Ageing in Li-ion Batteries

The operation of LIBs described in Section 2.1 is however an idealised version only including the sought after intercalation reactions, and ignoring the possible unwanted side reactions, which are what makes batteries age.

Ageing phenomena in Lithium Ion Batteries have been discussed extensively in the scientific literature, with overviews performed in for instance [63]–[66], where the authors have concluded that the main degradation comes from four unwanted side reactions.

- SEI growth
- Lithium plating
- Particle cracking in active material
- Positive electrode decomposition

In the following sections each of these will be explained in more detail.

SEI Growth

A layer of electrochemically passivating compounds needs to be formed on the surface of the graphite anode, since all commonly used electrolytes are unstable at potentials below 0.8 V vs. Li/Li⁺ [67] and graphite electrodes are operated well below this threshold (typically down to $\sim 0.05 \,\mathrm{V} \, vs. \,\mathrm{Li/Li^+}$). This means that where graphite electrode and electrolyte come in direct contact a redox reaction will occur in which the different carbonates and the Li⁺ in the electrolyte react with electrons from the electrode to form solids on the negative electrode material [68], [69]. These solids then form a protective layer on the negative electrode stabilising the system to lessen further reduction of electrolyte. Therefore the SEI layer can be said to be both a blessing and a curse since its existence helps stabilise the negative electrode and enables the usage of graphite as negative electrode operating at low potential, but it also irreversibely consumes Li, meaning that cycling capacity is lost upon SEI formation. The properties of the SEI will also have a significant influence on how the battery ages, as the permeability of Li⁺ to migrate through the SEI layer is an important factor in determining cell impedance.

The main formation of SEI will occur in the first cycles of a fresh battery, but since the SEI layer is somewhat porous to allow for Li^+ migration it will continue to grow continuously throughout the batteries service life. The exact mechanism through which SEI growth happens has not been fully clarified, but an overview by Single *et al.* [44] found that four long term growth regimes are suggested in literature:

(a) Diffusion of solvent/salt through SEI pores.

- (b) Electron tunneling through inner layer of SEI.
- (c) Electron conduction through SEI.
- (d) Diffusion of neutral radicals, typically Li interstitials.

where (a) assume SEI to be sufficiently porous for larger solvent molecules to reach electrode surface, (b) assume sufficient porosity for solvent molecules to reach within tunnelling distance ($\approx 2 \text{ nm}$ [70]) from the electrode. Electron conduction (c) makes no assumptions about porosity, but requires non-zero electrical conductivity of the SEI. Neutral radical diffusion (d) assumes mobility of neutral species, namely Li , through the SEI. The growth modes are graphically presented in Fig. 2.3.

As the process bottleneck is transport processes driven by concentration gradients rather than overpotentials its occurrence is not limited to duty cycling, but will also occur during storage where cells are not subjected to any load. This makes SEI growth particularly interesting in EV applications where vehicles are known to be parked in excess of 90% of the time [71], making SEI a likely main contributor to degradation of EV batteries.

The thickness of the SEI layer is however also affected by the cycling conditions. During the intercalation process, graphite will expand and contract causing mechanical stress to the SEI layer. This can in turn lead to crack formation and breakage in the SEI. If the cracks are deep enough they can expose pristine electrode material to electrolyte and thus cause further formation of SEI and corresponding capacity loss.

Lithium Plating

Lithium plating is another degradation process occurring on the negative electrode due to operation at low potential, where Li^+ from the electrolyte form metallic Li on the electrode surface rather than intercalate into the electrode. It happens when the intercalation process is slower than the charging process leading to the current being split into an intercalation and a plating current [72]. This can happen for two main reasons

- 1. Local saturation of graphite electrode.
- 2. Kinetically driven due to negative overpotential.


Figure 2.3: Schematic illustration of the four suggested growth models detailed in Section 2.3. Red and orange indicate regions where SEI growth is happening, arrows and curves indicate transport of species involved in reaction

Local saturation can happen due to slow intercalation meaning that surface layers of graphite are full despite overall concentration in particles are not critical. This is often caused by low temperatures and/or fast charging. Saturation can also happen due to overcharging where the graphite is near saturation throughout, which reduces the rate of diffusion.

The kinetically driven process occurs when, despite concentrations of hosted Li being below maximum, the overpotential of the Li plating reaction, $\eta = \phi_{\rm s} - \phi_{\rm l}$, drops below 0 V vs. Li/Li⁺. Here η denotes the reaction overpotential, $\phi_{\rm s}$ denotes solid phase potential and $\phi_{\rm l}$ denotes liquid phase potential. This means that the reduction of Li⁺ to metallic Li on the particle surface becomes thermodynamically favourable. The conditions for this to occur are similar to those for local saturation with low temperature and fast charging being main causes for a drop in negative electrode potential and rise in liquid phase potential. For a schematic visualisation of Li plating, see Fig. 2.4.

Lithium plating is, just like all metallic electroplating reactions, reversible with the reverse reaction dubbed "Lithium stripping". However in a battery, SEI is formed on the plated Li if exposed to electrolyte due to the low potential $(0 \text{ V } vs. \text{ Li/Li}^+ \text{ by definition})$. This can cause the metallic Li to become electrically isolated making it permanently lost to cycling. Isolated Li covered



Figure 2.4: Visual schematic of processes involved in Li plating.

in SEI is denoted as *dead lithium*. This process means that lithium plating can only be said to be partially reversible and causes irreversible capacity loss.

One further way that plated Li can be recovered is by subsequent insertion into the electrode regardless of external current [73]. This is assuming that there are available sites in the electrode host structure, meaning that plating has not occurred due to overcharge.

Modelling Lithium Plating

The plating and stripping of Li can be modelled as a kinetically limited process, meaning that it is governed by a Butler-Volmer equation. Since Li is not abundant on the electrode surface a concentration dependence must also be included in the model to avoid unlimited Li stripping occurring in normal operation. The concentration dependent Butler-Volmer equation can be written as

$$i_{\rm Li} = i_{0,\rm Li} \left(\frac{c_{\rm Li}}{c_{\rm Li,ref}} \exp\left(\frac{\alpha_{\rm a} F \eta}{RT}\right) - \frac{c_{\rm l}}{c_{\rm l,ref}} \exp\left(-\frac{\alpha_{\rm c} F \eta}{RT}\right) \right).$$
(2.7)

The concentration c_{Li} denotes the concentration of metallic Li and is calculated by solving the differential equation $\frac{\partial c_{\text{Li}}}{\partial t} = \frac{i_{\text{Li}}}{F}$ and $c_{\text{Li,ref}}$ denotes a reference concentration of plated Li, and is used as tuning parameter in most published work [47], [54]. The concentration of Li⁺ in electrolyte is denoted as c_{l} , and $c_{\text{l,ref}}$ denotes the reference concentration in electrolyte. In the ButlerVolmer equation R is the gas constant, F is the Faraday constant, T denotes temperature and $\alpha_{a/c}$ denotes anodic and cathodic transfer coefficients respectively. The exchange current density of the plating reaction, $i_{0,Li}$, is calculated as $i_{0,Li} = Fk_{Li}c_{l,ref}c_{Li,ref}$, where k_{Li} is the kinetic rate constant and the overpotential of the reaction is $\eta = \phi_s - \phi_l$. When η is positive, the anodic reaction of Li stripping is kinetically favourable, and when η is negative the cathodic Li plating reaction dominates.

Particle Cracking

As mentioned in Section 2.3 the intercalation and de-intercalation processes causes alternating mechanical stresses in the electrode materials. The repeated stresses can in turn cause material fatigue and crack formation and propagation [51].

This contributes to capacity loss not only through re-formation of SEI consuming cyclable Li, but in extreme cases the cracks can cause parts of particles to become electrically disconnected from the rest of the electrode. This leads both to a loss of active material that can host Li and to the loss of the Li that is intercalated in the portion of the electrode particle that is disconnected [63].

Positive Electrode Decomposition

As mentioned in Section 2.1 most commercially available positive electrode are transition metal oxides (TMOs) which are susceptible to ion dissolution and migration and irreversible detrimental changes to the crystal structure. Layered oxides (for example lithium nickel manganese cobalt oxide (NMC) and lithium nickel cobalt aluminium oxide (NCA)) can experience irreversible phase changes where the crystal structure decompose to disordered spinel or rock salt phases which are not capable of hosting intercalating Li . This can happen on entire surface layers of particles creating a passivating layer making the particle inaccessible to cycling, or locally with corresponding loss of active material. This process is accelerated at high potential/low lithiation [74].

Furthermore the transition metal in the positive electrode material can react with the electrolyte if highly oxidised nickel comes in contact with electrolyte. This causes electrolyte decomposition and the Ni ions can migrate to the negative electrode and form passivating surface film [66].

2.4 Characterisation Techniques

In this section a theoretical background is provided for the main charachterisation methods implemented in the studies is provided.

Incremental Capacity Analysis (ICA)

Incremental capacity is the derivative of cumulative capacity with respect to voltage, expressed mathematically as

$$ICA = \frac{\mathrm{d}Q}{\mathrm{d}U}.\tag{2.8}$$

This is useful as the voltage of an electrochemical cell is an expression of the chemical potential of the system, which follows Gibbs' phase rule, meaning that the slope of the chemical potential is corresponding to degrees of freedom in the thermodynamic system. As such, the voltage curve will exhibit plateaus and slopes corresponding to the solid state phases, and the transitions between them in the material. Plateaus on the voltage curve show up as peaks on the incremental capacity analysis (ICA) plot, and correspondingly slopes will show as valleys on an ICA plot. Voltage plateaus will be present when two or more phases coexist at the same potential, thus indicating a phase change between stages of lithiation for the electrode materials [75].

An example of the method is shown in Fig. 2.5, where ICA on individual electrodes with peaks marked is combined with full cell ICA, where the combined cell peaks are marked according to the electrode they originate from. For details on the phase transitions and methodology see **Paper B**.

By tracing the intensity of individual peaks as well as the distance between peaks, the ageing of individual electrodes can be assessed. In order for the slope of the voltage curve to be dominated by the material OCV curve, overpotentials in the incremental capacity test need to be low. Therefore these tests are performed at low C-rates (<C/10 for energy optimised cells) for clearer results.

Differential Voltage Analysis (DVA)

Differential voltage is the inverse of incremental capacity, being defined as the derivative of voltage with respect to cumulative capacity: $\frac{dU}{dQ}$. The main advantage of differential voltage analysis (DVA) relative to ICA is that the



Figure 2.5: ICA on charge and discharge of each electrode and a full, cylindrical cell at beginning of life (BoL). Electrodes are harvested and reassembled into half cells and cycled at C/10: (a) NMC/Li, (b) Gr-SiO_x/Li. (c) NMC/Gr-SiO_x full cell at C/20. Reproduced and adapted from **Paper B**.

analysis is performed relative to capacity. This makes it possible to track the individual electrode capacity by tracking distances between peaks during cycling, making it a powerful tool for assessing electrode ageing.

As the voltage of the cell is the difference of positive and negative electrode potential

$$U_{\rm cell}(Q) = U_{\rm pe}(Q) - U_{\rm ne}(Q).$$
 (2.9)

The derivative of the full cell voltage is the sum of the derivatives of the individual electrode potentials

$$\frac{\mathrm{d}U_{\mathrm{cell}}}{\mathrm{d}Q_{\mathrm{cell}}} = \frac{\mathrm{d}U_{\mathrm{pe}}}{\mathrm{d}Q_{\mathrm{pe}}} + \left(-\frac{\mathrm{d}U_{\mathrm{ne}}}{\mathrm{d}Q_{\mathrm{ne}}}\right).$$
(2.10)

This makes the assignment of peaks more intuitive since the individual electrodes and full cell can be made to share x-axis with relatively simple scaling, which enables accurate electrode balancing, see Fig. 2.6. From this Figure it can also be noted that capacity values can be calculated based on distances between peaks, which can then be used as trackers for the individual material ageing.

Intermittent Current Interruption (ICI)

Based on a procedure very similar to the pseudo-OCV used for ICA/DVA the intermittent current interruption (ICI) characterisation methods is based on a slow (dis-)charge process with regular current interruptions (10 s) to track the voltage during rest phase. Based on the voltage profile during rest, significant additional information can be retrieved from the ICI test compared to a pure pseudo-OCV test [76]. This is done by noting that the internal processes of a battery will show up at different time scales in a measurement, with very fast voltage changes (t < 2 ms) being attributed to electrolyte resistance, events in the somewhat slower time scale (t < 1 s) attributed to charge transfer processes, and slower changes (1 s < t < 10 s) attributed to diffusion processes. Of special interest is the diffusion related parameter k that can be extracted as

$$k = -\frac{1}{I} \frac{\mathrm{d}U}{\mathrm{d}\sqrt{t}} \tag{2.11}$$

when t > 1 s, where I is the current applied during (dis-)charge and the fraction $\frac{dU}{d\sqrt{t}}$ denotes the linear slope of the voltage versus square root of



Figure 2.6: DVA for each electrode combined with full cell for the LG MJ1 cell described in Table 3.1. Individual electrode DVA has been scaled by size and unused end capacity to achieve peak fitting, which allows assigning full cell peaks to corresponding half cell peak. Vertical lines mark material peaks that are used to trace capacity retention of electrodes during cycling. Reproduced and adapted from Paper E.



Figure 2.7: Schematic of ICI test visualised for (a) Linear fit versus square root of time. (b) Definition of dU_{reg} .

time in this time scale. This has been shown in [77] to correlate to diffusion parameter σ in the Warburg impedance as $k = \sigma \sqrt{\frac{8}{\pi}}$. The linear behaviour of voltage with square root of time is displayed in 2.7a.

The linear regression means that the analysis becomes relatively robust to noisy data and sensor precision, which can cause issues when estimating impedance from single data points. This makes it beneficial to also define a pure resistance parameter $R_{\rm reg}$ that describes the impedance calculated based on the regression extrapolated to t = 0 s as

$$R_{\rm reg} = \frac{dU_{\rm reg}}{I} \tag{2.12}$$

Hysteresis Analysis

It is reported in literature that SiO_x produces large hysteresis between charge and discharge voltage at the same lithiation [78], [79]. In mixed materials electrodes this can be utilised to investigate the relative activity of SiO_x by calculating the hysteresis between charge and discharge voltage at the same SoC

$$U_{\rm hyst} = U_{\rm chrg} - U_{\rm dchg}.$$
 (2.13)

If this is calculated using data from low current galvanostatic cycling the influence from overpotentials can be minimised and a good approximation of the voltage hysteresis of the material can be obtained. A large hysteresis is thus indicative of SiO_x being the electrochemically active species and a smaller hysteresis indicates that lithiation is occurring mainly in graphite.

2.5 Analysis of Variance (ANOVA)

The analysis of variance is a commonly implemented statistical tool to discern between noise and signal in a dataset. This is achieved by testing whether differences found between measurements can be explained from variance with a reasonable probability [80]. This implies finding the probability of a null hypothesis of all subset means of the dataset being equal

$$H_0: \mu_1 = \cdots = \mu_n$$

versus the alternative hypothesis that a difference exists,

$$H_1: \mu_i \neq \mu_j$$
 for some (i, j).

The foundation of ANOVA is the decomposition of any sampled data into three parts, overall mean, set variance and error. For example, consider a total of N samples from I individual subsets, with n samples from each dataset such that $N = I \cdot n$. Then a unique sample k from subset i, denoted as Y_{ik} , can be decomposed as

$$Y_{ik} = \mu + \alpha_i + \epsilon_{ik}, \qquad \epsilon_{ik} \sim N(0, \sigma). \tag{2.14}$$

The parameters can be estimated from the data as

$$\hat{\mu}_i = \overline{y}_{i.} = \frac{1}{n} \sum_k y_{ik} \tag{2.15a}$$

$$\hat{\mu} = \overline{y}_{..} = \frac{1}{N} \sum_{k} \sum_{i} y_{ik}$$
(2.15b)

$$\hat{\alpha}_i = \overline{y}_{i.} - \overline{y}_{..} \tag{2.15c}$$

where the dot notation implies average, such that $\overline{y}_{i.}$ is the average for all

observations from subset i.

This decomposition means that a dataset with no significant difference between subsets would have a low value of α compared to ϵ , and conversely for a dataset with significant differences. To test this a decomposition of the total sum of squares is defined as

$$SS_{\rm T} = SS_{\rm A} + SS_{\rm E}$$

with

$$SS_{\rm T} = \sum_{i} \sum_{k} (y_{ik} - \overline{y}_{..})^2, \qquad df_{\rm T} = N - 1$$
 (2.16a)

$$SS_{\rm A} = n \sum_{i} \hat{\alpha}_i^2, \qquad df_{\rm A} = I - 1 \tag{2.16b}$$

$$SS_{\rm E} = \sum_{i} \sum_{k} \hat{\epsilon}_{ik}^2, \quad df_{\rm E} = I(n-1).$$
 (2.16c)

Essentially this splits the variation in overall response between the variation in all groups $(SS_{\rm E})$ and variation between subsets $(SS_{\rm A})$. By normalising the sum of squares by degree of freedom we obtain a directly comparable metric, denoted as *mean squares*

$$MS_{\rm A} = \frac{SS_{\rm A}}{df_{\rm A}} \tag{2.17a}$$

$$MS_{\rm E} = \frac{SS_{\rm E}}{\rm df_{\rm E}}.$$
 (2.17b)

The expected values of the mean squares can be calculated as

$$E(MS_{\rm A}) = \sigma^2 \frac{n}{I-1} \sum_i \alpha_i^2 \tag{2.18a}$$

$$E(MS_{\rm E}) = \sigma^2. \tag{2.18b}$$

The expected values imply that inspecting the ratio between them would give good evidence against null hypothesis. Therefore the ratio $F = MS_A/MS_E$ is defined as test statistic, and the probability of obtaining a certain value for F under the null hypothesis, $P(F | H_0)$, is the output of the ANOVA test. Some hypothetical examples of how to interpret results of the ANOVA tests are shown in Table 2.2.

 Table 2.2: Examples of outcomes and interpretations of an ANOVA test on hypothetical experimental studies.

			-	
Ι	n	F	$P\left(F \mid H_0\right)$	Interpretation and comment.
10	2	5	0.03	H_0 can be rejected with 97% probability. Typically considered as significant.
10	2	0.5	0.37	H_0 can be rejected with 63 % probability. Typically considered as non-significant, although graphic inspection might indicate trend. H_0 can be rejected with 91.8 % probability.
7	60	3	0.082	Typically considered as non-significant as a minimum of 95% probability is required.

CHAPTER 3

Experiments

This chapter presents the test equipment used and details the test setup for all experiments conducted in this thesis.

3.1 Test Equipment

Cell tester Neware BTS-4000 A significant portion of the life cycle testing was performed using these cyclers. They are designed specifically for testing of cylindrical LIB cells with built-in cell holders. It has a voltage range up to 5 V and maximum current of 6 A.This corresponds to approximately 1.33C for the 2170 cells and 1.7C for the 1865 cells. It has a maximum sampling frequency of 10 Hz.

Potentiostat GAMRY Reference 3000 Electrochemical impedance spectroscopy (EIS) measurements were performed using a high-accuracy potentiostat. The voltage range is up to 15 V with a maximum current of 3 A. The frequency range of EIS testing is $10 \,\mu\text{Hz}$ to $1 \,\text{MHz}$.

PEC ACT50 Life cycle testing requiring either higher current or faster switching, ie high frequency, were performed on this cycler. The tester is

designed for a maximum of 50 A current with a minimum pulse duration of 2 ms for a voltage range of 0-5 V and a maximum logging frequency of 1000 Hz.

3.2 Test Objects

The studies reported in thesis utilise one of two test objects, either a 2170 Panasonic cylindrical cell from Tesla Model 3 or an LG MJ1 18650 cylindrical cell. An overview of the specifications of the cells are listed in Table 3.1.

Panasonic Tesla Model 3 cell

The Tesla Model 3 cell manufactured by Panasonic, is an energy optimised cell intended for use between 2.55 V and 4.18 V, with a capacity of 4.6 Ah for a weight of 68.45 g yielding an energy density of 242 Wh/kg. At such high energy densities the risk of Li plating is typically higher compared to a more power optimised cell, therefore all charging is performed with a moderate C/3 current to avoid skewing results due to substantial Li plating. Post-mortem activities were performed on this cell, and scanning electron microscopy images of the cross-section of the electrodes are shown in Fig. 3.1.



Figure 3.1: SEM of cross section of (a) positive NCA electrode and (b) negative SiO_x electrode. The metallic current collectors visible in lower part of images, the active material particles of various sizes and shapes above. Reproduced from **Paper C** under CC BY NC ND 4.0 license.

Parameter	Panasonic 2170	LG MJ1	
Manufacturer	Panasonic	LG	
Geometry	Cylindrical 2170	Cylindrical 18650	
Chemistry	NCA/Si-Gr	$\mathrm{NMC}/\mathrm{Gr}\operatorname{-SiO}_x$	
Capacity	$4.6\mathrm{A}\mathrm{h}$	$3.5\mathrm{A}\mathrm{h}$	
Weight	$68.45\mathrm{g}$	$49\mathrm{g}$	
Height	$70\mathrm{mm}$	$65\mathrm{mm}$	
Diameter	$21\mathrm{mm}$	$18\mathrm{mm}$	
U_{\max}	$4.18\mathrm{V}$	$4.2\mathrm{V}$	
U_{\min}	$2.55\mathrm{V}$	$2.5\mathrm{V}$	
$U_{ m nom}$	$3.6\mathrm{V}$	$3.63\mathrm{V}$	
Gravimetric energy density	$242\mathrm{Wh/kg}$	$259\mathrm{Wh/kg}$	

Table 3.1: Technical specifications of the Panasonic 2170 and LG MJ1 cells.

LG MJ1 cell

Similarly to the Tesla Model 3 cell, the MJ1 cell from LG is an energy optimised cell with a capacity of 3.5 Ah and an energy density of 259 Wh/kg despite the small 18650 footprint.

3.3 Reference Performance Test (RPT)

During cycling, regular check-ups are conducted to monitor the degradation of the cells. In all studies, except for the pulse charge study, these check-ups are performed using only slow ICA (dis-)charging. In the pulse charge study, however, each cell undergoes an ICI test during the check-up.

The frequency of these check-ups varies between studies, depending on the expected degradation [15]. However, the frequency is always based on full cycle equivalent (FCE), which allows for direct comparisons between full and partial SoC window cycling. FCE scales partial cycling to full cycling, meaning, for instance, that 10 cycles of $10\%\Delta$ SoC would be equivalent to 1 full FCE.

All reference performance tests (RPTs) conducted in the ageing tests of this study followed the same logic, with the only difference being whether an ICA or ICI were performed. This protocol is illustrated schematically in Fig. 3.2, with an example that includes the ICI test. The process is almost identical for the ICA test, with ICA replacing the ICI component.

The capacity test itself is conducted using a constant current, constant voltage (CCCV) charge cycle, beginning with an initial current of C/3 and a cut-off current of C/20 at U_{max} . Following this, a CC discharge is performed with C/3 current to U_{min} . To ensure accuracy, the capacity measurement is performed twice, and the average of the two measurements is used as the final capacity value for the corresponding RPT.

Moreover, the ICA test provides data for electrochemical analysis, partly by tracing the impedance through the pulse test. However, it also includes a full CC C/20 charge and discharge cycle between $U_{\rm min}$ and $U_{\rm max}$, which is required for both ICA and DVA purposes. For further details, see Section 2.4 and Section 2.4.

After the ICA test the final part of the RPT is comprised of charge and discharge pulses at three SoC levels. To obtain comparable SoC levels throughout the cycling, the cell is first fully charged by CCCV C/3 with cut-off current C/20 to U_{max} . After this the cell is discharged by CC C/3 current to a voltage level corresponding to 70% SoC and a charge and discharge pulse at the maximum current of tester (6 A/1.33C) is performed. The discharge and pulsing is then repeated for 50% and 30% SoC as well.

3.4 Electrochemical Impedance Spectroscopy

To enable further electrochemical characterisation, a subset of the cells performed recurring EIS sweeps. The impedance sweeps were performed between 1 kHz and 10 mHz with high accuracy setting to reduce impact of noise on the EIS results.

3.5 Intermittent Current Interruption

For the cells tested with ICI the implementation followed what is described by Geng et al. in [76] with 5 min of applied charge or discharge current of C/10 followed by a 10s rest period. The voltage limits were U_{max} and U_{min} as described in the cell data sheet, see Table 3.1.



Figure 3.2: The RPT sequence used for regular checkups during ageing tests with ICI test, (a) showing voltage profile, and (b) showing current profile.

3.6 Experimental Studies

The test matrices for the substudies were designed to investigate ageing as a function of SoC, temperature, and current pulsation frequency. These experimental ageing campaigns comprise main studies included in this thesis. The test conditions used for ageing testing related to dynamic battery usage are summarised in Table 3.2, the implemented test conditions for the investigation of Δ SoC is summarised in Table 3.3 and the test conditions for the statistical study are shown in Table 3.4. The Δ SoC study was divided into two parts: the "Small Δ SoC study", whose results are presented alongside the "Storage study" in **Paper B**, and the "Large Δ SoC study", presented in **Paper C**. Similarly the frequency studies were split into two parts, the part focusing on pulse discharge presented in **Paper A** and the pulse charge study presented in **Paper E**. Furthermore a study on required number of replicates for robust conclusions in LIBs ageing studies was performed and is presented in **Paper D**.

Frequency Studies

A key element of the project was to investigate the ageing effects of dynamic usage at different frequency ranges and conditions. This was done in two separate studies, one focused on pulsating discharge current with varying frequencies, described in detail in **Paper A**, and one study investigating dynamic charge and discharge, described in **Paper E**. Though connected in scope, they were not performed with the same test objects as discharge sub-study was performed on Panasonic 2170 cells and the charge study was performed on LG MJ1.

For the frequency studies, the tests are described in further detail in Table 3.2. The "Discharge study" and "Pulse Charge Category 1" were performed on Neware BTS-4000 and "Pulse Charge Category 2" was cycled on PEC ACT50 tester.

Small \triangle SoC Study

The objective of the small Δ SOC study study was to investigate the influence of the SoC window on degradation in cells with mixed negative electrode materials. To achieve this, a test matrix was designed with nine consecutive

			DDT	Duty cycle	T	
	Cells	I, MHZ	RPT	ratio	lest tag	
	2	1000	$67 \ \mathrm{FCE}$	50	$1000\mathrm{mHz}$	
	4	500	$50 \ \mathrm{FCE}$	67	$500\mathrm{mHz}$	
	4	250	$50 \ \mathrm{FCE}$	67	$250\mathrm{mHz}$	
D. 1	2	125	$50 \ \mathrm{FCE}$	67	$125\mathrm{mHz}$	
Discharge study	4	62.5	$50 \ \mathrm{FCE}$	67	$62\mathrm{mHz}$	
v	2	31.3	$50 \ \mathrm{FCE}$	67	$31\mathrm{mHz}$	
	4	15.6	$50 \ \mathrm{FCE}$	67	$16\mathrm{mHz}$	
	2	7.8	$50 \ \mathrm{FCE}$	67	$8\mathrm{mHz}$	
	3	3.9	$50 \ \mathrm{FCE}$	67	$4\mathrm{mHz}$	
1C reference	3	-	100 FCE	-	CC-ref	
	4	1000	40 FCE	50	1000 mHz PC-PD	
	4	1000	$40 \ \mathrm{FCE}$	50	$1000\mathrm{mHz}$ PC-NPD	
	4	500	$40 \ \mathrm{FCE}$	50	$500\mathrm{mHz}$ PC-PD	
Pulse Charge	4	320	$40 \ \mathrm{FCE}$	50	$320\mathrm{mHz}$ PC-PD	
Category 1	4	100	$40 \ \mathrm{FCE}$	50	$100\mathrm{mHz}$ PC-PD	
	4	100	$40 \ \mathrm{FCE}$	50	$100\mathrm{mHz}$ PC-NPD	
	4	10	40 FCE	50	$10\mathrm{mHz}$ PC-PD	
	4	-	40 FCE	-	CC-ref	
	Cells	f, Hz	RPT	Duty cycle ratio	Discharge pulse	
	2	1	$40 \ \mathrm{FCE}$	25	$1\mathrm{Hz}$ PC-PD-25	
	2	10	$40 \ \mathrm{FCE}$	25	$10\mathrm{Hz}$ PC-PD-25	
	2	50	40 FCE	25	$50\mathrm{Hz}$ PC-PD-25	
Pulse Charge	2	125	$40 \ \mathrm{FCE}$	25	$125\mathrm{Hz}$ PC-PD-25	
Category 2	4	1	$40 \ \mathrm{FCE}$	50	$1\mathrm{Hz}$ PC-PD-50	
	4	10	40 FCE	50	$10\mathrm{Hz}$ PC-PD-50	
	4	50	40 FCE	50	$50\mathrm{Hz}$ PC-PD-50	
	2	-	$40 \ \mathrm{FCE}$	-	1C-ref	

 Table 3.2: Summary of ageing tests performed in the frequency variation studies.

SoC windows, each defined by specific voltage cut-offs, to avoid SoC drift during cycling. The SoC windows consisted of nine consecutive 10 % Δ SoC intervals, starting at 5 % SoC and extending to 95 %. All cells were tested with a standard 1C discharge current and C/3 charge current. Since degradation typically occurs more slowly in partial SoC windows [15], [16], RPTs were performed less frequently, at intervals of every 150 FCE.

In addition to the cycling tests, this study also included a set of calendar ageing tests. These were conducted by charging the cells to a specific SoC and then leaving them without any load. After every 30 days an RPT was performed on the cells, with the addition of a full discharge and a CCCV charge to relevant SoC. Tests were performed at 15, 50 and 85% SoC.

Large Δ SoC Study

The large Δ SOC study study similarly focused on examining the effects of different SoC windows on ageing, but also incorporated the impact of temperature variations. This study featured three distinct SoC windows tested at two different temperatures.

In collaboration with partners at Uppsala University and the Royal Institute of Technology, the study also placed significant emphasis on post-mortem investigations to confirm and extend the findings from the in-situ characterisation. This involved opening several cells in an Ar-filled glovebox to extract samples from both pristine and aged cells and for the positive as well as the negative electrode. These were then investigated using a range of experimental techniques including inductively coupled plasma–optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and SEM/transmission electron microscopy (TEM). For details on the post-mortem techniques the interested reader is referred to **Paper C**.

All cycling tests for the Δ SoC studies were performed using the Neware BTS-4000 testers

Replicate Requirement Study

The primary objective of the replicate requirement study was to assess the intrinsic variability between cells. To achieve this, the experimental design was intentionally kept simple, thereby minimising the potential for test-induced

	# Cells	T, °C	$\mathrm{SoC}_{\mathrm{min}}$	${\rm SoC}_{\rm max}$	RPT	Test tag
	2	25	0	100	$50 \ \mathrm{FCE}$	R0-100
	2	25	50	100	$50 \ \mathrm{FCE}$	R50-100
Large ΔSoC	2	25	0	50	$50 \ \mathrm{FCE}$	R0-50
study	2	45	0	100	$50 \ \mathrm{FCE}$	H0-100
	2	45	50	100	$50 \ \mathrm{FCE}$	H50-100
	2	45	0	50	$50 \ \mathrm{FCE}$	H0-50
	2	25	5	15	150 FCE	5-15% SoC
	2	25	15	25	$150 \ \mathrm{FCE}$	15-25% SoC
Small ΔSoC	2	25	25	35	$150 \ \mathrm{FCE}$	25-35% SoC
study	2	25	35	45	$150 \ \mathrm{FCE}$	35-45% SoC
	2	25	45	55	$150 \ \mathrm{FCE}$	45-55% SoC
	2	25	55	65	$150 \ \mathrm{FCE}$	55-65% SoC
	2	25	65	75	$150 \ \mathrm{FCE}$	65-75% SoC
	2	25	75	85	$150 \ \mathrm{FCE}$	75-85% SoC
	2	25	85	95	$150 \ \mathrm{FCE}$	85-95% SoC
	2	25	15	15	Monthly	15% SoC
Storage study	2	25	50	50	Monthly	50% SoC
	2	25	85	85	Monthly	85% SoC

Table 3.3: Summary of ageing tests performed in the Δ SoC studies. All cells were
charged with C/3 current and discharged with an average current of 1 C.

	# Cells	$\mathrm{SoC}_{\mathrm{min}}$	$\mathrm{SoC}_{\mathrm{max}}$	$\mathrm{I}_{\mathrm{chrg}}$	$\mathrm{I}_{\mathrm{dchg}}$
Test A	8	0	50	$0.5\mathrm{C}$	$1\mathrm{C}$
Test B	8	50	100	$0.5\mathrm{C}$	$1\mathrm{C}$
Test C	8	0	100	$0.5\mathrm{C}$	$1\mathrm{C}$
Test D	8	0	100	$1\mathrm{C}$	$1\mathrm{C}$

Table 3.4: Ageing tests performed for number of replicates study.

variability. A total of 8 replicates per condition were cycled across four distinct test conditions, as summarised in Table 3.4. This approach was chosen to ensure that the variability observed could be attributed primarily to the inherent differences between individual cells, rather than external factors related to the test procedure.

All testing was carried out on LG MJ1 cells, which were selected for being well-characterised and often studied in academic literature [81]. The tests were performed using the Neware BTS 4000 tester.

CHAPTER 4

Results Extracted from Appended Papers

This chapter summarises the results obtained from the three studies described in Chapter 3 investigating how discharge current frequency and SoC windows affect battery degradation.

4.1 Effect of Dynamics in Cycling

The cycling of cells were conducted during 2020 and 2021, with initial results indicating surprisingly large spread in data between replicates. This prompted the addition of further tests in the instances where large spread was seen. This led to somewhat uneven distribution in number of cells tested, which can be seen from Table 3.2. The results presented below include all of the tested cells as no errors in test conditions could be found, so the spread is assumed to be a consequence of cell quality and should be taken into consideration for the study. These findings in cell-to-cell variability also prompted further investigation of the distribution of battery ageing, more details on which can be found in **Paper D** and a summary in Section 4.4.

The summarised degradation data for all the cells cycled with different discharge frequencies are presented in Fig. 4.1. As mentioned above, already



Figure 4.1: Capacity fade of all cells tested in the frequency study, together with the 1C reference. Worth noting significant spread in results between replicates. See Table 3.2 for test conditions.

from this figure a significant spread can be noted for the replicates, which makes analysis based directly on inspecting the capacity fade versus FCE difficult. However a weak trend can be noted, namely that the cells discharging with a lower frequency age at a slower rate compared to those at higher frequencies.

To clarify the results, another metric is introduced where the energy throughput at end of life (EoL), defined as 75 % of initial cell capacity, is calculated. This yields a single data-point per replicate which after grouping by frequency can be plotted as a box plot with the average and the spread for each set of replicates, see Fig. 4.2. From this plot the trend is more clearly visible with a tendency for the energy throughput to decrease with increasing frequency. This trend is however stronger in lower frequency (f < 100 mHz), and when only inspecting higher frequency no clear trend can be seen.

The surprisingly large spread between replicates still makes it hard to discern between noise and trend, so to be able to draw any conclusions statistical analysis is required. For this dataset, the ANOVA test is appropriate, as it is designed to check the null hypothesis of background noise versus an actual existing trend. In this work the ANOVA test is used and implemented in the R software [82]. That is, it seeks to investigate if the variations in the results can be explained by natural variance, or if that null hypothesis can be rejected, see Section 2.5 for further details.

The null hypothesis, H_0 , being that the actual means are the same for all data in the set, and any apparent differences are only due to the variance of the data. To assess whether the null hypothesis can be rejected the probability $P(H_0)$ is calculated for a given dataset. In this study $P(H_0) < 0.05$ is set as significance condition for rejecting the null hypothesis.

As a first step $P(H_0)$ is calculated for the full dataset resulting in $P(H_0) = 0.28$, or that there is a 72 % probability that we can reject null hypothesis. Since this is above the significance threshold, the null hypothesis can not be rejected for the full set.

However, as was noticed earlier, the trend is not equal across the dataset, but seems to be stronger in the frequencies below 100 mHz. Therefore a split of the dataset is introduced to assess whether a statistically significant trend can be identified in the low frequency region. By performing the ANOVA analysis for only f < 100 mHz a probability of $P(H_0 | f < 100 \text{ mHz}) = 0.028$ is obtained, meaning that in the lower frequency domain a statistically significant trend exists, and the null hypothesis can be rejected with 97.2 % probability.

On the high frequency part of the dataset on the other hand, the ANOVA test yields $P(H_0 | f > 100 \text{ mHz}) = 0.81$. This means that there is only a 19% probability that the null hypothesis can be rejected and no trend can be said to exist in this frequency range.

This strengthens the initial observation that there is a positive trend of cycle life when decreasing the cycling frequency, at least down to $\sim 4 \text{ mHz}$. However, the trend is not universal as all dynamic tests outperform the 1C reference case, which could be conceptualised as "zero" frequency by the convention of this study. This suggests that it could be of interest to further investigate ageing behaviour in the low frequency domain, preferably on a cell with less individual variance.

The trend that the high frequency cycling has little to no impact on the cycle life also fits well with the results found by Bessman *et al.* [83], who saw little influence when investigating f > 1 Hz. One should however keep in mind that even though no trend exists within the 0.1 Hz < f < 1 Hz domain, all these tests significantly outperform the 1C reference, so to realistically assess the cycle life of cells for a commercial application for instance, testing of dynamic cycling in this frequency range is definitely relevant.



Figure 4.2: Distribution of the energy throughput at EoL for cells cycled at different frequencies. Large spread is visible in numerous samples. Note that this does not include the 1C reference. Reproduced and adapted from Paper A.

4.2 Effect of dynamics in charging

In 2024 and 2025, an investigation into the dynamics of charging, as opposed to standard CC charging, was conducted on LG MJ1 cells (see Section 3.2 for details). The study focused on the effects of varying frequency and duty cycles in square wave pulse charging. Due to tester limitations, the experiments were divided into two categories with different mean currents. See Table 3.2 for test condition details.

The overall degradation results are shown in Fig. 4.3. A clear trend emerges: when comparing constant current (CC) charging to dynamic charging at similar current levels, dynamic charging consistently outperforms CC charging in terms of durability. However, this trend holds only when the pulse frequency exceeds 10 mHz. A similar trend is observed for both category 1 and category 2 tests, where CC operation proves to be the most detrimental to battery state of health (SoH). Category 1 data also aligns well with previous findings on cycling dynamics, showing that cases where the discharge current was dynamic outperformed those with constant current discharge.



Figure 4.3: Capacity fade for each pulse charge test condition, with data presented being mean for all replicates. (a) displays degradation data for cells in category 1. (b) shows degradation data for category 2. Reproduced and adapted from Paper E.

To gain deeper insights into these processes, electrochemical data from ICI tests were analyzed. Reconstructed half-cell data were used to assign ICA and DVA peaks to their respective electrodes. The peak assignment followed the method described in Section 2.4 and is displayed in Fig. 4.4.

To determine whether dynamic charging leads to qualitatively different aging mechanisms compared to constant current, we compared the ICA traces of cells at similar SoH levels. If dynamic and constant current charging induced fundamentally different aging mechanisms, we would expect to see distinct changes in peak intensity and voltage shifts in the ICA traces. However, as shown in Fig. 4.5, the peak evolution is remarkably similar across cells, suggesting that the fundamental aging mechanisms remain the same, though the rate of degradation varies with usage dynamics. From the ICA trace it is also clear that the main reduction in activity happens in peaks 1 and 2 which are attributed wholly or mainly to negative electrode (NE). It is therefore reasonable to assume that most of the degradation is taking place on the NE, and that this degradation is then accelerated in low frequencies and static conditions. Peak 1 is also known to be related to (re-)formation of SEI [84] and a large reduction in peak activity is indicative of significative SEI growth.

Although an average current of 2.5 A might appear moderate for a 3.5 Ah cell, these cells are highly energy-optimized. At high SoC levels, such currents



Figure 4.4: ICA and DVA traces of full cell with peaks assigned to respective electrode with (a) showing ICA and (b) DVA. Reproduced and adapted from Paper E.



Figure 4.5: ICA for beginning of life (BoL) reference plotted together with constant current reference and 1000 mHz, 500 mHz and 10 mHz pulse charge, pulse discharge at the same capacity retention. Reproduced from Paper E.

correspond to relatively fast charging. This, combined with the observed degradation occurring primarily on the NE, suggests the possibility of Li plating and subsequent SEI formation on plated Li.

Proving this hypothesis without invasive post-mortem analysis is difficult, however, an indication can be drawn from analysing the diffusive resistance k from the ICI test, see Section 3.5 for details. As this parameter will lump all diffusion related resistance together it is not possible to single out the resistance of the SEI layer or indeed any plated li, but typically the formation of a dense layer on either electrode will contribute disproportionately to the diffusive resistance as it is more difficult for Li⁺ to diffuse through a denser and more tortuous layer compared to a more porous one. In Fig. 4.6 the diffusion resistance at similar SoH levels is compared. From 4.6b, it can be observed that the diffusion resistance is considerably larger in the CC case, even though the overall ageing processes appear similar, as indicated by the comparable ICA traces. The left panel of Fig. 4.6 is somewhat noisy, but by averaging values in the 3.5-4.1 V range—chosen to minimize the influence of tail-end fluctuations—a clear trend emerges. The k-values for constant current 10 mHz cases are, on average, 8 % higher than those for 500 and 1000 mHz

While this does not provide conclusive evidence that dynamic charging reduces Li plating, the observed trends strongly suggest a potential benefit. Given the significant improvements in capacity retention—consistent with recent literature—dynamic charging emerges as a promising strategy for battery electric vehicles (BEVs) and other commercial LIB applications.

4.3 Effect of Low SoC Cycling

The study of different SoC windows was conducted in parallel with the frequency study and using the same Panasonic 2170 cell as test object. Further information about the cell can be found in Table 3.1. In this study comparatively less heterogeneity was found between samples, meaning that it was sufficient for all tests to be performed with 2 replicates, see Table 3.3 for further test condition information. For the smaller Δ SoC windows all tests were conducted at the same temperature, and for the large Δ SoC windows every test was performed in two temperatures, at 25 °C and 45 °C. The naming convention used for all figure legends reflect SoC window for small Δ SoC windows and temperature and SoC window for large Δ SoC windows.



Figure 4.6: Diffusion resistance parameter k as calculated from ICI test for cells of similar SoH.

All the data from the cycling study is summarised in Figures 4.7 and 4.8. From the data the overall trend that low SoC cycling has a detrimental effect on the capacity retention is clear. Worth noting in particular is that 5-15 % and 15-25 %SoC tests stand out with especially rapid degradation in the small Δ SOC study. This trend is more pronounced in the early stages of ageing with the capacity decay levelling out after approximately 1000 FCE, whereas for the large Δ SOC study the trend is continuous for all tests that cycle to low SoC. The dominance of the influence of low SoC windows on ageing can also be demonstrated by noting that all cases in large Δ SOC study that cycle to low SoC are closely grouped. As seen from Fig. 4.7 this happens regardless of the maximum SoC and the temperature. Ont he other hand, the tests that cycle with higher miniumm SoC, that is $SoC_{min} = 50$ %, show a clear temperature dependence, where a lower temperature reduces the rate of degradation.

The reason behind this strong SoC dependence can be investigated with in-situ techniques, especially utilising DVA and tracking peaks corresponding to each material in the electrodes. In Fig. 4.9 a comparison of DVA profiles for 5-15% SoC, Fig. 4.9a, and 85-95% SoC, Fig. 4.9b, is shown. For 5-15%, already at 150 FCE peaks S1 and S2 (see Fig. 2.6 for peak assignment), which are characteristic for SiO_x, are nearly lost. However in the 85-95% case S1 and S2 are still well-defined after 150 FCE. As cycling proceeds the SiO_x are completely lost in the low SoC case and the DVA profile is losing features



Figure 4.7: Capacity fade cells tested in large SoC windows. All cells shown in (a) with a subset of cells cycled to 0% SoC shown in (b) to improve visibility. Legends are consistent with test tag in Table 3.3. Reproduced from Paper C.



Figure 4.8: Capacity fade of cells tested in small Δ SoC windows. Legends are consistent with test tag in Table 3.3. Reproduced and adapted from Paper B



Figure 4.9: Comparison of DVA development with ageing for 5-15% case, shown in (a), and 85-95% case, shown in (b). The effect of low SoC cycling is clearly visible in loss of SiO_x related peaks in low SoC for 5-15% case. Reproduced and adapted from **Paper B**.

overall, except for the NCA peaks. This is indicative of inhomogeneous ageing in the electrode which leads to multiple lithiation stages coexisting in different locations in the cell leading to smearing out of equilibrium potentials.

Also visible from Figures 4.9a and 4.9b is the overall shift of the peaks leftward which can be seen as further indication that SiO_x , which contributes to the capacity in low SoC, is being lost. It can also be indicative of loss of lithium inventory (LLI), which is investigated in greater detail using DVA peak tracking, see below.

The decrease in active SiO_x can be further corroborated by analysis of the voltage hysteresis, ie the difference in voltage for the same SoC during slow galvanostatic charge and discharge cycling, see Section 2.4. The hysteresis calculation for a C/20 cycle is visually represented in Fig. 4.10a with repeated hysteresis calculations during cycling shown for 5-15% in Fig. 4.10b and for 85-95% in Fig. 4.10c respectively. It shows a clear disparity in hysteresis in low SoC (approximately < 15%) between the two cases. For the 5-15% cycling case, the hysteresis decreases from ~250 mV at beginning of life (BoL) to approximately 200 mV after 1200 FCE. For the 85-95% case the decrease is significantly smaller with hysteresis only decreasing to about 240 mV after 1200 FCE.

To extend this qualitative assessment of $Gr-SiO_x$ ageing, DVA was utilised



Figure 4.10: Comparison of the voltage difference between the charge and discharge part at the same SoC during C/20 cycling for (a) a full cell at BoL, (b) a cell cycled in 5-15% SoC window at three ageing stages, and (c) a cell cycled in 85-95% SoC window at different stages of ageing. Reproduced and adapted from Paper B.

to make quantitative analysis of ageing modes to further elucidate the degradation processes in the cells. This was done following a method detailed by Smith et al. [in 85] where by tracking the DVA peak distances during cycling, the overall capacity fade can be attributed to loss of active material (LAM) on each material as well as loss of lithium inventory (LLI). The results from DVA peak tracking are presented in Fig. 4.11 where Fig. 4.11a and (b) display all DVA curves with artifical offset, and 4.11c and (d) show the corresponding LAM and LLI trackers. Though the heterogeneity and resulting smearing/convolution of peaks caused some numerical issues and made the results somewhat jumpy, it still allows for concluding that LAM_{SiO_x} contributes to ageing in a low SoC cycling to a significantly larger extent than in high SoC cycling. In the 5-15 % case it contributes 7 % of overall ageing compared to 3 % in 85-95 % case. Also noteworthy is that the bulk of LAM_{SiO_x} happens in the first ~ 1000 FCE and flattens out for the rest of cycling, see Fig. 4.11c. This corresponds well with the overall capacity loss which show a more rapid capacity decay in the first ~ 1000 FCE to flatten out at a later stage, see Fig. 4.8, which indicates that degradation due to LAM_{SiO_x} contributes disproportionately to ageing until a significant portion of SiO_x is lost.

For both the tests investigated with DVA peak tracking, the main loss factor can be concluded to be LLI, see Figures 4.11c and (d). The LLI is particularly dominant for the 5-15% SoC cycling. Through post-mortem work performed at Uppsala University and described in detail in **Paper C** this is shown to be heavily influenced by the formation and reformation of dendritic SEI on SiO_x particles, which consumes Li^+ . Post-mortem analysis also revealed pore development in SiO_x particles that could also contribute to trapping of Li , and cause electrical isolation that leads to LAM.

For tests performed at high SoC the increase in capacity loss is attributed to LAM_{NCA} in the post-mortem investigation. In particular the findings show that particle fractures lead to voids in positive electrode particles and irreversible capacity loss.

4.4 Minimum replicate requirement

The findings from the previous studies indicate that cell-to-cell variance significantly affects battery ageing. Therefore, this factor was further investigated in a dedicated sub-study. This was done in a sub-study conducted in the first



Figure 4.11: DVA from all RPT through cycling shown for (a) 5-15% SoC cycling, and (b) 85-95% SoC window. (c) and (d) display key ageing factors tracked for each DVA during cycling. Reproduced from Paper B.

half of 2022 with an increased number of replicates — eight per test condition. This allowed for an assessment of when results stabilised and whether the number of replicates was sufficient. The test conditions utilised can be found in Table 3.4.

Four different methods were developed and assessed to determine the number of replicates needed for stable test results. This chapter highlights one of these methods, while further details can be found in **Paper D**.

An initial estimate of cell-to-cell variance can be obtained at BoL by measuring capacity and impedance of all tested cells. In this study it was found, following notation suggested in [32], that the average capacity of all cells was $\mu_{\rm C} = 3340$ mAh with a standard deviation of cell capacity of $\sigma_{\rm C} = 18.9$ mAh, which yields a relative coefficient of capacity variation of $\kappa_{\rm C} = 0.56$ %.

Cycles to End of Life

To evaluate the stability of ageing test results, a standard capacity decay model was implemented following [86]. This model predicts the number of cycles until a given capacity retention level, expressed as

$$Q = Q_0 \exp\left(-\frac{x}{\tau}\right)^{\beta} \tag{4.1}$$

with Q_0 , τ and β as fitting parameters and x being the number of full cycle equivalents. This model could then be fitted using different subsets of the full dataset to find the probability that for a given size of the subset it would over-estimate the number of cycles to EoL, $n_{\rm EoL}$ by more than 5%. This one-sided rejection condition was chosen because an underestimation of $n_{\rm EoL}$ is a conservative error which is unlikely to lead to significant warranty cost for the cell and/or equipment manufacturer.

To find the risk of overestimation, all possible $\binom{N}{k}$ combinations to sample k cells, where $k \in [2, N - 1]$, were fitted with (4.1). That allows for the calculation of $n_{\text{EoL},k,i}$ for each combination i of k cells, which could then be compared to $n_{\text{EoL},N}$ for the complete dataset (N = 8), which was taken as ground truth in the study. The risk of 5% overestimation can then be calculated by dividing the number of combinations which yielded $n_{\text{EoL},k,i} > 1.05 n_{\text{EoL},N}$ with the total number of combinations $\binom{N}{k}$.

Since the number of combinations is limited, the computed probability remains numerically sensitive. To address this, a more stable method is intro-
	Number of Replicates							
	2	3	4	5	6	7		
Test A	14	7	$\left(2.8\right)$	0.64	0.04	0		
Test B	35	28	21	14	7	1.1		
Test C	30	23	16	9.5	3.8	0.32		
Test D	15	7.8	3.3	0.85	0.07	0		

Table 4.1: Probabilities of 5 % or more overestimation of FCE to EoL for all numberof replicates, with the lowest number replicates with probability lessthan 5 % marked for each test condition.

duced. To obtain such a method it is assumed that the population of cycles to EoL is normally distributed, ie $n_{\text{EoL}} \sim \mathcal{N}(\mu_n, \sigma_n)$ where the point estimates $\hat{\mu}_n$ and $\hat{\sigma}_n$ of μ_n and σ_n cen be calculated for some number of replicates, k, to be

$$\hat{\mu}_{n, k} = \frac{1}{\binom{N}{k}} \sum_{i} n_{\text{EoL}, k, i}$$

$$(4.2)$$

$$\hat{\sigma}_{n, k} = \sqrt{\frac{1}{\binom{N}{k} - 1} \sum_{i} n_{\text{EoL}, k, i} - \hat{\mu}_{n, k}}$$
(4.3)

such that the distribution of $n_{\text{EoL},k}$ can be modelled as $n_{\text{EoL},k} \sim \mathcal{N}(\hat{\mu}_{n,k}, \hat{\sigma}_{n,k})$. The probability of overestimation is calculated as

 $1 - F(1.05 n_{\rm EoL,N})$

with F being the cumulative distribution function $F = \int_{-\infty}^{x} P(t) dt$.

The results of this algorithm are shown in Fig. 4.12, where the histogram shows the frequency of $n_{\text{EoL},k}$ with the fitted normal distribution overlaid in blue. The shaded orange area indicates the cumulative risk of overestimating $n_{\text{EoL},k}$ by more than 5% compared to ground truth, which can be seen for this particular case to be 7.03%. A dataset was considered sufficiently large if this overestimation risk remained below 5%.

This procedure was applied to all test conditions and replicate combinations



Figure 4.12: Histogram with fitted normal distribution for the number of FCEs estimated until EoL. Data to the right of dashed green line are cases where number of FCEs to EoL are overestimated by more than 5% compared to the reference case.

to determine the minimum required dataset size. The summary results are shown in Table 4.1, from which it can be concluded that at least four replicates are needed to reduce the risk of overestimation sufficiently. However, the required number of replicates varies depending on the test condition, as different conditions lead to different degrees of variability in the data.

It is worth noting that these results apply specifically to the tested cell type, while previous studies have reported required replicate numbers as high as 9–10 [30], [31]. To further explore the influence of cell-to-cell variance, the dataset was artificially modified to simulate different levels of ageing variability. The same method was applied to the modified datasets, where noise levels were artificially increased or decreased. The results, summarized in Table 4.2, indicate a clear dependence on cell-to-cell variance. Since the extent of ageing variability is unknown at the time of experimental design — unless extensive pre-tests are conducted, which would delay testing and increase costs — one potential solution is to include a standardized ageing test in commercial cell datasheets. Such a datasheet value would enable assigning the correct number of replicates to planned ageing tests.

Increase Variance							
	2	3	4	5	6	7	
Test A	24.7	17.0	10.5	5.1	1.3	0.0	
Test B	42.6	36.5	30.6	24.2	16.4	6.2	
Test C	38.7	32.7	26.7	20.2	12.5	$\left(\begin{array}{c} 3.7 \end{array}\right)$	
Test D	25.2	17.8	11.3	5.7	1.7	0.1	
Decrease Variance							
	2	3	4	5	6	7	
Test A	(4.9)	1.3	0.2	0.0	0.0	0.0	
Test B	25.8	17.6	10.7	5.1	1.3	0.0	
Test C	19.3	11.8	6.2	2.3	0.4	0.0	
Test D	5.5	1.6	0.3	0.0	0.0	0.0	

Table 4.2: Probabilities of overestimation of FCE to EoL, analogous to Table 4.1, with variance synthetically increased or decreased by 50%. The increased variance is shown above, and decreased variance below.

CHAPTER 5

Conclusions

In the presented work, test matrices were designed to comprehensively assess the influence of SoC and current dynamics on battery degradation. Based on these data, it can be concluded that dynamic cycling plays a critical role in the ageing of LIBs. A similar conclusion applies to SoC variations, where SiO_x doping in the negative electrode plays a dominant role.

Degradation is particularly sensitive to frequency in the lower range – approximately f < 100-500 mHz during discharge and f < 100 mHz during charging. At higher frequencies, the effect of frequency on degradation is less pronounced, although cells subjected to dynamic cycling still exhibit significantly improved durability compared to the constant current (CC) case. For charging, electrochemical analyses indicate reduced Li plating and SEI (re-)formation under dynamic conditions. Although further investigation is needed, these findings suggest that charging speeds could be increased without compromising durability.

Furthermore, a strong SoC dependence was identified, with the most rapid capacity loss occurring at low SoC levels (<25%), the slowest degradation observed in the mid-SoC range, and an accelerated degradation rate at high SoC. Cycling within smaller Δ SoC windows resulted in slower degradation compared to larger Δ SoC windows, consistent with previously reported findings [15]. The study also confirmed prior results regarding temperature effects, demonstrating that lower temperatures reduce the degradation rate. However, the influence of SoC was found to be dominant, particularly in low SoC cycling, suggesting that, in cells with mixed negative electrodes containing SiO_x, SoC dependence has a greater impact on cycling ageing than temperature.

The rapid degradation at low SoC levels is likely driven by SiO_x , contributing to LLI through unstable SEI formation and $\text{LAM}_{\text{SiO}_x}$ during cycling. Similarly, the increased degradation observed in high SoC windows is likely driven by accelerated LAM_{NCA}.

CHAPTER 6

Future Work

While many questions have been addressed throughout this project, but several compelling research questions have arisen beyond the scope of this PhD.

In particular, the field of dynamic charging presents several opportunities for further investigation. Extending the frequency ranges, exploring a broader range of duty cycles at low frequencies, and conducting cycle testing with modified pulse patterns are promising directions for future research. Additionally, further post-mortem analysis of the tested cells would be valuable to verify the findings from in-situ investigations, particularly regarding the correlation of pulse charging with lithium plating and SEI (re-)formation.

There are also significant opportunities to extend this research through physics-based modelling, given the rapid advancements in this field in recent years. Modelling the impact of ageing dynamics on key degradation mechanisms – such as lithium plating, particle cracking, and long-term SEI growth – would provide important insights to complement the experimental findings of this study.

Post-mortem investigations would provide valuable insights not only into dynamic cycling and charging but also into the intrinsic variability examined in the replicate requirement study. Examining the heterogeneity of ageing among replicates tested under identical cycling conditions could offer deeper insights into the factors contributing to cell-to-cell variance. This could also clarify whether cell design parameters influence the number of replicates required for statistically robust ageing assessments. Additionally, performing material characterisation for the Doyle-Fuller-Newman (DFN) model could enable the modelling of heterogeneous ageing dynamics through statistically distributed model parameters.

Addressing these open questions would improve our understanding of how batteries degrade under controllable yet realistic cycling conditions and could help refine charging algorithms while better adapting battery management systems to ageing under dynamic conditions. This is essential not only for bridging the gap between controlled laboratory environments and real-world testing, but also for supporting the continued mass-market adoption of electric vehicles.

CHAPTER 7

Summary of Included Papers

7.1 Low Frequency Influence on Degradation of Commercial Li Ion Battery

In this paper we present the influence of low frequency $(<1 \,\mathrm{Hz})$ current harmonics on ageing in a commercial LIB.

Problem

Battery electric vehicle usage is very different from the more idealised utilisation in laboratory studies of ageing, which typically utilise constant current charge and discharge to scope the degradation of battery cells. In this paper we seek to introduce an alternative testing methodology with parameterisable discharge patterns to closer emulate usage in a real application while maintaining governing parameters to a manageable set.

Contribution

In this paper, we introduce a testing method for parametrisable dynamic battery testing, which makes it possible to elucidate the influence of low frequency current harmonics on battery degradation using a standard battery tester. The focus in this paper is on discharge current harmonics, but could be implemented analogously for charge currents, or combinations of both.

The cycling resulted in statistically significant influence on ageing from current frequency in the region below f < 0.1 Hz, but no influence could be found in the region where f > 0.1 Hz. Furthermore, a clear preference for dynamic cycles over the reference constant current (CC) 1 C cycle was found, as the CC performed significantly worse than all pulse frequencies tested (0.04 Hz to 1 Hz).

Methodology

The test protocol is a square wave profile with an average discharge current the same as a standard 1 C discharge. This was implemented on a standard NEWARE BTS-4000 battery cycler with regular check-up tests performed every 50 Full cycles. In each check-up capacity, impedance and incremental capacity measurements were performed to assess battery degradation.

Author contributions

Kristian Frenander: Investigation, Conceptualization, Methodology, Writing - original draft, Writing - review & editiing, Visualization. **Torbjörn Thiringer**: Conceptualization, Writing - review & editing, Supervision, Funding acquisition, Project administration, Resources.

7.2 The state of charge dependence of degradation in lithium-ion cells from a Tesla model 3

In this paper, we present an ageing study of commercial cells with NCA positive electrode and mixed graphite/SiO_x negative electrode, with a focus on the SoC dependence of ageing.

Problem

Findings in the literature indicate that there is a correlation between SoC and both cycling and storage ageing of LIBs. However, the nature of this correlation is highly dependent on the battery chemistry and configuration. Understanding this influence is crucial to take into account when designing battery control systems and usage strategies to maximise battery durability.

Contribution

The capacity fade results for cells with an NCA positive electrode and a mixed graphite/SiO_x negative electrode cycled in sequential 10 % SoC windows are presented. Additionally, extensive in-situ analysis is performed to investigate the ageing mechanisms across different SoC windows, with a particular focus on the low SoC region.

Furthermore, calendar ageing results for three SoC levels (15 $\%,\,50\,\%,$ and 85 %) are reported.

This paper reveals an unexpected SoC-ageing correlation, where cells cycled at low SoC degrade more rapidly than those cycled at higher SoC. The optimal region for minimizing degradation is found to be between 35% and 75% SoC, with a slight increase in degradation above 75% SoC. In contrast, for calendar ageing tests, the trend is reversed, with high SoC cells degrading faster than those stored at low SoC.

In the low SoC region, SiO_x is found to contribute disproportionately to the rapid degradation due to the loss of cyclable SiO_x . This conclusion is supported by ICA, DVA, and hysteresis analysis, which also indicate that loss of lithium inventory (LLI) is the primary driver of overall capacity loss in cells cycled at low SoC.

Methodology

Nine consecutive 10% SoC windows were defined by voltage limits and cycling performed with 1 C constant current discharge and C/3 charge. Regular checkups with capacity, impedance and incremental capacity measurements were performed every 150 cycles. Each test was run with duplicate cells to ensure reproducibility of results, yielding a total of 18 cycled cells and 6 calendar aged cells.

The main techniques utilised to understand ageing processes are ICA and DVA. Using ICA to demonstrate qualitatively the loss of active silicon and heterogeneity in ageing, and DVA to seek to quantify loss of silicon and also LLI.

Author contributions

Niladri Roy Chowdhury: Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Investigation, Data curation. Alexander J. Smith: Visualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. Kristian Frenander: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing, Visualization, Data curation. Anastasiia Mikheenkova: Methodology, Writing – review & editing. Rakel Wreland Lindström: Writing – review & editing, Supervision, Funding acquisition, Resources. Torbjörn Thiringer: Conceptualization, Writing – review & editing, Supervision, Funding acquisition, Resources, Project administration.

7.3 Ageing of High Energy Density Automotive Li-ion Batteries: The Effect of Temperature and State-of-Charge

Similarly to **Paper B** we focus on the SoC influence on ageing in this paper. Here the focus is shifted to larger SoC windows and positive electrode degradation.

Problem

Understanding both the SoC and temperature influence on ageing in commercial EV cells is necessary to be able to develop optimise usage strategies for both drivers and manufacturers.

Contribution

In this paper we show that ageing on positive electrode due to TM dissolution happens at a higher rate in high SoC and high temperature conditions. Postmortem analysis also confirmed that LLI is the main cause for overall capacity loss. It also confirmed that loss of silicon capacity is many times higher than loss of graphite capacity and therefore is the main contributor to capacity loss on negative electrode. With similar findings from in-situ electrochemical analysis as in **Paper B** the post-mortem results corroborate the results of the parallel study as well.

Methodology

Three different SoC windows (0-50%, 50-100% and 0-100%) are defined and cycling is performed in two temperatures $(25 \,^{\circ}\text{C} \text{ and } 45 \,^{\circ}\text{C})$ for each of these SoC windows, with two duplicates performing each test, yielding a cycling test matrix of six tests and twelve cells.

Additionally extensive post-mortem analysis was performed on samples taken from cycled cells. This included electrochemical measurements (ICI, ICA, EIS) as well as microscopy (SEM, TEM), spectroscopy techniques (EDS, ICP-OES) and XRD.

Author contribution

Anastasiia Mikheenkova: Investigation, Conceptualization, Data curation, Visualization, Validation, Writing - orignial draft, Writing - review & editing. Alexander J. Smith: Investigation, Conceptualization, Visualization, Data curation, Writing - review & editing. Kristian Frenander: Investigation, Visualization, Data curation, Writing - review & editing. Yonas Tesfamhret: Investigation, Writing - review & editing. Niladri Roy Chowdhury: Investigation, Data Curation. Cheuk-Wai Tai: Investigation, Writing - review & editing. Torbjörn Thiringer: Supervision, Resources. Rakel Wreland Lindström: Supervision, Resources, Writing - review & editing. Maria Hahlin: Supervision, Resources, Writing - review & editing. Matthew Lacey: Supervision, Writing - review & editing.

7.4 Analysis of the number of replicates required for Li-ion battery degradation testing

In this paper we focus on the issues with cell-to-cell variability and its implications for performing laboratory ageing testing.

Problem

Due to inherent cell-to-cell variations, ageing test results can differ even among replicates undergoing identical testing. This variability makes it challenging to draw reliable conclusions when using a low number of replicates—a common limitation in battery ageing studies due to equipment constraints and cost. For equipment manufacturers, misjudging ageing behavior under different conditions can have serious repercussions.

Contribution

In this paper, we demonstrate that at least four replicates are required to obtain dependable results in battery ageing testing. Additionally, we introduce several novel methods for determining the number of replicates needed to obtain robust data.

Using a methodology to estimate population parameter spread and relative standard error (RSE), we define a maximum allowed RSE of 25%. Based on this threshold, we conclude that five to six replicates are necessary across all tests.

By fitting an ageing model and estimating the number of cycles to EoL, we determine that at least four replicates are required to keep the risk of overestimating cycles to EoL by more than 5% below a 5% probability.

Finally, by synthetically varying the data in line with naturally occurring differences, it can be confirm that the required number of replicates depends on cell-to-cell variability. Thus, it is suggested to incorporate a standard test for cell-to-cell variation as part of battery datasheets.

Methodology

Larger batches of cells, 8 replicates per test condition, were tested at four different test conditions. The data from the ageing testing was then analysed using several statistical methods to evaluate how many replicates were required to be able to draw reliable conclusions.

Author contribution

Kristian Frenander: Investigation, Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Conceptualization. **Torbjörn Thiringer**: Writing – review & editing, Resources, Methodology, Funding acquisition, Conceptualization.

7.5 Extending Battery Lifetime by Pulsed Charging

In this paper, we investigate the effects of pulse charging on lithium-ion battery (LIB) degradation, focusing on how dynamic charging influences battery lifetime compared to standard CC charging.

Problem

Over the years there has been mixed findings when it comes to benefits or drawbacks from a durability point of view when it comes to pulsed charging compared to CC charging. More recent publications show a tendency towards positive effects, and this paper seeks to clarify the degradation implications of pulsed charging and the effect of duty cycles and frequency on degradation.

Contribution

This study demonstrates that switching from CC charging to pulse charging can significantly reduce capacity fade. Key findings include:

- A 50 % reduction in capacity loss for pulse frequencies above 100 mHz compared to CC charging.
- The identification of 10 mHz as a pivotal frequency, where degradation levels match CC charging.
- Electrochemical analysis suggesting that pulsed charging reduces Li plating and SEI reformation, particularly at higher pulse frequencies.

Methodology

Two experimental categories were employed, testing LIB cells (LG MJ1, NMC/Graphite-SiO_x) under different charge/discharge waveforms:

- Category 1: Mean current of 2.5 A, using a square-wave 50 % duty cycle with pulse frequencies between 10 and 1000 mHz

• Category 2: Mean current of 1 C, tested at 1-125 Hz, with 25 % and 50 % duty cycle groups.

Each test group included multiple replicates, and periodic RPTs were conducted to assess capacity retention and impedance change. Electrochemical techniques such as incremental capacity analysis (ICA), differential voltage analysis (DVA), and intermittent current interruption (ICI) were used to investigate degradation mechanisms.

Author contribution

Kristian Frenander: Investigation, Conceptualization, Methodology, Data curation, Visualization, Writing – original draft, Writing – review & editing. Douglas Jutsell Nilsson: Methodology, Data curation, Writing – review & editing. Torbjörn Thiringer: Conceptualization, Writing – review & editing, Funding acquisition, Project administration, Methodology.

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Part II

Papers



Low Frequency Influence on Degradation of Commercial Li-ion Battery

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The layout has been revised.

Low Frequency influence on degradation of commercial Li-ion battery

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Abstract

The Tesla model 3 has rapidly become one of the most popular electric vehicles (EV), being the best selling EV in 2020 and the second best selling in 2021. In this paper the ageing implications of varying time scales in usage of the battery are investigated for the 2170 cells used in the Tesla model 3. It is shown that dynamic usage in the range of approximately 0.01 to 0.1 Hz has a statistically significant impact on ageing, while dynamic usage in range 0.1 to 1 Hz does not show significant impact on ageing. Furthermore the individual electrode ageing is investigated by non-invasive electrochemical techniques, revealing the profound impact on ageing from Si addition to the negative electrode, where it is shown that substantial part of the ageing comes from loss of Si in the negative electrode.

1. Introduction

In recent years the push to increase electrification of the vehicle fleets across the world has gained momentum and the market shares have been increasingly rapidly in many countries. During this period the Battery Electric Vehicle (BEV) with a Lithium-ion Battery (LiB) has matured into the most popular variant of electrified vehicle (EV). This process has been enabled by rapid development of the LiBs used in the automotive industry, but since the battery is still the largest and most expensive component in a BEV understanding their behaviour and optimising their utilisation remains an important topic for industry and research alike.

This development has lead to increased interest in many aspects of the LiB, from improving energy density and performance to prolonging service life. One of the chemistries that has been generating interest is Silicon negative electrodes. This is due to the high capacity of Si as negative electrode material, as it alloys with Li in a more efficient way that standard intercalation materials,

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yielding 4212 mA h g^{-1} [1] theoretical capacity and a practical capacity around 3579 mA h g^{-1} for $\text{Li}_{15}\text{Si}_4$ [2, 3, 4]. This is a very tangible improvement compared to 372 mA h g^{-1} for graphite [5]. Moreover, silicon's attractiveness is increased by the material's abundance and and non-toxicity [1]. However, large volumetric contraction and expansion [6] causes durability issues with unstable SEI, particle pulverisation and morphology changes [7] during alloying and dealloying. This rapid degradation of pure Si electrodes have hampered their industrialisation. In recent years the development of Silicon based electrodes has been rapid [8] and these drawbacks have been partially overcome, for instance by producing composite electrodes where the silicon works as a dopant to graphite electrode to add capacity. This technique is now used widely in commercial cells available off the shelf, but still only a relatively small body of literature is available concerning its durability effects, especially when considering an NCA positive electrode.

Liu et al. [9] have reported degradation data for cells comprising an NCA positive electrode and a Si-Gr composite negative electrode with static current and found little influence of the discharge current, but it should be noted that their investigation was limited to non-dynamic tests. Teichert et al. [10] investigated the ageing challenges for Ni-rich positive electrodes, specifically focusing on the ageing mechanisms occurring in the cells, with the investigation limited to the positive electrode. Farmakis et al. [11] performed interesting investigations comparing the ageing behaviour of cells with an NCA positive electrode versus pure Si or pure graphite, using standard galvanostatic cycling, and were able to conclude that a Si negative electrode was detrimental to battery lifetime. However they did not extend their investigation to include mixed materials.

Jossen and co-workers [12], have found that ageing implications are not homogeneous for the two materials making up the composite electrode. Instead it can be seen that the graphite is losing capacity less rapidly than the Si, leading to a shift of the OCV of the negative electrode, and corresponding change in cell OCV. They have also investigated how the fraction of Si added to the negative electrode affects the durability and found a negative correlation between the amount of Si and the capacity retention [13] and performed studies in the calendar ageing behaviour and reversibility of capacity loss of cells with Si-Gr composite electrodes [14]. Profatilova et al. [15] investigated the influence of porosity on the durability for Si-Gr electrodes and found that the influence of porosity on transport properties led to significantly different ageing when porosity decreased. Important to note is that these studies did not extended their scope beyond constant current cycles.

Interesting investigations of the influence of drive cycles on battery ageing was conducted by Baure and Dubarry [16] who compared drive cycles used in certification to real driving data, as well as Keil and Jossen [17] who investigated the effects of regenerative braking during dynamic driving, and different SOC levels, for non-parameterised discharge and drive cycles. Schmalstieg et al. [18] implemented parameterised customer profiles to investigate effects of waiting times and other parts of the usage behaviour, for constant current discharge cycling. Further important work was conducted by Peterson et al. [19] investigating realistic usage conditions for a Vehicle-to-Grid (V2G) user, including realistic drive cycles and investigating different customer profiles, however not including a discharge pattern that could be reduced to a small number of governing parameters. Bessmann et al. [20] implemented discharge profiles combining a DC discharge and AC harmonics, for frequency ranges above 1 Hz.

Despite the valuable and interesting research being published in the field, to the best of the authors' knowledge there are no papers where representative parameterisable discharge patterns are developed or used to investigate the effect of the discharge dynamics on the cell ageing. In order to fill this research gap, a novel test method for investigating the sensitivity to the dynamic pulses of driving is suggested in this paper, making standardised dynamic testing possible, allowing researchers to investigate ageing behaviour more akin to real world scenarios. This methodology can also be further expanded to investigate other usage parameters derived from real world driving and the highly variable nature of the current profiles that batteries are exposed to in EV applications.

Accordingly, the aim of this paper is to establish the influence on Lithiumion battery ageing due to low frequency current pulses, with a specific focus on cells with silicon doped composite electrodes.

The key novel contributions of this article are

- Reporting of cycling data for cells with NCA positive electrode and Si-Gr negative electrode.
- A proposal of a parameterisable dynamic discharge pattern and demonstration of its feasibility when implemented in a battery testing equipment.
- Proof of the possibility to use the low-SOC hysteresis as tool for noninvasive ageing assessment in composite electrode cells.
- Demonstration of a correlation of ageing and pulse harmonics in the range of 10 to 100 mHz, while showing no correlation for frequencies in the range 100 to 1000 mHz.

2. Experimental

2.1. Cells and setup

The 2170 cells tested for this study are from a Tesla model 3 car to ensure it is production status cells. Samples were also taken from cells to build halfcells for electrode characterisation. Its chemistry is a mixed silicon and graphite negative electrode paired with a Nickel-Cobalt-Aluminium (NCA) positive electrode. Some further technical details are given in Table 1.

To investigate the influence of the typically stochastic discharge behaviour, a suitable dynamic discharge pattern is developed. The main interest of this study was to investigate the effect of different time scales on the ageing behaviour, since different drive patterns give rise to vastly different time scales of discharge, quite dissimilar from the idealised steady state currents typically used in laboratory ageing studies.

Parameter	Cell specifications
Manufacturer	Panasonic
Geometry	Cylindrical 2170
Chemistry	NCA/Si-Gr
Capacity	$4.6\mathrm{A}\mathrm{h}$
Weight	$68.45\mathrm{g}$
Dimensions	$21\mathrm{mm} imes 70\mathrm{mm}$
U_{max}	$4.18\mathrm{V}$
U_{min}	$2.55\mathrm{V}$
U_{nom}	$3.6\mathrm{V}$
Gravimetric	$242\mathrm{W}\mathrm{hkg}^{-1}$
energy density	

Table 1: Technical specifications of the Panasonic 2170 cell.

A cycling protocol was developed where the cell would undergo different discharge cycles with a maintained mean current of 1C to yield comparable results. This was achieved by applying a rectangular wave discharge current of 1.33C during three quarters of a repeating cycle, while resting the remaining quarter of the cycle, see Figure 2 for clarification of the discharge profile. The total time of the repeating cycle is then varied to yield the different discharge protocols. As a reference cycle a standard 1C test was also performed.

The total time in the test matrix was varied to obtain a suitable distribution in the frequency domain by varying the total time according to $t_{total} = 2^N s$ where $N \in \{0, 1, \ldots, 8\}$, or from 1 s to 256 s with the frequency of the test defined as $f_{test} = 1/t_{total}$. This yields a frequency range from 4 mHz to 1 Hz. While the main purpose of the test design is to allow for direct comparison with standard 1C tests it can be interesting to note that the typical frequencies found in standard urban (Artemis urban) and highway (US06 and Artemis 130) drive cycles range from about 10 to 200 mHz with maximum occurrence around ~ 25 mHz, identified using fast Fourier transform (FFT) on the speed trace of the cycles. Thus, the tested frequency range is not dissimilar to what could be expected from real world applications. All tests were performed with a minimum of two replicates in a temperature of 25 °C.

2.2. Reference test

All cells underwent regular checkups every 50 full cycle equivalents (FCE) where the discharge capacity was measured at $I_{dchg} = C/3$ current after performing a C/3 CCCV charging with $I_{cutoff} = C/20$ at U_{max} . This cycle was repeated twice and the average of the two values was utilised as capacity figure for that reference test.

After determining the capacity of the cell an incremental capacity sweep was done at $I_{ICA} = C/20$, sweeping both charge and discharge direction between U_{min} and U_{max} .


Figure 1: Normalised frequency spectra from FFT on speed trace of two standard drive cycles, with (a) showing Artemis Urban, a drive cycle used to represent urban driving. Correspondingly in (b) the frequency spectrum from FFT on US06, a highway drive cycle, is depicted.

Table 2:	Tabular	representation	of reference	performance	test	(RPT)	as p	erformed	every 50
cycles of	cycle life	testing.							

Measurement	Procedure	Comment		
Capacity	CCCV Charge $I_{cutoff} = C/20$	Cut at U_{max}		
Repeat x2	$\begin{array}{c} \text{CC Discharge} \\ I = C/3 \end{array}$	Cut at U_{min}		
	$\begin{array}{c} \text{CC Charge} \\ I = {}^{C\!/_{20}} \end{array}$	Cut at U_{max}		
	$\begin{array}{c} \text{CC Discharge} \\ I = \frac{C}{20} \end{array}$	Cut at U_{min}		
	$\begin{array}{c} \text{CCCV Charge} \\ I_{cutoff} = C/20 \end{array}$	Cut at U_{max}		
Impedance	CC Discharge $I = C/3$ to 70%, 50%, 30% SOC	Break based on voltage corresponding to X% SOC		
	$ \begin{array}{c} 10 \text{ s pulse} \\ I_{pulse} = 1.3C \end{array} $	Max current on tester Charge and discharge		



Figure 2: Schematic visualisation of the pulse discharge pattern used in the study.

The final step of the reference test was a pulse test to measure resistance of the cell, run with 10 s pulses of $I_{pulse} = 1.3C$. The current level used in the pulse was set by the maximum current limit provided by the tester, see section 2.4. The pulses were applied at three different SOC levels of 30, 50 and 70% with both charge and discharge pulses applied to the cell. See Table 2 for clarification and a tabular representation of reference test procedure.

On top of this basic checkup test a subset of the cells also underwent further tests to obtain a more complete characterisation. The additional tests were Intermittent Current Interruption (ICI) test and Electrochemical Impedance Spectroscopy. The ICI test procedure is desribed in [21]. In this study it was implemented with $I_{ICI} = C/20$ applied for 300 s and current interruptions of 5 s and the test was performed during every reference test.

The cells that performed regular ICI were also characterised using regular electrochemical impedance spectroscopy (EIS) sweeps. However due to requiring specific equipment (see Section 2.4) and lead time for the test, these tests were only performed every 300 FCE to reduce stoppages. The lead time was mainly due to conditioning, as the cells needed to be brought to 50% SOC level for the test and then fully equilibrated for 12 h before the test was performed. The EIS sweeps were run between 10 kHz and 10 mHz with 10 points per decade and a 10 mV perturbation applied.

2.3. Individual electrode analysis

To enable half cell analysis electrode materials were harvested from a fresh cell and reconstructed into half cells with a lithium metal counter electrode. These cells were assembled into pouch cells, using electrode discs with $\emptyset 15 \text{ mm}$ with a $\emptyset 18 \text{ mm}$ lithium metal counter electrode and a Whatman 260 µm separator.

These single electrode cells were cycled using C/10 current to obtain reference OCV curve for electrodes. The Si-Gr electrode was cycled between 0.002 V and 1.5 V and the NCA electrode was cycled between 3 V and 4.35 V to obtain full voltage curves.

2.4. Test equipment

All cycling testing and the reference tests were performed using a Neware BTS4000 5V battery testing system with a maximum current of $I_{max,tester} = 6$ A. The EIS measurements were performed on a Gamry reference 3000 tester with a frequency range of 1 mHz to 300 kHz.

3. Results and discussion

The capacity fade results of the tests are shown in Figure 3. From this figure it can be noted that the spread in results is significant even between cells performing exactly the same test. This type of behaviour has been investigated for cells connected in modules or packs [22, 23] which experience slightly different conditions during ageing, but has not been investigated for cells performing identical tests. Despite the spread, there is a trend that can be noted which is that the capacity of the cells that are subjected to higher frequency pulses is decaying more rapidly than those performing pulses with lower frequency. This trend, and the noise in the data, can be seen more clearly from Figure 5 where the average energy throughput through the cells before reaching end of life is plotted versus the frequency applied in the test. As can be seen from the box plot, the data is noisy, but with a trend towards higher energy throughput before reaching end of life for the cells cycled with lower frequency pulses. This would indicate that more stationary loads on the battery, corresponding to less dynamic driving with more constant speed, would be beneficial for the mileage one can get out of an electric vehicle before it reaches end of life. It can also be noted that there is significant capacity recuperation in some tests, which occurs when testing is temporarily halted to perform EIS tests, see Section 2.2, as this led to a rest period for all cells before the tests were restarted. This behaviour has previously been reported in several previous works [24, 25, 26] and is believed to be related to negative electrode overhang storing excess capacity of lithium ions.



Figure 3: Capacity fade plots for all tested cells, split into four subplots based on frequency, with decreasing frequency from top left to bottom right. All replicates performing the same test are shown in the same figure. Each subplot also include average of the three 1C reference test for comparison.

3.1. Comparison with 1C reference

As 1C constant current discharge is a typical standard test in battery cycling studies, it is important to note that despite the large variance in the individual tests, durability is improved in all but one of the dynamic test cases when comparing to the average of the 1C reference tests, see Figure 3. This trend is also confirmed when including the resistance increase in the analysis, see Figure 4 where the 1C reference is displaying the fastest resistance increase as well as the fastest capacity decay when comparing with several different pulse test conditions.

The fact that even as ageing behaviour changes for different pulse discharge cases the dynamic cycling is always outperforming the 1C reference shows that accounting for dynamics in battery durability testing is a vital feature. Therefore test studies aiming to investigate cycle life of BEV batteries should take dynamic usage into account when designing tests. It also complements the findings of Keil and Jossen [17] which showed that including regenerative breaking pulses in cycling tests improved durability, where our results show analogous results for dynamic discharge as compared to static discharge.

The causes for this can not be clearly stated based on the tests performed in this study, but one hypothesis could be that periodic rest reduces local phenomena such as lithiation unbalance or local potential drops due to equilibration during rest phases. Pulses have also been mentioned previously in literature as a way to reduce concentration polarisation and utilisation of active material [27], so further speculation could be that the distribution of Li in the active material is improved by pulsing the current compared to constant current. This could help reduce material stress and decrease for instance crack formation in the material, but to verify these hypotheses further post-mortem analysis would be needed.

3.2. Splitting the dataset

The trend that lifetime decreases with higher frequency mentioned in Section 3 is more clearly present for lower frequencies, where as in higher frequencies the trend seems to be much weaker, or even non-existent. This can be further analysed by splitting the dataset into two subsets, where higher frequency pulses (f > 100 mHz) are analysed separately from lower frequency pulses. The differences in trends can be seen more clearly from Figure 6 where the linear trends for the subsets of data are shown together with the test data from the study. The slope is large for the low frequency pulses, but more or less flat for the higher frequency.

The reasons for choosing f = 100 mHz as the cut-off frequency is two-fold. Firstly it can be seen from the ageing data that it is around this frequency that the trends start diverging. Secondly, based on EIS sweeps on cells, the characteristic frequency for the charge transfer resistance and the double layer capacitance is between 100 mHz and 10 Hz and tending towards lower frequency as the cells age, see Figure 7. Combining these two observations, one hypothesis can be that for frequencies higher than $f \approx 100 \text{ mHz}$ the influence of the



Figure 4: Average capacity fade and resistance increase for four cases of pulsed discharge plotted as dashed lines with the average capacity fade and resistance increase for 1C case as reference, plotted with solid lines. In all cases the pulsed discharge tests are showing better durability compared to 1C.



Figure 5: Box plot of energy throughput at end of life for all test data grouped by pulse frequency. Large variance in the data can be noted for six out of nine test conditions, indicating surprisingly large spread in cell ageing performance.

pulsation is dampened by passing the current through the double layer capacitance. This will cause charging and discharging of double layer capacitance during pulsing, which will lead to the effective concentration in the particles not being significantly different in the different frequency cases. Previous research on pulse current in LiBs have not focused on this, but previous research on lead-acid battery technology have linked the influence of double layer to performance [28, 29]. This hypothesis would however require further study to draw more reliable conclusions.

3.3. ANOVA test on datasets

Even though the trends for the split datasets might look significantly different from direct inspection, the large variance in the test results means that there is a risk of misinterpreting pure variance as a trend. To verify that this is not the case further statistical analysis is performed on the datasets by applying the ANalysis Of VAriance (ANOVA) test. The ANOVA test, used here as implemented in the R software [30], finds with what probability a trend in results can be attributed to natural variance within the sample set. The null hypothesis being that the variations in results are indeed caused by variance and the means of all individual tests are the same, generating a utility test of

$$H_0: \mu_1 = \mu_2 = \cdots = \mu_i$$
 versus $H_1: \mu_u \neq \mu_v$ for some (u, v) .



Figure 6: Pulse frequency versus energy throughput at end of life for all tests conducted in study, together with linear fits of end of life versus frequency for the two subsets of data.

Based on the probability of rejecting H_0 , the presence of a trend in the data is assessed, with $P(H_0) < 0.05$ used as condition for a statistically significant trend.

Examining the full dataset without a split by frequency the probability of null hypothesis is $P(H_0) = 0.28$ meaning that the null hypothesis can be rejected with only 72% probability. This result cannot be considered significant with the standard requirement, so the variations in means is considered attributed to variance rather than trend.

However if the data is split by frequency it becomes clear that the trend is present in the low frequency region, as $P(H_0) = 0.028$ for tests with f < 100 mHz indicating that the null hypothesis can be rejected with 97.2% probability, which can be considered a statistically significant trend. Conversely, analysis of the data where f > 100 mHz yields that $P(H_0) = 0.81$, or null hypothesis can only be rejected with 19% probability, and accordingly no relation can be established. This further enforces the observation that at lower frequency the pulse duration has an influence on the ageing of the battery, but at higher frequency the effect is negligible. These observations are also align with the findings in previous studies of Bessman et al. [20]

3.4. Negative Electrode Decay

To track the individual electrode ageing without intrusive testing, the differential voltage curve of the full cell is recreated by a combination of positive



Figure 7: Nyquist plot of EIS sweep after 0, 300, 600 and 900 FCE respectively. Markers on curve denote certain frequencies in the sweep, and it can be noted that the characteristic frequency is getting lower throughout testing.

and negative electrode voltage curves, see Figure 8. Details on the half-cell implementation is found in 2.3. The capacity of the coin cells used for half cell characterisation needs to be scaled to full cell, and electrode balancing taken into account. Following the method proposed in Mussa et al. [31] the scaled electrode capacities, $Q_{neg/pos}$ are formulated as

$$Q_{neg} = s_{neg}q_{neg} + \sigma_{neg} \tag{1}$$

$$Q_{pos} = s_{pos}q_{pos} + \sigma_{pos} \tag{2}$$

with $q_{neg/pos}$ denoting the capacity measured in the coin cell, $s_{neg/pos}$ and $\sigma_{neg/pos}$ denoting the scale and slip factor respectively. Using the scaled capacities together with the voltage curves measured, allows the approximation of full cell voltage as the difference between the electrode potentials, $U_{cell} = U_{pos} - U_{neg}$ with $U_{neg/pos} = f(Q_{neg/pos})$ based on measured voltage on half cells.

By calculating the derivative of voltage with respect to capacity, dV/dQ, of these curves a Differential Voltage Analysis (DVA) can be performed. Overlaying the DVA curves from the half cells and the full cell, the peaks can be clearly assigned to a unique electrode, see Figure 8. This allows one to define proxies to track the capacity of the individual electrodes by tracking the distance in capacity between DVA peaks.

Following the method presented by Zülke et al. in [32] the distance between the peaks associated to each electrode, the relative capacity of the electrodes



Figure 8: Differential voltage for full cell at beginning of life, and each electrode at beginning of life. Two capacities are marked between horisontal lines on the plot to indicate the capacity until central graphite peak, and between the two visible NCA peaks. Q_1 serves as a proxy for estimating the capacity loss of the Si-Gr, and Q_2 serves as proxy for estimating the capacity loss of NCA.

can be tracked. For NCA the capacity defined as Q_2 in Figure 8 indicates the capacity available between the two phase shifts. Analogously for the Si-Gr electrode, the capacity, defined as Q_1 , until the central graphite peak appears, is taken as a proxy of the electrode capacity. This which however has an inherent weakness in not being able to distinguish between loss of active material and loss of lithium inventory due to only being referenced to one peak. The reason for using only one peak can be deduced from Figure 9a which shows how the relative slip of the electrodes makes the peaks associated with the negative electrode around 30% SOC and 65% SOC non-identifiable as degradation progresses.

These values can then be tracked throughout the ageing testing to indicate the individual ageing of each electrode, and the result is shown in Figure 9b. Due to peaks shifting in the DVA with ageing, the central graphite peak becomes indistinguishable, and unfortunately this means that Q_1 can not be calculated beyond 200 FCE. Yet the trend is clear from the data that can be obtained, showing that the negative electrode capacity is dropping swiftly, whereas the positive electrode capacity can be considered more or less unchanged throughout the test, with the fluctuations stemming from the noise of the measurement data.

This trend can be further investigated by the novel method of analysing the difference between charge and discharge voltage of ICA tests, as shown in Figure 10a. The difference is defined simply as $\Delta U = U_{chrg} - U_{dchg}$ for the same point



(b) Ageing proxies for negative and positive electrode.

Figure 9: Disappearance of distinct DVA peak for negative electrode capacity (a) and the ageing proxies for positive and negative electrode respectively (b).

in SOC.

For the ICA test, that is performed with a c-rate of C/20 it can be assumed that overpotentials in the cell are low, and thus the difference between charge and discharge can be attributed to hysteresis effects mainly. Silicon electrodes are known to show significant voltage hysteresis [33, 34], so a large difference between charge and discharge in the low SOC region, is an indicator of Si in the composite electrode. Furthermore, as the resistance in the cell increases with ageing, see Figure 4, any overpotential contribution to ΔU will increase with ageing, yielding the expected trend that ΔU would increase if there are no changes in the underlying OCP curves. It is however clear from the data that ΔU is decreasing in the lower SOC region, which is a clear indication that Si is being lost at a disproportionate rate during cycling. This aligns with the previous findings in literature that Si composites can have issues with cycle life, mainly due to large volumetric changes during charge and discharge [35, 36, 37].

The hypothesis that Si capacity loss is the main contributor to the initial negative electrode capacity loss is further corroborated with analysis of the Incremental Capacity Analysis (ICA) sweeps. ICA is the inverse derivate compared to DVA as dQ/dV such that valleys in the DVA show up as peaks in ICA. ICA sweeps performed during life testing is shown in Figure 10b, where the peaks associated with Si for low voltages, are quickly diminishing. As the cell reaches its end of life the peaks are completely gone, indicating that there is very little active silicon remaining in the negative electrode.

3.5. Future Work

Several interesting questions arise from the findings in this paper that would be interesting to investigate further. More detailed post-mortem analysis to further investigate the different ageing mechanisms involved and finding a more detailed physical explanation to why the degradation is faster in constant current cycling compared to dynamic cycling. Coin cell harvesting at end of life to be able to improve the results from voltage fitting shown in Section 3.4 would also be of value to further elucidate the internal processes.

4. Conclusion

After splitting the data it can be concluded that the investigated discharge harmonics does not have significant influence on ageing performance in higher frequencies, but there is a statistically significant trend in the region where f < 100 mHz. In this region, the energy throughput that the cells manage before reaching end of life increases with decreasing frequency. This indicates that slower dynamic loads would be beneficial for battery life compared to fast dynamic loads.

The reasons for this trend need to be investigated further, but a hypothesis for higher frequency is proposed, with the effect of higher frequency being smoothened out by double layer capacitance charge and discharge during cycling.



(b) Incremental Capacity plot with peaks associated with Si marked.

Figure 10: Voltage hysteresis (a) and Incremental Capacity plot (b) for the same cell at three stages of ageing. Both figures indicate near complete loss of active Si when cell is at end of life (EoL).

All tests performed with some form of dynamic load, outperform the standard 1C test performed for reference, which showed the poorest durability performance of all tests. This indicates that standard static tests are not fully representative for the dynamic use case that is experienced in real life applications, and for assessing durability performance test protocols that include dynamic usage should be considered.

Further findings indicate that the degradation of the cells are mainly due to capacity loss on the negative electrode side, and more specifically on the Si part of Si-Gr composite electrode. Previous studies suggest that this is due to volumetric expansion causing breakage of the SEI layer, and the lack of stable SEI layer causes rapid ageing. This trend is similar for all tested cells and show no discernible dependence on frequency.

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$_{\text{PAPER}}B$

The state of charge dependence of degradation in lithium-ion cells from a Tesla model 3

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The layout has been revised.

Influence of state of charge window on the degradation of Tesla lithium-ion battery cells

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Abstract

The Tesla Model 3 is currently one of the most popular electric vehicle (EV) and was the best selling EV in 2020. In this article, performance and degradation of 21700 cylindrical cells, taken from a new vehicle, were studied by cycling within 10% State of charge (SOC) windows. Cells tested in either very high and very low SOC windows show faster degradation than at moderate SOC. In particular, the shortest service life was for cells cycled below 25% SOC. The ageing mechanisms of the cells cycled in these most extreme windows have been monitored by non-destructive electrochemical methods including analyses of differential voltage, incremental capacity, and voltage hysteresis. The combination of loss of lithium inventory (LLI) accelerated in early cycling by SiO_x utilisation, paired with loss of active material (LAM) of SiO_x are responsible for the most rapid ageing, which is observed in the cells cycled in the 5-15% SOC window. Calendar ageing, however, is not accelerated by storage at low SOC. The results from this study offer an understanding of the distinct, SOC-dependent ageing patterns observed in the cells. This understanding of the ageing mechanisms in different cycling and storage conditions can be used to recommend improved customer usage patterns and substantially extend the lifetime of lithium-ion batteries in operation.

1. Introduction

The push for vehicle electrification across the globe has led to a surge in research interest in the field of energy storage systems. Various energy stor-

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age and conversion technologies like batteries, electrochemical capacitors, and fuel cells have been considered for use in vehicle applications. Among these, Lithium-ion batterys (LIBs) have emerged as the most common choice for energy storage in electric vehicles, owing to their high energy density [1], low rate of self-discharge [2], long cycle life [3] and higher energy efficiency compared to their predecessors[4]. However, even though the driving range of electric vehicles (EVs) has increased, it is still typically less than that achievable by combustion engine vehicles [5]. Moreover, EVs remain expensive in comparison to combustion engine vehicles [6, 7]. The most expensive component of an EV is the battery pack [8]. Thus, long lifetimes of LIBs are desired and demanded by consumers. An improved understanding of the ageing mechanisms is helpful to improve the lifetime of LIBs. Based on this understanding of the ageing process, better usage profiles can be suggested in order to extend battery lifetime. An extended lifetime of the on-board energy storage will make EVs cheaper and more competitive in the long run.

LIBs for EVs require high energy density to achieve sufficient driving range. Many advanced electrode materials have been developed to increase the energy density of the LIBs [1, 9, 10]. Nickel-rich layered oxide materials, including lithium nickel cobalt aluminium oxide (NCA) and lithium nickel manganese cobalt oxide (NCM) have been gaining popularity in EVs due to their high energy density and convenient cost to energy storage ratio [11, 12]. In combination with graphite-silicon oxide $(Gr-SiO_x)$ blended negative electrodes, they form promising prospects for increasing energy density. Unfortunately, the most energy-dense of these materials tend to have challenges in achieving sufficient cycle life. Some examples with tailored structures are proving exceptions to this rule (e.g. single-crystal NCMs [13]), but have not yet been implemented in EVs. However, at the negative electrode, $Gr-SiO_x$ blends have been able to mitigate the large volumetric changes and continuous side reactions associated with pure silicon electrodes, while retaining a high capacity appropriate for EVs [14, 15, 16]. In fact, one of the most popular EVs, the Tesla Model 3, which provides up to 500 kilometers of range per charge and available at an affordable price uses 21700 cylindrical cells with NCA as the positive electrode active material and blended $\operatorname{Gr-SiO}_x$ as the negative electrode active material [17]. However, the high energy density of NCA/Gr-SiO_x cells comes at the cost of relatively low cycle life in comparison to lower-energy, yet commercially-viable, cell chemistries such as LiFePO₄ (LFP)/Gr [18]. It is important to understand the ageing mechanism of these NCA/Gr-SiO_r cells in order to improve their performance and</sub> cycle life, especially in vehicular applications as it will have a greater impact on bringing down the resulting cost of ownership of EVs. Several studies have contributed to our understanding of the ageing mechanisms of $NCA/Gr-SiO_x$ electrodes [19, 20, 21, 22]. The calendar and cycle ageing behaviour of other commercial cells using $Gr-SiO_x$ negative electrodes has been studied in terms of morphology and electrochemical property changes [23, 24, 25]. A study carried out on similar $NCA/Gr-SiO_x$ cells identified and managed the reversibility of capacity losses that may otherwise lead to false conclusions from cycle ageing tests [26]. Benavente-Araoz and our colleagues have also studied the ageing of such cells when partially cycled in different state of charge (SOC) windows [27, 28]. These studies and others have shown that battery lifetime depends on several factors, e.g., temperature, rate of charging and discharging, depth of discharge (DOD), and the SOC window in which the cell is cycled [29, 30, 31, 32, 33, 34, 35, 36]. Generally high charging and discharging rate, high temperature and wider DOD are detrimental to the battery lifetime. In comparison, relatively few studies focus on the placement of the SOC intervals in the operational window on cell ageing, though faster ageing is often observed in high SOC windows for other automotive cell chemistries [37, 38, 39]. Lifetime testing of cells in narrow charge intervals is helpful in determining the SOC dependence of the cell degradation mechanisms. These kinds of studies are valuable to understand the ageing of different cell components as well as useful in ageing model development. We aim to improve the understanding of the SOC dependence of ageing in commercial, high-energy, NCA/Gr-SiO_x cells, with a focus on vehicle applications.

We use NCA/Gr-SiO_x cells harvested from a relatively new consumer EV in order to reveal specific SOC-dependent detriments to cell lifetime that are relevant to everyday consumers and drivers of EVs. In a parallel study, identical cells cycled in 50 and 100% Δ SOC windows are studied, with a focus on post mortem analysis [17]. In this work, we have targeted specific ageing processes by cycling the cells in narrow SOC windows of only 10% Δ SOC, with a focus on full-cell differential analysis during ageing. In both studies, the NCA/Gr-SiO_x cell shows different ageing behaviour in low SOC and high SOC windows. The results from this cycle ageing work on commercial NCA/Gr-SiO_x 21700 cells can be used to improve customer usage patterns and substantially extend the lifetime of the battery pack.

2. Experimental

2.1. Cells and cycling protocols

Panasonic 21700 cylindrical cells extracted from a relatively new 2018 Tesla Long Range Model 3 and containing $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Al}_{0.05}\text{O}_2$ (NCA), as positive electrode and Gr-SiO_x as negative electrode have been used in this study. At the beginning of the study the cells have undergone a low number of cycles in the vehicle on top of the formation performed during cell production. Throughout the paper beginning of life (BOL) refers to the state after dismantling of battery pack. Detailed technical specifications of the cell are provided in Table 1. Compositional characterization of the positive electrode can be found in our previous studies[40, 17].

Parameter	Cell specifications
Manufacturer	Panasonic
Geometry	Cylindrical 21700
Diameter	$21\mathrm{mm}$
Height	$70\mathrm{mm}$
Chemistry	$NCA/Gr-SiO_x$
Capacity	$4.6\mathrm{A}\mathrm{h}$
Weight	$68.45\mathrm{g}$
Maximum voltage	$4.18\mathrm{V}$
Minimum voltage	$2.55\mathrm{V}$
Nominal voltage	$3.6\mathrm{V}$
Gravimetric energy density	$242\mathrm{Whkg}^{-1}$

Table 1: Technical specifications of the Panasonic 21700 cell.

A NEWARE BTS-4000 battery cycler was used for cycling the cells in the laboratory with the temperature maintained around 25 °C. The cells were cycled in nine consecutive 10% Δ SOC intervals ranging from 5-15% SOC to 85-95% SOC. The cells were cycled using C/3 charging current and 1C discharging current, corresponding to three hours and one hour for a complete charge and discharge of the nominal capacity, respectively. The SOC windows used in this study were defined by cut-off voltages as listed in Table 2. The upper and lower cut-off voltages are not equal for the same SOC; this is to correct for polarisation and hysteresis observed during cycling.

Reference performance tests (RPTs) were performed regularly every 150 full cycle equivalent (FCE) to monitor the ageing behaviour of the cells. Full cycle equivalent is defined as normalisation to 100 %SOC, meaning that 10 cycles in 10 %SOC interval corresponds to 1 FCE. Each RPT consisted of an activation step in which the cell is charged to the maximum voltage at C/3 rate followed by two discharge and charge cycles to measure the C/3 capacity. A C/20 discharge and charge cycle is performed next, followed by discharge and charge pulses at 1.3C (6 A) at 30%, 50% and 70% SOC levels. Calendar ageing tests have been done to compare the ageing behaviour of the cells under cycling and stationary storage conditions. In the calendar ageing tests, the cells were stored at 15%, 50% and 85% SOC levels at 25 °C. An RPT was performed at the end of each month for the calendar-aged cells to check their capacity and performance. The cells were considered to reach their end of life (EOL) upon degradation to 80%of their initial capacity, which was typically reached after around two years of cycling including RPTs. Two duplicate cells have been tested under each ageing condition, bringing the total number of cells tested to 24.

SOC, %	$\mathrm{U}_{\mathrm{low}}$	$\mathrm{U}_{\mathrm{high}}$
5-15	$2.91\mathrm{V}$	$3.51\mathrm{V}$
15-25	$3.18\mathrm{V}$	$3.59\mathrm{V}$
25 - 35	$3.32\mathrm{V}$	$3.68\mathrm{V}$
35-45	$3.39\mathrm{V}$	$3.74\mathrm{V}$
45-55	$3.48\mathrm{V}$	$3.83\mathrm{V}$
55-65	$3.58\mathrm{V}$	$3.91\mathrm{V}$
65-75	$3.68\mathrm{V}$	$3.98\mathrm{V}$
75-85	$3.75\mathrm{V}$	$4.06\mathrm{V}$
85-95	$3.83\mathrm{V}$	$4.15\mathrm{V}$

Table 2: Voltage cut off limits used to define SOC windows in tests.

2.2. Characterisation of half cell electrodes

Non-cycled cells were cut open in an Ar-filled glovebox to harvest the electrodes for electrochemical characterization at BOL. One side of the active material coating was carefully removed by swabbing with N-methylpyrrolidone, dimethyl carbonate, and (for negative electrodes only) anhydrous methanol. Single-sided electrodes were punched, assembled, and vacuum-sealed in pouch cells with Whatman GF/A separator, 150-200 μL electrolyte (1 M LiPF_6 in ethylene carbonate/diethylene carbonate, 1/1 wt.), and lithium foil as counter/reference electrode. Several cycles were performed at an estimated C/10 rate (0.4 mA cm^{-2}) for formation, capacity analysis, and differential analysis. All half cell cycling was performed on our in-house, high-precision battery cycler built with Keithley 220 programmable power sources and in climate chambers at 25 °C. Positive electrode samples were cycled between 3.00-4.35 V vs. Li/Li⁺ and negative electrode samples were cycled between 0.002-1.50 V vs. Li/Li⁺. Differentiation for differential voltage analysis (DVA) and incremental capacity analysis (ICA) were performed using a moving average over 0.55% SOC and Gaussian filter over 3.0% SOC as proposed by Li et al. [41] and used in our previous work [42]. Scripts for tracking peak locations were written in MATLAB with the inclusion of predefined functions peakfit.m and Interactive Peak Fitter (ipf.m) available from https://terpconnect.umd.edu/~toh/spectrum/ [43].

3. Results

3.1. Capacity fade analysis

In Figure 1, the capacity retention of the cells cycled in different SOC windows are shown as a function of FCE, together with the capacity retention of calendar aged cells. The average percentage of capacity retention value of two cells cycled under the same conditions is shown for each case, together with an error bar indicating the spread between duplicates. Figure 1(b) shows a snapshot of the capacity loss at the same FCE highlights the trend of SOC dependence. The rate and amount of degradation overall is greatest for those cells cycled at low SOC (<25%). The least degradation occurs at moderate SOCs

(35-65%), with increased degradation again at high SOC (>65\%). The rate of degradation (interpreted qualitatively as the slope of the capacity retention curve), does change during the life of the cells. In particular, this rate decelerates after several hundred cycles for the cells cycled at low SOC. This rate of capacity fade remains high yet constant in each of the high SOC windows above 65% SOC. As the ageing does not worsen with SOC above this point, it may represent a threshold for a particular ageing mechanism, such as the onset of electrolyte instability at high voltage.

Calendar ageing results at room temperature, around 25 °C, of the cells stored at 15%, 50% and 85% SOC are shown in Figure 1(c), with average of duplicates shown with error bar, same as for Figure 1(a). Figure 1(c) clearly indicates that in the case when the cells are not cycled, a cell stored at high SOC (85% SOC) ages faster than a cell stored at moderate (50%) or low SOC (15%). In some cases, a recovery in the capacity of the cells can be observed, which coincides with breaks in cycling due to handling and restarts of tests. Deviations from homogeneous lithium distribution and negative electrode overhang have been found to be a reason for such capacity recovery [27, 44, 45]. The cycling and the calendar ageing patterns suggest that there are two distinct ageing mechanisms for the cell, one for the cyclic and another for the calendar ageing. It is well-known that the growth of the solid-electrolyte interphase (SEI) and other chemical degradation mechanisms are more active at high SOC [46]. The retention of the cells calendar aged at low SOC contrasts with the cycle ageing results and shows that capacity fade at low SOC is an active electrochemical mechanism caused by cycling through the SOC window. It is not simply a result of the amount of cumulative time spent at low SOC. In the next section, the ageing mechanism responsible for the rapid degradation of the cells cycled in the lowest SOC windows will be investigated. This primarily reflects the use and resulting degradation of the silicon oxide fraction of the negative electrode.

3.1.1. Identification of ageing modes with DVA

Differential voltage analysis is a useful technique to monitor the degradation pathways of the electrodes and track cell degradation [47, 48]. During charge and discharge, changes in the dominant electrochemical reaction (and thereby, the equilibrium potential) at either electrode are represented as peaks in DVA. In order to assign features to the respective electrodes, a fresh cylindrical cell was disassembled and electrode samples were harvested and reassembled into half cells versus lithium foil. Figure 2 shows the DV profiles of the positive electrode, the negative electrode, their sum, and the full cell recorded during a constant current discharge at C/20. By fitting differential voltage peaks of the summed half cells to those of the cylindrical cell, the single electrode profiles have been scaled and translated to reflect their complete capacities and balancing in the full cell. Key DVA peaks for the fresh full cell are labeled based on the component where there is a change in reaction. Peaks P1 and P2 indicate the transitions in NCA from reaction (1) to (2) and (2) to (3), respectively [29], which will be discussed further in section Incremental Capacity Analysis.



Figure 1: Normalised capacity retention of $c\overline{\mathbf{y}}$ cled and calendar aged NCA/Gr-SiO_x 21700 cells cycled with C/3 charge and 1C discharge currents. In (a) the capacity retention of the cycled cells are displayed, with the spread between duplicates indicated by error bars. In (b) a snapshot of the capacity loss at 1200 cycles is shown. In (c) the normalised capacity retention of the calendar aged cells is shown versus time in days. All capacity measurements performed with C/3 as described in Section 2.1.

Peak N1 corresponds to the transition between subsequent graphite deintercalation reactions forming LiC_{12} and LiC_{27} . Peak N2 represents, in actuality, several increasingly dilute graphite delithation reactions that can be lumped for this analysis. These peaks are distinct in the fresh cylindrical cell but rapidly smear out and only the largest remains visible during ageing. Peaks S1 and S2 are characteristic of the silicon oxide fraction of the negative electrode and represent its (de)lithiation reactions at high electrode potential (low cell SOC) [14, 49]. The capacity delivered between the labeled peaks can be interpreted as proportional to the usable active material. For the negative electrode, the capacity of each component q_k and fraction x_k is defined as follows, using the discharge capacity, Q_d , peak locations, Q_i , with units of mAh, and the fraction of graphite capacity, θ_j , in each region of the DV profile ($\theta_a=0.5, \theta_b=0.38$, and $\theta_c = 0.12$ during discharge [50]). The DV profile is split into regions a, b, and c based on the graphite peaks as illustrated in Figure 2. Due to kinetic limitations in real electrodes, the exact values of θ_i that are observed may vary from the thermodynamic values reported by Olson et al. and used herein.

$$q_{Gr} = \frac{Q_{N2} - Q_{N1}}{\theta_b} \tag{1a}$$

$$q_{Si} = (Q_d - Q_{N2}) - \theta_c q_{Gr} \tag{1b}$$

$$x_{Gr} = 1 - \frac{q_{Si,BOL}}{Q_{d,BOL}} \tag{1c}$$

Indicators for loss of active material (LAM) and the loss of lithium inventory (LLI) can be defined using these and other capacity spacings. Similar fitting is described in detail for half cells in our parallel work [17]. The calculation of LLI as written assumes that peak N1 is independent of graphite losses, which is expected to be true unless graphite losses are severe enough to exceed the rate of LLI.

$$LAM_{NCA} = 1 - \frac{Q_{P2} - Q_{P1}}{(Q_{P2} - Q_{P1})_{BOL}}$$
(2a)

$$LAM_{Gr} = \left(1 - \frac{q_{Gr}}{q_{Gr,BOL}}\right) x_{Gr}$$
(2b)

$$LAM_{Si} = \left(1 - \frac{q_{Si}}{q_{Si,BOL}}\right) (1 - x_{Gr}) \tag{2c}$$

$$LLI = \frac{Q_{N1,BOL} - Q_{N1}}{Q_d} \tag{2d}$$



Figure 2: DVA of a NCA/Gr-SiO_x full cell with NCA/Li and Gr-SiO_x half cells scaled and translated to fit characteristic peaks. Peaks labeled with P are from positive electrode NCA material, those labeled N are from negative electrode graphite material and peaks labeled S are from silicon oxide material.

Having assigned the DVA peaks to their respective active materials, their evolution with cycling is tracked to identify the relevant degradation modes in selected SOC windows. In principle, this approach is not so different (and utilises the same data) as approaches fitting the open circuit voltage reconstructed from half cell data [51, 52, 37, 53]. It is equally non-invasive and similarly quantitative, but by highlighting only the DV peak locations, it is numerically simpler and visually more intuitive than fitting the entire, undifferentiated voltage profile [50]. This straightforward dependency also ensures spurious fits made by this method can be easily identified and traced. It also provides direct, experimental quantification of contributions from each fraction of the blended graphite-silicon oxide electrode, which has recently been corroborated with similar model fitting [54, 53].

The DV profiles at each RPT from cells cycled in the most extreme SOC windows (5-15% and 85-95%) are shown in Figure 3(a) and 3(b). Automated peak detection with peakfit.m was executed as follows. All relevant features were fitted with Gaussian peak shapes. Segments of the DV profile were identified with empirical conditions that are specific to the cell and chemistry. The first segment spanned from the local minimum of differential voltage occurring between 0-1000 mAh on discharge and the minimum occurring between 1000-2000 mAh. Peaks P1 and N1 were identified with linear baseline subtraction within this segment. Peak P1 was labeled based on its larger area (Figure 2) while peak N1 was the smaller of the two. Though deconvolution was difficult



Figure 3: DVA from C/20 discharge profiles at each RPT for cells cycled (a) 5-15% and (b) 85-95%. From peak tracking, key ageing indicators are calculated for LAM of each component and LLI in (c,d). Duplicate cells are shown as filled and empty symbols for each indicator and dashed and dotted lines for the total capacity fade under each ageing case.

when the peak maxima overlapped, their consistent sizes enabled consistent labeling. The next segment spanned from the end of the first until the point when the cell voltage reached 3.45 V (this was visually confirmed for all fitted curves to correspond to the minimum in differential voltage before peak S1). Similarly, peaks P2 and N2 were identified as the largest (P2) and last (N2) peaks in this segment.

Early in life, the negative electrode peaks smear out and become less sharp, indicating a degree of lithiation heterogeneity and perhaps heterogeneous degradation within the negative electrodes. Qualitatively, the silicon oxide peaks S1 and S2 and lumped graphite peak N2 appear particularly decreased in the 5-15% ageing case.

The key ageing indicators described above are presented in Figure 3(c) and 3(d). The convolution of peak N1 with P1 observed in all test groups proved troublesome for fitting, and results in much of the jumpy LAM_{NCA} behavior

observed for the 85-95% ageing case. Nevertheless, different ageing patterns are identified at high and low SOC. At low SOC, LLI is particularly rapid during early cycling. This has also been observed at low SOC in our parallel study and coincides with the formation of an unstable, dendritic SEI on SiO_x particles [17]. This caused peak N1 to quickly pass P1 and improve the deconvolution effort. A concurrent increase in the graphite capacity is observed, which compensates in part for the rapid LLI and results in a slower net fade in cell capacity. Some gains of effective capacity are expected in graphite early in life, as mild exfoliation of the particles improves rate capability [55]. However, an actual increase of 20% as fitted for the 5-15% cycled cells is unlikely to be the case. This result may be an artifact from our fitting protocol, though similar results have been seen to a lesser degree in post mortem half cells under different cycling conditions [17]. It could also be that the initial graphite capacity calculated from DV fitting, q_{Gr} , is an underestimate at BOL. This could be related to discrepancies between the thermodynamic values of θ_i used for calculation and experimental observations that inherently include kinetic limitations. For an additional example, the lithium distribution within electrodes may homogenize during long-term storage prior to testing at BOL, both microscopically within particles and macroscopically, including the so-called overhang region of the negative electrode [56]. Upon continuous aging cycling, lithium is redistributed and becomes more concentrated near the surface of the particles and interface with the separator [57]. Such redistribution could feasibly result in an increase in the accessible graphite capacity during testing. We do not claim to resolve the nature of graphite capacity increases in this work. Regardless of its mechanism, we do show that the phenomenon of graphite capacity gains can help to offset early capacity losses due to LLI.

Surprisingly, LAM_{NCA} contributes significantly to the overall capacity fade as well at low SOC. However, cycling in the low SOC window also results in greater and more rapid LAM_{Si} . For the 5-15% cells, this contributes to a loss of 7% of the overall capacity, while it only contributes 3% for the high SOC case. While more challenging to resolve the early peaks in the 85-95% ageing case, LLI appeared to be slower and LAM_{NCA} less pronounced at high SOC, with improved confidence of fit in the final four RPTs. Due to the better fit at EOL, the value of post mortem analysis for separating electrode-specific contributions in the final aged state would be limited. It could provide the opportunity to investigate heterogeneity within the cell. However, in the current work, complementary in situ, non-invasive techniques are used to support further evaluation of these ageing modes.

3.1.2. Incremental capacity analysis

The inverse of DVA, incremental capacity analysis, has also been performed on the C/20 charge/discharge cycle of each RPT to better explain the ageing mechanisms active in the full cell [58, 59, 60, 42]. The full cell ICA profile is the combined electrochemical signature of both electrodes, and features correspond to lithiation equilibria in the active materials. It is important to assign the peaks to the alignment of individual materials and reactions in order to properly understand the ageing process. Based on the half cell ICA for positive and negative electrodes in Figure 4(a) and 4(b), respectively, the peaks in the full cell ICA for a fresh cell, shown in Figure 4(c) have been assigned. All peaks represent coupled reactions occurring at both electrodes, i.e., voltage regions without a change in the active electrochemical reactions in any component. For the positive and negative half cells, the lithium foil is assumed to operate as an ideal counter electrode at a constant reference potential. For all cell types, the charge and discharge profiles (positive and negative differential capacity, respectively) are observed to be reasonably symmetrical. Depending on charge or discharge, a voltage shift in peak locations is observed and attributable to hysteresis and overpotentials during galvanostatic measurement. Positive electrode peaks (1)-(4) represent several equilibrium potentials during delithiation and lithiation of NCA, as dependent on stoichiometry and the crystal structure. Thermodynamically, peak (3) as identified here could be split into two distinct stoichiometric regimes, but these peaks rapidly smear out with ageing and can be reasonably treated as one in this work. For the negative electrode, peaks 1 **3** represent the well-ordered lithium staging reactions in graphite. Peak **4** far broader and lower in magnitude than any of the graphite peaks, is unique to the alloying reaction of lithium with silicon [61]. In the full cell ICA profile, peaks are labeled to represent the combined contributions from NCA, graphite, and silicon oxide.

The evolution of the selected ICA profiles during cycling is shown in Figure 5(a). The blended negative electrode, as suspected, does not age uniformly. Initially, active silicon is lost rapidly while the graphite appears to remain intact. This is clear from the immediately reduced magnitude of peak $(4)^*$ during the first few hundred cycles. Several other peaks smear out rapidly, suggesting increased polarization and a degree of inhomogeneity within the electrodes. This inhomogeneous response occurs due to a distribution of lithiation states throughout the jellyroll, causing reactions to occur over a broader range of full cell voltage than in the fresh cell. From this cursory analysis, the loss of negative electrode active material appears to be the major cause of capacity loss in the cells cycled in the 5-15% SOC window.

Peaks (2)*(1) and (2)*(2) are initially separated due to the graphite transition from delithiation of the fully lithiated (stage I) graphite ($\text{LiC}_6 \rightarrow \text{LiC}_{12}$), to delithiation of stage II graphite ($\text{LiC}_{12} \rightarrow \text{LiC}_{27}$). However, with ageing, this transition moves to a different cell voltage, alongside smearing effects, revealing a single, combined peak of stable reactions in both NCA and graphite. An expected consequence of LLI would be the shift of this transition to higher cell voltage as the negative electrode becomes relatively less lithiated with longterm cycling [42]. The steady decrease in peak (1)*(1) with continued cycling, while most other peaks remain fairly constant, reflects a loss of capacity in the high-voltage region that could also be attributed to rapid LLI that stabilizes after approximately 2000 cycles.

In Figure 5(b) ICA is compared for cells cycled in 5-15%, 15-25% and 85-95% SOC windows. Partial loss of peak $(4)^*(4)$ even at high SOC indicates



Figure 4: ICA on charge and discharge of each electrode and a full, cylindrical cell at BOL. Electrodes are harvested and reassembled into half cells and cycled at C/10: (a) NCA/Li, (b) Gr-SiO_x/Li. (c) NCA/Gr-SiO_x full cell at C/20.

that loss of active silicon material can occur even without active cycling in the low SOC regime, though to a much lesser extent. This loss may also be due to full cycling experienced by the cell during RPTs. The amplitudes of peaks relating to the graphite reactions **3** have reduced more for the cell cycled in the 5-15% SOC window than for the cell cycled in the 15-25% SOC window. This can indicate that the cell cycled in the 5-15% SOC window has increased polarisation or heterogeneity. Each of these cells retain similar behaviour at moderate SOC, with similarities among them for peaks (2)*(2) and (3)*(2). This comparison of ICA again suggests that loss of active silicon in the negative electrode material dominates capacity loss when cycling in low SOC windows.

3.1.3. Hysteresis analysis

In this section, the evolution of the hysteresis voltage (the difference of cell voltage between charge and discharge) with ageing is investigated. This is measured at C/20 cycling rates in order to minimise overpotentials and kinetic effects and highlight the thermodynamic hysteresis. The huge mechanical strain and unstable solid electrolyte interface formation on silicon electrodes is well documented [62, 57], this mechanical strain also leads to voltage hysteresis [63, 64].

A large voltage hysteresis upwards of 250 mV is observed at low SOC (<20%) between the charge and discharge of a fresh Tesla Model 3 cell, as seen in Figure 6(a). From the capacity retention plots in Figure 1(a) it can be recalled that the cells cycled in the 5-15% SOC window degrade the fastest. ICA and DVA have suggested that the major cause of ageing for these cells is the loss of negative electrode active material, specifically silicon oxide.


Figure 5: Evolution of ICA from C/20 discharge and charge with ageing for (a) a cell cycled in 5-15% SOC at different FCE and (b) the comparison of ICA for cells cycled in 5-15%, 15-25%, and 85-95% SOC windows, each at 90% SOH.



Figure 6: Comparison of voltage hysteresis measured between C/20 charge and discharge for (a) a fresh cell, and at different FCE for cells aged by (b) 5-15% SOC and (c) 85-95% SOC cycling.

Changes in the hysteresis voltage with cycling for the cells cycled in the 5-15% and 85-95% SOC windows are depicted in Figure 6(b) and 6(c). The magnitude of hysteresis voltage at low SOC decreases with ageing cycling. This reduction in hysteresis voltage is most pronounced for the cells cycled in the 5-15% SOC window and much less for the cell cycled in the 85-95% SOC window. This reduction in hysteresis voltage is another indicator that the cells cycled at low SOC lose more active silicon oxide with cycling. With the loss of silicon oxide, the mechanical strain in the negative electrode decreases, resulting in a decreased hysteresis voltage. Another interesting trend which can be noted is that although the hysteresis voltage in the low SOC window decreases with cycling for the cells cycled in the 5-15% SOC window, it increases at mid and high SOC. The distribution of hysteresis across the full operational window is not observed for cells cycled at higher SOC and may represent increasing heterogeneity in the electrodes.

4. Discussion

The ageing results of the cells cycled in 10% Δ SOC intervals show that those cells cycled below 25% SOC have the shortest lifetimes. At higher SOC (>85% SOC), cells also exhibit accelerated ageing but to a lesser extent. Generally, rapid degradation of cells at high SOC is observed, since at high SOC the electrolyte is either near or outside its voltage stability window at both the negative and positive electrodes [65]. The voltage is lower than 1 V vs. Li/Li⁺ at the negative electrode and above 4 V vs. Li/Li⁺ at the positive electrode. This fact is corroborated by the cells tested for calendar ageing, there the cells stored at 85% SOC exhibit the fastest degradation.

One reason for the faster ageing of cells cycled in the 5-15% SOC window is that in the blended negative electrode, silicon oxide is highly active and utilised during such cycling condition. In the 15-25% SOC window, both silicon and graphite are utilised while above 25% SOC only graphite is being used [66]. All the electrochemical ex-situ analyses indicate that the cells cycled in the 5-15%SOC experience the greatest LAM_{NE} and preferentially lose active silicon from the blended electrode. The volumetric expansion and contraction of silicon during cycling is reported to stress the particles, leading to particle cracking and particle pulverisation upon repeated cycling. This can lead to the loss of electronic contact in the electrode and LAM_{NE} [67, 68] and we have observed such disconnection in post mortem analysis of other cells cycled 0-50% SOC [17]. These cracks may also propagate to the bulk of the negative electrode and reduce contact among the graphite particles, leading to further isolation of active material, further LAM_{NE} , and possible delamination from the current collector. Degradation of conduction pathways increases the polarisation, as observed in the ICA and DVA plots of the cells cycled in the 5-15% SOC window. In addition, repeated expansion and contraction affect the electrode active surface area, forcing damage and reconstruction of the passivating SEI layer [69, 70] and an increase in LLI, particularly during early cycles, as observed in Figure 3(c).

In the case of the positive electrode, LAM_{PE} is observed (in Figure 3(d)). The loss of active material can be attributed to a number of factors which are typical for the Ni-rich cathode materials: phase change, secondary particle cracking, loss of lattice oxygen with subsequent loss of active material, cation mixing and transition metals dissolution [71]. A number of studies indicate that particle cracking and loss of lattice oxygen resulting in gas evolution are typically triggered beyond 75% of the cathode delithiation [72, 27, 29, 73]. Our prior study conducted on the same type of cell has shown the relevance of the mechanism to the cell positive electrode [40]. The same study also indicated that cell cycled at high SOC suffer from electrolyte decomposition as a result of its reaction with NCA lattice oxygen.

5. Conclusion

The ageing of 21700 cells harvested from a Tesla Model 3 is critically dependent on the SOC range. Full-cell differential voltage, incremental capacity, and voltage hysteresis analyses on cells cycled in narrow SOC windows suggest several ageing processes. The cells tested at the highest and lowest SOC levels demonstrate faster ageing than those cycled at intermediate SOC. This implies that the extremes of SOC should be avoided during battery usage in order to extend battery service life. Cells cycled between 35-55% SOC exhibited the best performance retention. To extend this window, it is preferable to use higher SOC (to 65% SOC or above) than lower (to 25% SOC or below). The loss of active silicon oxide in the negative electrode appears responsible for the rapid ageing of the cells cycled in the 5-15% SOC range. The volumetric expansion of the silicon particles during cycling is expected to lead to particle cracking and disconnection, which was also observed and confirmed by post mortem analysis in our parallel work [17]. It is worth noting that the degradation observed when cycling in larger SOC windows (0.50%, 50-100%) and (0.100%) studied in our parallel work was more rapid (about 3 times faster degradation) than for the narrower SOC windows studied in this work. This is in line with previously reported data by for instance Gao et al. [58] and Zhu et al. [36] and may be explained by increased degradation when crossing a larger number of phase transitions in the battery materials at charge and discharge. Continuous volume changes during cycling put stress on the SEI layer, resulting in the destruction and formation of the SEI layer observed as LLI. The cells tested in the high SOC range age due to LAM_{PE} and electrolyte decomposition. Under this condition, LLI is also greater due to electrolyte instability. For this reason, high SOC should be avoided during the long-term storage of batteries to extend service life. This type of ageing study is effective at evaluating the SOC-dependence of ageing in batteries and can be used on other chemistries to select precise cycling cutoff points that optimise energy and lifetime.

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PAPER C

Ageing of High Energy Density Automotive Li-ion Batteries: The Effect of Temperature and State-of-Charge

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The layout has been revised.

Ageing of High Energy Density Automotive Li-ion Batteries: The Effect of

Temperature and State-of-Charge

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Abstract

Lithium ion batteries (LIB) have become a cornerstone of the shift to electric transportation. In an attempt to decrease the production load and prolong battery life, understanding different degradation mechanisms in state-of-the-art LIBs is essential. Here, we analyze how operational temperature and state-of-charge (SoC) range in cycling influence the ageing of automotive grade 21700 batteries, extracted from a Tesla 3 Long Range 2018 battery pack with positive electrode containing $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA) and negative electrode containing SiO_x -C. In the given study we use a combination of electrochemical and material analysis to understand degradation sources in the cell. Herein we show that loss of lithium inventory is the main degradation mode in the cells, with loss of material on the negative electrode as there is a significant contributor when cycled in the low SoC range. Degradation of NCA dominates at elevated temperatures with combination of cycling to high SoC (beyond 50%).

Graphical abstract



Keywords: Li-ion battery; EV battery; Ni-rich cathode; Battery ageing; Operation conditions

Introduction

The future of passenger road transport is electric. The phase-out of fossil fuel vehicles is now closer than ever, with targets such as the "Fit for 55" package within the European Green Deal aiming to ban petrol- and diesel-powered cars and vans from the European Union market by 2035 [1–4]. Lithium-ion batteries (LIB) are widely considered to be the key technology enabling electrification [5]. Solutions for prolonging battery life are motivated by reasons of economics and sustainability, particularly concerning the high energy demand of production and the scarcity of key materials [6–8]. A significant focus in degradation studies of electric vehicle (EV) grade batteries is placed on cycling conditions. Finding an optimal combination of cut-off potential together with cycling temperature can significantly prolong battery life [9].

In this study, we focus on the ageing and degradation of a Tesla 21700 cylindrical cell, which is composed of a blended graphite-SiO_x composite negative electrode and an NCA (LiNi_xCo_yAl_zO₂) positive electrode, both currently considered state-of-the-art in EV cells. Among the most widespread chemistries used for the positive electrode in LIBs (NCA, NMC, LFP, and LMO) NCA shows the higher gravimetric capacity and specific energy [10]. A number of comprehensive studies are performed on the NCA and analogous materials as well as on its operation in commercial cells [9, 11–15]. The results have demonstrated that the state of charge (SoC) range has a significant influence on the ageing of the cells. The choice of the appropriate SoC range as well as the temperature can significantly improve the cell battery life. However, the majority of research on battery systems is conducted on model systems in the laboratory and typically with a focus on the positive electrode. Nonetheless, automotive-grade cells are much more optimized which, as well as the larger form factor, can influence the degradation processes. In this work, we focus on the influence of temperature and state of charge (SoC) range (0-50, 50-100, and 0-100% SoC) through full cell electrochemical evaluation and postmortem analysis of harvested electrodes from automotive-grade batteries.

Battery ageing studies are complex due to the interrelation of multiscale processes, requiring multiple techniques for a profound analysis and often interpretations can be challenging due to technical limitations [16]. Most of the ageing studies are focused on cell, electrode, or material levels [17], but the challenge to distinguish individual ageing processes has motivated the classification of ageing mechanisms into three major ageing modes: loss of lithium inventory (LLI), loss of active material (LAM), and loss of electric conductivity also known as resistance increase (RI) [18–22]. LLI refers to processes that result in a loss of lithium ions available to participate in the redox process, such as the formation of the solid-electrolyte interphase (SEI), while LAM covers processes that involve loss or changes resulting in the lower electrochemical activity of the host material, including transition metal dissolution, irreversible phase transition, and particle disconnection as a result of particle cracking. RI is related to the degradation of current collectors and binder. LLI and LAM modes are shown to be dominant [22, 23].

The degree of ageing of a cell is often reported as its state of health (SoH), which is calculated as the ratio of an observed capacity to the initial or nominal capacity of the cell [24]. To understand the sources of capacity loss and resistance increase, various electrochemical characterization techniques are used, including incremental capacity analysis (ICA) and differential voltage analysis (DVA) [25]. ICA and DVA provide information about the close-to-equilibrium state of the cell. Bot of the analysis may be combined with techniques analyzing electrochemical dynamics such as electrochemical impedance spectroscopy (EIS) and current interruption techniques give insights into general ageing trends in the battery as well as possible sources of capacity loss and internal resistance growth. Such analysis is feasible for commercial cells, yet, the possibility of testing the electrodes in three-electrode cell setup or half-cells allows the deconvolution of separate resistance contributions [26]. The anode active material ageing is mainly caused by SEI instability, lithium plating, and the loss of electrical contact in the active material [27]. For the inactive components, binder decomposition, conductive additive oxidation, and current collector corrosion are highlighted as ageing causes [28]. The anode active material ageing is mainly caused by SEI instability, lithium plating, and the loss of active material electrical contact [29]. As for the positive electrode, generally, micro-cracking of secondary particles, structural disordering, phase transitions to inactive phases, transition metal dissolution, and reaction with electrolyte are listed [30, 31]. However, the extent of each mechanism is specific to different active materials. Especially, for Ni-rich materials these are shown to be dependent on the Ni content and type of doping [30, 32, 33]. The extent to which different degradation mechanisms contribute to overall ageing depends on the cycling conditions. For example, particle cracking of Ni-rich active material is prevalent at a high state of charge (SoC) [34], and degradation sensitivity towards temperatures has been shown before [11, 35]. Other detrimental processes can be accelerated with elevated temperatures, such as SEI thickening and dissolution [36].

The development of LIBs has been the subject of extensive research in both academic and industrial settings. However, there is still a gap between the results obtained from model systems and the actual batteries in use [37]. In order to address this issue, this study uses a combination of electrochemical and material studies to investigate ageing in state-of-the-art batteries and address the relevance of current ageing theories. The study aims to leverage access and skill in a large network to do an in-depth study of ageing processes in a relevant cell. Specifically, the cells were subjected to ageing tests at three different state-of-charge (SoC) ranges (0-50% SoC, 50-100% SoC, and full SoC) and two temperatures (22°C and 45°C) to identify the dominant agents of ageing. The data suggest that LLI is a major degradation mechanism. Additionally, LAM on the negative electrode is dominated by SiO_x capacity loss with negligible losses of the graphite. LAM on the positive electrode is more prominent for the cells operating at high states of charge and is associated with cation mixing and transition metal dissolution together with particle void formation.

Experimental

Materials

Laminated aluminum pouch material (Skultuna Flexible), 1 mol L⁻¹ lithium hexafluorophosphate dissolved in 1:1 v/v ethylene carbonate:diethyl carbonate (LP40, 1 M LiPF6 in 1:1 EC:DEC, Solvionic), lithium metal chips (Li, MTI Corporation, thickness 450 μ m, Ø 1.55 cm, 90 mAh cm⁻²), quartz capillaries (Ø 5 mm, wall thickness 0.01 mm, Hilgenberg), and glass fiber separators (Whatman® GF/A) were used as received. Trilayer Microporous Membrane (PP/PE/PP) separators (Celgard 2325, 25 μ m) were cleaned with ethanol and deionized water and dried under vacuum at 60°C for 12 hours in the glovebox).

Commercial cells cycling ageing

The two sets of 21700 cells were extracted from a battery pack of a relatively new Tesla 3 Long Range from the year 2018. The cells were cycled within 0-50%, 50-100% and 0-100% SoC ranges at constant temperatures: at 22°C and 45°C correspondingly using a NEWARE BTS-4000 battery tester within a constant temperature test chamber. The SoC levels during cycling were defined via voltage limits, in order to avoid drift in SoC with coulomb counting. In order to account for polarization during

cycling the voltage limit corresponding to 50% SoC is different depending on whether it is a charge or discharge to 50% SoC. The cycling test matrix and naming of the cells are based on cycling conditions and are listed in Table 1 (for more details see Supporting Information (SI) Table S1) where R denotes room temperature (22 °C), H denotes high temperature (45 °C) and numbers indicate cycling intervals during ageing in terms of % SoC. C/3 and 1C current rates were used as charging and discharging current respectively. After each 50 Full Cycle Equivalents (FCE) a reference performance test (RPT) was conducted. During RPT one cycle at C/3 charge and discharge rate was performed to initialize cells for RPT and ensure uniform test conditions throughout the RPT. Then two cycles with a CC-CV charge with C/20 cut-off at maximum voltage and C/3 discharge to minimum voltage was performed to measure capacity. An average of the two discharge capacity measurements is used as capacity value for that RPT. Furthermore, a C/20 full cycle is performed for incremental capacity analysis purposes, which is followed by discharge and charge pulses at the cycler maximum current of 1.3C (6 A) at 30%, 50% and 70% SOC levels to track impedance. A visual clarification of the RPT is included in SI Figure S 1. The cells were stopped when reaching ~75 % SoH, unless they had to be stopped earlier due to the time limitations of the project (an example of such is a cell cycled between 50-100% SoC at 22°C).

Sample name	SoC range	Upper Voltage	Lower Voltage	Temperature					
R0-50	0-50 %SoC	3.78V	2.55V	22 °C					
R50-100	50-100% SoC	4.18V	3.53V	22 °C					
R0-100	0-100% SoC	4.18V	2.55V	22 °C					
H0-50	0-50 %SoC	3.78V	2.55V	45 °C					
H50-100	50-100% SoC	4.18V	3.53V	45 °C					
H0-100	0-100% SoC	4.18V	2.55V	45 °C					

Table	1 -	Samp	le	matrix.
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State of Health (SoH) is defined as a capacity retention as measured during a C/3 discharge related to the initial capacity and expressed in percentage of initial capacity.

State of Charge was set by fix voltage levels to avoid drifting in SoC window during cycling. The voltage limits were set based on reference tests with relevant C rate (*i.e.*, 1C for voltage during discharge and C/3 for charge procedure, for the partial SOC window tests). For R0-100 and H0-100 cycling was performed between maximum and minimum voltage of the cell.

Cell tear down

All cells were discharged to 0% SoC (~2.55 V) before disassembly and opened in a dry, Ar-filled glovebox. For each cell, electrodes were carefully unrolled and cut in segments of equal size, respecting the orientation of the electrodes to one another as well as to the cell terminals. Segments were numbered 1 to 6 where 1 is the closest to the cell casing and 6 is the closest to the core. Additionally, segment 4, which was considered as central, was split on three equal parts within the height called U, C, and D, where U is the segment closest to the negative terminal, C is in the center and D is a segment close to the positive terminal. The heterogeneity of ageing within the cell was evaluated by selecting samples at three different positions in the height direction from the center of Region 4. The electrodes collected within the height of the cell U, C, and D were taken from ~15, 32, and 47 mm from the top of the cell (the scheme of the electrode's regions is shown in "Degradation inhomogeneity" section). Region 1 was the beginning of the roll. Region 4 was located at ~400 mm from the beginning of the positive electrode. Region 6 was at the end of the roll.

Afterwards, the segments were stored in individual pre-dried plastic bags and sealed in pouch bags. Electrodes were harvested at BoL from an unaged cell and at end of life (EoL) from cycled cells from each of the six test groups.

Electrochemical measurements of extracted electrodes

A Biologic MPG2 was used for post-disassembly electrochemical testing. One side of the active material coating on the extracted electrodes was removed using a scalpel. Positive electrodes were punched \emptyset 10 mm and the negative electrode using an \emptyset 11 mm puncher. The pouch cells were assembled with electrolyte LP40, Celgard 2325 separator in a half-cell configuration. A part of the cells from Region 4 was tested using a gold micro-reference electrode as a reference electrode [38]. The cells were cycled at room temperature between 2.55 and 4.2 V for the positive and between 1.5 V and 0.05 V for the negative electrode with a constant current of C/10 (275 μ A) after a 4 h rest. A combination of constant current cycling and ICI was performed to evaluate the electrode performance. ICI was carried out by introducing a 5-second rest every 5 minutes [39]. The ICI data were treated using the script developed by Lacey *et al.*[40]. To compare cells cycled at different conditions, the lithium diffusion coefficient *k* was averaged for the plateau region between 2 to 3 mAh g⁻¹.

Additional two-electrode, vacuum-sealed pouch cells were built and tested in the interests of evaluating lab-to-lab reproducibility (Uppsala University and KTH Royal Institute of Technology) and generating robust metrics of electrode capacity. These cells contained NCA or $Gr-SiO_x$ electrodes harvested from the cylindrical cells, lithium foil (Sigma-Aldrich) as a counter/reference electrode, Whatman® GF/A separator, and the same electrolyte. At KTH, cycling was done at an estimated 0.1C rate (NCA: 0.40 mA cm⁻², Gr-SiOx: 0.45 mA cm⁻²) on an in-house, high-precision battery cycler using Keithley 220 programmable power sources. Cycling of the NCA cells was occasionally conducted with higher cutoff voltages of up to 4.35 V vs. Li/Li⁺. In the cases with higher cutoff voltages, the discharge and differential voltage profiles are translated to match the initial discharge voltage of the corresponding three-electrode cell. The discharge curves are shown in SI Figures S2 and S3 (positive and negative electrodes correspondingly).

Test cell data already processed for ICI did not require additional smoothing for DVA. The other test cell data were smoothed using the strategy first suggested by Li *et al.*[41] and applied in our earlier work [42], with an initial moving average smoothing step over a 0.55% SoC span and a Gaussian filter over a 3.0% SoC span. The differential voltage parameter was obtained by numerical differentiation of the discharge curves (corresponding to the second complete discharge of each half-cell) and normalization by the discharge capacity (DV = $Q_d \cdot dV/dQ$). Peaks were identified manually using ipf.m, Interactive Peak Fitter [43]. All smoothing, peak identification, and differential voltage analyses were performed in MATLAB®.

Scanning electron microscopy and Energy-dispersive X-ray spectroscopy studies

A Zeiss LEO 1530 with an Oxford AZtec EDS system was used to perform scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS). SEM was performed using an acceleration voltage of 5 kV and a working distance of 6.5 mm for cross-section images and 5.0 mm for top-view images. Elemental distribution within the positive and negative electrodes was also measured with EDXS using acceleration voltage 20 kV and distance 8.5 mm. Cross section sample preparation of electrodes were done using ion polishing. The methodology is further described in our previous study [44].

Inductively coupled plasma - optical emission spectrometry

An Avio 500 Scott/Cross-Flow Configuration was used for elementary composition identification using inductively coupled plasma - optical emission spectrometry (ICP-OES). Disks of positive and negative electrodes were punched from each cell: room and 45°C ageing within 0-50%, 50-100%, and 0-100% SoC. Region 4 from positive and negative electrodes of each sample was used for comparison. One disk \emptyset 10 mm for positive electrode and two disks \emptyset 20 mm for negative electrode were used per sample. The followed detailed methodology for further sample preparation can be accessed in our previous study [44].

X-ray diffraction

The extracted powder from the 4th electrode segment in each cell was ground by hand in a mortar and pestle and sealed in quartz capillary in a dry, Ar filled glovebox using an epoxy glue. For the x-ray diffraction (XRD) data collection a STOE Stadi P diffractometer with Ge source and a Dectris Mythen 3K detector was used. The data was collected utilizing Cu K α radiation ($\lambda = 1.5406$ Å) in Debye-Scherrer mode and fitted using commercially available software TOPAS V6 [45].

Transmission Electron Microscopy

TEM lamellae of BoL and EoL samples were prepared using a Focused Ion Beam (FIB) on model Crossbeam 550 (Zeiss). The surface of the sample was masked with a carbon and a Pt layer. A 2 kV ion accelerating voltage was used for sample polishing. The lamellae were studied with STEM using a double aberration-corrected Themis Z (Thermo Fisher). The microscope was operated at 300 kV and equipped with a Super-X EDS detector. The aberrations in the condenser lens system were corrected up to 5th order. The collection angle of HAADF- and BF-STEM images were 63-200 mrad and below 35 mrad, respectively. Imaging acquisition and analysis were performed using Thermo Fisher Velox.

Results

Cell composition

In the opened 21700 cylindrical cells the positive electrode was measured to be 920×64 mm (both sides); the negative electrode was measured to be 65 mm height, with a coating length of 855 mm on the convex side of the coating and 920 mm on the concave side. The negative current collector measured 940 mm and had a clean copper part facing the cell casing. The separator oversized by 1 mm at the top and bottom of the negative electrode. SEM/EDXS analysis revealed that the positive electrode was composed of NCA, carbon conductive additive, and a polymer binder. The active material consisted of secondary particles of $Li_xNi_{0.96}Co_{0.05}Al_{0.05}O_2$ doped with ~1% W (confirmed with ICP and EDXS SI Figure S 5) and primary particles in a range of ~100 nm. W doping of NCA is known to increase electronic and ionic conductivity, decrease cation mixing, and mitigate particle cracking [46]. The negative electrode consisted of graphite with SiO_x particles, which had a coating or interphase layer with a thickness up to 100 nm. The use of SiO_x chemistry in the negative electrode was found to improve its specific capacity and lower degradation compared to pure Si [47]. The 21700 cells in the Tesla Model 3 2019 battery pack had similar chemistries of the positive and negative electrodes reported for Tesla Model S 18650 cells [35] and Panasonic cells [10, 13, 48].

SEM images of cross-sections of the electrodes showed that the positive electrode was doublecoated with an Al foil with a thickness of 15 μ m and a coating thickness of ~65 μ m (Figure 1- a). The active material loading was measured at ~22.9 mg/cm². The negative electrode consisted of a copper foil with a thickness of 8 μ m with a double-sided coating of ~85 μ m and a loading of ~11.7 mg/cm² (Figure 1–b). The separator extracted from the cell had a morphological similarity to polypropylene (PP)/polyethylene (PE) separators (SI Figure S4) and a coating on the side towards the positive electrode that was based on Al₂O₃ or Al(OH)₃, which are often used to improve thermal properties, puncture strength, and limit cross-talk between the cathode and anode [49–51].



Figure 1 – SEM images of electrodes cross-section: a – positive electrode, b – negative electrode.

Full cell degradation analysis

The present study investigates the long-term cycling performance of cells under different operational conditions, as shown in Table 1. Capacity loss was evaluated in the change in SoH with increasing number of FCE (Figure 2 - a). The observations of the capacity loss trends enable a comparative evaluation of cell performance under varied conditions. In the studied case, the capacity loss curve indicates a sublinear ageing trajectory, as the cells did not reach the knee point where degradation is expected to accelerate [52]. The last point of each dataset corresponds to the last measurement of remaining practical capacity before the cell was disconnected. The difference in end-of-life (EoL) capacity between cells will be taken into consideration for every trend analysis.

The capacity retention above 95% is similar for all ageing conditions, except for the cells cycled at 50-100% SoC at 22°C (R50-100), which exhibit better capacity retention. Cells cycled between 0-50% and 0-100% SoC (R0-50, H0-50, R0-100, and H0-100) at both temperatures show a similar trend of capacity fading down to 85% SoC, as depicted in Figure 2–b. The cells cycled at 50-100% SoC at both 22°C and 45°C exhibit a slower decay and longer lifetime compared to the other cells. Among these, the cells cycled at 22°C demonstrate superior performance compared to those cycled at 45°C. Furthermore, the cells cycled between 0-100% SoC at 22°C (R0-100) degrade quicker than the others.

In order to compare the rates of cell ageing, the number of FCE required for each cell to reach ~80% SoH are determined. For most conditions, the cycle life is around 600-700 FCE. However, the cells aged within the 50-100% state of charge (SoC) range have a significantly higher number of FCE compared to the rest of the cells. The H50-100 cell has undergone approximately twice as many cycles (~1200), while the R0-100 cell has undergone more than three times as many cycles (~2400). This suggests that cells cycled at high SoC (50-100%) at both room (22°C) and high (45°C) temperatures outperformed the other cells by a factor of 2 and 4 respectively.



Figure 2 – Percentage of capacity retention of 21700 Li-ion cells at different cycling conditions: a – full cycle life, b – the same cells cycled between 0-50 and 0-100% SoC at 22°C and 45°C are shown separately from high SoC cells.

The electrochemical behavior of cells was visualized using incremental capacity analysis (ICA). ICA profiles at BoL, an intermediate cycle number (MoL, 300 FCE), and EoL (~75% capacity retention) are depicted in Figure 3, illustrating the evolution of electrochemical behavior. The peaks identified in the fresh cell are attributed to regions of reaction stability in both electrodes and are labeled accordingly. During charging, NCA undergoes multiple phase transitions, including the transitions from hexagonal H1 to monoclinic M (reaction 0), intermediate monoclinic behavior (reaction 0), monoclinic M to hexagonal H2 (reaction 0), and hexagonal H2 to hexagonal H3 (reaction 0)[53, 54]. Lumped silicon oxide behavior is represented by reaction 0. Graphite (de)lithiation occurs through several well-ordered stages, with several lumped dilute stages exchanging until stage III (LiC₂₇, reaction 0), stage III exchanging with stage II (LiC₁₂, reaction 0), and stage II exchanging with stage I (LiC₆, reaction 0)[47, 55, 56]. The peak $\textcircled{0} \times \textcircled{0}$ is used to track the changes in the silicon oxide fraction of the blended negative electrode. All other ICA features arise due to convolutions of NCA and graphite (de)lithiation reactions. The evolution of these features supports qualitative discussion of the observed aging behavior.

In general, it is noted that as the cells age, the peaks become wider and less distinct. This can indicate the effects of lithiation heterogeneity within the electrodes. This uneven distribution of lithium can arise due to slowed reaction or diffusion kinetics and other localized aging processes [18, 57, 58]. Heterogeneity causes peaks to blend into one another, since it causes local differences in capacity within the cell and thus shifts the local electrode potentials. The reactions then occur, still sequentially in each particle, but over a distribution of times during charge/discharge and at different points of overall cell voltage. Heterogeneous ageing is also confirmed by local capacity measurements during post mortem analysis, see section "Degradation inhomogeneity". This trend is consistent across all cycling conditions and shows no clear dependence on temperature nor SoC window, with all EoL ICA profiles showing fewer distinct peaks. In particular, peaks $\Im \times \textcircled$ and $\Im \times \textcircled$, which are inherently less pronounced already at BoL, cannot be resolved visually in ICA after extended cycling. This likely represents increases in both resistance and heterogeneity in all cells.

For the H50-100 and R50-100 cases, shown in Figure 3 - b and e respectively, a shift of all peaks towards higher full cell voltage is visible. This is attributed to loss of lithium inventory (LLI) [47], by which electrode slippage shifts the operating windows of the electrodes to higher potentials.

In the cases where the cells were fully discharged during cycling, Figure 3 – a, c, d, and f, all show that peak $\textcircled{3} \times \textcircled{6}$ is lost, or greatly diminished, already after 300 FCE compared to H50-100 and R50-100 cells which clearly show the $\textcircled{3} \times \textcircled{6}$ peak. As the graphite peak are still clearly visible, this indicates uneven aging in the blended electrode with a rapid loss of active silicon oxide when discharging to (and charging from) 0% SOC during cycling. For H50-100, this characteristic peak ($\textcircled{3} \times \textcircled{6}$) is preserved, albeit shifted, during cycling, indicating retained activity of the silicon oxide fraction of the electrode. It is noted that the loss of this peak $\textcircled{3} \times \textcircled{6}$ in the R50-100 case, shown in Figure 3 – b, shows that active silicon may also be lost during cycling in a higher SOC window. However, higher resistance and local heterogeneity might also to some extent contribute to apparent losses of this weakly-prominent peak.

The shift in the trough between peaks $@\times •$ and $@\times •$ to higher voltages is an indicator for LLI [42]. However, this might only be possible to capture by tracking intermediate stages (see MoL profiles in Figure 3) and the observation that the trough deepens between NCA reactions ① and @. The latter becomes coincident with the trough between graphite reactions • and • (Figure 3 – e). In cases of increasing heterogeneity, the distinction between $@\times •$ and $@\times •$ may simply smear out to form one broad peak representing both concurrent equilibria. The gradual loss of peak height in $@\times •$ seen in all aging cases is a better indicator of LLI for cells containing NCA and graphite. For this to be true, the $@\times •$ peak must remain prominent and separated from the other smeared peaks (so that the decrease is not due solely to lithiation heterogeneity). In such cases, less of the fully-lithiated LiC₆ phase can be formed on charge once lithium is consumed at the negative electrode. Although selective LAM presents in some aging cases and increasing heterogeneity is observed throughout, the changes in peak $@\times •$ for all samples indicate that LLI always occurs to a significant extent.



Figure 3 – ICA comparison of BoL and EoL cells tested at various conditions: a - BoL cell with reaction specified; b - R0-50 cell cycled between 0-50% SoC at 22°C, c - H0-50 cell cycled between 0-50% SoC at 22°C, d - R50-100 cell cycled between 50-100% SoC at 22°C,

e – H50-100 cell cycled between 50-100% SoC at 22°C, f – R0-100 cell cycled between 0-100% SoC at 22°C, g – H0-100 cell cycled between 0-100% SoC at 22°C.

Post mortem analysis

Degradation inhomogeneity

The ICA of the full cell cycling data has indicated ageing heterogeneity within the cell. To address spatial heterogeneity, corresponding positive and negative electrodes from several regions were tested. The evaluation of heterogeneity was done to anticipate its effect for the following ex-situ tests. Local half-cell capacity was addressed for the positive and negative electrodes respectively in several different regions, where Region 1 corresponds to the cell casing and region 6 is the cell core (Figure 4). For the positive electrodes the H0-100 aged cell showed the most severe degradation in the central region. The least aged region (highest capacity retention) is the Region 6, located in in the core of the cell, while the most aged region is number 1, which is closest to the cell casing. The highest capacity loss was also for the negative electrode found in Region 1 (closer to the cell casing). The heterogeneity in ageing within the electrode roll was also done at various heights for the central Region 4 of the cell. For consistent comparison among cells the electrodes were cut at the same distance from the top of the cell. The most severe ageing for the positive electrode was detected for the middle height of the cell. This is consistent with the previous studies evaluating the capacity loss distribution within cylindrical cells [35, 59]. The negative electrode shows the opposite trend and the lowest capacity was found towards the bottom of the cell. For consistent comparison among cells the centre of Region 4 was chosen and the electrodes were cut at the same distance from the top of the cell.





Electrochemical analysis of capacity loss in the positive and negative electrodes

Upon reaching end-of-life (EoL), the cells were disassembled and the positive and negative electrodes from the center (Region 4) were evaluated in a half-cell configuration. Figure 5 presents the capacity loss of the positive and negative electrodes from aged cell expressed as a percentage of the cell

capacity at BoL. The capacity loss depicted in Figure 5 reveals that for the cells cycled at both temperatures between 0-50% State of Charge (SoC), the negative electrode exhibits higher capacity loss. Also, all cells cycled at 22°C demonstrated a dominant capacity loss in the negative electrode. On the contrary, the cells cycled at 45°C exhibited a relatively greater capacity loss of the positive electrode, compared to their 22°C counterpart, and when cycling at higher SoC the loss of capacity of the positive electrode was dominating. The positive electrode operating between 0-50% SoC at 22 °C (R0-50) demonstrated the lowest capacity loss. These observed trends are consistent with what is commonly observed for nickel-rich electrodes, as the majority of the degradation processes are linked to material delithiation beyond 0.75% of lithium content in the cathode material [20]. The results demonstrate that elevated temperature accelerates the degradation of the NCA-electrode, whereas the low SoC window (0-50%) is more detrimental for the Si-Gr electrode.



Figure 5 – Capacity loss evaluation of positive and negative electrodes harvested from the center of the jellyroll (region 4) of aged cells as a percentage of BoL capacity.

The difference in a used cyclable capacity window (Q_{window}) in a full cell configuration is presented in Figure 6. A decrease in the Q_{window} is generally coming from capacity loss and a change in positive *vs* negative electrodes capacity balancing [60]. The detailed analysis methodology for used capacity is presented by Birkl *et al.* [19]. The loss of cyclable capacity window is found to be similar for cells cycled at 22°C (all SoC window) and cell cycled 50-100% SoC at 45°C. Additionally, the LLI was analyzed for all aged cells and showed that LLI is responsible for most of the capacity loss in the studied cells. Interestingly, LLI are very close for all condition with a slight deviation for the cell cycled at 45°C between 0-100% SoC. LLI is often suggested as one of the main degradation mechanisms in LIB [23]. The observed LLI and it extend supports ICA presented in Figure 3.



Figure 6 – Comparison of a cyclable capacity window and LLI for the studied cells.

Intermittent current interruption (ICI) cycling protocols and analysis reveal solid state Li diffusion resistance coefficients, k [61, 62]. Changes of k can be due to an alteration of the effective diffusion length (for example, particle cracking or increased tortuosity), the formation of surface layers such as rock-salt, which introduce lattice mismatch along the diffusion path of Li⁺, or other structural changes in the active material [63, 64]. Figure 7 shows a comparison of the Li diffusion resistance coefficients of the extracted aged electrodes. For the aged positive electrodes, k increased most significantly for the H0-100 cell (~6 times). For other conditions such as R50-100, R0-100, and H0-50, the increase in k is approximately 2 times compared to BoL. As for the negative electrode, room temperature ageing did not increase k, but rather impose a slight decrease. The high-temperature cycling led to a decrease for the H50-100 and H0-100 aged cells, and ~1.5 times increase in k for the H0-50 aged cell. The increase of k on the negative electrodes might be influenced by an increase of graphite interlattice spacing during ageing [65].



Figure 7 – Comparison of Li diffusion resistance coefficient of cells aged within 0-50%, 50-100%, and 0-100% SoC at 22°C and 45°C for positive and negative electrodes.

Detailed analysis of the degradation of the NCA positive electrode

In order to evaluate loss of active material on the positive electrode (LAM_{PE}), a differential voltage analysis (DVA) was conducted and the results are presented in Figure 8. Three peaks were identified for all samples, where for the BoL sample peak P1 had a maximum at 0.85 mAh cm⁻², peak P2 at 1.9 mAh cm⁻², and peak P3 at 2.9-3.7 mAh cm⁻². The final peak is inconsistent among the test cells and not used for further fitting. The corresponding reference peak capacities in mAh cm⁻² (denoted Q_{P1} and Q_{P2}) are used to calculate characteristic peak spacings. Together with half-cell capacity (Q_d), they are marked in Figure 8 – a, b. The changes in key peak spacings and capacity for electrodes harvested from the cells cycled at various conditions are shown in Figure 8 – b, c in both mAh cm⁻² and % of BoL values. Degradation of NCA results in changes of both the position of the peaks Q_{Pn} (where n is number of the peak) as well as its relative quantity. Such quantities have previously been defined and tracked over ageing for similar cells [12, 42].

In modelling of cell balancing and post-mortem analysis, LAM is typically represented as a uniform scaling of the electrode potential profile [18, 19] (and, proportionally, the differential voltage profile) with fewer redox centers, less charge compensation and, therefore, decreased capacity. This uniform view of LAM_{PE} presents a proportional decrease in all positive electrode peak spacings in DVA and in the observed discharge capacity. However, the first peak spacing, $Q_{P1} - 0$ for the aged samples

(Figure 8 – b), is far out of proportion when compared to Q_d . Electrodes from the cells cycled at 45°C have particularly low values. The dramatic decrease in $Q_{P1} - 0$ represents that very little capacity is available from the first reduction reaction during the lithiation of NCA (①). On the other hand, the quantities $Q_{P2} - Q_{P1}$ and $Q_d - Q_{P2}$ (Figure 8 – c), representing subsequent sections of the discharge curve, are much more consistent and in proportion with one another. Observing proportionality among the remainder of the DV profile, we suggest the spacing $Q_{P2} - Q_{P1}$ as a better candidate for accurately estimating the thermodynamic LAM_{PE}. Latter represents the expected loss of capacity in the absence of rate limitation. This quantity removes artifacts arising from the switch between charge and discharge and is presented also in SI Table S 4. The quantity $Q_d - Q_{P2}$ may also be suitable, though it should include kinetic limitations at the end of discharge that may be coupled with limitations of the lithium foil counter electrode.



Figure 8 – DVA analysis of the positive electrodes extracted from Regions 4 and 5: a – representative BoL half cell potential and differential voltage profile of NCA/Li with characteristic peaks, spacings, and half-cell capacity marked; b – summary of capacity and DVA peak fitting and b – selected values compared to BoL.

Figure 9 depicts cross-sectional images of the positive electrode from fresh (Figure 9 – a) and 0-100% SoC aged at 45°C (Figure 9 – b) cells. Examination of the secondary particle microstructure reveals no significant particle cracking at 0% SoC, even under the most severe aging conditions.

However, in the aged cell voids within larger particles are visible, and in more detail a few particles exhibit cracking in their centers (SEM images for each cell can be seen in SI Table S2). A slightly larger intergranular spacing is observed in aged electrodes. The evaluation of cathode thickness shows an average increase of 13%, with a higher increase of 17% for electrodes cycled between 50-100% SoC (SI Table S3). This result does not agree with previous research that has shown partially reversible cracking in NCA [66], including also the BoL material harvested from the cells presented here [44]. Furthermore, a surface layer (sometimes called the cathode-electrolyte interphase or CEI) and decomposition products is visible on all samples except for BoL and EoL aged at 22°C 50-100% SoC and 45°C 0-50% SoC (BoL and H0-100 cases are presented in SI Figure S5). However, its thickness (around 200 nm corresponding to only to 0.3% of the BoL electrode thickness) does not account for an increase in the electrode volume.



Figure 9 – Cross section scanning electron microscopy image of positive electrode: a – fresh cell; b – aged within 0-100% SoC at 45°C cell.

The formation of a rock salt surface layer on the active material particles has been associated with an increase in resistance in lithium-ion batteries [63]. To investigate this phenomenon, transmission electron microscopy (TEM) was used to evaluate the formation of surface layers on fresh and aged electrodes. Figure 10 displays TEM images of the surface of NCA particles from both BoL and EoL (H0-100) samples. Surprisingly, no presence of rock salt layer was detected on the surface of NCA particles in any of the samples (a and b correspondingly). To further investigate this, the distribution of Ni was evaluated by EDXS over the TEM samples of EoL samples, as shown in (Figure 10 – c and d). No gradient of Ni concentration was observed, indicating that the surface layers on the particles were not responsible for any significant increase in resistance in these samples. Additionally, the nanoporosity is present in EoL (H0-100) electrodes and visible in Figure 10 – d which we address in an upcoming publication as a part of degradation related to the oxygen evolution.



Figure 10 – TEM images of electrodes extracted from fresh (a) and aged within 0-100% SoC at 45°C (b) cells together with EDXS mapping done for BoL and EoL H0-100 electrodes (c) and (d) correspondingly.

To better understand the structural changes in the bulk of the positive electrodes of lithium-ion batteries upon ageing, an XRD study was performed on powders extracted from the electrodes of both BoL and EoL cells. Rietveld refinement of this XRD data are presented in Table 2. Changes in the lattice parameters a and c, and the relationship between them, indicate structural changes in the electrode material. Additionally, the I_{003}/I_{104} ratio can be used to detect Ni/Li cation mixing [67–69], which occurs when the material deviates from hexagonal symmetry towards cubic symmetry, and a threshold value of 1.2 is often used to indicate this phenomenon [67, 70, 71].

The results of the XRD analysis indicate that there is a minor shift in the c lattice parameter in the studied samples, with a EoL maximum deviation of 0.2% from the BoL sample. This deviation is significant, considering that the c lattice parameter usually deviates by approximately 1% during cycling [44]. Notably, the cells cycled to high state of charge (R50-100, R0-100, H50-100, H0-100) experience such differences. Moreover, the c/a ratio remains close to the BoL values in all studied cases, showing xx. The I_{003}/I_{104} ratios of the aged electrode are also relatively close to the BoL values, except for the samples cycled between 50-100% SoC at 22°C and 45°C, which show lower values, close to 1.2. This indicate that the active material may experience a higher cation mixing in the upper SoC region. Overall, the XRD results suggest that there are structural changes in the electrode material cycled beyond 50% SoC.

		cicculouco.		
Sample	a, Å	c, Å	c/a	I_{003}/I_{104}
BoL	2.86160(3)	14.2464(3)	4.9785 (1)	1.316
R0-50	2.84837(6)	14.2410(6)	4.9997 (2)	1.382
R50-100	2.85500(4)	14.2771(5)	5.0007 (2)	1.186
R0-100	2.85416(5)	14.2781(5)	5.0026 (2)	1.292
H0-50	2.85216(4)	14.2900(4)	5.0102 (2)	1.389
H50-100	2.85618(4)	14.2731(4)	4.9989 (2)	1.269
H0-100	2.85623(3)	14.2732(3)	4.9972 (1)	1.378

Table 2 – X-Ray diffraction results conducted over the powders extracted from positive electrodes

The dissolution of transition metals is another common phenomenon observed in Ni-rich layered cathode materials [72, 73]. Here, an elemental analysis evaluation of the positive electrode was performed using ICP-OES to investigate the dissolution of transition metals. However, direct comparison of transition metal ratios may be misleading as it may neglect a correlated, net change in all of the transition metals. To avoid this, the negative electrodes from the corresponding part of the positive electrode were analyzed since the dissolved transition metals are expected to be reduced on the negative electrode [74].

The amount of Ni detected in the negative electrode coating of BoL and EoL cells was determined, and the results are presented in Figure 11. A comparison of BoL and EoL cells showed that, although there was a relatively large variation between samples, a greater Ni content was observed in the negative electrodes of cells cycled between 50-100% SoC. Furthermore, ageing at 45°C resulted in higher Ni dissolution and deposition on the negative electrodes compared to ageing at 22°C. The ICP-OES of the positive electrode was rather similar, and no further conclusions drawn from the data, see SI Figures S 8 and S 9.



Figure 11 – Ni detected in negative electrodes of BoL and EoL cells aged 0-50, 50-100 and 0-100% SoC and two temperatures: 22 °C (R0-50, R50-100, R0-100) and 45 °C (H0-50, H50-100, H0-100).

Detailed analysis of the degradation of the negative electrode

For the negative electrode, DVA was also performed to determine the extent of loss of active material on the negative electrode (LAM_{NE}) and to decouple the contributions from graphite and silicon

oxide. The capacity of the active graphite material was partitioned into three segments based on the sharp differential voltage peaks N1 and N3, illustrated in Figure 12 – a. If kinetic limitations can be reasonably neglected (i.e., if cycling at sufficiently slowly), the resulting segments $a (Q_{N1} - 0)$, $b (Q_{N3} - Q_{N1})$, and $c (Q_d - Q_{N1})$ contain 50, 38, and 12 % of the graphite capacity, respectively [56, 75, 76]. The observed capacities in each region, as well as the total electrode delithiation capacity, Q_d , is presented for each cycling condition in Figure 12 and Table S 5 (n SI) as the averages from multiple harvested electrodes from various regions within each test cell. Even in the blended electrode, region b, quantified as $Q_{N3} - Q_{N1}$, purely represents graphite activity with no contribution from the silicon fraction nor kinetic limitations. From the $Q_{N3} - Q_{N1}$ quantity, we can therefore estimate the total capacity of the graphite in the blended electrode, Q_{Gr} , where θ is the fraction of the thermodynamic graphite capacity in the respective region.

$$Q_{\rm Gr} = \frac{Q_{\rm N3} - Q_{\rm N1}}{\theta_b}$$

 $Q_{\rm Gr}$ are calculated at BOL and EOL for each ageing case and presented in Figure 12. $Q_{\rm Gr}$ serves as a quantitative metric of close-to-thermodynamic LAM_{Gr}. Knowing the effective graphite capacity, it is possible to deconvolute the activity of silicon from that of the dilute graphite stages at low extents of lithiation. This is achieved by subtracting the expected graphite contribution ($\theta_c \cdot Q_{\rm Gr}$) from the remaining capacity in region *c*.

$$Q_{\rm Si} = Q_d - Q_{\rm N3} - \theta_c \cdot Q_{\rm Gr}$$

The necessary assumption in this estimation is that both the silicon and graphite are fully delithiated following the 0.1C step to 1.5 V. Effectively, this resolves the silicon amount that is kinetically available, which may be somewhat less than the total silicon content determined by other techniques. In spirit, this method of separating the silicon contribution is the same as can be done with fitting the open circuit potential for blended electrodes [77]. However, this manual algebraic calculation provides simplified, quick quantification in concert with the analysis of the differential voltage profiles.

Furthermore, the high SoC kinetic limitations can also be evaluated. In the early stage of delithiation, the underutilization of the graphite is represented by Q_{ul} . Similar to $Q_{P1} - 0$ for the positive electrodes, this underlithiation can be due to kinetic limitations on the previous charge step, or isolated regions that have poor conductive connection.

$$Q_{ul} = \theta_a \cdot Q_{\rm Gr} - Q_{\rm N1}$$

The key to these measurements is that they, like in our case, must be slow enough so that the electrode approaches pseudo-OCP and peaks N1 and N3 are sharp and can be confidently fitted. Increasing heterogeneity within the electrodes can smear out these peaks, making such measurements particularly challenging at full-cell level.

The evaluation of BoL electrodes reveals that silicon initially contributes 17% (0.72 mAh cm⁻²) of the achievable capacity of 4.3 mAh cm⁻². Ultimately, in the various aging cases, 45-72% of this silicon capacity is lost, compared to a maximum of a few percent capacity loss of the graphite. In some cases, the graphite capacity even increases by EoL within the error. This is attributed to kinetic improvements with mild exfoliation and increases in the interlayer spacing of graphite [65]. Overall, the contribution from the graphite in the blended electrodes has had minimal impact on capacity fade in these cells. For each SoC range, the cells cycled at 22°C retained 5-10 % more silicon capacity than their counterparts cycled at higher temperature. However, the 22°C cells attained greater values of Q_{ul} , indicating greater kinetic limitations or more trapped lithium, though this value has greater variation among the test cells. Regardless, we suggest that this is tied to greater utilization of the graphite in the 45°C-cycled electrodes (having less active silicon). Even though the silicon degradation was severe in all cases, it was the least so for those cells cycled 50-100% SoC (R50-100 and H50-100), indicating that time spent in delithiated state was more detrimental for the silicon. It is noted that the cells cycled at high SoC still over the cell lifetime had several full cell cycles (from 0 to 100% SoC) during 30+ RPTs, and that this may to some degree have contributed to the observed losses of SiOx capacity.



Figure 12 – DVA of the negative electrodes extracted fromRegions 4 and 5: a – representative BoL half cell potential and differential voltage profile of Gr-SiOx/Li with graphite and silicon peaks and important capacities marked; b – summary of calculated values from DVA peak fitting and c – calculated values compared to BoL. Error bars represent the standard deviation among all test cells for each case.

A comparison of the negative electrode cross-section SEM images from samples harvested at BoL and EoL are shown in Figure 13. EDXS mapping was done to differentiate surfaces of SiO_x and graphite (SI Figure S7). The SEM images revealed an 11.6% increase in the electrode coating thickness in aged

cells within the 0-50% and 0-100% SoC ranges. This finding can be attributed to the expansion of the electrode during cycling. In addition to the thickness change, the morphology of the silicon (Si) particles in the electrodes also exhibited distinct differences between BoL and EoL cells, as evidenced by the SEM images shown in Figure 13.

The morphology of Si-containing particles was found to differ with respect to the SoC range of the cycled electrodes. Specifically, a development of a loose morphology around the particles upon ageing (Figure 13). Changes in morphology in the coating layer were also observed (Figure 13 – c, d). At higher magnification, the SEM images of the EoL sample also showed that the entire SiO_x particle was porous, with pore sizes in the range of tens of nanometers (Figure 13– e). Furthermore, the growth of SEI around SiO_x particle was dendritic and displayed a compositional gradient, as evidenced by the image contrast (Figure 13– e).



Figure 13 – SEM images of SiO_x particles in fresh and aged electrodes: a - top view of BoL negative electrode; b - top view of H0-100 negative electrode; c - cross section view of BoL

negative electrode; d – cross section view of H0-100 negative electrode; e – higher magnification of cross section view of SiO_x particle.

Discussion

The general trend across all ageing conditions shows sublinear dependence of capacity loss versus the number of FCE (Figure 2). It is generally proposed that such dependence is typical for the cells where degradation is mostly due to the side reactions, and this would then be the case for the cells studied herein [52]. The starting point for the study of the ageing contributions is an analysis of the ICA of the fresh and aged cylindrical cells during their ageing process (Figure 3). Regardless of cycling conditions, some of the peaks associated with both positive and negative electrodes disappear (Figure 3), which is attributed both to LAM and LLI. These results also showed that SiO_x electrochemical activity is decreased for the cells that is cycled down to 0% SoC such as R0-50, H0-50, R0-100, and H0-100 (Figure 3 – a, c, d, f). The electrochemical activity of NCA was also seen to decreased significantly for the cells cycled at 45°C and up to 100% SoC (Figure 3 – e, f). The ICA results also indicated heterogeneous degradation and this was later confirmed with post-mortem analysis. Inhomogeneous special degradation is a known phenomenon and depends on distributions of temperature, pressure, and electrolyte distribution in the battery cells [35, 59, 78]. It is worth to mention that in the studied cases this heterogeneity is present but yet not severe enough to lead to "knee point" which is typical for cells exhibiting higher degree of ageing heterogeneity.

LLI was analyzed post-mortem and was found to be similar in all conditions and the main cause for the loss of capacity, on the order of ~ 1 mAh cm⁻². Li-ions are typically lost in SEI formation, electrolyte decomposition and other side reactions which coincide with general ageing trends observed in cycling of the studied full cells. As Li⁺ is present in excess in the electrolyte, most of the capacity fade attributable to LLI is a consequence of electrode slippage, i.e., a gradually increasing mismatch in electrode-level SoC that results in underutilization of the electrodes.

LAM evaluation was conducted for both positive and negative electrodes. The positive electrode has shown 15% of LAM_{PE} on average and similar for most cases within statistical error (Table S 4 in SI). Thermodynamic LAM_{PE} is higher for ageing in full SoC range (R0-100 and H0-100). However, when the kinetic limitations are isolated and removed in half-cell DVA, the average figure for thermodynamic LAM decreases to 7.2%. As for the LAM_{NE}, of graphite was found to be insignificant, while SiO_x is shown to be around 60% on average. The average thermodynamic LAM_{NE} of the aged, blended electrodes overall is 9.7%. However, comparing the LAM_{NE} of cells aged at different condition is challenging because the deviation between ageing conditions of the most values are within the statistical error which can be attributed to heterogeneity within the cell. It indicates an importance of accounting for statistics in this kind of analysis.

Understanding LAM_{PE} extent was done using post mortem electrochemical characterization of the electrodes in a half-cell configuration. The ex-situ capacity evaluation of the electrode contribution indicated prevalent ageing of the negative electrode under most conditions and the positive electrode at 45°C cycled between 50-100 and 0-100% SoC. Lithium diffusion resistance trends show a similar increase of *k* for negative electrodes aged at 22°C (Figure 3 – b) and a significant increase when aged at 45°C between 0-50% SoC. As for the positive electrode, *k* shows the trend of increase from the narrow range (cycling within Δ 50% SoC) to the full range (cycling within Δ 100% SoC) and higher *k* at

higher temperature for most conditions (Figure 3-a). We have observed greater degradation of positive, Ni-rich electrodes cycled within the full range, as well as a higher temperature sensitivity, than has been reported for other cathode chemistries [11].

LAM_{PE} unites processes such as particle cracking resulting in inactivation of particles, transition metal dissolution, and phase transitions to less electrochemically-phases together with oxygen release [28]. From ex-situ studies, it is seen that high-temperature cycling affects the loss of active material more significantly. The study of oxygen evolution on materials extracted from the same BoL cell has been conducted previously by our group, showing CO₂ evolution as a result of reactions involving lattice oxygen and electrolyte [44]. The cells cycled between 50-100% SoC and 0-100% SoC has shown the presence of voids in larger particles. Particle cracking was evaluated for EoL samples and found present to a lesser extent than is generally discussed in the literature. It might be related to presence of W, grain boundary engineering and development of nanopores inside the primary particles decreasing the strain within the secondary particles. Instead, voids were found in the center of larger particles. Similar features have been previously reported for NMC and NCA [66, 79]. However, the cross-section study does not provide sufficient statistics on whether it is present for the entire sample due to the technique limitation. Our previous study conducted on BoL samples has also showed visible, reversible cracking [44].

A loss of active material into inactive phases was not observed by means of XRD (Table 2) nor TEM. The lack of structural deteriorations is also supported by TEM studies. The BoL and EoL samples have similar lattice parameters (Figure 7). The rock salt phase, to which the capacity loss and Li diffusion resistance increase is often attributed, was not observed neither for BoL nor for EoL samples (Figure 7). TEM EDX also confirmed that the Ni distribution to be homogeneous (Figure 7) and no inhomogeneous structure within primary particles was found, as had been previously reported [80]. However, the Rietveld refinement disclosed a difference in lattice parameters which can influence Li diffusion resistance [81–83]. Additionally, the thickness of the CEI and decomposition products visible with electron microscopy does not correlate with higher values of *k*.

Transition metal dissolution was identified through increased Ni concentration in negative electrodes samples upon ageing. It is possible that HF etching may induce Ni dissolution and migration from the positive electrode [73]. The Ni dissolution is significant in cells cycled within 50-100% SoC in both temperatures and increased at 45°C, which may be attributed to the higher number of cycles with these cells. The high-temperature cell (R0-100) and room-temperature cell (R0-100) completed 1950 and 2570 FCE respectively compared to ~800-1000 FCE performed by the rest of the cells. This agrees with previously observed trends for Ni-rich layered oxide cathodes (NMC811) before [72]. This indicates that the Ni dissolution might be rather determined by cycle number or operation time than associated to capacity fade.

Observed LAM_{NE} indicating mostly loss of SiO_x. XRD study of the negative electrode has supported that (SI figure S 10).SEM study has shown development of pores within the particles as well as a significant change in the particle surface which may result in Li trapping and electrical isolation [84]. Si particles are well-known for their surface reactivity [85]. A 45°C-related development of the SiO_x surface particles was observed and it might be one of the sources causing a significant change of *k* for high-temperature aged negative electrodes.
Additionally, the separator was investigated for pore reduction (Supporting information Figure S 11) and we have shown a significant change in the EoL sample which can cause a higher cell resistance by reducing ion conductivity [28].

The study conducted on post-mortem samples was analyzed for contributions introduced from cell disassembly. The SEM images showed no delamination of the active material from the current collector after taking the electrodes apart and mechanically removing one side. However, the comparison of ICI measured on the full cell (SI, Figure S 12) and half cells from extracted electrodes (Figure 7) has shown that the values of the lithium diffusion coefficient have increased almost threefold (~3.4 Ω s^{-0.5} cm² measured in full cell compared to ~10.1 Ω s^{-0.5} cm² calculated as the sum of the *k* measured in half cells). Here, the influence of the double contribution of the separator as well as less optimized cell geometry in addition to a much lower current used in the case of the full cell plays a substantial role. Yet, an evaluation of the contributions of each step to achieve an understanding regarding artefacts it may contribute is essential for these types of studies.

Cell geometry-dependent ageing has been also studied as it plays a significant role in cell degradation [86]. Interestingly, the positive electrode material experiences higher capacity loss in regions of higher temperature [87]. The ageing within the cell roll complies with trends reported earlier with higher degradation towards the outer part of the cell [35].

Conclusions

In summary, a comprehensive investigation of ageing in EV cells was carried out. By subjecting the cells to two different temperatures and three different SoC ranges, a thorough analysis of their longterm cycling performance was performed. The results revealed that LLI is a major factor in capacity loss and can be associated with degradation products deposited at both the positive and negative electrodes as well as extensive development of a dendritic SEI on the SiO_x particles. The latter played a crucial role in the capacity loss observed on the negative electrode in the studied cells. The LAMPE was found to be particularly prominent at higher operating cell potentials. Void formation within the secondary particles was observed as well as indications of cation mixing. The positive electrode ageing mechanisms were found to be enhanced at elevated temperatures. The analysis also identified other factors contributing to resistance increase, such as separator ageing. The study was done in holistic approach creating an extensive understanding of the degradation mechanisms in the relevant commercial EV cells. The wide range of methods was used to support the study: electrochemical (cycling voltammetry of full and half-cells, ICI), structural (XRD), microscopy (SEM, TEM), and compositional (ICP, EDXS) analysis. Additionally, the in-depth analysis such as DVA was used to understand the individual contribution of blended electrode compounds to the ageing $(i.g., loss of SiO_x)$ over graphite). These findings have both academic and industrial relevance.

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$_{\text{PAPER}}$

Analysis of the number of replicates required for Li-ion battery degradation testing

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The layout has been revised.

Analysis of the number of replicates required for Li-ion battery degradation testing

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Abstract

Aging prediction of Lithium Ion Batteries is of major importance for assessing both longevity and sustainability of any battery system. In addition to the aging itself, aging trajectories are also dependent on the cell-to-cell variability that is caused by production tolerances. To be able to accurately model and predict the aging of battery systems, researchers and manufacturers must thus take the cell-to-cell variability into account when modelling battery aging. This paper contributes to the methodology for including cell-to-cell variability in aging testing by generating empirical aging data for a large number of replicates of commercial battery cells and assessing prediction stability. The conclusion from several different methods of evaluation is that a minimum of 4 replicates is required to accurately capture cell-to-cell variability in aging testing and modelling. The typical variance for the tested cells was about 10% of the capacity lost at any given point in testing.

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1. Introduction

Lithium-ion batterys (LIBs) have seen a surge in importance over the decades since the first commercial introduction in 1991, spreading from handheld electronic devices to tailpipe-emission-free energy storage for cars and trucks, and being developed as an option for aircrafts[1] and ships [2]. This puts considerable pressure on the development of reliable, inexpensive, and energy dense LIBs.

Significant trade-offs must still be made between power density, energy density and durability, and all these aspects are negatively impacted by cell-to-cell variation [3, 4]. The cell-to-cell variation has also been shown to influence both the beginning of life (BOL) performance [5, 6] and the aging behaviour of LIB cells [7, 8]. Furthermore, variance in the cell-to-cell performance also affects the requirements for cell testing, both for durability and BOL performance, since the reliability of test results is highly affected by sample variance. Since battery aging is a complex process governed by the interplay of several conditions such as temperature and current rates [9], an extensive test matrix is needed to understand the influence of different parameters. Despite the influence of usage conditions being qualitatively similar between cells, the details are different for every new cell, meaning that in order to be able to model expected life-time, a full test matrix must be performed for every new cell under investigation. Given the limited nature of test resources, the trade-off between reliability and the ability to investigate multiple parameters using a limited amount of samples is of high interest.

There are several possible causes for the cell-to-cell variation, but it can be mainly attributed to the differences in the aging conditions due to pack inhomogeneities [8, 10] or manufacturing variability and the tolerances of the production process [11, 12]. In this work the focus is on investigating the requirements on testing that arise from production tolerance.

The cell-to-cell variance has been the subject of many interesting works in the scientific literature in recent years. Beck et al. [7] provide a good overview of the origins of cell-to-cell variations in both capacity and impedance, which was further extended by Tian et al. [13] who also provide an extensive overview of how to evaluate cell-to-cell variation. Numerous studies on the effects of cell-to-cell variations for pack configurations have been published, with most of them investigating the effects of inhomogeneities in parallel connections in modules and packs [14, 15, 16, 17] and others focusing on methods to quantify the variance between cells and filtering out cells that deviate too much from the average [18, 19]. The authors tend to mainly focus on BOL impact, and typically do not include aging and aging models in the scope of the papers. Gogoana et al. [3] investigated the influence of internal resistance matching on aging behaviour, finding that differences in internal resistance can have severe adverse effects when it comes to system durability compared to well matched internal resistance. These studies, and more, show the need to understand the inconsistencies between cells, both when it comes to designing battery packs and control systems and when investigating battery degradation.

The literature on how many replicates to test in order to handle the cellto-cell when performing aging tests is not very extensive, but Dechent *et al.* [20] published interesting work with detailed suggestions on how to design a test matrix for parameterising an aging model, based on larger-scale datasets published in [4, 21, 22] and two further internally generated datasets. Using sophisticated statistical methods they evaluate three different types of aging models to assess the appropriate number of replicates. They concluded that the more advanced the model, the more cells are needed, but typically on the order of 10 cells are needed for stability. However, they did not consider the actual output of the model. This work was followed by [23] where an automated method for determining appropriate number of replicates for a battery aging test is suggested. The method used is based on a linear degradation model to minimise the complexity of the analysis, and the assessment is based on the stability of the model parameters. Using this methodology, a recommendation of 9 replicates per test condition is suggested. However, the authors do not consider the scale of the deviations of the predictions of the model, nor do they investigate comparisons between tests to assess the severity of pairs of aging conditions.

In this work, we seek to build on this foundation by using more realistic models for battery degradation and generating our own designated datasets. The article will also contribute with an assessment of sample sizes required when assessing pairwise tests to assess influence of certain usage conditions, and also seek a pragmatic trade-off between the number of replicates and the stability of model predictions, with the specific contributions

- 1. A novel approach that enables assessing model stability for different number of replicates and cell inconsistencies.
- 2. A concrete and realistic suggestion of number of replicates to use in lifetime testing of LIBs.
- 3. Analysis of variance approach to assessing pair-wise aging data sets, to determine the severity of aging conditions.
- 4. Quantification of variability of capacity losses, as fraction of total capacity losses.

	SOC_{min}	SOC_{max}	I_{chrg}	I_{dchg}
Test A	0	50	$0.5\mathrm{C}$	1C
Test B	50	100	$0.5\mathrm{C}$	$1\mathrm{C}$
Test C	0	100	$0.5\mathrm{C}$	$1\mathrm{C}$
Test D	0	100	$1\mathrm{C}$	$1\mathrm{C}$

Table 1: Description of test conditions as implemented in the current study.

2. Experiments

2.1. Tested cells

For the purpose of investigating the spread in commercial cells, the 3.5 Ah INR18650-MJ1 cell from LG, a well studied commercial cell, was chosen. It is of format 18650 and is well described by Sturm *et al.* in [24] which have described a full set of physical parameters for this cell. Notable is that it uses a negative electrode doped with SiO_x , determined by Sturm *et al.* to be around 3.5 wt%, which means that with the significantly higher capacity of SiO_x roughly 30% of negative electrode capacity is in SiO_x . In total 32 of these cells were tested, divided into four groups of 8 cells, each group performing identical tests to investigate the spread in aging during identical testing.

2.2. Test Conditions

The four tests were designed to be similar to a simplified lifetime testing with different c-rates and different state of charge (SOC) levels and windows. As shown in [25] the low SOC region is expected to have a strong influence on the aging in cells with a silicon-graphite negative electrode, thus this parameter is varied in this test matrix to investigate the risk of false conclusions on data generated from such tests. All SOC limits and current conditions of the tests are described in Table 1. All tests were performed in room temperature in the lab, which is maintained at near 22 °C, using a Neware BTS4000 5V battery testing system with a maximum current of $I_{max,tester} = 6$ A.

2.3. Reference test

All cells underwent regular checkups every 40 full cycle equivalent (FCE) where the discharge capacity was measured at $I_{dchg} = C/3$ current after performing a C/3 CCCV charging with $I_{cutoff} = C/20$ at U_{max} . This cycle was repeated twice and the average of the two values was utilised as capacity figure for that reference test.

After determining the capacity of the cell, an incremental capacity sweep was performed in $I_{ICA} = C/20$, sweeping both the charge and discharge direction between U_{min} and U_{max} .

The final step of the reference test was a pulse test to measure the resistance of the cell, performed with 10 s pulses of $I_{pulse} = 1.3C$. The current level used in the pulse was set by the maximum current limit provided by the tester, see



Figure 1: Visual representation of progression of test procedure



Figure 2: Visual representation of the different sampling levels, from the unattainable overall population which is represented as the grey dots in this figure. Sampling ranges from the full sample of N replicates, shown as the set Ω_N in the figure, to the subsample of k replicates, shown as the set Ω_k in the figure.

section 2.2. The pulses were applied at three different SOC levels of 30, 50 and 70% with charge and discharge pulses applied to the cell. See Figure 1 for a graphic representation of the test procedure.

2.4. Data Structure and Notation

After processing of the cycling data is done, it yields four distinct sets of data for the four test conditions. Each of these datasets in turn contains N = 8replicates of cells performing the same test under identical conditions, where each replicate has unique measurements of capacity decay as a function of FCEs. Each replicate measurement is denoted as q_i for replicate *i*. The full set of samples, assumed to be taken from a larger unattainable population, are then denoted by $\Omega_N = \{q_i\}_{i=1}^N$. From the complete set of samples, sub-samples are extracted with different number of replicates k ranging from 2 to N-1. Such sub-samples are denoted Ω_k with $k = 2, \ldots, N-1$ indicating the number of replicates included in the sub-sample. It then follows that a sub-sample of kreplicates from the full test set can be extracted in $\binom{N}{k}$ different ways. A set of all combinations of sub-samples is denoted $\Theta_k = \{ \hat{\Omega}_{k,i} \}_{i \in \binom{N}{k}}$. To provide individual notation on which of the four test conditions the data is taken from a superscript index $M = \{A, B, C, D\}$ is introduced. The test conditions are described in Section 2.2. This superscript should be read such that Θ_k^B denotes all possible combinations of sub-samples with k replicates from the test condition B, and correspondingly Ω_N^B denotes the full sample of degradation data from the test condition B.



Figure 3: All test data for the four test conditions

3. Cycling Results

All the cycling results are summarised in Figure 3. It is interesting to note that the curve shapes of the aging trajectories are somewhat different, firstly Test A showing an increasing slope after around 50 cycles, only to seem to plateau again when approaching end of life (EOL) after 300 FCE. Test B displays a nearly linear trajectory with some of the replicates showing a tendency to drop faster in capacity after around 150 cycles. It is also noteworthy that Test B has significantly slower aging than the other tests, likely due to not cycling to 0 SOC. Test B also has a positive outlier with replicate 4 having significantly higher capacity retention compared to other replicates.

Test C has a curve shape more similar to what can be observed in Test A, however, a tendency towards a faster decrease can be noted towards the end of the cycling, potentially indicating that a knee effect could have been seen if the testing had progressed further. In terms of capacity retention Test C shows similar behaviour to Test A, indicating that it is the cycling in low SOC that dominates the aging, which aligns well with findings in [25] among others. Finally Test D shows an extremely rapid decline, and the test had to be terminated earlier than the others due to very low capacity retention after only some 200 FCEs. The capacity loss also shows a nearly linear decrease from about 50 FCEs onwards.



Figure 4: Standard deviation of capacity retention normalized by capacity loss in the corresponding point for all tests.

For all tests, the spread in results is non-negligible, with the standard deviations typically on the order of magnitude of around 10-20% of the total capacity loss when normalized with q_{loss} at the same point. These normalized standard deviations are displayed in Figure 4. Such non-negligible spread also motivates further study of the influence of cell to cell variance and its implications on both lifetime testing and modelling. In particular it emphasises the need for analysing the variance in data when seeking to calculate expected lifetimes and comparing different tests.

4. Statistical Analysis

A useful approach to assess the results from an experimental aging study is to compare the capacity throughput until reaching a certain state of health (SOH) level. This enables comparison of the severity of the aging tests with a higher value indicating less severe ageing. Using such a single value indicator of severity makes statistical analysis more convenient and is henceforth going to be used for the statistical analysis in this study. The metric of FCEs at EOL is denoted by n_{EOL} and defined as $n_{EOL,k,i}^M = \#FCE$ when SOH = 70% for the *i*th combination of k replicates taken from test condition M. This metric will be used throughout this section.

4.1. Beginning of life cell-to-cell variance

As all cells undergo an initial characterisation test, the production cell variance can be coarsely assessed by checking the mean and variance of the BOL capacity and impedance as suggested by Schindler *et al.* [14]. For the 32 cells tested in this study the average capacity at BOL was determined to be $\mu_q = 3340$ mAh with a standard deviation of $\sigma_q = 18.9$ mAh yielding a normalised standard deviation of $\frac{\sigma_q}{\mu_q} = 0.56\%$. The average charge impedance at 50% SOC and BOL was $\mu_Z = 42.5 \text{ m}\Omega$ with a standard deviation of $\frac{\sigma_Z}{\mu_Z} = 3.2\%$. For comparison purposes only normalised standard deviation of $\frac{\sigma_Z}{\mu_Z} = 3.2\%$. For comparison purposes only normalised capacity will be utilised for the rest of the statistical analysis, with each cell being normalised with its own initial value to generate comparable numbers for each cell.

4.2. Analysis of Variance

In order to distinguish between the noise, is variance between replicates, and the signal, is actual differences between datasets, Analysis of variance (ANOVA) methods can be a powerful tool. These methods calculate the probability that different samples are taken from datasets with the same mean, even though naturally occurring variance means that the point estimates of the means are different [26]. This makes it possible to compare the results of samples from two test conditions to assess whether one test condition leads to significantly different aging compared to another or if it is likely that variance is the explanation for any observed differences.

One specific method for doing this analysis is the *Paired t-test*, which calculates the ratio of difference between paired samples to the variance of said samples. If this ratio is large, it is unlikely that the data compared is taken from sets with the same mean. Thus the null hypothesis is that the mean difference between paired observations is zero

$$H_0: \mu_d = 0, \tag{1}$$

with the alternate hypothesis that the mean difference is non-zero

$$H_1: \mu_d \neq 0. \tag{2}$$



Figure 5: Graphic representation of the method used to find probability of false conclusion from T-test with sub-samples compared to full sample T-test.

Here μ_d denotes the difference in population mean between the paired observations, $\mu_d = \mu_1 - \mu_2$ for the observations from paired populations 1 and 2.

This means that a test statistic comparing the difference in mean values, μ_d with the variance in the population

$$s_d = \sqrt{\frac{\sum_{i=1}^{n} (d_i - \bar{d})^2}{n-1}}$$

is compared to the difference in means in the following way

$$t = \frac{\bar{d}}{\frac{s_d}{\sqrt{n}}}.$$

Thus, if the test statistic t is large, the likelihood that observations come from populations with the same mean is low, and can be used to determine whether the null hypothesis can be rejected or not.

This statistical test can then be used to asses the risk of drawing false conclusions from a set that has too small sample size for accurate conclusions. To investigate this, sub-sampling from the full dataset is implemented, such that all $\Omega_{k,i}^{M}$ is compared to all $\Omega_{k,j}^{O}$ for generic test condition M and O. Index i and j respectively indicate that all possible combinations of sub-samples are tested.

This seeks to simulate a situation where fewer replicates have been tested, and by finding the risk of drawing false conclusions based on that data, give a recommendation on minimum sample size. Thus paired t-test analysis is performed for each of the combinations with k replicates from test M combined with k replicates from another test O, yielding $\binom{N}{k}^2$ results for probability of rejecting the null hypothesis, denoted as $P_{k,i}$. This probability is then compared with the designated reference case where all available data for test M and O, Ω_N^M and Ω_N^O , are used to calculate P_{ref} . If the conclusion when using k samples is different to that from N samples it is counted as a false conclusion. The total probability of drawing false conclusions for k replicates is then defined as the fraction of false conclusions and total number of tests: $P(false)_k = \frac{\#false_k}{\#total}$.

By inspecting the data in Figure 6 it can be observed that as expected, the likelihood of false conclusions is reduced with increasing sample size. The exact trend is somewhat different for the different datasets due to the different aging patterns for the different tests, but in general it can be said that a minimum of four replicates is necessary to be sure to avoid false conclusions. There is also a clear trend that for the cases where the testing has proceeded further, ie higher FCE number, the likelihood of false conclusions decreases. So to some extent, the need for multiple replicates can be offset by letting the testing run for a longer period of time and approaching EOL. Though it is a considerable spread in the results, a general recommendation for at least four replicates sees the probability of erroneous conclusions become negligible.

4.3. Cycles to End of Life

One of the most common ways that aging test data is used, is to fit models for the capacity decay versus time or cycles. Thus a further metric for analyzing the



Figure 6: Risk of false conclusions from paired t-test analysis for all combinations of tests and number of replicates, as compared to the reference case where the full datasets are utilized.

number of replicates required for reliable results of aging testing, is to analyze the probability that models fitted with a subset of replicates yield results which are offset from results obtained using models fitted with the full population data by too big a margin. This approach is akin to the method used in [20, 23], but with the modification of using a fitting model capable of fitting typical curve shapes for degradation curves, rather than a linear fit. As this is done by fitting three parameters, it yields a more complex parameter set, and the analysis is instead performed on the EOL prediction rather than the parameter values.

For this article the model proposed in [27] is implemented, with the capacity decay modelled as

$$Q = Q_0 e^{-\left(\frac{x}{\tau}\right)^\beta} \tag{3}$$

with Q_0 , τ and β as fitting parameters and x the number of full cycle equivalents. To investigate the sensitivity of the model fits to the number of replicates utilized, a method to perform fits for all possible combinations of datasets and comparing them to the fit for the full set was implemented.

The algorithm to do so is relatively intuitive: with k being the number of cells utilized, for all $k \in [2, N - 1]$, sample all $\binom{N}{k}$ possible combinations of tests and fit the model for the resulting dataset Θ_k . Then, by using the fitted model, calculate n_{EOL} for each dataset and compare it to the result obtained when using the full dataset Ω_N . The dataset is then considered too small if there is more than 5% risk of overestimating n_{EOL} by more than 5%, ie $P(n_{EOL,k,i} > 1.05 * n_{EOL,N}) > 0.05$. This one-sided rejection criterion is based on the fact that an underestimation of n_{EOL} is a conservative error which is not likely to cause warranty issues in the mass market. An overestimation of n_{EOL} however, could lead to controls and limitations functions being too lenient, causing issues in the market and leading to significant warranty costs for car manufacturers.

Since the number of possible combinations is limited, the probability of overestimation calculated simply by dividing the number of overestimates for data in Θ_k with the full number of combinations becomes numerically very sensitive. To mitigate this, a more numerically stable metric is needed. To obtain this we assume that for the full population, the number of cycles until reaching EOL for a given test condition is a normal distributed parameter such that $n_{EOL} \sim \mathcal{N}(\mu_n, \sigma_n)$ where point estimates of population parameters μ_n and σ_n can be estimated for some subset Θ_k by

$$\hat{\mu}_{n,k} = \frac{1}{\binom{N}{k}} \sum_{i} n_{EOL,i,k} \tag{4}$$

$$\hat{\sigma}_{n,k} = \sqrt{\frac{1}{\binom{N}{k} - 1} \sum_{i} n_{EOL,i,k} - \hat{\mu}_{n,k}}$$
(5)

such that the sub-sample distribution is modelled as $n_{EOLk} \sim \mathcal{N}(\hat{\mu}_{n,k}, \hat{\sigma}_{n,k})$. Using this estimate of the population distribution, the probability of overestimation can be calculated as $1 - F(1.05 * n_{EOLN})$ with cumulative distribution function $F(x) = \int_{-\infty}^{x} P(t) dt$. This probability is visualised by the shaded area



Figure 7: Distribution of estimated number of FCEs until EOL for all combinations of three sets of data. All data to the right of the dashed line are overestimating FCE to EOL by more than 5% and would lead to erroneous model predictions. This is indicated for the histogram with red color and as the shaded area under the graph for the normal distribution.

under the probability distribution curve in Figure 7, which shows one typical examples where all $n_{EOL,k}$ have been calculated and plotted as histograms together with the fitted normal distribution.

As can be seen from Figure 7 there is a significant (7.03%) risk of overestimation in this case. The risk of overestimation for each corresponding case is summarised in Table 2. From this table it is clear that we have an expected behavior of a decreasing risk of overestimation with an increasing amount of replicates, but in order to reduce the risk below our suggested threshold of 5% a minimum of four replicates is required, with up to 7 cells required in the most challenging case. This indicates that when training a typical degradation model, at least four replicates are required on all tests to avoid false conclusions.

4.4. Population parameter distribution

In order to assess the reliability of measurements it is also useful to investigate the stability of the estimated population parameters for the distribution of remaining capacities of cells. In order for conclusions and fitted models to be reliable, the error in the estimates of mean and variance of the measurements need to be sufficiently low. One way to assess whether this is the case,

	Number of Replicates						
	2	3	4	5	6	7	
Test A	14	7	(2.8)	0.64	0.04	0	
Test B	35	28	$\underbrace{21}$	14	7	$\left(\begin{array}{c}1.1\end{array}\right)$	
Test C	30	23	16	9.5	3.8	0.32	
Test D	15	7.8	$\left(3.3\right)$	0.85	0.07	0	

Table 2: Probabilities of 5% or more overestimation of FCE to EOL for all number of replicates, with the lowest number replicates with probability less than 5% marked for each test condition.

is to investigate the standard error of the measured values. If we assume that the measured capacities q_i are normally distributed, the distribution can be estimated as $q_i \sim \mathcal{N}(\bar{q}, \hat{\sigma})$ where in turn the estimated variance $\hat{\sigma}$ is normally distributed with $\hat{\sigma} \sim \mathcal{N}(\sigma, s_n)$ where σ is the true, unknown, variance of the full population and s_n the standard error of the estimate. The standard error is decreasing by the square root of number of samples used for the estimate of population parameters, so to find a suitable number of replicates needed for an aging test, the standard error can be assessed.

In this paper it is done by a bootstrap-like approach, namely that for k replicates the mean and standard deviation are calculated for all $\binom{N}{k}$ possible combinations of replicates. This is done analogously to (4) and (5), but unlike in Section 4.3 the analysis is also reiterated for each individual capacity measurement in Θ_k , not just for the full set Ω_N . We thus obtain a set of mean and variance estimates from $\binom{N}{k}$ measurements for each reference performance test (RPT). Using this dataset the standard error can then be estimated by finding the mean and variance of the calculated population parameters \bar{q} and $\hat{\sigma}$.

To assess the suitable amount of replicates, a threshold for maximum allowed standard error is required. Such a value is however tricky to define, but following the methodology of Strange *et al.* [23] a relevant metric can be proposed by calculating the *relative standard error* (*RSE*), which is defined as

$$RSE = 100 * \frac{s_n}{\sigma}.$$
 (6)

The RSE should be interpreted as the boundary for how far from the true value, σ , the point estimate $\hat{\sigma}$ can be expected to be, with a certain confidence. This metric, can then be used to set a relevant threshold, and following Strange *et al.* a value of RSE = 25% is used. Assuming that the point estimates are normally distributed, RSE = 25% would mean that we can expect that the point estimate is deviating less than 25% from the true value with a confidence of 68%.

To calculate the RSE, the full population variance σ must be estimated, for this purpose the full dataset is used, ie $\sigma \approx \hat{\sigma}_N$. Given that both the variance and the standard error are dependent on how far the testing has progressed, it needs to be investigated whether the RSE is dependent on the duration of testing. The calculated RSE is shown in Figure 8, where it can be seen that RSE



Figure 8: The relative standard error plotted versus number of replicates for the four test conditions included in the study. Thicker black dashed line show the average value calculated for all RPTs for each number of replicates.

is not strongly dependent on the test progression, indicating that full population variance and standard error are increasing at similar rates as testing progresses. Therefore only the replicate-wise mean is reported in Table 3. From the same table it can be noted that using the threshold value of RSE < 25% as suggested in [23] a minimum of 5 replicates is required for most tests, with Test C actually requiring 6 replicates to reduce RSE sufficiently. It can also be noted that when using 2 replicates, as is quite common in literature, the RSE is in excess of 50% for all test conditions. This further strengthens the argument for utilising more than 2 replicates when performing lifetime testing to avoid false conclusions or overextending the analysis.

4.5. Synthetic data verification

As the scope of the paper only includes test data from one cell, to verify the feasibility of the approach, some manipulations of the data are performed to simulate more or less cell-to-cell variation.

The synthetic values of the degradation tests are calculated by comparing the offset in capacity retention of a cell *i* at RPT *j*, q_{ij} compared to the mean of all cell capacities at corresponding RPT, μ_{q_j} . This offset is then scaled 50% to emulate significantly reduced or increased cell-to-cell variance. The scaled offset is then added to the mean value to create the synthetic dataset. Repeating the process for all test conditions M, the synthetic data thus becomes

Table 3: Mean RSE values for the four test conditions in the study, with the smallest number of replicates yielding RSE less than 25% marked.

	Number of Replicates					
	2	3	4	5	6	7
Test A	56	37	27	$\left(\begin{array}{c} 20 \end{array}\right)$	14	9
Test B	57	40	30	(24)	18	12
Test C	62	46	36	28	(21)	14
Test D	58	41	31	$\left(\begin{array}{c}24\end{array}\right)$	17	12



Figure 9: Visualisation of data noise manipulation where all dashed lines show increased variance case, and dotted lines show the reduced variance case. This clarifies how all results tend closer to the overall mean when noise is reduced, and inversely for the increased noise case.

$$q_{ij,synth}^{M} = \mu_{q_j}^{M} + c \left(q_{ij}^{M} - \mu_{q_j}^{M} \right) \tag{7}$$

where c is the scaling factor, applied as c = 1.5 or c = 1/1.5 to increase or reduce variance. An visualisation of the results of the artificial data generation is displayed in 9.

The process described in Section 4.3 is then repeated for all the synthetically generated data to calculate the risk of overestimation of the number of FCEs to EOL. This was chosen as the most appropriate method to verify, as it is the most relevant to manufacturers. The results of the analysis performed with synthetically generated data are shown in Table 4. From these data, it can be seen that the required number of cells changes in an expected manner, with more cells required to obtain statistically certain conclusions when increasing variance, and conversely fewer cells are required when the variance is decreased. As expected, the pattern for the number of replicates required is preserved when

Increase Variance							
	2	3	4	5	6	7	
Test A	24.7	17.0	10.5	5.1	$\left(\begin{array}{c} 1.3 \end{array}\right)$	0.0	
Test B	42.6	36.5	30.6	24.2	16.4	6.2	
Test C	38.7	32.7	26.7	20.2	12.5	$\left(3.7 \right)$	
Test D	25.2	17.8	11.3	5.7	$\left(\begin{array}{c} 1.7 \end{array}\right)$	0.1	
Decrease Variance							
	2	3	4	5	6	7	
Test A	4.9	1.3	0.2	0.0	0.0	0.0	
Test B	25.8	17.6	10.7	5.1	$\left(\begin{array}{c}1.3\end{array}\right)$	0.0	
Test C	19.3	11.8	6.2	$\boxed{2.3}$	0.4	0.0	
Test D	5.5	$\fbox{1.6}$	0.3	0.0	0.0	0.0	

Table 4: Probabilities of overestimation of FCE to EOL, analogous to Table 2, with variance synthetically increased or decreased by 50%. The increased variance is shown above, and decreased variance below.

scaling the variance, so that tests A and D require fewer replicates to obtain robust results compared to tests B and C. This indicates that variance is unique for a specific test condition, but still the overall quality and cell-to-cell variance of a certain cell will affect how many replicates are required for robust test results to be obtained. This means that knowing the cell-to-cell variance before planning and starting a comprehensive aging test with a large number of test conditions is very valuable as this allows an appropriate number of cells to be assigned to each test condition.

5. Conclusions

The goal of this work was find a minimal sample size that can satisfy the requirements for confidence and reliability of battery aging data for experimental studies of battery aging. This should be applicable for industry and research alike when assessing the influence of different usage parameters on battery aging, but with a particular applicability for industry where reliable predictions on warranty level and risk of fall-out must be made. Based on three different assessment methods a general recommendation can be made that a minimum of n = 4 cells should be tested for each test condition to ensure reliability of the results. This can be adjusted slightly depending on the purpose of the study, but given that test resources are limited, even running four replicates will in practice often be difficult, considering the amount of aging aspects that need to be investigated.

Notable is that with a sample size of n = 2, even in the best case scenario with minimum spread, the risk of overestimating FCE to EOL by 5% was 14%, and ranging up to 35% in the worst case. Thus, for mass-market implementation, where significant costs are associated with wrong predictions on EOL and warranty levels, the cost of performing more tests should be offset by the reduced risk for unexpected warranty claims.

6. Discussions and Future work

The current study is limited to one type of battery at one temperature, therefore it would be valuable to complement the study with further battery types (chemistries, shape, energy/power optimized etc), temperatures and also different types of duty cycles. Such studies would be a very valuable complement to the results presented in this article.

It would also be interesting in future work to assess how the recommendations for number of replicates would differ between cells, and if an indicative test could be developed where an initial test to assess cell-to-cell variability could be run, and based on this test the appropriate amount of replicates is decided. This suggestion is reinforced by the analysis with synthetically scaled variance in Section 4.5, which shows that the appropriate number of replicates will be strongly dependent on cell quality. For instance a comparison of the standard deviation of BOL, capacity compared to the standard deviation of capacity after some 100 cycles of a simple standard cycle, could provide sufficient understanding of cell variability. To reduce overlapping efforts, this could be provided as a data sheet value from the cell supplier so that end-users would be able to make an informed decision on the appropriate replicate sizes.

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Extending Battery Lifetime by Pulse Charging

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 $Under\ review$

The layout has been revised.

Lithium-ion batteries are a fundamental component of achieving a carbon-neutral transport sector, since battery-equipped electric vehicles have become the most viable alternative to pure internal combustion engine vehicles. However, the ability to charge batteries at a fast enough rate without detrimental effects on battery durability remains one of the key challenges for technology to fully permeate society. In this paper, pulse charging is investigated with the goal of reducing the adverse effects on durability that the charging process results in. In turn, this enables maintained charge rates while dramatically reducing effects on battery lifetime compared to constant current charging. Results include data from battery cycling with different charge and discharge waveforms. Both frequency and duty cycle are varied between specimen groups and a reference is provided by a group subjected to constant current waveforms. It is evident from the presented dataset that the capacity loss incurred by charging the battery using a constant current scheme can be reduced by a substantial amount by switching to a pulsed waveform. A 50% reduction in capacity loss when the frequency is higher than 100 mHz for a square wave pulse charge is observed. Using only in-situ electrochemical analysis, strong indications were found that the dominating ageing processes occur on the anode side when constant current waveforms are used, suggesting that this method may prevent extensive lithium plating and corresponding solid-electrolyte interphase (SEI) formation.

Extending Battery Lifetime by Pulsed Charging

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1 Introduction

The need for carbon-neutral transportation has led to a surge of battery electric vehicles (BEVs) in the global transportation and logistical system. This was primarily facilitated by the great strides in lithium-ion battery technology, particularly the ever-higher energy-density storage capabilities that these devices are capable of [1].

This paper aims to explore possible improvements regarding one of the issues that still prevail – durability and charging performance, which have been identified as essential to be addressed for continued mass-market adoption [2].

Refining the current understanding of LIBs degradation, particularly how capacity loss correlates with different usage and charge patterns, can make significant contributions to societal development. This knowledge would aid manufacturers in optimizing charging strategies, ultimately supporting the global goal of increasing the share of electrified vehicles in the transport sector.

The most common approach for battery ageing experiments has long been to conduct tests under constant current (CC) conditions [3–6], primarily due to the simplicity of implementation and the ease of comparing results across studies. However, most real-world usage of batteries, particularly in BEV applications, differ significantly from the static nature of CC-experiments in a laboratory. Instead, actual operating conditions involve highly dynamic current patterns. These give rise to different degradation processes in the cells compared to when the cells are CC-cycled [7–9].

The influence of current dynamics on battery degradation has been a topic of interest for several years, yet the reported research findings have been inconsistent. Some studies report little to no impact – or even a negative influence – of dynamic

cycling on durability [10–13], while others indicate significant positive effects [7, 14– 16]. More recent publications in the field, notably by Geslin et al. [17] and Huang et al. [18] conclude that dynamic usage enhances the battery lifetime. These findings underscore the need for a deeper understanding of the degradation mechanisms occurring during dynamic battery usage, as this knowledge could lead to improved battery management strategies and extended lifetime.

If we accept the hypothesis that dynamic usage can improve battery lifetime compared to steady-state operation, it is important to recognize that 'dynamic usage' encompasses a broad spectrum of cycling patterns. Some authors have examined drive-cycle-like ageing patterns [7, 17, 19, 20], while others have focused on the characteristics of the current pulses with features such as intermittent rest periods and periods with reverse cycling [21–23]. Other studies have focused on the influence of high-frequency content in the waveforms, typically above 10 Hz, which originate from power electronics in the system. These studies consistently report that only a minute impact on battery degradation can be observed [24, 25], although the overall observed degradation has a more extensive spread when these contributions are considered and when multiple replicates are tested [26, 27].

In contrast, the effects of lower-frequency cycling, with pulse frequencies below 1 Hz, have received significantly less attention, despite drive-cycle analyses indicating that real-world battery operation is dominated by waveforms in this frequency range [28]. Earlier work [29] suggests positive effects from pulse charging in this frequency range, but further experimental data and verification are lacking. This leaves a research gap that this paper aims to contribute to filling.

Huang et al. [18] investigated a large set of different pulse charging schemes, varying both the frequency as well as C-rates and duty cycles on power optimised lithium nickel manganese cobalt oxide (NMC)-Graphite batteries. Their findings indicate significant improvement compared to CC charging in all pulsed scenarios with an interesting peak in degradation occurring around a pulse frequency of 1 Hz. It was also found that the durability improved in both higher (up to 2 kHz) and lower (down to 50 mHz) frequency ranges. These results raise important questions regarding the replicability of these trends across different cell designs and chemistries, as well as the underlying mechanisms driving degradation in the 1 Hz range — making further investigation into this frequency domain a compelling research avenue.

In a minor pre-study to this paper [30], the results indicated that the most influential region when considering battery capacity degradation in conjunction with pulse charging is found below 1 Hz, sparking further interest in pulse patterns in this frequency range. Those results were generated by cycling experiments conducted on the same type of energy-optimised cell (see Supplementary Table 2 for details) as used in the cycling experiments in this contribution. Motivated by findings in the pre-study, this paper aims to extend that investigation and provide deeper insights into the role of pulse cycling in battery ageing.

Publications in the field tend to agree on the positive impact on battery capacity that can be obtained by dynamic usage in general and pulsed charging in particular, though only a few studies have provided explanations of the phenomenon in terms of the effect of the underlying ageing mechanisms. By using physics-based models of SEI growth, Lv et al. [29] showed that pulse charging reduces the overall current density of SEI formation. However, no experimental results are available to support this conclusion further. It can also be noted that for higher frequencies Uddin et al. [13] concluded that SEI formation was negatively impacted by adding AC ripple, meaning that results from earlier studies remain inconclusive. Other authors have hypothesised that cell impedance is the dominant factor with maximum degradation occurring at the frequencies with the highest impedance [31] and correspondingly pulsing near the frequency of minimal impedance reduces degradation [32], but a clear correlation to actual ageing processes is not yet found.

As the conclusions from pulse charging studies are inconclusive regarding the frequency influence and duty cycles, this paper seeks to contribute to the field by investigating a wide frequency range using electrochemical characterisation techniques to elucidate further the differences in ageing observed when performing dynamic charging. The key contributions consist of:

- A charging method for significantly reduced degradation at equivalent current rate
- Identification of pulse duty cycle ratio as an important parameter for battery degradation
- Discovery of a relationship between pulse frequency and the variability in the onset of the transition to linear ageing.
- Identification of a critical degradation frequency at approximately 10 mHz, where degradation closely matches that of constant current charging.

2 Experimental

Two separate experimental setups were utilised in order to measure the effect on battery capacity retention as a function of charge- and discharge cycling with different current waveforms. Testing conducted at frequencies below 1 Hz was carried out on a Neware BTS 4000-5V6A tester, and testing requiring higher frequencies and higher currents was tested on a PEC ACT50. The latter being capable of higher currents with more rapid dynamics compared to the Neware system.

The testing performed is summarised in Table 1. Test tests are grouped in two overarching categories based on their average current, where within each category the pulse frequency were varied, see Sections 2.1 and 2.2 for further details.

Test condition	Test ID	$I_{\rm avg}$
Pulse charge, pulse discharge Pulse charge, no pulse discharge Constant current reference	PC-PD PC-NPD CC-ref	$2.5\mathrm{A}$
Pulse charge, 50 % duty cycle Pulse charge, 25 % duty cycle Constant current reference	PC-PD-50 PC-PD-25 1C-ref	$3.5\mathrm{A}$

Table 1: Summarised test descriptions and testIDs.

The overall approach was to expose the battery cell specimens to an identical average current over time while varying the duty cycle ratio and frequency between the specimen groups. The average current used was the nominal charge current that the manufacturer provided for the batteries. Thus, a specimen subjected to 50% duty cycle ratio would see twice the manufacturer-rated current for half of a period. This means that the cells were subjected to the same amount of energy transfer, regardless of duty cycle or frequency. The principle of the pulse duty and C-rate are visualised in Supplementary Fig. 1.

In total, 54 cells were tested, with all testing performed at room temperature that was maintained around 23 °C over the course of the experiment. The testing was split into two categories according to average current, see following sections.

2.1 Category 1 – mean current 2.5 A

Category 1 tests were performed with a maximum current of 5 A, dictated by the limitations of the tester. All tests in this category employed a square wave with a 50 % duty cycle for both charge and discharge, yielding an average current of 2.5 A. The frequency was varied in the 10-1000 mHz range. See Table 2 for the exact frequencies tested for each test condition.

The reference test for this category was a constant current case with 2.5 A charging and discharging. In order to facilitate the comparison of the effect of using different frequencies, a finishing constant voltage (CV) phase was used whenever maximum voltage was reached. This was required as the dynamic pulses will hit the cut-off voltage at different underlying state of charges (SoCs) due to the accumulation of overpotential. The transition from CC to CV occurred when the maximum voltage of 4.2 V was reached with a cut-off current defined as C/3. Analogously, during discharge, a constant current, constant voltage (CCCV) implementation was used, transitioning to CV when the lower cut-off voltage of 2.8 V was reached, with a cut-off current of C/3.

To test the hypothesis that charging is the dominant factor when comparing battery capacity loss between conventional and pulsed strategies, two specimen groups were tested, where only the charging was pulsed while the discharge was static. For each specimen group four replicates were tested, as the initial measurements with only two replicates showed a surprisingly large spread in the results.

Table 2:	Frequencies	tested	for	each	test
condition.					

Test Condition	Frequencies
PC-PD	10, 100, 320, 500, 1000 mHz
PC-NPD	100, 1000 mHz

2.2 Category 2 – mean current 1 C

Category 2 testing consisted of four specimen groups with two replicates each, cycling with a duty cycle of 25% at 4 C current, yielding an average of 1 C current for both charge and discharge. The specimen groups were tested at varying frequencies, from 1 Hz to 125 Hz, see Table 3 for details on included frequencies. There were severe issues with current control during the transition from CC to CV mode in these fast and high current cycles. To address this, a step-wise de-rating of current was implemented instead of CCCV operation. When the maximum voltage of 4.2 V was reached, the current was reduced to 95% of the current of the previous step, following $I_{\text{new}} = I_{\text{old}} * 0.95$. This was repeated until the current was reduced to 1 C. For these tests, the discharge was pulsed analogously with a lower cut-off voltage of 2.8 V and a cut-off current of 1 C. As the SoC and voltage increase, the average current is scaled down so that the average current is no longer 1 C. This means that the charging at higher voltages is somewhat slower. A 1 C CC charge- discharge cycle served as the reference test for this set of cells.

Category 2 also included tests that operated with 50% duty cycle ratio and 2C current, aiming at maintaining the same 1C average current, however, as with 25% duty cycle ratio the average current is reduced in high voltages. Three specimen groups, each with four replicates, were tested at this duty cycle ratio, with frequencies ranging from 1 Hz to 50 Hz. As with the 25% duty cycle tests, all specimen groups are referenced towards a 1 C CC test.

As the root mean square (RMS) values of the current is different between the duty cycle of 25 % and 50 % different heat generation was anticipated for the category 2 testes. To minimise the influence of this temperature difference, cooling fans were mounted just in front of the cells and kept active throughout the testing.

Table 3: Frequencies tested foreach test condition.

Test Condition	Frequencies
PC-PD-25	1, 10, 50, 125 Hz
PC-PD-50	1, 10, 50 Hz

2.3 Reference Performance Test

All cycling was performed with intermittent reference performance tests (RPTs) conducted every 40 cycles. The RPT consisted of a capacity measurement, an intermittent current interruption (ICI) test and an impedance measurement by 10s pulses. The RPT is visualised in Supplementary Fig. 2, showing an initial capacity measurement part followed by an ICI and the final impedance measurement through current pulses.

2.4 Intermittent Current Interrupt

ICI is a technique utilised to analyse impedance characteristics by applying a constant current of limited C-rate with periodic shorter rest periods, or current interrupts [33]. In this paper, ICI was implemented in accordance with the procedure described by Geng et al. [34] which allows for the calculations of both overall impedance and diffusion-related resistance for the entire voltage window utilised in the ICI test. The diffusion-related resistance, defined as the slope $k = -\frac{1}{I} \frac{\mathrm{d}U}{\mathrm{d}\sqrt{t}}$ during relaxation, can

also be related to the Warburg impedance σ in the Randles circuit by as $k = \sigma \sqrt{\frac{8}{\pi}}$ [35]. This relation facilitates a more detailed analysis of the electrochemical processes inside the cell, bringing in-situ testing closer to electrochemical impedance spectroscopy (EIS) testing in terms of retrieved information. Additionally, ICI also enables incremental capacity analysis (ICA) and differential voltage analysis (DVA), providing further insight into the degradation processes in LIBs under ageing test. This is done by removing the points on the capacity vs. voltage curve where the overpotential is not saturated, thus enabling the extraction of a pseudo-OCV curve that can be used to trace the slopes and plateaus of the open circuit voltage (OCV) curve [34]. This makes it a powerful tool for experimental ageing campaigns, such as the one described in this paper. For further details on the ICI method and its analysis, see Supplementary Method 2.

3 Results

The capacity decay results that the cycling experiments produced are found in Fig. 1. The mean overall capacity retention of each group of specimens is shown as a function of the number of charge/discharge cycles. Each group contains two or four replicates. The cells from category 1 are shown in Fig. 1a, and those from category 2 are shown in Fig. 1b. For both categories of data, it is clear that the CC reference cases degrade at a significantly faster rate than the tests where the current is pulsating. For the category 1 tests, it is particularly noteworthy that for all cyclings where f > 100 mHz, the specimen groups cluster together so that no statistically significant differences in ageing can be observed between the different tests, see Supplementary Method 1 for details. This is in line with the findings in [17], where frequencies significantly below 1 Hz in general are found to be dominant with regard to degradation patterns. It is also in good alignment with results from the pre-study [30].

For the category 2 testing, the pulse frequency does not appear to influence the congregation of the results, instead the clustering of the data seems to depend on the different duty cycle ratios. This is further expounded on in Section 3.1. The non-significant influence of frequency in this domain further corroborates the finding that low-frequency content in the current waveform is of high importance when considering battery degradation processes, with only a small fraction of the capacity loss seen in CC operation occurring in pulsed operation. Considering the specimen groups in category 1 with frequencies above 10 mHz, the average capacity retention after 400 cycles is 88 % whereas for frequencies below or equal to 10 mHz and constant current it is 67 %, meaning that degradation is roughly three times as rapid on average when



(a) Cells tested with 2.5 A average current. (b)

(b) Cells tested with 1 C average current.

Fig. 1: Relative capacity retention of tests cells for all tests in Category 1 showed in 1a. Normalised capacity retention for all tests in Category 2 (average current of 1 C) in 1b.

low frequency or CC charging is applied, with CC being the most detrimental to battery health.

3.1 Duty cycle ratio

The observed differences in capacity retention between the different groups of specimens reiterate that dynamic usage is a significant contributor to take into account when considering battery lifetime, given that the CC reference groups have the lowest capacity retention in both category 1 and 2.

Another pronounced detail in the dataset is the apparent dependence on the duty cycle ratio in category 2. In the second category, the specimen groups that are performing at 50 % duty cycle ratio age at an accelerated rate compared to those at 25 % duty cycle ratio. To further investigate this observation, a comparison between the number of cycles until a certain state of health (SoH) level was implemented. This was done by fitting the test data to a degradation function taken from [36]

$$q = q_0 \exp\left(-\left(\frac{n}{\tau}\right)^\beta\right) \tag{1}$$

where n is the number of cycles and q_0 , τ and β are fitting parameters. Using this fit, the intersection at 90% SoH was calculated to allow a direct comparison of the expected number of cycles that a battery can perform. The level of 90% was chosen to avoid excessive extrapolation as several tests did not degrade below 95% during the experimental ageing campaign. The dominant influence of duty cycle ratio is further highlighted by Fig. 2, which depicts the number of cycles expected until 90% SoH as a function of the duty cycle ratio with colour coding according to frequency. From this plot, it can be seen that the number of cycles until 90% SoH is mainly determined by the duty cycle, while the frequency has a much smaller impact in this range.



Fig. 2: Duty cycle versus number of cycle to 90% SoH for all tests in category 2 with colouring based on frequency.

This aligns well with the findings of the category 1 tests that all specimen groups cycled with frequencies above 100 mHz saw similar degradation patterns, indicating that above this frequency no significant lifetime gains can be found by further increasing it. However, as indicated by the correlation between duty cycle ratio and degradation, other aspects of dynamic usage are still important. In this case, it can be hypothesised that the reduction in charge current due to reaching maximum voltage might be the dominant factor affecting the ageing, given that 25 % will have a lower average current in high SoC charging.

3.2 Electrochemical analysis

To gain insight into the internal ageing processes, the results from ICI and its derived ICA and DVA curves were analysed. The ICI was used to trace the development of cell impedance, mainly focusing on the diffusive impedance during ageing. Both ICA and DVA techniques provide information about electrode-level changes by tracking peak shifts and their broadening and varying intensity over cycling. This was utilised to attempt to differentiate between the different degradation mechanisms occurring in continuous and pulsed cycling.

3.2.1 Incremental Capacity Analysis

As shown in Fig. 3 and Fig. 4, the peaks identified in the full cell can be attributed to the respective electrodes, allowing for an assessment of individual electrode ageing. This facilitates an evaluation of how the applied current regime influenced the degradation.

In Fig. 5 the ICA trace of constant current reference (CC-ref) and pulse charge, pulse discharge (PC-PD) at three different frequencies, 1000 mHz, 500 mHz and 10 mHz are compared. At the same SoH level, the degradation behaviour appears similar, but after 400 cycles – when the capacity retention is at 92 % and 69 % respectively – the ICA traces have diverged. This indicates that while the ageing incurred



Fig. 3: ICA performed on reconstructed half-cells with all peaks marked, grey markers for positive electrode (PE) peaks and white markers for negative electrode peaks. Red colour indicates processes taking place during charging of the full cell. 3a NMC/Li, 3b Gr-SiO_x/Li, 3c full cell with peak assignment to individual electrode for peaks in full cell. For details on half-cell reconstruction, see Supplementary Method 4.

at pulsed operation is not qualitatively different from that in CC operation, it progresses at a significantly slower rate when the current is pulsed. It is noteworthy that the decrease in activity is significantly larger in peaks 1 and 2, which are attributed fully or partially to the negative electrode (NE) compared to peaks 3 and 4, which are mainly attributed to the positive electrode (PE). This indicates that the most significant degradation is occurring on the NE. The significant flattening of peak 1, which is likely attributable to SEI growth and reformation [37], indicates that the continuous formation of the SEI layer is a strongly contributing factor to ageing. This can in turn also be affected by the presence of plated Li where new SEI is formed [38].

From Fig. 5b the clustering of cell degradation behaviour based on pulse frequency can also be observed, as 10 mHz PC-PD aligns nearly perfectly with the CC-ref while 500 and 1000 mHz align closely together. This further strengthens the observation that



Fig. 4: ICA Performed on reconstructed half-cells with all peaks marked, grey markers for positive electrode (PE) peaks, and white markers for negative electrode peaks. Red colour indicates processes taking place during charging of a full battery. 4a NMC/Li, 4b Gr–SiO_x/Li, 4c full cell with peak assignment to individual electrode for peaks in full cell.

at frequencies below the pivotal $100\,\mathrm{mHz}$ is of high importance to battery degradation, accelerating the process.

3.2.2 Identifying ageing by DVA

The inverse of incremental capacity analysis, differential voltage analysis (DVA), is a useful technique for tracking the development of electrode level capacity during ageing. This method utilises the features of the OCV curves, where voltage plateaus correspond to regions with coexisting solid-state phases and slopes indicate the dominance of a single phase. To accentuate these shifts the derivate $\frac{dV}{dQ}$ is calculated for the pseudo-OCV curve [39, 40]. By assigning the peaks to individual electrodes as in Fig. 4, which aligns with [41], the loss modes on each electrode can be traced. All DVA traces with the peaks marked can be found in Supplementary Figs. 3-8.



Fig. 5: ICA for beginning of life (BOL) reference plotted together with CC-ref and 1000 mHz, 500 mHz and 10 mHz PC-PD at the same capacity retention, 5a, or after the same amount of cycles, 5b.

One such indicator can be found from peaks 1 and 3 which can both be attributed to the NE, meaning that the distance between them, defined as $\Delta Q_{\rm NE} = q_{\rm FC,peak3} - q_{\rm FC,peak1}$, can be used as an indication of the loss of active material (LAM) on the NE. The alignment of two different electrode peaks at full cell peak 3 with the graphite central peak (3) being dominant, complicates the tracing of two separate peaks on the PE. However, since the charge is always concluded at 4.2 V, where the NE potential is relatively flat at low voltage, it is reasonable to assume that the end of charge occurs at a stable lithiation state for the PE. Thus, the proxy for LAM on the PE, defined as $\Delta Q_{\rm PE} = q_{\rm eoc} - q_{\rm FC,peak4}$, allows for tracking of PE degradation. Additionally, the relative slip between the electrodes can be quantified by investigating the relative difference between peaks 2 and 3, yielding $\Delta Q_{\rm PE-NE}$. Further details of the assignment of ΔQ_i and the alignment of electrode voltages can be found in Supplementary Method 3.

These three proxies — $\Delta Q_{\rm NE}$, $\Delta Q_{\rm PE}$, and $\Delta Q_{\rm PE-NE}$ — can be compared to SoH to provide information about different ageing modes across specimen groups. By normalising the capacities with the capacity at beginning of life (BOL), a direct comparison is possible, which is shown in Fig. 6. Analysing the trends for capacity loss, from Fig. 6a it is evident that the NE loses capacity at a similar rate to the overall cell capacity loss, with no clear separation between different specimen groups, as they all group close to the dashed line indicating ageing at the same rate.

The ageing of the PE, seen in Fig. 6b, is clearly slower, as indicated by all points lying above the trend line, suggesting higher relative capacity retention for the PE compared to the cell as a whole. This aligns with the findings from the ICA analysis, which also indicated that most degradation occurs on the NE side. However, Fig. 6b shows no significant separation among specimen groups, since all cases are similar.

Another trend emerges in Fig. 6c, where cells subjected to constant current or low-frequency testing (f < 100 mHz) appear above the trend line, while higher frequencies



(a) Normalised $\Delta Q_{\rm NE}$ plotted versus SoH. (b) Normalised $\Delta Q_{\rm PE}$ plotted versus SoH.



Fig. 6: Ageing mode proxies as identified from DVA traces plotted versus SoH, with black dashed lines indicating the symmetric relation between electrode capacity loss and cell SoH. The plots indicate significantly faster degradation on the NE compared to PE, and 6c indicates that the ageing is more asymmetric in the low-frequency or constant current cases.

group on or below the same trend line. A larger $\Delta Q_{\text{PE-NE}}$ shows a more significant separation between electrode capacities and indicates a faster degradation of the PE in these cases. Given that 1 C charging is a relatively elevated rate for highly energyoptimised cells, one potential explanation for the faster degradation of the NE in these cases could be more extensive Li plating compared to the situations where the frequency of the current pulses is higher.

3.2.3 Diffusive resistance from ICI

To complement the findings from the DVA peak tracking, it is also of interest to track the development of the resistive properties of the cells as they degrade. In Fig. 7, the diffusive resistance parameter k is displayed for the voltage window of the cell for two subsets of cells from category 1 (Fig. 7a) and category 2 (Fig. 7b). In all cases, the ICI tests are chosen such that the SoH level is similar for the cells to enable direct comparison. The k parameter does not seem to follow the same trend as the ICA traces which were not significantly different at similar SoH. Instead, there is a trend that the diffusive resistance increases more in the constant current case for category 2, or for the cases with a frequency below 100 mHz for category 1. The data for category 1 was gathered by a tester with lower precision, meaning that the results are noisier than those in category 2. In order to highlight the offset between the two groups even more, the average value of k for each specimen (calculated in the range between 3.5 and 4.1 V to avoid disproportionate influence of the data tails) is shown in Table 4. It can be seen that the average k for the low frequency cases is about 8% higher compared to the higher frequency cases.



Fig. 7: Diffusion resistance parameter k as calculated from ICI test for cells of similar SoH.

The separation in diffusive resistance could potentially be explained by a higher occurrence of Li plating in these tests as this could lead to the formation of a highertortuosity layer on the NE, which would increase the diffusive resistance. This supports the findings from DVA peak tracking, as that showed larger electrode separation in the low-frequency cases, indicating that the cases with faster degradation could be due to a higher presence of Li plating. This remains however a speculation on the

Table 4: Average k-values for testconditions in Fig. 7a.

Test Condition	$k_{\rm mean} \left[{\rm m}\Omega / \sqrt{{\rm s}} \right]$
1000 mHz PC-PD 500 mHz PC-PD 10 mHz PC-PD CC-ref	$2.89 \\ 2.86 \\ 3.16 \\ 3.07$

part of the authors, and to confirm the hypothesis post-mortem characterisation of the test objects would be required.

3.3 Transition to linear ageing

During the cycling, many of the cells exhibit a transition from slower to significantly accelerated ageing, typically following a linear trend. However, there is considerable variation in the onset of the linear trend, even among cells under identical conditions. This variation is influenced by the dynamics of the cycling, as illustrated in Table 5, which is extracted by visual inspection of data for each individual cell shown in Supplementary Figures 9 and 10. Note that all 25% duty cycles are excluded from the table, as none exhibit a transition to linear ageing. From the table, it is evident that several specimen groups contain cells that either do not transition to linear ageing at all, or transition to accelerated ageing after less than two hundred cycles. This seems more pronounced for cells subjected to dynamic charging, as compared to static conditions. Notably, for CC-ref and 1C-ref, the transition to linear ageing occurs almost synchronously across cells.

The spread in the transition to the linear ageing stage is notably larger in the cases with pulsed charging. For example, in the 100 mHz PC-PD case, one cell experiences linear ageing after 160 cycles, while two cells do not transition to linear ageing at all. This suggests that the non-homogeneity of ageing is exacerbated under dynamic usage conditions, which is consistent with previously reported data in the literature, such as by Uddin et al. [26].

Two hypotheses to explain this larger spread are: 1) inherent cell-to-cell variance from manufacturing [42], which is amplified by pulsed charging; or 2) a stochastic element in the onset of Li plating, which becomes more pronounced in cells that do not experience sustained periods of negative overpotentials on the NE. These two hypotheses are not mutually exclusive, and could both be contributing to the spread. However, further studies would be required to verify the cause of non-homogeneity in ageing behaviour during dynamic usage.

4 Discussion and conclusion

The goal of this paper was to demonstrate a durability-friendly charging method for LIBs with near-term applicability for battery and equipment manufacturers. This was achieved by implementing a simple, parameterisable pulse-charging algorithm in a

Case	Transition	Case	Transition	
$100\mathrm{mH}$	Iz PC-PD	$100 \mathrm{mH}$	100 mHz PC-NPD	
1	-	1	120	
2	-	2	200	
3	160	3	240	
4	200	4	360	
$1000 \mathrm{m}$	Hz PC-PD	1000 m	Hz PC-NPD	
1	320	1	280	
2	-	2	360	
3	-	3	-	
4	-	4	-	
320 mH	320 mHz PC-PD 500 mHz		z PC-PD	
1	200	1	200	
2	200	2	280	
3	-	3	-	
4	-	4	-	
CC-re	f	10 mHz PC-PD		
1	120	1	120	
2	120	2	120	
3	120	3	160	
4	160	4	200	
10 Hz PC-PD-50 50 Hz		50 Hz I	PC-PD-50	
1	140	1	140	
2	160	2	-	
3	-	3	-	
4	-	4	-	
1C-ref	2	1 Hz PC-PD-50		
1	60	1	100	
2	60	2	140	
3	60	3	200	
4	60	4	-	

Table 5: Knee effect points for tested cells, number of cycles where ageing transitions to linear. Dash indicates that not transition has occurred.

laboratory setting and showing that it significantly reduces degradation compared to constant current (CC) charging at the same average current.

Results show that increasing pulse-charging frequency improves battery durability, with optimal conditions yielding 97 % capacity retention after 400 cycles, compared to 70,% with CC charging. As the benefits plateau at approximately 100 mHz, implementing pulse charging does not require highly specialised hardware, making it feasible for integration into existing BEV systems without adding significant complexity or cost.

Through electrochemical analysis intermittent current interruption and derived techniques, it was shown that the primary ageing process could be attributed to the negative electrode suggesting that lithium plating and SEI reformation could be major contributors to the observed degradation. This indicates a strong dependence on the duration of charging pulses in lithium plating, although further studies, including post-mortem analysis, are needed to fully confirm this hypothesis.

Challenges remain in elucidating the exact details of the reduction of degradation, as the current lithium plating models cannot accommodate for these effects, and no further post-mortem capabilities were available within the scope of the article. Further model development in conjunction with post-mortem activities could serve to further explain the underlying effects of the reduction in ageing.

Nevertheless, this work represents a significant step forward in the development of durability-friendly charging algorithms. The implementation of the proposed charge algorithm could accelerate the widespread adoption of BEVs in the mass market, offering a more sustainable and cost-effective solution for battery longevity.

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