

The influence of electrochemical history on lifetime of commercial lithium-ion batteries

Alexander Dimitrijevic

Submitted in part fulfilment of the requirements for the degree of
Doctor of Philosophy at University College London

Electrochemical Innovation Lab
Department of Chemical Engineering
University College London
2024

Declaration

I, Alexander Dimitrijevic confirm that the work presented in my thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

The urgent need to address global warming has propelled the development and optimisation of lithium-ion (Li-ion) batteries, particularly those with high nickel content, due to their critical role in the electrification of transportation and renewable energy integration. However, despite their high energy density, these cells are susceptible to accelerated degradation, and continuous efforts to characterise and mitigate these degradation mechanisms are crucial for enhancing their performance under diverse applications, including high-demand sectors such as the automotive industry or the aerospace sector. Accordingly, this thesis presents a comprehensive study of the longevity and performance of commercial cylindrical Li-ion, addressing various key elements influencing battery life.

For instance, the predictive capability of high-precision coulometry (HPC) was explored and it was shown that high coulombic efficiency (CE) correlates with improved long-term capacity retention, as confirmed by the cycling data provided by an industrial partner. This early-life assessment became a reliable metric across different cell models, consisting of various chemistries and other design differences, reinforcing CE's utility in identifying cells with greater longevity potential before significant capacity loss is observed.

Furthermore, commercial cells were subjected to several variable current protocols at various temperatures, and it was shown, via various characterisation methods, that the protocols that prolonged time spent at high voltage and high SoC had the most detrimental effect on battery life, with dramatic power fade, solid electrolyte interphase (SEI) growth, and SiO_x additives degradation at the anode.

The time spent at high SoC emerged again as a prevalent metric during a calendar ageing study where the notable "spoon-shape" capacity fade was observed, marked by increased fade at 70-80% SoC with a partial recovery at 100% SoC. The effect has been shown to be temporary, as cells held at 100% SoC subsequently degraded faster upon cycling. The storage mechanisms involved were identified to be anode and SEI-dominated, as cathode characterisation revealed the material was relatively well preserved.

Impact Statement

Global warming is one of the most pressing challenges of our time, driven by the excessive emission of greenhouse gases. Electrification, primarily through renewable energy sources and the electrification of transport, plays a pivotal role in this transition. In this context, Li-ion batteries are essential, as they provide the energy storage solutions necessary for electric vehicles and grid-scale energy storage. By facilitating the decarbonisation of the transport and energy sectors, Li-ion batteries contribute significantly to reducing reliance on fossil fuels. Their ongoing rapid development and use aim to increase energy density, improve longevity, and reduce dependence on critical raw materials, ensuring that batteries can meet the growing global demand for cleaner energy solutions

The research presented in this thesis was carried out under the UK's Faraday Institution program on the battery degradation consortium, a collaborative initiative involving multiple universities and industry partners, with the goal of extending battery lifespan and establishing the UK as a leader in the electric vehicle sector. A joint project was also undertaken in collaboration with the European Space Agency (ESA) and a British cell provider for the space sector, ABSL Enersys Ltd, from which a grant was obtained to support it (from the ESA Open-Space Innovation Program) and has led to a 9 months stay at the European Space Power Laboratory to develop a reliable method to assess forecast of battery fade behaviour. This work led to a successful presentation at the conference European Space Power Conference in Elche, Spain and the project stemmed interest in future works that are already being carried out.

A further collaboration was undergone with WMG and a prominent OEM interested in exploring the issues of storage degradation, which led to an extensive study on calendar ageing of contemporary commercial cells, where 224 cells were involved, at four different temperature conditions, and only a relatively small part of this work is presented here. The work was supported by an Industry sprint grant of the Faraday Institution, as well as two of the main project consortiums (Degradation and Safebatt).

Further work was carried out at the Diamond Light Source in Harwell and the European Synchrotron Radiation Facility in Grenoble, France, from which work has been disseminated in peer-reviewed publications, or soon to be.

Lastly, outreach efforts through the Faraday Institution, UCell or PPL PWR, involving giving talks, demonstrations and workshops in electrochemical energy storage systems at science festivals, fairs and a range of schools have expanded the reach and social impact of this work. This dissemination and sparking the interest of younger generations was found to be greatly rewarding and useful in all aspects.

This thesis showed the reach of both private interests, as well as public funding from national institutes and organisations, or supranational entities, all driving the development and success of Li-ion batteries, in the context of global energy transition and electrification, to tackle climate change.

Acknowledgments

First and foremost, I would like to thank my supervisor, Dr Rhodri Jervis, for the patient guidance, support, encouragement and advice he has provided me with during this PhD. During this journey of ups and downs, he has shown me truly exceptional support and understanding and is an integral part of the work presented here. I feel lucky to have been under his mentorship, and would not have done it any other way.

I also extend my gratitude to Prof. Paul Shearing for granting me the possibility to join the EIL and their exceptional facilities at UCL for the opportunity to carry on excellent scientific research. In addition, I am grateful to the Faraday Institution, and particularly Fran Long and Matt Howard, for their constant support, the great training program organised for us, as well as their enthusiasm in helping me secure my internship carried out during my PhD.

I am also really thankful to Toby Neville and Dr Julia Weaving for the help they provided me in the lab and for their exceptional resilience and patience shown towards all of us throughout the years. I also thank my lab and beamtime partners Dr Anmol Jnawali and Dr Alice Llewellyn; Dr Francesco Iacoviello and Dr Wenjia Du for their kind help and shared moments; Dr James Robinson, Dr Rhodri Owen, Ami Shah and Michael Johnson, the whole team of Ucell and the great events we had all together and Dr Josh Bailey and the PPL PWR team. I also wanted to thank many friends for their help and their contribution making the EIL such an enjoyable place to be, such as Dr Drasti Patel, Dr Alessia Matruggio, Dr Renier Arabolla, Dr Pooja Vadhva, Dr Mateen Mirza, Scott Young, Alex Marinov (other Alex), Dr Shangwei Zhou, Emanuele Magliocca, Ed Yang, and many more.

I further thank my collaborators in the extensive High-Ni Sprint project that we had with WMG: Dr Eleni Fiamegkou, Veronika Majherova, Dr Meltiani Belekoukia, Dr Ashok Menon, Dr Dhammika Widanalage, Dr Melanie Loveridge and Prof. Louis Piper. I also thank Dr May Ching Lai for the TEM characterisation, as well as Dr David Hall and Dr Wesley Dose, for their help.

I also want to highlight my time spent at ESA during my internship and the wonderful support I received from Aurore Carré and Bob Witteveen, always so helpful

and enthusiastic about the many projects we carried out, as well as the team at the EPB section with Dr Jakob Asenbauer, Brandon Buergler and Geraldine Palissat. I am also grateful for the exceptional support I have received from the ESPL team, on the other side of ESTEC, Victor Lujan Cuenca, Thijs Lorrier, Natasha Klein and Jaromir Vacca, with whom I have learned a lot. I also extend my gratitude to Carl Thwaite, Rachel Buckle and the people of ABSL for their support, help and numerous chats we had, (using extra channels for some battery cycling!) and for allowing the project we had to come true, as it has brought me so much.

Lastly, I am also particularly grateful to Lola, my girlfriend, for her truly exceptional support and help she has given me during the last challenging months of writing, keeping me in one piece and allowing me to keep pushing. This probably would not have been possible without her. Furthermore, I am eternally thankful towards my family, and particularly to my dad, mum and brother, who have always been there for me, since the very beginning, and have been with me at every step of my journey.

Table of contents

Declaration	3
Abstract	4
Impact Statement	5
Acknowledgments	7
Table of contents.....	9
List of Abbreviations	12
List of Tables.....	15
List of Figures.....	16
1 Introduction.....	25
1.1 Motivation.....	25
1.2 Lithium-ion batteries.....	28
1.3 Objectives	29
2 Literature review	32
2.1 Fundamentals of the lithium-ion battery	32
2.2 Battery components	35
2.2.1 Positive electrode	37
2.2.2 Negative electrode.....	40
2.2.3 Electrolyte and solid electrolyte interphase.....	45
2.2.4 Separator.....	47
2.3 Degradation of lithium-ion batteries.....	48
2.3.1 Degradation mechanisms within Ni-rich lithium-ion batteries.....	48
2.3.2 Calendar ageing of commercial cells.....	55
2.3.3 Loss of active material, lithium inventory, and impedance growth as degradation modes	58
2.4 Fast charging and other varied protocols for lithium-ion batteries.....	60
2.5 Consideration of cell resistance and ion mobility over the state of charge ..	65
2.6 High-Precision Coulometry	70
2.6.1 Theory and applications.....	70
2.6.2 Setup and error mitigation	75
2.6.3 Interpretation of High-Precision Coulometry results	80
2.7 Conclusions and perspectives.....	86

3	Methodology	89
3.1	Electrochemical characterisation.....	89
3.1.1	Battery cycling	89
3.1.2	High-Precision Coulometry setup and consideration	91
3.1.3	Electrochemical Impedance Spectroscopy	98
3.1.4	Incremental Capacity and Differential Voltage Analysis	103
3.2	Variable current protocols derivation	106
3.3	Commercial cells opening and reassembly	109
3.3.1	Cell opening.....	109
3.3.2	Coin cell reassembly of the harvested electrode material	110
3.4	Imaging techniques	111
3.4.1	X-Ray Computed Tomography	111
3.4.2	Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy.....	113
3.5	Powder Diffraction Techniques	114
3.5.1	Neutron Powder Diffraction.....	114
3.5.2	X-ray Powder Diffraction.....	115
4	Predicting fade behaviour using High-Precision Coulometry	117
4.1	Introduction	117
4.2	Experimental	119
4.3	Beginning and end of life studies	122
4.3.1	Macrostructure assessment using X-ray Computed Tomography	122
4.3.2	Visual inspection after cell opening and SEM/EDX	125
4.3.3	Capacity check and Incremental Capacity Analysis	133
4.3.4	Electrochemical Impedance Spectroscopy	137
4.4	High-Precision Coulometry cycling.....	140
4.4.1	Batch-to-batch assessment	140
4.4.2	Overall assessment	155
4.4.3	Other factors linked to influence coulombic efficiency	158
4.5	Conclusions.....	162
5	Degradation effects of variable current protocols on commercial cells	165
5.1	Introduction	165
5.2	Experimental	167
5.3	Baseline fresh cells evaluation	169
5.4	MH1 and MJ1 studies at 0.7C with temperatures of 20°C and 0°C	174

5.4.1	20°C cycling.....	174
5.4.2	0°C cycling.....	181
5.4.3	Incremental capacity and differential voltage analysis.....	188
5.5	M50 study at 0.5C and ambient temperature	193
5.5.1	Cycling data results	195
5.5.2	Incremental capacity and differential voltage analysis.....	197
5.5.3	Electrochemical impedance spectroscopy.....	201
5.6	Conclusions.....	205
6	Multiscale degradation study of calendar ageing of Ni-rich 21700 commercial cells with Graphite containing SiO _x	208
6.1	Introduction	208
6.2	Experimental	209
6.3	Calendar ageing results	210
6.3.1	Capacity fade and resistance increase as a function SoC, storage time and temperature	210
6.3.2	Macrostructural deformation assessment using X-ray Computed Tomography.....	214
6.4	Post-mortem characterisation	218
6.4.1	Visual inspection.....	218
6.4.2	Cathode material characterisation	221
6.4.3	Anode material imaging.....	223
6.5	Conclusions.....	225
7	Conclusions and Future Work	227
7.1	Conclusions.....	227
7.2	Future work	231
	References.....	235
	List of Publications and Conferences	270
8	Appendix.....	271
8.1	Appendices of Chapter 4.....	271
8.2	Appendices of Chapter 5.....	273
8.3	Appendices of Chapter 6.....	275

List of Abbreviations

BMS	Battery Management System
BoL	Beginning-of-Life
CC	Constant Current
CE	Coulombic efficiency
CEI	Cathode Electrolyte Interphase
COTS	Commercial Off-the-shelf
CV	Constant Voltage
DoD	Depth of Discharge
DEC	Diethyl Carbonate
DMC	Dimethyl Carbonate
EC	Ethylene Carbonate
ECM	Equivalent Circuit Model
EE	Energy Efficiency
EDX	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EMC	Ethyl Methyl Carbonate
EoL	End-of-Life
ESA	European Space Agency
ESPL	ESA Space Power Laboratory
EV	Electric Vehicle
FSR	Full-Scale Resolution
HC	Hard Carbon

HEV	Hybrid Electric Vehicles
HPC	High Precision Coulometry
HPPC	Hybrid Pulse Power Characterisation
IR	Internal Resistance
LCO	LiCoO_2
LFP	LiFePO_4
Li-ion	Lithium-ion
LMO	LiMn_2O_4
LNO	LiNiO_2
NCA	$\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$
NMC111	$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$
NMC532	$\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$
NMC622	$\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$
NMC811	$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$
NMP	N-Methyl-2-Pyrrolidone
OCV	Open Circuit Voltage
PE	Polyethylene
PP	Polypropylene
PTC	Positive Temperature Coefficient
PVDF	Polyvinylidene Fluoride
RMSE	Root-mean square error
RSL	Rock-salt layer
RTD	Resistance Temperature Detector
SEI	Solid Electrolyte Interphase

SEM	Scanning Electron Microscopy
SoC	State of Charge
TM	Transition Metal
XAS	X-ray Absorption Spectroscopy
XRD	X-ray Diffraction
VC	Vinylene Carbonate
VCP	Variable Current Protocol
VE	Voltage Efficiency
X-Ray CT	X-ray Computed Tomography

List of Tables

Table 2-1. Characteristics of most the common cathode materials available and studied for Li-ion batteries.	38
Table 2-2. Table showing four key parameters that contribute to errors in capacity measurement identified. Adapted from Smith et al. ¹⁸⁴	75
Table 2-3. Summary of the five main degradation processes and their effect on Lithium inventory, as described by Smith et al ¹⁹³	81
Table 3-1. Main characteristics of the battery cycling systems used throughout this thesis.....	90
Table 3-2. Summary of various cyclers used with their temperature control and measurements methods, respective precision and accuracy in ppm, and CE values measured above one for the first 25 cycles, with omission of the first 4 cycles.....	95
Table 3-3. Specifications of the Nikon XT H 225.	112
Table 4-1. Summary of the cell types used with electrode chemistry information, rated capacity and voltage range.	119
Table 5-1. Summary of the cell models used with dimensions, rated capacity and electrode chemistry information.	168
Table 5-2. Summary of some of the main cycling conditions and parameters used.	169

List of Figures

Figure 1-1. Diagram comparing various secondary battery technologies as a function of volumetric and specific energy densities. Reproduced from B. J. Landi et al. ²⁴ ...	27
Figure 2-1 Schematic of the charge and discharge processes of a lithium ion cell. It is noted that the separator is not represented in this image. Reproduced from A. Patil et al. ³⁴	33
Figure 2-2. Reconstructed tomograms showing the microstructure of a commercial cell. The yellow line shows a possible path taken by a Li^+ ion. Reproduced from D. Finegan ⁴³	34
Figure 2-3 (a) Schematic view of Li^+ charge during charge (b) Schematic view of Li^+ charge during discharge. Reproduced from Jow et al. ⁴⁴	35
Figure 2-4. Diagram showing the electrochemical potential of certain materials compared to lithium for the anode (red) and the cathode (blue). Reproduced from B. J. Landi et al. ²⁴	36
Figure 2-5. SEM micrograph a) showing two trenches milled into NMC cathode and b) a cross section of cathode clearly visualising active material particles and the carbon binder domain. Reproduced from Entwistle et al. ⁵⁶	39
Figure 2-6. a) and c) cell charge potential vs. Li/Li^+ as a function of lithiation state in a Li-graphite and hard carbon half-cell respectively, with stages marked for corresponding voltage plateaus, b) and d) schematic representation of the ordered crystal structure in lithiated state for graphite and hard carbon respectively, as well as differential capacity with respect to anode potential curve for hard carbon in d). Reproduced from Shellikeri et al. ⁶⁹	42
Figure 2-7. Anode-level data collected from an MJ1 18650 commercial cell with volume representation of the negative electrode material obtained via X-ray CT, and evidencing SiO_x additives particles. Reproduced from Heenan et al. ⁸³	44
Figure 2-8. Schematic figure of the Initial SEI formed on the graphite anode, the effect of acid-mediated thermal decomposition reactions on the structure of the SEI, and the further reduction of electrolyte leading to the thickening of the SEI. Reproduced from Heiskanen et al. ⁹⁴	46
Figure 2-9. Causes and effects of degradation mechanisms occurring within Li-ion batteries. Reproduced from Birkl et al. ¹⁰⁴	48
Figure 2-10. Differential capacity vs. cell voltage of NMC-graphite cells recorded at a 0.1 C-rate. The peaks represents their corresponding phase transitions with H1, H2 and H3 assigned to the three hexagonal phases and M the monoclinic one. $\text{C6} \rightarrow \text{LiC}_6$ indicates the lithiation of graphite. Reproduced from Jung et al. ¹⁰⁸	49
Figure 2-11. A map of relationship between discharge capacity, thermal stability and capacity retention of various NMC materials ratio. Reproduced from Noh et al. ¹¹³ ..	51
Figure 2-12. a) Schematic showing the tensile strain concentrated in the surface region of the rock-salt platelet, generated by retraction of the a-parameter of the layered phase upon delithiation. b) HRTEM view of the rock-salt/layered interface from a one-cycle particle, showing the bending of the lattice planes in the layered phase caused by the retraction of its a-axis. Reproduced from Zhang et al. ¹²⁴	52

Figure 2-13 (a) The oxidation states of transition metal ions in various NMCs. (b) Amount of Ni^{4+} ions as a function of state of charge in various NMCs states. Reproduced from M. Dixit et al. ¹²⁷	53
Figure 2-14. Atomic configurations for the structure of (a) LiMO_2 , where M = transition metals (Ni, Co, and Mn), and the schematic structures for each of the defects, (b) Li vacancies (V_{Li}), (c) oxygen vacancy (V_{O}), (d) excess Ni (Ni_{Li}), (e) Li/Ni exchange ($\text{Li}_{\text{Ni}}-\text{Ni}_{\text{Li}}$), and (f) Ni migration (Ni_{mig}). Reproduced from Min et al.. ¹³¹	54
Figure 2-15. Schematic illustration of transition-metal migration in layered oxides. The transition metals can move from octahedral sites in the transition-metal layer (A) via tetrahedral sites in the lithium layer (B) into octahedral sites in the lithium layer (C). Reproduced from Kleiner et al. ¹²⁰	55
Figure 2-16. a) Illustration of the CO_2 -based shuttle mechanism of self-discharge; b-d) mass flow model of the rates of reversible self-discharge and irreversible. SEI formation, including corrosion-type electron transfer for three different SoC levels. Left and Right column: anode and cathode potentials vs. SoC level. Inset: capacity retention during calendar ageing. Reproduced from Zülke et al.. ¹⁴⁰	57
Figure 2-17. a) Capacity fade over SoC for different storage periods of NCA/Graphite cells and b) DVA of a fresh cell. The dotted vertical line represents the SoC location of the central graphite peak. Reproduced from Keil et al.. ¹⁴⁵	58
Figure 2-18. Varying V and C-rates protocols for new chargers of Lithium ion cells, resulting in the standard CCCV protocol. Reproduced from Chen et al.. ¹⁵³	61
Figure 2-19. Cycle life of cylindrical Li-ion batteries under high charging load conditions at $I_{\text{max}}=4.5\text{ C}$, $V_{\text{max}}=4.2\text{ V}$ (a) and $I_{\text{max}}=4.5\text{ C}$, $V_{\text{max}}=4.3\text{ V}$ (b). Cycle life upon standard CCCV-charging ($I_{\text{max}}=1\text{ C}$, $V_{\text{max}}=4.2\text{ V}$) is indicated in curve (c). Reproduced from Notten et al.. ¹⁵⁴	62
Figure 2-20. Five step current charging protocol. Reproduced from Liu et al.. ¹⁵⁵	63
Figure 2-21. Varying cycling procedures and profiles considered by Abdel-Monem et al.. ¹⁵⁷	64
Figure 2-22. IR over SoC for four fresh batteries. Reproduced from Wang et al.. ¹⁶²	66
Figure 2-23. IR over SoC with consideration of temperature (left) and number of cycles (right). Reproduced from Wang et al.. ¹⁶²	66
Figure 2-24. 3D plots of the Nyquist spectra for the studied battery at SoC values of 7.5% to 93.0%. Reproduced from Huang et al.. ¹⁶⁷	67
Figure 2-25. Li mobility over SoC obtained from GITT applied to NMC811/Li half-cells. Reproduced from K. Marker et al.	68
Figure 2-26. Comparison between the IR derived from the GITT, ICI method and EIS. The IR (R) of NMC811 in Cell 1 at various OCP of the electrode (E) derived from the GITT with data selection interval 5–40 s, the ICI method and the EIS fitting ($R_0 + R_1 + R_2$) during charging and discharging are plotted in a, b, respectively. The maximum of y-axis is set to 200 Ω to show the differences of the data above 3.7 V. The error bars originate from the standard deviation of the linear regression. Reproduced from Chien et al.. ¹⁷¹	69
Figure 2-27. Inconsistent GITT diffusivity values reported in the literature. All data points are from the same material system, NMC111. In addition to the orders-of-magnitude inconsistency in the values, the qualitative dependency on Li composition is also discrepant among reports. The sky blue markers labelled lithiation/delithiation	

indicate measurements from nominally identical samples but with reversed current directions. Reproduced from Kang et al. ¹⁷²	70
Figure 2-28. Coulombic Efficiency values for Li/MoS ₂ AA commercial cells at various voltage limits and cycle histories. The horizontal lines indicate the mean values for each voltage cycling range.....	73
Figure 2-29. Top panel: CE values from 30 LCO/Graphite different commercial 18650 cells charged and discharged at C/24 at 30 °C, 3.0-4.2V range. Bottom panel: average and standard deviation of said cells.	74
Figure 2-30. Illustration of the endpoint correction. Left figure: The data in black represents the measured data collected from the cycler, while the red data point indicates the point at which the voltage limit is crossed (determined by linear interpolation). Right figure: illustration of how capacity is corrected for charge that is transferred beyond fixed voltage limits. Reproduced from T. Bond ¹⁹⁰	77
Figure 2-31. RMSE (averaged from 2 cells) of CE data collected using the UHPC in 4 different configurations as indicated. “T” refers to temperature control of instruments, and “V” refers to voltage stabilisation of instrument power supply. Reproduced from Bond et al. ¹⁸⁹	78
Figure 2-32. Illustration depicting the discharge endpoint slippage (ΔD) and charge endpoint slippage (ΔC) of a Li ion cell. Reproduced from Smith et al. ¹⁹³	82
Figure 2-33. Capacity fade and HPC data for 18650 commercial cells with various additives. Reproduced from Smith et al. ¹⁹⁹	83
Figure 2-34. Capacity (a), Coulombic efficiency (b) and Coulombic inefficiency per hour (c) versus time for pouch cells cycling at 30°C during cycling with various C-rates. Reproduced from Burns et al. ²⁰⁰	84
Figure 2-35. Various display of CE found in more recent literature. a) specific capacity and CE plot vs cycle number of NMC 811/graphite coin cells reassembled with NMC 811 electrode material left at ambient air storage for 3 months and 1 year compared to fresh material. Reproduced from Jung et al. ²⁰¹ b) capacity and CE plot vs cycle number of NMC811 half-cells coin cells with two distinct upper-voltage cut-off. Reproduced from McNulty et al. ²⁰² c) CE calculated from anode-free cells cycled with a voltage range of 3.6–4.5 V and 1.25–4.5 V. Reproduced from Genovese et al. ²⁰³ d) CE vs cycles plot of pristine Li _{1.2} Mn _{0.6} Ni _{0.2} O ₂ (LRMO) cathode material (blue) and a modified sample Li _{1.2} Mn _{0.6} Ni _{0.2} O _{2-δ} (M-LRO) with oxygen vacancies and a reduced Mn structure (red). Reproduced from Li et al. ²⁰⁴	85
Figure 3-1. a) CE value with four different corresponding quadratic fit depending on the number of values skipped for said fit, and their corresponding R ² and RMSE values. The CE of the first cycle is 0.982, not displayed in this figure. b) Additional 5 th degree polynomial and logarithmic fits carried out skipping the first two values.....	92
Figure 3-2. CE values for two cells from the same cell type and batch cycled on Novonix and Diatron, and their respective RMSE values. Cycling was done at C/5 and the first 50 cycles are on display.	93
Figure 3-3. Precision and Accuracy values measured in ppm for Ultra High Precision Cycler, High Precision Cycler and Maccor Series 4000 cyclers. Reproduced from Bond et al. ¹⁸⁹	96

Figure 3-4. Temperature measured of LCO/HC – 2004 – 01 cycled on the Novonix, the ambient temperature measured, and their respective ones for LCO/HC – 2004 – 03 cycled on the Digatron, for the first 6 cycles.	98
Figure 3-5. A Nyquist plot with each region of the spectrum specified. Reproduced from Abdem Monem et al. ²⁰⁹	99
Figure 3-6. Example of three-electrode EIS measurements for (a) positive and negative electrodes and (b) the sum of three-electrode measurements and the full cell plot. Reproduced from Raccichini et al. ²¹⁶	100
Figure 3-7. Nyquist spectrum of a fresh commercial cylindrical 18650 cell (NMC111/Graphite). The data is not fitted. Highlighted are R_{Ω} and R_{ct} and how they are obtained graphically from the graph.	102
Figure 3-8. Exemplary C/25 electrochemical ICA behaviour for several labelled battery materials in half-cell configuration. Reproduced from Dubarry and Anseán ²²⁰	104
Figure 3-9. a) The full-cell voltage and b) the DVA spectra of each anode and cathode half-cell curves from a NCA commercial cell. This allows for a reconstruction of the 18650 full-cell by a superposition. Reproduced from Keil et al. ¹³²	106
Figure 3-10. Schematic representation of all variable current protocols used in this thesis, the C-rate applied per interval and how much time it would take to complete for both 0.5C and 0.7C equivalent. a) is the commonly used CCCV, b) the VCP, c) the LowEnd and d) the LowStart. This is only representative for the charge sequence.	108
Figure 4-1. Illustration of the potential use for high-precision coulometry.....	118
Figure 4-2. Coulombic efficiency, discharge capacity and normalised discharge capacity values for 15 cycles for four M50 cells: two cycled at C/5 and two at C/10.	120
Figure 4-3. Summary of the procedure applied to the cells throughout this chapter.	121
Figure 4-4. Reconstructed tomograms of the commercial 18650 cells as received. The tomograms correspond to a) to c) LCO/HC, d) to f) LCO/Graphite and g) to i) NMC/Graphite. Each tomogram is labelled by the ID of the cell and the year of manufacture of the batch it corresponds to. The scale bar displayed represents 10mm.	124
Figure 4-5. LCO/HC – 2013 cell separator visual inspection after cell opening displaying a) the side of both cathode and anode closer to the core of the electrode assembly, and b) the outer side.	125
Figure 4-6. NMC/Graphite – 2015 separator visual inspection after cell opening. a) shows both separators with a delaminated patch of cathode material located towards the core, magnified in b). c) displays of the cathode once the cell opened in the glovebox, with the suspected delaminated cathode material, located close to the intercalated aluminium tab of the cell.	127
Figure 4-7. SEM micrographs of the cathode material of a) and c) LCO/HC – 2013 at $\times 1000$ and $\times 2500$ magnification respectively and b) and d) NMC/Graphite – 2015 at $\times 5000$ and $\times 15000$ magnification respectively, with their respective representative element table in e) and f).....	128

Figure 4-8. SEM micrographs of the cathode material of LCO/HC – 2013 a) and b) at $\times 1300$ and $\times 3700$ magnification respectively. c) is the elemental table of the EDX performed on the particle identified in b).	129
Figure 4-9. SEM micrographs of the anode material of a) and c) LCO/HC – 2013 at $\times 2000$ and $\times 4700$ magnification respectively and b) and d) NMC/Graphite – 2015 at $\times 3000$ and $\times 15000$ magnification respectively.	130
Figure 4-10. a) Portion of NMC/Graphite – 2015 cathode examined showing both intact and partially delaminated material with b) an SEM micrograph of the area at $\times 350$ magnification. c) EDX elemental map of Fluorine of d) the feature observed in the delaminated area, as well as f) with $\times 2500$ and $\times 1200$ magnification, respectively. e) and g) micrographs evidencing the Aluminium current collector exposition. at $\times 1500$ and $\times 10000$ magnification, respectively.	132
Figure 4-11. Results of BoL and EoL capacity checks at C/10 carried out before and after the 70 cycles of HPC for LCO/HC cells where a) displays the voltage curve over capacity and c) is the incremental capacity vs cell voltage (dQ/dV), with b) and d) being the corresponding magnified region of relevant areas (marked with a black rectangle) for a) and c) respectively.	134
Figure 4-12. Results of BoL and EoL capacity checks at C/10 carried out before and after the 70 cycles of HPC for LCO/Graphite cells where a) displays the voltage curve over capacity and c) is the incremental capacity vs cell voltage (dQ/dV), with b) and d) being the corresponding magnified region of relevant areas (marked with a black rectangle) for a) and c) respectively.	135
Figure 4-13. Results of BoL and EoL capacity checks at C/10 carried out before and after the 70 cycles of HPC for NMC/Graphite cells where a) displays the voltage curve over capacity and c) is the incremental capacity vs cell voltage (dQ/dV), with b) and d) being the corresponding magnified region of relevant areas (marked with a black rectangle) for a) and c) respectively.	136
Figure 4-14. Nyquist spectra and R_{Ω} and R_{ct} values for cells “LCO/HC” (a and b), “LCO/Graphite” (c and d) and “NMC/Graphite” (e and f). For the Nyquist plots, only the positive $-Z''$ values are displayed for clarity.....	139
Figure 4-15. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of Cells LCO/HC, b) CE values plotted for each batch, comprised of the averaging of its component cells, and c) the representative lifetime capacity fade for each batch. Error bars represent standard deviation (SD).	143
Figure 4-16. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of LCO/Graphite cells, b) CE values plotted for each batch, comprised of the averaging of its component cells, and c) the representative lifetime capacity fade for each batch.	146
Figure 4-17. a) Schematic representation of lithium ion diffusion between anode active material and overhang region. Cases represented are in (a) during storage at high SoC where the Li ions from the anode active region is accepted into the overhang. (b) during subsequent storage or cycling at low SoC, ions nestled in the overhang region are released back into the active anode region. Reproduced from Gyenes et al. ²⁶⁸ . b) Orthoslice of LCO/HC – 2014 – 01, displaying the top part of the electrode assembly and the cap, where the overhang of the anode is observable in the highlighted area.	148

Figure 4-18. Normalised discharge capacity of the capacity check cycles of the lifetime data and the percentage of capacity recovered as opposed to the capacity measured with the cycle prior for a) cells LCO/HC and b) LCO/Graphite.	150
Figure 4-19. For all batches of LCO/HC and LCO/Graphite cells, a) lifetime data with the capacity checks removed with a b) magnified region of the first 1000 cycles. c) is the CE for the “01” cells and d) is the normalised ΔV obtained from all cells.	152
Figure 4-20. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of NMC/Graphite cells, b) CE values plotted for each batch, comprised of the averaging of its component cells, and c) the representative lifetime capacity fade for each batch.	154
Figure 4-21. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of all cells cycled on the Novonix cycler, b) CE values plotted as a result of the averaging of all cells and c) cycled on the Digatron setup only. d) is the normalised capacity fade lifetime data of all batches of all cells and e) a magnified region displaying only the first 1000 cycles.	157
Figure 4-22. a) ΔV and b) its normalised value for all cell types.	158
Figure 4-23. CE values, discharge capacity and normalised discharge capacity values of the last 10 cycles prior interruption for capacity check and the 10 cycles after it for a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite cells.	160
Figure 4-24. CE values, discharge capacity and normalised discharge capacity values for cells cycled directly without capacity check first compared with the first 10 cycles of the cells shown previously on the Novonix for a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite. Insets for CE are displayed to allow for an assessment of the differences shown particularly for the first cycle.	161
Figure 5-1. Cycling profiles with voltage and current applied for the first cycle for a) CCCV, b) VCP, c) LowEnd and d) LowStart, on an MJ1 cell as an example.	166
Figure 5-2. a) Voltage vs capacity curves, b) incremental capacity analysis, c) dVdQ and d) dVd(SoC) plots of fresh MH1, MJ1 and M50 cells.	170
Figure 5-3. a) and b) DVA plot with explanation of relevant peaks for MH1 and M50 cells respectively. c) and d) key distances between relevant peaks, referred to as “Q” that will be tracked throughout this chapter. The data in a) & c) and b) & d) is identical but replicated for clarity of labelling.	172
Figure 5-4. IR values across the battery SoC through full charge followed by discharge obtained by HPPC, measured at 20°C.	173
Figure 5-5. a) and b) Measured discharge capacity, c) and d) normalised discharge capacity, e) and f) measured CC and CV capacity per charge per cycle and g) and h) CV capacity and time contribution in percentage per charge per cycle for MH1 and MJ1 respectively at 20°C.	175
Figure 5-6. a) and b) Total cycle, charge and discharge times per cycle number, and c) and d) time spent in CC and CV during charge per cycle for MH1 and MJ1 cells respectively.	177
Figure 5-7. a) and b) Measured overpotentials during charge and discharge, c) and d) average voltages per cycle (charge, charge without CV and discharge), e) and f) polarisation (ΔV) considering CC and CV for charge compared to charge without CV, and g) and h) normalised polarisation.	179

Figure 5-8. Coulombic efficiency per cycle of a) MH1 and b) MJ1 cells. An inset is displayed in b) while allowing a comparison between both cells types.	180
Figure 5-9. a) and b) Measured discharge capacity, c) and d) normalised discharge capacity, e) and f) measured CC and CV capacity per charge per cycle and g) and h) CV capacity and time contribution in percentage per charge per cycle for MH1 and MJ1 respectively at 0°C.....	183
Figure 5-10. a) and b) Total cycle, charge and discharge times per cycle number, and c) and d) time spent in CC and CV during charge per cycle for MH1 and MJ1 cells respectively.	184
Figure 5-11. a) and b) Measured overpotentials during charge and discharge, c) and d) average voltages per cycle (charge, charge without CV and discharge), e) and f) polarisation considering CC and CV for charge compared to charge without CV, and g) and h) normalised polarisation.	186
Figure 5-12. CE per cycle of a) MH1 and b) MJ1 cells.	187
Figure 5-13. Voltage profiles of a) MH1 LowStart, b) MH1 LowEnd and c) MJ1 LowStart at various cycles displaying a positive voltage recovery during discharge.	188
Figure 5-14. Incremental capacity analysis for MH1 cells at a) 20°C and c) 0°C respectively, and MJ1 cells at b) 20°C and d) 0°C respectively.	190
Figure 5-15. dVd(SoC) plots for MH1 cells at a) 20°C and c) 0°C respectively, and MJ1 cells at b) 20°C and d) 0°C respectively.	191
Figure 5-16. Calculated DVA markers for a) MH1 and b) MJ1 cells, with subsequent losses fraction of capacity from each marker compared to the fresh cell during the ageing for c) MH1 and d) MJ1 cells.....	193
Figure 5-17. Discharge capacity and average temperature per cycle for the VCP_01 and LowEnd_02 cells between cycles 25-50.....	194
Figure 5-18. Normalised discharge capacity per cycle for all M50 cells, cycled at ambient temperature.	195
Figure 5-19. a) Capacity contribution of the CV phase for charge in percentage and measured overpotentials for b) charge and c) discharge.	197
Figure 5-20. a) Incremental capacity analysis, b) dVdQ, c) dVd(SoC) plots and d) inset of the dVdQ plot focusing on the SiO _x phase transitions.....	199
Figure 5-21. a) DVA plot of the diagnostic cycles performed on LowEnd_02 and b) inset focusing on the evolution of the two SiO _x peaks.....	200
Figure 5-22. a) Calculated DVA markers and subsequent calculated capacity losses in percentage.	201
Figure 5-23. Nyquist spectra of a fresh M50 cell measured during discharge at 100%, 95%, 75%, 50%, 5% and 0% SoC.	203
Figure 5-24. Calculated R _Ω and R _{ct} values for all cells at 100%, 95%, 75%, 50%, 5% and 0% SoC.	204
Figure 6-1. Capacity retention of cylindrical cells calendar aged at different storage SoC and temperatures for a) 0°C, b) 25°C, c) 45°C and d) 60°C. The coloured crosses represent cell failure. Data collected by Dhammika Widanalage at WMG.	211
Figure 6-2. Capacity retention of cylindrical cells calendar aged as a function of time for the batches stored at a) 0°C, b) 25°C, c) 45°C and d) 60°C. Data collected by Dhammika Widanalage at WMG.	212

Figure 6-3. Resistance data obtained from DCIR measurements for cells calendar aged at a) 0°C, b) 25°C, c) 45°C and d) 60°C as a function of time. Data collected by Dhammika Widanalage at WMG.	213
Figure 6-4. Cycling performed after storage of cells at 80% and 100% SoC of the 25°C and 70 weeks batch. The capacity recovery at cycles 50, 100 and 200 are due to pauses during the cycling. Further cycling carried out by Eleni Fiamegkou at WMG.	214
Figure 6-5. Reconstructed tomograms of the cylindrical cells from various SoC, storage time and temperatures. The tomograms correspond to a) and b) two fresh cells, c) and d) 80% SoC at 25°C stored for 29 and 52 weeks respectively, e) and f) 90% and 100% SoC respectively at 25°C stored for 52 weeks and g) and h) 80% SoC stored for 70 weeks at 25°C and 60°C respectively. Annotations highlight the area of influence of the intercalated Al tab, where some electrode deformation is observed in cells stored for 52 weeks or longer. The scale bar displayed represents 10mm. ...	216
Figure 6-6. Reconstructed tomogram of a fresh cell with highlights of the tab area of influence, radial strain and compressive stress due to the geometric arrangement of the jelly-roll.	218
Figure 6-7. Photographs of the disassembled cylindrical cells, at a) fresh, b) 80% SoC and c) 100% SoC, from the 25 °C and 70 weeks batch. Particular attention is brought to the state of the cathode, anode and their corresponding side of the separator..	219
Figure 6-8. Photographs of anode side of the separator from a cell stored at 100% SoC, from the 25°C and 70 weeks batch, with distinction between areas at the outside and close to the core of the jelly-roll.	220
Figure 6-9. Coin cell voltage over capacity of harvested cylindrical cell's cathode material vs Li. Inset is displayed for clarity to ass total discharge capacity. The data represents the second C/20 cycle after assembly.	222
Figure 6-10. a) NPD of the cathode material of fresh, 30% SoC, 60% SoC, 80% SoC and 100% SoC cell of the 25 °C and 52 weeks batch. b) XRD of the cathode material of fresh and 80% SoC cells of 29 and 70 weeks of the 25°C batch.	223
Figure 6-11. SEM/EDX of SiO _x particle in a cell aged for 70 weeks at 100% SoC and 25°C, where a) is the SEM microgram, b) Silicon EDX signal, where an uneven signal represents the particle degradation; c) the Fluorine signal, which indicates electrolyte decomposition and d) the Carbon signal which is a proxy for the SEI formed on the surface. Images obtained by James Gott from WMG.	224
Figure 8-1. Nyquist spectra of BoL and EoL at 50% SoC of a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite cells.	271
Figure 8-2. Coulombic efficiency values with consideration of the first cycle for each batch on average for a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite cells.....	272
Figure 8-3. dVdQ plots for MH1 cells at a) 20°C and c) 0°C respectively, and MJ1 cells at b) 20°C and d) 0°C respectively.	273
Figure 8-4. LowStart_02 cathode sample a) microgram showing formation of intragranular crack in a primary particle and b) inset showing structural changes from layered structure to RSL (yellow rectangle) towards the crack region. c) and d) represent the average core-loss EELS spectra of LowStart_02, LowEnd_02 and Fresh arranged from top to bottom where the fine structure EELS is shown for c) the Oxygen K-edge and d) the Nickel L ₃ /L ₂ edges. Vertical dashed lines indicate relevant, expected	

peak positions and are shown as a guidance to the eye. Data gathered by May Ching Lai from Cambridge University.	275
Figure 8-5. NPD data of a) all cells, and refined data and residuals for b) fresh, c) 30% SoC, d) 60% SoC, e) 80% SoC and f) 100% SoC of the 25°C and 52 weeks batch.	276

1 Introduction

1.1 Motivation

The generalised use of hydrocarbons as fuels since the beginning of the 20th century has helped our society to grow economically in an unprecedented way. This growth is also characterised by a rapid population increase, alarming pollution levels due to fossil fuel use, and serious issues regarding global warming. Another issue is the fact that hydrocarbon sources of energy are being depleted, which will lead to a logical rise of the price in oil and natural gas, as they will be rarer and more difficult to extract. Numerous expert panels, policy-makers and scientists, have repeated numerous times that new energy sources and energy storage technologies need to be implemented rapidly, and are part of the solution to efficiently resolve these issues^{1–3}. These viable technologies already exist, and just need more consideration, funding or development in order to be fully adopted.

Electrification is widely recognised as a pivotal strategy in combating global warming, primarily due to its potential to significantly reduce greenhouse gas emissions⁴. The transition from fossil fuel-based energy systems to electrified alternatives, particularly when powered by renewable energy sources, directly addresses the root cause of global warming by decreasing the reliance on carbon-intensive energy⁵. This shift is especially critical in sectors such as transportation and industrial processes, where electrification can lead to substantial emission reductions^{6–8}. Moreover, advancements in battery technologies and the development of sustainable energy storage solutions further enhance the effectiveness of electrification, making it a cornerstone of global decarbonisation efforts⁹. Several publications have highlighted that a full electrification and energy transition to better tackle climate change is possible and reachable if action is taken on a global scale^{10–13}. However, another extensive and thorough study tempered this optimism, and showed the exact opposite, hinting that such a transition is only ever possible with a shift in paradigm in perspective and in reducing global consumption, increasing recycling and better use of resources; which only highlight the complex task ahead, at all levels¹⁴.

To respond to this global problem, batteries are currently considered the most suitable technologies to store energy, allowing electricity to be stored efficiently and with a high energy density, being a key element necessary in domains such as portable electronics. Both primary (single-use) and secondary batteries exist, however, secondary devices seem to have received the most interest and are seen as the overall best option^{15,16}. As Figure 1-1 displays, Li-ion batteries are presented as an integral solution for energy storage, as they offer high specific and volumetric energy densities, a long cycle lifetime, a low self-discharge rate, and a high operational voltage¹⁷. Indeed, they will be able to have a major role in reducing the emissions of CO₂ and more toxic gases as they are expected to limit the necessity of the use of fossil fuels and the internal combustion engines used for transportation. It is relevant to state that most of the research and progress achieved regarding Li-ion technology presented in this thesis is motivated by the economic incentive of its early application within portable electronic devices, and in more recent years, due to advancements in energy density, safety and cost reduction, the automotive industry. Replacing every single current internal combustion engine car with hybrid-electric (HEV) or electric vehicles (EV) could potentially represent a trillion pounds market¹⁸. This economic incentive has stimulated research and drawn a lot of funding from governments and private companies, with the ultimate goal of electrifying the automotive sector.

At the cell level, the gradual reduction in capacity over time is well documented, with causes that differ based on the materials used and the operating environment. This capacity fade stems from both the active cycling of the cell (cycle-related losses) and from degradation mechanisms that persist regardless of cycling, collectively known as calendar ageing¹⁹. Calendar ageing is particularly crucial in applications where Li-ion batteries experience long periods of inactivity, such as in electric vehicles, which may remain idle for up to 96% of their lifespan^{20,21}. This form of ageing encompasses all processes that contribute to the cumulative degradation of a battery, independent of the charge-discharge cycles. Unlike cycle ageing, where mechanical strain and lithium plating are primary factors, calendar ageing is characterised by the growth or modification of passivating layers that consume active lithium^{22,23}. Understanding the mechanisms behind calendar ageing is essential for improving the longevity and reliability of EV systems, making them competitive with internal combustion engines.

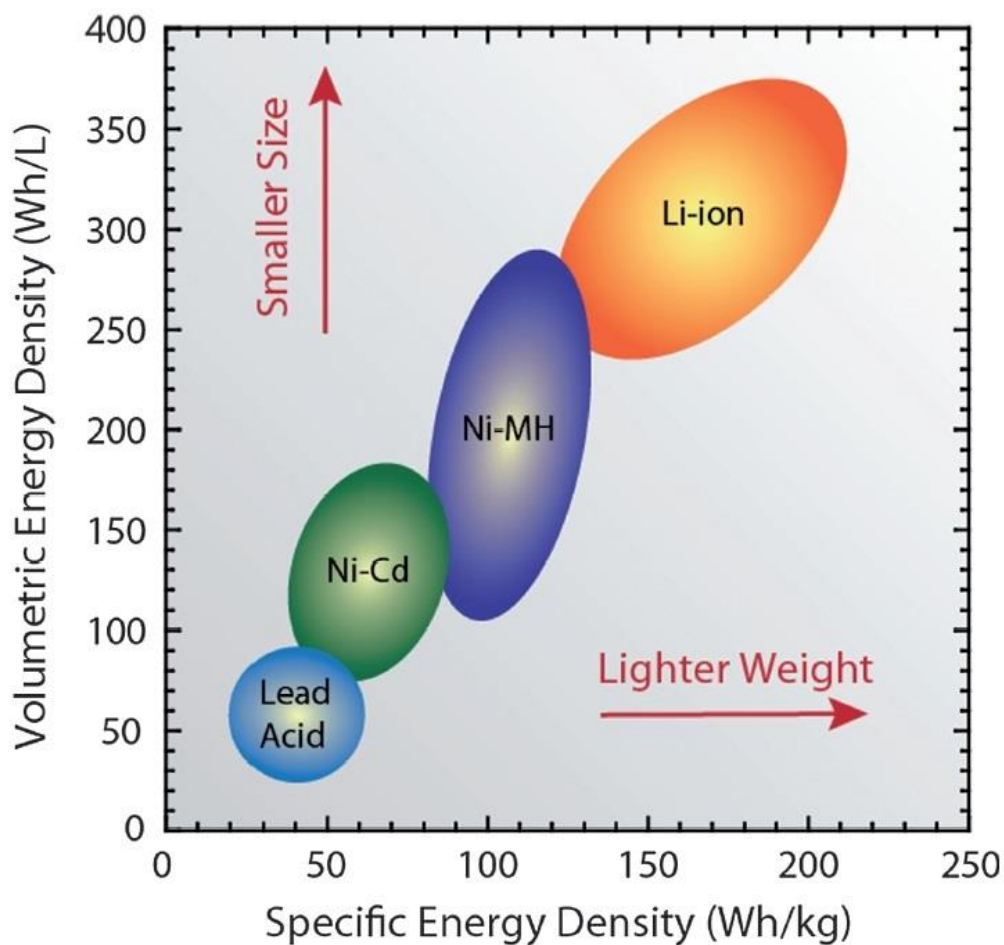


Figure 1-1. Diagram comparing various secondary battery technologies as a function of volumetric and specific energy densities. Reproduced from B. J. Landi et al.²⁴

Li-ion batteries have been extensively studied over the past decades. There have been major improvements and breakthroughs regarding the materials used for the cathode material (such as LiCoO_2 (LCO), LiFePO_4 (LFP), $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC) etc.) or overall design (such as cylindrical jellyroll electrode structure or electrolyte choice). However, despite the progress made in the past years, there is still much to learn in the interplay between material properties (such as crystallography, morphology and microstructure) and performance, with complex degradation modes affecting the long-term cycle life of batteries. This is especially true when failure happens or to estimate a forecast of said failure. Furthermore, there is a growing demand for these batteries to have an ever-increasing energy density, operate in more challenging conditions and be more efficient and cheaper, while safety remains a priority. There is, globally, a wider range of combinations of active materials within the

battery and many various temperatures, pressures and external conditions under which they can operate, which complicate the understanding of degradation mechanisms (both short and long terms) and failure.

The recent advancements in X-ray imaging, particularly in lab applications, have seen the technique being applied to electrochemical devices in numerous innovative ways^{25–27}. The non-destructive nature of X-ray computed tomography allows operando experiments to be conducted and the evolving microstructure of batteries to be studied throughout their lifetime. More established characterisation techniques such as X-ray diffraction have also found widespread use in operando and in situ experiments of batteries to follow the evolving crystallography during charge and discharge²⁸, enabling understanding of the behaviour of Li intercalation compounds under working conditions. More recently, micro-focused synchrotron radiation has allowed spatially resolved XRD to be carried out, producing 3D maps of the battery microstructure where each pixel contains a full X-ray diffractogram²⁹. These are just some examples that have become major milestones over the years that have helped deepen our understanding of the complex processes involved in Li-ion batteries.

1.2 Lithium-ion batteries

Li-ion batteries present several advantages compared to other types of batteries, notably due to their high energy and power density, which make them suitable candidates to tackle the global energy transition issue. Historically, lithium has been studied since the 1950s as a potential battery material³⁰ but took off in the 1970s when the price of oil nearly quadrupled during the oil crisis of 1973-74³¹, stimulating research on alternative energy sources and storage. In 1976, Stanley Whittingham, while working for Exxon Mobil, started exploring the integration of intercalated materials within Li-ion battery systems such as titanium disulphide and he soon realised that lithium metal tended to form dendrites, potentially complicating the commercialisation of this new promising cell³². Shortly after, John Goodenough showed that LCO presented the most promising results as a cathode material for said cell, with both high voltages and current densities achieved³³. After several advancements and testing of other materials, it was in 1991 that Sony commercialised

for the first time a Li-ion battery with a carbon-based anode, changing the landscape of energy storage technologies. This was the first demonstration of what we now call the Li-ion battery. Since then, a whole new generation of devices have been created and have revolutionised our society with the portability aspect as the main feature, such as smartphones and laptops, and this is why Li-ion batteries are the most suitable candidates to take part in the electrification of the automotive industry over the next decades³⁴. This pioneering research carried out over the years saw Whittingham, Goodenough and Yoshino recipients of the Nobel Prize in Chemistry in 2019, crowning the age of Li-ion batteries³⁵.

The well-established design, choice of materials, consequent investments in fundamental research, early commercialisation and the large-scale construction and establishment of Giga Factories across the UK, Europe and the world demonstrate that Li-ion batteries are here to stay. The mutual interests of the public sector, industry and consumers seem to indicate that this will be the case. Only major breakthroughs such as Solid-state, and Li-metal anode that show to work and be reliable, especially on long-term cycling will convince the industry to readapt the current supply chain and assembly lines of the current state of Giga Factories³⁶. While progress has been made in other cell technologies, such as Sodium-ion, Lithium-Sulphur, Potassium-ion³⁷ or Lithium-Air, it will take a leap for a major shift in the current EV, grid-storage or the defence and space sector to adopt them on a large-scale. Of these technologies, Sodium-ion seems to be the most technologically advanced, with major battery companies recently offering these cells, where a particular benefit is that the technology allows for drop-in materials replacement in existing manufacturing lines³⁸.

1.3 Objectives

The primary goal of this project is to understand degradation within Ni-rich cathode materials of Li-ion batteries. As further comprehension of these complex mechanisms is reached, mitigation or alternatives will be able to be used by manufacturers. Experiments were also carried out on older cathode materials such as the previously introduced LCO or lower Ni ratios within NMC materials. However, there is a vast range of degradation mechanisms that are still not fully understood, that occur

in a wide range of different temperatures, voltage, applied currents, materials, cell configurations or SoC of the battery, and as it will be shown, the anode will also be prevalent throughout this work as a significant driver of degradation.

It is also important to state that this project aims to study purely degradation mechanisms of the electrodes of Li-ion batteries, but also to take into consideration real-world application of such parameters, particularly for the automotive industry where high-Ni NMC materials are a priority for the next generation of vehicles³⁹. Hence, an attempt to combine conventional electrochemical characterisation techniques but also real-world engineering applications is investigated in this thesis. An example can be the use of commercial cylindrical cells in most experiments (and as such, as a full-cell system configuration) rather than coin cells in half-cell configuration, to study materials and systems more relevant to automotive applications.

Contributing to the already extensive literature available on forecasting capacity fade and performance, a project was carried out using HPC to attempt to provide a reliable forecasting fade behaviour technique, when put in the context of the space sector, where this is capital, as it will be shown in Chapter 4. The study was immensely helped by the provision of very long-term and extensive existing data of cells used, with the aim of confirming the potential of the HPC methodology applied.

Furthermore, Chapter 5 covers the development of various specific variable current protocols (VCPs), where the goal was to show precisely at which stage of the SoC of the battery the main degradation mechanisms contribute to capacity or power fade, and to mitigate it by adjusting the charging protocol. This was done at various temperatures and C-rates as well, and a wide range of parameters and metrics were followed, such as polarisation values, overpotentials, time spent at each charging stage etc. Particular attention was drawn to the time spent at high voltage and high SoC during cycling, that each protocol maximises or minimises, as it has been widely accepted as a sensitive SoC area in literature, prone to SEI growth and cathode structural disordering.

Lastly, Chapter 6 shows a part of another collaboration project introduced previously, which focuses on the calendar ageing of cells, with an extensive test matrix of 224 cells at four different temperatures. It tackled the study of the notable “spoon-

shape” effect observed in several other studies, and yet still poorly understood, despite the various explanations proposed by different papers.

As such, this thesis attempts to address the critical questions: how do specific degradation mechanisms within high-Ni lithium-ion batteries contribute to capacity and power fade, and how can these insights guide long-term cell lifetime forecast, enhanced real-world cycling protocols or improved cell storage conditions? Central to this investigation is the dynamic and complex interplay of known primary degradation mechanisms such as SEI growth or cathode structural disordering. Key stressors, such as prolonged high-voltage operation and high SoC, accelerate these mechanisms and trigger linked processes that further restrict lithium transport, increase impedance, and trap lithium, cumulatively affecting the operational effects: capacity and power fade.

This work also attempts to provide insight into the effect of temperature, which was key for instance, in the consideration of the right cycling conditions for the HPC study, as it is directly linked to SEI growth and parasitic reactions for instance. By decoupling the contributions of individual electrodes, the goal was to identify and pinpoint more accurately the underlying primary degradation mechanisms or modes of the positive or negative electrode. Direct observations via various imaging techniques of the electrode materials, or the indirect assessment of individual key markers via diagnostic tools such as incremental capacity and differential capacity analysis (ICA and DVA, respectively), proved themselves useful in this decoupling effort.

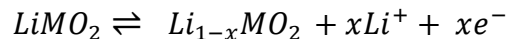
Furthermore, it is important to highlight that these studies were carried out on commercial 18650 or 21700 cylindrical, legacy and recent cells of various chemistries. It attempts to provide a broad overview of some of the evolution of cell designs, and materials (such as the move from hard carbon to graphite, and the increase of Ni content within NMC cathodes), as well as attempting to show that reliable and relevant data and information can be obtained from these commercial cells, despite some unknown parameters that is implied from working with them, such as the cell's electrolyte additives, rarely disclosed by manufacturers.

2 Literature review

2.1 Fundamentals of the lithium-ion battery

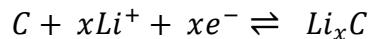
The main components of a Li-ion battery are: a positive electrode (referred to as the cathode), a negative electrode (referred to as the anode), and an electrolyte capable of transferring Li^+ ions. For Li-ion batteries, while cathode materials vary, the latest and most promising designs include layered metal-oxides (here represented as LiMO_2 , where M is a transition metal), and the anode is usually graphite-based. During the use of the battery, over charge/discharge cycles, the lithium ions are exchanged between the electrodes via the electrolyte. However, there is a significant change in the crystallographic structure of both the anode and cathode materials during (de)intercalation. During the discharge of a cell, lithium ions move from the anode to the cathode, while during the charge, this process is reversed, with an accompanying change in the oxidation state of the transition metal (TM) when Li^+ intercalates and deintercalates. The ions are intercalated within the electrodes' crystal lattices, and subsequently removed in a series of topotactic reactions⁴⁰. These reactions are presented in the equations below. These are half-reactions, different for both the negative and positive electrodes, where for each equation, the half arrowhead pointing towards the right represents the charge direction and discharge when pointing to the left:

At the positive electrode:



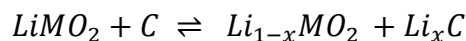
Equation 2-1

At the negative electrode:



Equation 2-2

Overall:



Equation 2-3

Usually, within a Li-ion battery, the electrodes are soaked in the liquid electrolytic solution for optimum conductivity within the cell and optimising the lithium ions transport processes. However, for safety purposes and to avoid internal short circuits (one of the main reasons for cell failure^{41,42}), a separator is integrated into the cell design. This microporous layer is electrically insulating but allows for Li ion transport through the electrolyte that permeates its pores, facilitating ion exchange between the electrodes. A design for a typical Li-ion cell is presented in Figure 2-1 below:

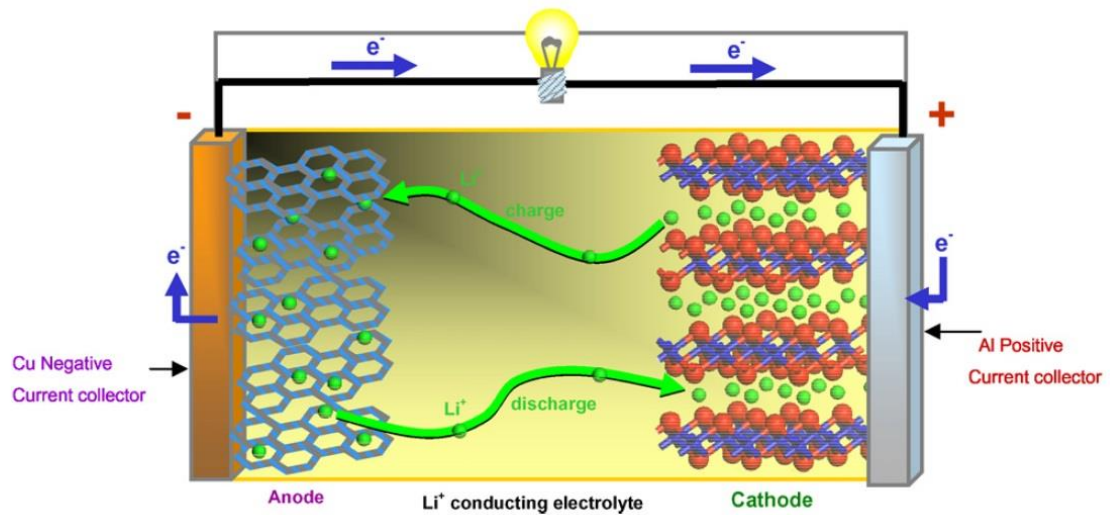


Figure 2-1 Schematic of the charge and discharge processes of a lithium ion cell. It is noted that the separator is not represented in this image. Reproduced from A. Patil et al.³⁴

Therefore, the potential path of a Li^+ ion within a Li-ion cell is displayed in Figure 2-2:

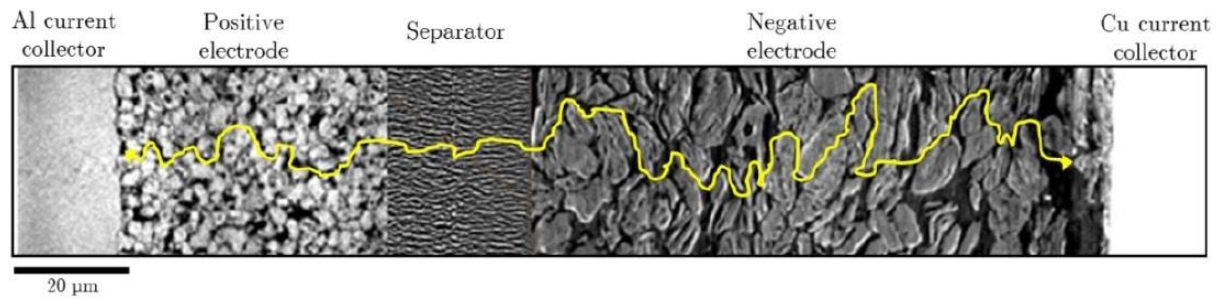


Figure 2-2. Reconstructed tomograms showing the microstructure of a commercial cell. The yellow line shows a possible path taken by a Li^+ ion. Reproduced from D. Finegan⁴³.

In more details, each Li^+ ion undergoes a specific solvation/de-solvation process unique to the charge/discharge process the battery is undergoing as shown in Figure 2-3.

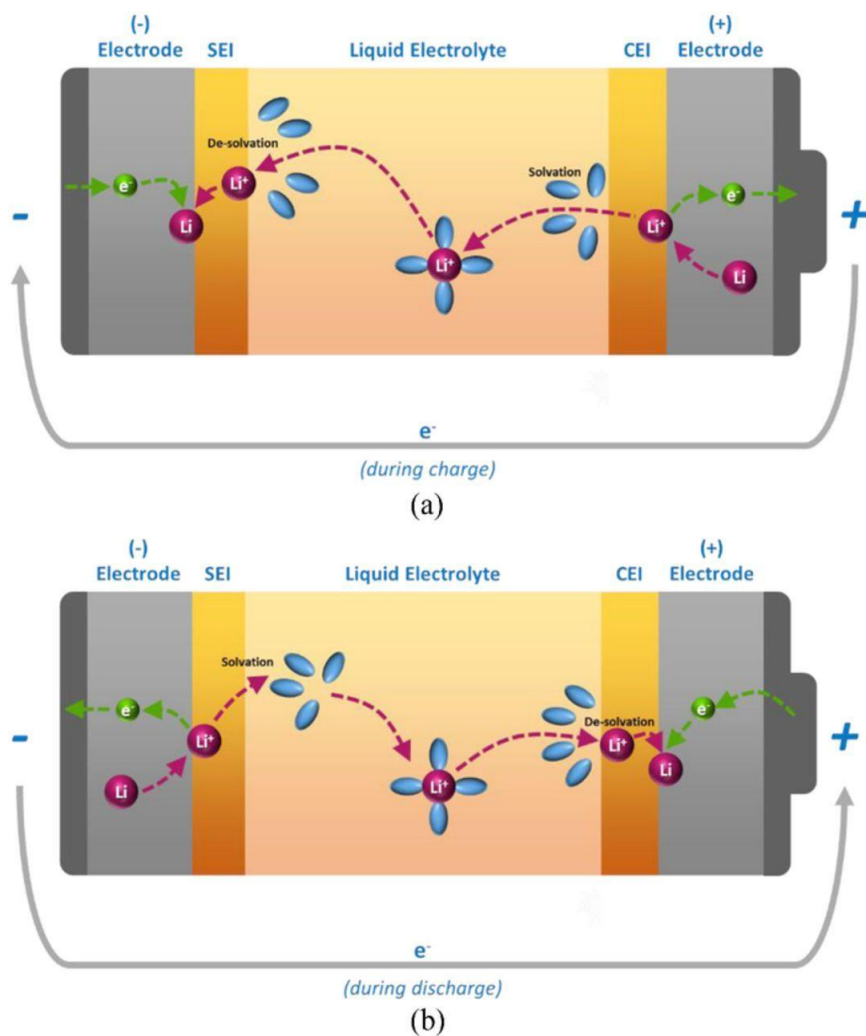


Figure 2-3 (a) Schematic view of Li⁺ charge during charge (b) Schematic view of Li⁺ charge during discharge. Reproduced from Jow et al.⁴⁴

Furthermore, regarding the energy that a typical cell produces, the maximum energy release is defined by the change in the Gibbs free energy: ΔG° . This accounts for the whole battery system, and is defined in Equation 2-4⁴⁵:

$$\Delta G^\circ = -nFE^\circ$$

Equation 2-4

Where n is the number of electrons produced per mole, F the Faraday constant and E° the standard electromotive force in Volts. The electromotive force (E) is defined numerically by the Nernst equation, as the chemical difference of the components between the whole Li-ion battery. However, not all this theoretical available energy is converted to electrical energy, as a significant part of it is lost as heat due to polarisation losses linked to the activation energy needed, and the formation of a mixture of reactants and products at the surface or within the electrodes, creating various gradients, due to the reactions taking place⁴⁶. These losses are related to the material used for each component of the cell. Additional losses are also due to Li⁺ diffusion, tortuosity⁴⁷, and these losses tend to be higher with higher rates, and therefore voltage efficiency tend to decrease with higher currents. For example, Billaud et al. showed in a study that magnetically orientating electrode particle in a way that reduces tortuosity, rate performance of a cell can be significantly improved⁴⁸.

2.2 Battery components

Li-ion batteries have evolved quite significantly over the past decades, regarding materials used, overall structure and many other aspects. From the early stages titanium disulphide and lithium cobalt oxide for the cathode material to new materials like layered metal oxides or the inclusion of vanadium, many transition metals have been investigated. Regarding the material at the anode, it has been consistently based

on graphite since the first battery commercialised by Sony in 1991. Generally, the materials used for both electrodes are summarised in Figure 2-4 but will be studied into more details in the following sections. It shows that a lot of research needs to be done in order to include the most promising materials in commercially viable Li-ion cells.

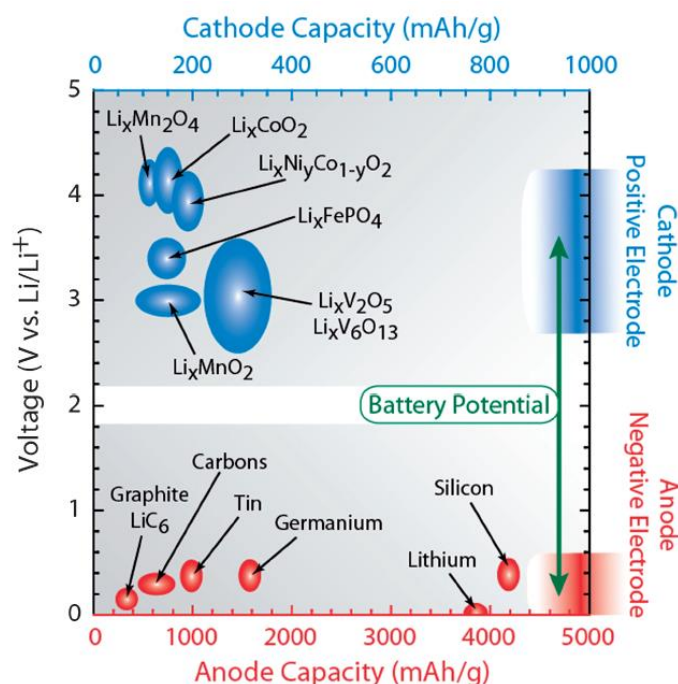


Figure 2-4. Diagram showing the electrochemical potential of certain materials compared to lithium for the anode (red) and the cathode (blue). Reproduced from B. J. Landi et al ²⁴.

As it becomes apparent, a high voltage is desirable for a potential commercial cell. In combination with high energy density electrode materials, a high voltage window allows more energy available for use⁴⁹. However, increasing the voltage window can lead to overcharge, increased flammability and to potentially trigger a whole range of various degradation mechanisms⁵⁰.

2.2.1 Positive electrode

As stated previously, layered transition metal-oxides are usually used as cathode material for most Li-ion cells, coated on an aluminium current collector. The metal used is usually a transition metal such as cobalt, nickel or iron combined with other elements, such as manganese or aluminium etc. Their high energy density and good reversible capabilities are suitable for the required function. Hence, the most common materials used are Lithium Manganese Oxide (LMO), Lithium Cobalt Oxide (LCO), Lithium Iron Phosphate (LFP), Nickel Manganese Cobalt Oxide (NMC) and Nickel Cobalt Aluminium Oxide (NCA). The principal characteristics, mainly found in the Linden's Handbook of batteries⁵¹ are summarised in Table 2-1, below.

Table 2-1. Characteristics of most the common cathode materials available and studied for Li-ion batteries.

Material	Specific capacity (mAhg ⁻¹)	Brief comment
LiCoO ₂ (LCO)	155	High theoretical capacity, but expensive, thermally unstable at high currents and ethical concerns linked to cobalt
LiMn ₂ O ₄ (LMO)	100 -120	Quite low capacity and known capacity fade over time, but low cost, thermally stable and low environmental impact
LiFePO ₄ (LFP)	160	Cheap, thermally stable and durable but low rate capability and elevated self-discharge
LiNi _{1-x-y} Mn _x Co _y O ₂ (NMC)	140 - 200	Safe and cheap compared to others. Variable capacity depending on stoichiometry. High voltage and capacity
LiNi _{1-x-y} Co _x Al _y O ₂ (NCA)	160 - 210	High specific capacity, voltage window and long life span. But presents safety issues and high cost ⁵²

The ethical problems stated in Table 2-1 for the use of cobalt are linked to the fact that most of the cobalt used around the world comes from Sub-Saharan African mines where child labour and even sometimes slavery (renamed “forced labour”) is used to extract it⁵³. LiCoO₂ was probably the material of choice for the positive electrode for over a decade since its inception, however, it is preferable to find other alternatives in order to avoid these humanitarian problems surrounding the extraction of cobalt, especially for such a large market as the electrification of the whole automotive industry. In addition, safety problems linked to high flammability related to

LCO have led to the more wide-spread adoption of materials where the Co is replaced by Ni and Al (NCA) and Mn (NMC).

These cathode materials are generally enhanced by manufacturers using various carbon coatings and doping to either cope with a low electrical conductivity, to improve stability or protect the material from reaction with the electrolyte. Common additives revolves around the use of carbon in various forms such as graphite, carbon nano-tubes, carbon fullerene-based structures, or the incorporation of graphene lattices⁵⁴. This addition is determined by elements like chirality²⁴, purity, length, and the cathode based material. Additional coating materials has been extensively studied and usually tends to increase rate capability and the low-temperature performance for LMO cathode based cells for example⁵⁴, or enhance overall conductivity by increasing the electrode porosity, and hence, shortening the solid-state diffusion distances in LFP cells^{55,56}. An example of NMC cathode material shown by SEM evidencing the conductive carbon and binder domain.

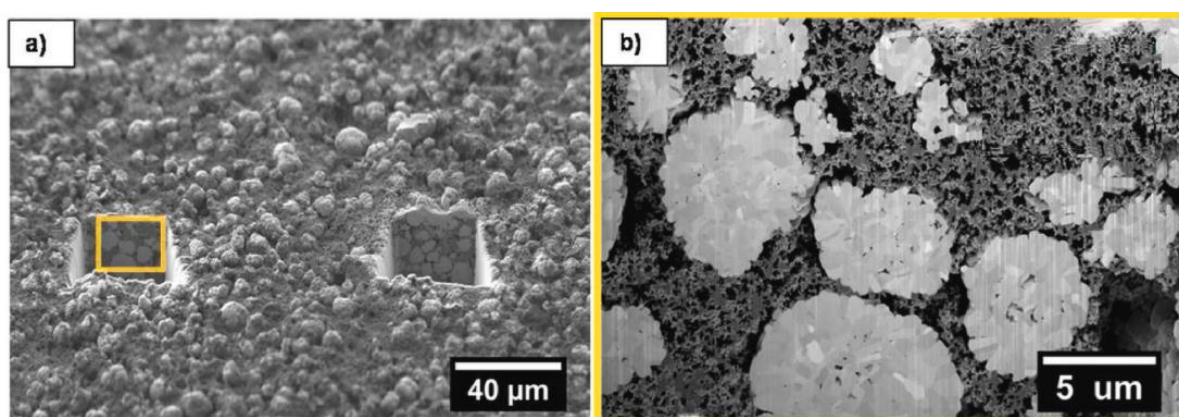


Figure 2-5. SEM micrograph a) showing two trenches milled into NMC cathode and b) a cross section of cathode clearly visualising active material particles and the carbon binder domain. Reproduced from Entwistle et al.⁵⁶

However, the research for positive electrode materials is extensive and goes beyond the scope of this review. Indeed, some papers highlight the complexity of this aspect, stating that parameters such as geometric and transport tortuosities, or pore constriction and twistedness are crucial for the understanding of cathode performance, and that more research and development of new models need to be done⁴⁷. In a more

immediate future and as it will be shown in this review, manufacturers are actively looking into Ni-rich based cathode with lower cobalt content, based on the NCA and NMC chemistries⁵⁷. As the Ni content is increased within their stoichiometry, energy density is also enhanced as it equivalent to approaching LiNiO_2 (LNO). However, LNO, despite its promising energy density and lower cost did not become a commercial reality for manufacturers as it also presented major drawbacks such as the control of the precise material composition during synthesis, and chemical, thermal and mechanical stability issues⁵⁸. Hence, other cations were found to partially replace nickel within the electrode. Cobalt is used to control the stability of the 2D parameter of the layered structure as a whole during Li extraction⁵⁹, while either Mn or Al were added in order to thermally and structurally stabilise the material. This resulted in the NMC and NCA chemistries, where a trade-off between capacity, stability and cost was found, and became viable materials for the automotive sector, where high energy density and low cost are a must. Therefore, this current area of research is extremely active and have led to hundreds of papers and several reviews, and has established the NMC cathode material with increasing Ni content as current state of the art. Hence, the study of its behaviour and specific degradation mechanisms has become the central part of this thesis.

2.2.2 Negative electrode

The negative electrode material has been mostly carbon-based since the first commercialisation of the Li-ion battery made by Sony in 1991. Graphite is extensively used in commercial cells with graphitic particles smaller than 30 μm , coupled to a copper current collector, as Al has a tendency to alloy with Li at these specific potentials⁶⁰. Typically, it is the disorder of the carbon-based material that determines the specific capacity and overall performance². For example, petroleum coke was used in the original 1991 Sony battery, with a specific capacity of 180 mAhg^{-1} , while the theoretical specific capacity of graphite of graphite is 372 mAhg^{-1} . Petroleum coke is highly disordered compared to graphite, resulting in a lower specific capacity.

Soon after, hard carbon (HC) followed as a reliable material of choice to be used in commercial Li-ion batteries before being almost universally replaced by

graphite^{61,62}. Unlike graphite, HC consists of a disordered arrangement of graphitic and amorphous regions, which provide abundant storage sites for lithium ions. This material offers higher reversible capacities and better performance at low temperatures compared to traditional graphite anodes^{63,64}. Additionally, HC demonstrates improved safety, as it is less prone to forming lithium dendrites compared to graphite, which can cause short circuits and battery failure. The structural disorder also contributes to a broader voltage plateau during discharge, making HC suitable for both high energy and high power applications in advanced battery technologies, and also as a negative electrode for newer or future battery technologies such as Sodium and Potassium-ion batteries^{65–67}. However, the renewed interest in HC is significantly slowed by the low initial CE, large initial irreversible capacity, and voltage hysteresis⁶⁸. Additionally, in addition to the intercalation displayed by graphite, HC materials also rely on adsorption processes at above 80% lithiation⁶⁹. Comparison between graphite and HC anodes discharge potentials are shown in Figure 2-6, below.

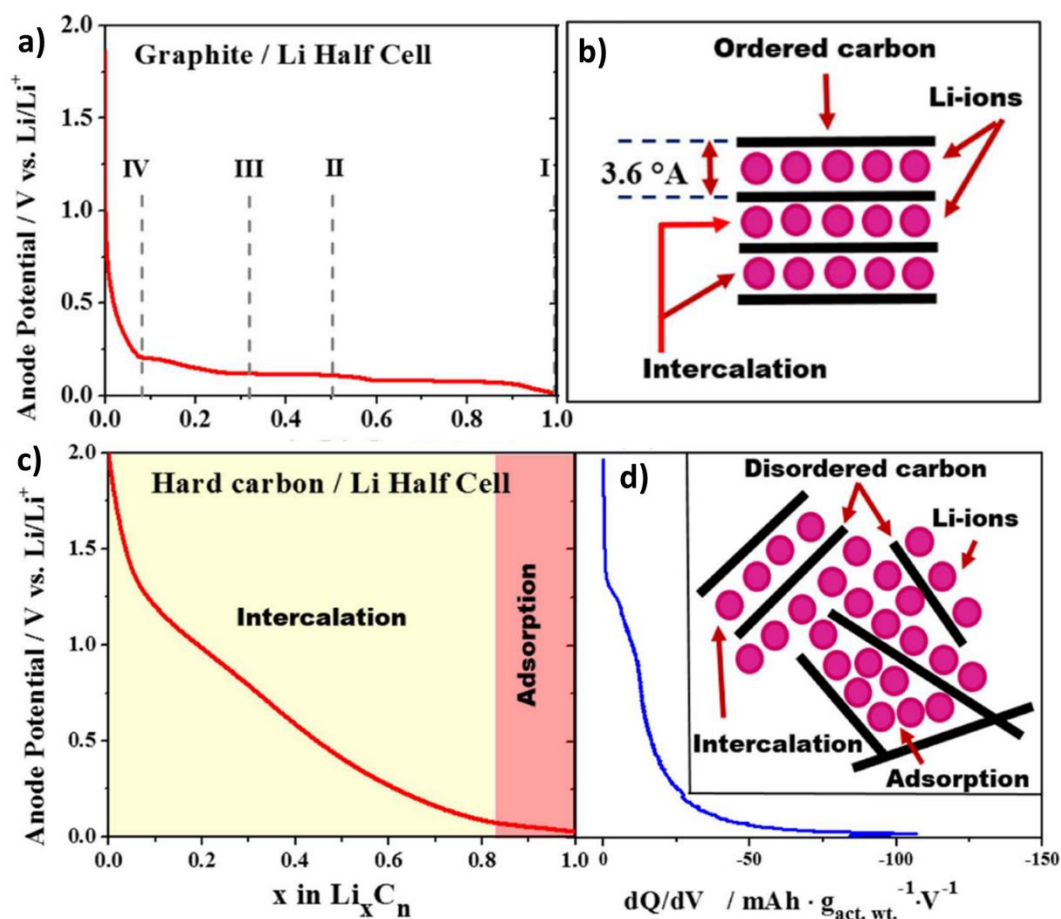


Figure 2-6. a) and c) cell charge potential vs. Li/Li^+ as a function of lithiation state in a Li-graphite and hard carbon half-cell respectively, with stages marked for corresponding voltage plateaus, b) and d) schematic representation of the ordered crystal structure in lithiated state for graphite and hard carbon respectively, as well as differential capacity with respect to anode potential curve for hard carbon in d). Reproduced from Shellikeri et al.⁶⁹

However, graphite remains the essential anode material of choice in commercial Li-ion batteries due to its balanced capacity, stability, and cost-effectiveness compared to emerging alternatives, solidifying its role as a fundamental material in Li-ion technology⁷⁰. Two main types of graphite are available in battery applications: natural and synthetic graphite. Natural graphite, which is mined and then processed, is known for its anisotropic crystalline structure, which can hinder fast lithium intercalation unless particles are further processed or coated, while synthetic graphite is produced through high-temperature carbonisation of petroleum or similar materials, offering a more consistent and thermally stable structure, albeit at a higher cost⁷¹. Furthermore, the crystalline domains of natural graphite align more uniformly,

offering excellent conductivity and high lithium storage potential due to large crystalline structures, as opposed to synthetic graphite, which is isotropic, with randomly oriented crystals, which generally benefits cycling stability but at a higher manufacturing cost and slightly lower energy density⁷². Both forms have distinct performance advantages, and manufacturers frequently blend them in commercial applications, capitalising on the high capacity of natural graphite and the stability of synthetic graphite, optimising cost-effectiveness and cycle life.

In future developments, and as recalled in Figure 2-4, there are materials with greater specific capacity than carbon for the anode. The greatest potential is silicon, due to its high gravimetric energy density where theoretically, four lithium atoms could be incorporated per silicon atom, compared to carbon where there is only one Li atom for six C atoms, resulting in LiC_6 . A composite association of silicon and graphite, or other carbon-related structures, is achievable and has been already conceived⁷³. Indeed, with a theoretical specific capacity of 4200 mAhg^{-1} , this material presents itself as a great candidate, however, it has been shown that silicon undergoes drastic volume changes during Li-ion alloying overcharge and discharge cycles, resulting in a problematic mechanical instability⁷⁴. In a similar way, pure Li metal is also considered a future anode material due to one of the highest energy densities available but also its use in future generations of batteries such as Lithium-Sulphur and Lithium-air technology. However, its use in commercial batteries remains a challenge as it has been known for its poor long-term cyclability and the fact that Li has a tendency to deposit in dendritic form through cycling which leads to internal short-circuits and subsequent thermal runaway and explosion hazards⁷⁵.

More recently, anodes containing both graphite and silicon (typically as silicon oxides, SiO_x) have become widespread in the battery industry, following their initial introduction in 2013⁷⁶. The trend has been to gradually increase the silicon content, providing substantial benefits to anode capacity and cell energy density. Silicon, while offering enhanced anode capacity, is typically associated with faster capacity loss during cycling. Unlike graphite particles, silicon-containing anodes do not fully passivate due to the large volumetric changes (up to 280% volume increase) and inherent instability of the SEI^{77,78}, which can result in electrode pulverisation and promote continuous electrolyte decomposition^{79,80}. The instability of the SEI layer on silicon, which undergoes dynamic changes in surface area during cycling. A recent

study using a composite anode demonstrated that the capacity loss rate of silicon is eight times higher than that of graphite⁸¹. SiO_x is employed to mitigate these effects, as it exhibits lower expansion ($<100\%$ volume increase) and a more stable SEI consisting of Li_2O and lithium silicates⁸². A stable, Li-ion conducting SEI layer is crucial on the anode surface, as once these layers are formed, they prevent further electrolyte decomposition, enabling reversible Li-ion cycling⁷⁶. Figure 2-7 represents SiO_x additives within a graphite anode material from a cylindrical commercial cell (LG MJ1) identified via X-ray Computed Tomography (X-ray CT), with identifiable SiO_x additives particles in a study by Heenan et al.⁸³ SiO_x particles show an average of 2-3 Vol.% of the total anode material.

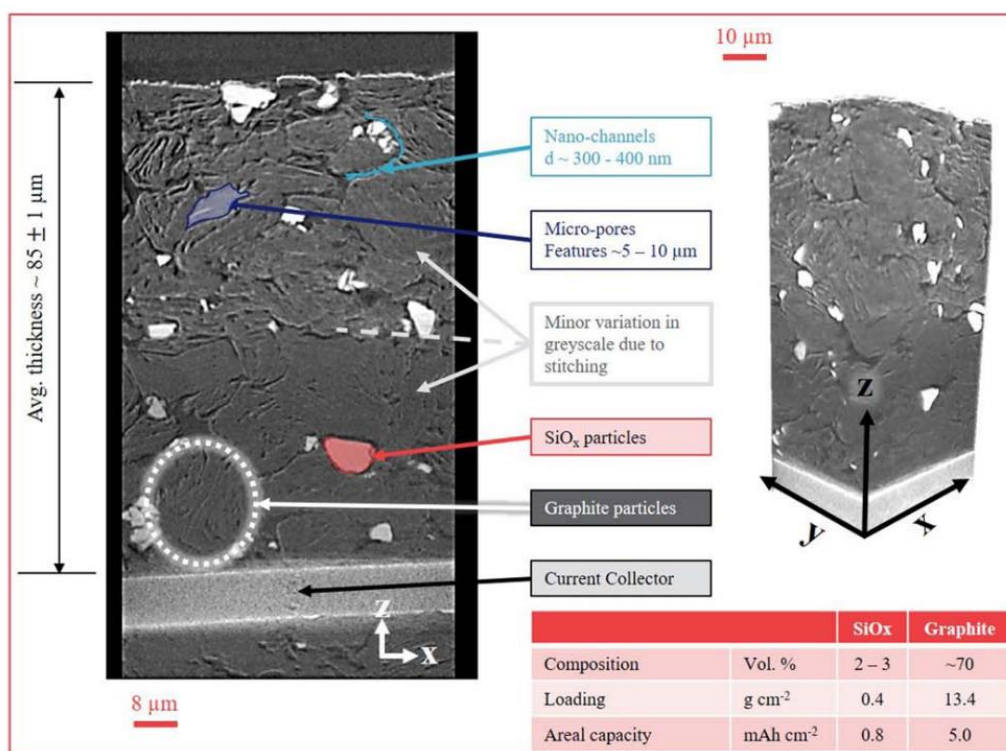


Figure 2-7. Anode-level data collected from an MJ1 18650 commercial cell with volume representation of the negative electrode material obtained via X-ray CT, and evidencing SiO_x additives particles. Reproduced from Heenan et al.⁸³

Beyond graphite and silicon, there are a wide range of possibilities regarding hard carbons such as nano-tubes, fullerene and graphene. Indeed, it has been studied for quite some time by Dahn et al. that the quantity of hydrogen sites within the carbon was linked to the capacity of the cell, due to the fact that lithium tends to bind to hydrogen sites⁸⁴. As such, an additional promising path for the development of anode

material is the use of graphene, with a theoretical specific capacity of 744 mAhg^{-1} , twice that of graphite. There is a significant potential regarding graphene, but a significant breakthrough still has to come⁸⁵.

2.2.3 Electrolyte and solid electrolyte interphase

The key function of the electrolyte is to conduct ions without conducting electrons. It comes in various forms within Li-ion cells, however, the majority of the time, it tends to be non-aqueous, as lithium reacts violently with water⁸⁶ and the voltage of Li ion cells (usually over 4V) far exceeds the breakdown voltage of water. Hence, organic solvents are normally employed in the electrolyte. Most commercial cells use a liquid electrolyte, which presents better overall performances and available at lower costs. A typical commercial Li-ion battery will have a liquid electrolyte, result of a mixture of LiPF_6 salts and alkyl carbonates (mostly ethylene carbonate, diethyl carbonate, vinylene carbonate and dimethyl carbonate) which act as a stabiliser and improve conductivity⁸⁷. It is important to state that the mentioned organic solvents are volatile and flammable, and are the cause of numerous safety issues regarding batteries operation. Companies and battery manufacturers have a wide range of choice regarding electrolyte additives in order to improve performance or stability, but most of them are not disclosed as protected by IPs and industrial secrecy. Common additives are present to reduce flammability, protect the cathode material or protect the Al current collector from corrosion, among others⁸⁷.

Furthermore, it is crucial to notice that a complex phenomenon within Li-ion batteries happens within the electrolyte: the formation of a SEI. It is the inevitable formation over time of layers of reactants which can include dendrite-like structures over the surface of the electrodes; almost always at the negative electrode⁸⁸ but can also occur at the cathode⁸⁹. The anode reduces the electrolyte and additives to form the SEI, but this actually protects the anode from further reaction. This leads to around a 10% loss of Li inventory on the first cycle⁹⁰, but the formation of a suitable SEI is vital to prevent further electrolyte degradation or loss of Li during operation. Electrolyte additives such as vinylene carbonate (VC) help a formation of a suitable SEI by being involved in the Li deposit phenomenon⁹¹. This has been described long time ago by

several authors, and Peled proposed a concept now universally accepted of a SEI⁹², through which lithium ions can move, but preventing the electrons to reach the molecules species of electrolyte susceptible of reduction. Any defect in the layer protection will result in lithium corrosion, and irreversible energy loss⁹³. Because of the high surface area of the porous negative electrode, this feature is more critical in Li-ion batteries, and is a possible source of ageing, either on cycling or on rest. Figure 2-8 describes the SEI formation process as described by Heiskanen et al.⁹⁴ The SEI initially forms from the decomposition of the electrolyte, primarily resulting in the creation of lithium ethylene dicarbonate (LEDC) and lithium fluoride (LiF). As the SEI evolves, it thickens due to ongoing electrolyte decomposition, becoming more inorganic and porous^{95,96}. This porosity allows more electrolyte to reach the graphite surface, further growing the SEI. Over time, this repeated process increases the SEI's thickness, which raises resistance and diminishes battery capacity⁹⁷.

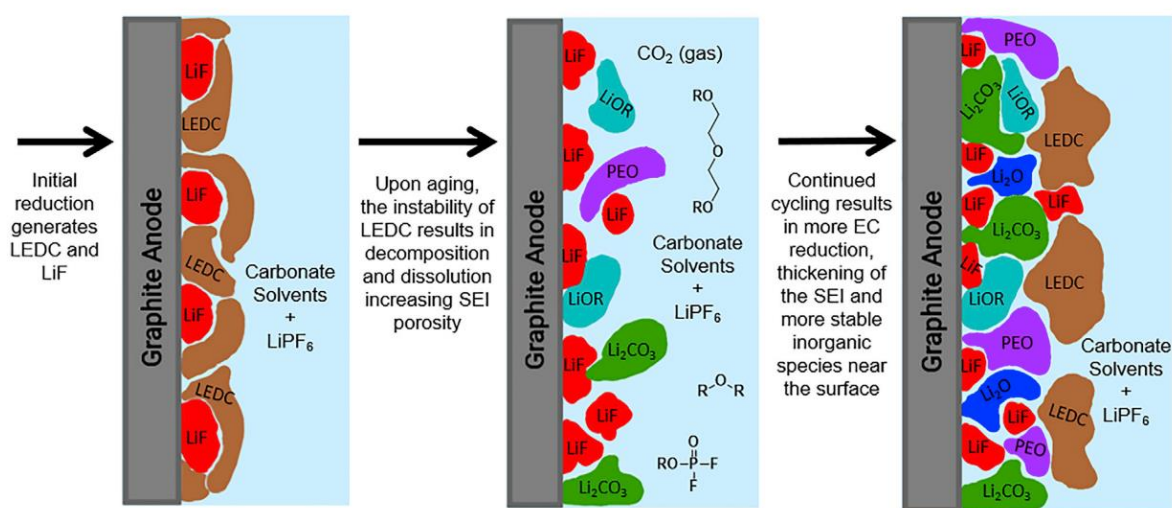


Figure 2-8. Schematic figure of the Initial SEI formed on the graphite anode, the effect of acid-mediated thermal decomposition reactions on the structure of the SEI, and the further reduction of electrolyte leading to the thickening of the SEI. Reproduced from Heiskanen et al.⁹⁴

One of the key goals of Li-ion battery development is the creation of an all solid-state electrolyte cell. Such a cell will considerably reduce the safety risks due to improved stability, increase the energy density of modules and pack due to a more space-efficient design and use of Li metal anode⁹⁸. However, despite a real interest by car companies and battery manufacturers, the development of scalable solid electrolyte cells are still in their early stages and a major breakthroughs are expected

in the upcoming years⁹⁹. This is due to a very low conductance of candidate materials, stability issues and potential scalability problems in manufacturing¹⁰⁰.

2.2.4 Separator

The separator's purpose is to avoid contact between both electrodes in order to prevent internal short circuit and is hence placed between them, but still allows the transfer of ions. Separators design and choice of material have not converged yet and the research is quite open-ended. Indeed, a wide range of separator materials is available for different applications such as energy density operation or high power operation. Materials available are: microporous separators, non-woven, ion exchange and supported liquid membranes and solid ion conductors¹⁰¹. For most commercial cells, however, a thin microporous polymeric membrane of thickness comprised between 10 and 30 μm is used. This microporous membrane is usually polyethylene (PE), polypropylene (PP), or a combination of both¹⁰².

Separators need to be chemically, mechanically and thermally stable, permeable and must include a viable and efficient *shutdown* mechanism. The most common separators used are called Celgard membranes, and consist of a tri-layer arranged microporous membrane in the form PP-PE-PP. Its shutdown mechanism occurs when the temperature is too high (which can potentially lead to failure and subsequent thermal runaway), the inner polyethylene layer will melt and fill the pores of the outer polypropylene layers, avoiding the transfer of ions, and subsequently *shut down* the cell, mitigating or stopping the thermal runaway¹⁰³.

2.3 Degradation of lithium-ion batteries

2.3.1 Degradation mechanisms within Ni-rich lithium-ion batteries

There are an extensive range of degradation mechanisms involved in Li-ion batteries, at multiple scales and elements within the whole battery configuration. Elements defined from the battery manufacturing processes to conditions of operations¹⁰⁴, as shown in Figure 2-9.

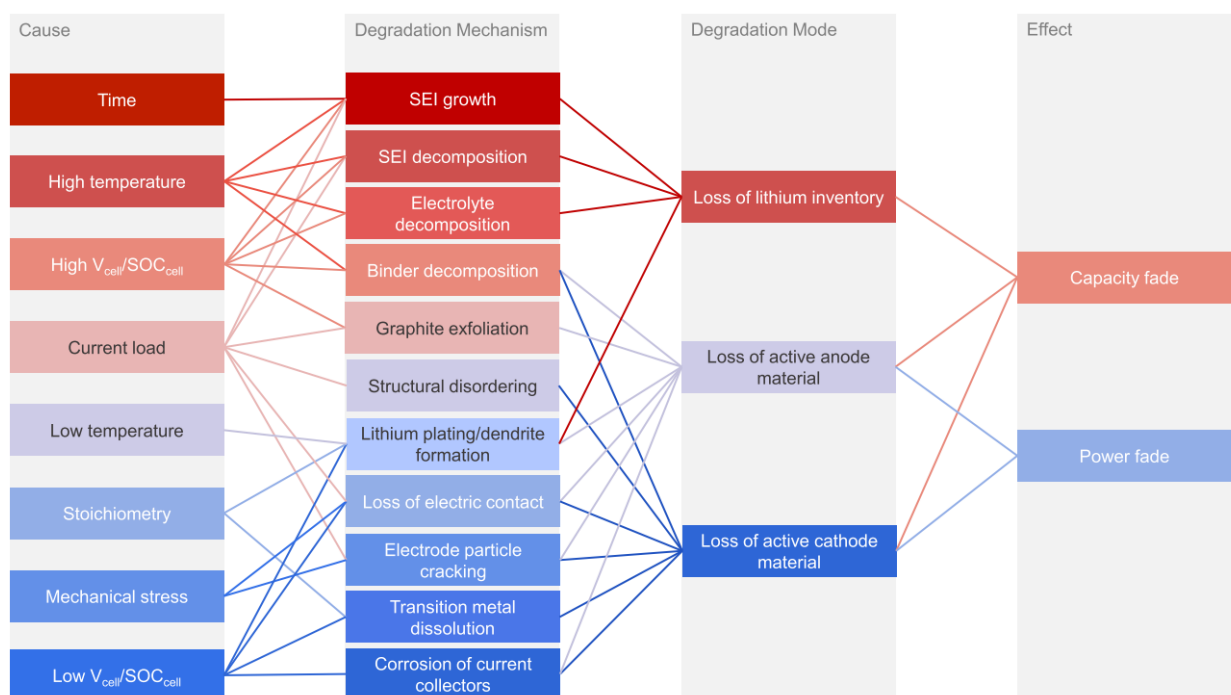


Figure 2-9. Causes and effects of degradation mechanisms occurring within Li-ion batteries. Reproduced from Birkel et al.¹⁰⁴

In this review, the main material of focus will be Ni-rich cathode material and specifically of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, referred to commonly as NMC 811 throughout the literature. The higher Ni compositions provide higher energy densities at high levels of delithiation but are prone to releasing oxygen, especially at high SoC¹⁰⁵. An advantage is that Li^+ ions diffuse faster in the NCM 811 cathode material than NMC 532¹⁰⁶. In

many aspects, NMC 811 is closer in behaviour to Lithium Nickel Oxide (LNO) cathode material but also shares common characteristics as lower content NMCs¹⁰⁷. Some differences in the various phase transitions of the electrodes as opposed to other NMC chemistries are observable¹⁰⁸, as shown in Figure 2-10. As it is observable, the main difference is that the M→H2 and H2→H3 phase transitions have not been reported in literature for NMC 622 and 111 as opposed to NMC 811. Overall, these differences are due to the reduced Ni content, which leads to enhanced electrostatic repulsion between oxygen layers for NMC 811, and introduces greater lattice strain during lithium de-intercalation, especially near full delithiation. M→H2 is not as pronounced in NMC622 or NMC111 for instance, due to their lower Ni proportions and more stable hexagonal structures, while H2→H3 reflects a transition towards higher covalency in Ni-O bonding as more lithium is removed for NMC811, marked by a sharp collapse in the c-lattice parameter¹⁰⁹. These additional phase transitions occur at higher voltage regions (from 3.8 V to 4.2 V) making this area particularly sensitive for the cathode material and as it would be shown, prompt features such as oxygen release.

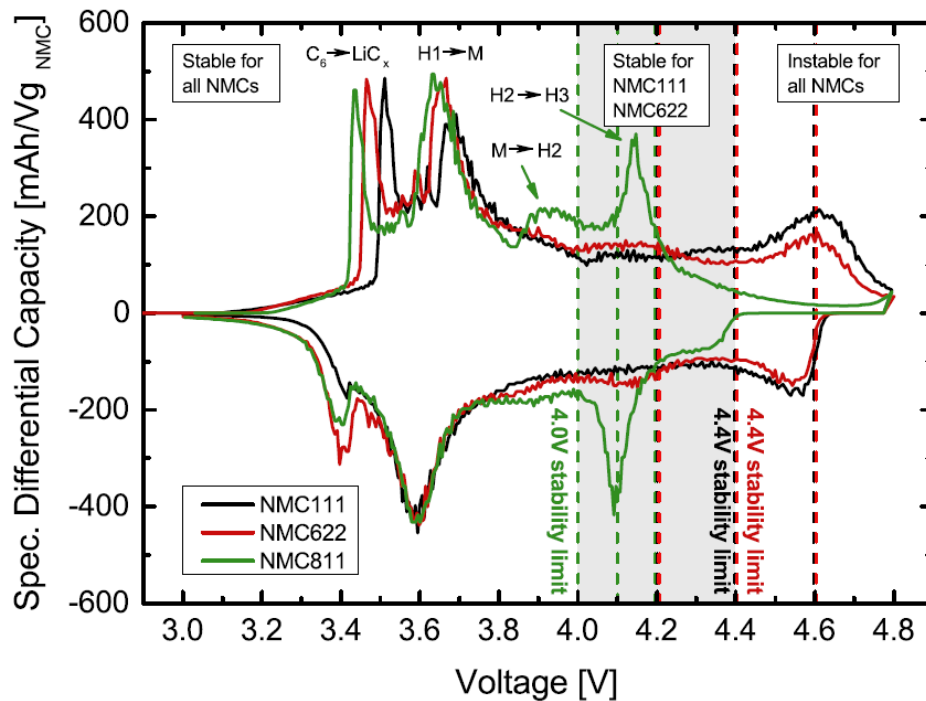


Figure 2-10. Differential capacity vs. cell voltage of NMC-graphite cells recorded at a 0.1 C-rate. The peaks represents their corresponding phase transitions with H1, H2 and H3 assigned to the three hexagonal phases and M the monoclinic one. $C_6 \rightarrow LiC_6$ indicates the lithiation of graphite. Reproduced from Jung et al.¹⁰⁸

Different chemistries of NMC have also different properties. An example is that NMC 811 is extremely sensitive to air exposure, particularly moisture present in the air. A study was made to assess the surface contamination over a year of NMC 811 compared to NMC 111. The cells were cycled (coin cells) to also assess their specific capacity. Results showed that the NMC 811 surface developed a 10nm thickness layer of mostly of Nickel carbonate species mixed with some hydroxide and water. No significant changes were seen on the surface of NMC 111. Gas chromatography was used to quantify the carbonate species when NMC particles were dissolved in hydrochloric acid and formed carbon dioxide. This lead to growing polarisation within the electrode, delithiation voltage peak in the very first charge and reduced cycling stability¹¹⁰.

For layered transition metal oxide compounds have increasing electrochemical potential as extraction of Li⁺ ions proceeds and decreases during the insertion of the ions. Charge neutrality is hence maintained by changes in the oxidation state of the components of the material's transition metals¹¹¹. On another hand, redox reactions occurring at the oxygen anions are also believed to play a part in this compensation, especially at high levels of delithiation¹¹², or in Li rich compounds. Overall, Noh et al. highlights that a balance between stability (thermal and structural) and overall capacity has to be found, as it is displayed in Figure 2-11, as it seems like a trade-off between the two at the current state of research¹¹³.

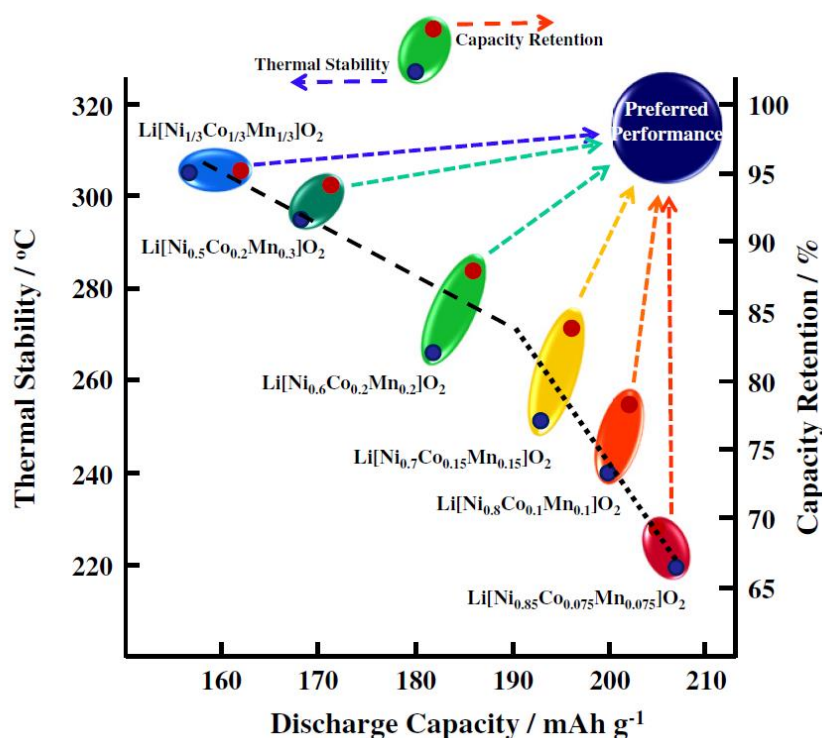


Figure 2-11. A map of relationship between discharge capacity, thermal stability and capacity retention of various NMC materials ratio. Reproduced from Noh et al.¹¹³

For Ni-rich NCA materials, the strong Al–O bonds (despite the low percentage of Aluminium) give it better structural stability and lower chemical reactivity than LiNiO_2 (for example), as they minimise the release of oxygen from the oxide material¹¹⁴. Oxygen loss occurring at high voltages from the cathode structure is a significant cause of degradation because it can lead to structural reorganisation to spinel or rock-salt layer (RSL) structures at the surface of the particles as it has been widely reported in literature^{92–97}, which lead to significant effects on Li insertion rates and an increase in impedance¹²². Furthermore, it has been shown that there is also potential during the same process of a release of highly reactive triplet O_2 which can react with the electrolyte¹²³. Figure 2-12 represents in a) a schematic of the tensile strengths leading to RSL platelet formation and b) a high-resolution transmission electron microscopy (HRTEM) view of the rock-salt/layered interface.

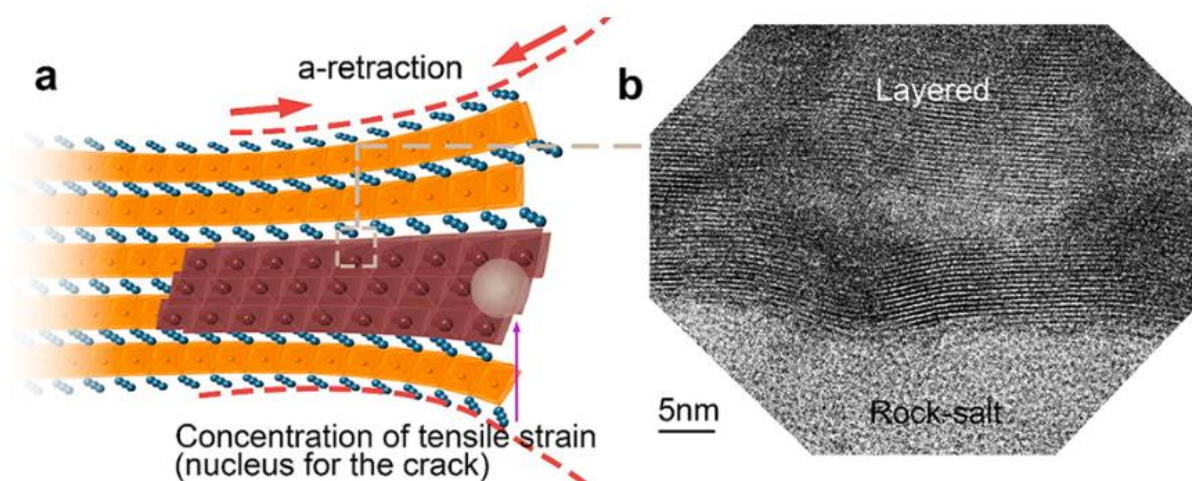


Figure 2-12. a) Schematic showing the tensile strain concentrated in the surface region of the rock-salt platelet, generated by retraction of the a-parameter of the layered phase upon delithiation. b) HRTEM view of the rock-salt/layered interface from a one-cycle particle, showing the bending of the lattice planes in the layered phase caused by the retraction of its a-axis. Reproduced from Zhang et al.¹²⁴

Cation mixing usually leads to a strong correlation with structural stability. It involves cation disorder between transition-metal sites and lithium sites. For instance, the Ni has a tendency to be formed as Ni^{2+} rather than Ni^{3+} because Ni^{3+} is, according to crystal-field theory, more unstable¹²⁵. Compared to the well-ordered phase, the disordered phase requires a higher activation energy for Li diffusion due to its smaller distance between the slabs¹²⁶, or transition-metal ions (particularly Ni ions) occupying the Li sites, as it will be discussed further on. In addition, on the surface, highly reactive Ni^{4+} ions have been found to accelerate electrolyte decomposition, leading to electrolyte depletion and a thick solid-state electrolyte interface layer¹²⁷. Another process that can occur is that these Ni^{4+} ions tend to reduce to the Ni^{2+} state with O_2 triplet release¹¹³. Overall, it has been shown that the presence of Ni^{3+} tends to increase with Ni content of NMC cathodes and that Ni^{4+} increases rapidly as a function of SoC, with an overall higher number of ions as the Ni content increases¹²⁷, as shown in Figure 2-13. Therefore, it results in a higher tendency within higher Ni content NMCs to have oxygen triplets release and gas production in the cathode-electrolyte interphase.

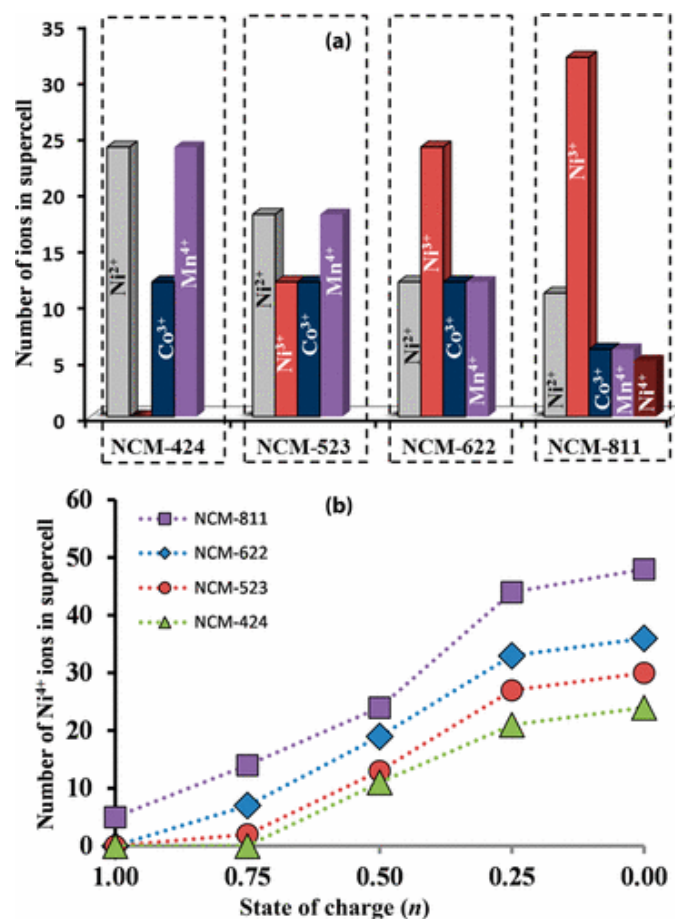


Figure 2-13 (a) The oxidation states of transition metal ions in various NMCs. (b) Amount of Ni⁴⁺ ions as a function of state of charge in various NMCs states. Reproduced from M. Dixit et al.¹²⁷

However, the poor interfacial and structural stability of Ni-rich NMC or NCA is still a challenge for manufacturers to implement their large-scale manufacturing and applications. Indeed, the fading mechanism in Ni-rich cathodes is linked to each phase transition, which involves Ni²⁺ content, over-lithiation/over-delithiation, oxygen loss and the lithium salts on the surface¹²⁸. For the Ni-rich cathodes, the Li⁺/ Ni²⁺ cation mixing (facilitated by the fact that both cations have similar size) is an important factor that has significant influences on the high initial capacity loss and poor cycling performance. Ni²⁺ are prone to be oxidised to form actively deformed Ni³⁺ ions by the Jahn-Teller effect during the delithiation process, the Li interlayer (LiO₆) then collapses, causing the blockage of Li⁺ diffusion pathways during lithiation process¹²⁹. This anisotropic change in c-lattice parameter dimensions during charge/discharge cycles as Li ions circulate tends to produce intergranular cracking at the boundary between primary particles, which lead to poor connectivity between said primary

particles¹³⁰. The interaction between several vacancies sites of potential TM/Li exchanges is displayed in Figure 2-14.

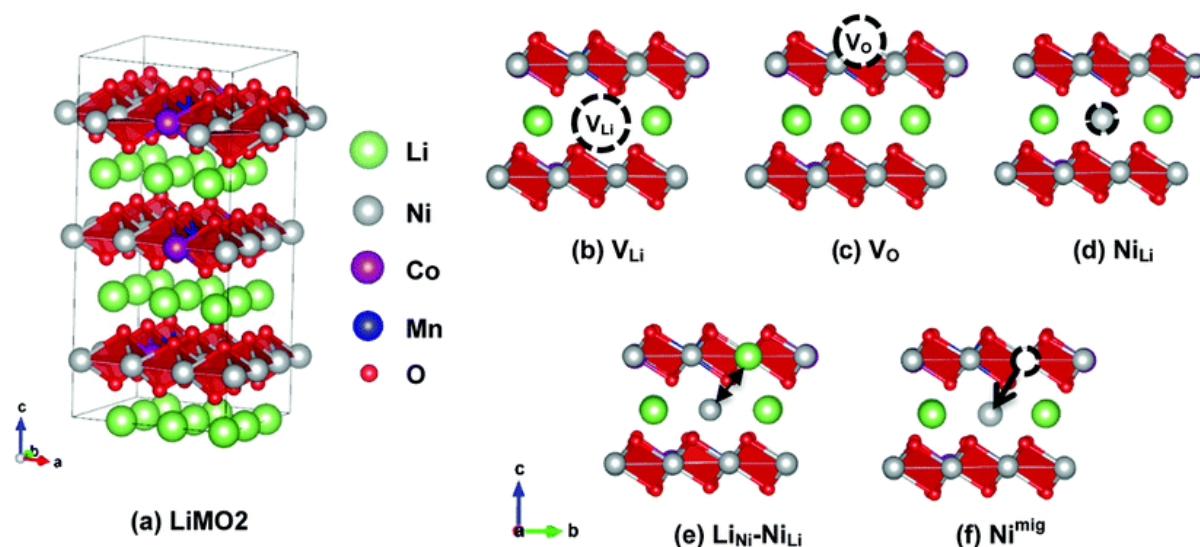


Figure 2-14. Atomic configurations for the structure of (a) LiMO_2 , where M = transition metals (Ni, Co, and Mn), and the schematic structures for each of the defects, (b) Li vacancies (V_{Li}), (c) oxygen vacancy (V_{O}), (d) excess Ni (Ni_{Li}), (e) Li/Ni exchange ($\text{Li}_{\text{Ni}}\text{-Ni}_{\text{Li}}$), and (f) Ni migration (Ni^{mig}). Reproduced from Min et al.¹³¹

The Ni particles migration towards Li sites is the subject of interest as one of the main drivers for bulk degradation within cathode materials and particularly NMC cathode materials as outlined by Kleiner et al¹²⁰. Through long-term in-situ XRD experiments, for over 100 cycles, the study revealed an irreversible transition-metal motion within the host structure to Li sites. However, it is speculated that this migration could be reversible if said particle reaches the tetrahedral orientation of the inter lattice crystallographic structure, as shown in Figure 2-15. In highly delithiated (charged) states, transition metals tend to occupy tetrahedral sites in the lithium layer. The energy barrier for this migration is lower in the charged compared to the discharged state because the neighbouring octahedral lithium sites are empty. Delithiated, disordered structure as in “the irreversible state” is thermodynamically more stable as “the reversible state”; thus, such migration is energetically more favourable. This disordered structure may tend to the release of oxygen, especially in the case of nickel-rich layered oxides, as Co tends to stabilise the structure and so the lack of Co in these materials means they are more prone to oxygen loss¹⁰⁸.

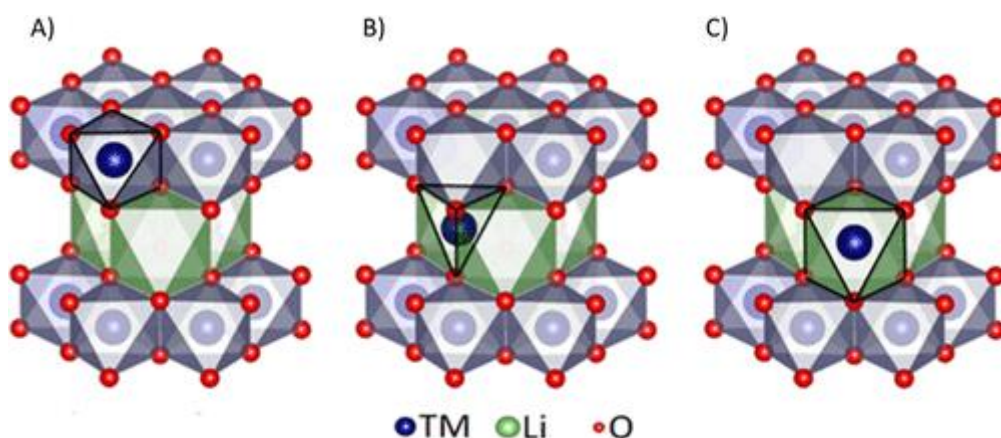


Figure 2-15. Schematic illustration of transition-metal migration in layered oxides. The transition metals can move from octahedral sites in the transition-metal layer (A) via tetrahedral sites in the lithium layer (B) into octahedral sites in the lithium layer (C). Reproduced from Kleiner et al¹²⁰.

This section, focusing on the positive electrode material, highlights the difficulty in studying primary degradation mechanisms in isolation, due to their intricate interconnections and feedback loops, as well as the overlapping impact of external factors like temperature, SoC, and cycling rates⁷⁹. As will be shown in the next sections, the interactions with the negative electrode further exacerbate this interplay.

2.3.2 Calendar ageing of commercial cells

Numerous studies on the topic of calendar ageing have highlighted a significant dependence of this process on a cell's SoC, temperature and time of storage, whereby the those factors are, the more degradation is undergone by the cell^{132–134}. It has been observed that the loss of available lithium, primarily due to side reactions at the negative electrode, is accelerated at higher SoC levels due to the increased potential difference between electrode interfaces and the electrolyte. In cells with graphite-silicon oxide composite anodes, capacity fade during calendar ageing is largely attributed to lithium loss at the anode, a phenomenon linked to the presence of silicon¹³⁵. Under such conditions, the solid SEI on silicon exhibits more dynamic and less passivating behaviour compared to that on graphite, leading to increased degradation^{23,136}.

It is widely recognised that Li-ion batteries experience accelerated capacity degradation and increased impedance as temperature rises, consistent with the Arrhenius law¹³⁷. This phenomenon occurs due to the exponential increase in the rate of chemical reactions with higher temperatures which then drives faster ageing. This relationship also holds true for calendar ageing and the associated side reactions that contribute to battery degradation, such as the formation of passivating films or the loss of active material¹³⁸. Essentially, the higher the temperature, the more rapidly the battery ages, and this effect is similarly correlated with the SoC. As the SoC nears saturation, the rates of side reactions increase, though as these degradation processes slow over time, the overall ageing effects become dependent on the square root of time, as described by the following derived extended Arrhenius equation¹³⁹:

$$T_{age} = A_0 \cdot e^{\frac{SoC - SoC_0}{b}} \cdot e^{\frac{T - T_0}{c}} \cdot \sqrt{t}$$

Equation 2-5

Where SoC_0 and T_0 are reference conditions, A_0 is the scaling factor for $\sqrt{t}$ and a and b are the model parameters for SoC and temperature respectively.

Some studies have documented a "spoon-shaped effect," where capacity recovery is observed at 100% SoC compared to 80% SoC. Zülke et al. suggested that in NCA/graphite cells, this effect is driven by a cathode-driven shuttle mechanism, induced by CO_2 from electrolyte decomposition, which competes with SEI formation for lithium, thus suppressing irreversible capacity loss at higher SoC levels¹⁴⁰. Figure 2-16 illustrated this mechanism, as shown in the study. Zilberman et al. proposed that this effect could be related to lithium storage in inactive anode overhang areas in NMC/Si-Gr cells, where these regions, soaked in electrolyte, participate in an equalisation process that allows for lithium storage¹⁴¹. This process, driven by the flat open-circuit voltage (OCV) of graphite at high SoC, is slow and relies on interparticle transport¹³⁵. The overhang areas, primarily a safety feature to prevent lithium plating at the current collector, can later supply extra lithium to the active anode area during post-storage cycling, leading to more lithium accumulation at 100% SoC than at 80% SoC¹⁴².

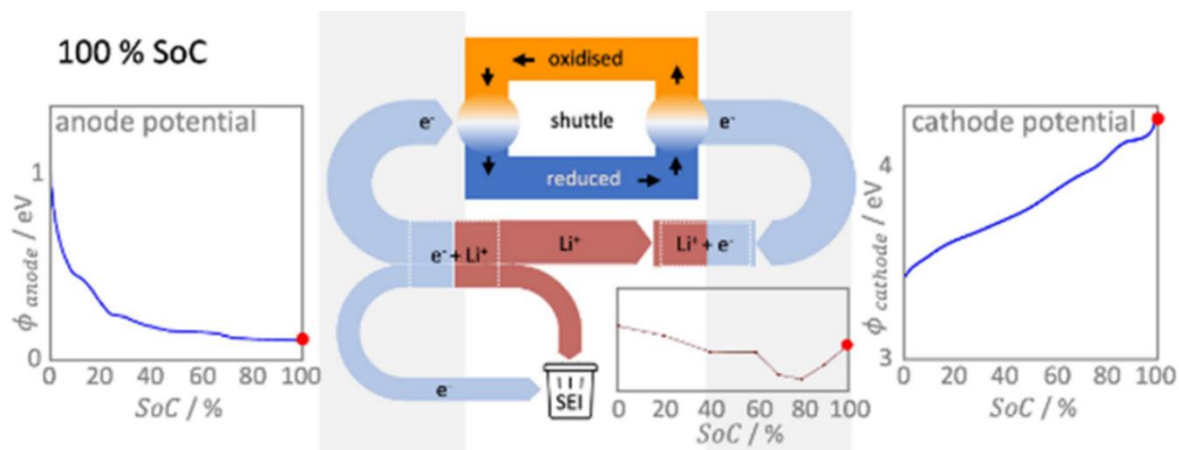


Figure 2-16. a) Illustration of the CO₂-based shuttle mechanism of self-discharge; b-d) mass flow model of the rates of reversible self-discharge and irreversible. SEI formation, including corrosion-type electron transfer for three different SoC levels. Left and Right column: anode and cathode potentials vs. SoC level. Inset: capacity retention during calendar ageing. Reproduced from Zülke et al.¹⁴⁰

Although several potential mechanisms for the "spoon-shaped" effect have been proposed, a comprehensive understanding has yet to be established. The material composition of the electrodes plays a crucial role in calendar ageing, with cells containing NMC layered-oxide cathodes suffering significant capacity loss at voltages above 4.4 V (vs. graphite) due to oxygen loss and structural deterioration^{143,144}. Similarly, the anode composition is critical, as previous studies have shown that anodic side reactions and the formation of passivating electrode-electrolyte interfaces are key contributors to capacity loss in calendar-aged cells. An observation provided by Keil et al. show that the capacity drop more significantly after 50-60% SoC, corresponding to the step right after the LiC₁₂ to LiC₆ has occurred within the graphite, as shown in Figure 2-17, indicating in this a more anode-driven fade mechanism¹⁴⁵.

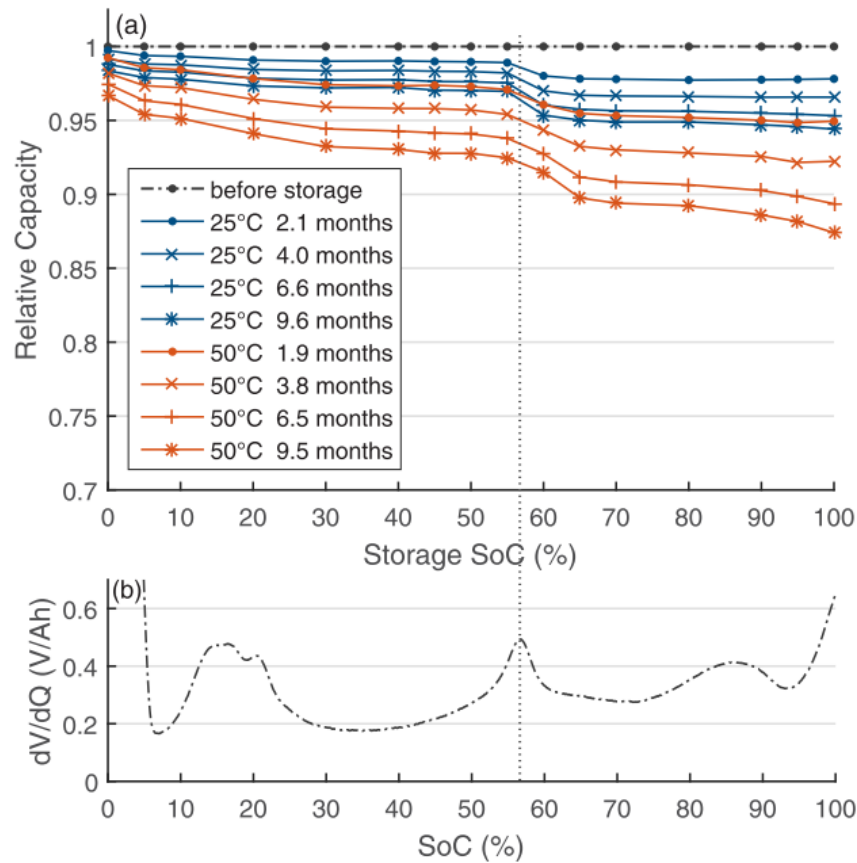


Figure 2-17. a) Capacity fade over SoC for different storage periods of NCA/Graphite cells and b) DVA of a fresh cell. The dotted vertical line represents the SoC location of the central graphite peak. Reproduced from Keil et al.¹⁴⁵

2.3.3 Loss of active material, lithium inventory, and impedance growth as degradation modes

Aforementioned primary degradation mechanisms can generally be categorised into three core degradation modes: Loss of Active Material (LAM), Loss of Lithium Inventory (LLI), and impedance growth. Some overlaps do exist and while they represent some simplifications, numerous papers have been using these three core concepts throughout their studies.

LAM refers to the reduction in the amount of electrochemically active material in the battery, which directly impacts the battery's capacity. Active sites within the materials in the cathode and anode participate in the intercalation and de-intercalation of lithium ions during charging and discharging. Over time, these materials can degrade, lose

their structural integrity, or become electrochemically inactive or electronically isolated, leading to a decrease in the battery's capacity. LAM encapsulates most of the structural degradation of electrodes for instance, such as cracking, particle fracture, pulverisation, formation of RSL, cation disordering and the formation of antistes defects, or electrode surface passivation, as mentioned previously.

On the other hand, LLI refers to the reduction in the amount of cyclable lithium in the battery. The inventory of lithium ions available for intercalation and de-intercalation in the electrodes is finite, so when lithium ions are permanently lost due to side reactions or other mechanisms, the battery's capacity diminishes because fewer lithium ions are available to participate in the electrochemical reactions. Most LLI processes involve the SEI (first its formation, and then its evolution, growth and thickening), Li plating or other Li depositions or irreversible side reactions

Furthermore, impedance growth refers to the increase in the internal resistance (IR) of the battery over time, which reduces the battery's power output and efficiency. Higher impedance means that it is more difficult for lithium ions to move through the electrolyte and across the electrode/electrolyte interfaces, which can lead to slower charge/discharge rates and higher energy losses, and is the main contributor to more pronounced power fade, instead of capacity fade. SEI layer thickening, electrolyte degradation and formation of RSL, are all major contributors of impedance increase within batteries. As such, it can be summarised:

- LAM covers structural degradation and isolation of active materials.
- LLI includes mechanisms that permanently trap lithium or remove it from the cyclable inventory.
- Impedance growth encompasses processes that increase the difficulty of lithium ion movement within the cell

Each of these processes is interconnected, and a single degradation mechanism can contribute to multiple types of degradation, as it has been mentioned for the SEI formation and evolution, or the formation of RSL. Overall, these concepts provide a comprehensive framework to understand the complex and intertwined mechanisms that lead to battery degradation.

2.4 Fast charging and other varied protocols for lithium-ion batteries

The goal of an ideal charging protocol is to charge a battery in as fast as possible while avoiding putting the cell under too much stress. This would allow cars to be charged at charging points in a relatively short amount of time, mitigating the phenomenon of range anxiety, found in most studies regarding potential EVs customers^{146,147}. Unfortunately, the physics needed to fulfil the demand for these characteristics have always resulted in trade-offs so far¹⁴⁸. As an example, thinner electrodes will result in better Li ion diffusion, withstanding higher current for fast charging, but will have the consequence of leading to a lower energy density (as a proportionally higher volume of the cell is taken up by non-active materials such as the separators and current collectors). Hence, several protocols discussed in this review present an attempt to optimise the need for fast-charge, but taking into account battery cycle life. Regarding discharge, for practical applications, it remains out of a controlled environment whether it is for a user usage of a phone or car. In lab-simulated situations, such discharge protocols can be simulated by using various car driving cycles to get better insights into how a discharge protocol would look during the lifetime of a commercial battery¹⁴⁹.

The standard protocol for charging commercial Li-ion batteries is the constant current constant voltage (CCCV) charging. The most common discharging protocol for discharge as found in literature studies for battery cycling usually consists of a simple CC discharge. However, several papers in literature have studied other charging protocols. Overall, optimised charging procedures aim to provide a short charging time, good capacity utilisation and a high-energy efficiency¹⁵⁰. The other parameter to include is the maintaining of a long cycle life, hence, mitigating degradation¹⁵¹. If said protocols are intended for real-world applications, such as fast charging protocols for the automotive industry, fast charging is not enough, as the battery pack cycle life has to be kept as long as possible. Unfortunately, fast charging and discharging a lithium battery (at above $C/2$) will also lead to accelerated capacity fade, shorter life-time,

potentially problematic internal cell temperature rise and other safety concerning aspects like dendrite growth and lithium plating¹¹⁸.

Most existing charge/discharge protocols are done at constant current and constant voltage (CCCV), which has become a standard. It consists of a constant current charge until the point when the manufacturer's upper voltage limit is reached (4.2 V in most NMC and NCA commercial cells) and then the voltage is kept constant as the current drops until a cut-off current is reached. Figure 2-18 illustrates this protocol. Such protocols are widely applied in academia to study the degradation mechanisms of cells or induce abuse conditions or in industry at the fast charging stations for EVs. while C-rates are often varied in the assessment of cells in academia and industry¹⁵², they tend to consist of separate experiments at different constant currents. Varying the C-rate within a single cycle is much rarer, as CCCV seems to have become self-evident early in battery research as the most energy-efficient charging protocol in while studying new technologies for chargers for Li-ion batteries¹⁵³.

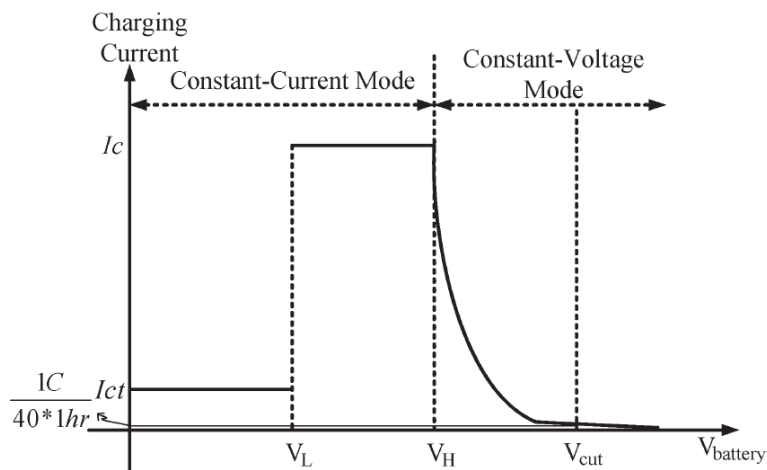


Figure 2-18. Varying V and C-rates protocols for new chargers of Lithium ion cells, resulting in the standard CCCV protocol. Reproduced from Chen et al..¹⁵³

Another study by Notten et al. in 2005 proposed a “boost charging” method for ultra-fast charging¹⁵⁴. This study showed that charging an almost empty cell to 1/3 of its SoC at very high C-rates has reduced negative effects on its capacity fade over time. It combined this varying C-rate method (4.5C until 30% SoC, then back to 1C) with long-term studies to see the potential negative effects on capacity. This was carried out on LCO cathodes, within 18650 and prismatic cells. Their results are shown

in Figure 2-19. The study also confirmed negative effects on capacity fade while having 4.3V as a cut-off voltage for 4.2V rated cells.

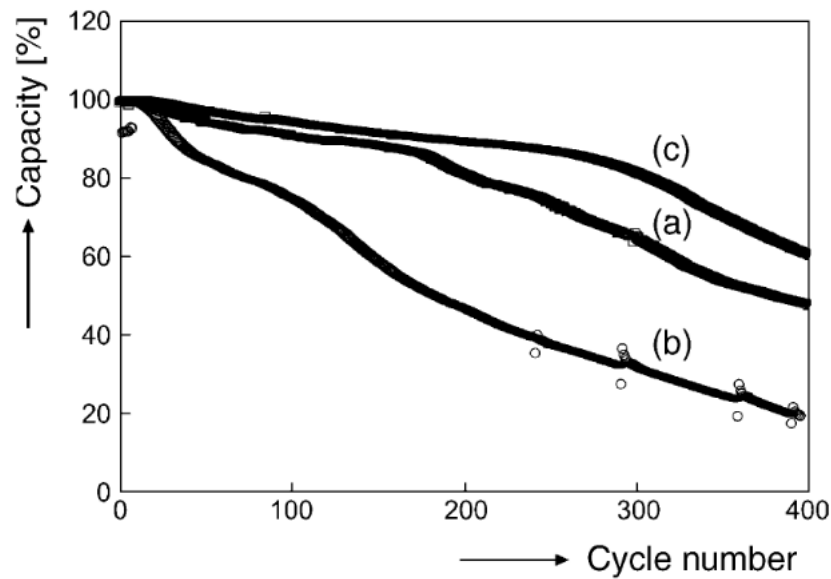


Figure 2-19. Cycle life of cylindrical Li-ion batteries under high charging load conditions at $I_{max}=4.5\text{ C}$, $V_{max}=4.2\text{ V}$ (a) and $I_{max}=4.5\text{ C}$, $V_{max}=4.3\text{ V}$ (b). Cycle life upon standard CCCV-charging ($I_{max}=1\text{C}$, $V_{max}=4.2\text{ V}$) is indicated in curve (c). Reproduced from Notten et al..¹⁵⁴

A multiple-stage constant-current charging was proposed in 2011, where the operation starts with the largest current in the first stage followed by sequentially stepwise reduced currents, called the Taguchi methods, based on an algorithm of the same name¹⁵⁵. The method consists of 5 steps of different C-rates, decreasing over the SoC by a small step of roughly 0.1C to 0.25 according to various protocols (Figure 2-20). The study reached a max C-rate of 1.45C, increasing the time of charge by 11% compared to standard CCCV methods. The Taguchi method was used again for another study with similar results¹⁵⁶.

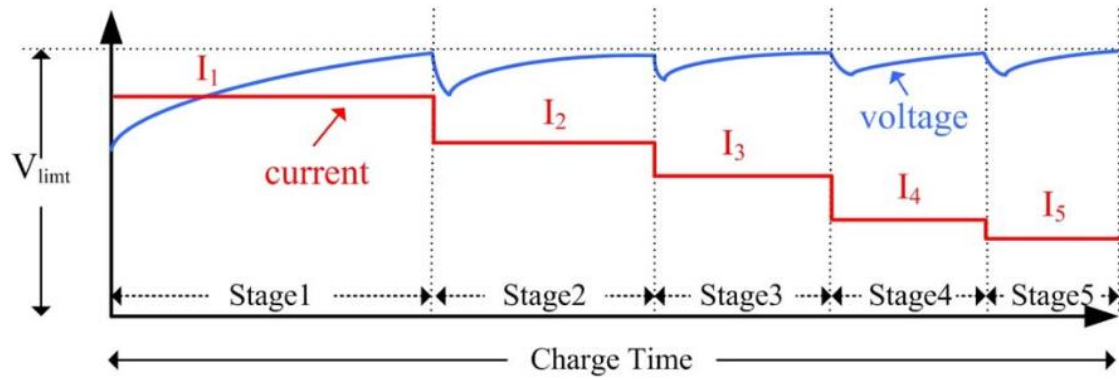


Figure 2-20. Five step current charging protocol. Reproduced from Liu et al..¹⁵⁵

A study on dynamic C-rates for charge/discharge was published in 2017 by Abdel-Monem et al.¹⁵⁷. Several protocols were considered (outlined in Figure 2-21), and EIS and surface temperature measurements were performed. The maximum C-rate reached, both during CCCV and CC-CVNP (defined by the authors as “Constant Current–Constant Voltage with Negative Pulse”), was 4C, with a LFP 7Ah commercial cell. Again, the same pattern of generally decreasing the C-rate over time and SoC is prominent. As a result, the CCCV protocol led to the least performant result (Case 1 procedure), while Case 2 and 3 resulted in the best overall performances, with also good results with Case 5 and 6. The effects of the procedures was measured regarding the discharge capacity losses over time. The negative pulse, according to the EIS measurements, seems to reduce the ohmic resistance, charge transfer resistance, and the passivation resistance. Yet, the most significant temperature rise was observed for Case 1, 2 and 3, while still relatively low ($\sim 5^{\circ}\text{C}$).

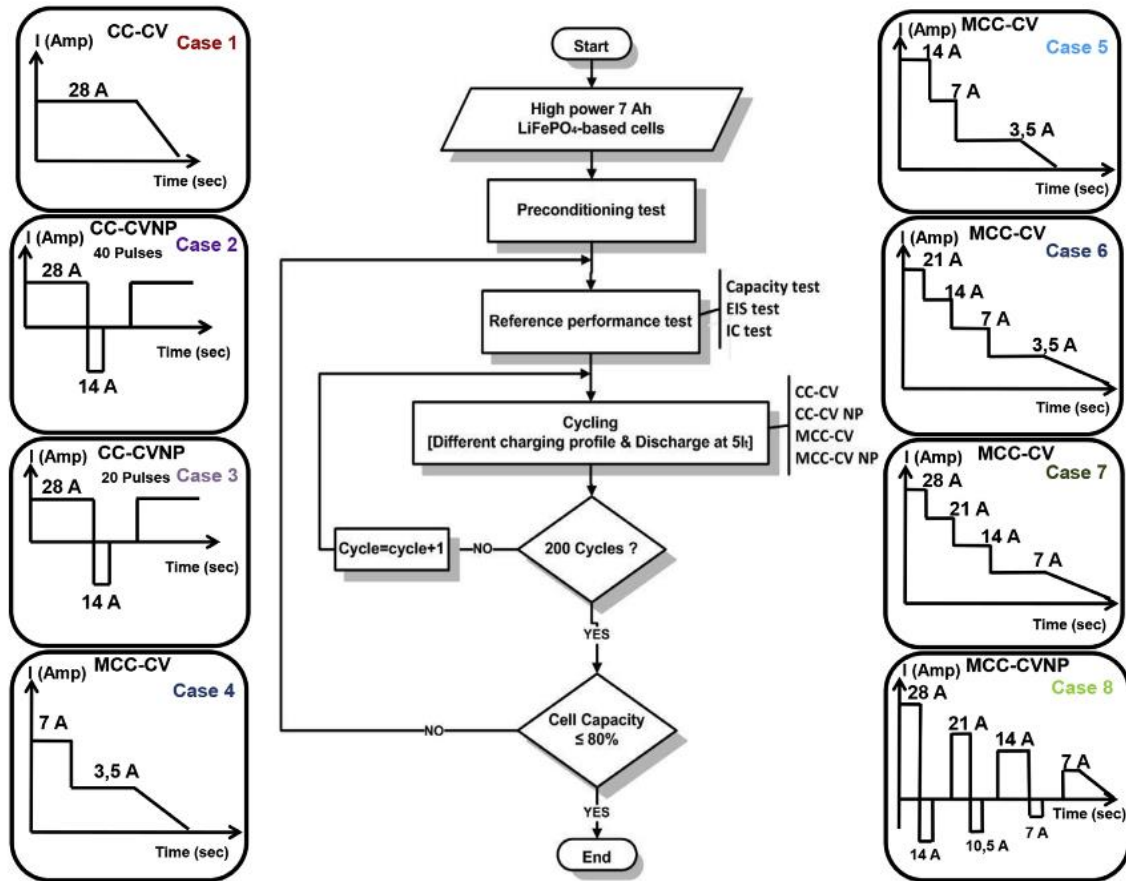


Figure 2-21. Varying cycling procedures and profiles considered by Abdel-Monem et al.¹⁵⁷

A subsequent study by the same authors was then released in 2018, focusing on the thermal aspect of these varied protocols¹⁵⁸, considering three different temperatures of operation (25, 10°C and 45°C), for two different pouch cells chemistries (NMC 111 coupled with Lithium Titanium Oxide (LTO)) using two different protocols (CCCV and CC-CVNP similar to Case 1 and 2, respectively, from the previous study). The study showed that at 10°C, the CC-CVNP protocol allowed a better fast charging as it helped raise the internal cell temperature due to the presence of more Joule heating effect. The cell warmed up; hence, its IR was lower. For the NMC, no significant data was relevant for 45°C as the patterns were similar.

More recently, variable currents over cycling have been considered from a modelling point of view, and not as the main subject of their studies^{159,160}. Zou et al. considered the aforementioned as “model-free studies as heuristic that propose suboptimal solutions”. However, the resulting optimal protocol suggested by the

algorithm used was a solution similar to CCCV, with constant temperature, despite what the previous studies suggested in this review. Lastly, Attia et al. considered even more patterns for varied protocols from various studies and car manufacturers' patents. However, despite keeping the trend of starting at high C-rate at low SoC, it still investigated the subdivision of the SoC window in more sub-regions (without the use of pulses), such as an intermediate 60-80% SoC, to promising results with improved charging times and mitigation of degradation¹⁶¹.

2.5 Consideration of cell resistance and ion mobility over the state of charge

When considering the IR of Li-ion cells when plotted over their SoC, as presented in several studies to follow, similar trends and patterns appear, as highlighted in both experimental¹⁶² and modelling studies^{163,164}. The IR is higher from 0-20% SoC, lower from 20-50%, at its lowest from 50% to 80%, and rises again from 80-100% (Figure 2-22) – this characteristic 'u-shape' is seen in many cell chemistries in literature. It was also found experimentally that the IR is affected by temperature of operation (the lower the temperature, the higher it gets) and cell ageing (the higher the number of cycles of a cell, the higher it gets) (Figure 2-23). When the resistance of a cell is at its highest (here, from 0-20% SoC), more significant temperature rises are expected as current is passed. In previously introduced studies, a compromise is often found for IR measurements where a single SoC point is considered and measurements carried out consistently taken at said SoC, to avoid the aforementioned variations.

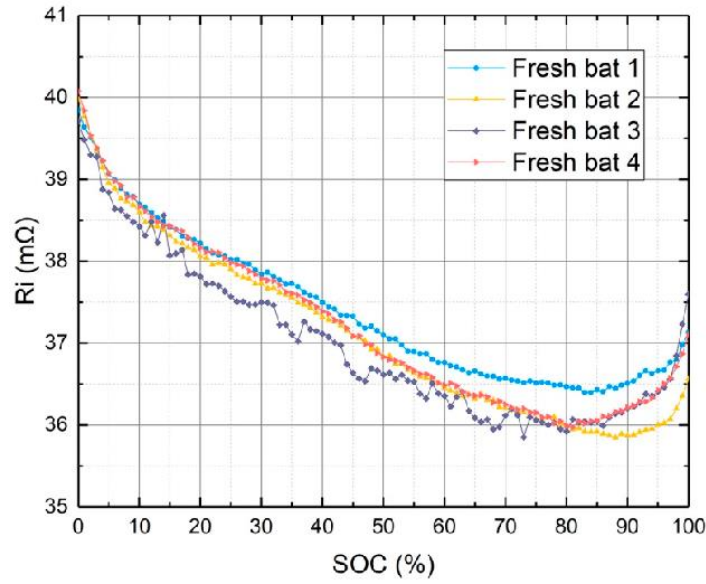


Figure 2-22. IR over SoC for four fresh batteries. Reproduced from Wang et al.¹⁶²

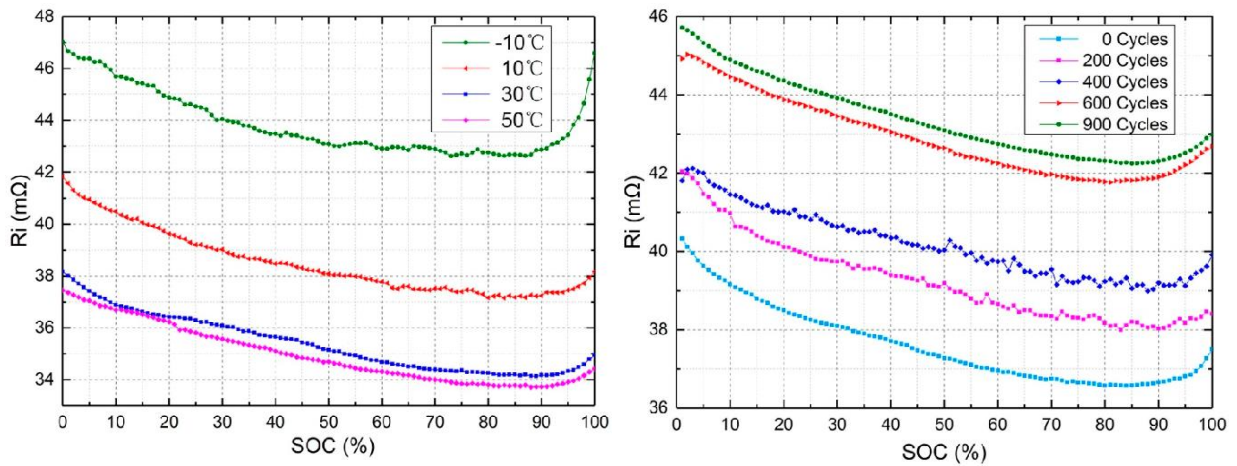


Figure 2-23. IR over SoC with consideration of temperature (left) and number of cycles (right). Reproduced from Wang et al.¹⁶²

Impedance also appears to follow these variations according to the SoC as well. Like IR, the components of impedance, such as the ohmic resistance (related to the electrolyte, separator, and current collectors) and the charge-transfer resistance, also exhibit significant dependence on SoC. At higher SoCs, the charge-transfer resistance generally increases due to reduced availability of active sites for Li-ion intercalation and deintercalation¹⁶⁵. The ohmic resistance appears to generally display less variation but may still experience minor changes due to electrolyte degradation or surface film evolution, such as SEI thickening, which can influence ionic transport

across electrode interfaces¹⁶⁶. This dependency highlights the dynamic nature of a battery's internal processes and underscores the importance of EIS in understanding battery performance and degradation over time. An illustration of impedance over SoC of cells are displayed in Figure 2-24, from an extensive EIS study from Huang et al. performed on several commercial cells¹⁶⁷.

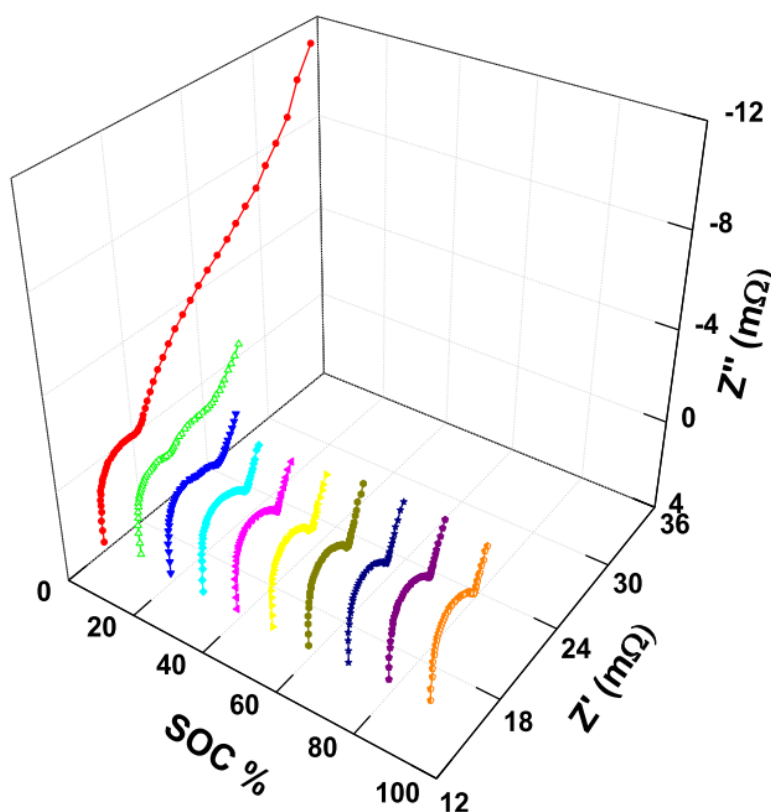


Figure 2-24. 3D plots of the Nyquist spectra for the studied battery at SoC values of 7.5% to 93.0%. Reproduced from Huang et al.¹⁶⁷

Another aspect to consider is the Li ions mobility within the cell, depending of the SoC. It can be speculated that it is at its highest from 50-80% according to the papers cited because IR is at its lowest during this SoC window. In a paper by K. Marker et al.¹⁶⁸, using the galvanostatic intermittent titration technique (GITT) combined with in-situ NMR, demonstrated an effectively higher Li ions mobility in this range for NMC811 half-cells. GITT provides a Li ion mobility value over a defined voltage window by applying short current pulses interrupted by long period of rest time to allow the cell to reach back its equilibrium state. The mobility is then calculated via an equation of known parameters, which varies according to experiments^{169,170}. As it

is shown in Figure 2-25 and noted by the authors, the first region (defined by $x < 0.1$) overestimates quite significantly the mobility because the cell potential did not fully relax when the following current pulse was applied during their experiment.

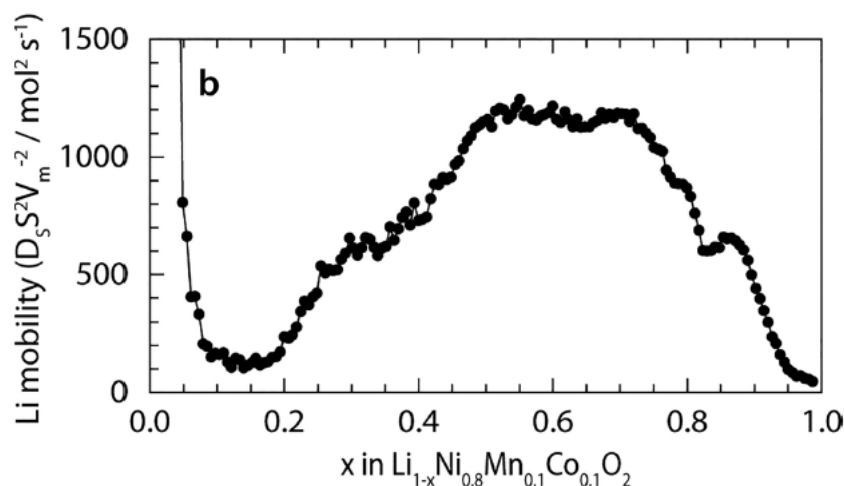


Figure 2-25. Li mobility over SoC obtained from GITT applied to NMC811/Li half-cells. Reproduced from K. Marker et al.

For potential charging applications, regarding the other end of the SoC window (80-100%), it would be preferable to lower the C-rate due to numerous reasons presented: higher IR, lower Li ions mobility and also the formation of potentially highly reactive singlet oxygen at above 80% SoC^{121,123}. Indeed, it has been demonstrated for HE-NMC and NMC 811, that these reactive oxygen species identified by operando emission spectroscopy, were released at higher SoC and led to the formation of CO and CO₂, as a result of problematic chemical reactions with the electrolyte and other safety issues. Its impact on cell capacity fade was also related. The problematic regions were found to be around 80% SoC for most NMC cells, but quite significant above 90% SoC for NMC 811 and 70% SoC for HE-NMC. It is important to note that relatively high currents were also used in these experiments. These two apparent and distinct battery characteristics (Impedance and Li-ion mobility) have been shown to be related in many aspects, as shown by Chien et al.¹⁷¹, where similar R vs SoC curves were obtained using GITT, EIS and ICI (defined in this case as intermittent current interruption), as displayed in Figure 2-26.

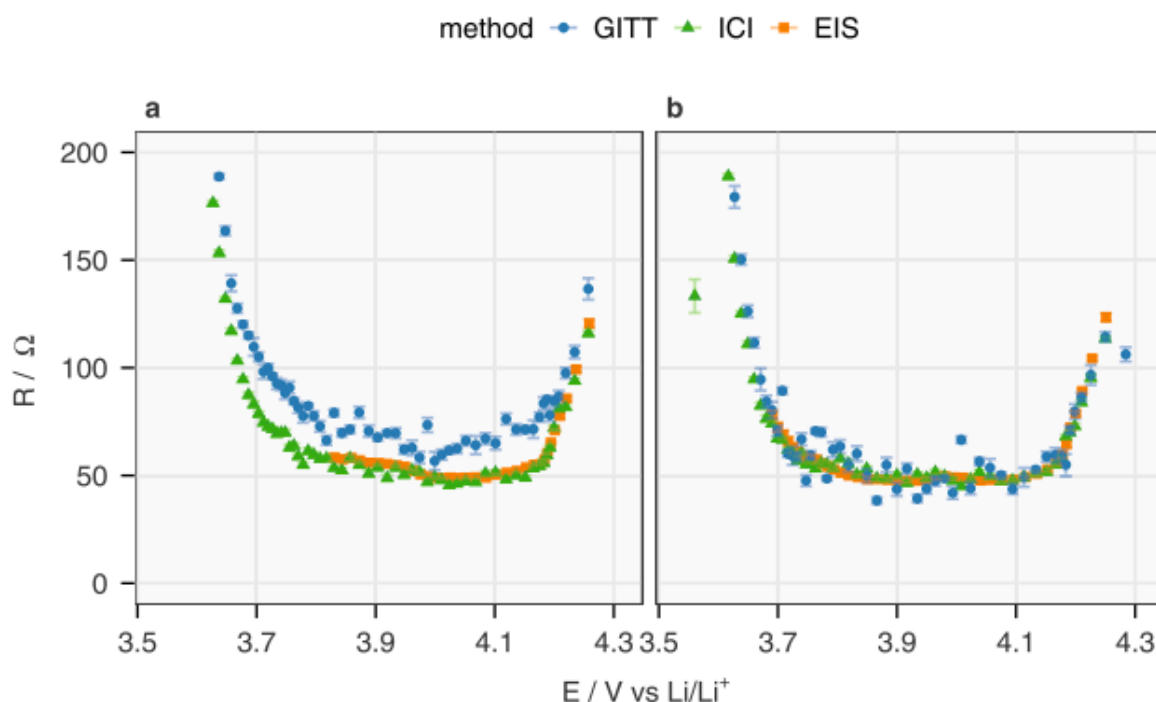


Figure 2-26. Comparison between the IR derived from the GITT, ICI method and EIS. The IR (R) of NMC811 in Cell 1 at various OCP of the electrode (E) derived from the GITT with data selection interval 5–40 s, the ICI method and the EIS fitting ($R_0 + R_1 + R_2$) during charging and discharging are plotted in a, b, respectively. The maximum of y-axis is set to 200 Ω to show the differences of the data above 3.7 V. The error bars originate from the standard deviation of the linear regression. Reproduced from Chien et al.¹⁷¹

However, a review published by Kang et al. highlighted significant variations in GITT measurements. Several studies were considered and significant variations were observed due to various reasons such as composition-dependent reaction overpotentials, non-diffusion-limited samples, errors in relaxation analysis methods, finite size and non-planar geometry effects, uncertainty in surface area estimation, contributions from the counter electrode, composition-dependent diffusivity, parasitic current and factor measurement¹⁷². The GITT from said studies are shown in Figure 2-27.

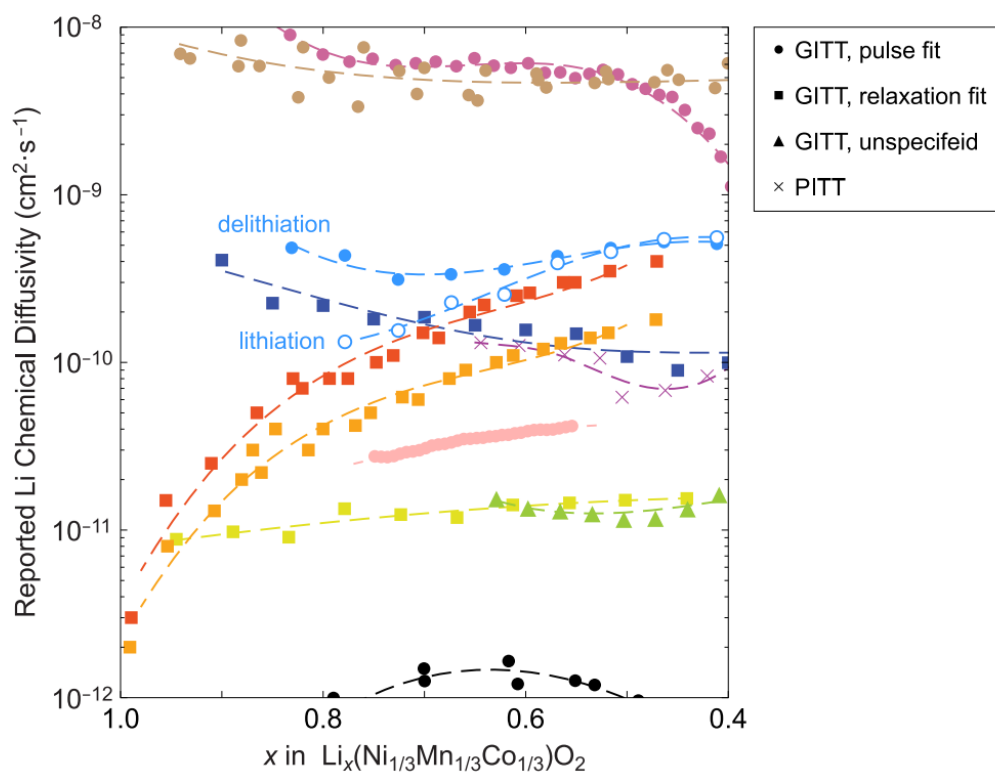


Figure 2-27. Inconsistent GITT diffusivity values reported in the literature. All data points are from the same material system, NMC111. In addition to the orders-of-magnitude inconsistency in the values, the qualitative dependency on Li composition is also discrepant among reports. The sky blue markers labelled lithiation/delithiation indicate measurements from nominally identical samples but with reversed current directions. Reproduced from Kang et al.¹⁷²

These behaviours underscore the complex interactions between the electrochemical processes within a battery and its SoC. A better understanding of these interplays could allow for specific adjustments of charging loads taking into account each SoC region, reducing stress on the cell.

2.6 High-Precision Coulometry

2.6.1 Theory and applications

A better understanding of the aforementioned degradation mechanisms and modes leads to better forecast capabilities as well. For this purpose, HPC is a potential

pathway, as it has been presented in the literature. It involves the accurate measurement of CE, also called Faradaic efficiency, is indicative of the age of the concept itself. Faradaic efficiency shares a namesake with Michael Faraday as it was first detailed in his landmark research “The Laws of Electrolysis” in 1834, with the concept simply coined as “current efficiency” and to account for what was referred to as “side reactions”¹⁷³. In more contemporary terms, CE can be defined as displayed in Equation 2-6 below:

$$CE_n = \frac{Q_{d,n}}{Q_{c,n}}$$

Equation 2-6

Where $Q_{d,n}$ and $Q_{c,n}$ are the discharge and charge capacities respectively of the battery system for each n^{th} cycle. A cycle with index n is defined as, for any charging/discharge procedure:

1. Starting from a lower-voltage limit, a cell is charged by a current source up to a set and fixed upper-voltage limit where the current is turned off. The total amount of charge that has left the current source and therefore passing into the cell during this period is defined $Q_{c,n}$.
2. The cell is then immediately discharged (i.e. involving no rest period) via a current sink back down to the same fixed lower-voltage limit. The total current discharged through the sink coming from the cell is $Q_{d,n}$.

Therefore, CE describes the charge efficiency by which electrons are transferred in batteries and is the ratio of the total charge extracted from the battery to the total charge put into the battery over a full cycle. Batteries have other ways of measuring efficiency, such as voltaic efficiency (VE) and energy efficiency (EE). VE represents the ratio of the average discharge voltage to the average charge voltage, and is analogous to voltage polarisation¹⁷⁴. Losses occur because the charging voltage is always higher than the rated voltage to activate the chemical reaction within the battery. Energy efficiency of Li-ion batteries lays, on the other hand, around 90%¹⁷⁵.

If CE_n is less than 1 for any cycle number n , it is assumed that side-reactions are effectively taking place within the cell and are hence not useful for storing energy. These side reactions are henceforth referred to as *parasitic reactions* and are a net

loss of energy of the cell per each cycle. The term is defined as the unwanted chemical reactions that consume active material, reversibly or irreversibly, where that material would otherwise carry out useful work in an electrochemical system (for instance, Lithium in a Li-ion cell). These parasitic reactions occur in all electrochemical systems and have been studied in this way for Li-ion cells as early as the late 1980s¹⁷⁶.

In essence, the CE of a cell is always less than 1 due to inevitable parasitic reactions that occur either due to thermodynamic instability of the materials in a cell or to kinetic effects from a current source/sink being applied as shown in a paper from Broussely et al. in 2005¹⁷⁷. In the case for Li-Ion cells specifically, despite the efficiency of a cell remaining high after many cycles (~ 0.995), parasitic reactions are always present. Though the CE of Li-ion batteries is high, as they are required to undergo many thousands of cycles for most cases, even a small parasitic loss each cycle will build up over the lifetime of the cell, and therefore even small improvements in early CE can make a significant difference to capacity fade over that many cycles¹⁷⁸. By measuring CE, we can account for all the charge that is not being used effectively and therefore have a quantitative measurement of the rate of total parasitic reactions per cycle. This logic and premise are the basis of what high precision coulometry (HPC) measurements aim to achieve. The aforementioned approach to measuring CE to account for parasitic reactions only works when the setup is very precise, accurate and consistent. This is because the CE is so high for Li-ion cells that small variations in measurement each cycle can lead to a large spread of values per cycle. Many CE values are reported in literature but their cycle-to-cycle variation is very high, around $\pm 0.5\%$, indicative of noisy and erroneous measurements since CE values are not expected to change significantly cycle to cycle.^{179–181}

Early beginnings and initial attempts at measuring CE with these considerations can be traced back to 1989 in a study by Murray and Alderson, where the authors carried out high precision measurements on Li/MoS₂ commercial cells¹⁸². However, their values resulted to be consistently in the range of 100.2 - 100.7%, revealing a physical impossibility with respect to the conservation of charge, hence highlighting limitations with the measurements. These erroneous results were attributed to two key problems. Firstly, the sample period (Δt) was limited to a 15 second interval, far too high and secondly, the measurement equipment was too noisy resulting in erroneous

current measurements over each cycle. These CE values are displayed in Figure 2-28 below.

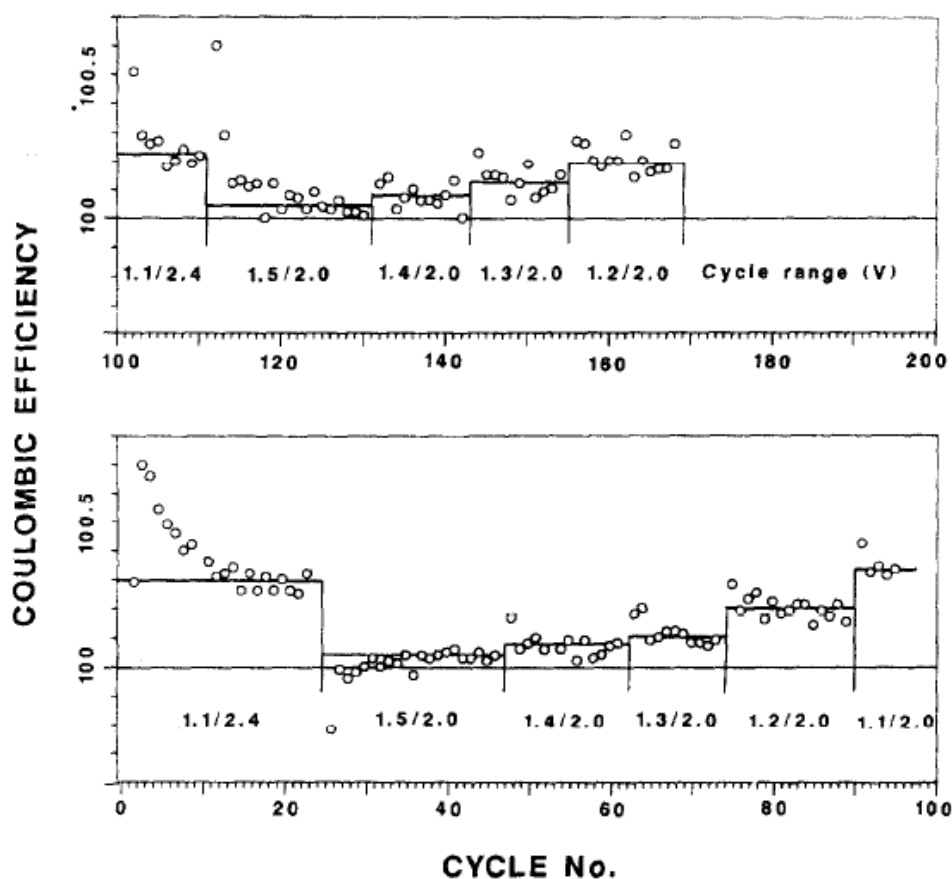


Figure 2-28. Coulombic Efficiency values for Li/MoS₂ AA commercial cells at various voltage limits and cycle histories. The horizontal lines indicate the mean values for each voltage cycling range.

Much more successful attempts and developments of the method and setups were made by Jeff Dahn's group, resulting in publications in 2010 detailing procedures to achieve successful HPC acquisition^{183,184}. As such, Smith et al. achieved more realistic values of CE (0.996 – 0.999) with lower standard deviation (see error-bars) with a custom setup. Not only are these figures in line with physical limitations (conservation of charge) but also arise from 30 LCO/Graphite commercial 18650 cells, ensuring their validity too. The results are displayed below in Figure 2-29; these represent how typical CE values from HPC studies are found since then in literature.

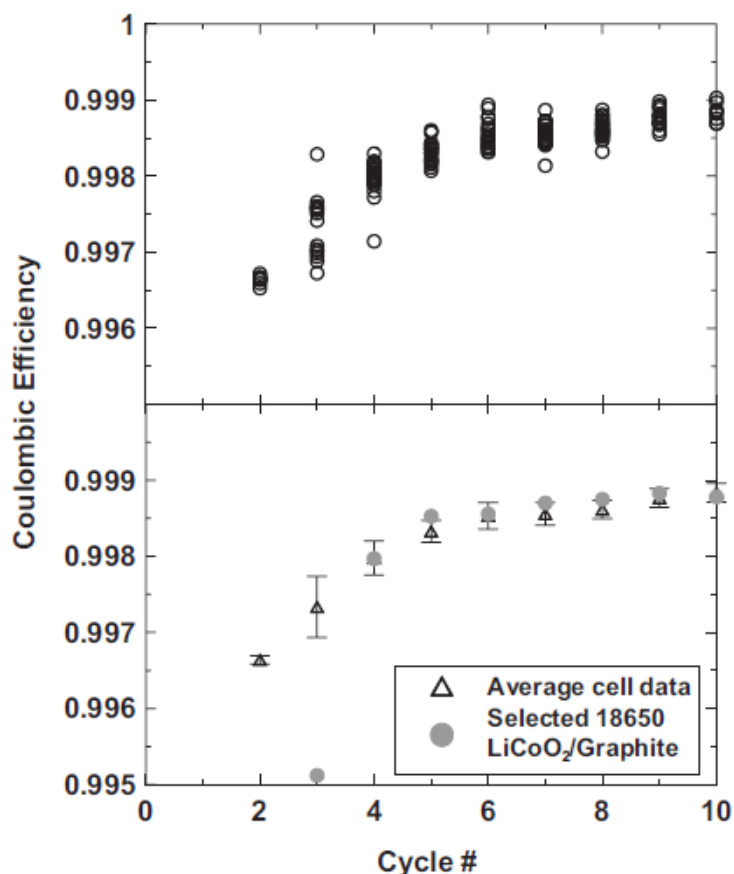


Figure 2-29. Top panel: CE values from 30 LCO/Graphite different commercial 18650 cells charged and discharged at C/24 at 30 °C, 3.0-4.2V range. Bottom panel: average and standard deviation of said cells.

One can see that the CE of the cells tends to increase with cycle number initially; this increase gradually tapers off to a plateau, settling on a more consistent CE value just after reaching 20 cycles. It is implied later on in the paper that this profile, created from fresh cells, is due to the consolidation of the SEI layer on the negative electrode. The first few cycles consume active material in the cell irreversibly and generate the SEI in the process, this shows up as high level of parasitic reactions, gradually tapering off as the layer forms more slowly with cycling. This still happens after the initial formation cycles to ensure valid SEI with the cells¹⁸⁵. Furthermore, Harlow et al. found that electrolyte oxidation at the positive electrode is the primary cause of the departure of the CE from unity for already aged cells and that increasing the cycling temperature or potential leads to lower CE values, indicating that parasitic reactions occur at a greater rate at higher temperatures and higher voltages¹⁸⁶. Early on, the technique showed potential to being able to provide an early qualitative

assessment and forecast of lifetime performance of cells¹⁸⁷, as it will be shown in the following sections, and strive towards battery materials leading to ever higher theoretical CE¹⁸⁸.

2.6.2 Setup and error mitigation

To achieve such low scatter and variability in CE measurements, Smith et al. were meticulous in their consideration of which factors contribute most to noise when measuring CE. Firstly, they identified four parameters that introduce error when calculating capacity, detailed in Table 2-2 below, the percentage error associated with capacity calculation is given by the symbol ΔQ .

Table 2-2. Table showing four key parameters that contribute to errors in capacity measurement identified. Adapted from Smith et al.¹⁸⁴

Source of Error	Symbol	Equation for ΔQ contribution	Explanation
Current Measurement	ΔI	$\Delta Q = \Delta I \cdot t_{cycle}$	Any error in current multiplied by the total time length of a cycle gives the wrongly measured quantity of charge that half-cycle.
Sample Interval	Δt	$\Delta Q = I \cdot \Delta t$	Between two samples, the current source may change its polarity introducing error once per half-cycle.
Voltage Measurement	ΔV	$\Delta Q = \frac{dQ}{dV} \cdot \Delta V$	Errors in voltage measurement might lead to the voltage cut-off being inaccurately placed, this can cut or add some capacity at the ends of each half-cycle.
Temperature Stability	ΔT	$\Delta Q = \frac{dV}{dT} \cdot \frac{dQ}{dV} \cdot \Delta T$	Changes in cell voltage due to temperature are calculated and treated as a voltage error in the same way as the above case.

Note that since CE is the ratio of discharge capacity over charge capacity, we refer to the error per half-cycle, as this will lead to the error when calculating said ratio.

By calculating these values, it is possible to see how much contribution each of the four parameters have to the error of the final measurement. This was done for a number of different commercial cyclers on the market at that time and it was concluded that none could provide the precision needed, and as a result, a custom solution was developed by the group, detailed at length in the paper.

Further improvements were made in the data post-processing, by the use of interpolation and “endpoint subtraction”¹⁸⁹, best illustrated in Figure 2-30, where an illustration of charge over-shoot is observable on the left image. Due to the fact that any charging system must sample a finite number of data-points, it will always overshoot the “true” upper-voltage limit and lower-voltage limit. This is because the control system in most charging systems sends the command to stop charging/discharging once they have met the upper or lower set voltage limits (i.e. above or below this limit respectively). As such, there is a time delay, and in this time the current source/sink will continue to deliver/receive current beyond this limit¹⁹⁰. Due to the precision requirement of the measurement, Bond et al. explain that extra current must be accounted for and the “true” capacity of the charge or discharge is given by the following two equations, referencing the illustration presented in Figure 2-30.

$$Q_D = Q'_D - A_1 - B_1$$

Equation 2-7

$$Q_C = Q'_C - B_1 - A_2$$

Equation 2-8

Where Q_C and Q_D are the true values of charge and discharge capacity respectively; A_1 and B_1 are the capacities due to charging beyond the voltage limit and below it, respectively, A_2 being the following cycle’s charging capacity.

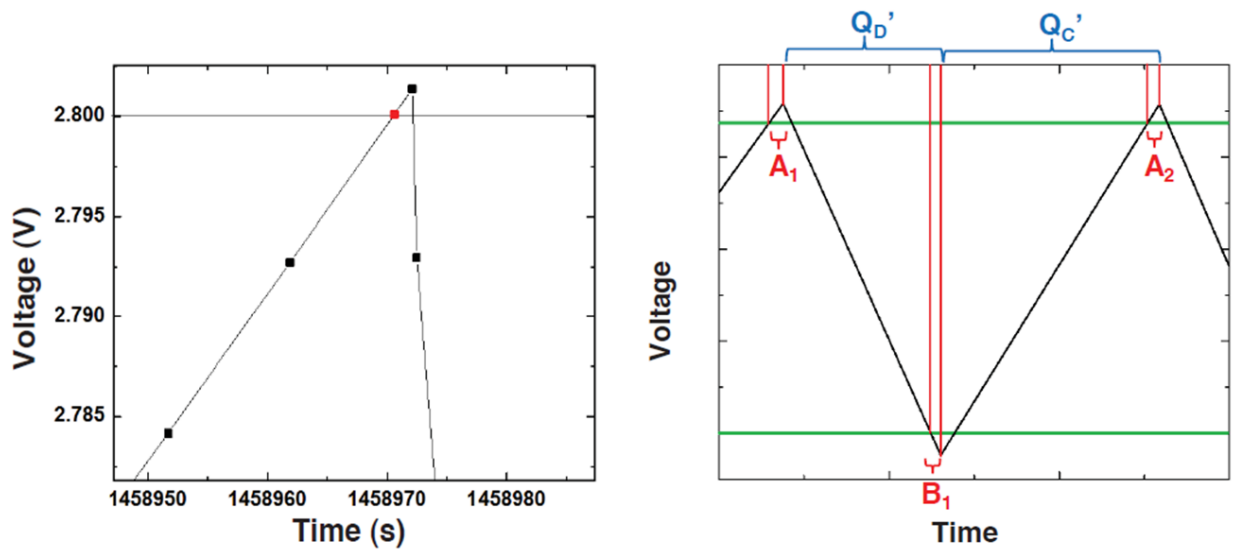


Figure 2-30. Illustration of the endpoint correction. Left figure: The data in black represents the measured data collected from the cycler, while the red data point indicates the point at which the voltage limit is crossed (determined by linear interpolation). Right figure: illustration of how capacity is corrected for charge that is transferred beyond fixed voltage limits. Reproduced from T. Bond¹⁹⁰.

To find the total capacities beyond the overshoot, the exact time-stamp at the voltage limit is needed, then integrated to the current from that time-stamp until the end of charge. To find this voltage-limit time-stamp, linear interpolation is to be used between the two data-points immediately above and below the voltage limit, followed by integration. The procedure is then repeated for measured current readings. Additional improvements were then implemented leading to a new HPC setup that was upgraded and coined as an Ultra-High Precision Charger (UHPC). Improvements include:

1. True measurement of the current source/sink's output and input (rather than assuming constant current charge/discharge as previously done).
2. Temperature control of each cell, current sources and digital multi-meters.
3. Increased data sample rate.
4. Voltage stabilisation of power supplied to current sources and digital multi-meters.

From these modifications, the greatest impact was found to be, by far, the measurement of the current value itself according to the study¹⁸⁹. Before, the current source was calibrated then assumed constant at the value it was set to, while in reality

it was found to fluctuate greatly. The second most impact was found in controlling the temperature of the cell, current sources and digital multi-meters. This provided a significant reduction in error as illustrated in the extracted Figure 2-31, shown below. A later perspective on temperature control was provided in 2019 by Zülke et al., who recommended that HPC studies should be performed in cooling thermal baths for consistency and results reproducibility purposes¹⁹¹. However, the emphasis was made on commercial high-power cells done at high rate (1.5C in their study), which led to self-heating of 14K in thermal chambers as opposed to 2K in comparison for cells cycled in a thermal bath. At such high rates, the self-heating appears to be heavily affecting the CE values.

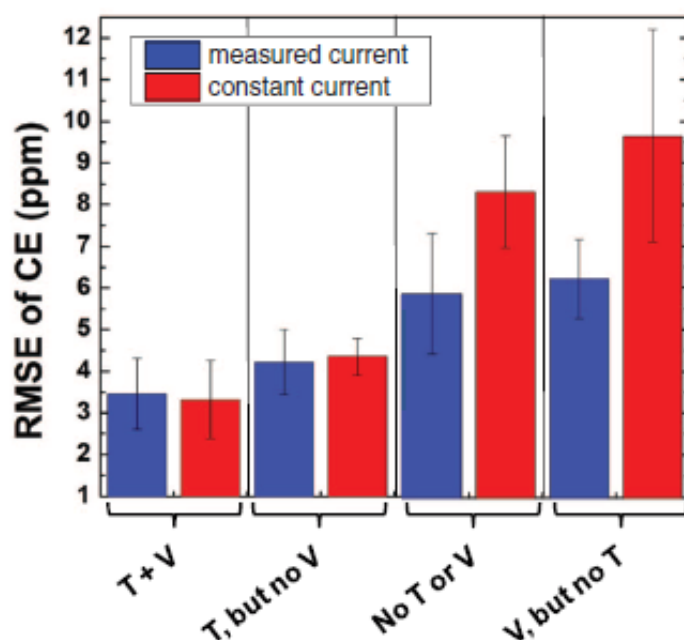


Figure 2-31. RMSE (averaged from 2 cells) of CE data collected using the UHPC in 4 different configurations as indicated. “T” refers to temperature control of instruments, and “V” refers to voltage stabilisation of instrument power supply. Reproduced from Bond et al.¹⁸⁹

The error, or rather, precision of the readings is obtained by employing a quadratic fitting function and then calculating the root mean square error (RMSE) of the data in relation to the fitting function. This is a commonly used statistical method in measuring the spread of data, and also referred to as polynomial regression. It is

defined as in Equation 2-9 where x_d is the measured data point, x_f is the point on the fitted quadratic function and N is the total number of data-points.

$$RMSE = \sqrt{\frac{(x_d - x_f)^2}{N}}$$

Equation 2-9

Bond et al. advise for the use of a quadratic function for the fitting of the data with the lowest possible number of parameters, as to capture the parabolic trend and initial gradient of CE during the first cycles. It is also stated that the first couple of cycles are simply excluded during fitting as they can be significantly lower than when stabilisation is reached. The term “accuracy” is also introduced, which in the context of HPC (as opposed to the more traditional understanding of the term), refers to the measured differences between CE datasets. This accounts for the combined effects of both channel-to-channel (due to the difficulty to have identical channels) and cell-to-cell variations (due to the variations between cells, despite being of the same model and batch). It uses the same RMSE formula, but this time, each CE value of each dataset is compared between each other. The RMSE are typically given in ppm, due to their very low values, in this context.

In Figure 2-31 we can see that the most significant contributions came from using “measured current” i.e. the blue bars and there is little advantage in stabilising input voltage from the electrical grid. The uncertainty bars even overlap significantly, indicating there may be no advantage at all. Conversely, it was found that increasing the data sample rate provided little advantage except only at the start and end of charge. Therefore, a large sample interval during the middle of charging and discharging can save on collecting unnecessarily large data and instead, only fast sample rate at the ends of the charge/discharge curve.

Beyond the setups proposed previously, other alternatives have been found in literature to try to approach the desired precision and accuracy for an HPC measurements without the use of expensive cyclers and equipment such as Novonix. Wilhelm et al. for instance used a BaSyTec CTS battery test system for a study on LFP commercial 18650 cells, with the addition of 20 mΩ shunts in their setup¹⁹². In this way, the voltage drop across each shunt is then measured with an external

equipment, in this particular case, an ultra-low noise, 24-bit sigma-delta analog-digital converter. This enables the measurement of the currents flowing into and out of each battery cell with a higher resolution and precision than the battery test system itself¹⁸⁹. Error measurements and RMSE values were not provided during the study, but CE showed results satisfactory according to the literature presented previously.

2.6.3 Interpretation of High-Precision Coulometry results

There have been several studies made into the physical interpretation of high-precision CE results, specifically in relating the evolution of CE vs. cycles, to cell cycle-life predictions. A 2011 study by Smith et al. attempted to account for all parasitic reactions observed when measuring CE by linking CE to some well-known degradation mechanisms¹⁹³. The paper uses what it refers to as “Lithium accounting model”. Essentially, it models a Li-Ion cell as composed of 4 separate parts: the positive electrode, negative electrode, SEI and electrolyte. Since Lithium is conserved (no nuclear processes occur) then some parasitic reactions will move Lithium from one location to another (irreversibly) and this, along with reactions that do not involve Lithium, will account for all parasitic reactions, and ultimately cause degradation. The authors go on to describe five parasitic processes that either increase, decrease or are negligible to the amount of active Lithium within the cell, and these are summarised in Table 2-3, along with the degradation process causing them. The total amount of changing Lithium is expressed in terms of capacity first, then converted into parasitic “currents” which are the charge lost or gained per unit time.

Table 2-3. Summary of the five main degradation processes and their effect on Lithium inventory, as described by Smith et al¹⁹³.

Name of Process	Description of Parasitic Reaction	Effect on Lithium inventory
SEI Growth and Repair	As the electrolyte and negative electrode react, they form the SEI. This consumes Lithium and electrolyte material irreversibly but the rate of reaction decreases over time.	Decreases
Electrolyte Oxidation at Positive	Due to a large potential difference at the interface of the electrolyte and positive electrode, some electrolyte material is oxidised and often deposits on the surface of the positive. Each electron deposited by the electrolyte adds to the overall cell capacity and pulls Lithium salt out of the electrolyte.	Increases (but depletes electrolyte)
Electrolyte Shuttle	The electrolyte may oxidise at the positive as above but does not deposit but shuttles between the negative and positive therefore increasing self-discharge but not affecting the "Lithium inventory".	None
Transition Metal Dissolution	The metal oxide material at the positive may be thermodynamically unstable and dissolve into the electrolyte at higher voltages. It will then collect charge at the negative and bring it back to the positive inducing a shuttle mechanism.	None
Positive Electrode Damage	The positive electrode may crack or undergo fatigue due to volume changes under cycling. This cracking can lock away Lithium permanently if there is no conductive path to access it.	Decreases

The authors also introduce the "charge endpoint slippage" and "discharge endpoint slippage", best illustrated by Figure 2-32, where Δ_c and Δ_d represents the slippage for charge and discharge respectively. Slippage represents how voltages curves do not return back to their original position when plotted against capacity. This is necessarily the case due to capacity fade of a cell over time and a CE lower than 1. Therefore, these slippages were attributed by Smith et al. to the parasitic currents in a cell and they only took into account the ends of the curve rather than points along it¹⁹⁴.

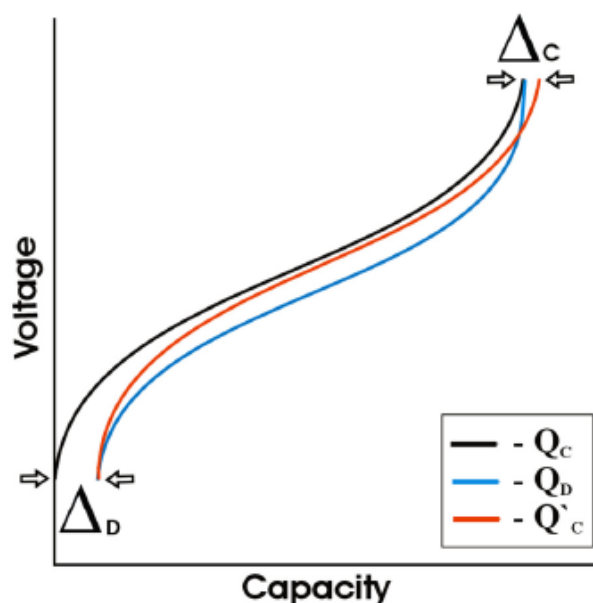


Figure 2-32. Illustration depicting the discharge endpoint slippage (ΔD) and charge endpoint slippage (ΔC) of a Li ion cell. Reproduced from Smith et al.¹⁹³

Furthermore, and as it has been discussed in previous sections, the majority of the SEI forms within the first few cycles of a cell's lifetime and the cell will then slow SEI formation fairly rapidly, meaning that parasitic reactions are relatively higher for the first cycles of a cell's lifetime. It should also be noted that any cells that are purchased commercially will have already undergone formation and therefore the extent of CE during formation is not knowable in these cases. It has been shown in numerous studies that the quality of the SEI layer can dramatically determine how the cell performs.^{195–197} Ellis et al. use these observations to try and determine the best possible formation cycle that a cell should undergo to ensure better functioning using HPC in combination with other techniques such as EIS. In this particular case, the preferred formation protocol, a hotter 60 °C with longer voltage hold, as opposed to colder temperature and shorter holds, revealed higher CE and no lasting effect on long-term cycling or increase in impedance compared to standard protocols. The study concluded that the better CE was primarily due to reduced charge end point capacity slippage, suggesting a reduction in parasitic redox reactions at the positive electrode, and an SEI that was becoming more inorganic over time¹⁹⁸.

Smith et al. shows that using HPC and EIS, it is possible to analyse and predict the onset of “rollover failure” of cells with various electrolyte additives¹⁹⁹. Figure 2-33

displays the Capacity fade and HPC data of five identical pairs of 18650 NMC/Graphite cells that have been built with five different electrolyte additives. The HPC measurements, coupled with extended cycle life data, helped identify the additive combinations that improved the lifetime of the cells. Traditional testing methods were unable to distinguish which cell would fail first based on short-term measurements alone, however, the HPC measurements provided insights into the performance of each additives and predicted the onset of rollover failure (also known as “knee point”) for each cell. The authors highlights that the short-term HPC data was collected during weeks, as opposed to potential years for lifetime data.

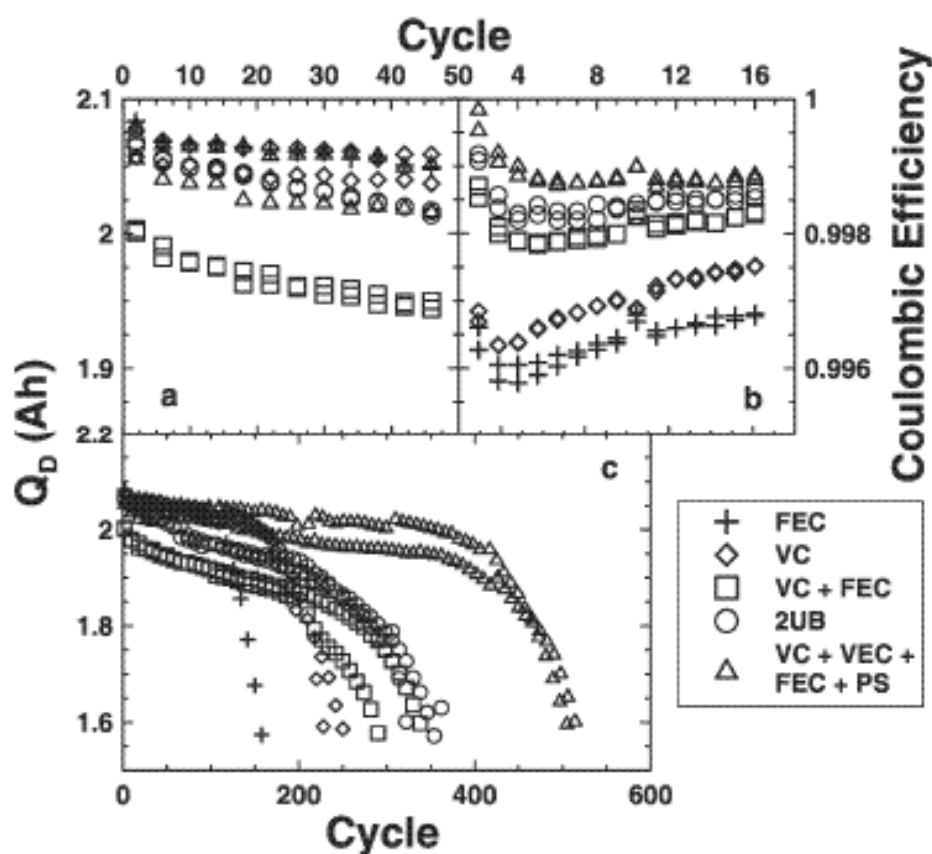


Figure 2-33. Capacity fade and HPC data for 18650 commercial cells with various additives. Reproduced from Smith et al.¹⁹⁹

Another study from Burns et al. used HPC profiles to determine the effect of Lithium plating on CE. Due to the inefficiency of the lithium plating and stripping during the operation of the cell, this action is captured as parasitic reactions by HPC²⁰⁰. Lithium plating (favoured by low temperature and high C-rate), when occurring within

a cell, becomes evident with lower CE values, as illustrated in Figure 2-34. Cells were also opened and examined to confirm the presence of plated lithium during post-mortem studies.

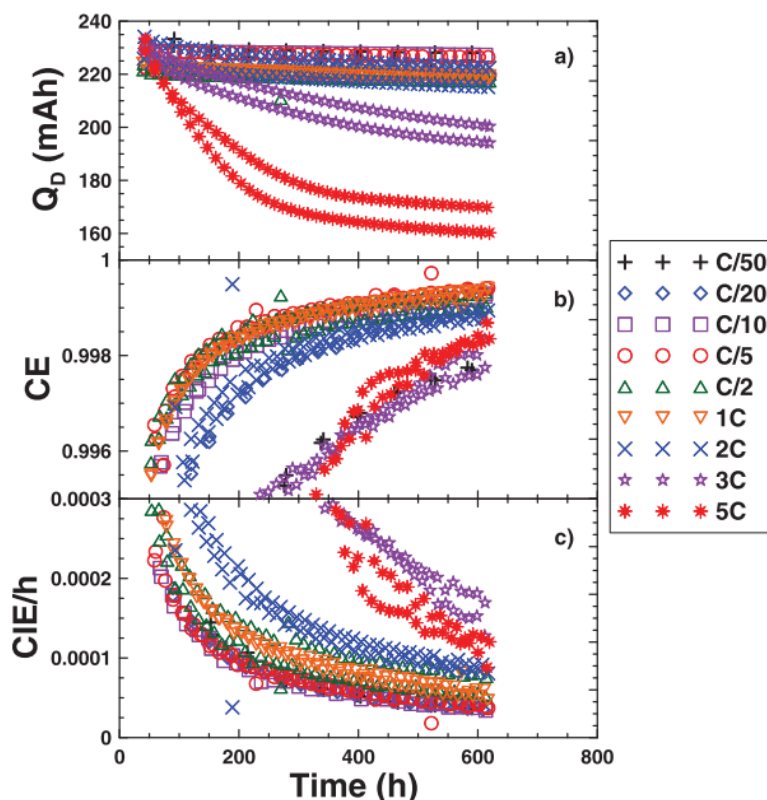


Figure 2-34. Capacity (a), Coulombic efficiency (b) and Coulombic inefficiency per hour (c) versus time for pouch cells cycling at 30°C during cycling with various C-rates. Reproduced from Burns et al.²⁰⁰

More contemporary uses of CE in literature are displayed in Figure 2-35. A typical representation is usually when shown on the right axis in combination with a capacity vs cycle number plot, as observable in a) and b). It can arise from coin cell materials assembled from altered or damaged electrode and assess their differences, such as NMC 811 material exposed to ambient air in Jung et al.²⁰¹ or the study of the validity of a certain configuration or method, such as Li-NMC 811 half-cells coin cells as studied in McNulty et al.²⁰². Other studies include the assessment of performance or validity of solid-state electrolyte cells, or anode-free or zero excess lithium metal batteries, such as presented in Genovese et al.²⁰³. Further uses arise from new synthesised or modified material performance assessment against a known baseline

material, such as the study of Li et al. of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ material against a new variant with additional oxygen vacancies and reduced Mn²⁰⁴.

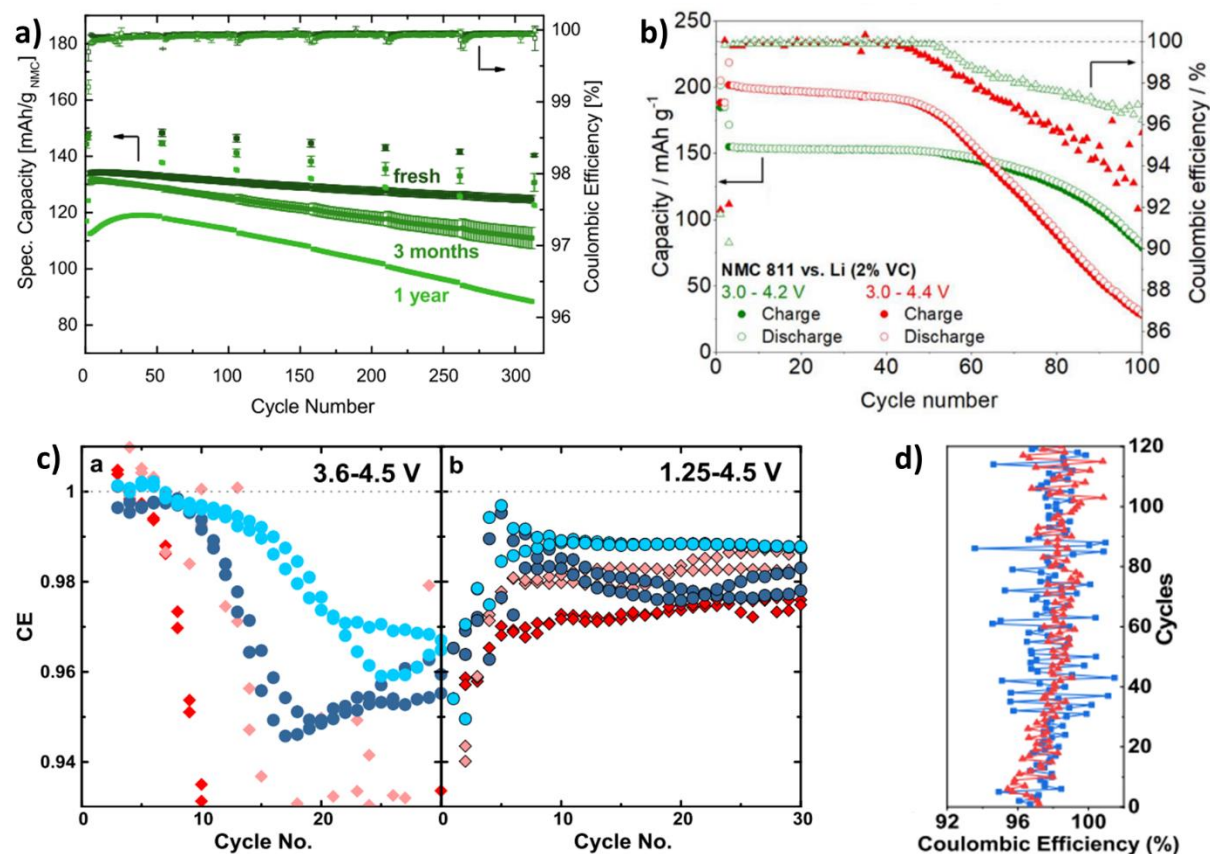


Figure 2-35. Various display of CE found in more recent literature. a) specific capacity and CE plot vs cycle number of NMC 811/graphite coin cells reassembled with NMC 811 electrode material left at ambient air storage for 3 months and 1 year compared to fresh material. Reproduced from Jung et al.²⁰¹ b) capacity and CE plot vs cycle number of NMC811 half-cells coin cells with two distinct upper-voltage cut-off. Reproduced from McNulty et al.²⁰² c) CE calculated from anode-free cells cycled with a voltage range of 3.6–4.5 V and 1.25–4.5 V. Reproduced from Genovese et al.²⁰³ d) CE vs cycles plot of pristine $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ (LRMO) cathode material (blue) and a modified sample $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-\delta}$ (M-LRO) with oxygen vacancies and a reduced Mn structure (red). Reproduced from Li et al.²⁰⁴

2.7 Conclusions and perspectives

The Li-ion battery is a prime candidate for the electrification of the automotive industry and the energy transition to a more sustainable future. As a result, it has been extensively studied in the literature, and the industry is extremely attentive to any ground-breaking discovery in this domain. Ni-rich cathode materials like NMC 811 and high-nickel content NCA have been prioritised by the industry for several years. Despite novel cathode materials, doping strategies or coatings published in literature over the years, manufacturers still rely on traditional NMC and NCA cathode chemistries and graphite-based anode materials, and it is expected to remain like that until a significant breakthrough appears either on solid-state electrolyte or next generation of batteries (Sodium-ion, Lithium-Sulphur, Lithium-air etc.). As it was more the focus of this review, it is crucial to deepen the understanding of Ni-rich cathode materials for the current and next generations of Li-ion batteries. This is in consideration of its coupling with graphite, which has established itself as a fundamental pillar of Li-ion technology for several decades now, consistently used in commercial cells as the negative electrode material of choice.

Primary degradation mechanisms have been evidenced throughout this chapter, and are at play within both positive and negative electrodes, and have been shown to have complex interactions and cross-talk. Indeed, SEI growth, lithium plating, and structural changes in electrodes often trigger or exacerbate each other, creating complex multi-scale interactions. For instance, mechanical fracture of electrode particles exposes fresh surfaces, accelerating SEI growth and lithium inventory loss, while dissolved transition metals from one electrode can deposit on another, further complicating degradation. Additionally, many experimental conditions simultaneously activate multiple mechanisms, making it challenging to decouple their individual effects. Comprehensive models are required to capture these interdependencies, and to manage to fully integrate the complex physical and chemical interactions observed in real-world conditions demanded by applications in the EV or aerospace sectors, for example. Each electrode contributes uniquely to cell degradation, often through pathways influenced by cross-talk and the dynamic environment within the cell, and their decoupling could be a starting point of choice. In the absence of three-electrode

cell setups for operando diagnostics, alternative methodologies such as the use of electrochemical proxies, ICA or DVA, half-cell configuration coin cells or direct ex-situ characterisation all can provide individual electrode degradation information.

Additionally, SoC has been identified as a critical parameter influencing degradation pathways as well, with distinct mechanisms dominating at specific SoC ranges. For instance, at high SoC, structural instability due to oxygen release and lattice collapse in Ni-rich cathodes exacerbates capacity fade. SEI growth, electrolyte decomposition and the rate of parasitic reactions have also been shown to increase at these high SoCs and voltages, while at low SoC, lithium plating risks increase, particularly under low-temperature conditions. The middle SoC range often exhibits higher Li ion mobility and reduced impedance, suggesting that SoC-specific protocols could mitigate stress on the electrodes. For instance, most VCPs presented in this review seem to start charge at high C-rates and then decrease it until the top of charge, which is in appearance counterintuitive given that impedance has been shown to be high and Li mobility low in this low SoC area. A VCP tailored to these dynamics represents a significant innovation and has been suggested and adopted in literature and industry, but a detailed mechanistic understanding of their efficacy is still needed. By modulating current in specific SoC regions, VCP could aim to minimise degradation by avoiding conditions prone to lithium plating and overpotential-induced damage. Experimental studies presented in this thesis will evaluate how these adaptive cycling strategies affect cell performance, both at the macroscopic scale and at the microstructural level.

The review also highlights the significance of CE as a critical metric for understanding and predicting the performance and longevity of Li-ion batteries, as very long-term cell cycling is quite capital and time extensive, and sometimes simply not possible in real-world situations. HPC has proven to be an invaluable tool for detecting minute losses in efficiency, which often result from parasitic reactions such as SEI formation, electrolyte decomposition, and lithium plating. These reactions, while typically minor on a per-cycle basis, accumulate over time, leading to capacity fade and reduced battery lifespan. Despite its clear potential, as highlighted in several studies, the full capabilities of HPC are yet to be fully realised in commercial battery diagnostics. The potential for the method's ability to provide early indicators of battery degradation offers a path forward for the development of more durable and reliable

energy storage systems. However, challenges related to measurement and setup accuracy and the need for more standardised methodologies must be addressed to fully integrate this technique into widespread use. Although several studies reached a couple of thousands cycles, SoH levels below 50% or non-linear fade behaviour were only occasionally reached, and as such, it was identified that a definitive study with very long-term cycling data was lacking, to provide a final answer confirming or not the potential systemic use of HPC as a reliable forecasting tool. Lastly, several studies highlighted that knee-point or rollover fade could be predicted. Given the complex interactions of all primary degradation mechanisms and how challenging these non-linear fade behaviours are to predict, particular attention to this will be taken during HPC tests to follow in this thesis.

Lastly, this section highlighted the overall complexities of understanding calendar ageing, embodied mainly by the "spoon-shape" effect, which presents a multifaceted nature and varying interpretations in the literature. Different studies attribute the apparent capacity increase at 100% SoC for instance, to mechanisms like anode overhang lithiation combined or not to a cathode-driven shuttle mechanism, while others suggest this increase was tied to reversible processes that mask irreversible losses during prolonged storage. Others highlight the impact of SiO_x particle expansion or side reactions at the electrode interfaces. Moreover, factors such as storage conditions (duration, temperature and SoC) and cell chemistry critically influence the observed degradation patterns, which complicates the identification of potential universal phenomena. Understanding the spoon-shape effect necessitates separating the overarching degradation mechanisms from localised and punctual phenomena, like the apparent temporary capacity gained at 100% SoC. These must be analysed independently to accurately model the ageing process and predict the performance for subsequent cell cycling.

3 Methodology

3.1 Electrochemical characterisation

3.1.1 Battery cycling

For the battery cycling carried out in this thesis, several cyclers were used. A BioLogic BCS-815 Potentiostat (BioLogic, Seyssinet-Pariset, France), a Maccor high-precision test system model 4300 Desktop Automated System (MACCOR, USA), a Novonix UHPC 2A (Novonix Battery Testing Services Inc., Belford, Canada) and a Digatron MCT-2-6-16/10-6-16/10-18-8 HD cycler (Digatron Industrie-Elektronik GmbH, Aaschen, Germany). Their main characteristics are summarised in Table 3-1, with the specification if the cycler is used in Chapter 4, which focuses on HPC. The accuracy is expressed in percentage of the full-scale resolution (FSR) of the voltage and current ranges. Each cell was connected to the rack using a universal cylindrical cell Gamry holder, able to accommodate both 21700 and 18650 models, and a thermocouple (fixed with Kapton tape on the mid-section of the cell) which allowed a directly integrated temperature measurement into the final dataset. The software used is the BT Lab v1.65 which allows cycling, testing and possess data analysis modules which are directly integrated. For cycling, the ModuloBat module was used as it allowed all the basic tools for standard cycling as well as EIS (detailed in 3.1.3) directly available to add to the chain of command within the same script. As the determination of a precise protocol is an intrinsic part of this project, the precise procedures and protocols will be specified in detail in the relevant sections of this report.

Table 3-1. Main characteristics of the battery cycling systems used throughout this thesis

Manufacturer	Model	Ranges	Accuracy	Used in Chapter 4 (HPC)
BioLogic	BCS-815	200 μ A – 5 A 0 – 10 V	0.015 % FSR	No
Maccor	4300	300 μ A – 5 A 0 – 5 V	0.02 % FSR	No
Novonix	UHPC 2A	100 μ A – 10 A 0 – 5 V	0.005 % FSR	Yes
Digatron	MCT-2-6-16/10-6-16/10-18-8 HD	300 μ A – 5 A 0 – 6 V	0.05 % FSR	Yes

Whenever possible, every cell setup and holder were kept as a 4-wire connection; that is, for each electrode, two cables were used: one for current and one for voltage reading. This allows for better voltage measurements as opposed to a 2-wire connection, effectively excluding the voltage drop caused by the contact and cable resistances. This is the case for all the cycling done in Chapter 4, when manual soldering of the cables was performed on each cell. The rest of the cycling in other chapters was done using standard cell holders provided by the manufacturer of each cycler.

The main cells used throughout this thesis are three cell models from LG Chem (Seoul, South Korea): MH1, MJ1 and M50 of dimensions 18650, and 21700 for the latter. Three additional 18650 models were used in Chapter 4, but are referred to as cells “LCO/HC”, “LCO/Graphite” and “NMC/Graphite” throughout, due to confidentiality agreement with the project’s industrial partner and cell provider, as it will be further explained. The cells were cycled at 20°C, 0°C or ambient temperature (in a climate-controlled lab environment) depending on the experiment, and this will be specified when relevant.

3.1.2 High-Precision Coulometry setup and consideration

This section describes the various setups used namely for the results presented in Chapter 4. The goal was to compare a known HPC cyclers with a less precise/accurate equipment, to compare the cycling information obtained. For this purpose the two cyclers used are:

- Novonix UHPC 2A module (Novonix Battery Testing Services Inc., Belford, Canada) and its respective environmental thermostatic chamber (Resistive heating method and Peltier cells cooling method).
- Digatron MCT- 2-6-16/10-6-16/10-18-8 HD (Digatron Industrie-Elektronik GmbH, Aachen, Germany). Combined with Vötsch VT 3050 environmental chamber is announced at $\pm 0.5\text{K}$ as per the user manual, resistive and compressor cooling.

3.1.2.1. Cyclers precision and accuracy calculations

The Novonix cycler is known for its use for HPC cycling as it is one of its main selling points, and hence the Digatron system's precision/accuracy will be compared to it to ensure its potential validity for HPC acquisition. However, as discussed in Chapter 2 Section 2.6, the intrinsic characteristics and resolution of the circuitry alone are not sufficient to determine the validity of HPC cycling, and the setup as a whole must be considered. This includes elements such as temperature control and measurements, holders, cables etc, that have been shown to have an effect on CE.

To obtain objective and coherent precision and accuracy values for a designated setup, the procedure detailed in Bond et al. was followed¹⁸⁹. This was done as this study was shown to be one of the only one that provided quantifiable values of precision and accuracy, and hence, allowing comparison a different setup compared to one that is known to be up to HPC standards. A quadratic fit of the CE values of a designated cycled cell is obtained, and then Equation 2-9 is used to calculate the RMSE for precision, giving its value then converted in parts per million (ppm). As observable in Figure 3-1, a) a better polynomial fit (namely, as a higher degree polynomial) could be applied in order to increase the coefficient of determination R^2 ,

but it has been kept as such to allow a comparison between our present setups and values obtained in literature. Indeed, the study suggests a 2nd order polynomial to account for the “long-term curvature that is commonly seen in CE data”, and is not intended to attempt to come up with a predictive model¹⁸⁹. As it will be shown in this chapter, different cell types and chemistries possess different sets of patterns in CE values. Furthermore, the study calls for the exclusion of “the first few data points” of the dataset due to the poor fit to the parabolic curve, accounting for what appears to be the first 4 cycles excluded for a fit in an illustrative figure found in the study. Figure 3-1 shows the effect the omission of various cycles has on the fit and the subsequent RMSE values. b) displays a 5th order polynomial and logarithmic fits of the data, skipping 2 values, showing a hypothetical better fit for modelling purposes, which would here defeat the purpose of comparison. After consideration, it was decided that all further values of RMSE for precision and accuracy were obtained by skipping the first cycle only. It is also capital to specify that in order to have coherent calculations useful for comparative purposes, CE values as a ratio are ought to be used, and not CE as a percentage value: this will effectively add two orders of magnitudes of error to the RMSE.

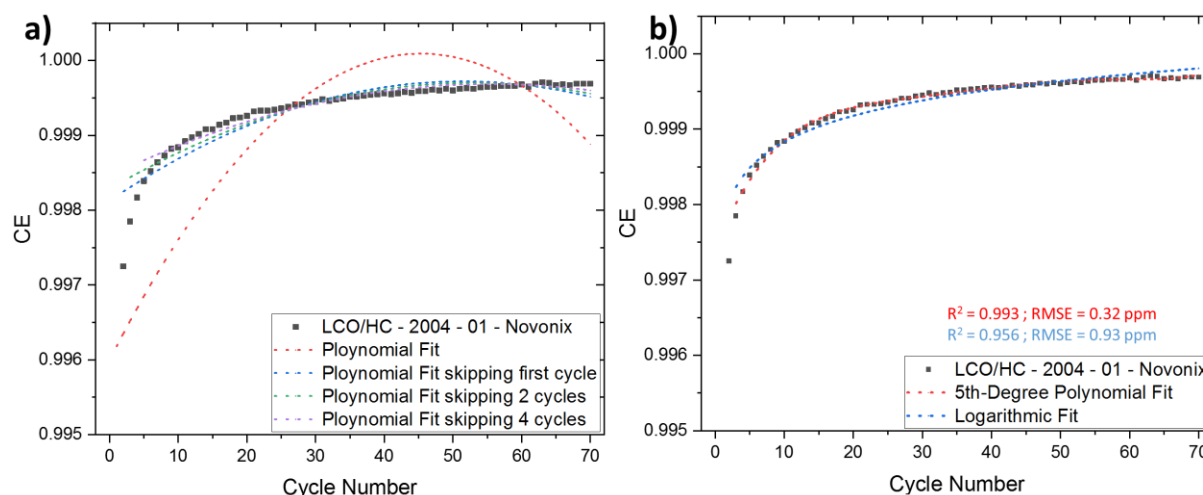


Figure 3-1. a) CE value with four different corresponding quadratic fit depending on the number of values skipped for said fit, and their corresponding R^2 and RMSE values. The CE of the first cycle is 0.982, not displayed in this figure. b) Additional 5th degree polynomial and logarithmic fits carried out skipping the first two values.

RMSE values for accuracy were calculated in a similar way. As discussed in Chapter 2 Section 2.6.2, in the context of HPC and as opposed to the more traditional understanding of the term, accuracy in the Bond et al. study refers to the measured differences between CE datasets. This effectively accounts for the combined effects of both channel-to-channel and cell-to-cell variations. It uses the same RMSE formula, but this time, each CE value of each dataset is compared with each other. A procedure for this would theoretically imply to cycle the same individual cell on different channels; which is not possible as once cycled; said cell would not be in the same condition for an identical cycling on a different channel. Hence, for the RMSE value for accuracy, cells from each batch were considered as identical for the calculations, accounting only for channel-to-channel variations. Figure 3-2 below displays as an example the CE of two cells coming from the same batch from the same cell type cycled on the Novonix and Digatron systems.

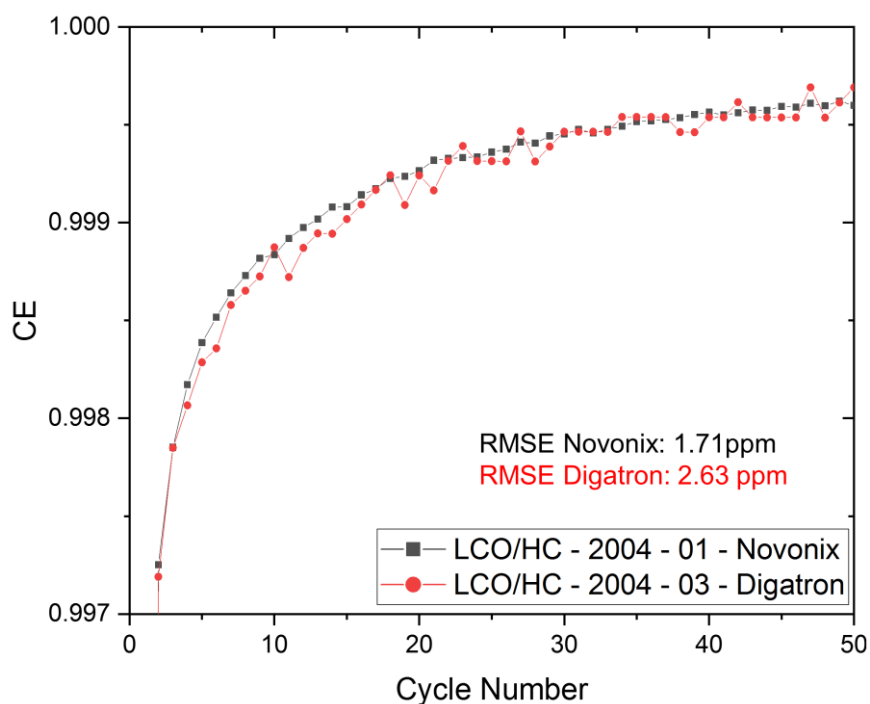


Figure 3-2. CE values for two cells from the same cell type and batch cycled on Novonix and Digatron, and their respective RMSE values. Cycling was done at C/5 and the first 50 cycles are on display.

In addition to both cyclers used for this chapter, values from cells from Chapter 5 were also considered for comparison. Those were charged and discharged using a Biologic cycler while left in an ammo box in an ambient temperature laboratory, with the temperature measured with a type K thermocouple. Table 3-2 summarises all values obtained for precision and accuracy in ppm, the number of cells considered to obtain such data and their respective ways for temperature control and measurement methods. The precision obtained in our setup is notoriously low and close, in the same order of magnitude, while the Novonix ones are smaller (0.761 ± 0.730 ppm as opposed to 1.01 ± 0.438 ppm). The accuracy measured is slightly higher for both cyclers compared to the data found, with a difference between the two, as the Digatron is higher here as well. In comparison, the values for the Biologic cycler setup display precision and accuracy values a whole order of magnitude higher. This is in accordance with the literature discussed in Chapter 3 Section 2.6.2, where temperature control was identified as a key factor in improving both precision and accuracy. It is therefore expected that a setup of a cycler in theory more precise, leads to a less precise setup value if less rigorous methods of thermal control are used.

In addition, a new parameter was also added which accounts for the number of CE values measured to be above 1 for the first 25 cycles. 25 was chosen as it was a number available for all cells used in this thesis, as sometimes cycling was interrupted for various reasons after 25 cycles, notably for diagnostic cycles done at lower rates. An additional factor was also the omission of the first 5 cycles for this value. In theory CE values above 1 are not possible; however, it has been shown, as it will be discussed that throughout this chapter, that values above 1 have been observed for the first few cycles, heavily influenced by the storage conditions of cells. These values then settle and stabilise below one, if an appropriate HPC setup is used and values above 1 are rarely if at all measured. Hence, this parameter displayed in the table below offer an additional proxy for the validity of a potential HPC setup: with this consideration, while no CE values have been observed to be above 1 for the Novonix and Digatron setups, the cells cycled on our Biologic setup have displayed on average 6 values (standard deviation being 2.35) above 1.

Table 3-2. Summary of various cyclers used with their temperature control and measurements methods, respective precision and accuracy in ppm, and CE values measured above one for the first 25 cycles, with omission of the first 4 cycles.

Cycler manufacturer	Temperature Control and measurement	Cells used for statistics	Precision (ppm)	Accuracy (ppm)	CE values > 1, for 25 cycles (first 5 omitted)
Novonix	Thermo-electric (Peltier) and RTD	13	0.761 ± 0.730	3.26 ± 2.76	0
Digatron	Coupled with environmental chamber (resistive and compressor) and Thermocouple type K	22	1.01 ± 0.438	9.06 ± 3.02	0
Biologic	Ammo box in ambient temperature lab and Thermocouple type K	12	11.6 ± 8.14	18.3 ± 9.02	6 ± 2.35

Comparing the values of the setups used during this thesis to available values in literature, displayed in Figure 3-3, the values obtained for precision are similar in the same order of magnitude as the UHPC and HPC setups of Bond et al., the presented calculated values for accuracy are an order of magnitude lower. This could be partly attributable to our assumptions used to calculate the accuracy value, as no known grand standard for precisions are available for this purpose. The other cycler mentioned in the study is a Maccor series 4000, showing higher values of one and two order of magnitude for precision and accuracy respectively. It is important to note that this comparison is from 2013, and that improvements have been made by manufacturers since then, and why for our setup, despite different theoretical resolution values for each cycler, we obtain similar precision and accuracy overall when the whole setup is considered. We confirm, however, that temperature control is key in order to obtain valid and coherent HPC data.

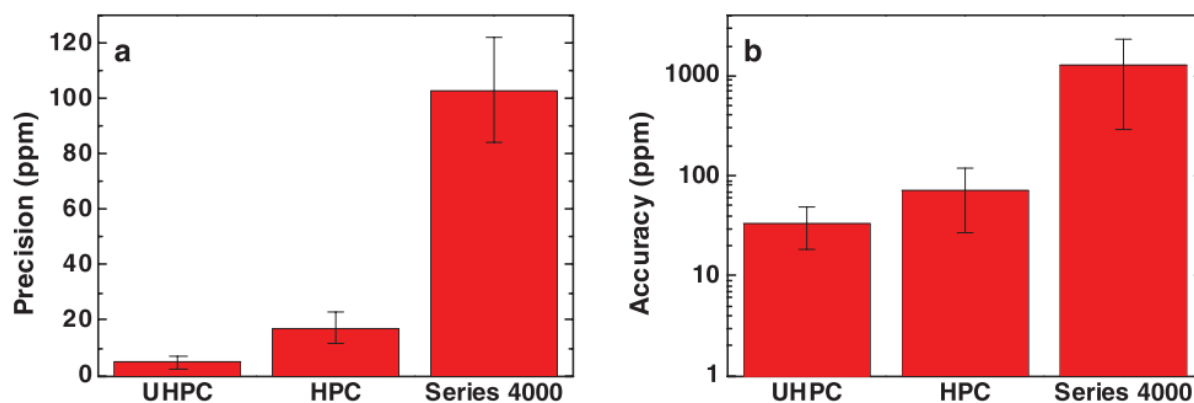


Figure 3-3. Precision and Accuracy values measured in ppm for Ultra High Precision Cyclers, High Precision Cyclers and Maccor Series 4000 cyclers. Reproduced from Bond et al.¹⁸⁹

3.1.2.2 Thermal aspect

The temperature assessment and the interaction between cell-level and ambient temperature is beyond the scope of this thesis; however, a display of the measured temperatures for the first few cycles is available in Figure 3-4. For cell ID, information can be found in the experimental section in 4.2. The figure displays the measured temperature of cell LCO/HC – 2004 – 01 cycled on the Novonix cycler, the ambient temperature measured on that cycler, and their respective ones for LCO/HC – 2004 – 03 cycled on the Digatron for the first 6 cycles. The temperature pattern changes are observable, and are more prominent for LCO/HC – 2004 – 03, where the highest measured temperature corresponds to the fully discharged state. This shows effectively better cooling provided by the Novonix setup, with a more stable cell temperature.

Per the user manual, the accuracy and stability of the Novonix thermal chamber are announced at $\pm 0.2^{\circ}\text{C}$ ($\pm 0.02^{\circ}\text{C}$) and resistance temperature detector (RTD) accuracy will vary according to the material used (Copper, Nickel or Platinum) but will be between 0.15°C and 0.425°C depending on the source^{205–207}. The Digatron setup uses type K thermocouples, the accuracy typically being between 1.5°C and 2.5°C ²⁰⁷, and the temperature accuracy and stability of the Vötsch VT 3050 environmental chamber is announced at $\pm 0.5\text{K}$ as per the user manual. Figure 3-4 illustrates the differences in levels of precision of measurements of temperature: the thermocouple

in this setup only allows for steps of 0.1°C , as opposed to the more precise RTD. Furthermore, the more precise Peltier cooling appears to keep the cell's temperature more constant for LCO/HC – 2004 – 01 (less than 0.2°C oscillations in total as opposed to 1.7°C oscillations for LCO/HC – 2004 – 03), despite measured variations in ambient temperature more significant for the Novonix, particularly around the 20-25 h mark. It is possible that more significant temperature variations occur within the Digatron setups, but were simply not measured accurately by the thermocouple. It is important to note that the oscillations of all cells cycled on the Digatron are still below the 2K variations recommended by Zülke et al¹⁹¹. Moreover, the ambient circuit temperature value for the Novonix could potentially be given by a 4-wire RTD closed-loop including in the chamber, which is also used for the feedback climate control loop. Whether it is an average value or not is simply unknown. The cell holders are also provided with an on-board RTD sensor. For the Digatron setup, a single thermocouple was kept in the centre of the environmental chamber (from a vertical and horizontal perspective) for the ambient temperature value, while another thermocouple was placed in the central section of each 18650 cell and held in place with aluminium tape. It is important to note that the cells cycle altogether in the same chamber, further exacerbating the complex thermal interactions. The core takeaway observed in the presented setups, beyond the technical differences of the used equipment, is that cells cycled on the Novonix cycler appear to be kept at a more constant temperature than on their Digatron counterparts.

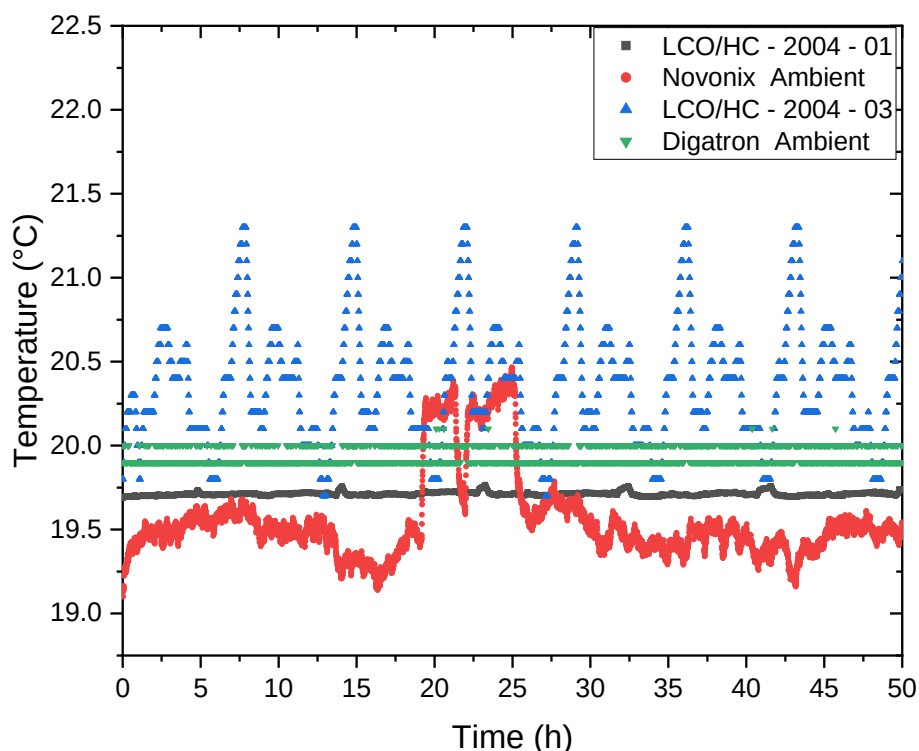


Figure 3-4. Temperature measured of LCO/HC – 2004 – 01 cycled on the Novonix, the ambient temperature measured, and their respective ones for LCO/HC – 2004 – 03 cycled on the Digatron, for the first 6 cycles.

3.1.3 Electrochemical Impedance Spectroscopy

Prior to or after the cycling of cells, electrochemical impedance spectroscopy (EIS) was carried out, which is a technique widely used with batteries as it is a non-destructive method to estimate parameters of a cell, such as its SoH²⁰⁸. It usually involved no change in the setup, making the technique easy to implement in the test matrix. It consists of the application of an AC potential to a cell and then measuring the current through it. Hence, the application of a sinusoidal potential excitation results in an AC current signal which can be fitted and analysed as a sum of sinusoidal functions (Fourier series). From the fitted data, a Nyquist plot can be obtained, as displayed in Figure 3-5. Each section of the spectrum is attributed to a specific electrochemical or chemical phenomenon occurring within the whole cell system, and their evolution can be tracked over time by repeating EIS acquisitions. Generally, the higher frequency corresponds to conduction processes (also referred to as induction processes), the middle region as the charge transfer region while the lowest frequency

part represents various diffusion effect, such as the lithium diffusion in the electrolyte and electrodes²⁰⁹. With EIS, it is possible to explore and isolate the individual contributions to the impedance made by the various physical components and electrochemical processes occurring in a battery.

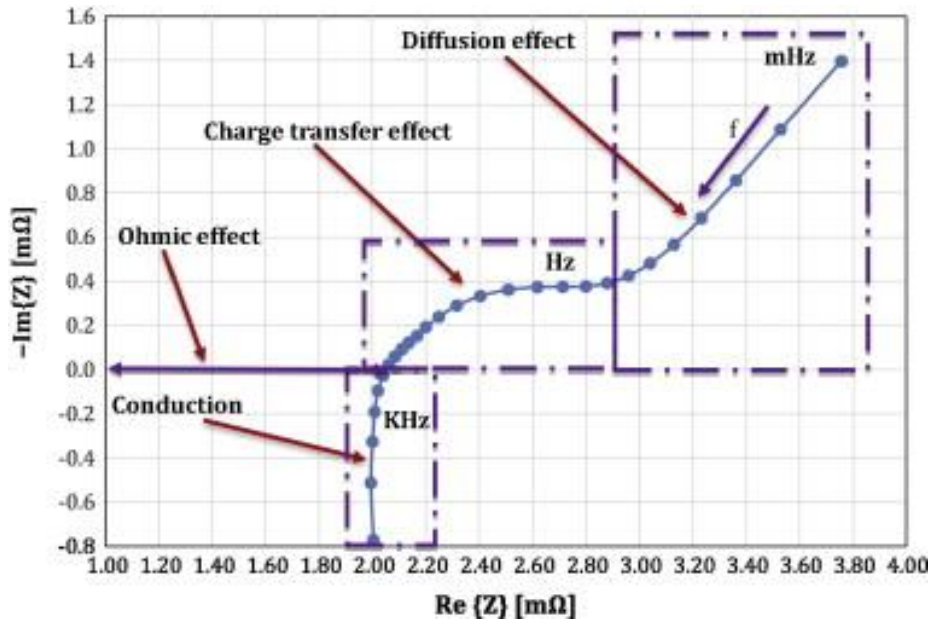


Figure 3-5. A Nyquist plot with each region of the spectrum specified. Reproduced from Abdem Monem et al.²⁰⁹

Each individual component of the battery system can be approximated by a semi-circle, representing an “ideal conductor”, and depending on the fitting model, a Nyquist plot can then be derived from the series of individual semi-circles. The impedance of a battery will change at different voltages, state of health, ageing and configuration⁷⁸. Differences between cell models are often linked to the porosity, tortuosity factor and overall electrode morphology^{210,211}. While it is challenging to directly attribute an electrochemical process occurring just from a Nyquist plot, some features seemed to have been understood.

The depression of the semicircle, rather than a perfect semi-circular arc (which would be an ideal conductor), is often attributed to factors such as surface inhomogeneities, non-uniform current distribution, or variations in local electrode characteristics that affect charge transfer dynamics^{212,213}. This leads to deviations from

ideal charge-transfer kinetics, and this depression is commonly modelled with a constant phase element to account for the non-ideal capacitive behaviour²¹⁴. The depressed semi-circle(s) in the mid-frequency region, for most commercial cells for instance, represent processes occurring in both the anode/electrolyte and the cathode/electrolyte interphases²¹⁵. In addition, the Nyquist plot in a full cell represents the overall impedance of the whole system: a half-cell (NMC/Li for example) will lead to different Nyquist plots and is useful to try and decouple each electrode contribution to the overall impedance of a cell. For operando and in situ measurements, a three-electrode cell configuration, with a reference electrode (Li, Ag or Pt) included in the cell system (usually coin cells or Swagelok cells in a lab environment), can facilitate three Nyquist plots: of the cathode, the anode and the overall spectrum as if it was a full cell configuration²¹⁶, as displayed in Figure 3-6.

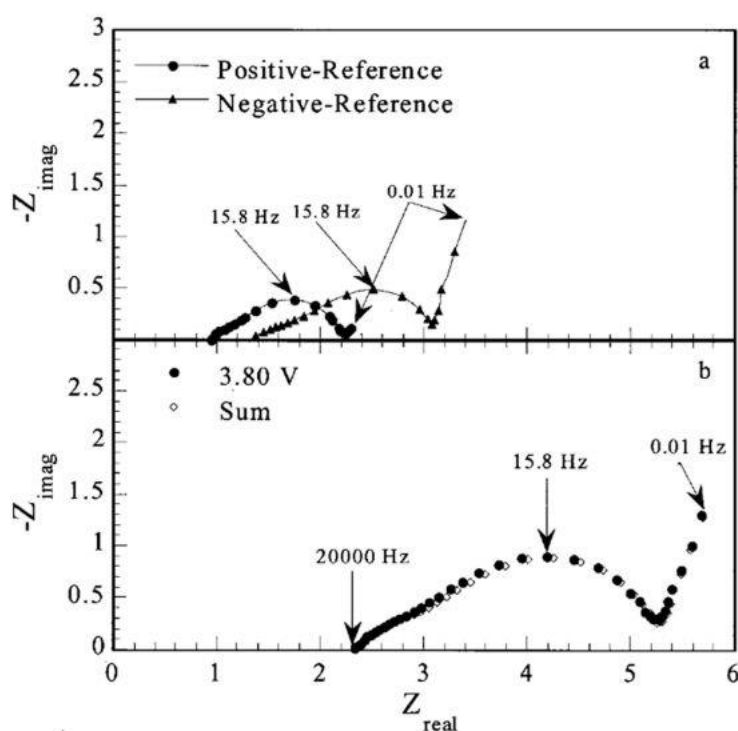


Figure 3-6. Example of three-electrode EIS measurements for (a) positive and negative electrodes and (b) the sum of three-electrode measurements and the full cell plot. Reproduced from Raccichini et al.²¹⁶

EIS throughout this thesis was either performed using the BioLogic cycler using its Potentiostatic EIS function of the ModuloBat of the BCS-815 using 10mV perturbation, ranging from 100 kHz to 100 mHz, with 6 points per decade acquisition; or on a Metrohm Autolab AUT84755 (Metrohm, Herisau, Switzerland) using a current

perturbation (Galvanostatic control) of 30mA, ranging from 1 MHz to 10 mHz. All tests followed a 3h (Chapter 4) or 2h (Chapter 5) rest periods after reaching the desired SoC. The higher frequency value of 100 mHz was chosen instead of 10 mHz for example, due to the time needed for the PEIS to complete at 10 mHz as a lower boundary. Many points for PEIS were collected, so it was decided that 100 mHz will give enough impedance information while allowing enough ageing of the cells to start observing capacity fade. Indeed, the boundary of 100 mHz may reduce the information regarding the diffusion region, but does not affect the charge transfer region. This data is then used to plot the Nyquist impedance plots, which will be the main focus regarding EIS data throughout this report. This plot is comprised of Z' on the real axis, which represent the real measured resistance of the cell and the Z'' data on the imaginary axis. This plot can provide a relevant following of the evolution of the impedance of various components of the cell, as shown previously in the literature review.

To interpret EIS data, several options are possible. For the bulk of this thesis, the data will be displayed as Nyquist spectra such as the one shown in Figure 3-7. In multiple cases, the spectrum will be displayed without the high-frequency “tail”, removing the negative values of $-Z''$. It is a common feature in commercial cells and can be attributed to inductive effects²¹⁴, such as the cell lead and cable connections, and as such the measurement setup itself, as well as components within the cell such as interconnections, current collectors and tabs²¹⁷. Furthermore, all Nyquist plots in this thesis will be presented with equal axis length value: despite the axis not resulting in a square shape (like found in some papers), the axis have the same proportions as to not deform any features of the spectrum. This is ensured by selecting the option “Link Axis length to scale with X:Y ratio =1” in the plotting software used, Origin (2018b version, OriginLab). As such, the integrity of the Nyquist plot is preserved, while relevant visual information can be appropriately displayed.

The figure also displays how Ohmic Resistance (R_Ω) and the Charge Transfer resistance (R_{ct}) are obtained graphically, inspired by a method previously used by Dose et al., where R_{ct} is equivalent to the “mid-frequency semicircle” in said study²¹⁸. R_Ω is the intercept of the spectrum with the real axis (effectively the value of Z' when $-Z''=0$) and was calculated via linear interpolation using the closest data points. R_{ct} is then the Z' value equal to the subtraction of R_Ω to the Z' value which corresponds to

the local minimum representing the end of the mid-frequency semicircle (formed or not of two semi-circles itself). This process was automated in with Python scripts.

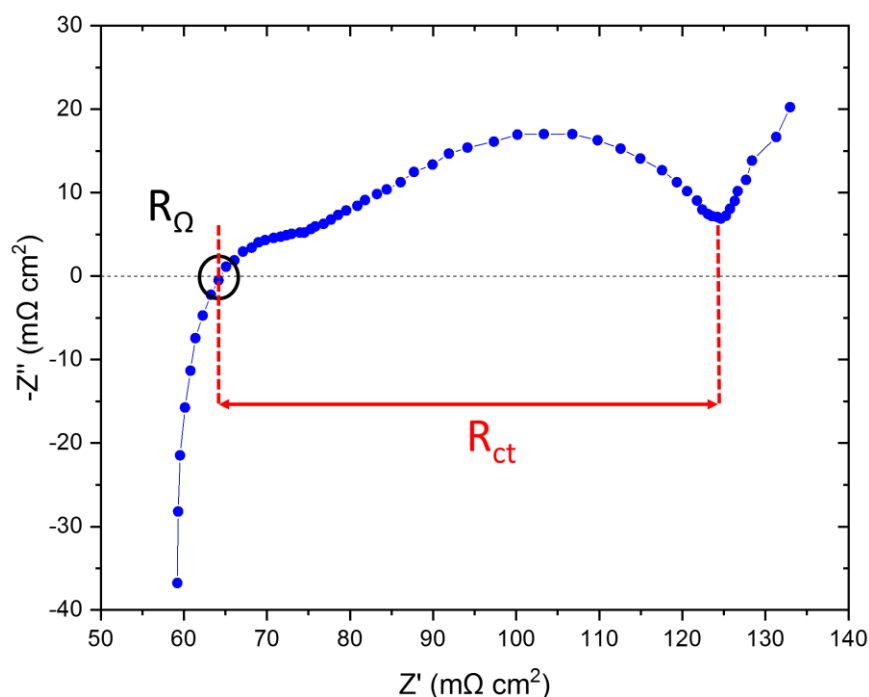


Figure 3-7. Nyquist spectrum of a fresh commercial cylindrical 18650 cell (NMC111/Graphite). The data is not fitted. Highlighted are R_Ω and R_{ct} and how they are obtained graphically from the graph.

The results of this method were then compared to the more common method of fitting the Nyquist spectrum to a predetermined equivalent circuit model (ECM), which then allows for the extraction of the individual resistances, including (in this case) the discrimination between the two components of the mid-frequency semicircle. The fitting was done using the programs RelaxIS and ZView. However, as multiple types of commercial cells, of several dimensions and various electrode chemistries (for both cathode and anode) were used during this thesis, the spectra were deemed too different, with strong variations in mid-frequency features batch-to-batch (as later shown in Chapter 6 for example). This impeded the possibility of having a set ECM and known values for other components (such as CPE items) to obtain resistance variations (for cell ageing for instance), with different cell types necessitating different ECMs to reduce errors. For example, cells “NMC/Graphite” introduced in Chapter 4 display a single mid-frequency semi-circle, which makes the estimation of the individual contribution of the SEI/Anode and CEI/Cathode to R_{ct}

unreliable. In some cases, EIS data acquired as cells were ageing was too different and the error values were too great compared to the early life spectra when the same ECM was used.

Overall, the fitting and extraction of SEI/Anode and CEI /Cathode individual resistances was deemed too ambitious for the commercial cylindrical cells presented in this thesis, and the method illustrated in Figure 3-7 was used throughout this work. It provides trackable, consistent and reliable values for R_{Ω} and R_{ct} , and keeps a cautious and transparent approach with the charge transfer area of the Nyquist plot.

3.1.4 Incremental Capacity and Differential Voltage Analysis

ICA (also referred to differential capacity analysis) and DVA are the common names given to diagnostic tools which represent the plots dQ/dV and dV/dQ respectively, where V is the voltage and Q the capacity passed during a cycle. Throughout this thesis, these were implemented on diagnostic/capacity checks cycles, done at C/20, in order to minimise polarisation effects and access a better resolution of phase transitions²¹⁹. As such, these diagnostic cycles provided a significant amount of information, where DVA, ICA and EIS were applied consistently. Dubarry and Anseán also highlight the importance of filtering and smoothing the data to obtain a good balance between accurate representation, and noise reduction²²⁰. For this purpose, sophisticated methods and algorithms have been found in literature, such as the use of extended Kalman filtering²¹⁹, and other smoothing techniques, but for this thesis, a filtering of data to retain only one data point per mV, and an additional rolling mean of 3 data points were used, leading to satisfactory results. This was applied to both ICA and DVA.

3.1.4.1 Incremental capacity analysis

ICA is a powerful diagnostic tool used in the study of Li-ion batteries. The core concept behind ICA is the calculation of the differential capacity (dQ/dV), which represents the change in the battery's charge (Q) relative to its voltage (V). This plot

of dQ/dV as a function of voltage can reveal subtle changes in the electrochemical processes occurring within the battery, including phase transitions, degradation mechanisms, and loss of lithium inventory²²¹. The calculation of dQ/dV is typically performed by taking small increments of charge and voltage during the charging or discharging process and computing their ratio. The peaks in a dQ/dV plot correspond to specific electrochemical events within the battery. Each peak is associated with a phase transition in the electrode materials, which typically involve lithium ions moving in or out of a crystal structure. The position (voltage) and height of these peaks provide insights into the SoH and SoC of the battery.

A decrease in the amplitude of dQ/dV peaks can indicate a loss of active material (LAM), while shifts in peak positions might indicate changes in the electrode's structure or composition, such as phase transformations or the development of microstructural defects, or increased resistance within the cell^{222,223}. The movement or disappearance of peaks in the dQ/dV curve may indicate the loss of lithium inventory (LLI), where lithium becomes trapped in inactive phases or the SEI²²⁴. Figure 3-8 below displays the dQ/dV plots of several well-known and well-used battery materials in half-cell configuration (vs Li as a counter electrode).

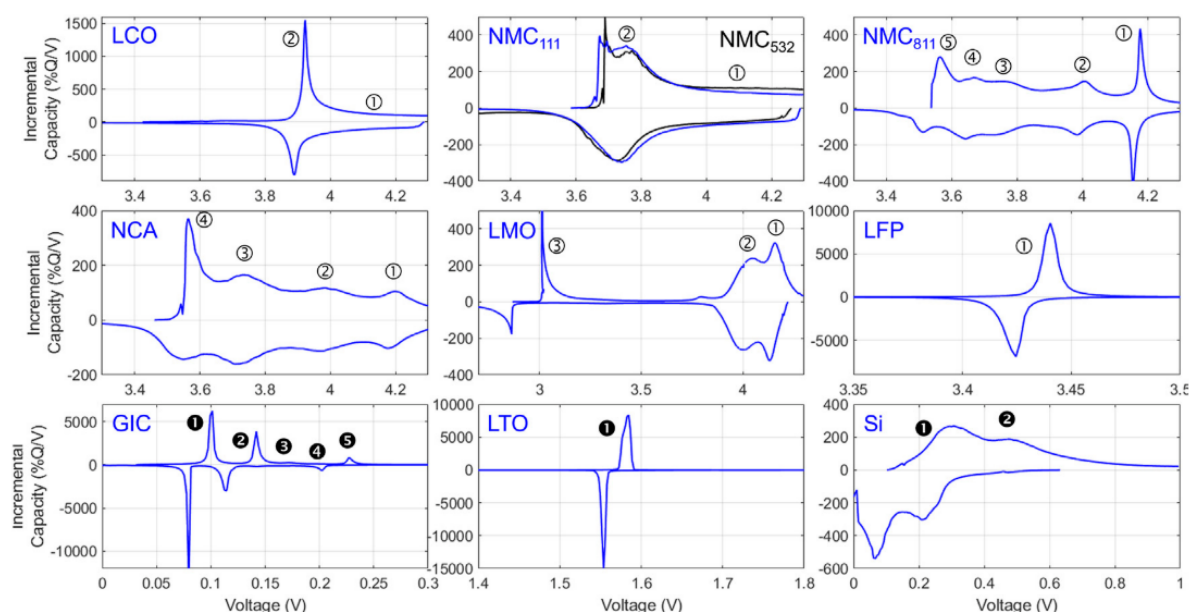


Figure 3-8. Exemplary C/25 electrochemical ICA behaviour for several labelled battery materials in half-cell configuration. Reproduced from Dubarry and Anseán²²⁰.

3.1.4.2 Differential voltage analysis

Differential Voltage Analysis (DVA), often denoted as dV/dQ , is a complementary technique to ICA. While ICA focuses on the changes in charge (dQ) as a function of voltage (V), DVA examines the changes in voltage (dV) as a function of the charge (Q) passed, and is, as such, more sensitive to more nuanced voltage changes associated with certain phase transitions, as it is the case for SiO_x additives in graphite anode for example²²⁵, not present in dQ/dV plots.

Sharp changes in the slope of the dV/dQ plot correspond to specific electrochemical processes, such as phase transitions within the electrode materials. Unlike ICA, which shows peaks where these transitions occur, DVA exhibits troughs or inflection points at these transitions. The steepness of the slope in a dV/dQ plot indicates the extent of the voltage change per unit of charge, with more significant changes corresponding to more critical or pronounced phase transitions²²⁶. Regions where the voltage changes slowly with respect to charge (flat or nearly flat regions in the dV/dQ plot) correspond to voltage plateaus in the charge-discharge curve. These plateaus are typically associated with two-phase regions in the electrode materials, where lithium is intercalating or deintercalating at a relatively constant voltage²²⁷. DVA is also particularly useful for assessing the balancing between the positive and negative electrodes in a battery, referred to as slippage. In a study published by Dose et al., DVA was used to track slippage in graphite/NMC811 cells over hundreds of cycles and the analysis showed that after around 300 cycles, the graphite anode's potential at the end of charge began to increase, which led to the cathode being driven to higher potentials, accelerating degradation mechanisms such as transition metal dissolution and rock-salt layer formation²¹⁸.

As an example, Figure 3-9 below displays the charge and discharge curves, and subsequent DVA spectra of anode and cathode half-cells reconstructed from a commercial NCA cell, extracted from a calendar ageing study performed by Keil et al.¹³² Notable differences in peak placement, magnitude, plateaus, as well as the available capacity are clearly shown.

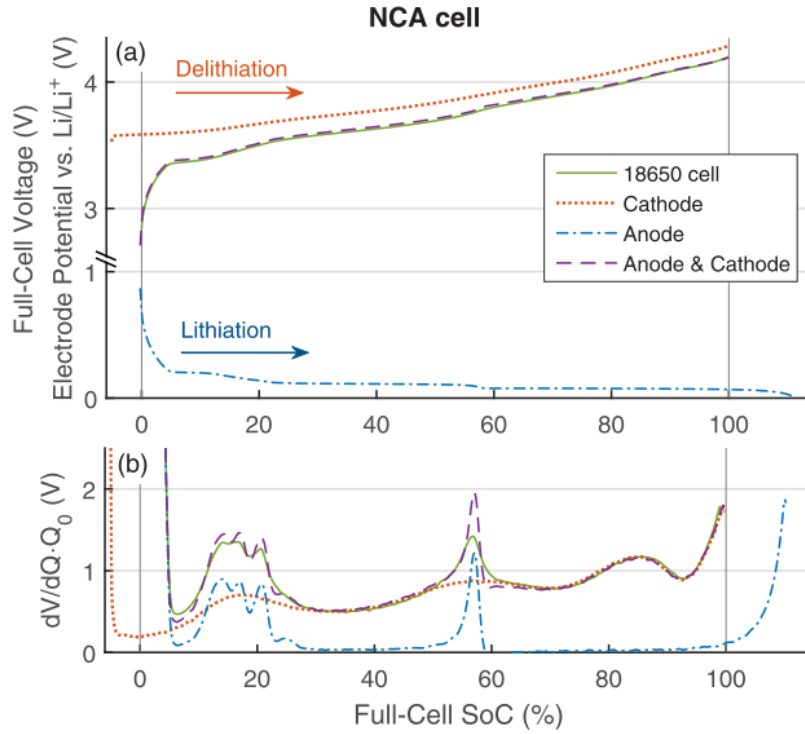


Figure 3-9. a) The full-cell voltage and b) the DVA spectra of each anode and cathode half-cell curves from a NCA commercial cell. This allows for a reconstruction of the 18650 full-cell by a superposition. Reproduced from Keil et al.¹³²

3.2 Variable current protocols derivation

Following the literature review previously presented, two potential main areas for degradation have been identified: low and high SoCs. While exact SoC values would vary slightly depending on the study, parameters or cell configuration, the values kept for all subsequent variable current protocols experiments are as such:

- Low SoC area: from 0% to 20%.
- Middle SoC area: from 20% to 80%.
- High SoC area: from 80% to 100%.

This divides the capacity into three main regions where the cells have been shown to have distinct resistances and ion mobility values in the literature. Hence, instead of applying a constant current, a more varied and control application of current will be displayed in experiments conducted in Chapter 5, and will be compared to the universally used CCCV. Figure 3-10 displays said protocols, with the notions of current

applied and time taken for all subdivided intervals. a) displays CCCV, while b) shows the protocol referred to as VCP, which presents a high current in its middle 20-80% SoC area, and low current in the low and top of the SoC. c) represents LowEnd, which starts cycling at high current, and then drops significantly reaching 80%, while d) LowStart displays the opposite with a slow start until 20% SoC, followed by high current until CV phase.

Additionally, C-rate of the cycling needed to be chosen. The C-rate represents the current applied as a function of the cell capacity. As an example, if the capacity of a cell is 5 Ah, and the current applied for its cycling is 5 A, then the cell is considered to be cycled at 1C. It means that the whole capacity of the cell is attained during charge or discharge in 1h, regardless of the absolute current. It is a practical way to compare cells of different capacity. Hence, for these experiments, a C-rate for the CCCV protocol and a C-rate equivalent for the other protocols were chosen and kept as the same. Indeed, the goal with these protocols is to propose a fair comparison to the universal CCCV, and as such, charge the cells with the same total charge passed, taking the same amount of time to do so. The C-rate equivalent had also to be selected in consideration of other external factors, and in this case, it was the maximum C-rate recommended by the manufacturer. Three cell models were selected: two with the maximum recommended C-rate to be 1C, and one with it being 0.7C. As such, the equivalent C-rate chosen was 0.7C and 0.5C respectively. Figure 3-10 represents C-rates and time per interval for both C-rate equivalents.

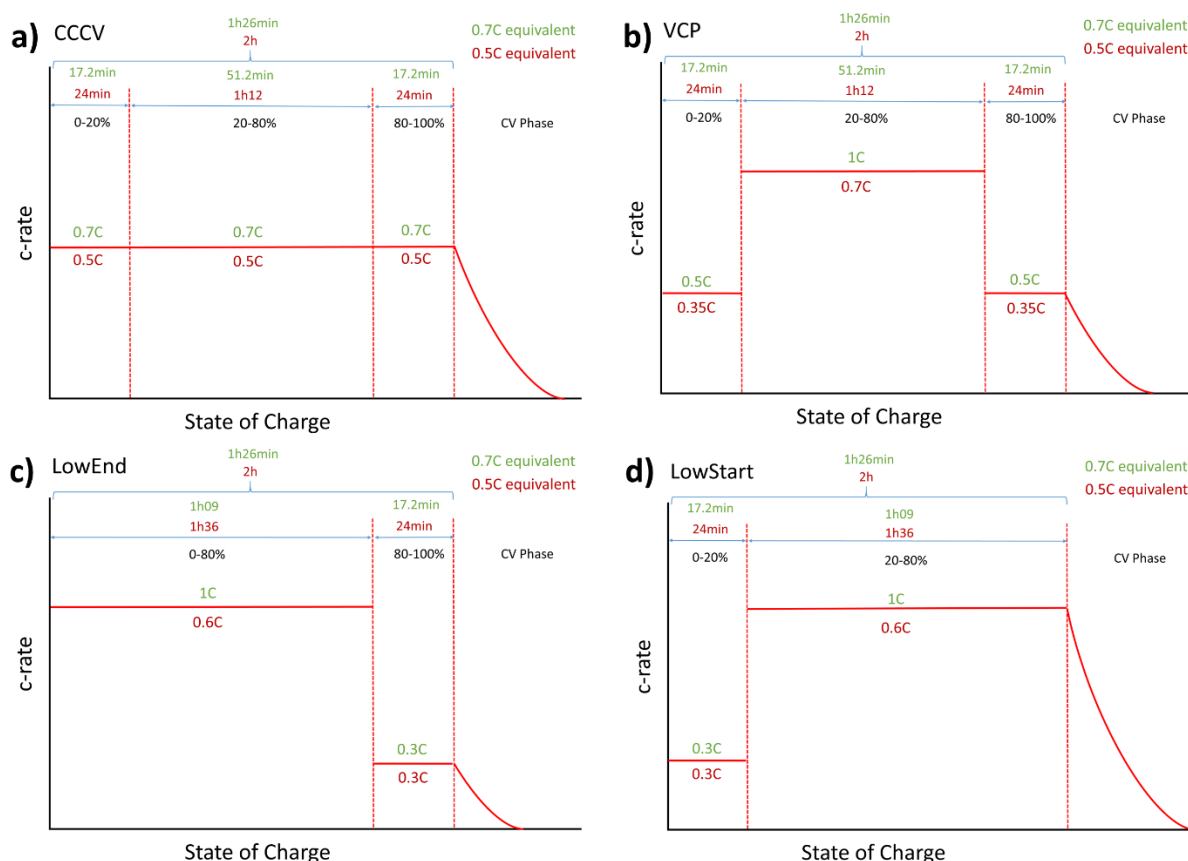


Figure 3-10. Schematic representation of all variable current protocols used in this thesis, the C-rate applied per interval and how much time it would take to complete for both 0.5C and 0.7C equivalent. a) is the commonly used CCCV, b) the VCP, c) the LowEnd and d) the LowStart. This is only representative for the charge sequence.

It can already be apparent that a more significant CV phase is to be expected for cells like LowStart, due to the simple fact that the current at which CV phase I started for this protocol is higher than other protocols, as the current in such phase decays in the same fashion while the voltage is hold: exponentially²²⁸. This indicates that it is expected that such protocol will maximise time spent at high voltages (in CV phase) compared to the other variants. Lastly, some voltage limits were also devised for each step, to avoid reaching CV phase directly as the impedance and overpotential of the cell increase as the cell ages. Lastly, some minor approximations were taken in the derivation of the variable current protocols. For instance, for LowEnd at 0.7C, when the last interval was set at 0.3, the exact calculate C-rate for the 0-80%SoC interval should be 1.05. This was deemed minor, and the measured capacities of the cells cycled with these protocols corroborate this, as their initial capacities were within normal cell-to-cell variations.

3.3 Commercial cells opening and reassembly

3.3.1 Cell opening

At end-of-life (EoL), after cell cycling was completed, the experimental plan usually called for the cells to be opened. This allowed for visual inspection of the electrode assembly, application of various imaging techniques, and harvesting of electrode material. However, due to the risk of short circuit and Lithium reacting with air, a specific procedure needs to be followed in order to open commercial cylindrical cells for imaging techniques like the subsequent scanning electron microscopy (SEM) analysis presented in section 4.3.2, as most commercial cells are shipped at around 30% SoC, a first discharge cycle was needed. For this purpose, a slow discharge protocol is applied to remove as much Lithium from the graphitic anode as possible and limiting the possibility of it catching fire in the subsequent opening procedure. A C-rate of C/10 is first applied until the recommended low cut-off voltage recommended by the manufacturer (2.5V for most models, although two cells used in Chapter 4 were notable exceptions). Then the cell is left to rest for 4h, where some voltage recovery is expected during this time. Once the rest period is over, a C-rate of C/20 is then applied, followed by a four-hour rest period again. The procedure is then repeated with C/50 and C/100 C-rates and then left to rest for 4h and ideally overnight.

Then, the cells were taken to an MBraun Lab Star glovebox in Argon environment (MBraun, Garching, Germany). The top part of the cell is carefully removed with a pipe cutter and the exposed tab (positive aluminium tab connected to the cap) is covered in Kapton tape to avoid any short-circuit during the following steps. The outer case is then teared and peeled using pliers until the electrode assembly can be removed or extracted from the remaining stainless-steel casing. The jellyroll is subsequently left to wash in a beaker filled with Dimethyl Carbonate (DMC) for 1min, if the goal is to perform further imaging and characterisation. This is not done if the electrode is to be harvested and reassembled in coin cells. This washing is done in order to remove as much remaining electrolyte and Lithium salts from the electrode assembly as possible. The electrodes are then left in the glovebox to dry at least overnight. The material used in such electrodes is air sensitive, and particularly to CO₂ and moisture, hence an ideal way to transport the samples to the imaging or

spectroscopy instrument of choice would a vacuum transfer. It is a crucial aspect for techniques such as XPS as it is more surface/species sensitive²²⁹, but a contact with air of several minutes in between the glovebox and the SEM chamber or other imaging devices was deemed acceptable for the larger scale morphological studies during this thesis. Indeed, the bulk should not be affected, and the surface changes would be minimal for SEM and Energy-dispersive X-ray spectroscopy (EDX) analysis.

3.3.2 Coin cell reassembly of the harvested electrode material

When electrode material was to be harvested and reassembled, it must be done the same day the cylindrical cell is opened, as described previously. Active material (whether cathode or anode) was carefully removed from one side of the electrode assembly using anhydrous N-Methyl-2-Pyrrolidone (NMP) in the glovebox (Sigma Aldrich, St. Louis, USA) to expose the current collector. This was performed by sticking a cut portion of the jellyroll with Kapton tape on Plexiglas and proceeded with extreme caution to gently rub the material with soaked magic erasers. It has been found that letting a small quantity of NMP soaking on the surface of the electrode for a duration of 15min to ease and shorten the scraping process of one of the sides of the electrode, without soaking in any way to the other side of the electrode assembly. This is done until the current collector is clearly exposed and washed with DMC. The punching of the coin cells discs can then be performed; different disc sizes were used throughout this thesis.

The material harvested was then re-assembled in coin cells (CR2032, Hohsen Corp., Osaka, Japan). A three-layer polyolefin membrane served as a separator (Celgard 2325, Celgard, LLC.), and the electrolyte employed was 1.0 M lithium hexafluorophosphate, LiPF_6 , in a mix of Ethylene Carbonate, Ethyl Methyl Carbonate and Dimethyl Carbonate (1 M LiPF_6 in a 1:1:1 by wt EC:EMC:DMC + 1% Vinylene Carbonate (VC), Soulbrain MI). The quantity used per coin cell was 60 μL and all cells were put together in a glove box under an argon atmosphere (with careful monitoring to be O_2 and H_2O < 0.5 ppm). Once reassembled, the coin cells must be left at least 8h or overnight at rest (voltage monitoring can be done at that stage, if reassembled

in half-cells vs Li). Prior any cycling, two C/20 cycles were performed to allow for reformation, and only the second cycle is deemed stable enough for capacity check or ICA and DVA.

3.4 Imaging techniques

3.4.1 X-Ray Computed Tomography

X-ray computed tomography (X-ray CT) is a non-destructive imaging technique that provides three-dimensional (3D) visualisation of the internal structure of objects. The fundamental principle of X-ray CT relies on the differential absorption of X-rays by materials with varying densities and atomic compositions. When an object is exposed to a collimated beam of X-rays, the varying degrees of absorption create a shadowgraph or radiographic image. As the object is rotated around a fixed axis, multiple two-dimensional (2D) images (or projections) are captured from different angles. These projections are then processed using a mathematical algorithm, such as filtered back projection or iterative reconstruction techniques, to generate a 3D volumetric image of the object's internal structure. The resultant 3D images offer high spatial resolution and enable the identification of features such as cracks, voids, and inclusions within the material. In order to perform X-ray CT, a Nikon XT H 225 (Nikon Metrology, Leuven, Belgium) was used. This tomograph, usually used for the scan of relatively large objects due to its high energy source, large working distance and simple geometric magnification, can reach a resolution down to 3 μm pixel size. The main specifications can be found in Table 3-3. While multiple filament sources were available (Copper, Silver, Molybdenum and Tungsten), Tungsten was used for all the scans, as it is the heaviest element available and hence provides a more penetrant wave which leads to better contrast.

Table 3-3. Specifications of the Nikon XT H 225.

Detector	Focal Spot size	# of Bits	Active pixels	Max frame rate at 1x1 binning	Max frame rate at 2x2 binning
Perkin Elmer 1620	3 μm up to 7 W and 225 μm at 225 W	16-bit	2000x2000	3.75 fps	30 fps

To initiate a scan, the sample is mounted on the rotational stage within the Nikon chamber. For optimal scanning with high contrast, the absorbance must be maintained between 15-20%, determined by the ratio of the reference (blank) image to the sample image. Achieving this requires real-time adjustments to the beam energy and current until the desired absorbance is obtained, just before the acquisition begins. For consistency across all scans, the following parameters were generally kept constant:

- Beam energy: 190 kV
- Beam current: 100 μA
- Power: 19.0 W

However, due to variations in X-ray emissions from the filament over time, these parameters occasionally required adjustments within a range of ± 12 kV, corresponding to a power variation of ± 2.0 W. Additionally, the number of pictures per frame was set to 1. Although the option to use more pictures per frame is available, which would result in a smoother scan by averaging the images per frame, this would also significantly increase the total scan time. Prior cycling, all cells were scanned to detect any macrostructural defects or impurities.

The raw scan data must then be processed and reconstructed to be usable by the image analysis software, done using CT Pro 3D (part of the Nikon software suite). The software allows the user to adjust parameters to find the centre of rotation—since most samples are not perfectly aligned with the detector—and to correct major artifacts, usually present at the dense material edges of the sample. For data export, various quality options are available: 8-Bit, 16-Bit, and Floating 32-Bit. The latter was chosen for all scans, resulting in significantly larger file sizes but also slightly better contrast

and smoothness. The resulting .vgi file is then opened in Avizo 9.4.0 (FEI VSG, France) for image analysis. Basic rendering of the tomograms along all three axes was performed to identify major macrostructural features of the cells.

3.4.2 Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy

Following the opening of a cell following the procedure in 3.3.1, samples from the electrode assembly, samples of roughly 1 cm² taken from different zones of the electrode. At least two samples were taken and mapped, one from a central region of the electrode and another one closer to one of the extremities. The SEMs used were a Zeiss EVO MA10 (Zeiss, Oberkochen, Germany) for results of Chapter 4 and a Thermo Fisher Scientific Scios (PFIB-SEM, EDX and SIMS) (Thermo Fisher Scientific, Waltham, Massachusetts, United States) for Chapter 6; with a Lanthanum hexaboride (LaB₆) source, and a Ga source, respectively. Parameters like the magnification or energy used will be specified in each micrograph used in this report. The working distance was always kept in the optimal 8.5-10 mm range, which is also the optimal distance for the EDX analysis. On the Zeiss microscope, said EDX analysis was performed using an INCA X-Act detector (Oxford Instruments, United-Kingdom), coupled with the INCA acquisition software.

To show the best approximation possible of the sample observed, a mapping of said sample is performed. For each sample, at least three different regions of interest are selected, and within each, at least three different points of interest are chosen for imaging and potential EDX analysis in order to complete a mapping.

3.5 Powder Diffraction Techniques

3.5.1 Neutron Powder Diffraction

Cell opening also allowed for sample preparation for the application of various powder diffraction techniques. As an example, neutron powder diffraction (NPD) is a powerful analytical technique that leverages the wave-like properties of neutrons to probe the atomic structure of materials. In an NPD experiment, a neutron beam is directed at a powdered sample and as the neutrons interact with the nuclei in the sample, they are scattered in different directions. The intensity and angles of these scattered neutrons are recorded and used to construct a diffraction pattern. This pattern contains information about the crystal structure, atomic positions, and other structural details of the sample material. Unlike X-rays, which interact primarily with the electron cloud surrounding atoms, neutrons interact directly with the nuclei of atoms. This difference provides NPD with several unique advantages such as its sensitivity to light elements, such as lithium, which are often difficult to detect with X-ray diffraction. This makes NPD especially useful in the study of Li-ion batteries, where the distribution and behaviour of lithium within various phases can be monitored²³⁰. Neutrons also possess a magnetic moment, allowing NPD to probe the magnetic structure of materials. This is particularly important in the study of materials that exhibit magnetic ordering.

NPD has become an essential tool in Li-ion battery research, Ni-rich NMC and NCA materials and it is uniquely suited to detect and quantify the extent of Li-Ni intermixing due to its sensitivity to lithium, providing insights into how this affects the structural stability with antisites defects, by monitoring the (003) and (101) reflections associated with the R-3m space group^{231–233}.

In this thesis, NPD was collected in transmission on the high-resolution neutron powder diffractometer, Echidna²³⁴, at the Australian Nuclear Science and Technology Organisation (ANSTO), at a wavelength of 1.622 Å. For the measurement, approximately 2 g of powder scraped from the electrodes was packed into a vanadium can. Data was collected over an angular range of 2.75°–163.95° for a duration of 1h.

3.5.2 X-ray Powder Diffraction

Furthermore, X-ray Diffraction (XRD) can also be used on the same samples. XRD is a widely used analytical technique for determining the atomic and molecular structure of a crystal. In XRD, X-rays are directed at a material, and the pattern of diffraction is measured. As the X-rays interact with the electron clouds of the atoms, they are diffracted in specific directions that depend on the arrangement of the atoms. The resulting diffraction pattern provides a fingerprint of the crystal structure, which can be analysed to determine various structural parameters such as lattice constants, crystallite size, and phase composition²³⁵. The intensity and angle of the diffracted X-rays are measured to create a diffraction pattern. By analysing this pattern, one can infer the crystal structure, lattice parameters, and other structural details. The fundamental principle behind XRD is Bragg's Law, which relates the angles at which X-rays are diffracted to the spacing between planes of atoms in the crystal, and described in Equation 3-1:

$$n\lambda = 2d\sin\theta$$

Equation 3-1

Where n is an integer, λ is the wavelength of the X-rays, d is the distance between atomic planes, and θ is the angle of incidence.

XRD has proven to be a prominent technique used in the study of Li-ion batteries, especially for characterising cathode materials like Ni-rich NMC and NCA materials²³⁶. Specific peaks and lattice parameters derived from XRD provide critical insights into the structural changes that occur during battery operation such as the tracking of the c-lattice parameter, which corresponds to the length of the unit cell along the c-axis in layered materials like NMC, is particularly important in battery research. Changes in the c-lattice parameter during cycling can indicate the degree of lithium intercalation and deintercalation. For instance, an expansion in the c-lattice parameter is often observed during lithium insertion, while a contraction occurs during lithium extraction^{237,238}. Additionally, in XRD patterns of NMC811 material, the (003) and (104) peaks are key indicators of the material's structure and health. As lithium is extracted (during charging), the (003) peak tends to shift to higher angles (indicating a contraction of the c-lattice parameter), and as lithium is inserted (during discharging),

it shifts to lower angles (indicating an expansion of the c-lattice parameter)²³⁹. Furthermore, the (104) peak provides insights into cation intermixing in the material, as an increased intensity of the (104) peak relative to the (003) peak can suggest increased Li-Ni intermixing^{129,240}, as exposed previously.

In this thesis, XRD experiments were carried out on a Malvern Panalytical Aeris XRD with Cu K-alpha (1.5418 Å) radiation in the Bragg-Brentano mode. Data was collected directly between 10 and 75° (2θ) scattering angles. The samples were spun during the measurement for improved statistics.

4 Predicting fade behaviour using High-Precision Coulometry

4.1 Introduction

The study presented in this section accounts for a collaboration project carried out between UCL, the ESA Space Power Laboratory (ESPL) and ABSL Enersys Ltd. It was co-funded by the Faraday Institution and ESA via a grant obtained from the Open-Space Innovation Programme: <https://activities.esa.int/4000139791>. Cells and legacy data for some cells were provided by ABSL and represent commercial sensitivities, and therefore are generally described in this work without specific reference to manufacturers.

As presented previously, there is a need to be able to rapidly characterise cell fade behaviour, and this is particularly true for space missions of various durations. Indeed, for a supposed mission of 10 years duration, the cell manufacturer/provider does not have 10 years to characterise various cell types or batches to assess which one performs best and select it for said mission. Space applications are also naturally much more restrictive in terms of replacing faulty cells or monitoring performance than other applications, and therefore selecting highly reliable or predictable cells is vital. While proven older and reliable cells exist, new research and improvements through the years are compelling enough to select recent models. Improvements affecting energy/volumetric density, a central pillar for the space sector, and extending the cell lifetime are key for improved performance, but involve risk and liability as to knowing for sure the long-term cycling performance of these newer cells. Many ways of attempting to predict fade behaviour exist in literature and are subject to extensive internal private research and models as well, and High-Precision Coulometry (HPC) was jointly identified as a potential technique to be studied for this very purpose. The goal was to assess if it was possible to provide a robust estimation with a sufficient level of confidence of fade behaviour, which will be available in addition to other ways or existing models.

As such, three well-studied commercial 18650 Li-ion cell types of various chemistries were provided by ABSL, where each cell type is composed of three different batches, each displaying different long-term fade behaviours. The core difference for this study is that long-term cycling data was also made available. These thousands of cycles provide actual information on the capacity fade and subsequent knee points, going well beyond what is usually presented in HPC literature, attempting to provide a more definite answer to the question: does initial cycling HPC data match the actual long-term cycling performance of a specific cell, batch or cell type? An illustration of this postulate is presented in Figure 4-1 below.

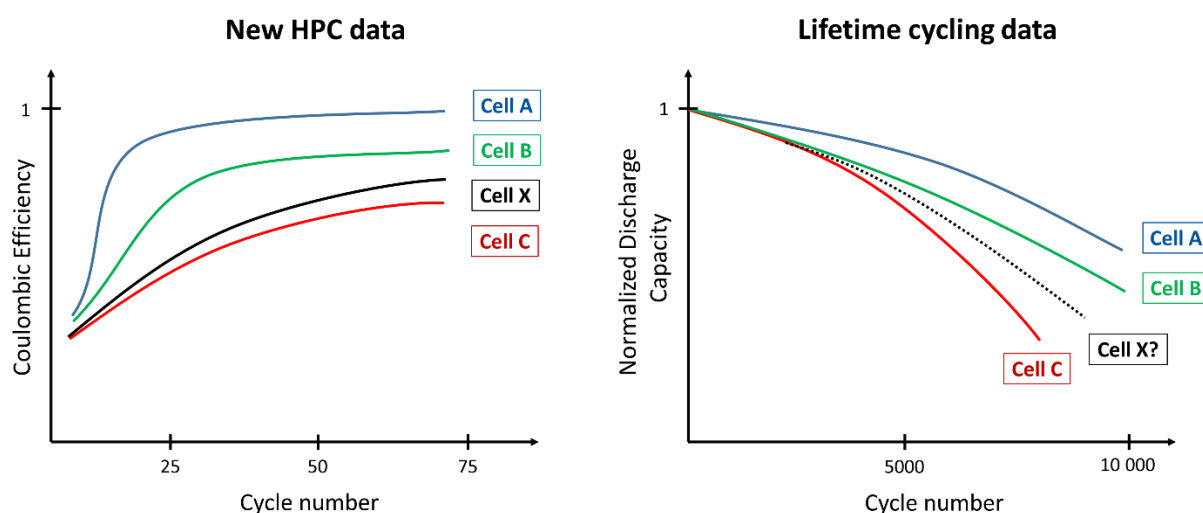


Figure 4-1. Illustration of the potential use for high-precision coulometry.

Relevant information about the cells obtained, such as electrode materials, the number of batches used (and how many cells were used for cycling per batch), batch year of manufacturing, capacity and voltage range can be found in Table 4-1. For these studies, the cells' names and models will not be disclosed, and they will be referred to as cells "LCO/HC", "LCO/Graphite" and "NMC/Graphite", hinting at their respective cathode and anode materials. The same goes for some of the lifetime data, where only the relevant information extracted from the provided dataset will be presented in this thesis as the lifetime data is a property of ABSL. However, it has been specified by the company that the lifetime data shared is accurate for their respective batches and is representative of expected fade behaviour. Therefore, and

in the context of this project, for any individual cell acquired by ABSL, two scenarios are possible:

- The cell underwent lifetime characterisation under various profiles and cycling conditions or other tests (mechanical, vibrations, abuse, post-mortem opening etc.), or used for actual missions. Some of this cycling data has been shared for this project.
- It underwent storage under fixed conditions, presently 20°C and at <10% SoC for all cells. The cells shared by ABSL for cycling and characterisation for this project come from this batch. This is effectively already considered as calendar ageing, which is important to take into account throughout this study.

Table 4-1. Summary of the cell types used with electrode chemistry information, rated capacity and voltage range.

Cell ID	Batches (cells per batch)	Batch years	Cathode/Anode material	Rated Capacity (Ah)	Voltage Range (V)
LCO/HC	3 (4)	2004 2013 2014	LCO/Hard carbon	1.5	2.5 – 4.2
LCO/Graphite (labelled as high energy)	3 (4)	2008 2011 2014	LCO/Graphite	2.4	3.0 – 4.2
NMC/Graphite (labelled as high power)	3 (4)	2015 2017 2020	Nickel Manganese Cobalt (assumed NMC111)/Graphite	2.0	2.0 – 4.2

4.2 Experimental

The core HPC cycling presented in this chapter has been carried out at C/5 for 70 cycles. This C-rate value was selected with a preliminary experiment involving four 21700 LG M50 cells (which will be introduced further in the following chapters) cycled

on the Novonix setup, two at C/10 and the other two at C/5. As can be seen in Figure 4-2, while 16 mAh on average less capacity is accessed during discharge for the two cells cycled at C/5, it appears that their CE values consistently sit right above the CE values for the cells cycled at C/10. Seeing no major changes in CE values and pattern, C/5 was therefore the selected C-rate for the remainder of this study, effectively halving the time of the 70 HPC cycles compared to C/10, improving the speed at which this diagnostic could deliver its results, while also keeping a C-rate low enough to reduce self-heating, i.e. a measured cell temperature close to identical as the ambient set cycling temperature. Furthermore, the cycling was performed at 20°C and with no CV phase, as high temperature and time spent at high voltages have been shown, as discussed previously, to increase the rate of parasitic reactions, and as such, result in lower CE values¹⁸⁶.

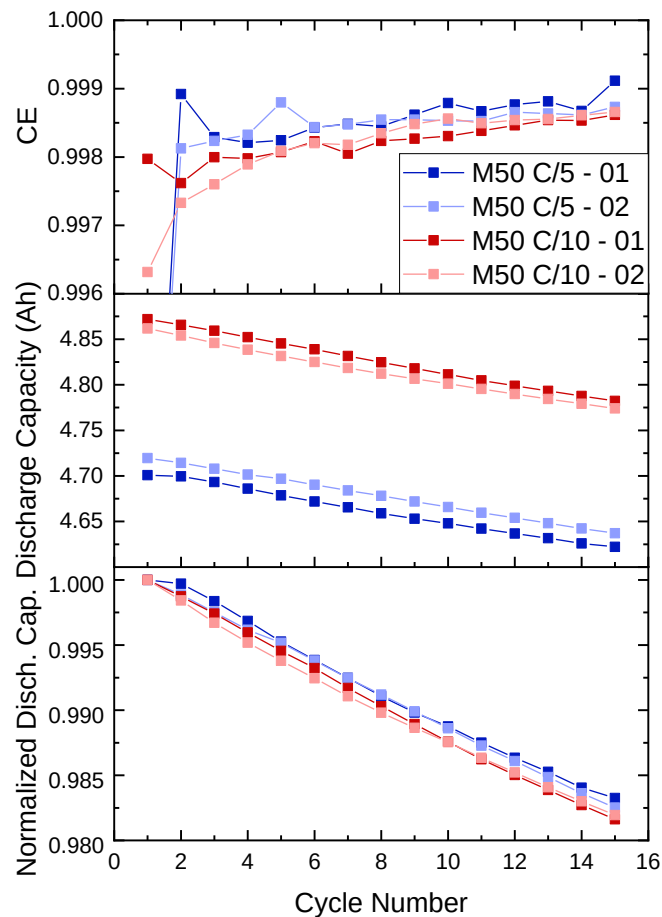


Figure 4-2. Coulombic efficiency, discharge capacity and normalised discharge capacity values for 15 cycles for four M50 cells: two cycled at C/5 and two at C/10.

Moreover, as illustrated in Figure 4-3, the cycling procedure applied to the cells throughout this chapter is as follows. Firstly, a discharge to 0% SoC was carried out for all cells, as they were delivered in the conditions they were stored at, below 10% SoC. This was immediately followed by a capacity check at C/10, consisting of a full CC charge and a CV phase, and a CC discharge. Subsequently, for all cells with ID “03” and “04”, a C/10 charge and discharge were performed to the defined SoC for the EIS acquisition, 50% SoC for cells “03” (full charge followed by a discharge to 50%SoC) and 100% SoC for cells “04” of each batch. This consists of the beginning-of-life (BoL) diagnostic cycle throughout this study. This is then followed by a C/10 discharge to 0%SoC where the bulk of the cycling at C/5 for 70 cycles with no CV phase. Subsequently, EoL characterisation was performed, mirroring the BoL diagnostic cycle. Originally, cells “02” were intended to perform 70 cycles, but they were interrupted due to a lab electrical failure. As they began their cycling without BoL inspection, their CE displayed different trends which will be discussed in this chapter. Furthermore, 10 additional cycles at C/5 were performed on “01” cells after the EoL cycle, to further study the CE trend after interruption. These 10 cycles were preceded by a C/10 discharge as well. Additional cells were provided as well for opening, visual inspection and SEM/EDX presented in the following sections. They were opened as described in the procedure in Section 3.3.

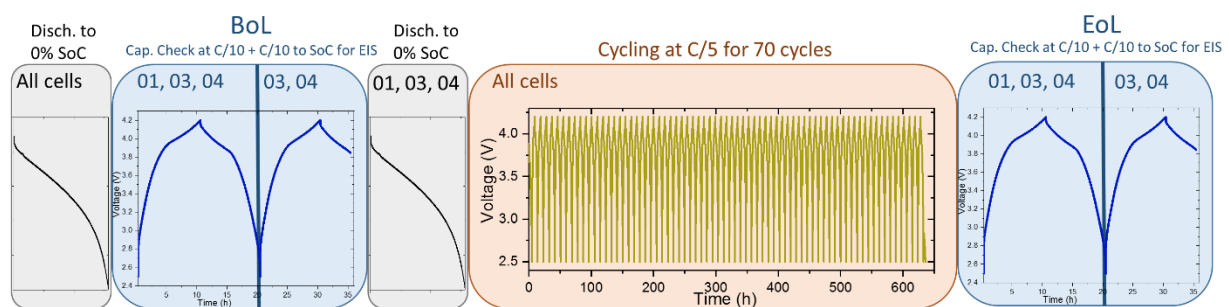


Figure 4-3. Summary of the procedure applied to the cells throughout this chapter.

Taking as an example a cell from “LCO/HC – 2004”:

- LCO/HC – 2004 – 01: Cycled on Novonix 70 cycles
- LCO/HC – 2004 – 02: Cycled on Novonix with no BoL or EoL, ~7 cycles (due to interruption)
- LCO/HC – 2004 – 03: Cycled on Digatron 70 cycles + EIS at 50% SoC
- LCO/HC – 2004 – 04: Cycled on Digatron 70 cycles + EIS at 100% SoC

Furthermore, the EIS was performed using a current perturbation (Galvanostatic control) of 30mA, ranging from 1 MHz to 10 mHz, with 10 points per decade acquisition, following a 3h rest period.

4.3 Beginning and end of life studies

The BoL and EoL studies presented in this section serve the purposes of illustrating the differences in cell design, macro and microstructure, chemistry and electrochemical fingerprints to emphasise the leading differences that will be observed in CE during the main cycling in the section that will follow, 4.4.

4.3.1 Macrostructure assessment using X-ray Computed Tomography

Prior to the cycling of the cells, each cell sent by ABSL was scanned using the Nikon XTH 225 for X-ray CT to assess the cell's internal macrostructure. Tomograms of the cells are displayed in Figure 4-4, showing the 'jelly-roll' electrode assembly structure, typical of 18650 commercial cells. The tomograms displayed have been taken at the $\frac{3}{4}$ height mark starting from the bottom, to show a representative slice of the overall electrode assembly. Firstly, it can be noticed that within each cell type, design changes are visible from batch-to-batch, representing adjustments made by the manufacturer. For cells "LCO/HC" for instance, the addition of a mandrel at the core of the cell has been made for the 2013 and 2014 batches, as opposed to its first iteration in 2004. Mandrels are found in certain cell models, providing mechanical stability to the wound jelly-roll layers and ensuring that the cell maintains its shape during assembly and operation²⁴¹. Additionally, what is most likely a nickel tab on the outer part of the jelly-roll is present for said 2004 batch, and absent in the others. For LCO/Graphite cells, which possesses a thicker mandrel located at its core (around 280 μm thick for cells "LCO/HC" as opposed to around 500 μm for cells "LCO/Graphite"), the earlier batch from 2008 does not have an outer nickel tab like its later iterations from the 2011 and 2014 batches. NMC/Graphite cells on the other hand does not appear to have observable macrostructural design changes from batch-to-

batch, but display what appears to be an aluminium tab embedded within the central layers of the jelly-roll and a nickel tab (verified by EDX) at its core. Additionally, a thinner electrode assembly is visually apparent, consistent with its high power rate denomination. This was taken from several measurements from the tomograms from the copper to the aluminium current collector, encompassing a whole electrode assembly layer and were found to be around 200 μm , 175 μm and 80 μm for cells “LCO/HC”, “LCO/Graphite” and “NMC/Graphite” respectively. Furthermore, a small deformation of the electrode assembly is observable for LCO/Graphite – 2008 – 01 at its core and close to the mandrel, which form appears analogous to the deformation present in all NMC/Graphite cells. With these initial observations, it appears that no major defects are present within the cells scanned prior to the following cycling, despite the age of some of the cells.

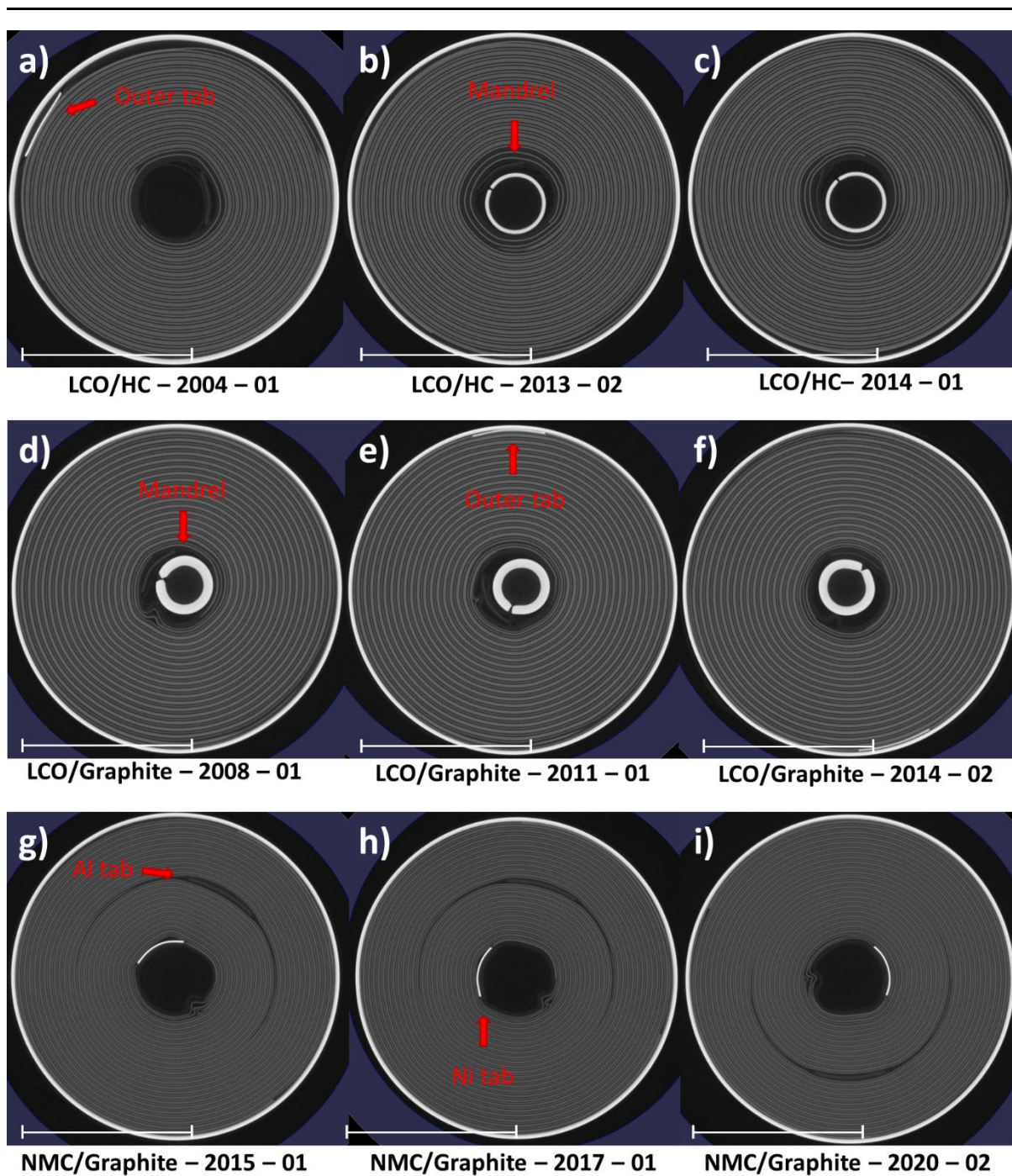


Figure 4-4. Reconstructed tomograms of the commercial 18650 cells as received. The tomograms correspond to a) to c) LCO/HC, d) to f) LCO/Graphite and g) to i) NMC/Graphite. Each tomogram is labelled by the ID of the cell and the year of manufacture of the batch it corresponds to. The scale bar displayed represents 10mm.

Following the 70 HPC cycles and an additional capacity check cycle, the cells were scanned again to assess for any changes in their macrostructure. The EoL scans are virtually identical to the ones of the cells as received and displayed in Figure 4-4.

This suggests that two or three slow cycles at C/10 and 70 cycles at C/5 are not sufficient to induce sufficient macrostructural changes, expected over this short and low C-rate cycling history²⁴².

4.3.2 Visual inspection after cell opening and SEM/EDX

Two additional cells of “LCO/HC” and “NMC/Graphite” were then slowly discharged following the procedure in Section 3.3.1 and subsequently opened for visual inspection and SEM/EDX. A cell from the LCO/HC – 2013 batch was opened and the visual inspection of its separator is displayed in Figure 4-5. Representative sections of the inner and outer parts are displayed for the cathode and anode sides. The harvested separators present a consistent brown colour, with a notable darker shade of brown band observable towards the whole longitudinal central area. These features seem consistent with post-mortem and subsequent visual inspections in the literature for cells stored at high SoC, high temperature, long storage time or that underwent high-rate cycling^{243–245}. Towards the core, where there is more mechanical strain, darker circular grey stains are observable on the separator, which might be an indication of localised concentric lithium depositions arising from local drier spots²⁴⁶.

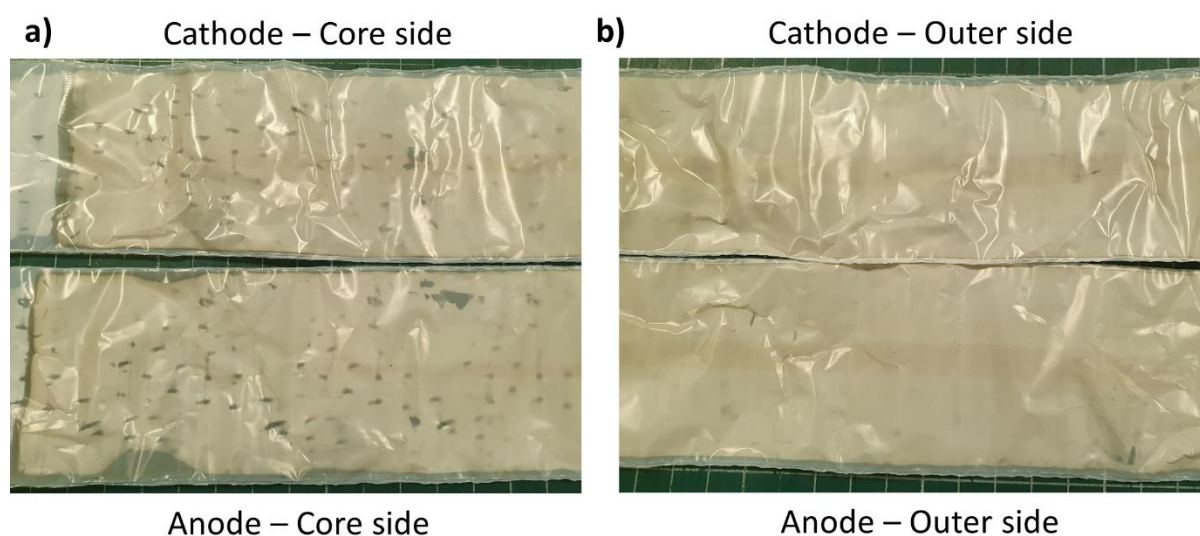


Figure 4-5. LCO/HC – 2013 cell separator visual inspection after cell opening displaying a) the side of both cathode and anode closer to the core of the electrode assembly, and b) the outer side.

Afterwards, a separate cell from the 2015 batch of “NMC/Graphite” was opened, and the relevant visual observations are shown in Figure 4-6. The cathode material displays partial delamination which occurred on the internal side (side of the electrode facing the inner part of the cell) on the area close to the intercalated aluminium tab. The tab itself is located closer to the core of the cell. The delamination location closer to the centre of the electrode assembly is facilitated by the additional inner strain sources usually observed at these locations during post-mortem studies^{247,248}. Another aspect that might facilitate this is the fact that after the cap has been removed during opening, the cell is left to rest 30 min to allow some electrolyte evaporation, as per the procedure. This effectively allows for some drying effect which might render the electrode assembly more brittle and to stick to the separator. Moreover, the electrodes of NMC/Graphite cells are notably thinner, as it has been shown with the X-ray CT assessment, which could encourage an easier delamination. This, however, is the only instance throughout this thesis that this has been observed, as this is usually more prevalent for anode graphite material to partially or fully delaminate during the opening procedure, depending on how aged/damaged it is. On the other hand, and in comparison to the overall state of the “LCO/HC” cell, NMC/Graphite’s separator is more analogous to a “fresh” cell state, being white, without any trace of yellow tones. No major feature is displayed by the anode material or the anode side of the separators. Overall, these observations are indications that despite storage in what could be considered favourable conditions to minimise degradation (20°C and < 10% SoC), due to the age of the cells, it is effectively undergoing inevitable calendar ageing evidenced by the various features discussed; 10 years and 8 years for LCO/HC – 2013 and NMC/Graphite – 2015 respectively.

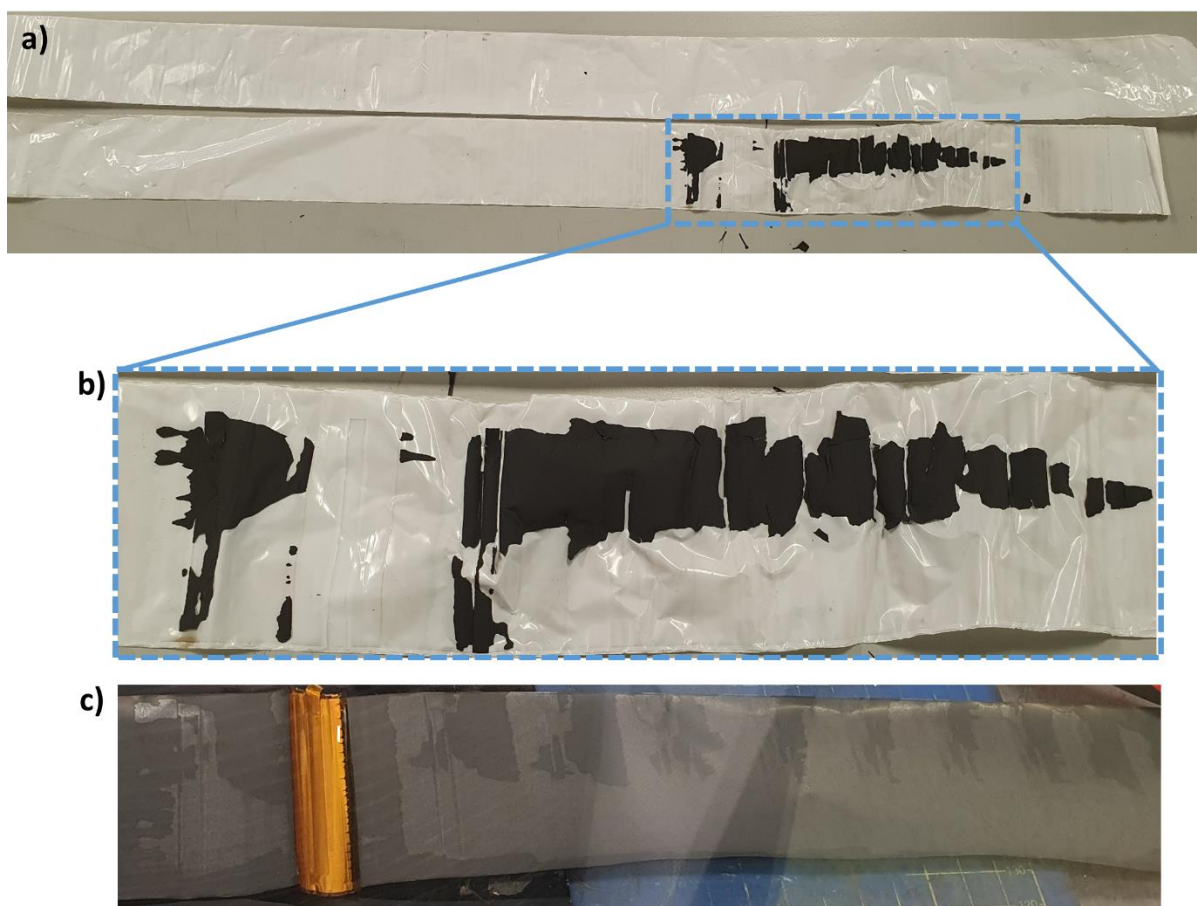


Figure 4-6. NMC/Graphite – 2015 separator visual inspection after cell opening. a) shows both separators with a delaminated patch of cathode material located towards the core, magnified in b). c) displays of the cathode once the cell opened in the glovebox, with the suspected delaminated cathode material, located close to the intercalated aluminium tab of the cell.

Subsequent SEM and EDX analyses, as shown in Figure 4-7, reveal, as expected, LCO cathode material for the “LCO/HC” cell and what appears to be NMC material for NMC/Graphite cells, as expected. As mentioned previously, the exact ratio of NMC of “NMC/Graphite” was not provided by the cell supplier during this project, but EDX analysis shown in f) suggests an almost equal ratio of nickel, manganese, and cobalt, leading to the assumption that the current cathode material is an NMC 111. Secondary NMC particle agglomerates have been measured in the range of 8 to 15 μm , which themselves consist of thousands of smaller primary particles which are hundreds of nm in size. For “LCO/HC”, LCO particles are observable in the range of roughly from 8 to 20 μm , and the conductive carbon added to the electrode material is particularly visible in c), appearing as the darker stain. The Fluorine evidenced by EDX

in e) is usually attributable to leftover Li electrolyte salts species^{249,250} or the presence of the binder²⁵¹.

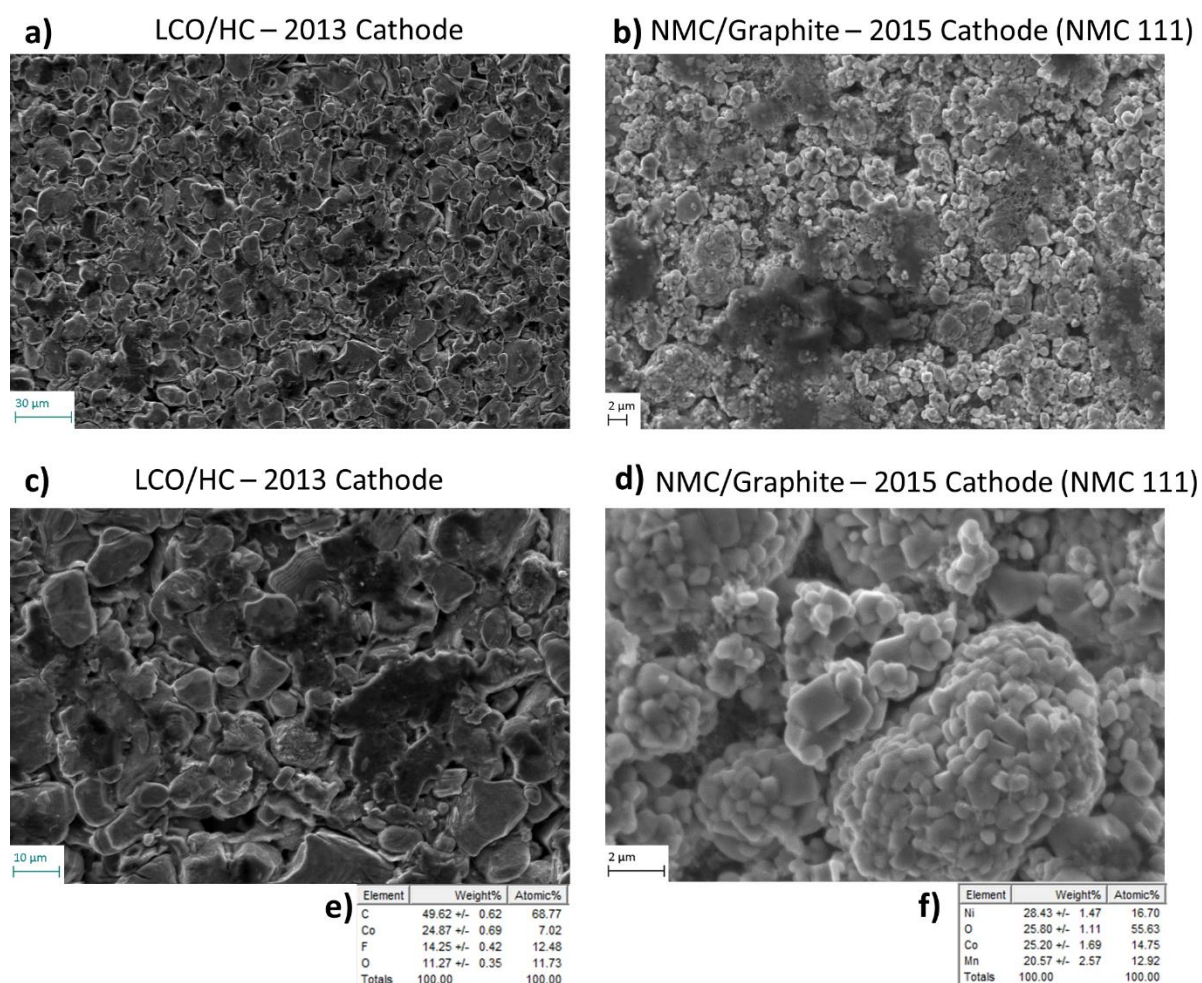
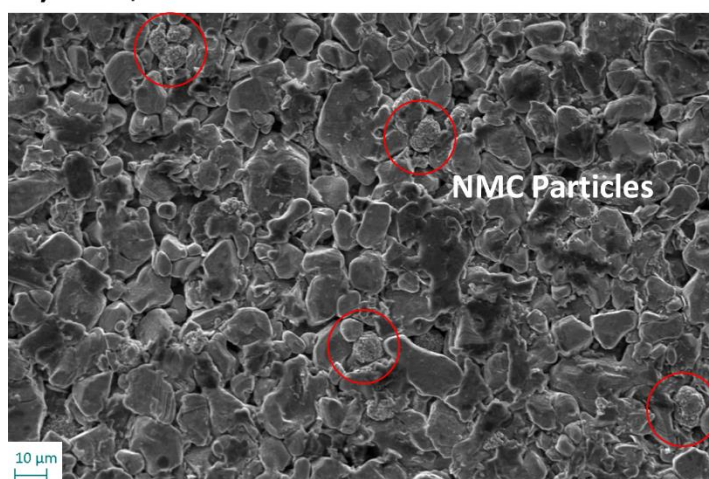


Figure 4-7. SEM micrographs of the cathode material of a) and c) LCO/HC – 2013 at $\times 1000$ and $\times 2500$ magnification respectively and b) and d) NMC/Graphite – 2015 at $\times 5000$ and $\times 15000$ magnification respectively, with their respective representative element table in e) and f).

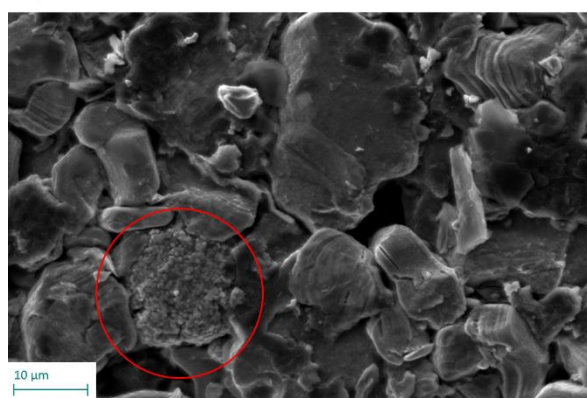
However, a more in-depth mapping investigation of the cathode material of the “LCO/HC” cell revealed the presence of a multitude of individual NMC secondary particles embedded within the LCO material, as shown in Figure 4-8. The EDX in c) performed on the particle isolated in b) indicates a ratio with marginally more Ni compared to the one observed in Figure 4-7 f) observed for NMC/Graphite cells, suggesting that the embedded particles could be NMC particles, although the ratio could be more dominated by Ni in this case. The accuracy of EDX does not allow a clear conclusion on this matter, although additional particles analysed ranged from

roughly 30 to 35 Ni weight%. This surprising observation raises questions about whether this was done intentionally or not by the manufacturer, as a doping strategy or a simple impurity respectively. One could suppose that the manufacturer produces cells of various chemistries, and slurry from the NMC batch would be residual in some of the machines, leading to this accidental contamination. It is unlikely that this contamination occurred during the opening process performed in our study, as the cell from “LCO/HC” was opened before the “NMC/Graphite” cell in the glove box, and no cross-contamination was deemed possible. If the blend is deliberate by the manufacturer, ICA carried out in 4.3.4 revealed no characteristic NMC peaks, and as such, likely negligent electrochemical contribution from these particles.

a) LCO/HC – 2013 Cathode



b) LCO/HC – 2013 Cathode



c)

Element	Weight%	Atomic%
Ni	34.63 +/- 0.93	17.58
O	24.20 +/- 0.62	45.07
Co	16.08 +/- 1.03	8.13
Mn	14.26 +/- 1.56	7.74
F	5.92 +/- 0.41	9.28
C	4.91 +/- 0.31	12.19
Totals	100.00	100.00

Figure 4-8. SEM micrographs of the cathode material of LCO/HC – 2013 a) and b) at $\times 1300$ and $\times 3700$ magnification respectively. c) is the elemental table of the EDX performed on the particle identified in b).

The imaging of the anode material for both cells reveals the HC microstructure of “LCO/HC” and the graphite of “NMC/Graphite”, shown in Figure 4-9. The HC anode is composed of irregularly shaped and sized particles, in the range of 2 to 40 μm . On the other hand, the graphite observable in b) displays particles ranging approximately from 12 to 32 μm , more consistent in size as well as more spherical in shape. The calendaring effect is also visually more pronounced as opposed to the observed HC. The micrograph in d) displays PVDF binder particles embedded within the microstructure.

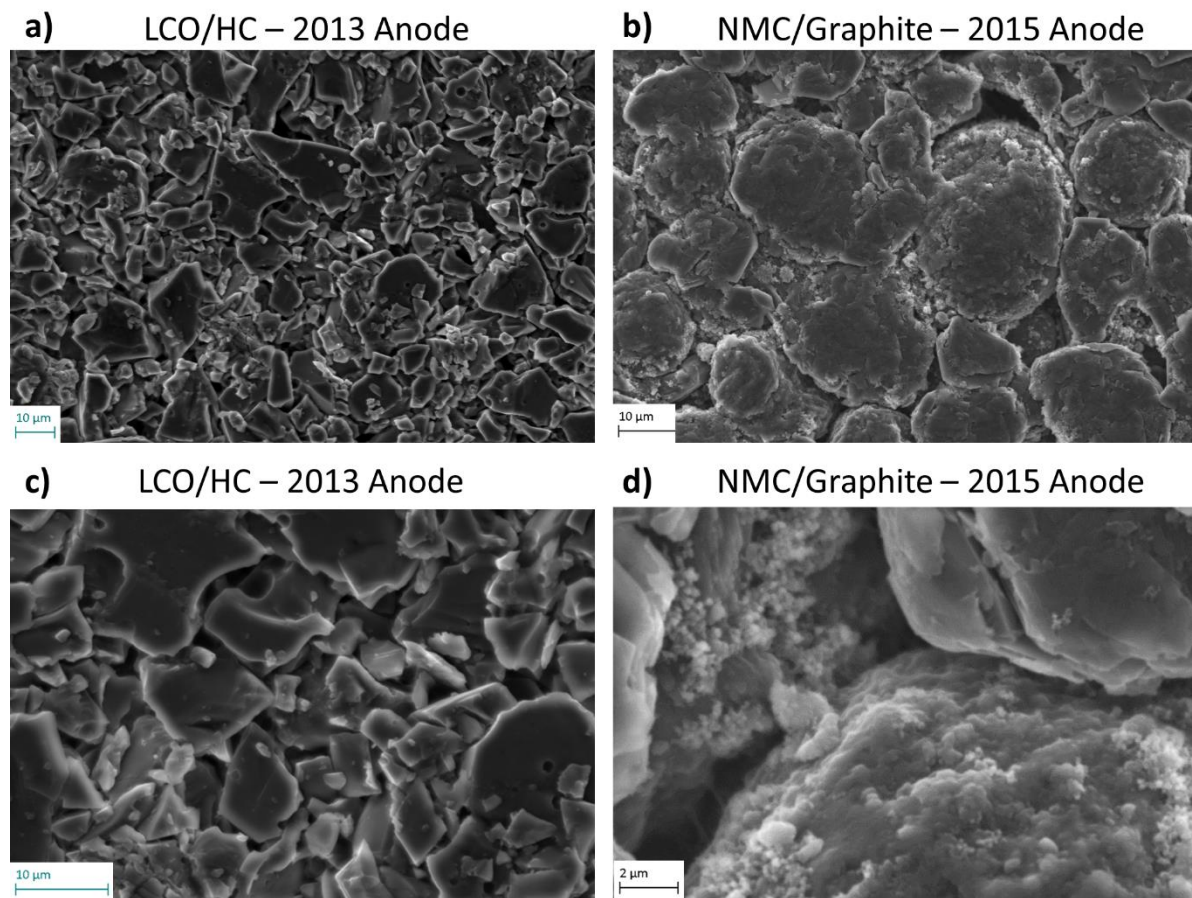


Figure 4-9. SEM micrographs of the anode material of a) and c) LCO/HC – 2013 at $\times 2000$ and $\times 4700$ magnification respectively and b) and d) NMC/Graphite – 2015 at $\times 3000$ and $\times 15000$ magnification respectively.

Further investigation was performed in the delaminated area using the SEM, as shown in Figure 4-10. The micrographs display the site of the fracture of the cathode material, where the right side corresponds to an intact area as opposed to the left side, which is the delaminated area, observable in b). Visual inspection suggested that

regions observed in a) are only partially delaminated; however, the SEM imaging in turn reveals a total delamination of the cathode material, exposing the aluminium current collector in some areas, visible in e) and g). Voids in these regions are also observable, as well as uncalendared and spherical secondary NMC particles. Further sites close to the location of the fracture show some features identified by EDX as fluorine between around 20 to 50 μm in size. These structures could be agglomerates of Li salts from the electrolyte, which could have arisen during the drying of the electrolyte after removal of the cap, where the cathode could have detached in dryer spots, and stuck to the separator. Another hypothesis is that these features appeared during the transfer of the electrode material from the glovebox to the SEM vacuum chamber, where the material is exposed to air for roughly 5 min. However, these features are only visible on the delaminated side of the cathode, and not on the intact side. Furthermore, nothing indicates that these were not already present within the electrode material and that they are indicative of weaknesses within the microstructure. No additional elements can confirm either of these hypotheses. The strain and tension present when the cell was closed and the electrode assembly compacted may have kept everything under pressure and no effect could have been noticed or the performance affected. Indeed, given the performance of NMC/Graphite cells throughout this chapter, it is unlikely that these were features prominent enough to cause any effect on normal cell operation unless this is an issue with this cell specifically. Overall, these initial observations evidences the differences within cell types and batches, as well as signs of ageing.

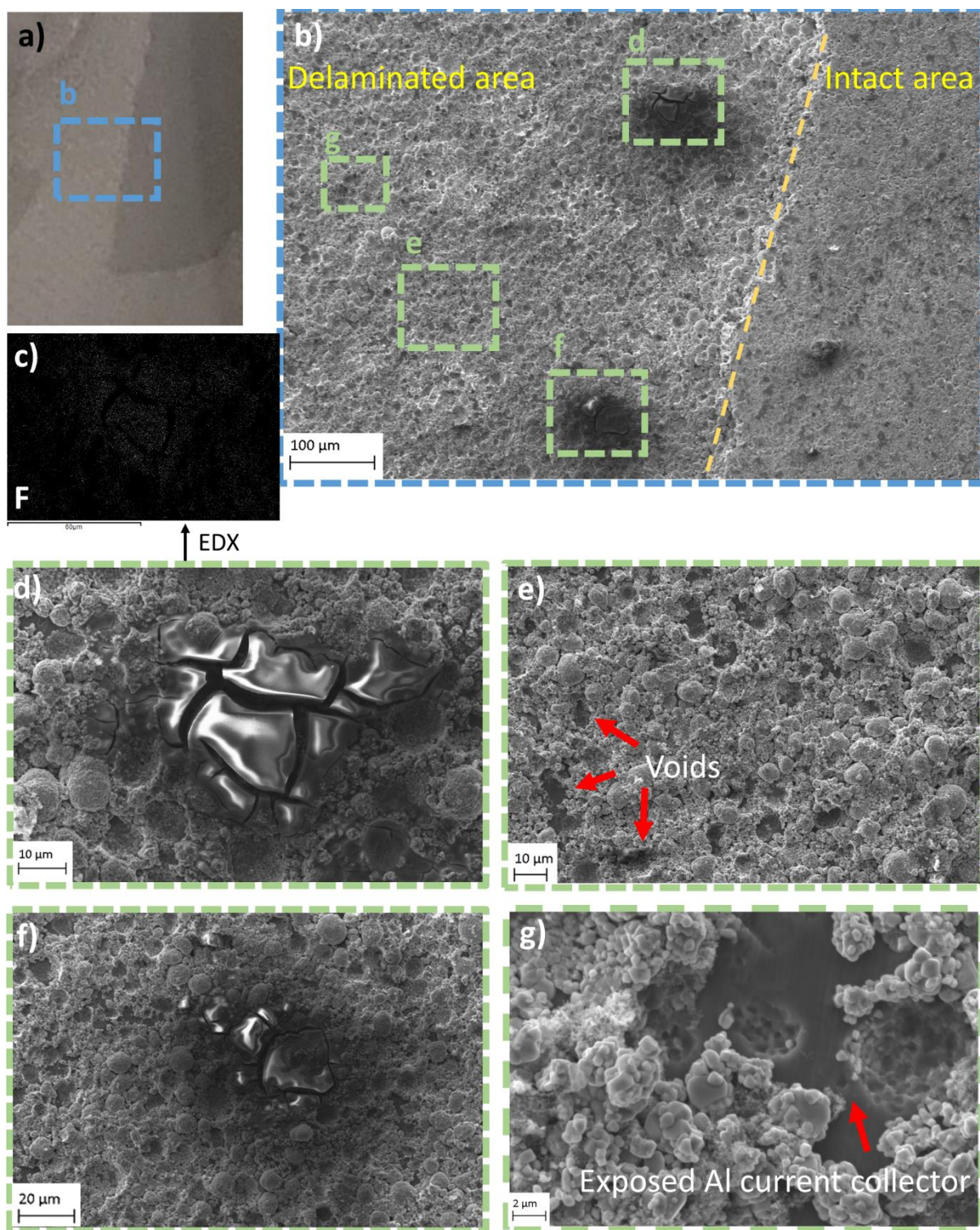


Figure 4-10. a) Portion of NMC/Graphite – 2015 cathode examined showing both intact and partially delaminated material with b) an SEM micrograph of the area at $\times 350$ magnification. c) EDX elemental map of Fluorine of d) the feature observed in the delaminated area, as well as f) with $\times 2500$ and $\times 1200$ magnification, respectively. e) and g) micrographs evidencing the Aluminium current collector exposition. at $\times 1500$ and $\times 10000$ magnification, respectively.

4.3.3 Capacity check and Incremental Capacity Analysis

Figure 4-11 displays the capacity checks conducted for cells “LCO/HC”, ID “01” cells, and the resulting ICA. For each cell, both at the BoL and EoL capacity checks, there is a small loss of capacity after 70 cycles of cycling at C/5, as is to be expected. Furthermore, as shown in the dQ/dV curve, there is only one broad peak for all LCO/HC cells, where single phase transition happens relatively slowly at around the 4 V mark, consistent with what is observed in literature for LCO cathode and HC anode materials²⁵². There is a small but noticeable resistance increase, characterised by a shift towards the right for all peaks in the charge direction for the dQ/dV , and towards the left in the discharge direction, and measured to be exactly 13 mV in the charge direction for all three cells. Additionally, the expected flattening of the peak is observable for all cells, particularly visible for LCO/HC – 2014 – 01, attributable to degradation mechanisms such as loss of active material²⁵³. Moreover, ICA showed no relevant and characteristic phase transition attributable to NMC presence in the cathode material, as evidenced by SEM/EDX in the previous section and as such, the electrochemical contribution of these individual embedded NMC particles could be considered negligible overall.

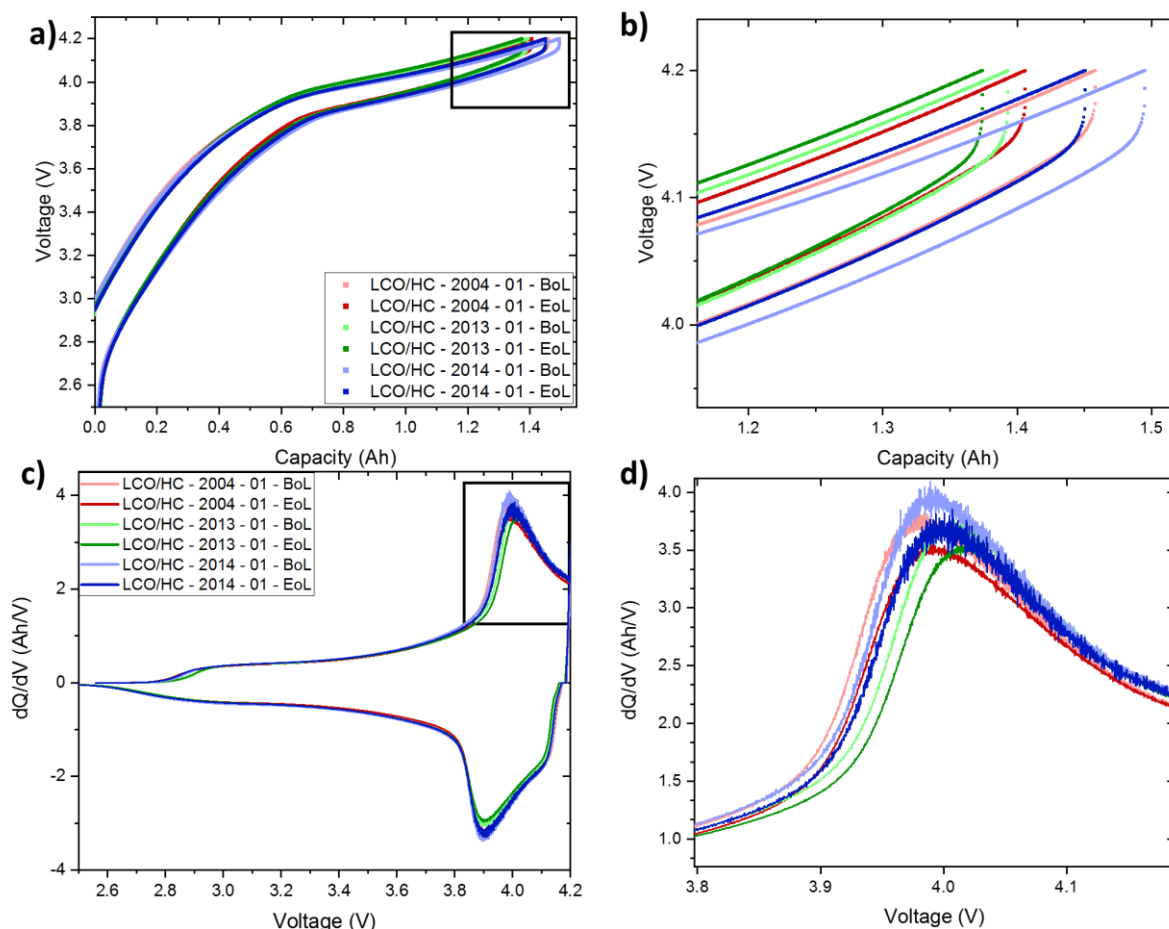


Figure 4-11. Results of BoL and EoL capacity checks at C/10 carried out before and after the 70 cycles of HPC for LCO/HC cells where a) displays the voltage curve over capacity and c) is the incremental capacity vs cell voltage (dQ/dV), with b) and d) being the corresponding magnified region of relevant areas (marked with a black rectangle) for a) and c) respectively.

LCO/Graphite's BoL and EoL capacity check cycle and resulting dQ/dV plot are displayed in Figure 4-12 with minor capacity losses and peaks shift measured at EoL. It can also be observed from the ICA plot that the cell from 2008 does present different first peak features at around 3.75 V, which may be attributed solely to graphite with no contribution of the cathode material, based on several studies on ICA of various materials^{220,254,255}. This specific difference in features could be explained by the use of different blends of graphite (artificial or natural), a different calendar process or other additives. The 2011 and 2014 batches on the other hand, are more consistent with each other, and the manufacturer could have corrected batches following the 2008 iteration. A small split of the peak is present in the BoL cycle for the 2011 batch but disappears at the EoL to match closely with the 2014 batch. An opening and

subsequent SEM/EDX and XRD investigation could help elucidate these distinctions for LCO/Graphite's first peak feature in future work.

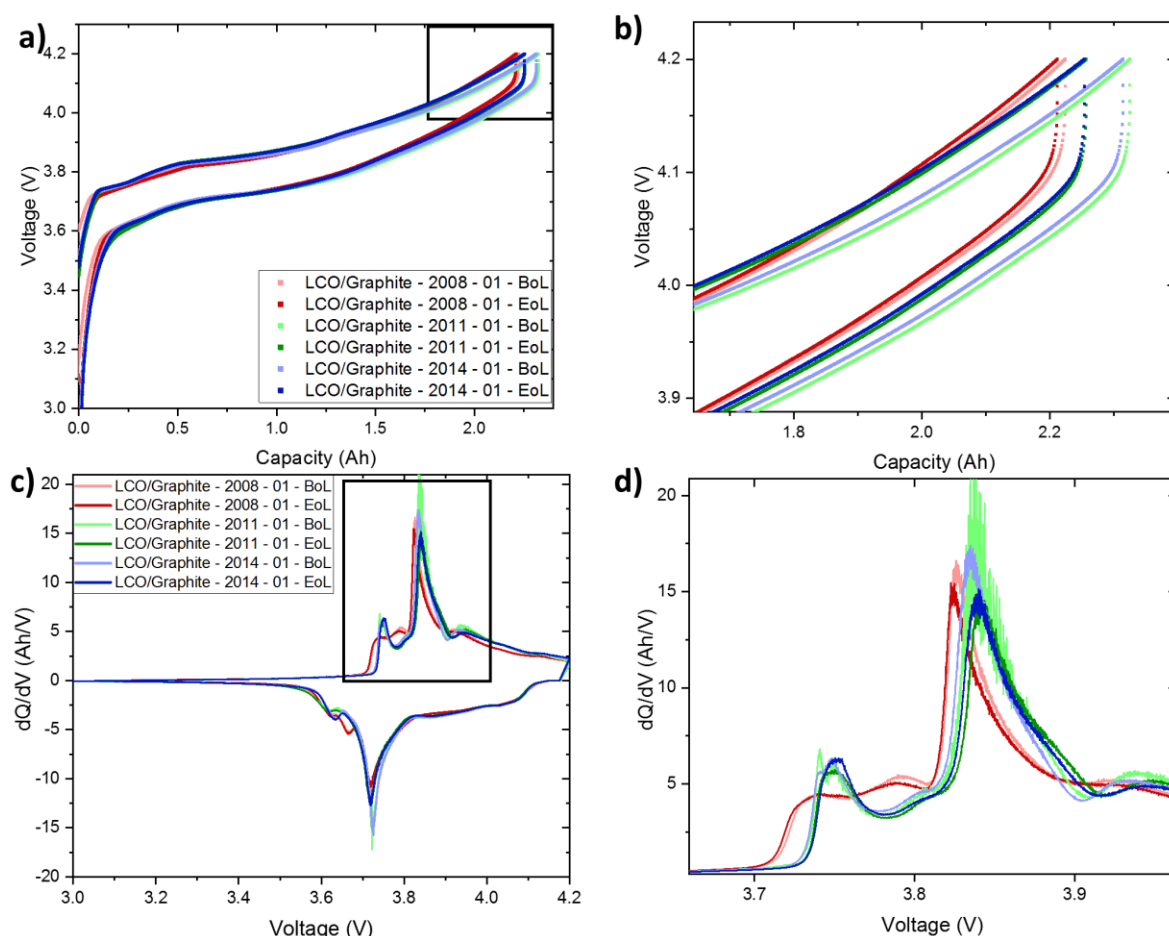


Figure 4-12. Results of BoL and EoL capacity checks at C/10 carried out before and after the 70 cycles of HPC for LCO/Graphite cells where a) displays the voltage curve over capacity and c) is the incremental capacity vs cell voltage (dQ/dV), with b) and d) being the corresponding magnified region of relevant areas (marked with a black rectangle) for a) and c) respectively.

Figure 4-13 displays the capacity checks conducted for “NMC/Graphite”, “01” cells, and the resulting ICA. It is important to note that the voltage range of these cells is 2.0 to 4.2 V, as this cell type is referred to as “high-power” cell. Indeed, a larger voltage range allows for higher rates and allowing higher overpotentials before reaching the upper cut-off voltage, although no peak was evidenced from 2.0 V to 2.5 V. As such, for clarity, the displayed figures are shown from 2.5 V to 4.2 V. NMC/Graphite cells distinctively display the least changes during BoL and EoL, evidencing the minimal overall degradation during the 70 cycles. Minor drops in

capacity shows a much better consistency of this cell type compared to the other cells. From the dQ/dV figures, while some features of the peaks have been flattened for all batches as expected, there is virtually no shift of the peaks towards the right (for charge), especially for the larger peak at 3.65 V, indicating minimal increase in resistance after 70 cycles. The dQ/dV features are also consistent with lower Ni content NMC/Graphite cells^{220,255}, corroborating the results obtained with EDX and further establishing NMC 111 as the cathode material of NMC/Graphite cells.

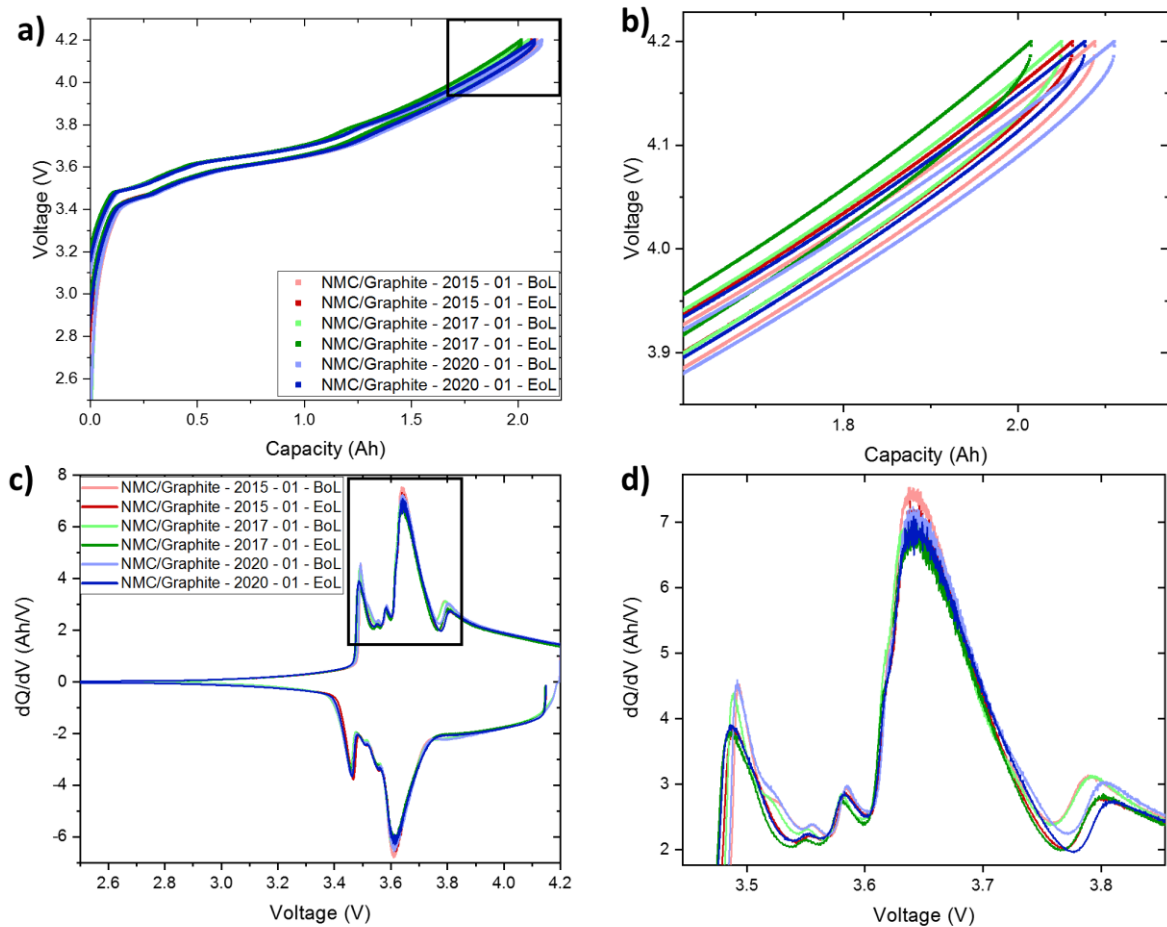


Figure 4-13. Results of BoL and EoL capacity checks at C/10 carried out before and after the 70 cycles of HPC for NMC/Graphite cells where a) displays the voltage curve over capacity and c) is the incremental capacity vs cell voltage (dQ/dV), with b) and d) being the corresponding magnified region of relevant areas (marked with a black rectangle) for a) and c) respectively.

Furthermore, the Voltage vs Capacity plot also evidence the different polarisation for each cell, observable with the differences in the voltage curves between charge and discharge. The comparison of the average charge and discharge

voltage curves per cycle, ΔV and its normalised value, will be studied the following sections, but a first assessment can already be made from the capacity check data. For instance, at 3.8 V, a voltage hysteresis between the charge and discharge curves were measured to be approximately of 180, 125 and 48 mV for cells “LCO/HC”, “LCO/Graphite” and “NMC/Graphite” respectively, emphasising further the differences from an electrochemical standpoint between each cell type. Despite the inherent differences observed between the various cell types, linked to their respective chemistries, no major degradation proxies or capacity and power fade are clearly observable so far for all cells.

4.3.4 Electrochemical Impedance Spectroscopy

EIS was carried out as part of the BoL and EoL diagnostics after initial charge and discharge for the capacity check on cells “03” and “04” for each cell type. The Nyquist spectra and extracted R_{Ω} and R_{ct} are displayed in Figure 4-14, where the high-frequency negative values have been omitted for clarity. The full spectra are found in appendices, in Figure 8-1. The Nyquist spectra displayed are the ones from cells ID “03”, collected at 50%SoC in the discharge direction, and the same scale was kept for resistance values for all cells in b), d) and f), to allow visual comparison.

Firstly, the data collected for cells “LCO/HC” in a) and b) demonstrate the different states and variations in EIS signature between batches, much more pronounced than for both “LCO/Graphite” and “NMC/Graphite” cells. The 2004 batch for instance, presents much lower overall R_{ct} values as opposed to the other batches at 50% SoC BoL. Moreover, while there is an expected increase in all resistance values from BoL to EoL, the highest relative increase is noted for the R_{ct} of the 2013 cells. Such increase is typically attributed to the growth of the SEI layer and changes in porosity, which result in reduced lithium concentration and a decrease in the exchange current density^{256–258}. Furthermore, it appears consistently that for all R_{ct} values, the 50% SoC is higher than its 100% SoC counterpart. On the other hand, R_{Ω} the values are analogous regardless of the SoC for the 2013 and 2014 batches but this is not true for the 2004 batch, where a higher R_{Ω} value is measured at 50% SoC. This batch appears to present a decreasing R_{Ω} as the SoC increases, as opposed to

the other batches, and for most of the other cells as well. Overall, the EIS for cells “LCO/HC” indicates significant differences between batches, particularly for the oldest batch (2004), which could indicate ageing signs, or simply potential changes in electrode material synthesis, calendaring or electrolyte additives made by the manufacturer.

LCO/Graphite cells display more consistency between values among batches as opposed to cells “LCO/HC”, although similar features previously explored are identifiable as well. R_{Ω} differences between 50% and 100% SoC are again minimal and consistent for all batches, and a minor difference is observable for 2008’s cells at BoL. The key differences arise from the magnitude of the increase of R_{ct} : it was measured to be higher for 2011 and 2014 batches, and lower for the 2008 batch. Hence in this case, the batch with less electrode surface reactions and SEI formation appears to be the original 2008 batch, particularly visible for LCO/Graphite – 2008 – 04, with its EIS collected at 100% SoC.

Furthermore, for NMC/Graphite cells it is observable that all batches display more prominent consistency and hence minor changes of R_{Ω} and R_{ct} . The values are overall much lower, across SoC, BoL and EoL. This is likely due to the thinner electrode material, and as such, less material to contribute to resistance against Li ions transfer²⁵⁹. Furthermore, the 70 cycles appear to have induced virtually no observable degradation detectable purely by EIS. Additionally, the mid-frequency region displays what appears to be a semi-circle with its two distinct components to be minimal, as opposed to “LCO/HC” and “NMC/Graphite” cells, as these features are more prominent and distinguishable.

Overall, despite the differences in values and trends discussed, it is important to note that differences between BoL and EoL are still relatively low, as the rate and duration of cycling are still considered to be relatively lenient, which is particularly true for NMC/Graphite cells. As such, with just the BoL and EoL data from EIS and ICA, coupled with the X-ray CT macrostructural assessment, a definitive conclusion of better cells or batches remains delicate. However, minor changes identified in early life might then result later on in major differences, exacerbated during very long term cycling. Henceforth, the HPC results will be studied in the following sections.

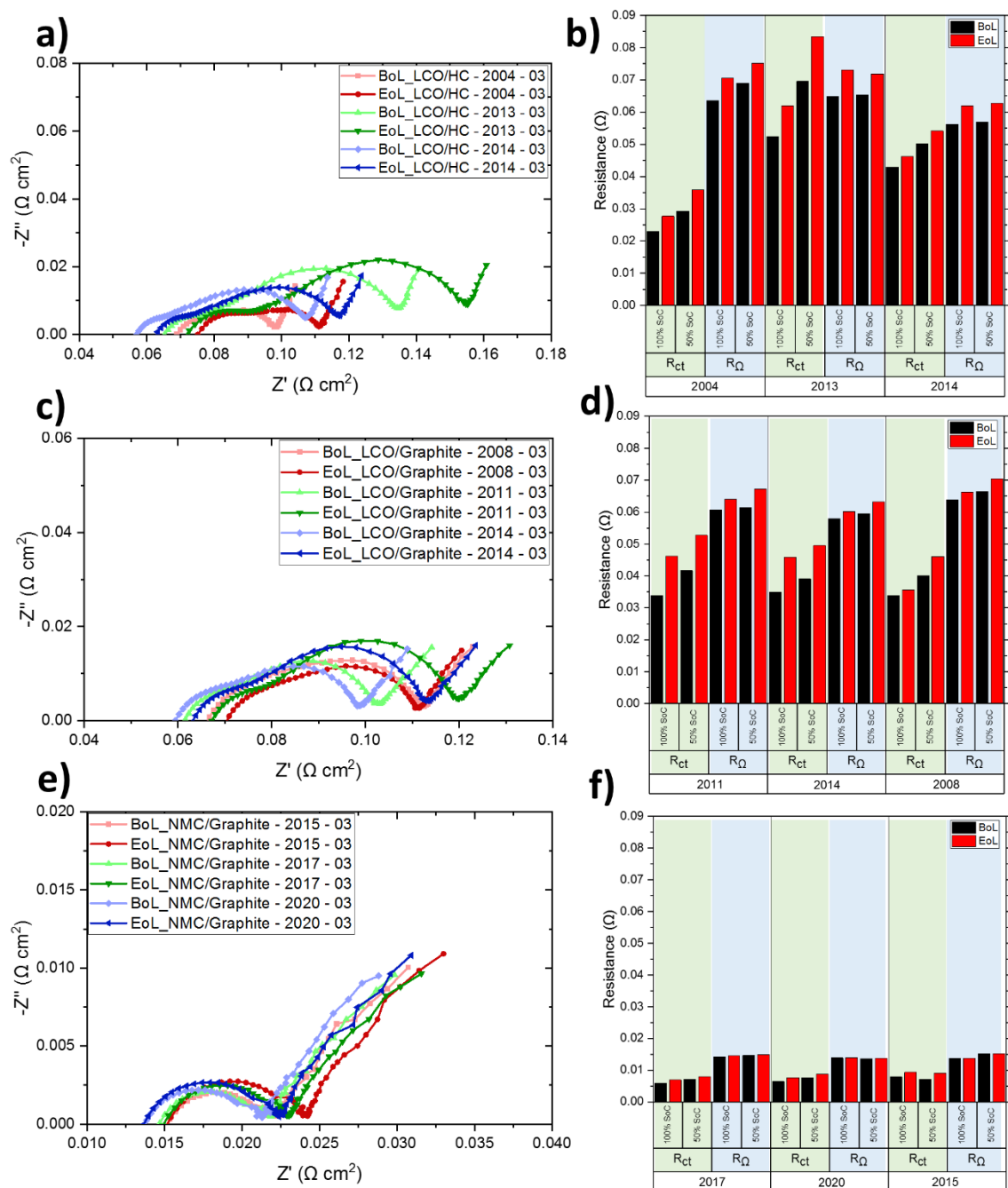


Figure 4-14. Nyquist spectra and R_{Ω} and R_{ct} values for cells “LCO/HC” (a and b), “LCO/Graphite” (c and d) and “NMC/Graphite” (e and f). For the Nyquist plots, only the positive $-Z''$ values are displayed for clarity.

Overall, this section has showed the major and minor differences in materials and design of all cell types used in this chapter. As such, it is important to highlight

how the HPC method will be applied to a varied test matrix, to potentially evidence its reliable application across a wide range of cell chemistries.

4.4 High-Precision Coulometry cycling

The HPC 70 cycles were performed with the considerations described previously and the CE values will be displayed alongside the measured discharge capacity and the normalised discharge capacity values plotted against the cycle number. Potential differences in CE values for cells cycled on the Novonix system (01 and 02) or the Digatron (03 and 04) cyler will also be discussed when relevant, considering the possible setup differences previously reviewed. These values will also be presented with the lifetime data shared to allow a direct comparison of qualitative indications given by CE. The first assessment made will be to address batch-to-batch differences within each cell type, with some specific comparisons made between batches of “LCO/HC” and “LCO/Graphite” which will be followed by an overall comparison of cell types compared together.

The representative lifetime data shared for this project comes from different quantities of cells and protocols performed by ABSL. The core information is that the cycling data was obtained cycling at C/2 CCCV charge and CC discharge to 90% DoD. The upper cut-off voltage for “LCO/HC” and “NMC/Graphite” cells was the standard 4.2V, but 4.1V for LCO/Graphite cells. The company confirmed that the data gave an accurate and representative overview of the capacity fade that can be expected from each batch, although it will vary depending on rate, DoD and cut-off voltages. The lifetime cycling was carried on either until cell failure or other reasons for interruption, and each case will be mentioned specifically when relevant.

4.4.1 Batch-to-batch assessment

Figure 4-15 displays the CE, discharge capacity, and normalised discharge capacity for LCO/HC cells, as well as the average CE per batch and the corresponding lifetime data. Three cells were cycled for each batch, one using the Novonix system

and the two others coming from the Digatron hardware, as previously stated. The CE value of the very first cycle is omitted in most of the figures that follow, as it is significantly lower than the following cycles. It is a practice commonly reflected in the literature^{185,260}, and figures with it available for all batches of all cells are placed in appendices, in Figure 8-2. What appears from the data is that the discharge capacity and normalised discharge capacity show great consistency between batches, no matter which cyclier was used, and as such indicate persistent differences in available capacity between each batch. For instance, the 2014 batch presents higher capacity and better capacity retention, as opposed to the 2004 and 2014 batches. Differences arise from CE values. We observe converging values for the cells labelled as “01”, which were cycled on the Novonix, stabilising at plateau between 0.9996 and 0.9997 after 40 cycles, with the CE values of the 2013 batch being above the others. More variations and spread are observable for cells “03” and “04” for each batch, cycled on the Digatron system. A spread is likely observable for the cells cycled on the Digatron cyclier, assuming that the CE values obtained from the Novonix system are closer to the “true” value, and may be a result of the differences found specifically in accuracy calculations displayed discussed in 3.1.2.1. However, the only average that appears to be higher than the “true” value is likely to be LCO/HC – 2013 – 04 from the 2013 cells, whereas the other 03 and 04 cells are usually lower than their 01 counterparts. From all the data gathered, the averaging in b) evidences that 2013 batch’s CE values are the highest, above 2004’s which itself is above 2014’s, with a significant spread for 2013 and 2014’s cells.

The lifetime data in c) indicates cycling carried out at C/2 with intermittent capacity checks at slower C-rates, resulting in a notable recovery of the capacity of different magnitudes for each batch, indicating the extent of resistance increases, or polarisation (also termed power fade). The most prevalent information obtained is the clear worse performance of the 2004 batch compared to the others, with rapid capacity fade after 2100 cycles and cycled until failure, as opposed to the other batches which retained significant capacity even after thousands of cycles and could have carried on for more cycling. Considering our initial postulate about the trends in CE and resulting lifetime data, it appears that it is not verified for LCO/HC cells batches, as the overall CE values of the 2004 batch, the worst performer, are almost as high as the one from 2013. The 2014 batch, which could be considered the best performer, even if it has a

more pronounced downtrend starting after 5000 cycles, displays the lowest CE values of the three batches. This is mainly because the “03” and “04” cells lower the total average. When considering only the 01 cells cycled on the Novonix, CE values for the 2013 are the highest, while LCO/HC – 2004 – 01 and LCO/HC – 2014 – 01 are closely matched, sitting at around 0.0001 below the 2013 batch. Overall, from the presented data, the drastic difference in long-time performance exhibited by the 2004 batch is not reflected on the measured CE of its initial cycles.

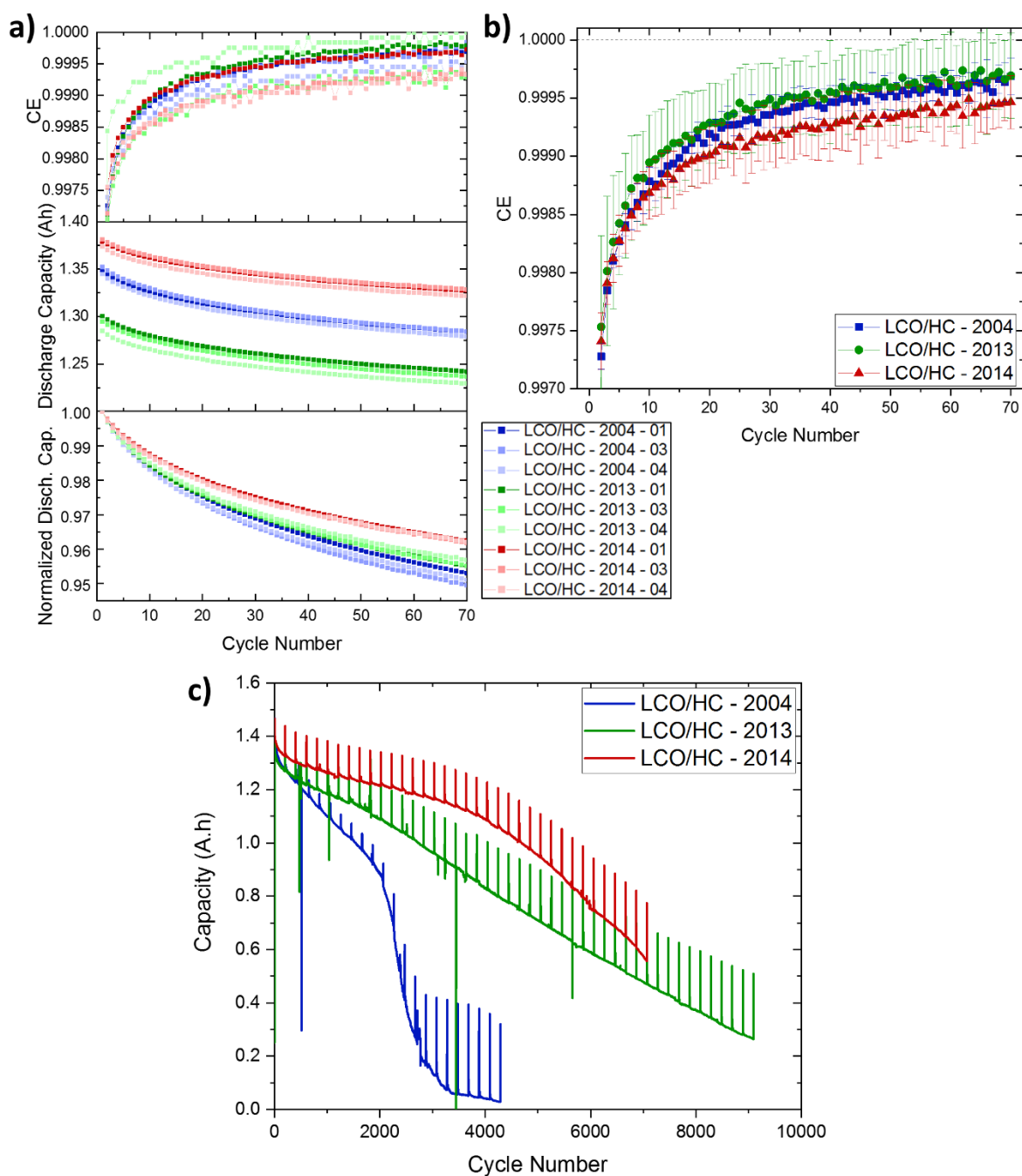


Figure 4-15. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of Cells LCO/HC, b) CE values plotted for each batch, comprised of the averaging of its component cells, and c) the representative lifetime capacity fade for each batch. Error bars represent standard deviation (SD).

The same data for LCO/Graphite cells is available in Figure 4-16. Batches' discharge capacity and their normalised values are once again consistent with each other, although some minor differences in trends are observable for normalised values, such as LCO/Graphite – 2014 – 04 showing higher capacity retention than its

other counterparts from the same batch. 2008 cells also display, as shown in the normalised capacity plots, a recovery of capacity at the beginning of cycling, to reach above unity for the first 8 cycles, as opposed to the other batches. These cells show better cycling retention, and match the BoL and EoL investigations as they also displayed the lowest capacity fade that was measured in the EoL. Once again, the “01” cells CE values are more consistent with each other, even more so here, as they all sit at a 0.9996 plateau for most of the cycling. Overall, more spread is once again observable for the remainder of the cells. However, this time, there is no outlier from the 03 and 04 cells with CE values higher than the ones displayed by cells 01, cycled on the Novonix.

Overall, the CE values stabilise a lot quicker at their plateau (between cycles 10 and 15), compared to LCO/HC cells, a difference that might be attributable to the anode material, as the cathode is assumed to be similar, although the use of various electrolyte additives or other components might have an effect as well. However, lower and slowly increasing CE values for LCO/HC cells, manifest a higher presence of parasitic reactions as opposed to LCO/Graphite cells in the initial cycles before stabilisation at cycle 40. A possible contributing factor might be that HC in LCO/HC cells has a higher propensity for SEI formation and surface reactions compared to graphite. This is due to the fact that it has micro-pores in its structure where Li ions can get trapped during the lithiation process and are hence not readily available for reversible cycling, lowering CE^{68,261}. Furthermore, the material can react with surface functional groups, such as oxygen-containing groups, during the lithiation process which can lead to irreversible capacity loss and lower CE as well²⁶². Additionally, as well as the intercalation displayed by graphite, HC materials also rely on adsorption processes at above 80% lithiation as shown by several studies, which could also contribute to lower CE, particularly at top of charge^{69,263}.

The lifetime data provided shown in c), indicates that the 2008 and 2014 batches failed at a similar time, while the 2011 one did so around 1000 cycles earlier, at 2550. The failure is characterised here by the broad oscillations between capacity values between 0.05 Ah and a much higher value, for several cycles before the cycling was interrupted. These could be attributable to drastic resistance increases leading to reaching cut-off voltages almost immediately and as such, skipping steps in the cycling protocol, or due to the formation of soft-shorts which can cause high self-discharge

rates, effectively allowing charge for longer periods of times^{42,264}. While the 2011 batch displays the initial highest capacity retention up to 900 cycles, it is the first batch to fail. The CE data summarised in b), in this case, shows a good correlation between CE and lifetime capacity fade, with notably 2011's cells with the lowest CE value and the first to fail. However, as mentioned previously, the "01" cells display nearly identical CE values once the plateau is reached, and hence complicates the possible distinction between batches. The 2008 batch is also the batch identified to have a different graphite peak feature with ICA during the BoL and EoL capacity checks, which could be considered here as the best performer.

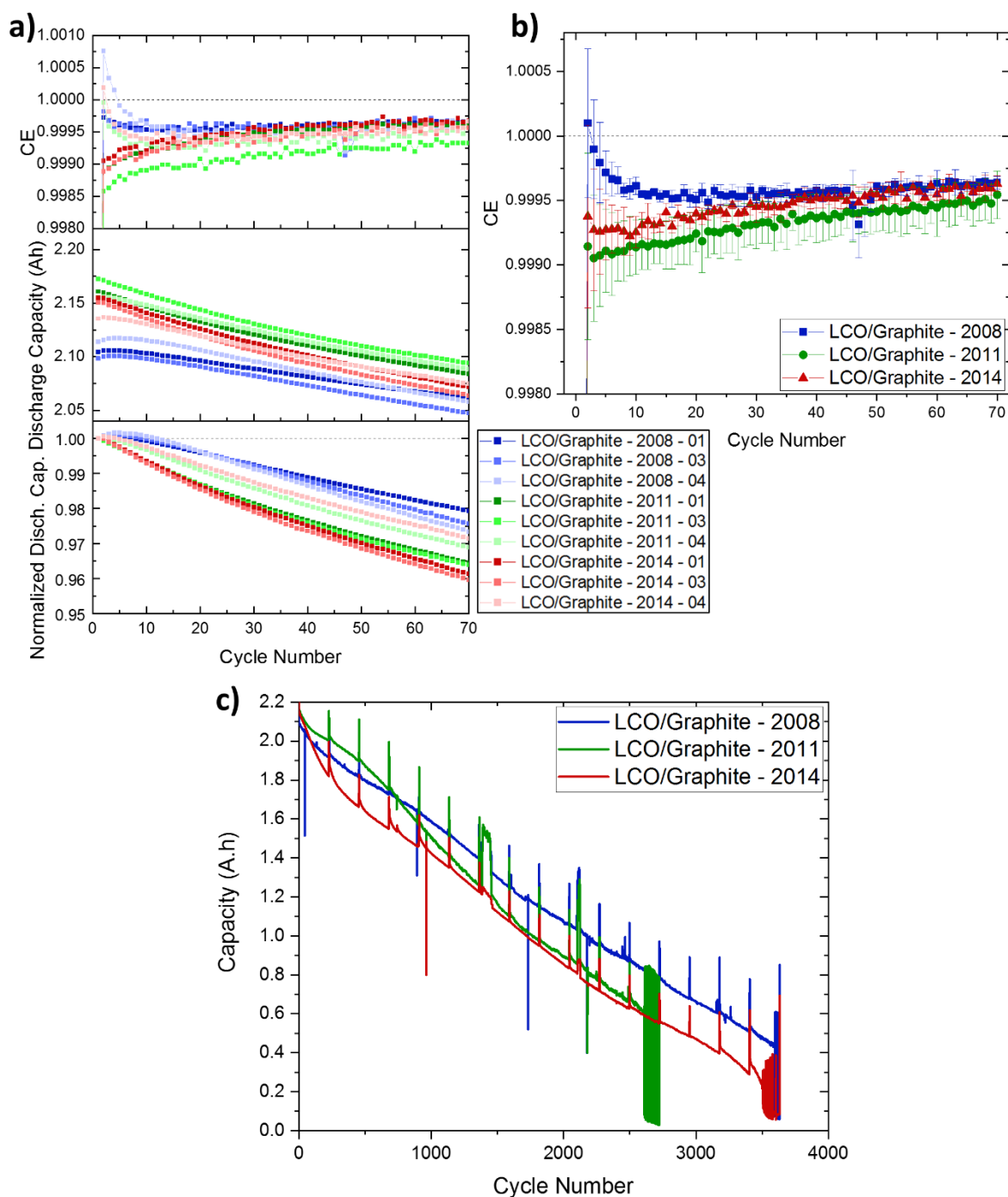


Figure 4-16. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of LCO/Graphite cells, b) CE values plotted for each batch, comprised of the averaging of its component cells, and c) the representative lifetime capacity fade for each batch.

Moreover, for cells "LCO/Graphite", several cells display an initial CE value higher at cycle 2 as opposed to the following cycles, in a downward trend, as opposed to most other cells, which show a gradual increase in CE in the first few cycles. This

is particularly true for the 2008 batch where all cells display this behaviour, as well as other cells. CE values above unity or on a downward trend for the first few cycles, have been explained by several studies highlighting the role of the overhang area of the anode. The overhang refers to areas of the graphite anode in a Li-ion battery that does not have a cathode counterpart directly opposite it. This area exists because the negative electrode in a Li-ion cell is designed slightly larger than the positive electrode to ensure 100% cathode-anode overlap and to prevent lithium plating at the border area (usually the nearest edge) of the graphite anode^{265,266}. The overhang regions tend to be located at the innermost and outermost winding of the battery's jelly roll, but can vary in location and size depending on manufacturer and cell model¹³⁵. These regions are still ionically connected to the lithium electrolyte reservoir and as such, can have an impact on the battery's CE measurements and capacity determination, though as they are not diametrically opposite a cathode region, the ion transport pathway from these areas of the anode is longer and therefore more kinetically hindered than for the bulk of the anode electrode²⁶⁷. The analysis of Li-ion battery ageing requires distinguishing between irreversible and reversible capacity changes, and the overhang regions can contribute to reversible capacity changes in very early life.

For instance, Gyenes et al. observed high SoC storage cells exhibited CE greater than unity during their first cycles after storage, as the Li ions nestled in the overhang contributed more predominantly in the discharge direction for the very first few cycles, as they slowly diffused out of the overhang towards the active anode material²⁶⁸. Eldesoky et al. indicate that a constant voltage hold at the lower voltage cut-off (2.5 or 3.0 V for most cells) for around a day will lead to the drainage of most of the Li ions nestled in the overhang area²⁶⁹. Furthermore, CE values higher than one appears to be more prominent the higher the storage SoC, the higher the temperature of storage and the longer the duration of storage^{142,192}. A schematic representation of the overhang interactions is found in Figure 4-17, along with an orthoslice of the very top part of LCO/HC – 2014 – 01, displaying the additional length of the anode material. As such, the CE of cells from 2008 represents well the longer storage time underwent by these older cells. Regardless, over time, Li could diffuse to overhang regions of the anode, even with lower temperatures. Interestingly, the oldest cells available, from the 2004 batch of LCO/HC, do not show a CE values above unity despite 18 years of calendar ageing. A potential explanation for this could be linked to specificities of the

HC material at the anode of these cells specifically. LCO/HC cells do possess an overhang like all other cells, as shown in Figure 4-17 b) below.

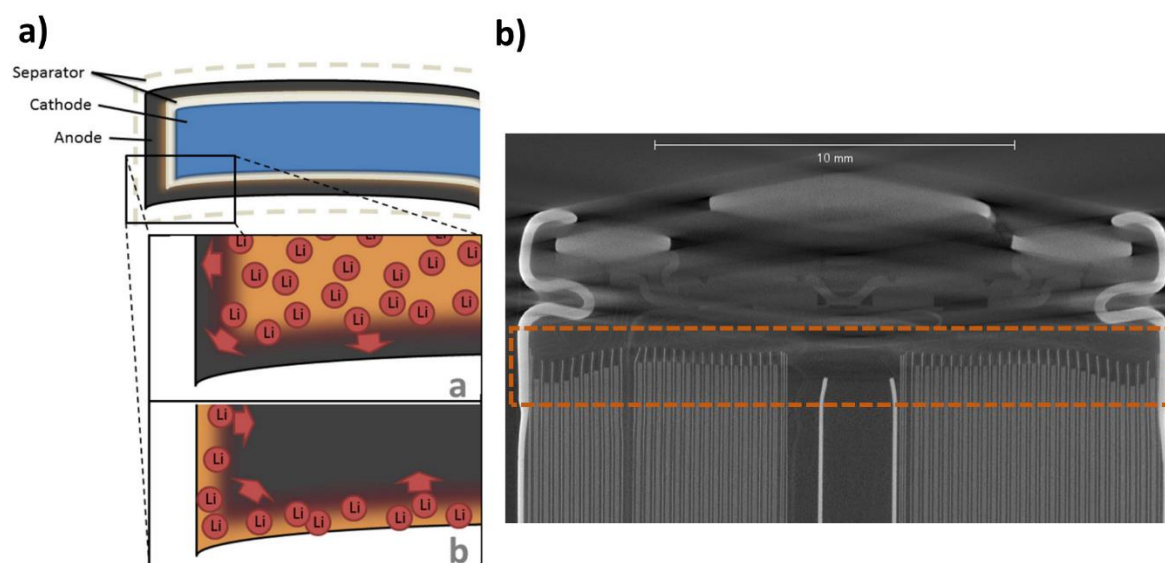


Figure 4-17. a) Schematic representation of lithium ion diffusion between anode active material and overhang region. Cases represented are in (a) during storage at high SoC where the Li ions from the anode active region is accepted into the overhang. (b) during subsequent storage or cycling at low SoC, ions nestled in the overhang region are released back into the active anode region. Reproduced from Gyenes et al.²⁶⁸. b) Orthoslice of LCO/HC – 2014 – 01, displaying the top part of the electrode assembly and the cap, where the overhang of the anode is observable in the highlighted area.

Furthermore, Figure 4-18 displays in more detail the capacity check cycles of the lifetime data the “LCO/HC” and “LCO/Graphite” cells. Said capacity checks were carried out at a slower rate ($C/10$) every 200 cycles and the percentage of capacity recovered is calculated from the ratio of the discharge capacity measured in the cycle prior the capacity check, with the measured capacity of the capacity check cycle. This confirms the magnitude of capacity recovery of the 2004 batch of LCO/HC, which appears after the rapid fade underwent after 2100 cycles, while the other batches present more linear behaviour, matching the overall fade as well. This is indicative of a more prominent and dramatic power fade for the 2004 batch, as much more capacity becomes available when slower rates are applied, leading to a much more significant lower overpotential response from the purely R_Ω . While $C/2$ cycling shows an available capacity close to 0 Ah in the lower plateau region of 2004 cells, a slow discharge cycle shows as high as 23% capacity available. For 2004’s cells, EIS evidenced a higher R_Ω value for 50% SoC as opposed to 100% SoC, unlike the rest of the cells. While the

difference is minor at BoL, this change might become exacerbated over long-term cycling, unlike the other cells which appear exposed to the same stable R_{Ω} throughout their whole SoC. As such, this increasing purely ohmic component of the resistance, combined with the CE values, could be an early proxy for the fade to come.

A suspected mechanism for this rapid and sudden power fade might be attributable to rollover failure, which is a sudden and significant loss of capacity that occurs after a prolonged period of apparently “typical” cycling. Ma et al. identified that impedance growth at the positive electrode and the associated increase in the DC resistance, leading to a rapid decrease in high-rate capability and evidenced by an increase in polarisation, play a crucial role in causing rollover failure²⁷⁰. It is challenging to predict as well and is highly dependent on many parameters such as cell chemistry, electrolyte additives and cell design.

LCO/Graphite’s lifetime data shows a more linear fade behaviour for all batches, and a very high capacity recovery in the last capacity check when the cell was already most likely failing. The batch from 2011 being the worst performer and the first one to fail does display a higher capacity recovery after 1000 cycles for over 600 cycles at above 10%, before reducing again at around 5%, right before the onset of failure. Moreover, EIS also showed a relatively more prominent R_{ct} increase for the 2014 cells but has not been evidenced either by a particularly lower CE of said batch or the lifetime data, as the capacity recovery values are in the same order of magnitude. In this particular case, it might not be parasitic side reactions contributing to a thickening of the SEI layer, but other mechanisms at play that lead to more fundamental degradation of the active material (such as cathode restructuring or oxygen losses).

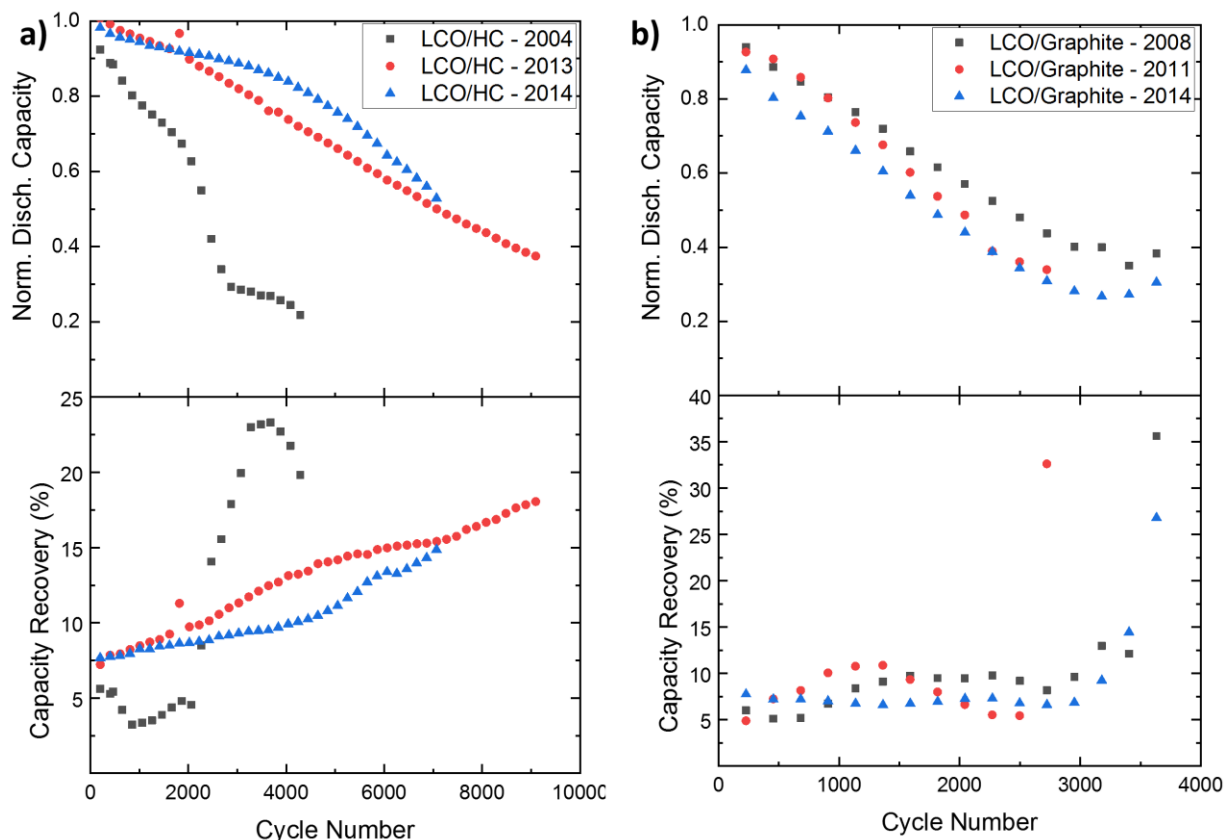


Figure 4-18. Normalised discharge capacity of the capacity check cycles of the lifetime data and the percentage of capacity recovered as opposed to the capacity measured with the cycle prior for a) cells LCO/HC and b) LCO/Graphite.

Furthermore, Figure 4-19 displays the lifetime data, “01” cells CE values from the Novonix hardware and normalised polarisation per cycle (ΔV) from all cells from all batches of cells “LCO/HC” and “LCO/Graphite” to allow a more detailed comparison. The capacity fade of LCO/HC batch 2004 is more analogous with LCO/Graphite cells (particularly visible in b)), although the mechanism might be different: power fade/rollover for 2004’s cells compared to the more linear fade of all LCO/Graphite cells. On the other hand, the 2013 and 2014 batches of LCO/HC cells display much better cycling retention. What is observable in c) with CE is that while LCO/HC batches start at a lower point, they do consistently overcome LCO/Graphite’s values once they reach their plateau at around 40 cycles. However, while LCO/HC – 2013 – 01 does present a significantly higher CE, the values for the 2013 and 2014 batches are very closely matched, a trend which does not reciprocate as the 2004 cells display much worse lifetime data.

The ΔV in d) evidences the differences in polarisation evolution for each batch of each cell type. The different trends and behaviours for each cell type are apparent, as they are closely related to the cell's chemistry, and good consistency is also displayed batch-to-batch. However, LCO/HC Batch 2004 here does display the highest increase in normalised ΔV , reaching values above 1, as opposed to the other batches. Increase in polarisation is also linked to overall resistance increase, and once again, the higher R_{Ω} measured at 50% SoC for the 2004 batch could be a proxy in early life, as this will be exacerbated with long-term cycling. LCO/Graphite cells display a more rapidly increasing polarisation, with an initial dip for the first 5-6 cycles. While the 2011 and 2014 batches display a higher increasing trend, 2008's normalised ΔV is significantly lower. As it is the best performer for "LCO/Graphite" cells (same lifetime as 2014's cells but with a better capacity retention at failure), the normalised polarisation and CE are in good agreement with lifetime data.

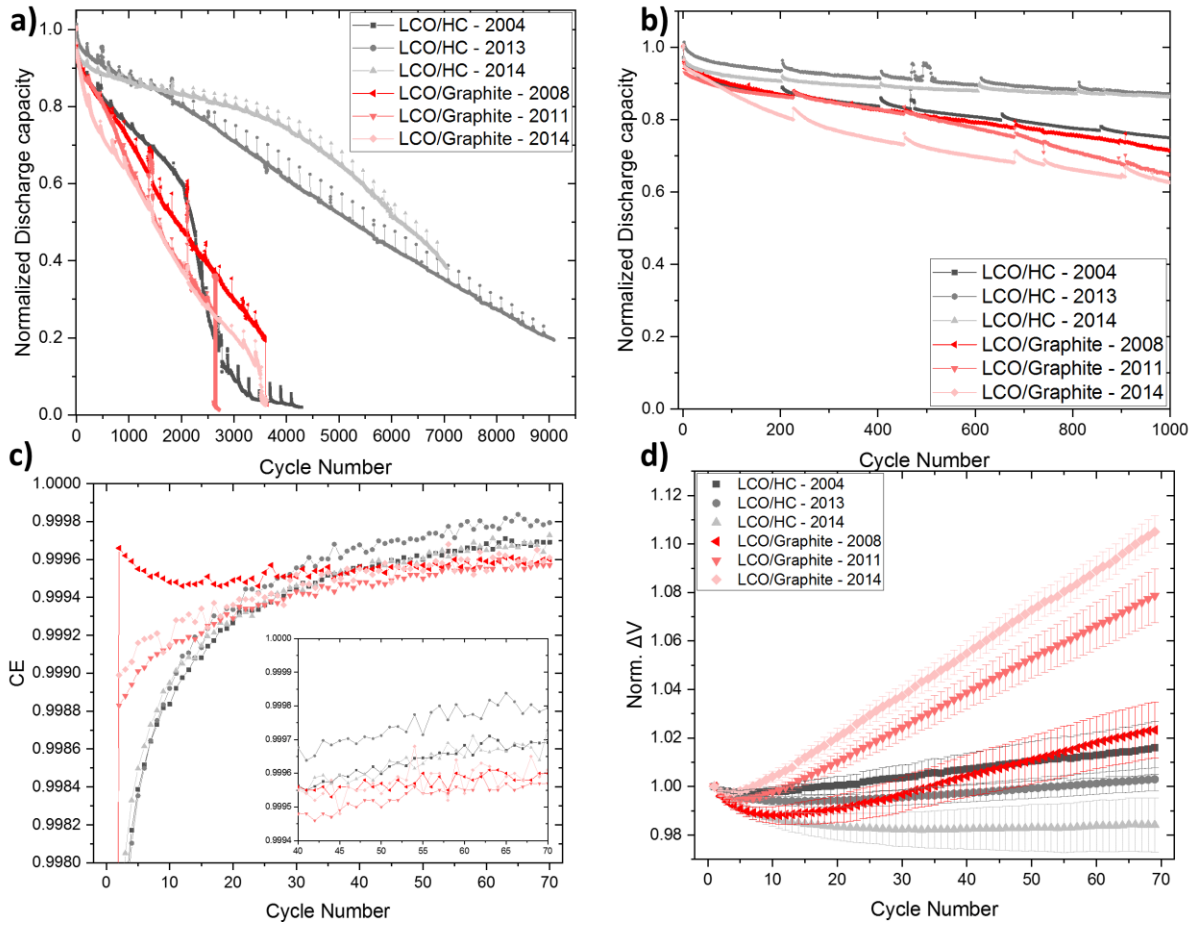


Figure 4-19. For all batches of LCO/HC and LCO/Graphite cells, a) lifetime data with the capacity checks removed with a b) magnified region of the first 1000 cycles. c) is the CE for the “01” cells and d) is the normalised ΔV obtained from all cells.

Furthermore, Figure 4-20 displays the CE, discharge capacity, and normalised discharge capacity for NMC/Graphite cells, as well as the average CE per batch and the corresponding lifetime data. The data of LCO/HC – 2014 – 04 is not available, as it was not cycled due to a channel failure. NMC/Graphite cells displays the highest CE values of all cell types, reaching a plateau and stable values immediately on cycle 2. The consistency in the capacity measured batch-to-batch is quite high, and the differences are minor with a difference of approximately 7 mAh for all cells of all batches throughout cycling. The normalised capacity values also show that there was no capacity fade observable during these 70 cycles, with capacity values rising above unity, with only a few cells dipping below 1 again before the end of cycling. However, considering the non-normalised capacity values, these changes are minor, and the capacity is simply exceptionally stable.

CE values then presented are high and convergent for cells 01, sitting consistently between 0.9997 and 0.9999 for the duration of the cycling. The values displayed by the cells 03 and 04 cycled on the Digatron system sit at around 0.0002 below, on average, but again show good consistency between all batches. Despite the differences in accuracy, perhaps more evident with the other cell types, 2017 cells appear to sit consistently higher for both 01 and 03/04 cells, and said batch could be considered among the best performers. Indeed, the lifetime data shows cycling that was interrupted for reasons other than rapid fade behaviour or failure, as for example the 2020 batch displays more than 80 % retention in capacity despite 16 000 cycles at C/2, and it could be assumed that the other batches could have undergone similar retention in capacity. This is why it is challenging to be able to differentiate in any way between batches for NMC/Graphite cells due to its consistently higher and analogous CE values, initial capacity values, closely matched lifetime data, and initial impedance values previously measured.

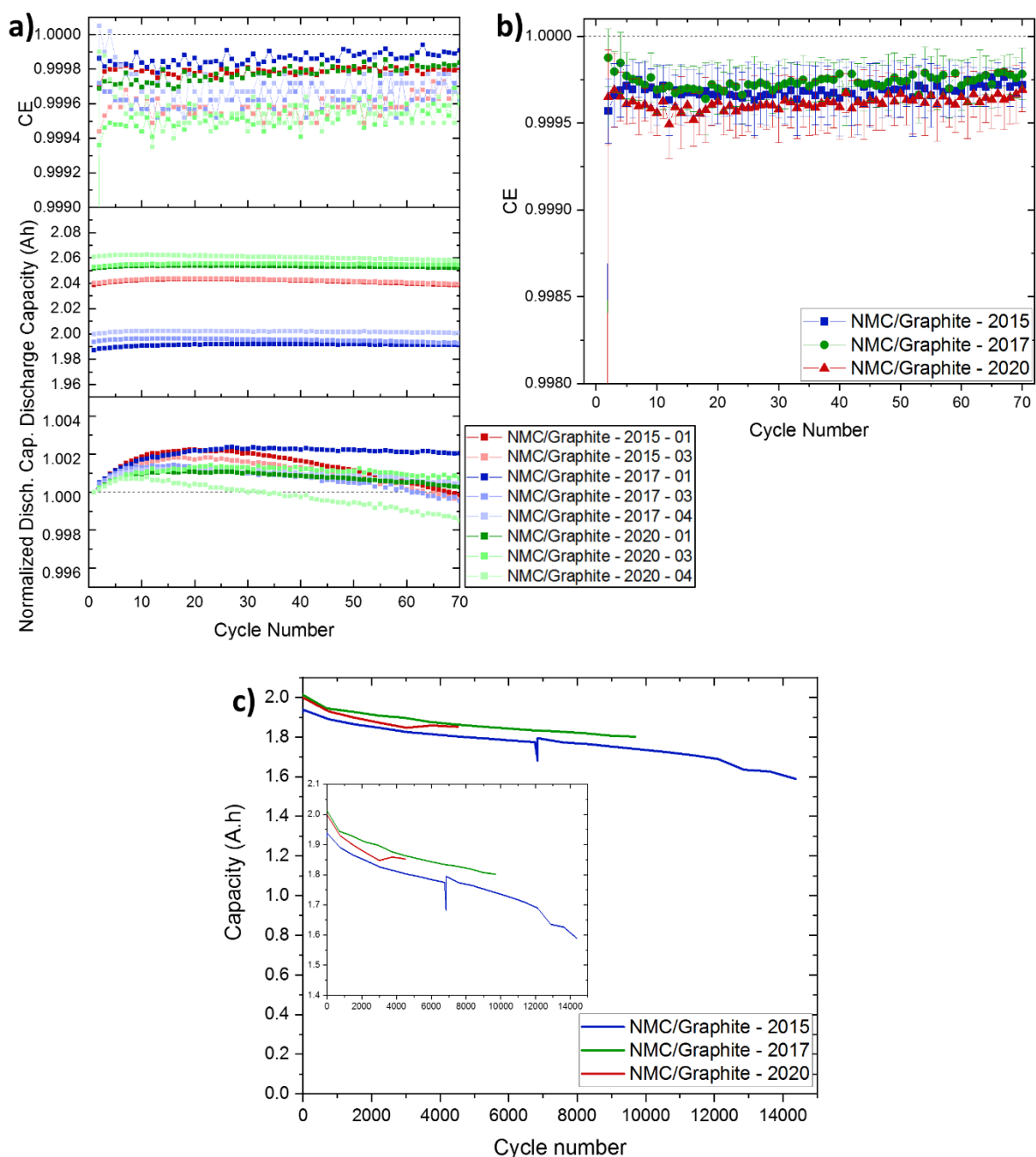


Figure 4-20. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of NMC/Graphite cells, b) CE values plotted for each batch, comprised of the averaging of its component cells, and c) the representative lifetime capacity fade for each batch.

Throughout this study, it became apparent that CE values measured on the Novonix sit consistently higher than the ones measured on the Digatron, although one exception was noted for one singular cell: LCO/HC – 2013 – 04. This could affect the consistency and reliability using this HPC method when cycling is performed on two

different cyclers. This notable discrepancy could be explained by a difference in the endpoint correction carried out at the top of charge and discharge, as shown in Figure 2-30. As the resolution of the Digatron cycler is lower than the Novonix (0.05 % vs 0.005 % FSR respectively), this might trigger an earlier software endpoint correction for the Digatron as high cut-off voltage is reached sooner as the steps are larger, as opposed to the Novonix where an additional minute amount of charge is passed before triggering the end of charge/discharge. Another element that may contribute to this is also the difference in temperature during cycling. As Shown in Figure 3-4, around 0.2°C oscillations were measured by cells cycled on the Novonix setup as opposed to around 1.5 to 1.8°C in total for cells on the Digatron system. This makes these cells subject to slightly higher temperature on average, which in turn increases the rate of parasitic reactions, and in turn leads to a lower CE value, albeit, only around 0.0002 to 0.0005 per cycle.

4.4.2 Overall assessment

Overall, batch-to-batch differences were shown to be challenging, where major differences in performance were not necessarily reflected on CE measurements, despite some good correlations for LCO/Graphite cells, but also displayed the impossibility of making clear identification of rollover or non-linear fade behaviour for the LCO/HC cells from the 2004 batch purely based on CE measurements. The surprising consistency of NMC/Graphite cells also rendered clear dichotomy between batches difficult, although other proxies and parameters like impedance and normalised polarisation did help.

However, another assessment is available when considering solely cell type comparisons. Figure 4-21 displays the CE of the three cell types cycled on the Novonix hardware, their discharge capacity, and their normalised discharge capacity, as well as the total CE average of all cells in b) and the average for the cells cycled only on the Digatron system. By comparing the CE values in a), b) and c), it becomes apparent that despite the differences and setups, spread and accuracy, and temperature control, the information provided by both cyclers is qualitatively the same. It can be interpreted overall as: cells “NMC/Graphite” will perform better than “LCO/HC”, which

themselves will perform better than “LCO/Graphite”; and lifetime data in d) indicates that this is true. Indeed, while starting at a lower value, the CE values of LCO/HC cells overcome LCO/Graphite’s at around 40 cycles. However, the differences between batches evidenced in the previous section encourage caution when taking these results at face value. Considering CE alone, it appears that this metric is heavily correlated to cell types and hence, the cell’s electrode material and key design choices. Another key contributor could be the choice the electrolyte additives (consumed or not during formation cycles), which is not studied here and is difficult to assess with commercial cells due to the secrecy of their use and consumption during formation, but can have a significant impact^{87,271,272}. As such, it would appear that overall cell design and chemistry have a greater qualitative impact on a cell’s long-term capacity retention than batch-to-batch adjustments and optimisation.

This is further emphasised by the difference in behaviour, trend and cycle number at which a stable CE plateau is reached for all cells, closely correlated to the cell’s chemistry. This is also reflected in the trends of capacity fade during the first 70 cycles, where a more pronounced fade is observable for LCO/HC cells (matching well the “arch-like” sigmoid curve behaviour of its CE value), a more linear fade for LCO/Graphite cells, and a very stable behaviour for NMC/Graphite cells. This matches well the core fundamental postulate of CE, where the lower the measured CE, the more side reactions are taking place, and the less is used as actually accessible charge.

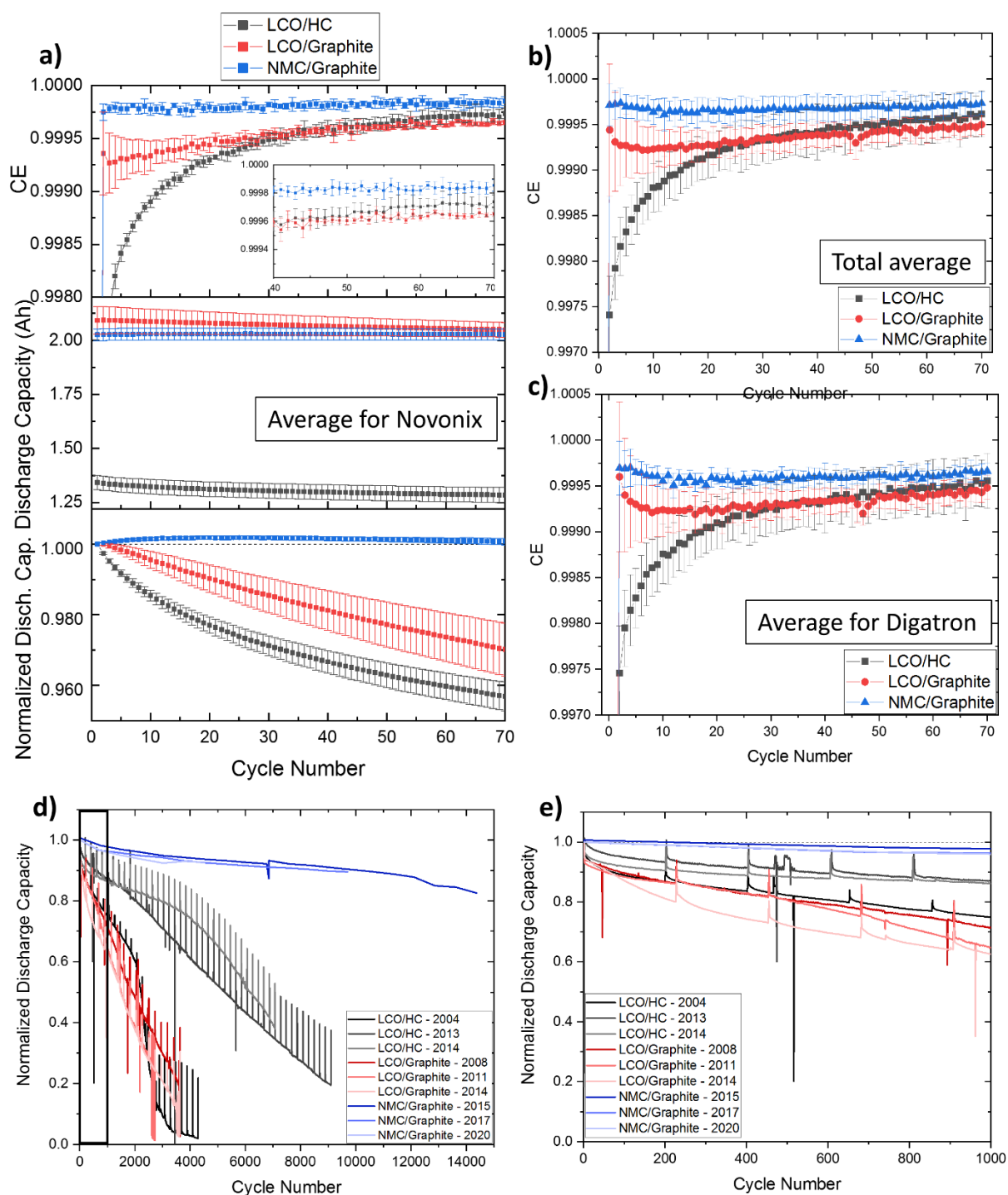


Figure 4-21. a) CE values, discharge capacity and normalised discharge capacity values vs cycle number of all cells cycled on the Novonix cycler, b) CE values plotted as a result of the averaging of all cells and c) cycled on the Digatron setup only. d) is the normalised capacity fade lifetime data of all batches of all cells and e) a magnified region displaying only the first 1000 cycles.

Furthermore, a look at the polarisation and normalised polarisation is possible when the data from all cells, from both cyclers, divided by cell type is considered, as shown in Figure 4-22. The normalisation starts at Cycle 2 to account for the variations of cycle 1, for all cells. While absolute values show relative stability, the normalised values display different trends for each type, with a more pronounced increase for LCO/Graphite cells, stability for LCO/HC cells and even a decrease for NMC/Graphite. Despite overall similarity in impedance and particularly similar R_{Ω} values, LCO/Graphite displays a high polarisation, which is therefore linked here to other causes such as the overall electrolyte properties such as salts concentration or electrode material properties such as particle size^{273,274}. This further reinforces the utility of ΔV in combination with EIS, to serve as additional proxies for longer-term fade assessment primarily obtained from HPC.

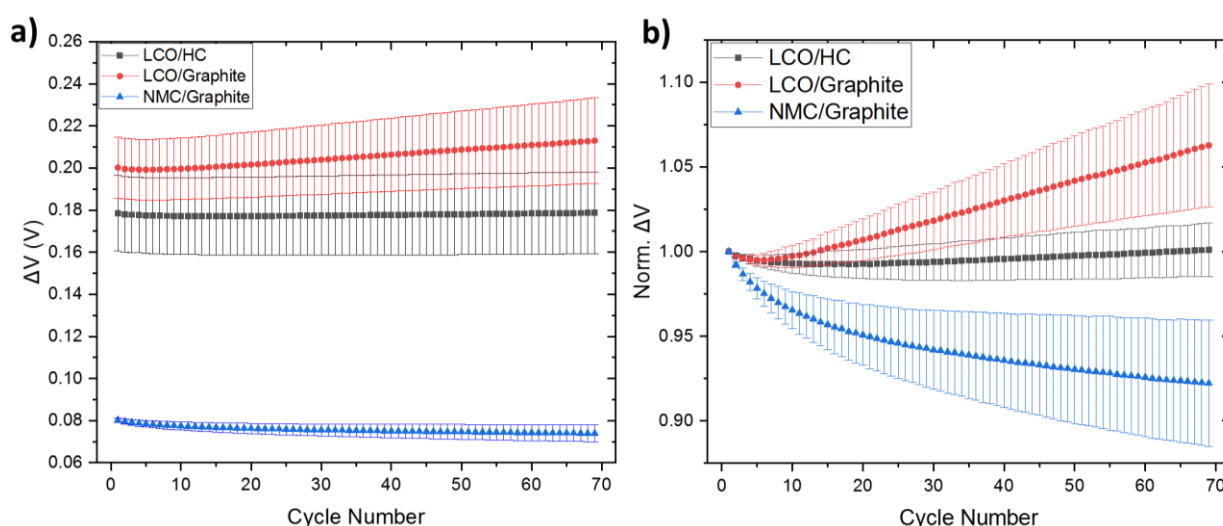


Figure 4-22. a) ΔV and b) its normalised value for all cell types.

4.4.3 Other factors linked to influence coulombic efficiency

On top of the data presented, further cycling was performed on cells “01” cycled on the Novonix setup. After the end of cycling capacity check and an X-ray CT scan for all cells, cycling was resumed for 10 cycles. This was originally planned for accuracy measurements and an attempt to account for channel-to-channel variations

for each cyclers, as recounted in section 3.1.2.1, but the data obtained served a different purpose and use, presented here.

As observable in Figure 4-23, there is an apparent correlation between the pattern in capacity recovery (or drop) following resuming of cycling with CE. For LCO/HC cells, for example, an increase of measured capacity on cycle 71 leads to a significant dip in CE as well. Conversely, NMC/Graphite cells depicts the opposite behaviour: when the capacity dips when cycling is resumed, CE on the other hand, increases as opposed to its last value before interruption, reaching even values above unity. For LCO/Graphite cells, the cell showing a capacity recovery (LCO/Graphite – 2008 – 01) presents a drop in CE values, while this time, the other two cells presenting a minor drop in capacity shows a relatively flat trend in CE. Recalling the discussion presented for the dQ/dV plot in Figure 4-12, the cells from the 2008 batch does present different first peak features at around 3.75 V, showing evidence of a difference of material in the anode, later adjusted for the remaining batches. This could potentially explain the difference in the behaviour of CE and capacity recovery for this batch as opposed to the others.

It is important to note that the interruption consisted of a capacity check starting with a C/10 discharge after the HPC cycling was done, and after that, the X-ray CT acquisition shown in Section 4.3.1 was performed and completed in the following two days for all cells. Consequently, the following 10 cycles followed, resulting in an interruption of cycling of less than 48 hours in total. This does not allow, in theory, the slow diffusive processes that enable the Li ions to nestle in the anode overhang, and the process is further complicated here as the interruption happens around a fully discharged state, where there should be no Li in the anode.

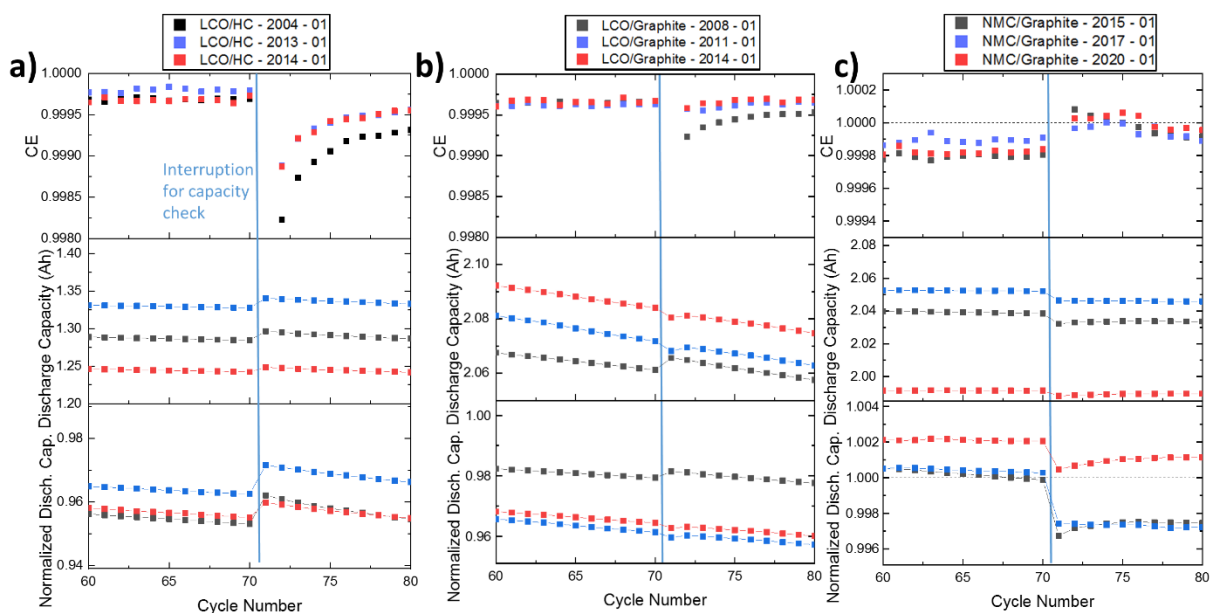


Figure 4-23. CE values, discharge capacity and normalised discharge capacity values of the last 10 cycles prior interruption for capacity check and the 10 cycles after it for a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite cells.

Furthermore, a second cell per batch for all cell types was used during this experiment, labelled “02” for each batch, which was cycled on the Novonix setup as well. These were cycled with the original objective to assess CE values starting above 1, observed particularly for the 2008 batch of LCO/Graphite, with the supposition that without an initial capacity check cycle, as it was previously done, exacerbated values above 1 could be observed, as it has been shown in other studies for more extreme storage conditions^{192,268}. Hence, they were cycled at C/5 as previously, only preceded by a C/10 discharge. Figure 4-24 shows the cycling of these cells compared with the first 10 cycles of the “01” cells of each batch assessed previously in this chapter. Only seven or eight cycles were performed as the cycling was interrupted due to an electrical shutdown in the lab.

The CE values for these newly cycled cells compared to the previous batches that included BoL, start at more significantly lower CE values for the first cycles. Said values are also quite consistent, with more spread present for NMC/Graphite cells, and the lowest being for LCO/HC cells, below 0.950 as opposed to approximately 0.974 for LCO/Graphite. CE values for cells “LCO/HC” do not reach the previously measured CE value in 7 and 8 cycles, characterised again by the slow CE increase shown previously. On the other hand, the plateau appears to be reached by

LCO/Graphite – 2008 – 02 after 3 cycles, while it is the case after 6 cycles for LCO/Graphite – 2011 – 02 and LCO/Graphite – 2014 – 02. This feature is consistently more rapid for NMC/Graphite cells, reaching the plateau after 3 to 5 cycles. When considering the normalised discharge capacity values, there is a creep above unity more pronounced for the newly cycled cells of “LCO/Graphite” and “NMC/Graphite”, while a more pronounced trend in fade for LCO/HC “02” cells is observed. This could however be accounted for by starting the normalisation at the 2nd cycle, to account for the extra cycle (or two for cells 03 and 04) undergone by the other cells.

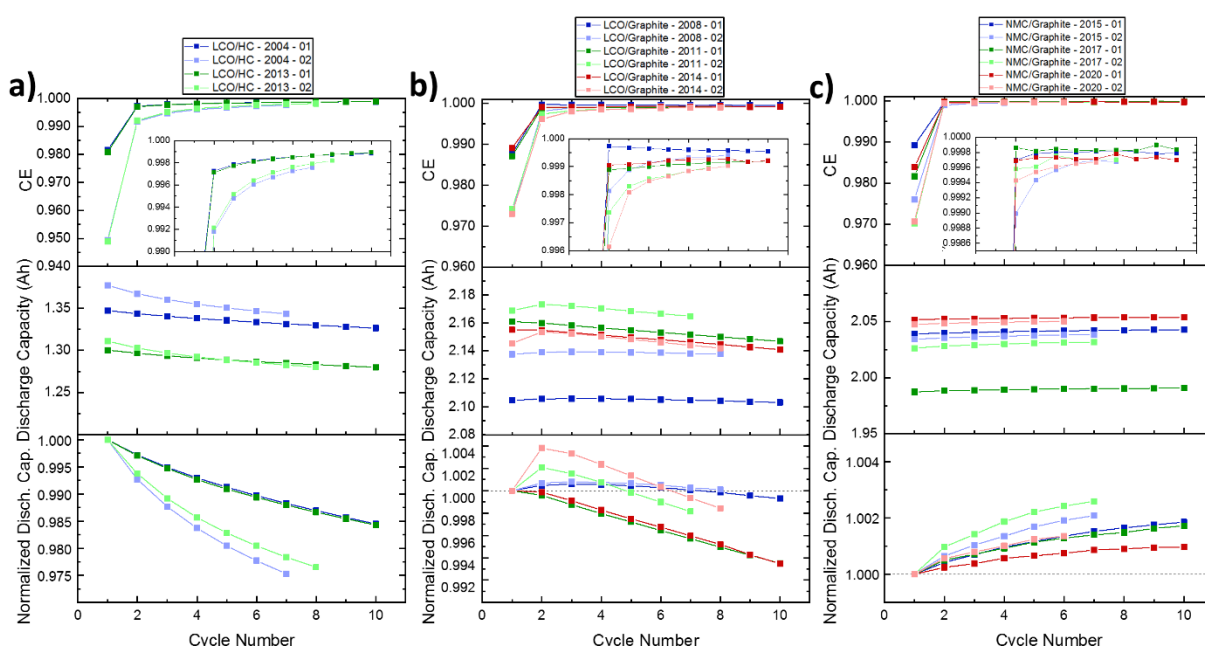


Figure 4-24. CE values, discharge capacity and normalised discharge capacity values for cells cycled directly without capacity check first compared with the first 10 cycles of the cells shown previously on the Novonix for a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite. Insets for CE are displayed to allow for an assessment of the differences shown particularly for the first cycle.

These additional investigations show how highly responsive and reactive CE is, and how it is heavily linked to the electrochemical history of the cell. The storage condition (SoC, temperature and duration) but also the cycling procedure itself have been shown to lead to significant variations, and as such, for comparative purposes, it is capital to keep consistent cycling procedures in order to properly assess it.

4.5 Conclusions

During this chapter, HPC cycling was carried out on three different cell types of various chemistries, each comprised of three individual batches. It was found that despite the challenges to accurately predict the minor differences in performance between batches, a good correlation was found between CE and long-term cycle life between cell types, validating our initial postulate. The lifetime data provided by the industrial collaborator was paramount in this study, effectively confirming the early cycling trend, with several thousands of cycles that were carried out on hundreds of cells, providing a comprehensive understanding of the whole lifetime of a wide array of batteries. This was identified previously as lacking in literature with HPC studies, often missing very long-term cycling, confirming the early-life trends identified. As such, this study supports the potential of HPC as highlighted in these previous publications, providing a framework for its application with a certain degree of confidence and advocating for its integration into existing forecasting models and prognosis tools.

Prior to cycling, X-ray CT and SEM/EDX were used on the cells, and it was evident that some cells showed signs of calendar ageing with investigations performed after cell opening. Evidence found on the separator of LCO/HC cells correlated with other post-mortem studies analogous to long storage or high-rate cycling effects. X-ray CT further emphasised the differences in design and electrode assembly between the cells, such as mandrel, tabs and electrode thickness, as well as the chronological evolution from batch to batch. Indeed, it was paramount to emphasise that the presented HPC procedure could be applied to a test matrix of cells varying in chemistry and with major design differences.

While ICA and capacity checks before and after the 70 cycles of HPC presented challenges in identifying elements indicative of long-term behaviour, EIS, voltage polarisation measurements and their normalised values proved crucial in this study, serving as additional proxies for longer-term exacerbation effects. For instance, EIS indicated higher R_{Ω} for the worst batch of LCO/HC, which could be linked to the dramatic power fade observed in its lifetime data. While rapid capacity fade was evident after 2,000 cycles, slower capacity checks showed higher recovery for that

batch, suggesting power fade was more prominent for this batch in particular, which could be attributed to the rollover fade mechanism.

In the end, CE measurements did correlate with long-term performance for the various cell types presented. For instance, NMC/Graphite cells, which demonstrated the least capacity fade, also consistently exhibited the highest CE during testing. Similarly, LCO/HC cells showed better capacity retention and higher CE compared to LCO/Graphite cells. The study found, however, that it was crucial to allow sufficient cycles to capture CE patterns and trends. Notably, LCO/HC's CE surpassed LCO/Graphite's only after 40 cycles, highlighting the importance of allowing CE to stabilise and fully capture differences that might arise after the few first cycles, which have been shown prominent for cells with HC as anode material. As such, the hypothesis, as announced previously, that “higher CE demonstrates a longer cycle-life”, is verified, at least for the presented cell models. It is however important to highlight that non-linear degradation behaviour, such as the dramatic rollover/power fade observed for one of the batches remained unpredictable by HPC in this chapter, probing caution, or the use of other diagnosis and prognosis tools. Despite this, the work in this chapter critically emphasises the link between SEI build-up and parasitic reactions measured by CE on the long-term performance of a battery, highlighting the importance of the measurements of “imperceptible processes and reactions” within Li-ion batteries, as suggested by Zhao et al.¹⁷⁸

It can be seen here, after the consideration of the multiple cycling conditions of various cells and various batches of each cell model, that CE is a highly sensitive parameter. Its pattern is not only linked to the storage conditions (duration of storage, temperature and SoC) but it is also linked to each cell model, here studied as different chemistries for cathode and anodes. On top of that, it has been shown that the resulting CE patterns are heavily dependent on the cycling protocol itself applied to each cell. While a plateau, for instance, for LCO/Graphite cells was reached relatively quickly, only after cycle two, after the BoL acquisition was done, this was not the case for a cell of the same batch cycled at the same C-rate but without a C/10 charge/discharge prior.

Finally, the experiments were conducted on two different cyclers in two different setups, which led to differences as well in the resulting data. While capacity values

between batches were closely matched between cyclers, differences arose for CE values. Although theoretical calculations of both setups' precision and accuracy were within the same order of magnitude, different trends were noted, particularly notable for NMC/Graphite cells. Indeed, while "NMC/Graphite"'s CE was highest and closest to unity, values recorded by the Digatron setup were consistently lower compared to the Novonix. However, key findings such as LCO/HC's CE eventually surpassing LCO/Graphite's, which then correlated with the lifetime data, were correctly identified by both setups. This provides a certain degree of confidence about this method, emphasising that major differences between cells, such as their chemistries and major design differences, and their expected lifetime, could be identified early by what could be considered "conventional" equipment. However, it has been shown that it is crucial to maintain consistency in test matrices, ensuring identical cycling conditions and temperatures for all cells. It can be concluded here that if one wants to build a database out of various cell models or batches, it is imperative to keep the exact same protocol for each cell, as well as identical storage conditions and cycling equipment.

5 Degradation effects of variable current protocols on commercial cells

5.1 Introduction

The performance and longevity of Li-ion batteries are dependent on their cycling protocols, which dictate how the cells are charged and discharged over time. In this study, the degradation mechanisms of three commercially available Li-ion battery cells — MH1, MJ1, and M50 — were investigated under varying cycling conditions. The cells were subjected to cycling protocols designed to explore the effects of varying the C-rate across three core SoC regions (0-20%, 20%-80% and 80%-100%) while maintaining consistent total charge delivery over the same time period. This approach ensured a fair comparison between the protocols, isolating the impact of different equivalent C-rates on cell performance and degradation. By systematically varying the C-rate in the low, middle, and high SoC regions, the study aimed to pinpoint the specific impact of each region to the overall degradation processes. These studies were conducted at equivalent C-rates of 0.5C and 0.7C, at 20°C, 0°C and ambient temperatures depending on the cells used for each batch

Key metrics such as capacity retention, impedance growth, but also other factors such as time spent at each stage, polarisation and overpotential shifts were closely monitored across the different cycling protocols. This detailed examination across multiple protocols and temperatures provides crucial insights into the degradation patterns of these cells, offering valuable information for potential optimisation of battery management systems. These findings are also put in perspective in a broader context by having a comparison to the most commonly used CCCV protocol and having a consistent discharge phase at selected C-rate 0.5C or 0.7C, without any variation in current. This allows for a clear decoupling of cause and effects by only varying charge, as well as leaving discharge “out of control” in a broader automotive sector context, which is up to the EV or portable electronic device use by the customer.

As such, a consistent application of a driving cycle could have been used instead of a standard CC discharge phase, but this goes beyond the scope of this thesis.

Moreover, the various current profiles and procedures were derived following the principles enunciated in section 3.2 and as such, the profiles and current patterns of each of the four variable current profiles are displayed in Figure 5-1. In a) a standard CCCV protocol is represented, followed by b) a VCP, where a higher current is applied in the middle SoC area, while lower current is applied at the beginning and end of charge. Furthermore, c) illustrated a protocol referred to as “LowEnd”, which starts with a higher current in the 0-20% SoC area followed by lower current, and then d) “LowStart” which, conversely, starts at lower current, and is then followed by a higher current prior to the CV phase.

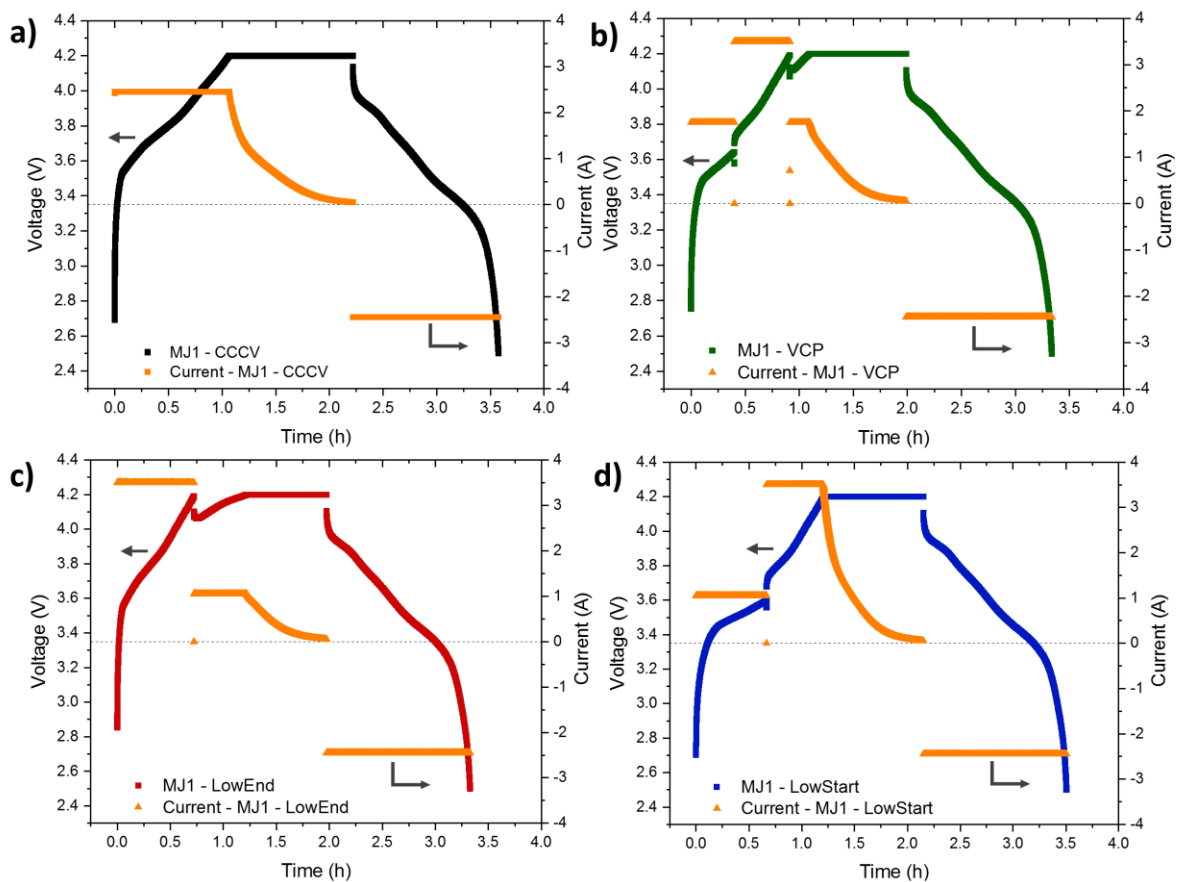


Figure 5-1. Cycling profiles with voltage and current applied for the first cycle for a) CCCV, b) VCP, c) LowEnd and d) LowStart, on an MJ1 cell as an example.

The goal is to illustrate the effect these various patterns have on capacity and power fade, and impedance (either via proxy or direct measurement with EIS), at various temperatures, with the variable current protocols cycle time matching the time for an equivalent CCCV protocol. Indeed, two main cycling studies will be performed in this chapter:

- 20°C and 0°C on 18650 MH1 and MJ1 cells, 0.7C equivalent
- Ambient temperature on 21700 M50 cells, 0.5C equivalent

These simple variations in charge current distributions lead to significant changes in capacity retention and performance, as it will be presented.

5.2 Experimental

Table 5-1 summarises the main characteristics as well as the cathode and anode materials as reported in several studies that used these cells. For instance, it was reported that the MH1 possesses an NMC 811 cathode²⁷⁵ and graphite anode with no SiO_x additive, as explicitly specified by Jnawali et al.²⁷⁶ For the MJ1 cell model, Sturm et al.²²⁵, Heenan et al.⁸³ and Li et al.⁷⁸ all report the cathode material to be NMC 811 with the anode material being graphite containing SiO_x with various measurements provided by X-Ray CT (giving SiO_x 2-3 vol%) and EDX (SiO_x 4.64% by weight of all anode materials including non-active O, F and Cu). Furthermore, in a recent paper, Chen et al.²⁷⁷ experimented on M50 cells and reported in details the composition of active materials using ICP-OES where the cathode consisted of doped Li_xNi_{1-y-z}Mn_yCo_zO₂ with an approximate atomic ratio of Ni: Mn: Co: Al = 82.9: 5.1: 10.6: 1.4, while the anode was comprised of 90% graphite and 10% SiO_x (by weight). Finally, the rated capacity (nominal capacity) is given by the specification sheet provided by the manufacturer.

Table 5-1. Summary of the cell models used with dimensions, rated capacity and electrode chemistry information.

Cell	Dimensions	Rated Capacity (Ah)	Cathode material	Anode material
LG MH1	18650	3.2	NMC 811	Graphite
LG MJ1	18650	3.5	NMC 811	Graphite/SiO _x
LG M50	21700	5.0	~ NMC 811 (Ni: Mn: Co: Al = 82.9: 5.1: 10.6: 1.4. (Atomic ratio))	Graphite/SiO _x (C : SiO _x = 90 : 10 (by weight))

Furthermore, Table 5-2 summarises some of the main components of the cycling performed on the aforementioned cells. MH1s and MJ1s were cycled at 20°C and 0°C for 400 cycles or until failure (which will be relevant for cycling at 0°C) at 0.7C equivalent (0.7C defined at CCCV, and equivalent C-rate for the VCP cells). On the other hand, M50s were cycled using duplicates for all single protocols for around 500-700 cycles, at ambient temperature (climate control lab environment). For all cells, the CV phase end conditions are the same, as specified by the manufacturer: 50 mA cut-off current. An additional condition was added: a 2h maximum time, to somewhat limit the time spent during CV for cells cycled at 0°C as it will be illustrated in this chapter. Additionally, capacity checks were performed at C/20 with the same CV phase conditions, at beginning and end of cycling for either MH1s and MJ1s, or periodically (50, 100 and around 300 cycles) for M50s, accompanied by EIS diagnostics collected at 100%, 95%, 75%, 50%, 5% and 0% SoC during discharge. SoC points were reached using C/10 followed by 2h of rest. Voltage limits were considered as well as secondary conditions to collect EIS data due to subsequent capacity fade and as such, a shift in voltages at which the defined SoC points were defined, but these were not triggered as the fade was not as significant (one cell reached the 80% SoH limit after >650 cycles). The cycling C-rates were chosen as to respect the maximum recommended currents set by manufacturers during charge, accommodating for all steps of the variable current profiles (1C for MH1 and MJ1, 0.7C for M50), and as

such, MH1 and MJ1 cells were cycled at 0.7C equivalent, while M50s were cycled at 0.5C equivalent.

Table 5-2. Summary of some of the main cycling conditions and parameters used.

Cell	Cycling	Temperature of cycling	EIS	CV phase end conditions
LG MH1	0.7C equivalent 400 cycles or until failure	20°C and 0°C	-	50 mA cut-off current or 2h
LG MJ1	0.7C equivalent 400 cycles or until failure	20°C and 0°C	-	50 mA cut-off current or 2h
LG M50	0.5C equivalent Various (most cells 500-650 cycles)	Ambient temperature	100%, 95%, 75%, 50%, 5% and 0% SoC (Discharge)	50 mA cut-off current or 2h

5.3 Baseline fresh cells evaluation

An initial capacity check of all cells as received (considered as “fresh”, as opposed to “pristine”, as the cells undergo formation cycling procedures prior to their sale) allows for some initial assessment of differences between the cells, shown in Figure 5-2. While the different voltage curves over capacity are presented in a), ICA presented in b) shows noticeable similarities between all three cell models, including all four main peaks of well-documented NMC811/Graphite systems^{108,278}, as well as a minor peak identified between the first and second main peaks at around roughly 3.55V. DVA presented in c) and d), however, reveals a core difference between M50/MJ1 cells and the MH1, which are the two notable SiO_x peaks occurring below 20% SoC in d) dVd(SoC) plot. This is in agreement with the literature on DVA performed on cells with graphite and known SiO_x additives. This, however, evidences that SiO_x signature peaks are only detectable in DVA, as opposed to ICA, for the present full-cell configuration. This can be caused by the fact that these particles show

large potential hysteresis during lithiation and delithiation, together with less pronounced plateaus^{23,279}, while ICA primarily shows capacity changes as a function of voltage rather than the nuanced shifts in electrode potential that DVA allows to visualise with regard to changes in capacity. Furthermore, the volume expansion of silicon particles during lithiation can cause mechanical stress and changes in the electrode structure which can then affect the local electrode potential²⁸⁰, which again is better encapsulated by DVA.

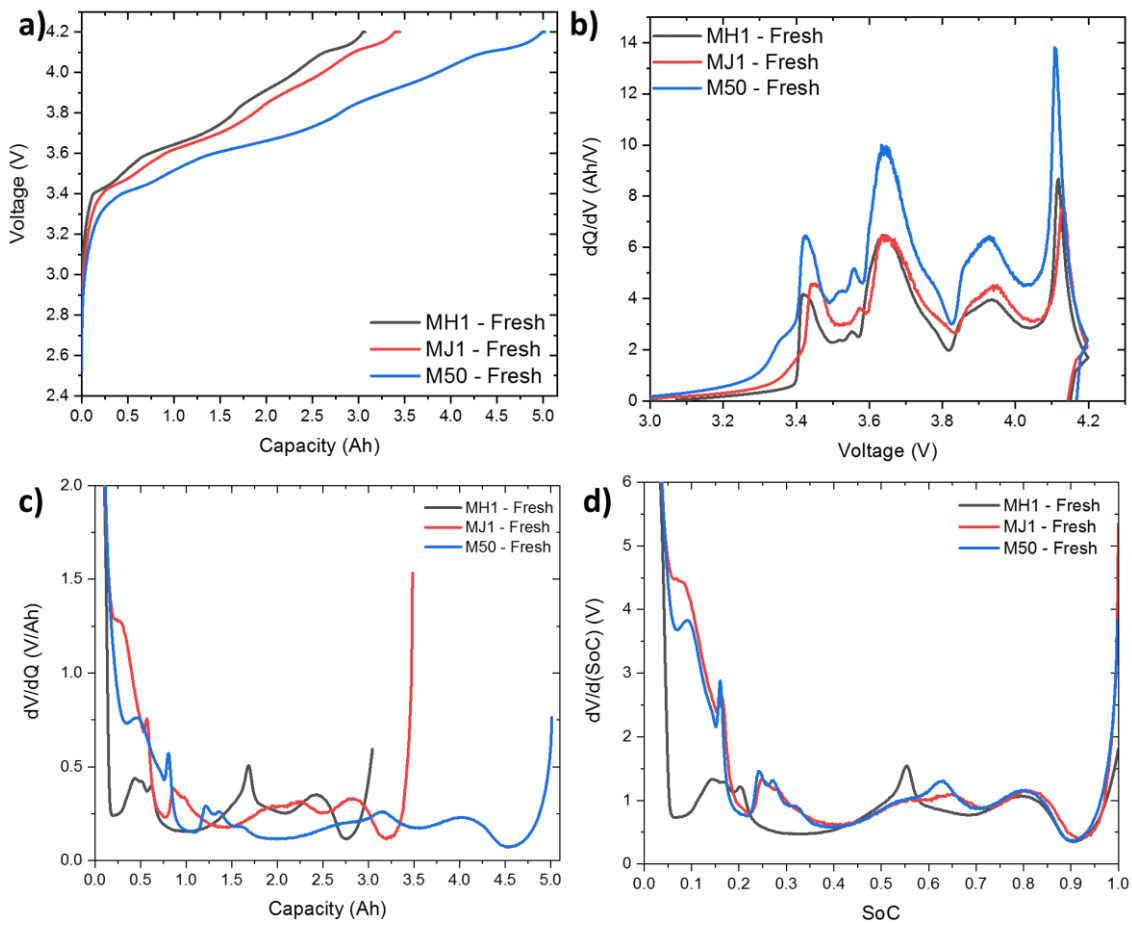


Figure 5-2. a) Voltage vs capacity curves, b) incremental capacity analysis, c) dVdQ and d) dVd(SoC) plots of fresh MH1, MJ1 and M50 cells.

Distances between particular peaks (referred to as “Q”, measured in Ah) were chosen to track capacity storage capabilities related to characteristic features of each individual electrodes and their relative changes, as it has been carried out by several studies^{23,140,281}. The peaks and Q representation taken for each cell type throughout this chapter are displayed in Figure 5-3. These intervals are supported by literature,

originating from three-electrode setups to find each individual electrode's contribution, and were used as references for the DVA shown later in this chapter. Below is a more detailed explanation of what each "Q" means, explained for the M50 cell.

The peaks observed between 0% and 15% SoC can be attributed to the lithiation of silicon, as supported by existing literature by multiple studies^{141,282–284}, confirming that the silicon component of the SiO_x/Graphite composite anodes undergoes lithiation during the early stages of charging, tracked as Q2 and Q3. Additionally, the total capacity of the cell is denoted as Q_{cell}, while Q1 represents the distance between 0% SoC and the central graphite peak, occurring at around 3.3 Ah. This central graphite peak marks the transition from the medium to the low voltage plateau in the anode potential, which happens when the graphite anode reaches 50% lithiation¹³², as will be further explained. Q5 represents the distance between the central graphite peak and 100% SoC, where a change in Q5, without corresponding changes in the anode capacity (Q1) and the cathode capacity (Q6), suggests a shift in electrode balancing or a loss of cyclable lithium inventory, thus altering the operating window of the electrodes^{285,286}. A second NMC811 cathode signature is present on the immediate left of the 50% lithiation graphite peak but this feature will not be tracked as no distinguishable and identifiable peak is available.

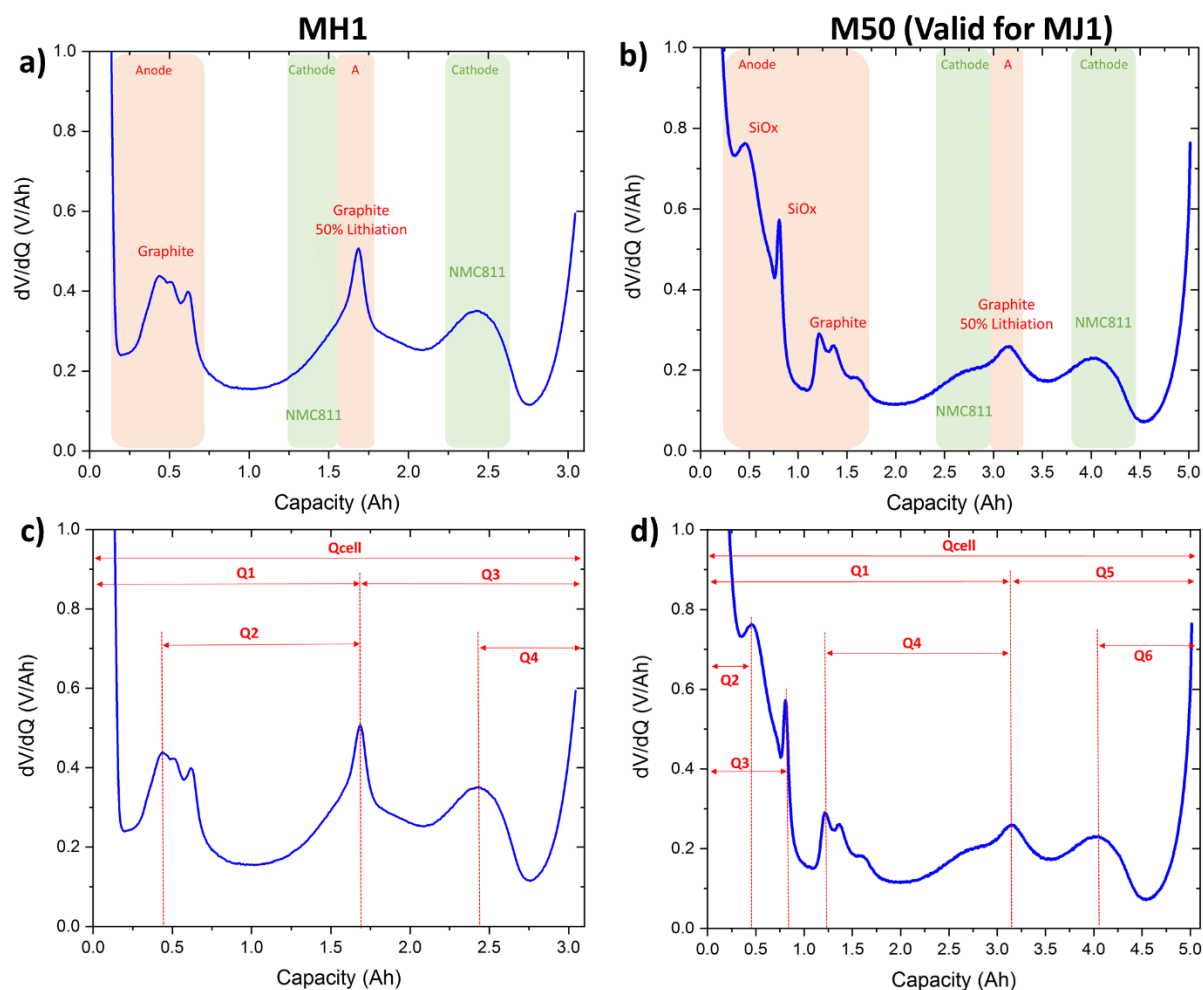


Figure 5-3. a) and b) DVA plot with explanation of relevant peaks for MH1 and M50 cells respectively. c) and d) key distances between relevant peaks, referred to as “Q” that will be tracked throughout this chapter. The data in a) & c) and b) & d) is identical but replicated for clarity of labelling.

Furthermore, IR values throughout the whole SoC of these cells were obtained via hybrid pulse power test (HPPC) and displayed in Figure 5-4. These pulses of C/10 applied for 30min each was followed by 1h rest periods, throughout the whole SoC window leading to 20 IR data points for each cell. Each data point was calculated using Ohm’s Law, using the voltage drop from the moment the current of the pulse was finished, until the end of the relaxation period of 1h. This approach effectively captures multiple resistive components within the battery system, as described in the literature previously introduced. Specifically, the immediate voltage drop upon cessation of the current pulse represents the purely ohmic component, while the subsequent voltage relaxation over seconds to minutes reflects the charge transfer resistance at the electrode-electrolyte interfaces²⁸⁷. Lastly, the extended relaxation over the 1-hour rest

period allows for the capture of polarisation and diffusion-related processes associated with lithium-ion migration within the solid and liquid phases²⁸⁸, as such the IR values presented here give a complete overview of these processes at defined SoC data points.

However, due to limit voltages of 4.2 V during charge and 2.5 V during discharge, the latest data points (100% SoC during charge and 0% SOC during discharge) are not displayed as the duration of these last pulses was not 30min. This figure reveals analogous IR values for the three cell models, following an overall u-shape during charge with a higher IR value at 0% SoC, as well as an IR increase measured at 50% SoC. This was consistently observed for commercial cells with graphite anodes throughout this thesis (and not for cells “LCO/HC”) in the previous chapter, with HC anode for instance) and therefore it is hypothesised that it is to do with the 50% lithiation graphite phase change. During discharge, a noticeable higher value is detected at around 70% SoC (30% DoD) while the largest values are detected at 5% SoC (95% DoD). These IR values above 1 Ω (not displayed in the figure), are six times larger than the 0%SoC data point during charge of the MH1 cell for example, due to the electrodes acting in blocking conditions, at these low SoCs²⁸⁹.

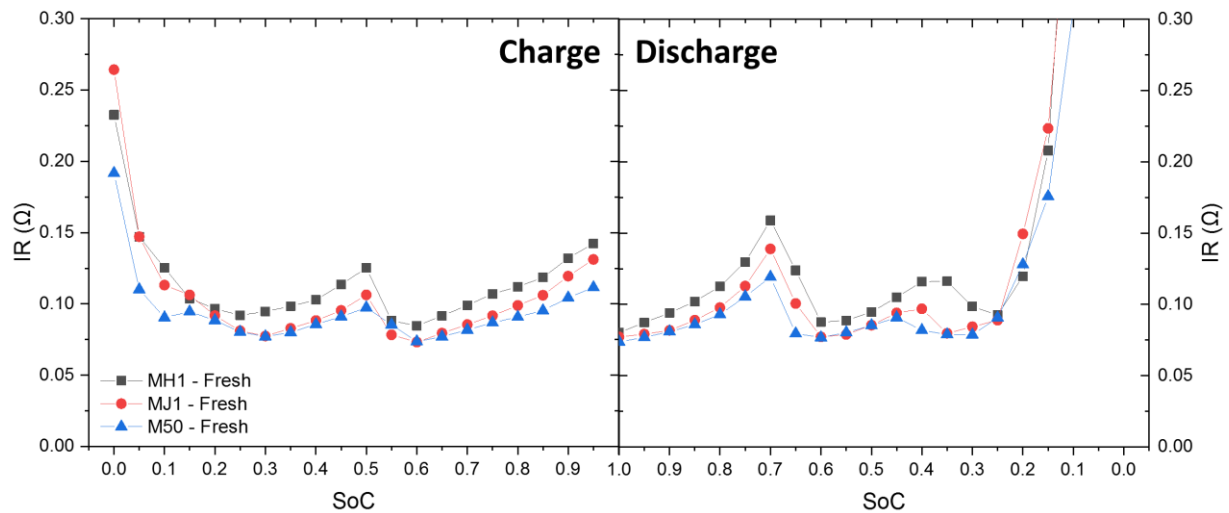


Figure 5-4. IR values across the battery SoC through full charge followed by discharge obtained by HPPC, measured at 20°C.

Therefore, these preliminary results show analogous IR values for all cells as well as phase transitions information for both cathode and anode materials provided

by their respective dQ/dV plots, but noticeable differences provided by DVA, notably the presence of the two SiO_x peaks for both M50 and MJ1 cells.

5.4 MH1 and MJ1 studies at 0.7C with temperatures of 20°C and 0°C

5.4.1 20°C cycling

The measured discharge capacity, normalised discharge capacity, CC (referred to as “CC” from either the CCCV cell or the sum of the various CC steps of the variable current profile cells) and CV capacity per charge, and its time contribution in percentage per charge per cycle are displayed in Figure 5-5. The main discharge capacity fade data reveals widely different performances of the various cycling protocols used. The protocol that leads to the worst fade for both cell models is the “LowStart” protocol; with a dramatic fade for the MH1 reaching almost 20% SoH and around 55% for the MJ1 variant after 400 cycles. Conversely the “LowEnd” MJ1 cell proposes the best capacity retention at around 80% for the MJ1s. For the MH1, the CCCV proposes the best capacity retention, but stands below the VCP variant for the MJ1. It is important to note that the cycling of the VCP MH1 and CCCV MJ1 cells were interrupted due to a channel failure (and not a cell failure), and as such, did not reach 400 cycles. Moreover, the distribution of capacity passed during charge either as CC or CV shown in e) and f) reveals that the LowEnd cell is the one that has the least contribution of CV phase overall (capacity and % of time of charge), maximising the capacity obtained from its CC phase. In essence, this means that the cell is closest to its thermodynamic SoC (or has lower overpotential) at the upper cut off voltage, meaning that a greater proportion of the charging of the cell is delivered at the higher (and constant) current than during the voltage hold, which would be beneficial for practical vehicle charging, for example. This is then followed by VCP, CCCV and LowStart cells in that order. The overall trend for all cells is that as cycling occurs, the contribution from CC phase reduces, and as such, CV phase increases, creating an overlap for instance, for both LowStart cells at around 250 cycles and 330 cycles for MH1 and MJ1 respectively. This is indicative of resistance increases causing greater

overpotential during ageing. By close to the end of cycling, MH1 LowStart spent around 90% of time of charge in CV, contributing to more than 80% of charge capacity.

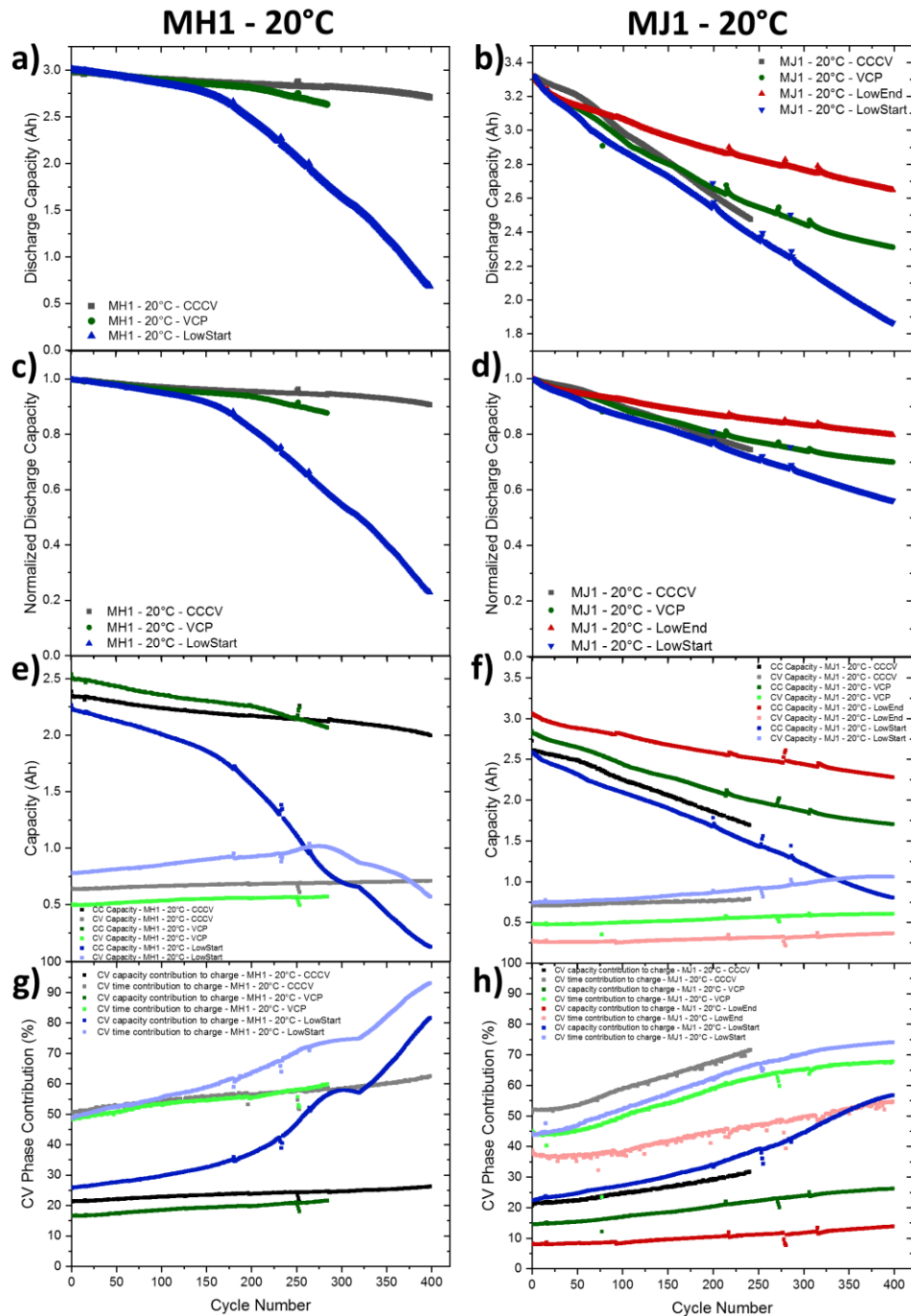


Figure 5-5. a) and b) Measured discharge capacity, c) and d) normalised discharge capacity, e) and f) measured CC and CV capacity per charge per cycle and g) and h) CV capacity and time contribution in percentage per charge per cycle for MH1 and MJ1 respectively at 20°C

Various time components are then displayed in Figure 5-6, such as cycle, charge and discharge time per cycle number, as well as time spent in CC and CV during charge for each cell. This reveals that only the LowStart cell reached the CV phase 2h time limit trigger (showed in c) and d)), before dropping again below said limit after 362 cycles, matching a collapse of all time metrics (total cycle, charge and discharge). This already evidences a significant increase in cell impedance, creating overpotentials and as such reducing the voltage window and triggering the CV phase earlier and for longer²⁹⁰. This also exacerbates the time the cell spends at high voltage (4.2 V here). Additionally, as evidenced for the MH1 cells, CC and CV times are similar at BoL for all cells (comprised between roughly 1h and 1h12min) followed by their divergence. Moreover, the cycle time for MJ1 decreases slightly for the first 150 cycles, before increasing again due to a slight drop in charge time, as opposed to the MH1 cells time that constantly rises. Conversely, the discharge time constantly drops, likely due to the overall increased aforementioned impedance.

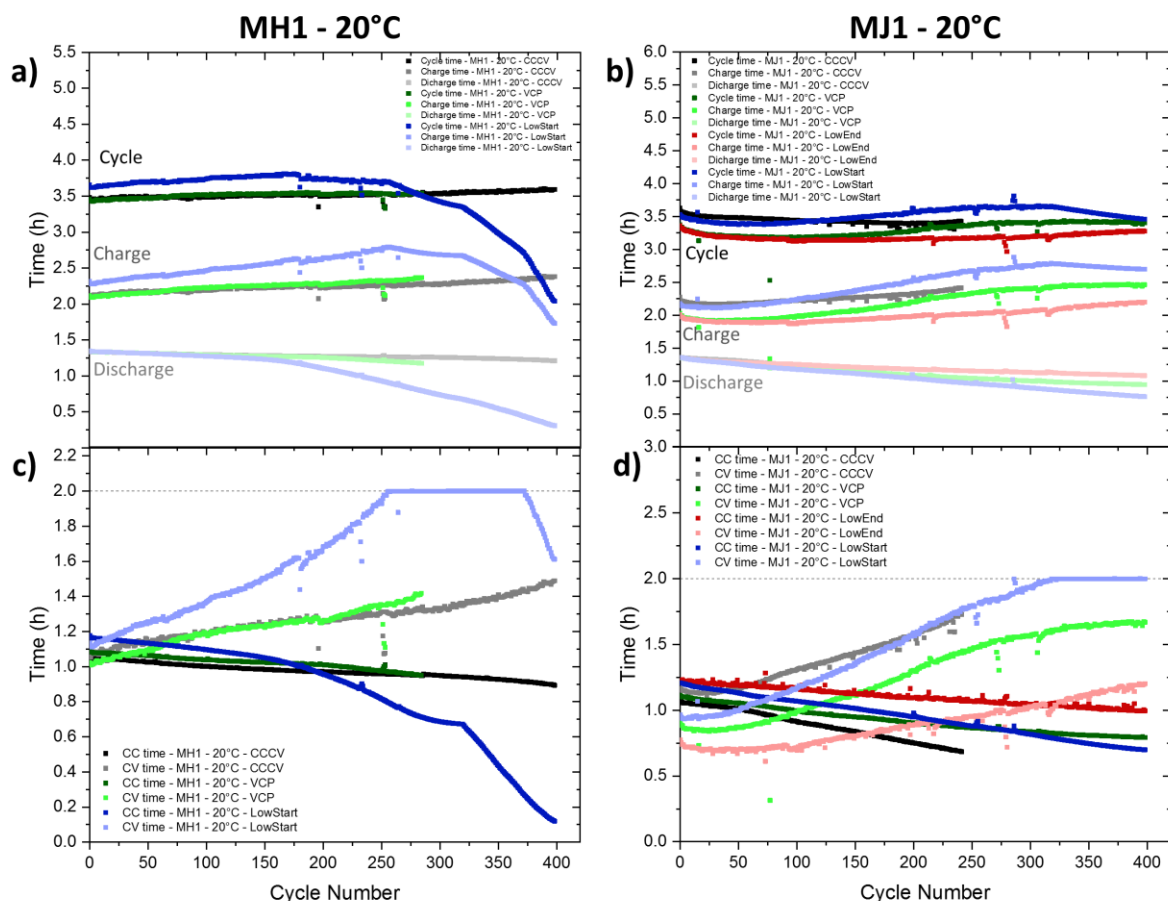


Figure 5-6. a) and b) Total cycle, charge and discharge times per cycle number, and c) and d) time spent in CC and CV during charge per cycle for MH1 and MJ1 cells respectively.

Furthermore, as displayed in Figure 5-7, the overpotentials in both charge and discharge directions were tracked. That is the first recorded data point when current is effectively applied to the cell, after the end of the previous step. It is directly related to the current applied (per Ohm's law) and as such is identical for all cells in discharge at BoL but not charge, as the C-rate applied for each cells is different. For example, LowStart initially displays the lowest overpotential as the C-rate applied is the lowest of all cells (0.3C vs 1C for LowEnd for example). Directly relating these overpotentials to a known resistance value via Ohm's law is not possible due to the contribution of activation and polarisation components during sustained cycling^{288,291}, but are nonetheless a good proxy of increased impedance at either 0% and 100% SoC, and particularly the purely ohmic component, R_{Ω} ²⁹². As such, the MH1 LowStart cells presents a steep increase of charge overpotentials at roughly 300 cycles, and a gradual decrease in discharge overpotentials starting around 200 cycles. This trend is

also followed by its MJ1 variant, although less pronounced. This evidences further the increase in impedance previously mentioned.

Additionally, the polarisation ΔV per cycle is studied, with a distinction between the conventionally calculated polarisation (average voltages of full charge, including CV phase, and average discharge voltage, integrated over capacity) and the ΔV discarding the CV phase (only CC during charge integrated). Different ΔV values are shown for each cell, directly linked to the protocol used, but as displayed in g) and h), a dramatic increase in the normalised ΔV is present for both LowStart cells (more than three times and twice for ΔV disregarding CV for MH1 and MH1 respectively). The tracking of the normalised polarisation values presents good correlation with the capacity fade observed previously. This shows the increase of voltage hysteresis of the various cells depending on their protocols, a multifaceted indicator of underlying degradation processes such as increased impedance and LAM^{293,294}. The MH1 LowStart cells present a gradual decrease in the average discharge voltage, and a rapid increase of the average charge voltage, following the trend indicated by the overpotentials in a), and as such, a rapid increase in impedance particularly in the fully discharge state.

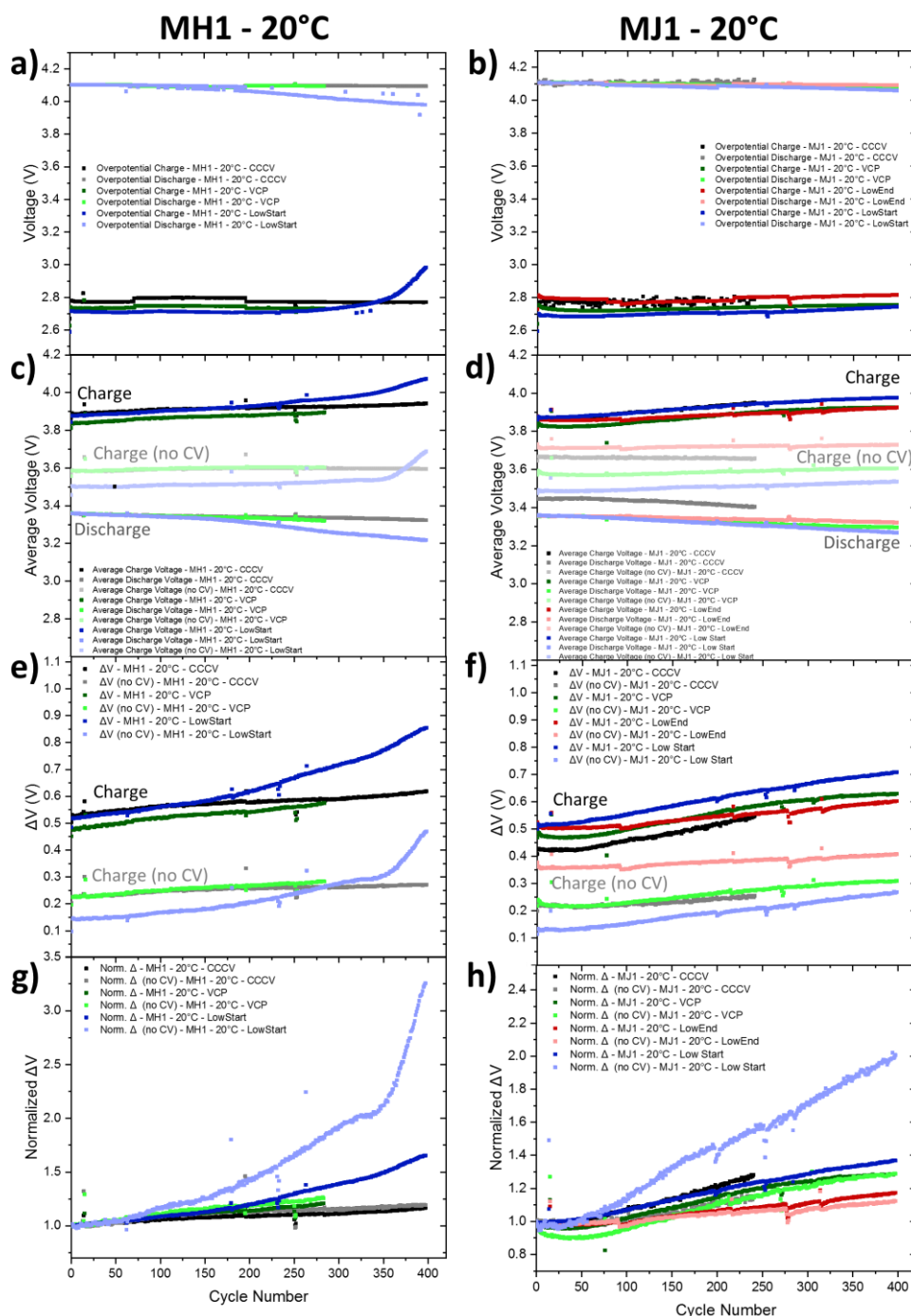


Figure 5-7. a) and b) Measured overpotentials during charge and discharge, c) and d) average voltages per cycle (charge, charge without CV and discharge), e) and f) polarisation (ΔV) considering CC and CV for charge compared to charge without CV, and g) and h) normalised polarisation.

Lastly, CE for each cycles of all cells are displayed in Figure 5-8. CE shows good correlation between the fade behaviour observed as well, with the LowEnd cell displaying the highest, followed by VCP, CCCV and LowStart as shown in the inset of b). MH1 LowStart shows the most dramatic drop in CE (below 0.98 per cycle close to

end of cycling, a direct loss of 20 mA calculated for said cycle due to coulombic inefficiency), and as it has been discussed previously, is directly linked to Li plating, parasitic reactions and SEI growth, which can be both reversible and irreversible.^{200,295,296} All these components have been found to consistently happen at higher voltages²⁹⁷, and the LowStart protocol has shown to maximise the time spent at these high voltages as opposed to other cells, as the high C-rate right before the CV ensures a longer current decay during the CV phase. This can then lead to a subsequent increase in impedance (particularly visible at 0% SoC) as the metallic plated Li blocks active graphite sites and the SEI growth increases R_{ct} ^{298,299}.

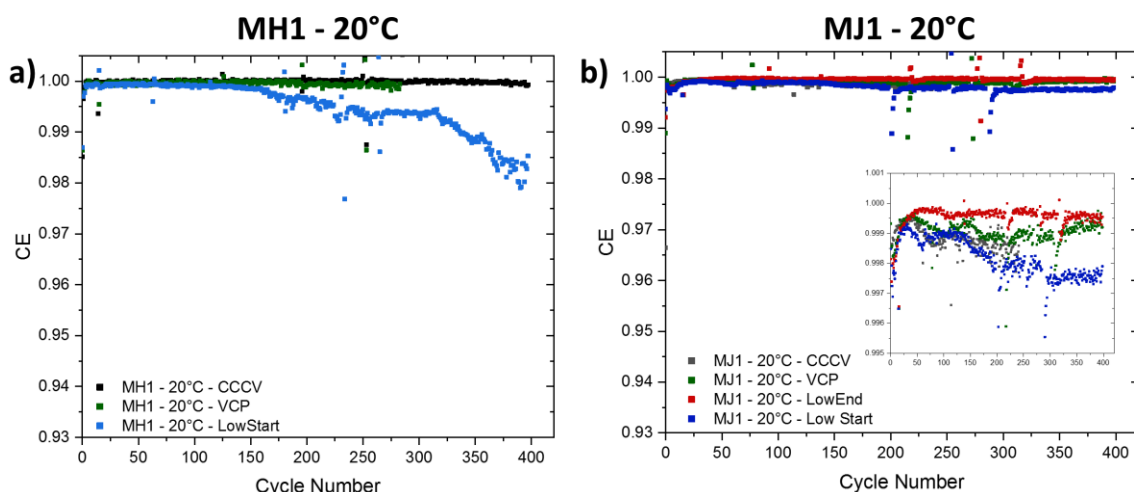


Figure 5-8. Coulombic efficiency per cycle of a) MH1 and b) MJ1 cells. An inset is displayed in b) while allowing a comparison between both cells types.

Overall LowStart presents the worst performance by a significant margin, while LowEnd presents the best capacity retention. Distinction between VCP and CCCV are not yet conclusive, and will be studied further at 0°C. It would appear here that the time spent at higher voltages (which happens to be the longest for the LowStart protocol) is a key component for increased power fade and impedance increase, as evidenced particularly by overpotentials, polarisation and CE.

5.4.2 0°C cycling

For this section, the same metrics and parameters considered previously during the 20°C study are presented for the cycling performed at 0°C. As shown in Figure 5-9, a clearer trend appears for the performance of all protocols: LowEnd provides the best capacity retention, followed by the VCP cells, CCCV and lastly LowStart, for both MH1 and MJ1 cells. It is important to note that the cycling was interrupted due to cell failure for all cells except MJ1 LowEnd, which reached the 400 cycles limit with around 40% SoH, and the MJ1 CCCV, which was cycled for 50 cycles due to channel availability, and follows the fade (and other metrics) set by the MJ1 LowStart cell, with significant overlap. As will be exposed further in this chapter, the “failure” notion of the cells needs to be redefined, as the cells successfully all underwent a diagnostic cycle following the interruption of the present cycling. Indeed, a slower C-rate allowed for cycling while the 0.7C applied immediately triggered the CV phase and a loop to discharge on the cycler due to drastic overpotentials present. As such, it is clear here that a dramatic power fade has occurred with low temperature cycling, with the cell inability to sustain 0.7C anymore, while still having a significant amount of capacity. Figure 8-3 in the Appendix shows the DVA of said diagnostics cycles, which reveal a discharge capacity between 1.9 and 2.1 Ah, and 2.1 and 2.5 Ah for MH1 and MJ1 cells respectively.

It is important to note that the MJ1 cells present a significantly better capacity retention than the MH1 cells at this temperature, where the MH1 LowEnd cell reached 179 cycles before power failure, as opposed to the 400 reached by the MJ1 variant. A definitive answer on why this is the case is challenging, as the only known difference is the presence of SiO_x in the anode for the MJ1. Despite the fact that it contains SiO_x (which might be thought of as a source of degradation, side reactions and impedance increases) the MJ1 has better performance. It should be noted that this is a more modern cell and came after the release of the MH1, so improvements made by the manufacturers could have been applied to the design of this newer cell. Such improvements can be electrode material manufacturing, calendaring processes or choice of electrolyte additives, which can have a significant impact on cycling performance, particularly at low temperatures, as shown in several studies such as the use of butyl acrylate in combination with LiBF₄³⁰⁰, or the addition of 1-ethyl-3-

methylimidazolium tetrafluoroborate³⁰¹. Furthermore, despite showing better capacity retention, the VCP cells fail relatively soon after the LowStart cells (1 cycle and 42 cycles after for MH1 and MJ1 cells respectively). This could indicate the prevalence of the power fade component over the energy retention aspect of the present observed degradation. Figure 5-9 g) and h) show that since the BoL, all the cells spend around 60% of their time in CV phase during charge due to reduced kinetics¹⁴⁶ and increased impedance³⁰² at low temperatures, followed by a rapid increase in time and capacity provided by the CV phase, particularly pronounced for the Low Start cells. e) and f) further shows that all MH1 cells undergo a power failure after the overlap in CV capacity contributing more than CC during charge occurs; indeed, the MH1 LowEnd failure occurs a couple of cycles after said overlap as well. Conversely, the overlap does not occur for the MJ1 VCP cell despite subsequent power failure, and for the LowEnd cell, which did not fail.

Additionally, a peak appears for all LowStart cells for the capacity contributed to charge metrics: the capacity provided by the CV phase (in e) and f)) increases initially until roughly 45-50 cycles for both MH1 and MJ1 cells, before decreasing until subsequent power failure. This then leads to a “shoulder-like” feature shown in g) and h). Said features are also observable for MH1 LowStart when cycled at 20°C, shown in Figure 5-5.

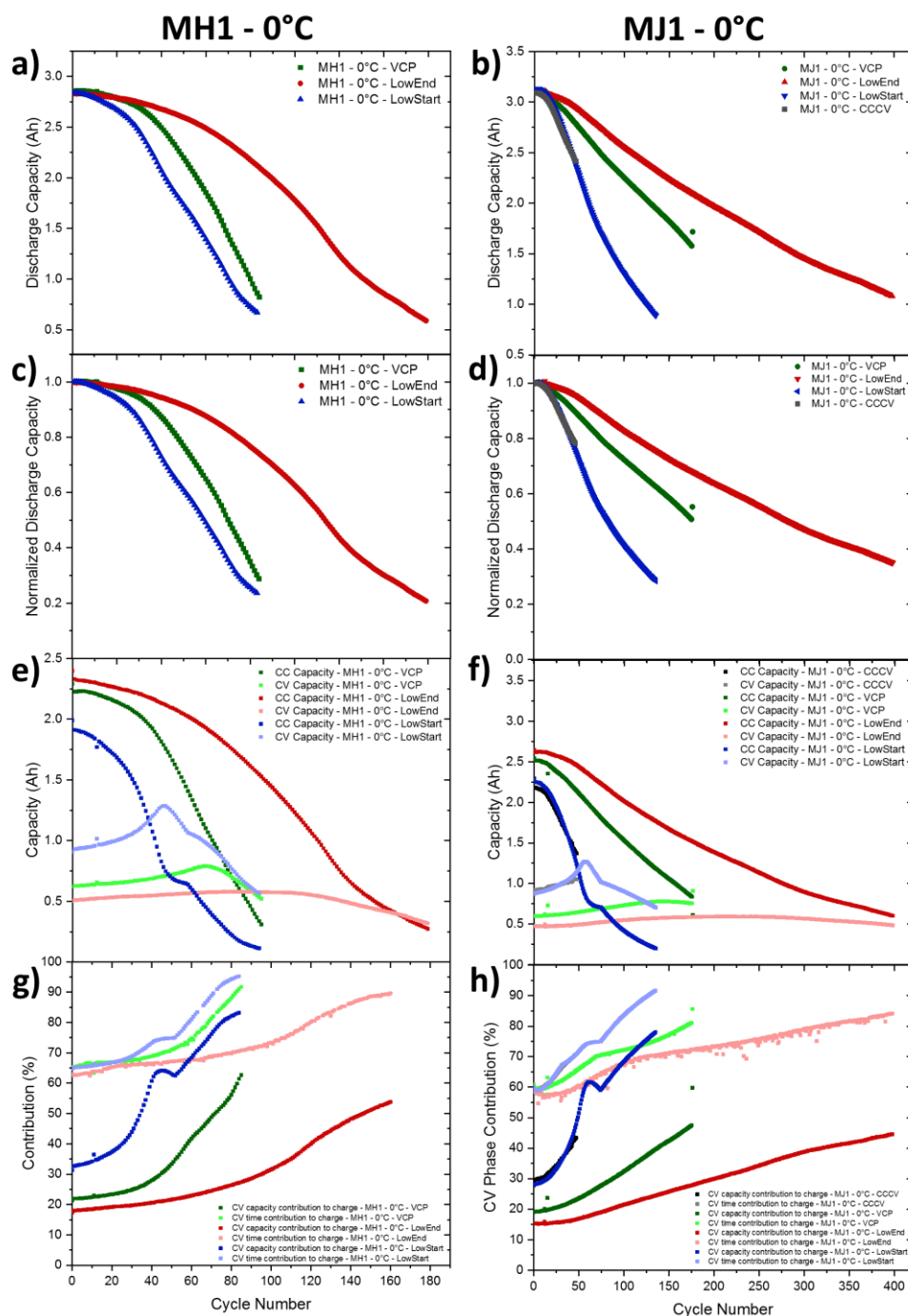


Figure 5-9. a) and b) Measured discharge capacity, c) and d) normalised discharge capacity, e) and f) measured CC and CV capacity per charge per cycle and g) and h) CV capacity and time contribution in percentage per charge per cycle for MH1 and MJ1 respectively at 0°C

The time components displayed in Figure 5-10 indicate that the 2h time trigger limit for the CV phase is reached quite early (after 2, 6 and 23 cycles for MH1 LowStart, VCP and LowEnd respectively), and slightly delayed depending on the protocol for MJ1 cells, with again LowEnd delaying this trigger point the most. Additionally, all cells

present an initial increase in total cycle time due to an increase in charge time, where it is particularly visible for the MJ1 cells. The cycle number where this pattern reversal occurs corresponds to the cycle number where the 2h time limit in CV is reached, as time for the CV remains constant (2h) while the time spent in CC consistently drops for each cycle as impedance builds up.

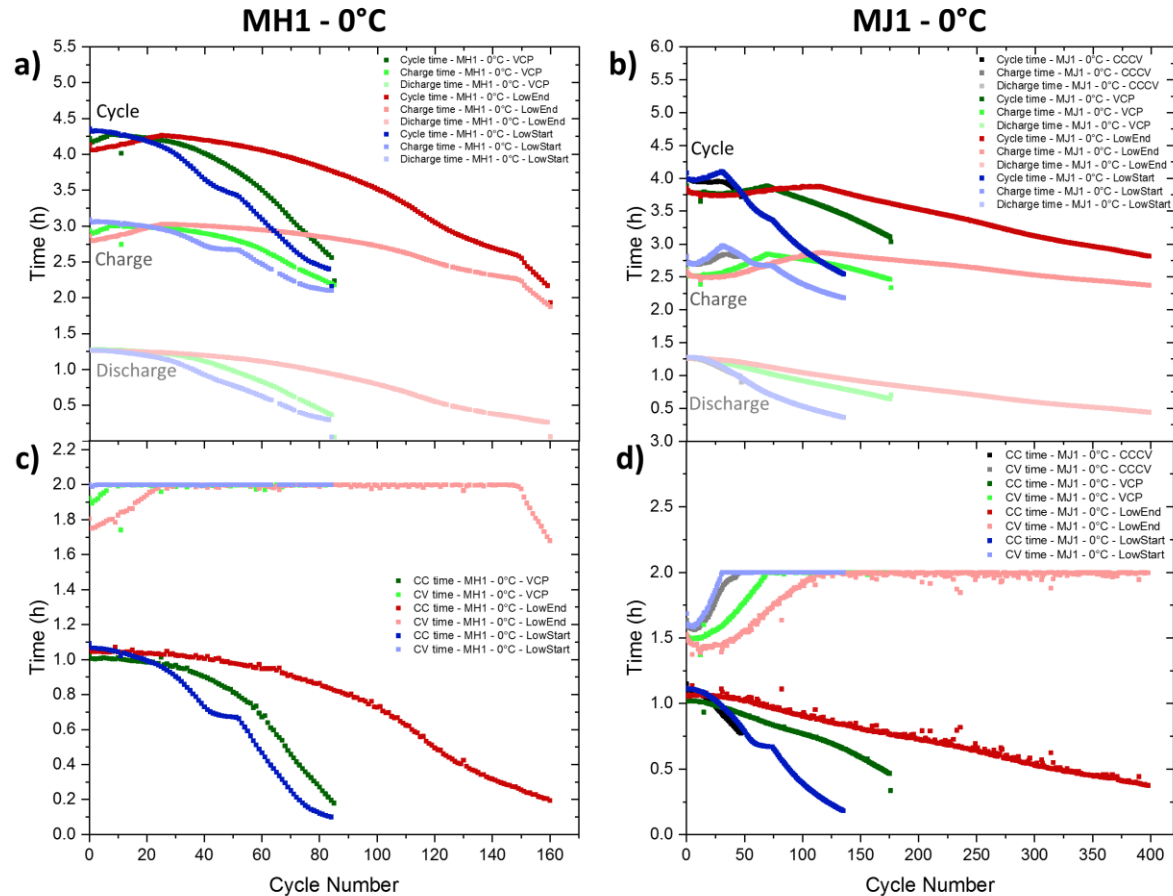


Figure 5-10. a) and b) Total cycle, charge and discharge times per cycle number, and c) and d) time spent in CC and CV during charge per cycle for MH1 and MJ1 cells respectively.

This is confirmed by the assessment of the overpotentials observed in Figure 5-11 a) and b) where dramatic increases are visible for the MH1 cells of the charge overpotentials prior to power failure, as well as a gradual overpotential decrease in discharge. Although less dramatic, these observations stand as well for the MJ1 cells, while still prominent for both charge and discharge for the LowStart variant. These rapid increases in overpotentials are supported by a rapid increase in average charge and discharge voltages, and as such subsequent parabolic increase of ΔV right before

the onset of power failure. This, however, is not as quite clearly observed for the MJ1 VCP cell which, despite failure, does not present the radical increase in overpotential and polarisation values, and presents patterns more analogous to its LowEnd variant which did not fail after 400 cycles. These observations show a rapid impedance increase in the two SoC points with the highest measured initial impedance (100% SoC but more importantly 0% SoC, as shown in Figure 5-4) which lead to exacerbated power fade, on the onset of failure.

At low temperatures, the SEI layer on the graphite anode tends to grow more thick and inhomogeneous due to reduced Li-ion mobility and increased charge transfer resistance^{303–305}. Over many cycles, the SEI layer becomes increasingly resistive, contributing to the high overpotentials observed at 0% SoC. Furthermore, during cycling, the SEI layer can crack due to the mechanical stresses induced by volume changes in the graphite. This cracking can expose fresh graphite to the electrolyte, leading to additional SEI formation and lithium consumption³⁰⁶, further increasing the IR and causing the parabolic rise in polarisation. This mechanism aligns with the significant power fade observed as the cell's ability to handle high current deteriorates .

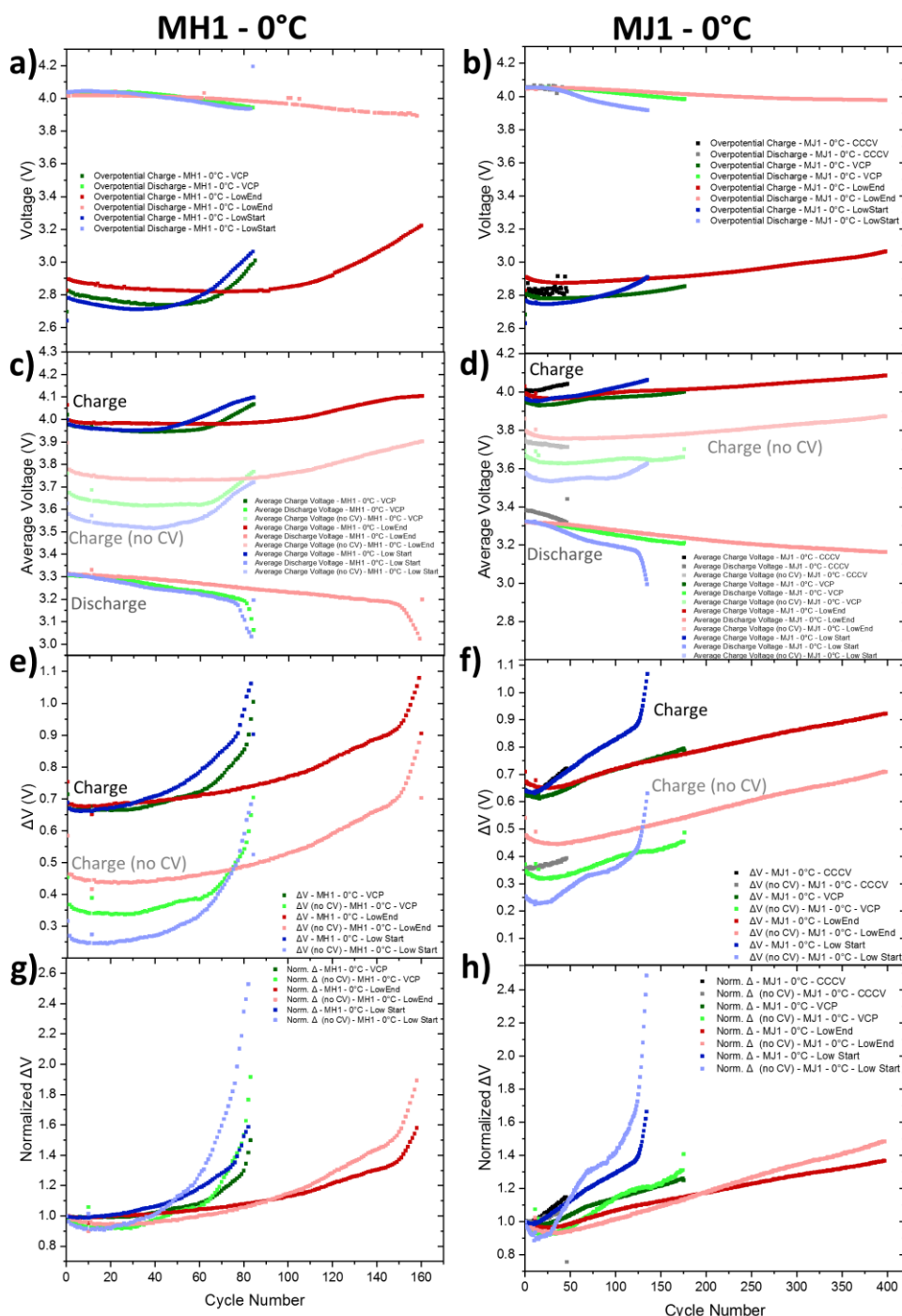


Figure 5-11. a) and b) Measured overpotentials during charge and discharge, c) and d) average voltages per cycle (charge, charge without CV and discharge), e) and f) polarisation considering CC and CV for charge compared to charge without CV, and g) and h) normalised polarisation.

This is further explained by that Li consumption by parasitic reactions, as shown by the CE displayed in Figure 5-12. The measured CE for MH1 cells is very low (reaching below 0.95 per cycle for LowStart and VCP cells) proxy for significant SEI

growth and plating, although further characterisation would be necessary to differentiate between the two. Comparatively however, the measured CE for MJ1 cells is higher (never reaching below 0.983 for all cells). This notable difference between the two cells could potentially be explained by additives in the electrolyte, as shown in several studies, with minor additions of additives (such as VC and VEC) lowering the rate electrolyte of oxidation led to higher CE and less Li plating^{199,307}.

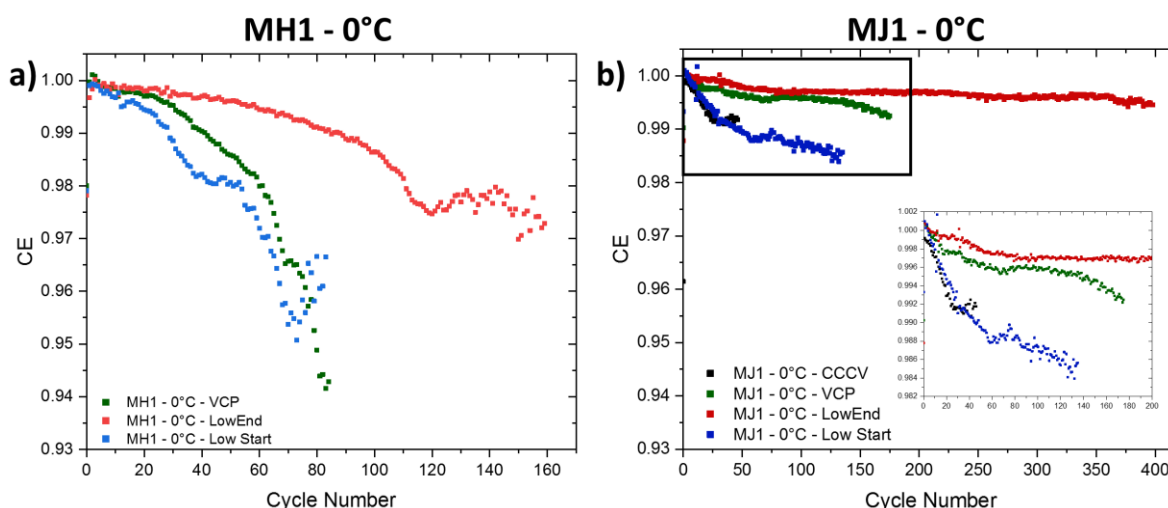


Figure 5-12. CE per cycle of a) MH1 and b) MJ1 cells.

Lastly, an increase of voltage during discharge was observed for several cells cycled at 0°C exclusively; feature displayed in Figure 5-13 below. This recovery is observed closer to the bottom of discharge, between roughly 2.8 V and 3.0 V, for three cells (MH1 LowStart and LowEnd, and MJ1 LowStart), close to their subsequent failure. This has been observed in 21700 commercial cylindrical cells by Hu et al.³⁰⁸ during cycling at -20°C and -30°C displaying different voltage changes during charge at 0.5C. The paper highlights that the plated lithium can partially re-intercalate into the anode, causing a temporary voltage increase before it drops again. This can also occur with the SEI layer (thicker and more unstable at lower temperatures³⁰⁹), which can temporarily break down or rearrange, which can then reform and stabilise at low SoCs, causing fluctuations in cell voltage, including temporary voltage recovery³¹⁰. Increased impedance might have a role as well, as it has been shown to be significant at low SoC, causing a temporary voltage bump before the cell continues to discharge to the cut-off voltage. This might also be exacerbated by reduced electrolyte dynamics and lower viscosity with reduced ion mobility at low temperatures³¹¹. During discharge,

as the battery heats up due to Joule heating due to very high impedance at low SoC, the electrolyte's viscosity decreases, improving ion transport and which could lead to a temporary increase in voltage as well. Despite these features observed only at -20°C and -30°C by Hu et al., the significant signs of SEI growth and Li plating shown by the present cells are coherent with this voltage feature, even at 0°C.

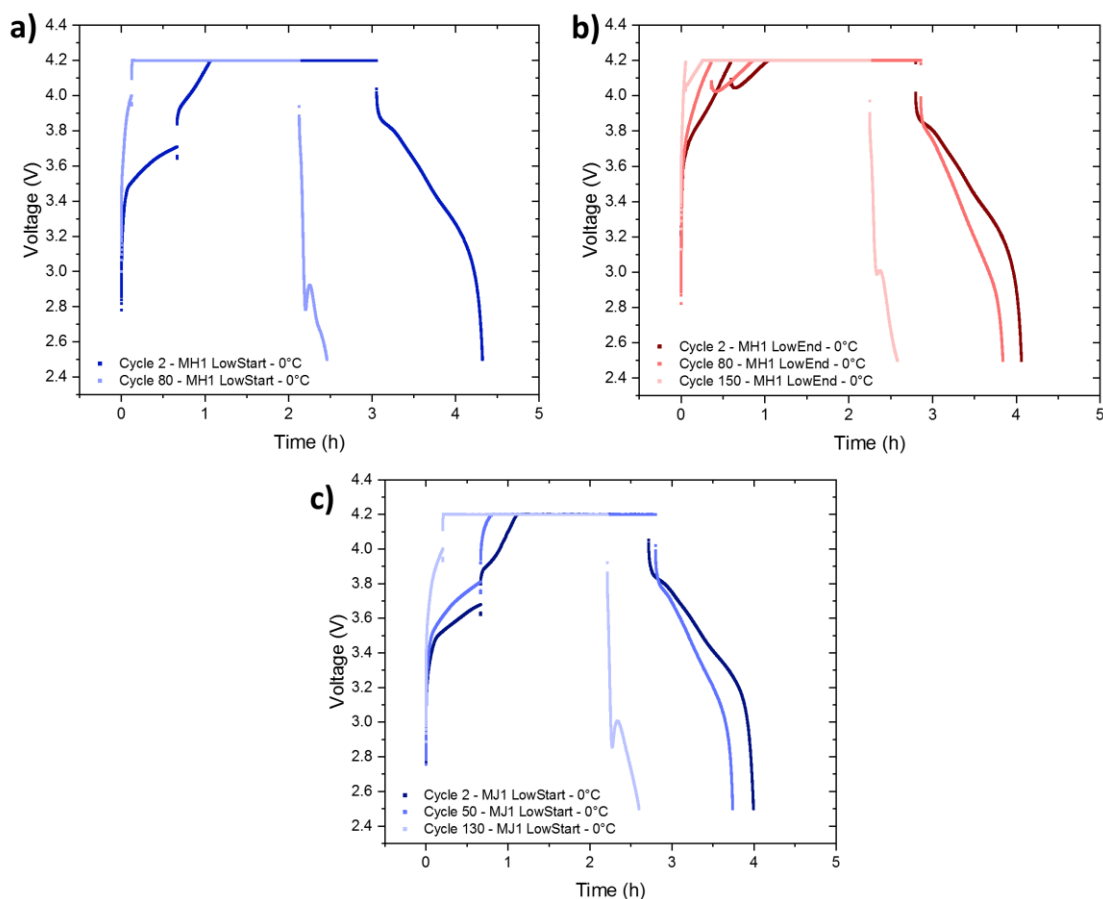


Figure 5-13. Voltage profiles of a) MH1 LowStart, b) MH1 LowEnd and c) MJ1 LowStart at various cycles displaying a positive voltage recovery during discharge.

5.4.3 Incremental capacity and differential voltage analysis

The ICA performed on the MH1 and MJ1 cells cycled at both temperatures is displayed in Figure 5-14. For the 20°C cells displayed in a) and b), the dQ/dV plot of a fresh cell is also included for reference. It is important to note that the diagnostic cycle for MJ1 VCP and LowEnd cells was not preceded by a discharge, as a such, the first peak is missing from the plot for VCP due to starting at a higher voltage. The MH1

cells show a dramatic difference between the CCCV and LowStart protocols, notably for the first peak which is observed between 3.4-3.55V. This peak, attributed to the early stages of lithiation of graphite, stages IV and III, LiC_{24} to LiC_{18} and LiC_{18} to LiC_{12} respectively³¹², and appears to be severely affected for the LowStart cell in both shift to the right (which corresponds to increased impedance and LLI), and loss of maximum value (which correlates to LAM²²⁰). As such this can be then applied to the 2nd peak, with smaller shift and severe LAM. Said peak is attributed to the graphite stage II LiC_{12} to LiC_6 as well as the initial stage of delithiation of the NMC 811¹⁰⁸, with the 3rd peak including the final stages of graphite lithiation (stage I) as well as another intermediate NMC811 phase transition. The last peak is solely related to NMC811, as the $\text{H2} \rightarrow \text{H3}$ phase transition, associated with a prominent c-lattice parameter volume contraction^{109,278}. This last peak appears to be the least affected for all cells, with no shift and only minor LAM for the MH1 LowStart cell, which provides evidence that, overall, the anode seems to be more degraded by the cycling as opposed to the cathode. Additionally, the shift and LAM observed in the 2nd and 3rd peak may be more linked to the anode degradation compared to the cathode, as the two overlap there. MJ1 cells present similar trends, with a more shifted 1st peak, and then relative LAM losses observed for the 2nd and 3rd peaks with the least prominent observed for the LowEnd cell, followed by VCP, CCCV and LowStart.

Both MH1 and MJ1 cells cycled at 0°C present more dramatic ICA features, as the 1st peak is not present anymore, which is only correlated to severe LAM (due to structural degradation or permanently stuck Li ions), LLI and impedance growth, where the lithiation associated with that peak can no longer occur due to the significant reduction in the amount of active material and availability of Li, pointing at severe anode degradation, SEI growth and plating, as shown previously. Despite this, the last peak associated with the cathode is still prominent, showing that the cathode degradation is not the main factor at play. It is important to note that the diagnostic cycle was performed after the previous failure, and as such, done at a different cycle numbers: it can then be observed that the MH1 LowEnd cell presents analogous ICA markers after 162 cycles compared to the LowStart cell after only 84. Similarly, the MJ1 LowEnd cell present a similar state of degradation as the VCP variant, despite having undergone more than 200 cycles during previous cycling.

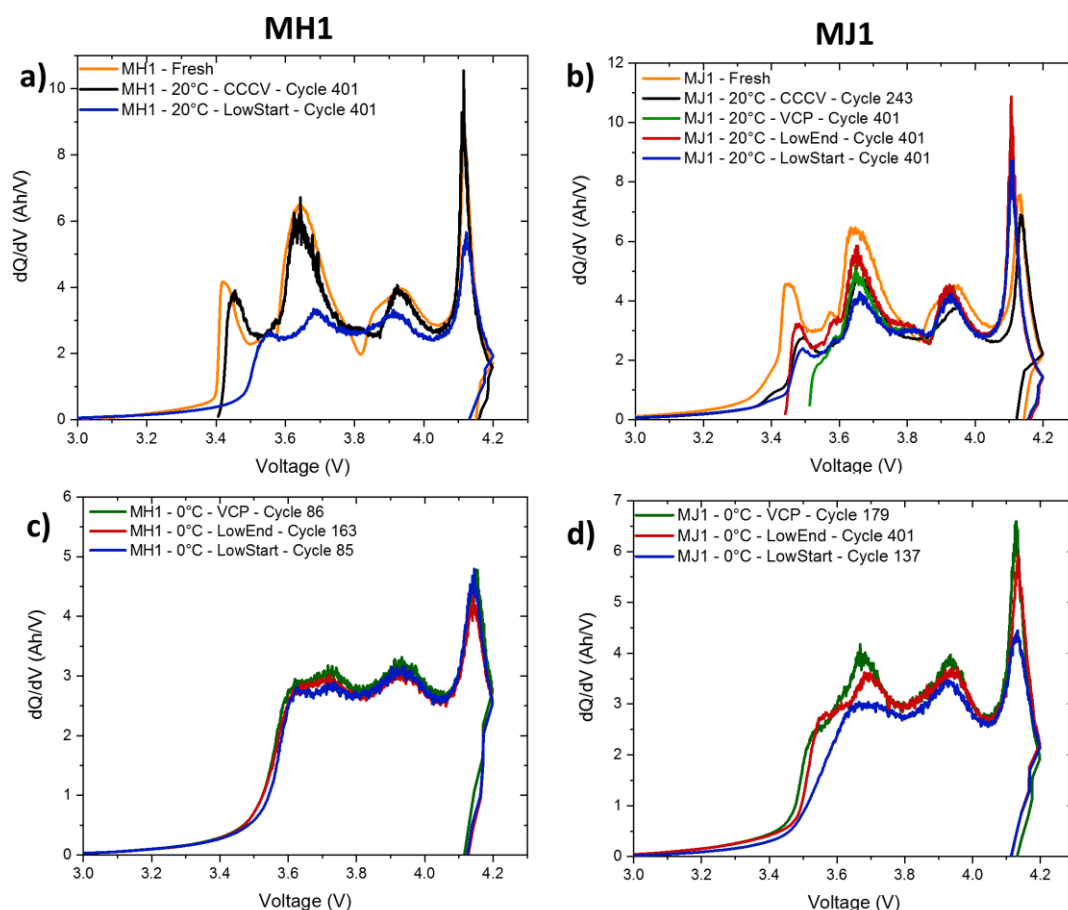


Figure 5-14. Incremental capacity analysis for MH1 cells at a) 20°C and c) 0°C respectively, and MJ1 cells at b) 20°C and d) 0°C respectively.

Additionally, the $dVd(\text{SoC})$ plots of the cells are shown in Figure 5-15. The MH1 CCCV cell shows some broadening and flattening of the first two peaks, associated with graphite, despite its good capacity retention, representing a phase transition occurring at a broader voltage range; while there is minimal change on the 3rd peak representing the NMC811. The LowStart variant shows dramatic flattening and broadening of the two graphite peaks, emphasising the LAM of the graphite. For the MJ1 cells, the fresh cell shows the first two peaks, associated with SiO_x phase transitions, as discussed previously. All other cells lack said peaks, after the 400 cycles, except the CCCV cell with a somewhat observable peak, because its diagnostic cycle was done after 242 cycles. It shows that at this rate, the total disappearance of the SiO_x markers occur between these cycle numbers. Their disappearance causes all other peaks to shift towards the left (particularly the graphite peaks), as these graphite phases occur now at lower SoC. Peaks flattening and

broadening is also observable, with magnitude matching the capacity fade measured for each protocol.

The cells cycled at 0°C show more extreme broadening of peaks to the point where both graphite peaks are barely identifiable, particularly the first one. The cathode peak still subsides, and differences in LAM are still available between the MJ1 cells for instance. The LowStart cathode shows for example more LAM than the VCP and LowEnd cell.

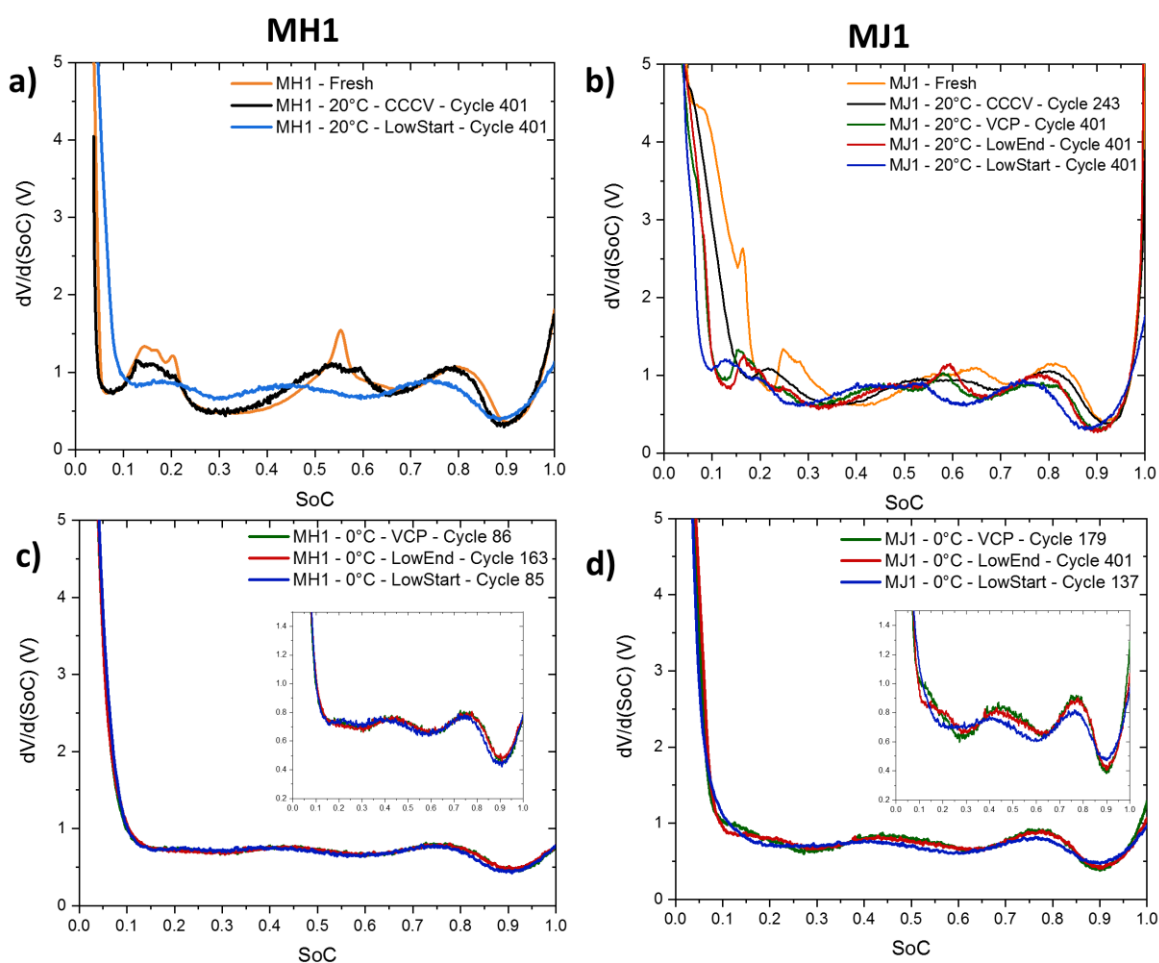


Figure 5-15. dVd(SoC) plots for MH1 cells at a) 20°C and c) 0°C respectively, and MJ1 cells at b) 20°C and d) 0°C respectively.

Furthermore, the intervals between key DVA peaks (referred as “Q”), as well as their resulting losses are shown in Figure 5-16 below. These DVA markers were calculated from the dVdQ plots, displayed in Figure 8-3 in Appendix. This analysis was not performed on the cells cycled at 0°C due to their dramatic peak broadening/disappearance. For the MH1 cells in a) and c), it can be seen that more

losses are observed at the anode for LowStart, particularly prominent for the Q2, at above 50%, showing a significantly reduced interval between the various graphite stages, due to the structural changes occurring. Q3 and Q4, however, present similar losses compared to the CCCV variant at around 20% for Q4. Notably, this makes the cathode proportionally the greater contributor of degradation for the CCCV cell. Therefore, it would appear that around 20% of cathode derived degradation would occur after 400 cycles inevitably, while the LowStart cell present significant additional anode driven degradation on top of this.

Figure 5-16 b) and c) shows the total disappearance of the SiO_x markers, except for Q2 of the CCCV cell. As discussed previously, this is linked to the fact that the dramatic increase in size of SiO_x particles induces stress in the electrode and leads to mechanical failure, cracking, pulverisation leading to electronic contact losses from the neighbouring graphite particles, and as such, failing to contribute to subsequent cycling⁷⁹. As opposed to the MH1 cells, the MJ1 cells main losses (excluding SiO_x markers) come from Q1, as opposed to Q4 (Q4 for MJ1 is equivalent to Q2 for MH1), meaning that the main losses are caused by a more prominent shift in the 50% lithiation graphite peak. This could be partly explained by the fact that the SiO_x peaks have disappeared, and as such, graphite lithiation processes occur at lower SoC, as shown previously. In any case, the anode presents the main losses when compared to Li inventory losses and the cathode. However, the LowEnd cell presents significantly less loss (around 4%) as opposed to all other cells (12-14%) for Q6. This would indicate that the protocol is also beneficial for the cathode, due to the fact that less time is spent at higher voltages, reducing likely oxygen release and RSL formation³¹³. However, both the anode and cathode do not exist in isolation in the cell, and cathode degradation modes such as O_2 release can and do have effects at the anode in the form of SEI disruption and growth as shown in two studies by Bernardine et al.^{314,315}

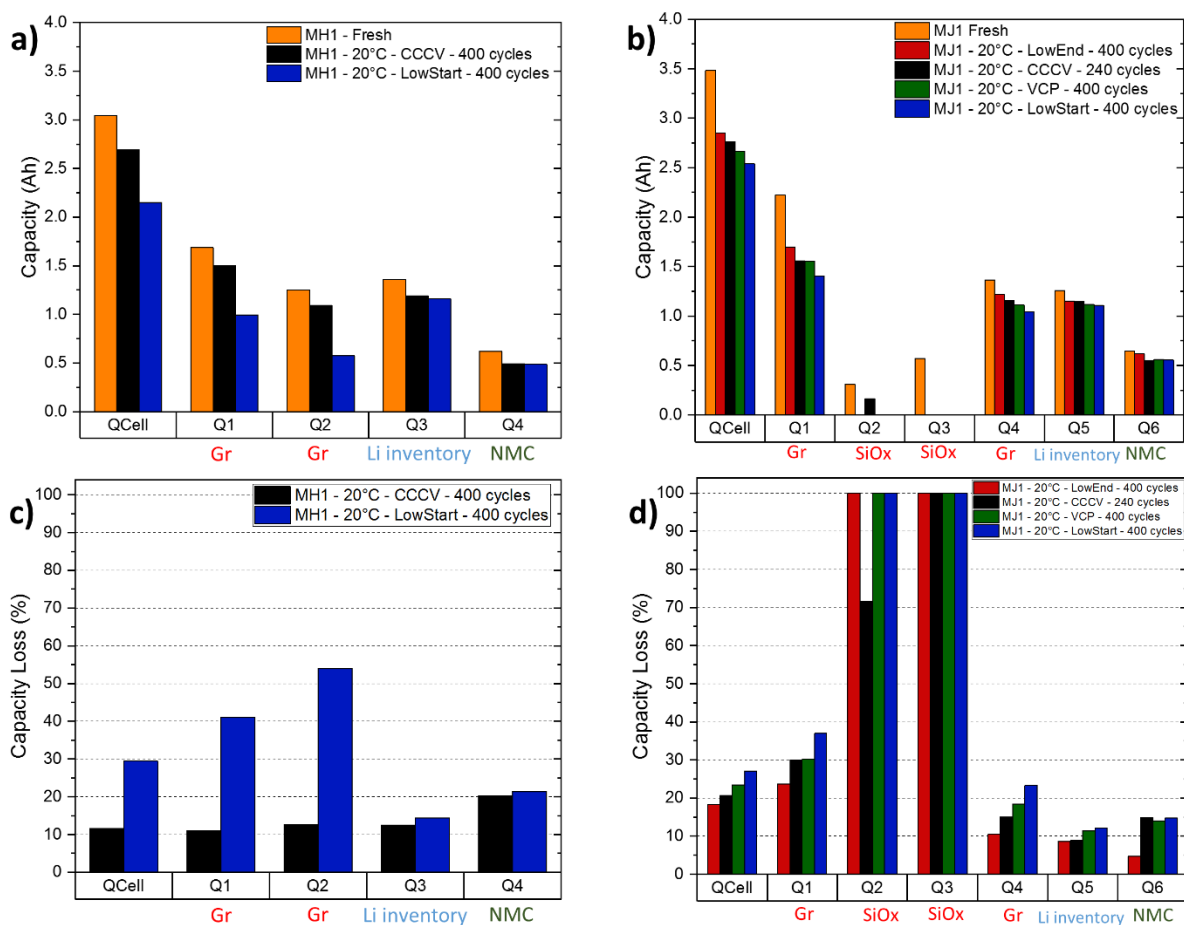


Figure 5-16. Calculated DVA markers for a) MH1 and b) MJ1 cells, with subsequent losses fraction of capacity from each marker compared to the fresh cell during the ageing for c) MH1 and d) MJ1 cells.

Therefore, it would appear that the anode, and particularly for the cycling carried out at 0°C, is the main driver of capacity fade, as opposed to the cathode, which remains relatively preserved, for the most degraded cells and particularly the LowStart protocol. This is in addition to the SEI growth, Li plating and impedance growth discussed previously.

5.5 M50 study at 0.5C and ambient temperature

The same procedures were then repeated with M50 cells, also from LG Chem, but of a larger format (21700), presence of SiO_x additives in the anode and particularly relevant in industry (interests from an OEM, involved in the work presented in the next

chapter) and in literature with several papers (introduced previously) published using said cells in their experiments. The cycling was then repeated at 0.5C with duplicates for each protocol, cycled at ambient temperature in an ammo box, with measured oscillations in temperature of roughly 17-26°C. This had a measurable direct impact on the monitored temperature of each cell, and as such, other cell characteristics and parameters. The discharge capacity and measured average temperature per cycle of two cells, VCP_01 and LowEnd_02 are displayed in Figure 5-17, as they illustrate this particularly well. The correlation between temperature and discharge capacity per cycle is evident, where a higher average temperature led to a slight increase in measured capacity during the same cycle, or the following one, and as such, this should be taken into consideration throughout this study. Furthermore, a lower cut-off voltage of 2.8 V instead of 2.5 V chosen previously was selected, to avoid any risk of over discharge of these large format cells.

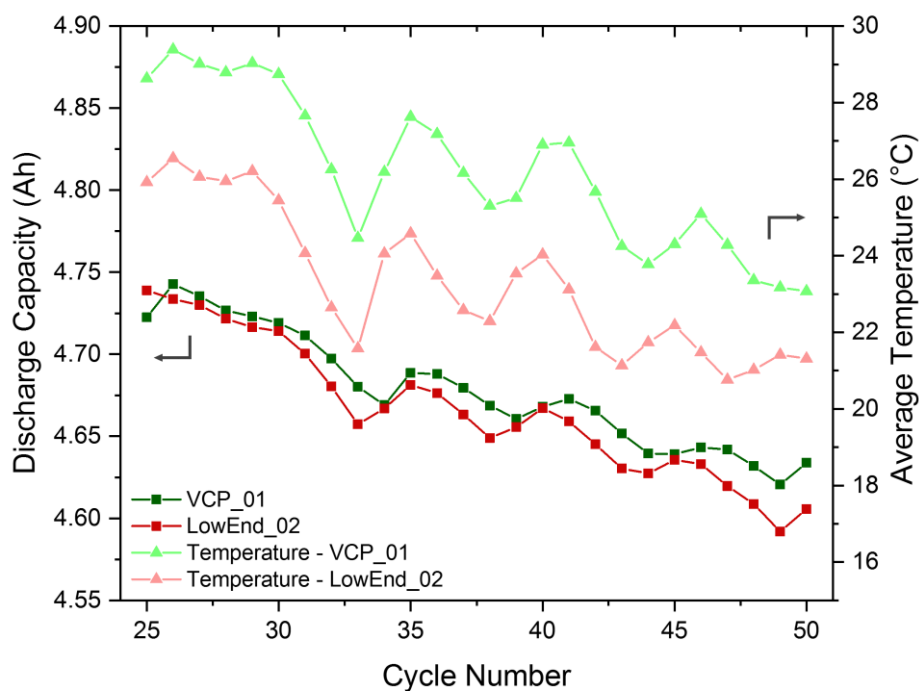


Figure 5-17. Discharge capacity and average temperature per cycle for the VCP_01 and LowEnd_02 cells between cycles 25-50.

5.5.1 Cycling data results

The measured discharge capacity and normalised discharge capacity of all cells are displayed in Figure 5-18. On top of the aforementioned oscillations in capacity, several interruptions of cycling are to be noticed, on top of the diagnostic cycles for capacity check and EIS. These were due to lab shutdowns or electrical failure. Overall, the cells show better capacity retention compared to the MJ1 cells, for example, despite the extra cycles, likely due to the lower C-rate used here with only one cell (LowStart_02) below 80% SoH after 670 cycles. The LowStart cells once again show the worse capacity retention, with a consistent capacity loss trend, followed by the CCCV batch (with CCCV_01 performing significantly better than 02 prior to its interruption of cycling), with VCP and LowEnd cells being the best performers.

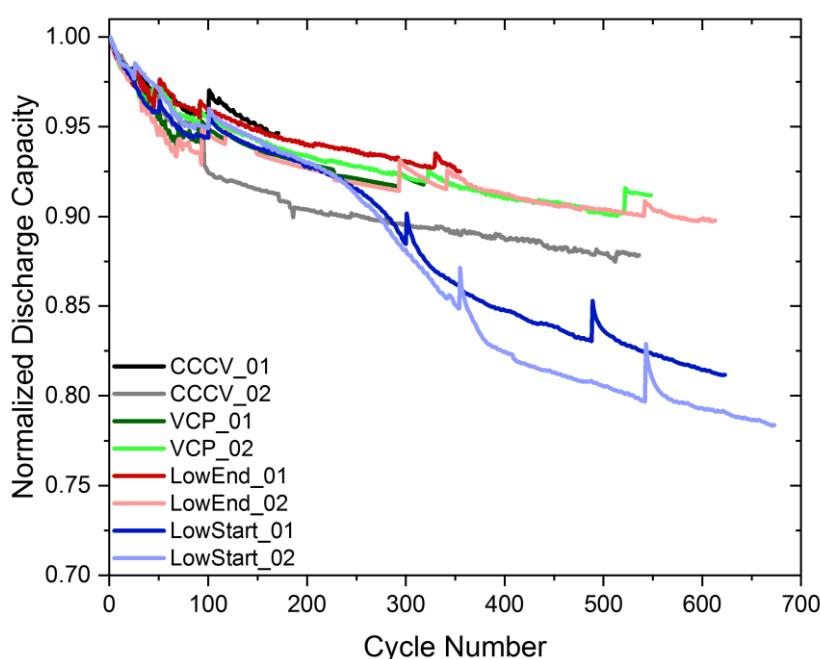


Figure 5-18. Normalised discharge capacity per cycle for all M50 cells, cycled at ambient temperature.

Subsequently, as it can be observed in Figure 5-19, the percentage of the CV phase contribution during charge shown in a) displays a similar pattern as observed for the previous batches. LowEnd cells have consistently less contribution, followed by VCP, CCCV and LowStart cells. However, this value seems quite consistent across all cells, excepts for the LowStart protocols were either a dramatic increase is

observed (immediately following an interruption) or a gradual increase before reaching a plateau. The overpotentials during charge shown in b) display dramatic increases following most interruptions before readjusting, and the same pattern is followed as well compared to the previous cells, where LowEnd shows the highest overpotentials, while LowStart show the lowest, due to the C-rate applied as charging starts. A significant increase is then measured and sustained until the end of cycling by the LowStart cells for both overpotentials, despite punctual interruptions. This follows the trend previously observed of higher impedance growth at top and bottom of the SoC, emphasising how detrimental the LowStart protocol appears for cycling, despite the lower C-rate compared to the previous studies.

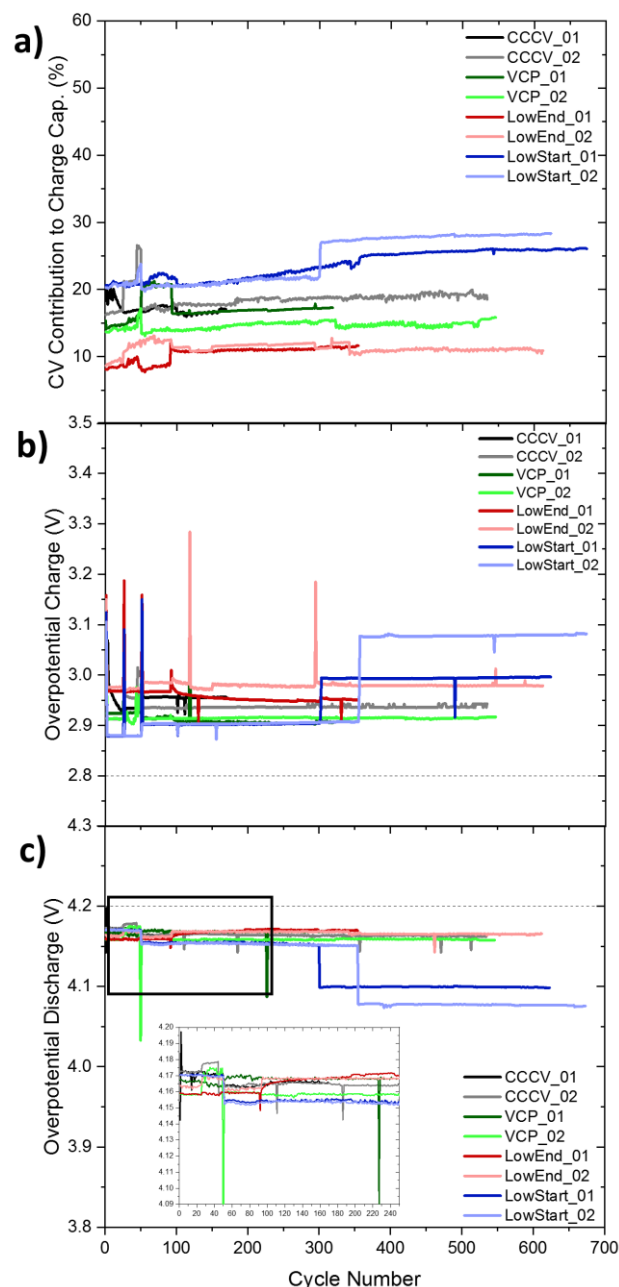


Figure 5-19. a) Capacity contribution of the CV phase for charge in percentage and measured overpotentials for b) charge and c) discharge.

5.5.2 Incremental capacity and differential voltage analysis

The ICA and DVA of the cells cycled for the longest (> 495 cycles) are displayed in Figure 5-20. As shown previously, the 4th peak seems to be the least affected, with some minor LAM identified due to the nearly identical peak shape and location across all cells. Conversely, the 1st peak, attributed to early graphite lithiation is the most affected with more severe identified LAM for LowStart while the LowEnd and VCP

display the least. However, this peak is shifted by a near identical amount for all cells, showing either similar LLI or impedance for this specific phase transition. Additionally, the 2nd peak shows little shift, but measurable LAM following the same pattern as the 1st peak. The 3rd peak displays a notable narrowing, but otherwise little change for all cells, consistent with the finding of the previous cells as well, indicating minor changes in the last graphite stages or intermediate cathode delithiation process M→H2, monoclinic to second hexagonal¹⁰⁸.

The DVA then shows some minor shift and change in features for the 50% lithiation of graphite stage and the cathode peak. The first graphite peak, however, shows a loss of the distinctive sub peak features, indicating LAM affecting the initial phases of graphite, consistent across all cells. As shown in c), and as seen before, said peak is also shifted earlier, making these phase transitions occur at earlier SoC. Furthermore, and contrary to the previous cells, all M50s still display markers of SiO_x activity during cycling as shown in b) and c). Despite the additional cycles (500-650 compared to 400 cycles previously), the SiO_x appears to not be completely cracked, pulverised and isolated (as suggested by literature), indicating that the C-rate could be a major contributor to SiO_x additives degradation and as such, a key parameter for their longevity. Otherwise, this would mean that, again, the manufacturer improved the nature or inclusion of these SiO_x additives, as the M50 cell came after the MJ1 cell chronologically. As seen in d), the most affected peak is the 2nd one showing significant shift and severe LAM, and can be even considered absent for both LowStart and CCCV cells.

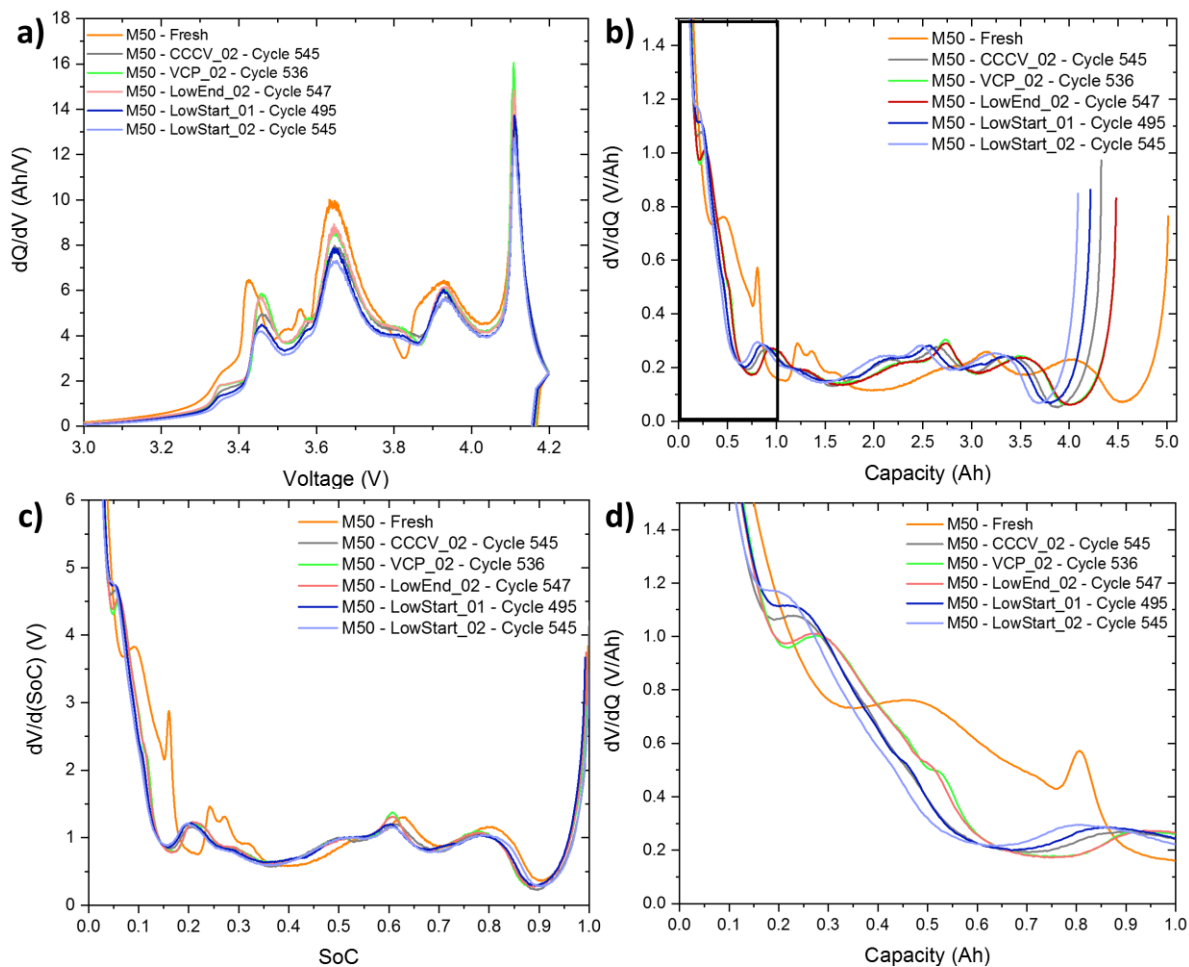


Figure 5-20. a) Incremental capacity analysis, b) dV/dQ , c) $dV/d(SoC)$ plots and d) inset of the dV/dQ plot focusing on the SiO_x phase transitions.

To further investigate SiO_x longevity, all diagnostic cycles with DVA performed on LowEnd_02 are shown in Figure 5-21, and present a comprehensive evolution of the two SiO_x peaks. It can be seen that the 1st SiO_x peak displays, as the cell ages, a peak sharpening and narrowing, when compared to the broader fresh peaks. This indicates that the attributed phase transitions occur at a narrower voltage range compared to the fresh state. This is the opposite of most commonly observed DVA markers, as the observed LAM usually leads to peak broadening due to loss of active sites²¹⁹. Furthermore, the 2nd peak is still quite present in cycle 295, while barely showing at cycle 547, and as such, significant LAM occurred in that interval.

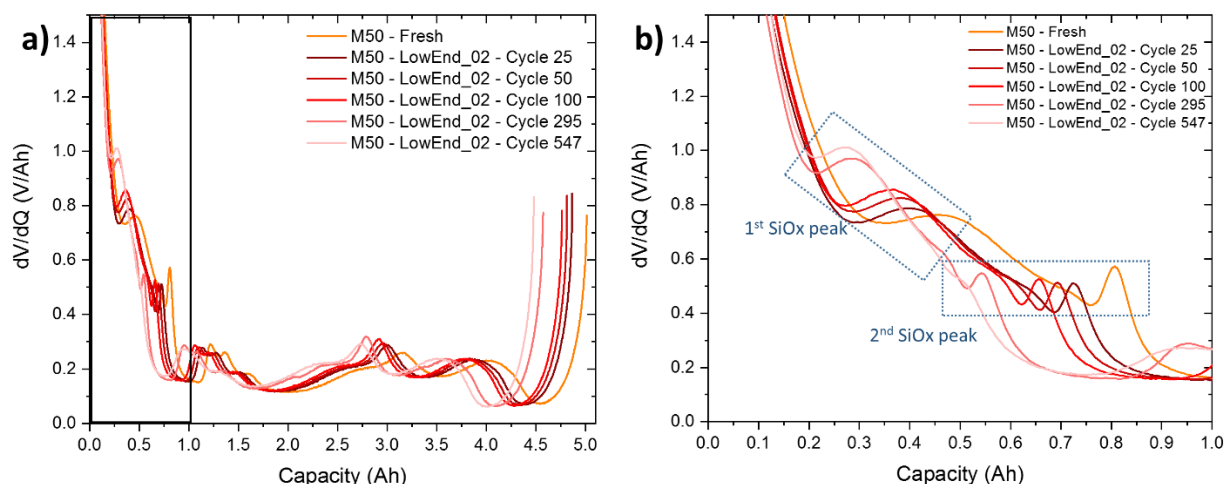


Figure 5-21. a) DVA plot of the diagnostic cycles performed on LowEnd_02 and b) inset focusing on the evolution of the two SiO_x peaks.

Subsequently, the various intervals between key peaks were calculated and are displayed in Figure 5-22, as previously. As expected, LowEnd and VCP cells present the least losses for all intervals, and are even the only cells to retain a 2nd peak, highlighting that their protocols are also beneficial for SiO_x longevity as well, on top of purely graphite and cathode markers. Their percentage of losses for Q6 (cathode) is also significantly lower (1.5-2.5%) than what was observed for MH1s and MJ1s, likely due to the reduced damage caused by 0.5C as opposed to the 0.7C cycling. Conversely, LowStart 02, 01 and the CCCV cells present the most losses in that order, with Q1 (anode), Q4 (graphite) and Q5 (LLI) being the most prominent respectively.

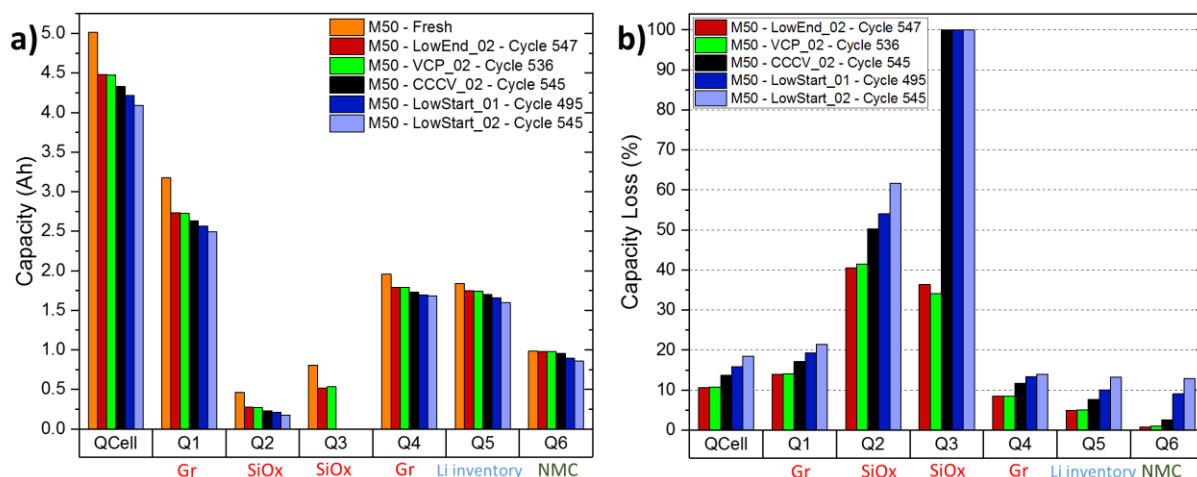


Figure 5-22. a) Calculated DVA markers and subsequent calculated capacity losses in percentage.

Overall, this shows, despite a lower C-rate, a prominently anode-driven fade behaviour for the M50 cells. Despite this, cathode degradation is still present for LowStart cells, while greatly reduced for other variants, confirming that a longer duration at high voltages is primarily damaging for the anode and exacerbates SEI/plating mechanisms. However, time at higher voltages is damaging for the cathode as well (as discussed previously) and drives various degradation modes, however, the subsequent effects of these degradation products on cross-over to the anode appear here to be more significant for capacity loss³¹⁶. Lastly, the difference in C-rate also appears to have greatly affected the longevity of SiO_x.

Moreover, TEM imaging was performed on cathode material extracted from Fresh, LowStart_02 and Low_End_02 cells after the cycling was finished and subsequent cell opening. The work was carried out by May Ching Lai from Cambridge University and part of the results of the study are displayed in the Appendix in Figure 8-4 for a further assessment of cathode degradation.

5.5.3 Electrochemical impedance spectroscopy

Furthermore, EIS was performed during the diagnostic cycles, at various stages during discharge. The Nyquist spectra of a fresh M50 cell during its first cycle are displayed in Figure 5-23, below. As can be seen, a notable increase in both R_{Ω} and R_{ct} occurs at both 5% and 0% SoC which is consistent with the measured IR in Figure

5-4. Higher values can also be appreciated for 100% SoC, although less prominent. It becomes apparent that the 5% and 0% SoC charge transfer semi-circle is much more irregular (and likely composed of two main distinct semi-circles) and significantly larger than the other SoC data points, composed of a single well-defined semi-circle. This evident change for 5% and 0% SoC likely indicates the presence of additional interfacial phenomena or alterations in the electrochemical processes, likely transport through the SEI³¹⁷, or concentration gradients caused by diffusion limitations and electrolyte starvation near the electrode surfaces at these SoCs, further hindering the charge transfer processes¹⁶⁶. This impedance data follows the trends introduced by the IR vs SoC measurements via HPPC in Figure 5-4, in the baseline fresh cells characterisation. Indeed, the timescales observed in the pulse-relaxation approach align with frequency-dependent resistance behaviours seen in the Nyquist plots, where the ohmic component dominates at high frequencies (short timescales), charge transfer resistance is prominent at mid-range frequencies, and diffusion processes dominate at low frequencies (long timescales).

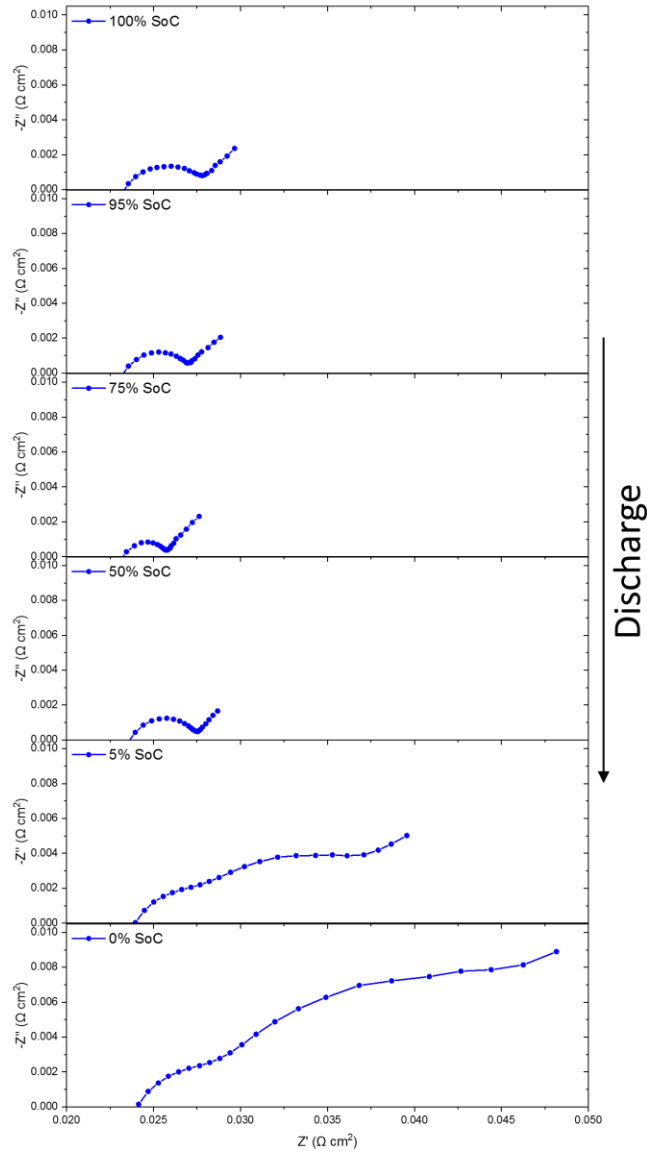


Figure 5-23. Nyquist spectra of a fresh M50 cell measured during discharge at 100%, 95%, 75%, 50%, 5% and 0% SoC.

Subsequently, the R_{Ω} and R_{ct} values from the impedance data were extracted and are displayed for all cells at each of the SoCs in Figure 5-24. Error bars represent the SD of the 2 cells per protocols for fresh state, 50 and 100 cycles. Additionally, the values for both LowStart_01 and 02 are displayed for the diagnostic cycles 495 and 545 respectively. For values at all SoCs, LowEnd and VCP cells display consistently lower R_{Ω} and R_{ct} compared to CCCV and particularly LowStart cells, matching well the studies done previously.

Furthermore, the R_{Ω} values across all SoCs are relatively consistent at around 24 m Ω , except for 0% SoC, with a starting value for all cells around 37 m Ω . A

significant increase for both R_{Ω} and R_{ct} is also notable at this SoC after just 25 cycles, which is also observed for R_{Ω} at 100% SoC. This matches the overpotentials tracked for the LowStart cells, direct results of increase impedance, particularly from the purely ohmic component.

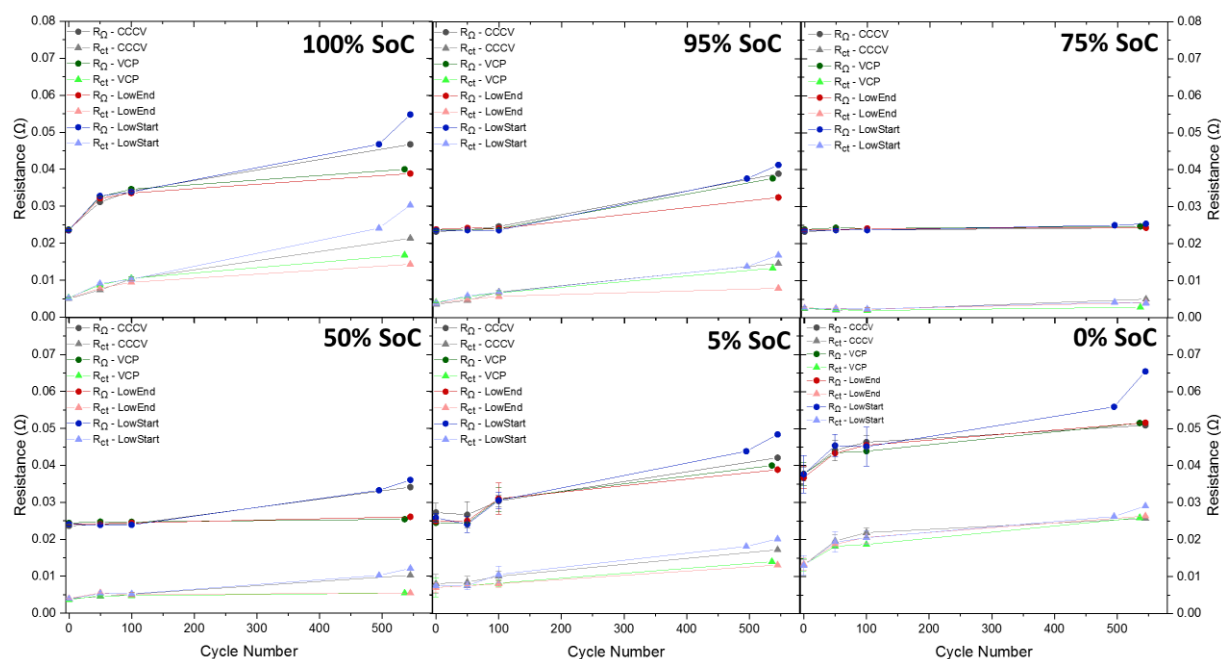


Figure 5-24. Calculated R_{Ω} and R_{ct} values for all cells at 100%, 95%, 75%, 50%, 5% and 0% SoC.

Conversely, virtually no changes in both R_{Ω} and R_{ct} are seen for all cells at 75% SoC, which remain almost identical even after 500 cycles. This denotes a mid-high SoC stability area, as the electrode materials might be operating in their most stable potential window. In this regime, the state of lithiation is such that neither the high-voltage degradation processes (such as electrolyte oxidation) nor the low-voltage processes (such as SEI thickening) are prominently active, major causes to changes in R_{Ω} and R_{ct} ²¹⁴. This stability appears to be leading to negligible changes in interfacial resistance and charge transfer resistance during cycling. This stable area could be extended to reach 50% SoC as well, as the same behaviour is observed for LowEnd and VCP cells, however, the CCCV and LowStart cell present measurable increases in resistance, analogous to the increase measured at other SoCs for all cells.

One possible contributing factor for this, as shown previously in Figure 5-22, is that the LowStart and CCCV cells both show more significant losses for the anode markers (both SiO_x and Graphite), which could lead to the significant 50% lithiation step (LiC_{12} to LiC_6) occurring at this SoC and increasing measured resistance values, while LowEnd and VCP cells would have this phase transition happening at lower SoCs. This however might contradict Figure 5-20 c) which shows a cathode feature appearing at precisely 50% SoC. However, due to slippage and accumulated overpotentials, the cycling to SoC for the EIS acquisition might lead to slightly different voltages where it is performed. As mentioned at the beginning of this chapter, voltage limits were considered for this very purpose, but were never triggered, and the voltage difference measured between all cells for the 50% SoC acquisition was < 95 mV.

5.6 Conclusions

During this chapter, several commercial cylindrical cells with NMC811/Graphite chemistry with (MJ1 and M50) and without (MH1) SiO_x additives were cycled at 20°C, 0°C and ambient temperature. The study analysed the impact of different cycling protocols on the performance and degradation, focusing on capacity retention, impedance growth, and the evolution of other metrics such as polarisation, CE and overpotentials across cycling. The results indicated that the cycling protocol significantly influences the longevity and stability of the cells, especially at higher rates and 0°C with the "LowStart" protocol consistently leading to the most severe degradation across all measured parameters. This protocol induced rapid capacity and power fade, a pronounced increase in polarisation and substantial impedance growth, particularly visible at low SoCs. In contrast, the "LowEnd" protocol demonstrated superior capacity retention and minimal impedance increase, particularly evident at low temperatures, suggesting a more controlled and balanced approach to cycling that mitigates detrimental effects on both the anode and cathode. Time spent at high voltages, particularly during the CV phase appears to be the key difference between the protocols, and this led to major differences in performance and fade behaviour.

At 20°C, the "LowStart" cells exhibited the worst performance, with a significant drop in capacity after 400 cycles, attributed to increased impedance and Li plating,

which severely hindered charge efficiency. Conversely, the "LowEnd" protocol maintained around 80% capacity retention under the same conditions, highlighting its effectiveness in prolonging battery life. Similar trends were observed at 0°C, where "LowEnd" again outperformed other protocols, with the "LowStart" protocol leading to early power failure and drastic overpotential increases, reflecting severe anode degradation. At 0°C, severe power fade was observed, as cells underwent diagnostic cycles after an apparent failure and demonstrated significant capacity still accessible (at lower rates), which shows that the ability to deliver power was the limiting cycling factor at this temperature, caused by dramatic impedance increase and SEI/plating degradation.

Subsequent ICA and DVA further confirmed the detrimental effects of aggressive cycling protocols. The "LowStart" protocol led to a significant loss of active material, especially in the anode, as evidenced by the disappearance of key lithiation peaks and the broadening of the remaining peaks, indicating severe LAM, LLI and increased impedance. In contrast, the "LowEnd" and "VCP" protocols showed more moderate degradation, with less pronounced shifts and retention of key peaks, suggesting a more stable cycling environment. Further EIS studies performed on M50 cells confirmed particularly more prominent impedance growth at 5%, 0% SoC, and 100% SoC as well, confirming the significant overpotential changes observed, showing that these metrics can be used as reliable tools to track IR and impedance at these two key SoC points. For instance, this shows good potential for integration within existing BMS systems, as their measurement can be directly extracted from each change of charge direction. It was also shown that a stable SoC region existed at around 75% SoC where no changes in ohmic and charge transfer resistances were observed, despite other evidence of degradation and capacity fade.

The findings underscore the importance of selecting appropriate cycling protocols to enhance the durability and performance of Li-ion batteries, where it is particularly evident under varying temperature conditions and higher rates. The evidence suggests that protocols minimising high voltage exposure and maintaining balanced charge distribution between CC and CV phases during charge are key in reducing degradation rates and prolonging cell life. Attia et al. compiled several variable current protocols from many known industry patents and papers, and they all appeared to show charging protocols analogous to the LowEnd protocol used through this

thesis¹⁶¹. Significant variations and differences are notable, such as an increased subdivision of the SoC and variations of C-rates applied, but the same overall idea of starting with a high C-rate and gradually reducing it until the end of charge persists, as further emphasised by a review by Tomaszewska et al.¹⁴⁷, particularly true for fast-charging uses. The work presented in this study presents evidence as to why these protocols appear to be so widely used, and not a different type of protocol such as VCP pattern, for example. Overall, however, the widely used CCCV appeared to be a reliable and easy-to-implement compromise, sitting consistently between LowEnd and LowStart for most metrics, except the MH1 20°C where it was the best performer, although a LowEnd cell was lacking for that batch.

Lastly, the study kept track of the behaviour of the SiO_x behaviour via DVA as the cells were cycled and it was found that the C-rate is a driving factor of SiO_x degradation and subsequent isolation with the anode material, as no corresponding DVA markers were found at 0.7C after 400 cycles for all MJ1cells, while M50 LowEnd and VCP were still showing a presence of both characteristic peaks after > 500 cycles for instance. This provides evidence on a possible C-rate dependency of the durability of these particles, although caution must be kept as these were observed on two different cell models, and the manufacturer might have improved the nature and inclusion of the SiO_x additives, for better long-term performance.

6 Multiscale degradation study of calendar ageing of Ni-rich 21700 commercial cells with Graphite containing SiO_x

This project was carried out in collaboration with WMG as part of an industry sprint project (EPSRC Faraday Institution Ni-Sprint project (FIRG053)) with a prominent OEM. It was also supported by the Degradation project (FIRG060) and the SafeBatt project (FIRG061)). It consisted of storing 224 commercially available M50 cells at different SoCs and temperatures for durations of up to 70 weeks, with regular capacity checks by the way of reference performance tests. Due to the large and collaborative nature of the project, only selected results will be shown in this chapter, largely pertaining to the investigations around cathode degradation that were led by UCL, though results from others in the project are used to give context and completeness to the results discussed.

Alexander Dimitrijevic, Eleni Fiamegkou and Meltiani Belekoukia opened and harvested the electrode material for the post-mortem characterisation. A.D. collected and prepared the electrode samples for NPD, which was performed at ANSTO by Maxim Avdeev. Ashok Menon helped with the interpretation of the NPD results, and performed the XRD and analysed the results. Dhammika Widanalage supervised and provided the storage and reference performance cycling data of the cells. A.D. and E.F. performed all X-Ray CT imaging and A.D. prepared the coin cells from harvested electrode materials. All contributed to the conceptualisation of the study and interpretation of results, as well as Wesley Dose, Melanie Loveridge, Louis Piper and Rhodri Jervis, which also provided supervision and sourced the funding of this study.

6.1 Introduction

The widespread adoption of Li-ion batteries in EVs is driving significant advancements in battery technology, with an emphasis on extending battery life and

improving performance. However, despite these innovations, a critical challenge remains: the understanding and mitigation of calendar ageing—the degradation that occurs when batteries are not in active use. This issue is particularly pertinent given that electric vehicles spend approximately 96% of their operational lifespan in a state of rest, often under varied environmental conditions and SoCs, as discussed previously²⁰. Such periods of inactivity can lead to substantial capacity fade and resistance increase, even in the absence of cyclic loading.

Calendar ageing is influenced by a complex interplay of factors, including temperature, SoC, and storage duration, all of which contribute to the long-term reliability and safety of batteries. This study undertakes a comprehensive investigation into the calendar ageing of cylindrical Li-ion cells, where a total of 224 cells were systematically stored and studied to quantify the impact of storage conditions, with a focus on varying SoC, temperatures and storage time. The experimental design enables a robust assessment of the degradation mechanisms, capturing the nuanced effects of SoC and temperature on capacity fade and resistance increase.

6.2 Experimental

After an initial capacity check, the cells were divided into 4 groups, each being stored at one of four temperatures: 0°C, 25°C, 40°C, and 60°C. A total of 224 cells were used for this study, and in each temperature group, triplicate cells were charged and then calendar-aged at a SoC value ranging from 0-100 %. To monitor the capacity degradation of the cells, a reference performance test (RPT) was carried out periodically for all cells. It consisted of the application of a CCCV (CV until current reached 10 % of initial capacity) and discharged in the range 2.5 – 4.2 V at a rate of C/3. A subsequent cycle was then performed where a direct current internal resistance (DCIR) measurement was applied during discharge: a 30s 2C pulse at 50% SoC. After the RPT, the cells were charged to the respective ageing SoC at C/20, where calendar ageing was resumed. After the calendar ageing process was completed, cells were taken off the cycler and stored at 30% SoC and 10 °C before subsequent selected cell disassembly and/or characterisation of the harvested electrodes (to minimise further calendar ageing, beyond that imposed deliberately on the cells).

Some post-mortem characterisation was performed, and for that purpose, the cells were opened for visual inspection and the cathode material was harvested and reassembled in individual coin cells carefully following the procedure introduced in 3.3.

6.3 Calendar ageing results

6.3.1 Capacity fade and resistance increase as a function SoC, storage time and temperature

Figure 6-1 represents the capacity retention of the aged cells at various temperatures, time intervals and SoCs. Overall, the “spoon-shape” effect previously discussed is immediately apparent for most conditions, where the 70% and 80% SoC present an apparent worse capacity retention, with a net measurable recovery at 100% SoC. This is perhaps less evident for 60°C, displaying the most fade (some cells reaching below 80% after 70 weeks) and where also the most cells failed, where one coloured cross represents the failure of the whole data point (cell triplicate). The cells stored at lower SoC tend to fare better (at around 3% capacity loss at 25°C for instance) than those at higher SoC faring worse (at around 6–7% capacity loss at 25°C). Furthermore, and as expected, cell stored 0°C present significantly better retention compared to 25°C and 45°C with analogous values, although all cells 90% SoC-70 weeks failed for the latter.

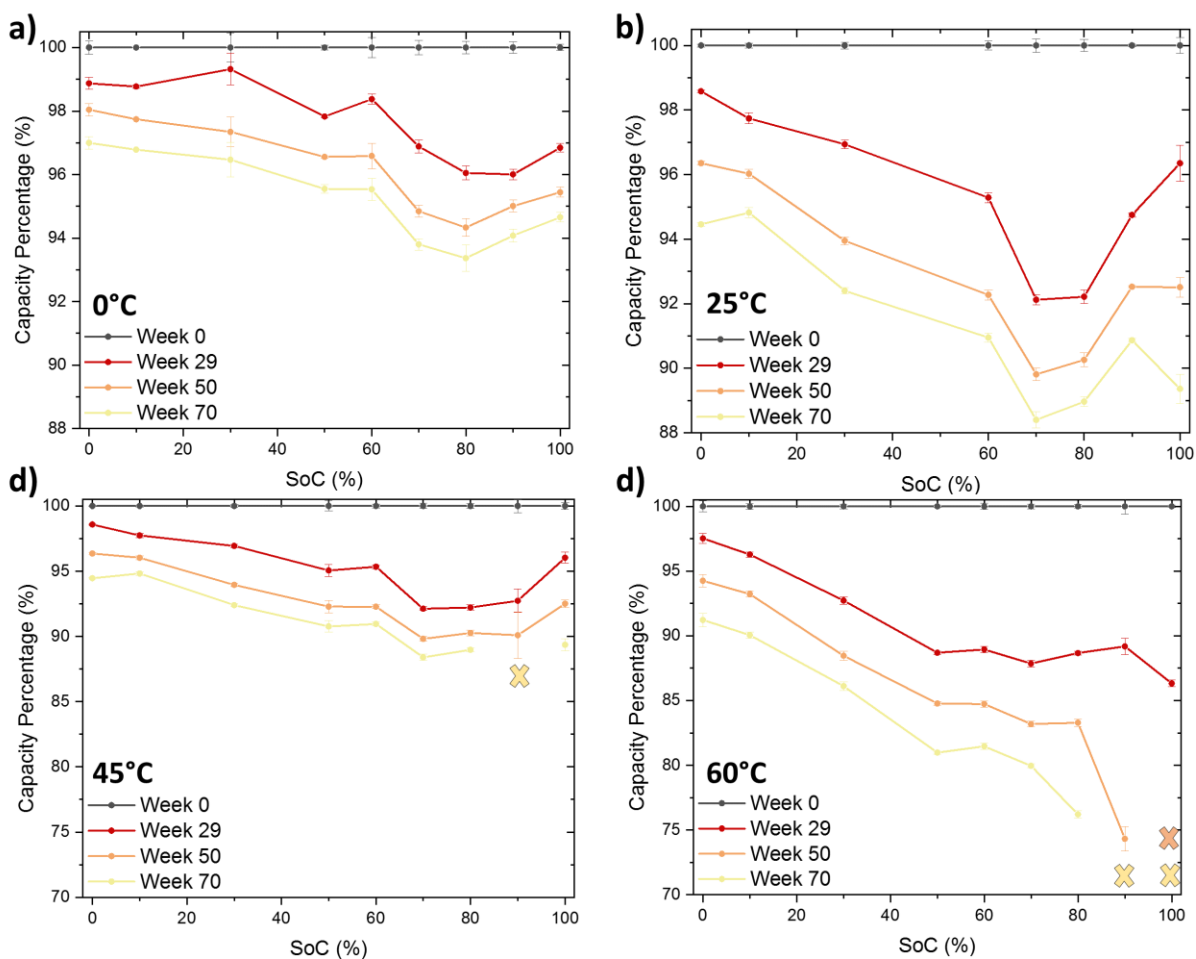


Figure 6-1. Capacity retention of cylindrical cells calendar aged at different storage SoC and temperatures for a) 0°C, b) 25°C, c) 45°C and d) 60°C. The coloured crosses represent cell failure. Data collected by Dhammika Widanalage at WMG.

Furthermore, Figure 6-2 shows the calendar-ageing capacity fade of the cylindrical cells as a function of time stored. It shows that the capacity losses appear to be in two main stages, involving a large initial drop during the first 4 weeks, followed by a more linear decay. The magnitude of the initial drop and the slope of the linear decay appear to be dependent on the SoC as well, with the largest drops observed for cells stored at above 70% SoC. As shown previously, the cells stored at SoC between 0 and 30% showed the best capacity retention and less pronounced aforementioned two-stage fade mechanism. This trend was similar across all temperatures investigated. Overall, it becomes apparent that the main SoC turning point seems to be 60% SoC, with significant drops in capacity occurring at 70% and above. This follows well the findings of Keil et al. where this 50-60% SoC area corresponds to the associated 50% SoC lithiation graphite peak identified by DVA¹⁴⁵.

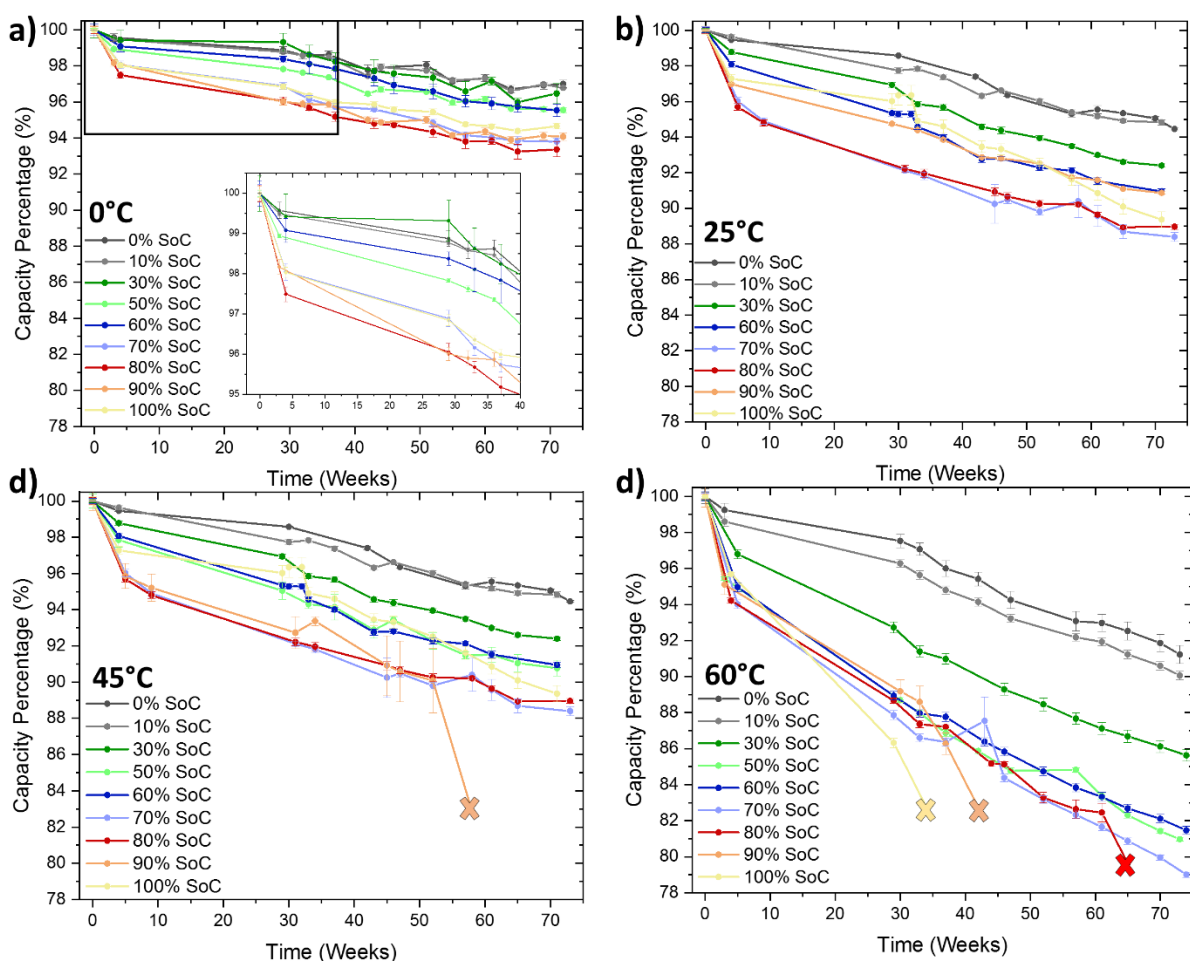


Figure 6-2. Capacity retention of cylindrical cells calendar aged as a function of time for the batches stored at a) 0°C, b) 25°C, c) 45°C and d) 60°C. Data collected by Dhammika Widanalage at WMG.

As part of the RPT, the DCIR test was also performed, and the resistance data was extracted to better understand the trends seen in capacity loss, displayed in Figure 6-3. At lower temperatures (0 and 25°C), only a minor resistance increase was observed after 70 weeks (1–5 mΩ), with little correlation with SoC observed. Conversely, at higher temperatures (45°C and 60°C), the resistance change was far more dramatic (6–20 mΩ) and showed a clear dependence on SoC. It can thus be seen that resistance increase caused by SEI build-up and electrode deformation is a significant source of calendar ageing, exacerbated at high temperatures and SoC. Notably, however, the resistance trends do not match the “spoon-shape”, with 100% SoC appearing consistently observed to show the most dramatic resistance increases. This gradual resistance increase over the SoC is consistent with what Keil et al. observed for NCA and NMC/Graphite cylindrical cells, but not for LFP cells¹³²,

suggesting potential mechanisms linked to the cathode material. The interesting question is then, if 100% SoC shows the greatest resistance increase (as might be expected), why does it show, in many cases, a slight increase in capacity?

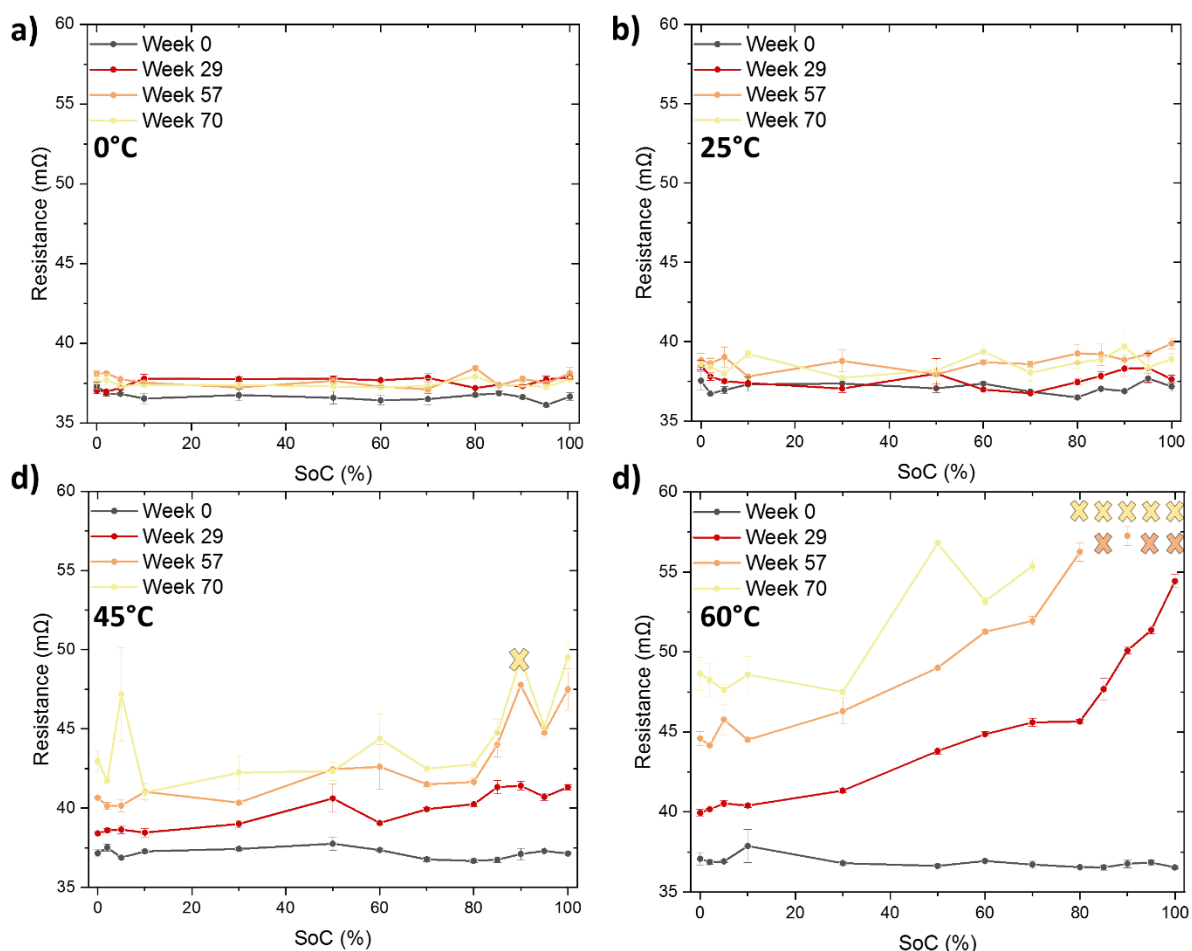


Figure 6-3. Resistance data obtained from DCIR measurements for cells calendar aged at a) 0°C, b) 25°C, c) 45°C and d) 60°C as a function of time. Data collected by Dhammika Widanalage at WMG.

Furthermore, two cells were cycled after their storage time, the capacity over cycle number data being displayed in Figure 6-4, to assess post-storage cycling performance. Two cylindrical cells aged at 80% and 100% SoC for 70 weeks were subsequently cycled repeatedly at C/3. Their initial capacities were 4.50 Ah and 4.52 Ah for the 80% and 100% SoC conditions, respectively, consistent with the values seen in Figure 6-1, which indicated that no additional degradation was added between the end of the calendar ageing and the cycling. During cycling, the cell at 100% SoC degraded at a faster rate than the 80% SoC one, suggesting that the observed spoon-

shaped effect is, at least, temporary, and that storing cells at 100% SoC offers no long-term advantage over 80% SoC. This finding is supported by greater degradation observed in cells stored at 100% SOC, as will be shown in the following post-mortem analysis.

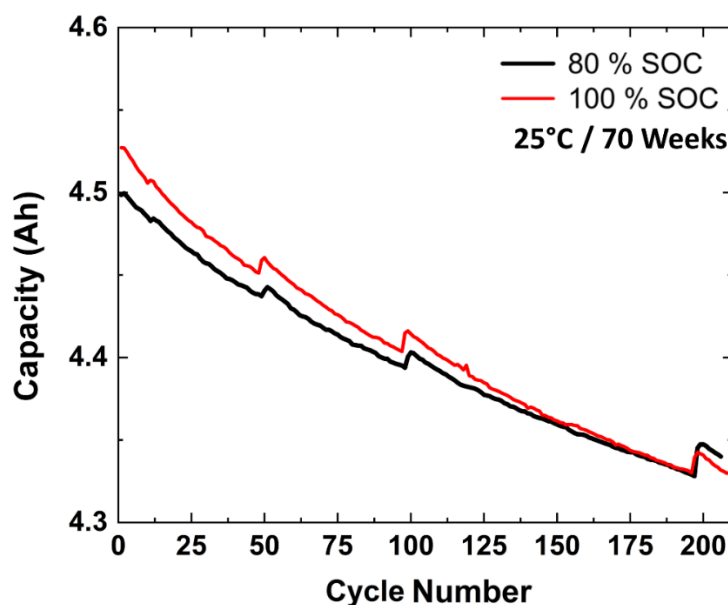


Figure 6-4. Cycling performed after storage of cells at 80% and 100% SoC of the 25°C and 70 weeks batch. The capacity recovery at cycles 50, 100 and 200 are due to pauses during the cycling. Further cycling carried out by Eleni Fiammegkou at WMG.

6.3.2 Macrostructural deformation assessment using X-ray Computed Tomography

X-Ray CT was performed on several cells after their respective time in storage was over, and the reconstructed tomograms are shown in Figure 6-5. As previously done, the orthoslices of the tomograms displayed have been taken at the approximate $\frac{3}{4}$ height mark starting from the bottom of the cell. The figure highlights the supposed area of influence of the intercalated Al tab has on macrostructural deformations. This tab is embedded within the jelly-roll longitudinally across the whole cell, and connected to the positive interface at the top cap. It is analogous to the one observed from cells “NMC/Graphite” in Chapter 4. While no visible deformation is observed in a) – c) from the fresh cells and a cell stored for 29 weeks, localised undulations (“wrinkling”) are observed for the other cells exclusively in the highlighted area, on the side of the tab,

close to the core. While a deformation appears minor for cells stored during 52 weeks for all SoCs at 25°C, it becomes much more significant for the cell displayed in h), corresponding to 60°C, evidencing the preponderant role of high temperature for macrostructural deformations, and affecting several layers of the jelly-roll in the area. Though similar deformations have been seen in cells with extensive cycle history, this is, to the author's knowledge, the first time this has been observed in calendar-aged cells that have undergone minimal cycling, where the RPT was carried out 11-12 times for the most aged cells at 70 weeks. Another study was found to have used X-ray CT on cylindrical commercial cell during calendar ageing, but it was to show how the CID was broken for cells stored at 70°C due to gas generation³¹⁸.

Furthermore, the deformations observed seem to be consistently slightly offset to the left part of the tab influence area, from the presented top-down view. This could be due to the fact that the winding of the jelly-roll is clockwise and as such, some slight radial forces could be applied in that direction, leading to that offset²⁴⁷. Overall, it would appear that macrostructural deformation are more linked to storage temperature, and secondly, to time (despite no significant differences between 52 and 70 weeks), rather than the SoC. Indeed, 80%, 90% and 100% SoC, display the worst capacity fade but show no clear differences in jelly-roll deformation.

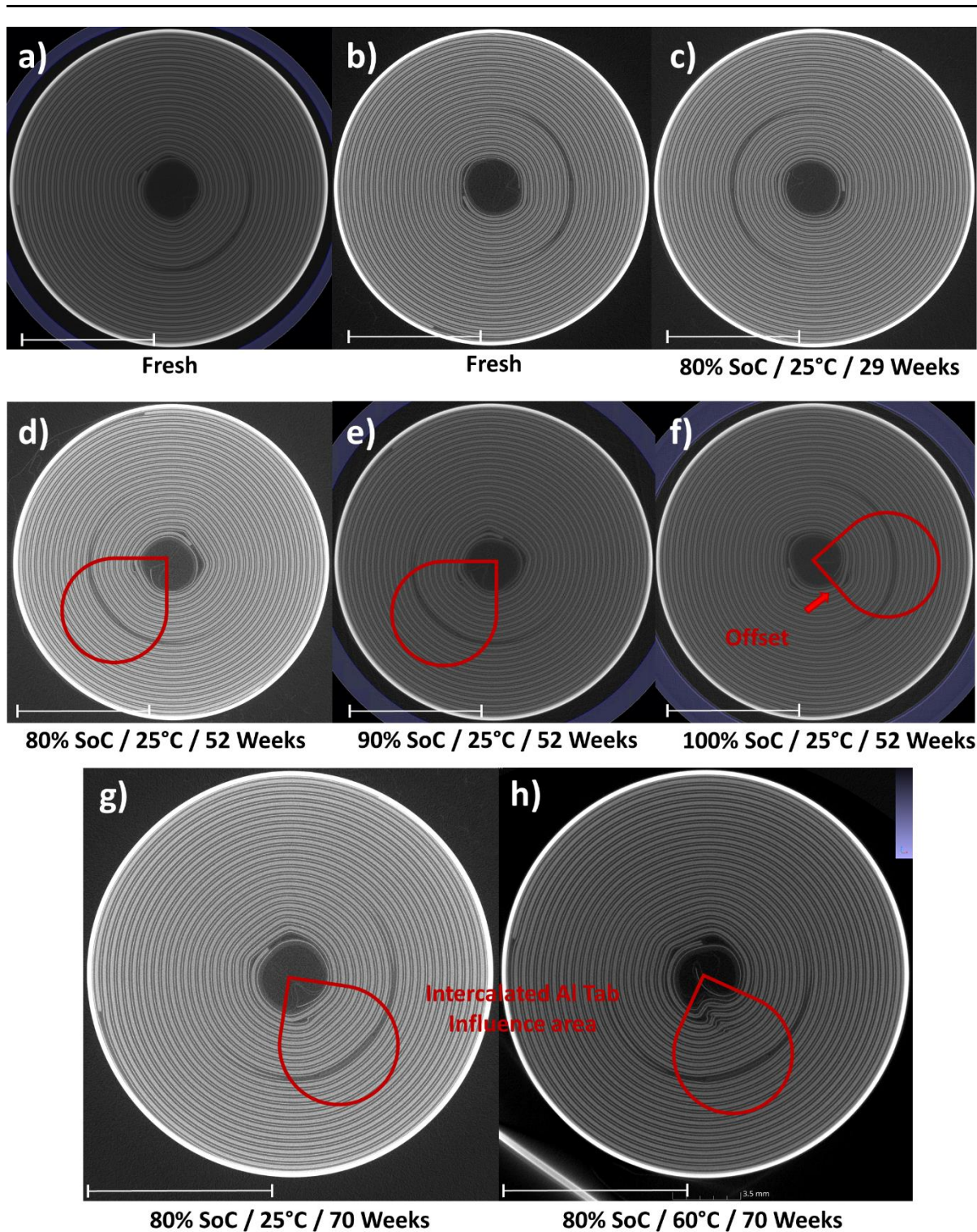


Figure 6-5. Reconstructed tomograms of the cylindrical cells from various SoC, storage time and temperatures. The tomograms correspond to a) and b) two fresh cells, c) and d) 80% SoC at 25°C stored for 29 and 52 weeks respectively, e) and f) 90% and 100% SoC respectively at 25°C stored for 52 weeks and g) and h) 80% SoC stored for 70 weeks at 25°C and 60°C respectively. Annotations highlight the area of influence of the intercalated Al tab, where some electrode deformation is observed in cells stored for 52 weeks or longer. The scale bar displayed represents 10mm.

Figure 6-6 illustrates the radial tensile strain more prevalent on the outer layers of the jelly-roll and the radial compressive stress forces on the electrode assembly closer to the core²⁵. The area of influence of the tab is also displayed, showing the asymmetric application of these straining and compressive forces. These forces lead to deformation when applied for extended periods of time and at higher temperatures, and can lead to cracking-induced delamination and buckling delamination from straining and compressive forces respectively^{215,319,320}, as will be evidenced during cell opening in the following section. These forces exacerbate mechanisms prevalent during high-temperature storage such as SEI growth and gas generation due to electrolyte decomposition such as biphenyl polymerisation as evidenced by Matadi et al.²⁴⁶ Furthermore, it has been shown that high temperatures can degrade the binder, exacerbating the SEI layer instability and electrode structural stability. While decomposition reactions such as dehydrofluorination typically become pronounced at higher temperatures (above 200°C in most cases), Maleki et al. highlighted that PVDF can experience plasticisation or softening under prolonged exposure to elevated temperatures but still well below its decomposition point³²¹. This leads to detachment of the active material or delamination, particularly in cells experiencing mechanical stress or expansion due to gas evolution from other aforementioned degradation processes³²². As such the binder's role at 60°C would likely be as a facilitator of structural instability rather than a primary driver. This deterioration not only weakens the binder but also contributes to pore blockage in the electrode, hindering ion transport and increasing overall impedance, which could partly explain the evolution of previously measured resistance values from the RPT, with a particularly drastic increase at high temperatures.

Notwithstanding, the deformations observed previously seem to be stemming consistently from the same site of nucleation of these forces, within the tab area of influence, with a slight offset. This is at least the case for the very first deformation site, as Kok et al. showed on extensive cycling (0.7C/1C charge/discharge for more than 1000 cycles) on the same M50s cells³²³. The cycling did indeed lead to deformation in that exact same area, but was rapidly followed by more pronounced deformation on the same level of the electrode assembly, but on the opposite side of the core. Another study by Spielbauer et al. evidenced a similar site of deformation with a different cell model and manufacturer (Samsung 25R), also in possession of a

similarly placed interlaced tab³²⁴, and the same site was noticed as well by Pfrang et al. for a Sanyo URE, even with the presence of a mandrel at the core of the electrode assembly²⁴⁷. Furthermore, Jnawali et al. cycled MJ1 and MH1 cells, which do not possess a similarly intercalated tab and the subsequent jelly-roll deformation appeared with no specific set nucleation site location, despite being consistently around the core-area²⁷⁶.

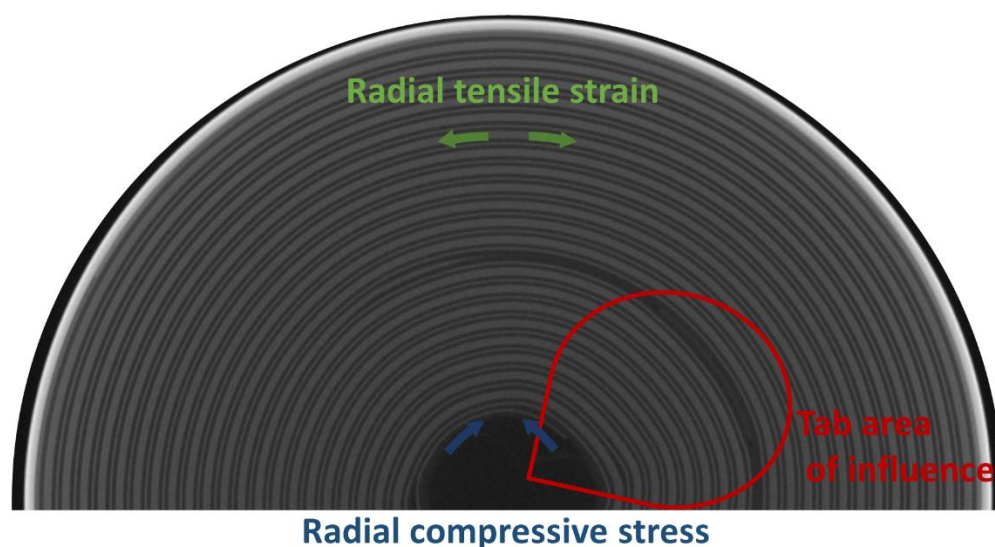


Figure 6-6. Reconstructed tomogram of a fresh cell with highlights of the tab area of influence, radial strain and compressive stress due to the geometric arrangement of the jelly-roll.

6.4 Post-mortem characterisation

6.4.1 Visual inspection

Figure 6-7 displays the degree of visual degradation to the electrode material assembly, with attention brought to the cathode, anode and their corresponding side of the separator. The anode material experienced more pronounced degradation related to its storage condition, as opposed to the cathode material. This observed reduced mechanical stability of the anode can lead to loss of active material and an increase in cell resistance^{325,326}. Indeed, in cells aged for 70 weeks at 25 °C, the anode in the 80% SoC cell remained visually intact, whereas the anode from the 100% SoC cell exhibited significant cracking and delamination. Although this might be expected,

as higher lithiation levels could cause greater electrode expansion and less stable electrolyte interactions, it contrasts with the capacity data, which showed that the 80% SoC cell actually suffered more capacity loss, consistent with the spoon-shaped effect. The separator on the side of the cathode remains clear white and analogous to its “fresh” state, and it is particularly striking for the 100% SoC cell when compared to the severe delamination observed on the anode side of the separator. The cathode material also displays for all conditions, a distinctive sheen. This initial visual inspection suggests no visual signs of cathode degradation at this stage of the investigation.



Figure 6-7. Photographs of the disassembled cylindrical cells, at a) fresh, b) 80% SoC and c) 100% SoC, from the 25 °C and 70 weeks batch. Particular attention is brought to the state of the cathode, anode and their corresponding side of the separator.

Local notable differences were also observed about the magnitude of anode degradation. Figure 6-8 shows photographs of the separator vs anode of the 100%

SoC cell of the 25 °C and 70 weeks batch. This prominence in differences of visually assessable degradation varying according to the location in the jelly-roll, being more significant overall closer to the core, is reported on opened 18650 cells as well in a study by Spielbauer et al²⁴⁸. Here it can be observed that the area of the separator closer to the portion of the electrode assembly of the outer winds of the jell-roll is uniformly black (small amounts of uniform deposits of graphite material), while on the contrary, the area closer to the core of the jelly-roll displays partial and total areas of anode delamination, where the graphite anode effectively sticks to the separator. This can be explained by the radial compressive stresses more present towards the centre of the electrode assembly, which have been illustrated previously. It has also been suggested that the volumetric changes of the SiO_x particles impacts the stability of the anode material³²⁷, and might be particularly impactful towards the core of the electrode assembly.



Figure 6-8. Photographs of anode side of the separator from a cell stored at 100% SoC, from the 25°C and 70 weeks batch, with distinction between areas at the outside and close to the core of the jelly-roll.

6.4.2 Positive electrode material characterisation

Figure 6-9 represents the voltage vs capacity plot of the coin cells of harvested cathode material (vs Li^+/Li) of cells stored at 80% and 100% SoC of the 25°C and 52 weeks batch. For both 80% and 100% SoC coin cells, the ordinal “1” represents a disc of cathode material harvested close to the core of the electrode assembly, and “2” closer to the outer part. The same system was kept for the Fresh cell’s coin cells, where “1” is closer to the core and “4” is closer to the most outer part. The purpose of constructing these coin cells from the harvested electrode is to decouple the cathode degradation from the anode and remove any effects of cell balancing or loss of Li at the anode, as the Li half-cell provides an effectively unlimited reserve of Li to re-lithiate the aged cathode. It can be observed that some capacity loss has occurred upon the calendar ageing for the cathode material, compared to the fresh material, but a distinction as to which storage condition led to the most losses is inconclusive. When averaging both coin cell’s discharge capacities for each SoC, 80% SoC would suggest a slightly higher capacity retention; however, the differences observed could be due to an error induced during the cell opening, disassembly, harvesting and reassembly process, which albeit, appears less significant for the four coin cells from the fresh cell. Furthermore, the 80% SoC and 100% SoC cells appear to show a greater capacity retention from the material collected at the outer part of the jelly-roll as opposed to the one closer to the core. However, it appears that it is not the case for the fresh cells, likely for the same reason as exposed previously. This would be consistent with the aforementioned discussion on the reduced material stress underwent by the outer jelly-roll part of cylindrical cells.

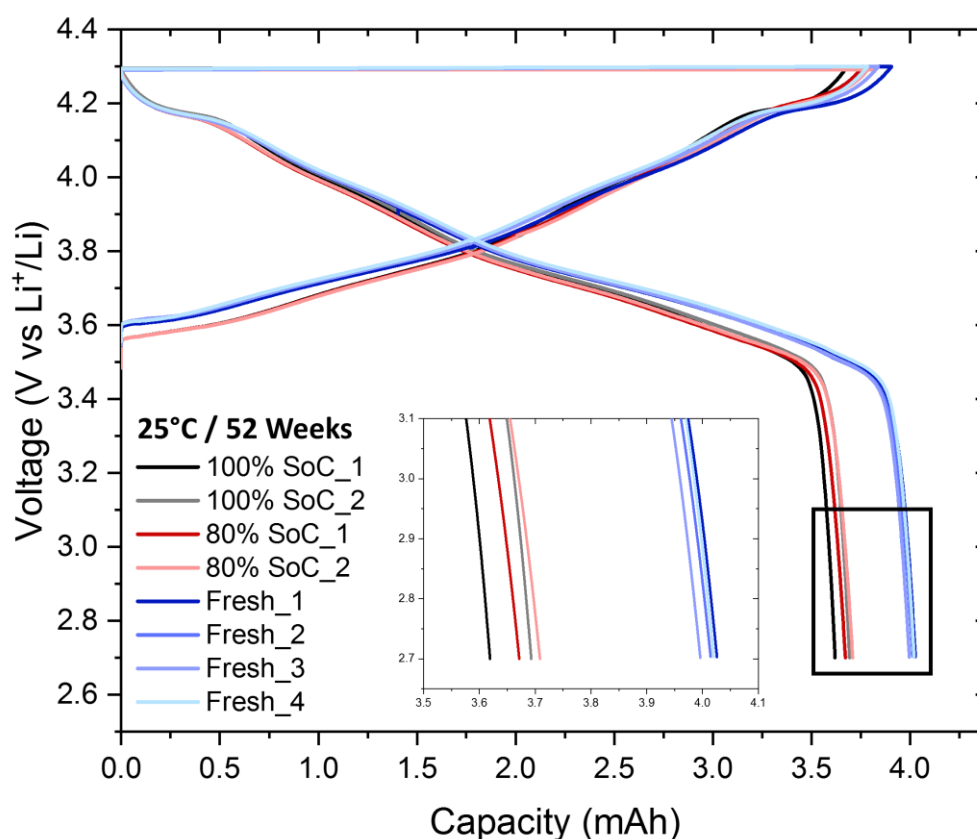


Figure 6-9. Coin cell voltage over capacity of harvested cylindrical cell's cathode material vs Li. Inset is displayed for clarity to assess total discharge capacity. The data represents the second C/20 cycle after assembly.

Lastly, Figure 6-10 displays the NPD and XRD data obtained from harvested cathode material at various SoC from the 25°C and 52 weeks batch for the NPD data, and at 80% SoC at 25°C, for the cells stored during 29 and 70 weeks for the XRD data. A fresh cell sample was also included in both experiments. The Neutron diffraction data was normalised, to account for a particularly small (003) peak and increasing background detected for the 60% SoC cathode material only. These were found to be due to instrumental and sample related parameters, such as the lower quantity of powder material in the sample vials. The original diffraction data, as well as individual plots with refinements and residuals are displayed in Appendix in Figure 8-5. As such, a) shows no notable differences in intensity for the key peaks attributed to Li-Ni intermixing, the (003) and (101) reflections associated with the R-3m space group, which would indicate Li-Ni antisite defects within the crystal structure or other cation disorder^{232,233}. The XRD data emphasises this as well with no additional phases or changes in intensity found for the (003) and (104) peaks¹⁰⁶. The diffraction data

evidences good structural integrity and absence of cation disordering for all samples, whether they are classified by SoC at 52 weeks, or the 80% SoC over 29 or 70 weeks.

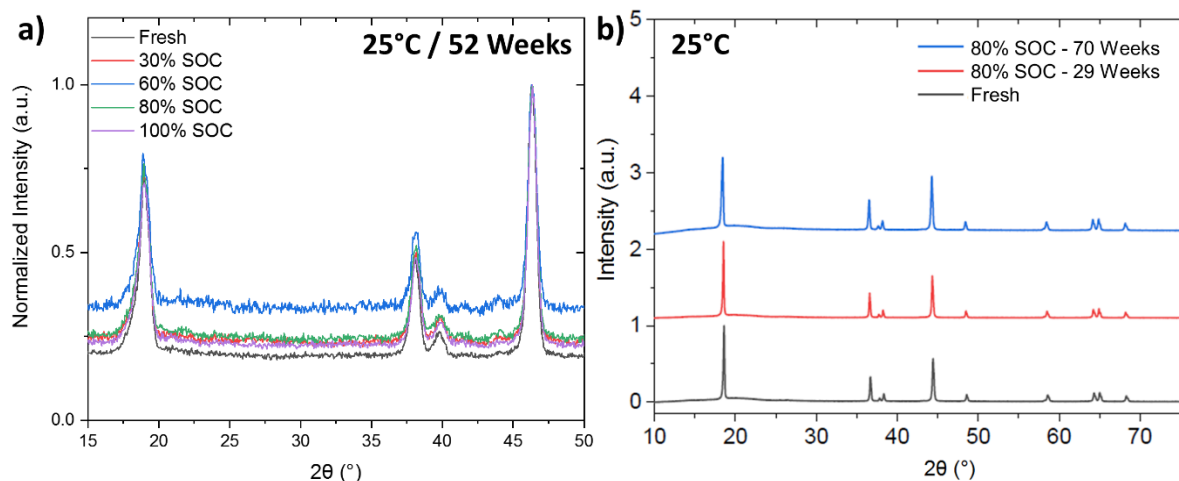


Figure 6-10. a) NPD of the cathode material of fresh, 30% SoC, 60% SoC, 80% SoC and 100% SoC cell of the 25 °C and 52 weeks batch. b) XRD of the cathode material of fresh and 80% SoC cells of 29 and 70 weeks of the 25°C batch.

Overall, these studies show little changes from the cathode material after the calendar ageing, and all evidence point toward an anode/SEI driven measured capacity fade instead. Fundamentally, this suggests that cathode-driven mechanisms that has been proposed in literature and introduced earlier, such as the shuttle mechanism based on oxygen loss at the cathode (in the form of CO_2 , which reduces to oxalate at the anode) proposed by Zülke et al.¹⁴⁰, does not seem to be applying here.

6.4.3 Negative electrode material imaging

Furthermore, the anode surface and morphology were examined using SEM/EDX, and the imaging is displayed in Figure 6-11, highlighting SiO_x particles within the anode of a cell aged for 70 weeks at 100% SoC and 25°C. The microgram in a) reveals significant deterioration and alteration in the SiO_x particles, known for their surface reactivity, as well as how the particle in the centre appears electronically isolated from the rest of the graphite material, with total or partial loss of contact,

depending on the areas. This has been shown to lead to LLI, reducing the availability of Li ions, trapped within the separated SiO_x structure^{79,279}. The analysis further shows evidence for electrolyte decomposition, with fluorine species accumulating on the degraded SiO_x particles, as shown in c), and a carbonate species shell forming on the silicon particles, potentially creating an insulating SEI layer, as shown in d), as it has been discussed in other studies^{23,328}.

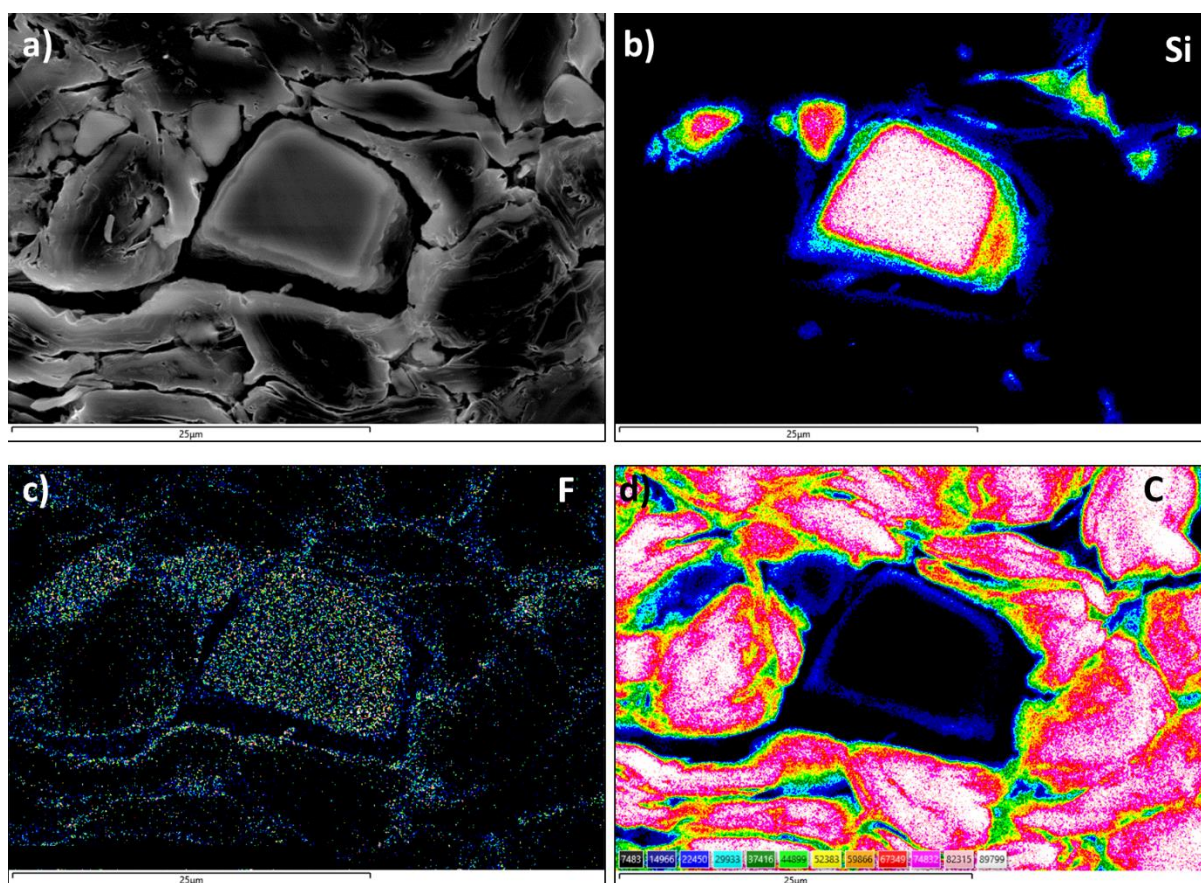


Figure 6-11. SEM/EDX of SiO_x particle in a cell aged for 70 weeks at 100% SoC and 25°C, where a) is the SEM microgram, b) Silicon EDX signal, where an uneven signal represents the particle degradation; c) the Fluorine signal, which indicates electrolyte decomposition and d) the Carbon signal which is a proxy for the SEI formed on the surface. Images obtained by James Gott from WMG.

Subsequent work on this project, carried out at WMG, appears to be confirming the degradation undergone by the SiO_x particles within the anode, and as such, points towards the anode as the core contributor to the various fade behaviours observed. Indeed, experiments such as three-electrode cell data from harvested electrode

material, as well as SIMS all indicated SiO_x damage and further carbonate deposits on these particles, respectively. This suggests that the formation and reformation of SEI at the anode and particularly on the SiO_x particles is the core mechanism at play here, and has been generally described as a prominent ageing mechanism by multiple studies, as the consumption of lithium ions leads to LLI and capacity losses^{329–331}. Furthermore, the additional lithium for the apparent high capacity measured at 100% SoC during the RPT might come from electrochemical electrolyte decomposition, which is supported by fluorine species detected by EDX on the degraded silicon particles. The contribution of the anode overhang, where Li ions diffuse to a greater extent when stored at 100% SoC, and they slowly reincorporated in the electrochemical system during cycling, especially during discharge (from which the capacity is measured during the RPT), is not to be discarded as well¹⁴².

6.5 Conclusions

The studies described in this chapter provided an in-depth examination of the effects of various storage conditions on the degradation of 224 commercial cylindrical 21700 M50 Li-ion cells, focusing on capacity fade and resistance increase as influenced by temperature, SoC and storage duration. The observed degradation followed a two-stage pattern, with an initial sharp decline in capacity during the first few weeks of storage, followed by a more gradual and linear decay. The degradation was more pronounced at higher SoC levels (above 70%) and elevated temperatures, particularly at 60°C, where significant capacity loss and cell failure were observed. The "spoon-shaped" effect, wherein capacity retention improved at 100% SoC, was prominent for all cells at 0°C, 25°C and 45°C, but less evident at higher temperatures, further emphasising the detrimental impact of high temperature on battery life.

Post-mortem analysis, including visual inspections and cathode material characterisation, revealed that the degradation was unlikely to be cathode-driven, contrary to some proposed mechanisms in the literature, like the cross-talk shuttle mechanism proposed by Zülke et al. The cathode material exhibited negligible structural changes, as evidenced by NPD and XRD, indicating that cathode-driven degradation mechanisms, such as cation disordering, oxygen loss, and antisite

defects, were not the dominant factors in this study. The fade observed and spoon-shape effect must, then, primarily be caused by processes occurring at the anode and within the SEI layer.

Macrostructural deformations, analysed via X-ray CT, were found to be influenced predominantly by storage temperature and time, rather than SoC. These deformations were consistently observed in specific areas of the jelly-roll, particularly within the embedded aluminium tab area of influence close to the core, where radial tensile and compressive stresses were more pronounced. The findings indicate that high temperatures exacerbate these mechanical stresses, facilitated by binder decomposition, leading to potential cracking and delamination, which further contribute to cell degradation. These are subsequently exacerbated in the area located at the core, where more prominent partial to total delamination was observed. Further work suggests that the overall degradation mechanisms at play during this study is the SEI growth and reformation, particularly on the SiO_x particles within the anode, leading to particle fracture and their electronic isolation, and more fade observable as SoC increases, but more characterisation is needed to confirm this. Indeed, the overall trends and “spoon-shape” effect have been observed in literature within cells without SiO_x additives in their negative electrodes as well.

Lastly, the ‘spoon-shape’ slight uptick in capacity retention for 100% SoC cells was shown to be misleading and temporary, with cells aged at 100% SoC showing more rapid cycling-induced decay than their counterparts at 80% SoC. This apparent better capacity retention is suggested to be from electrolyte oxidation at the SEI of the SiO_x particles, providing additional Li ions during the subsequent capacity check. The contribution of the anode overhang in this extensive storage time, cannot be discarded as well for the additional Lithium inventory at this high SoC. Overall, this study highlights the critical importance of carefully controlling storage conditions, particularly temperature and SoC, to minimise degradation and extend the life of Li-ion cells. Indeed, it became evident that there are no advantages gained by storing cells at above 50-60% SoC, which might become challenging in real-life applications and consumers EVs, given the amount of time they spend at rest, 96%, as previously shown.

7 Conclusions and Future Work

7.1 Conclusions

This thesis investigated the impact of electrochemical history on the lifetime of commercial Li-ion batteries using various commercial cylindrical cells. The research focused on understanding how different cycling protocols, storage conditions, and temperatures influence battery degradation, specifically through capacity fade and resistance increase. Each chapter targeted a specific aspect of battery performance, providing a comprehensive understanding of the degradation mechanisms under different conditions.

Chapter 4 explored the use of HPC and EIS to link initial conditions to long-term degradation and fade behaviour, showing that CE had the potential to propose reliable predictions about the differences between the likely performance of various cell types. The study demonstrated that consistent test protocols were, however, essential for meaningful comparisons across cell models, highlighting that variations in cycling equipment and procedures could significantly affect results.

Chapter 5 examined the effects of different cycling protocols on NMC811/Graphite cells with and without SiO_x additives, revealing that the cycling protocol significantly influenced degradation, particularly at high rates and low temperatures. The "LowStart" protocol led to severe degradation, including rapid capacity and power fade, and impedance growth, while the "LowEnd" protocol mitigated these effects, mainly due to the difference of time spent at higher voltages and prone to impedance growth. The research emphasised the importance of selecting appropriate protocols to enhance cell durability, noting that the commonly used CCCV protocol provided a good balance between performance and degradation, but that reducing the C-rate towards the top of charge (maintaining an overall average c-rat that was the same as the CCCV) can provide benefits to cell lifetime.

Chapter 6 focused on the impact of storage conditions on cell degradation, analysing 224 cylindrical cells stored under various temperatures and SoC. The study found that high SoC and elevated temperatures accelerated degradation, with an

observable characteristic spoon-shape effect with a small capacity recovery for cells stored at 100% SoC. The findings underscored the absence of observed significant degradation on the cathode material and suggest anode-driven and SEI mechanisms at play to explain the capacity losses and resistance increase.

The collective findings from this thesis provide a robust framework for understanding the degradation mechanisms in commercial cylindrical Li-ion batteries. The studies presented in this thesis consistently demonstrated that the electrochemical history, including cycling protocols, storage conditions, and initial cell status, play a crucial role in determining the long-term performance and lifespan of Li-ion batteries. Additionally, the research emphasises the variability between different cell models and batches, making it clear that universal protocols or assumptions cannot be applied across different Li-ion batteries for different uses and environments. Each cell chemistry and design may respond differently to the same conditions, necessitating customised approaches for testing and evaluation, as the work here focused mainly on Ni-rich and graphite cells.

A key finding from Chapter 5 was the emphasis shown on fade behaviour by time spent at higher voltages, as was the case with the LowStart protocol and tracked via the time spent at CV per cycle. This was particularly true at low temperatures and higher rates, but even cycling of a cell using this protocol at 20°C led to a SoH% of around 20% only. This was shown to lead to a dramatic power fade, led by an increase in impedance (particularly prominently visible at 0% SoC, by far the most intricate SoC region), also evidenced by proxy via tracking of overpotentials and polarisation. This influence of high voltages has been widely reported in the literature, but it was particularly evident with these various protocols. However in these experiments, more than the cathode structural disordering and subsequent RSL formation and oxygen release, evidence suggests a prominent role at the anode, related to SEI growth (at 20°C and ambient temperature) and Li plating (evident at 0°C). This could also partly explain the minimum degradation observed in Chapter 4, albeit done at C/5 for 70 cycles, as there was no CV phase used during cycling, which is a process that prevented degradation but also incidentally shortened the HPC acquisition greatly. Indeed, throughout this thesis, it was shown that a significantly long period of time is spent in CV phase (>50% of the time of charge, at BoL) for most of the cycling carried

out (particularly prominent at either 0.7C or 0°C), something perhaps overlooked in the literature.

Furthermore, several cells used during this thesis possessed SiO_x additives in their anode electrode, which were mainly added by manufacturers aimed at enhancing energy density due to the high specific capacity of silicon. However, the studies show that the cycling rate significantly influences the degradation behaviour of these SiO_x particles, with notable differences in longevity between 0.5C and 0.7C. In most cycling, substantial power fade appeared to be one of the main drivers for cell failure, particularly at higher cycling rates, as evidenced by the pronounced increase in impedance and the disappearance of key SiO_x lithiation peaks after several hundred cycles. While SiO_x additives boost significantly energy density, their short-lived longevity, particularly at high cycling rates, necessitates careful consideration of their use in applications where long-term power retention is critical. For instance, cells “NMC/Graphite”, characterised in Chapter 4, a cell specifically referred to as “high-power” by the manufacturer (and with no SiO_x), notable for its thinner electrode, displayed the highest CE and exceptional cycle life (SoH still above 80% after 14 000 cycles at C/2, 90% DoD). The question of whether this was a conscious decision by the manufacturer or an unintended consequence of their design choices leading to the production of this 'high-power' cell remains unknown. In any case, there are various cell designs and models for various purposes, and careful use of either high-energy or high-power cells, for the appropriate demand, will also ensure the greatest lifetime from the cell application.

The work presented in this thesis attempted to also show that reliable data and valid experiments can be performed on commercial cells, where not all parameters are known, especially the electrolyte additives, which have been shown to have a potentially significant impact on the performance of a cell. However, several studies have published helpful and reliable parameters on known cells, such as electrode material ratios and other key elements to help in that matter, particularly useful for modelling purposes, as it was shown for the cells presented here: MH1, MJ1 and M50. In Chapter 6, a study was performed solely on M50 21700 commercial cells, where this time, the consistency of the cells was an experimental advantage, to track small losses of capacity over calendar ageing. Additionally, a reliable and working cell opening procedure was used to reassemble harvested cell material into coin cells for

individual electrode studies. This was also repeated in the other chapters with a successful application on HPC or variable current charging protocols and the tracking of various performance markers on commercial cells. However, these studies also showed that temperature monitoring while cycling these cells was key, where the oscillation of ambient temperature has a measurable impact on the measured capacity. Lastly, Chapter 4 showed that whenever possible, the use of cells from the same batch is key as well, despite the opacity of the nomenclature used by manufacturers on serial numbers (although guesses can be made). When in control of this, as our cells were provided by ABSL with clear knowledge of various batches, notable and yet consistent differences between cells of different batches were observed, which could compromise the validity of experimental data if this is unknown. For instance, Keil et al., while conducting a calendar ageing study on several 18650 cells, observed that cells from a later production batch with slight material modifications showed reduced cathodic side reactions, leading to significantly better capacity retention from a same cell model¹⁴⁵. Indeed, variations in manufacturing processes, design changes or electrolyte additives can have a profound impact on a cell's performance.

Furthermore, the proposed HPC approach in this thesis was validated using commercial cells, which offer the advantage, yet again, of manufacturing consistency. However, a significant limitation lies in the proprietary nature of commercial formulations, particularly with respect to electrolyte additives, which remain undisclosed by manufacturers, as discussed previously. Alternatively, applying this technique using laboratory-scale cells, such as self-assembled coin or pouch cells, would allow for full control and transparency over electrolyte additives and material choice. Nonetheless, achieving the same level of consistency as commercial cells in laboratory-scale fabrication presents considerable challenges, as reproducibility in small-scale cell production is inherently difficult. As an example, McNulty et al. display cycling data of NMC811/Li coin cells where the CE drops below its stable plateau despite only 50 cycles and the addition of VC in the electrolyte²⁰². As such, the trade-off dilemma between consistency and opacity becomes apparent for commercial/self-assembled cells.

7.2 Future work

Further studies would be to build up on top of the foundations presented in Chapter 4, with HPC cycling and EIS of different cell models of recent and more commonly used chemistries, such as Ni-rich cathode materials, with considerations of the challenges mentioned in the previous paragraph. Improvements and optimisation could be achieved on the setup, as well as an increase in repeats and statistics to improve the level of confidence at which this technique can qualitatively provide an assessment and most importantly: assess how this technique works using a reduced DoD. The experiments presented in this thesis made use of the full voltage window of the cells to assess the CE values. For the space sector, for instance, certain orbit profiles, such as low Earth orbit (LEO), involve a reduced DoD, to go only as low as 20-40%. By attempting the CE assessment in this window only, notable changes are to be expected. Indeed, by staying at a constantly high SoC, limited chemo-mechanical processes take place within the electrochemical system, emphasising mostly the contribution of the anode and the SEI processes, while relieving some stress at the cathode and its intercalation processes. This will incidentally provide the unique advantage of having an even shorter characterisation time, as the whole voltage window will not be used, and a more accurate representation of the real protocol used for these procedures.

The cells studied here with graphite and HC anodes presented widely different CE behaviour and as such, widening the inventory of electrode materials used will be, in this case, invaluable. This will enable and facilitate material optimisation, as the cathode and anode will be decoupled. Furthermore, more in-depth studies could be performed to isolate each individual contributor to CE. By varying additives and materials in in-house assembled coin cells with other known variables and parameters, a comprehensive test matrix could be devised. These future endeavours would benefit from correlating results with imaging and spectroscopy techniques. XRD lattice change parameters within cathode and anode materials would be a primary focus, alongside X-ray CT for macrostructural electrode changes through cycling, which use has been demonstrated in this thesis.

Furthermore, after the results shown in Chapter 5, in addition to the set of electrochemical characterisation tests already performed, spectroscopy techniques ought to be applied to assess some key aspects of the redox states of the electrode materials studied. As discussed in the literature review, operando studies would have to be prioritised to assess changes in real time between each step of the variable current protocols. Such operando studies could be in a three-cell electrode setup (to also assess each individual electrode's EIS), using pouch cells in a synchrotron environment using XRD, to follow the evolution of the c-lattice parameter of the cathode material, particularly in the high SoC region, or XAS, where the evolution of the oxidation states of the Ni ions could be tracked. Particular attention should be directed towards the assessment of the Ni⁴⁺ ions which seem to be more present at higher SoC and are prone to reduction to Ni²⁺ with oxygen release, as previously mentioned, of which EELS data in the thesis indicate that cathode restructuration and RSL formation does occur. The lower C-rate applied during the VCPs compared to the higher C-rate in the CCCV or LowStart in the region would potentially lead to differences in concentration. This information will be then linked to the EIS, as this study showed already a greater contribution of impedance in the lower SoC region. Furthermore, additional work on oxygen release at the cathode/electrolyte interphase could be carried out, whether on the identification of the different oxygen isotopes such as works of Roy et al.³³², or the distinction between singlets and triplets oxygen atoms^{105,123}, and those could then be linked, in various in-situ and operando studies, to the varied protocol.

As it has been shown, however, anode and SEI processes appeared to have been the major driver of capacity and power fade behaviour observed, and as such, further characterisation could be carried out. As such, SEM could be employed, particularly in cells containing SiO_x additives, as demonstrated in Chapter 6, to identify the physical detachment of damaged SiO_x particles from the bulk anode material. This detachment leads to the permanent entrapment of Li ions within said particles and subsequent LAM. EDX could then be utilised to detect the presence of electrolyte decomposition products on the surface of these particles as well. Additionally, opening the cells and conducting visual inspections would allow for the identification of lithium plating, characterised by its distinctive colour. Furthermore, the various stages of graphite lithiation could be precisely identified using XRD, with a spatial focus on the

distribution and phase transitions of the anode material, similar to the approach taken by Wilhelm et al.¹⁹²

It was also shown throughout this thesis that cells cycled at 0.7C exhibit significantly higher degradation linked to the SiO_x DVA marker compared to those cycled at 0.5C, suggesting a pronounced impact of the C-rate on capacity fade. However, this observation is complicated by the fact that the 0.5C cycling was applied to a newer cell model (M50), which may include advancements in SiO_x additives or other manufacturing improvements made by the manufacturer not present in the cells subjected to 0.7C (MJ1). To accurately correlate the longevity of SiO_x-enhanced anodes with cycling rate, a comprehensive study with a well-defined testing matrix could be conducted using the same cell model across different cycling rates. Additionally, coupling these experiments with DVA in the same way it was carried out in this thesis would provide further insights into the specific longevity expected of the SiO_x additives under varying cycling conditions.

In addition, it was shown in Chapter 5 that the cells cycled at 0.7C and 0°C exhibited an increase of voltage close to the end of discharge when close to failure after severe degradation and power fade. While it is likely that this occurs due to significant impedance at 0% SoC and as such, significant Joule heating and temporary re-lithiation of the anode from the thick SEI/plating, further investigations could be carried out, at different and colder temperatures. The appearance of this feature would be monitored for each cycle, and other electrochemical parameters (Overpotentials, polarisation etc.) would then be correlated to it. Subsequent cell opening could also be performed to confirm the plating and/or SEI thickening.

Lastly, the calendar ageing study presented in Chapter 6 was carried out on SiO_x-containing commercial cells demonstrated that the cathode of said cells was relatively well preserved and indicated that the anode and related SEI formation linked to the SiO_x additives were responsible for the observed degradation. X-ray fluorescence (XRF) analysis could be employed to assess potential transition metal migration from the cathode to the anode, a degradation pathway known to occur in Li-ion batteries under certain conditions^{333,334}. Moreover, the ‘spoon-shaped’ recovery of capacity, observed for cells stored at 100% SoC, warrants deeper investigation, as these cells demonstrated poor cycling performance following storage compared to

80% SoC counterparts. Further studies could also reproduce a similar test matrix with similar cell chemistry devoid of SiO_x additives (such as the MH1 cell model) to assess whether the spoon-shaped recovery effect is also present and to elucidate the underlying degradation mechanisms independent of SiO_x .

References

- 1 B. Scrosati, J. Hassoun and Y. K. Sun, Lithium-ion batteries. A look into the future, *Energy Environ. Sci.*, 2011, **4**, 3287–3295.
- 2 M. Endo, C. Kim, K. Nishimura, T. Fujino and K. Miyashita, Recent development of carbon materials for Li ion batteries, *Carbon N. Y.*, 2000, **38**, 183–197.
- 3 H. Shareef, M. M. Islam and A. Mohamed, A review of the stage-of-the-art charging technologies, placement methodologies, and impacts of electric vehicles, *Renew. Sustain. Energy Rev.*, 2016, **64**, 403–420.
- 4 *US-UK Battery Technology Research and Innovation Summit 2022*, 2022.
- 5 European Commission, *Horizon Europe strategic plan 2025-2027 analysis*, 2023.
- 6 A. Sattar, D. Greenwood, M. Dowson and P. Unadkat, *Automotive Lithium ion Battery Recycling in the UK Based on a feasibility study*, 2020.
- 7 L. Gaines and R. Cuenca, Costs of lithium-ion batteries for vehicles, , DOI:10.2172/761281.
- 8 E. Kallitsis, L. Lander, J. Edge, L. Bravo Diaz, A. Brown, G. Kelsall, G. Offer and A. Korre, *Safe and sustainable lithium-ion batteries*, 2022.
- 9 International Energy Agency, *Global EV Outlook 2023*, 2023.
- 10 Energy Transitions Commission, *Material and resource requirements for the energy transition*.
- 11 European Commission, *Eu Net-Zero Industry Act: Making the Eu the Home*, 2023.
- 12 V. Lundaev, A. A. Solomon, T. Le, A. Lohrmann and C. Breyer, Review of critical materials for the energy transition, an analysis of global resources and production databases and the state of material circularity, *Miner. Eng.*, 2023, **203**, 108282.

-
- 13 European commission-JRC, *Critical raw materials and their role in the European aerospace and energy sectors*, 2017.
 - 14 S. P. Michaux, *Assessment of the Extra Capacity Required of Alternative Energy Electrical Power Systems to Completely Replace Fossil Fuels*, 2021.
 - 15 R. M. Salgado, F. Danzi, J. E. Oliveira, A. El-Azab, P. P. Camanho and M. H. Braga, The latest trends in electric vehicles batteries, *Molecules*, 2021, **26**, 1–41.
 - 16 B. Dunn, H. Kamath and J. M. Tarascon, *Science (80-.)*, 2011, 334, 928–935.
 - 17 J. Nelson, S. Misra, Y. Yang, A. Jackson, Y. Liu, H. Wang, H. Dai, J. C. Andrews, Y. Cui and M. F. Toney, In operando X-ray diffraction and transmission X-ray microscopy of lithium sulfur batteries, *J. Am. Chem. Soc.*, 2012, **134**, 6337–6343.
 - 18 McKinsey's, Automotive Revolution & Perspective Towards 2030, *Auto Tech Rev.*, 2016, **5**, 20–25.
 - 19 M. R. Palacín and A. De Guibert, Batteries: Why do batteries fail?, *Science (80-.)*, , DOI:10.1126/science.1253292.
 - 20 E. Nagler, *Standing Still*, 2021.
 - 21 K. Liu, T. R. Ashwin, X. Hu, M. Lucu and W. D. Widanage, An evaluation study of different modelling techniques for calendar ageing prediction of lithium-ion batteries, *Renew. Sustain. Energy Rev.*, 2020, **131**, 110017.
 - 22 D. I. Stroe, M. Swierczynski, S. K. Kær and R. Teodorescu, Degradation Behavior of Lithium-Ion Batteries During Calendar Ageing - The Case of the Internal Resistance Increase, *IEEE Trans. Ind. Appl.*, 2018, **54**, 517–525.
 - 23 J. D. McBrayer, M. T. F. Rodrigues, M. C. Schulze, D. P. Abraham, C. A. Apblett, I. Bloom, G. M. Carroll, A. M. Colclasure, C. Fang, K. L. Harrison, G. Liu, S. D. Minter, N. R. Neale, G. M. Veith, C. S. Johnson, J. T. Vaughey, A. K. Burrell and B. Cunningham, Calendar aging of silicon-containing batteries, *Nat. Energy*, 2021, **6**, 866–872.
 - 24 B. J. Landi, M. J. Ganter, C. D. Cress, R. A. DiLeo and R. P. Raffaele, Carbon

-
- nanotubes for lithium ion batteries, *Energy Environ. Sci.*, 2009, **2**, 638–654.
- 25 R. F. Ziesche, T. Arlt, D. P. Finegan, T. M. M. Heenan, A. Tengattini, D. Baum, N. Kardjilov, H. Markötter, I. Manke, W. Kockelmann, D. J. L. Brett and P. R. Shearing, 4D imaging of lithium-batteries using correlative neutron and X-ray tomography with a virtual unrolling technique, *Nat. Commun.*, 2020, **11**, 1–11.
- 26 T. M. M. Heenan, C. Tan, J. Hack, D. J. L. Brett and P. R. Shearing, Developments in X-ray tomography characterization for electrochemical devices, *Mater. Today*, 2019, **31**, 69–85.
- 27 T. M. M. Heenan, C. Tan, A. J. Wade, R. Jervis, D. J. L. Brett and P. R. Shearing, Theoretical transmissions for X-ray computed tomography studies of lithium-ion battery cathodes, *Mater. Des.*, 2020, 108585.
- 28 K. Märker, P. J. Reeves, C. Xu, K. J. Griffith and C. P. Grey, Evolution of Structure and Lithium Dynamics in LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) Cathodes during Electrochemical Cycling, *Chem. Mater.*, 2019, **31**, 2545–2554.
- 29 D. P. Finegan, A. Vamvakeros, C. Tan, T. M. M. Heenan, S. R. Daemi, N. Seitzman, M. Di Michiel, S. Jacques, A. M. Beale, D. J. L. Brett, P. R. Shearing and K. Smith, Spatial quantification of dynamic inter and intra particle crystallographic heterogeneities within lithium ion electrodes, *Nat. Commun.*, 2020, **11**, 1–11.
- 30 R. D. Weaver, Secondary Lithium-Chlorine Batteries, *19th Annu. Power Sources Sources Conf.*, 1965, 113–115.
- 31 S. Alpanda and A. Peralta-Alva, Oil crisis, energy-saving technological change and the stock market crash of 1973-74, *Rev. Econ. Dyn.*, 2010, **13**, 824–842.
- 32 M. S. Whittingham, Electrical Energy Storage and Intercalation Chemistry, *Science (80-.)*, 1976, **192**, 1126–1127.
- 33 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, Li_xCoO₂ (0 < x ≤ 1): A new cathode material for batteries of high energy density, *Solid State Ionics*, 1981, **3–4**, 171–174.
- 34 A. Patil, V. Patil, D. Wook Shin, J. W. Choi, D. S. Paik and S. J. Yoon, Issue and challenges facing rechargeable thin film lithium batteries, *Mater. Res. Bull.*,

-
- 2008, **43**, 1913–1942.
- 35 A. K. Stephan, The Age of Li-Ion Batteries, *Joule*, 2019, **3**, 2583–2584.
- 36 J. Liu, Z. Bao, Y. Cui, E. J. Dufek, J. B. Goodenough, P. Khalifah, Q. Li, B. Y. Liaw, P. Liu, A. Manthiram, Y. S. Meng, V. R. Subramanian, M. F. Toney, V. V. Viswanathan, M. S. Whittingham, J. Xiao, W. Xu, J. Yang, X. Q. Yang and J. G. Zhang, Pathways for practical high-energy long-cycling lithium metal batteries, *Nat. Energy*, 2019, **4**, 180–186.
- 37 Y. Xu, F. Bahmani, M. Zhou, Y. Li, C. Zhang, F. Liang, S. H. Kazemi, U. Kaiser, G. Meng and Y. Lei, Enhancing potassium-ion battery performance by defect and interlayer engineering, *Nanoscale Horizons*, 2019, **4**, 202–207.
- 38 K. M. Abraham, How Comparable Are Sodium-Ion Batteries to Lithium-Ion Counterparts?, *ACS Energy Lett.*, 2020, **5**, 3544–3547.
- 39 A. Manthiram, B. Song and W. Li, A perspective on nickel-rich layered oxide cathodes for lithium-ion batteries, *Energy Storage Mater.*, 2017, **6**, 125–139.
- 40 X. W. Lou, D. Deng, J. Y. Lee, J. Feng and L. A. Archer, Self-supported formation of needlelike Co₃O₄ nanotubes and their application as lithium-ion battery electrodes, *Adv. Mater.*, 2008, **20**, 258–262.
- 41 S. Santhanagopalan, P. Ramadass and J. (Zhengming) Zhang, Analysis of internal short-circuit in a lithium ion cell, *J. Power Sources*, 2009, **194**, 550–557.
- 42 E. Darcy, Screening Li-ion batteries for internal shorts, *J. Power Sources*, 2007, **174**, 575–578.
- 43 D. P. Finegan, UCL, 2016.
- 44 T. R. Jow, S. A. Delp, J. L. Allen, J. P. Jones and M. C. Smart, Factors limiting Li⁺ charge transfer kinetics in li-ion batteries, *J. Electrochem. Soc.*, 2018, **165**, A361–A367.
- 45 M. Winter and R. J. Brodd, What are batteries, fuel cells, and supercapacitors?, *Chem. Rev.*, 2004, **104**, 4245–4269.
- 46 M. Yoshio, R. J. Brodd and A. Kozawa, *Lithium-Ion Batteries*, Springer New York, New York, NY, 2009, vol. 58.

-
- 47 S. J. Cooper, D. S. Eastwood, J. Gelb, G. Damblanc, D. J. L. Brett, R. S. Bradley, P. J. Withers, P. D. Lee, A. J. Marquis, N. P. Brandon and P. R. Shearing, Image based modelling of microstructural heterogeneity in LiFePO₄ electrodes for Li-ion batteries, *J. Power Sources*, 2014, **247**, 1033–1039.
- 48 J. Billaud, F. Bouville, T. Magrini, C. Villevieille and A. R. Studart, Magnetically aligned graphite electrodes for high-rate performance Li-ion batteries, *Nat. Energy*, 2016, **1**, 16097.
- 49 J. L. Shi, D. D. Xiao, M. Ge, X. Yu, Y. Chu, X. Huang, X. D. Zhang, Y. X. Yin, X. Q. Yang, Y. G. Guo, L. Gu and L. J. Wan, High-Capacity Cathode Material with High Voltage for Li-Ion Batteries, *Adv. Mater.*, 2018, **30**, 1–8.
- 50 L. Madec, L. Ma, K. J. Nelson, R. Petibon, J. P. Sun, I. G. Hill and J. R. Dahn, The effects of a ternary electrolyte additive system on the electrode/electrolyte interfaces in high voltage Li-ion cells, *J. Electrochem. Soc.*, 2016, **163**, A1001–A1009.
- 51 P. A. Locke, *Basic concepts and examples of effective risk communication panel summary: getting the message out.*, New York, Vol. 4., 2011, vol. 101.
- 52 K. J. Park, J. Y. Hwang, H. H. Ryu, F. Maglia, S. J. Kim, P. Lamp, C. S. Yoon and Y. K. Sun, Degradation Mechanism of Ni-Enriched NCA Cathode for Lithium Batteries: Are Microcracks Really Critical?, *ACS Energy Lett.*, 2019, **4**, 1394–1400.
- 53 N. Tsurukawa, S. Prakash and A. Manhart, Social impacts of artisanal cobalt mining in Katanga, Democratic Republic of Congo, *Öko-Institut eV - Inst. Appl. Ecol. Freibg.*, 2011, **49**, 65.
- 54 K. S. Chen, R. Xu, N. S. Luu, E. B. Secor, K. Hamamoto, Q. Li, S. Kim, V. K. Sangwan, I. Balla, L. M. Guiney, J. W. T. Seo, X. Yu, W. Liu, J. Wu, C. Wolverton, V. P. Dravid, S. A. Barnett, J. Lu, K. Amine and M. C. Hersam, Comprehensive Enhancement of Nanostructured Lithium-Ion Battery Cathode Materials via Conformal Graphene Dispersion, *Nano Lett.*, 2017, **17**, 2539–2546.
- 55 A. Eftekhari, LiFePO₄/C nanocomposites for lithium-ion batteries, *J. Power*

-
- Sources, 2017, **343**, 395–411.
- 56 J. Entwistle, R. Ge, K. Pardikar, R. Smith and D. Cumming, Carbon binder domain networks and electrical conductivity in lithium-ion battery electrodes: A critical review, *Renew. Sustain. Energy Rev.*, 2022, **166**, 112624.
- 57 S. T. Myung, F. Maglia, K. J. Park, C. S. Yoon, P. Lamp, S. J. Kim and Y. K. Sun, Nickel-Rich Layered Cathode Materials for Automotive Lithium-Ion Batteries: Achievements and Perspectives, *ACS Energy Lett.*, 2017, **2**, 196–223.
- 58 M. Bianchini, M. Roca-Ayats, P. Hartmann, T. Brezesinski and J. Janek, There and Back Again—The Journey of LiNiO₂ as a Cathode Active Material, *Angew. Chemie - Int. Ed.*, 2019, **58**, 10434–10458.
- 59 P. Ge and M. Fouletier, Electrochemical intercalation of sodium in graphite, *Solid State Ionics*, 1988, **28–30**, 1172–1175.
- 60 R. Kostecki and F. McLarnon, Microprobe study of the effect of Li intercalation on the structure of graphite, *J. Power Sources*, 2003, **119–121**, 550–554.
- 61 C. Pearson, C. Thwaite and N. Russel, The Use of Small Cell Lithium-Ion Batteries for Small Satellite Applications, *18th Annu. AIAA/USU Conf. S*, 2003, 1–11.
- 62 G. J. Dudley, J. De Roche, F. Tonicello and C. Thwaite, Electrical/thermal model of a Sony 18650HC Li-Ion cell, *Eur. Sp. Agency, (Special Publ. ESA SP*, 2005, 499–505.
- 63 E. Buiel and J. R. Dahn, Li-insertion in hard carbon anode materials for Li-ion batteries, *Electrochim. Acta*, 1999, **45**, 121–130.
- 64 H. Azuma, H. Imoto, S. N. I. Yamada and K. Sekai, Advanced carbon anode materials for lithium ion cells, *J. Power Sources*, 1999, **81–82**, 1–7.
- 65 Z. Guo, Z. Xu, F. Xie, J. Jiang, K. Zheng, S. Alabidun, M. Crespo-ribadeneyra, Y. Hu, H. Au and M. Titirici, Investigating the Superior Performance of Hard Carbon Anodes in Sodium-Ion Compared With Lithium- and Potassium-Ion Batteries, *Adv. Mater.*, 2023, **35**, 2304091.

-
- 66 H. Au, M. Crespo-Ribadeneyra and M. M. Titirici, Beyond Li-ion batteries: performance, materials diversification, and sustainability, *One Earth*, 2022, **5**, 207–211.
- 67 Y. Li, A. Vasileiadis, Q. Zhou, Y. Lu, Q. Meng, Y. Li, P. Ombrini, J. Zhao, Z. Chen, Y. Niu, X. Qi, F. Xie, R. van der Jagt, S. Ganapathy, M.-M. Titirici, H. Li, L. Chen, M. Wagemaker and Y.-S. Hu, Origin of fast charging in hard carbon anodes, *Nat. Energy* 2024, 2024, 1–9.
- 68 L. Xie, C. Tang, Z. Bi, M. Song, Y. Fan, C. Yan, X. Li, F. Su, Q. Zhang and C. Chen, *Adv. Energy Mater.*, 2021, **11**, 2101650.
- 69 A. Shellikeri, V. Watson, D. Adams, E. E. Kalu, J. A. Read, T. R. Jow, J. S. Zheng and J. P. Zheng, Investigation of Pre-lithiation in Graphite and Hard-Carbon Anodes Using Different Lithium Source Structures, *J. Electrochem. Soc.*, 2017, **164**, A3914–A3924.
- 70 J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen and D. Bresser, The success story of graphite as a lithium-ion anode material-fundamentals, remaining challenges, and recent developments including silicon (oxide) composites, *Sustain. Energy Fuels*, 2020, **4**, 5387–5416.
- 71 Y. P. Wu, E. Rahm and R. Holze, Carbon anode materials for lithium ion batteries, *J. Power Sources*, 2003, **114**, 228–236.
- 72 A. Eldesoky, M. Bauer, S. Azam, E. Zsoldos, W. Song, R. Weber, S. Hy, M. B. Johnson, M. Metzger and J. R. Dahn, Impact of Graphite Materials on the Lifetime of NMC811/Graphite Pouch Cells: Part I. Material Properties, ARC Safety Tests, Gas Generation, and Room Temperature Cycling, *J. Electrochem. Soc.*, 2021, **168**, 110543.
- 73 Y. Zhang, X. G. Zhang, H. L. Zhang, Z. G. Zhao, F. Li, C. Liu and H. M. Cheng, Composite anode material of silicon/graphite/carbon nanotubes for Li-ion batteries, *Electrochim. Acta*, 2006, **51**, 4994–5000.
- 74 J. H. Lee, W. J. Kim, J. Y. Kim, S. H. Lim and S. M. Lee, Spherical silicon/graphite/carbon composites as anode material for lithium-ion batteries, *J. Power Sources*, 2008, **176**, 353–358.

-
- 75 D. Lin, Y. Liu and Y. Cui, Reviving the lithium metal anode for high-energy batteries, *Nat. Nanotechnol.*, 2017, **12**, 194–206.
- 76 G. G. Eshetu, H. Zhang, X. Judez, H. Adenusi, M. Armand, S. Passerini and E. Figgemeier, Production of high-energy Li-ion batteries comprising silicon-containing anodes and insertion-type cathodes, *Nat. Commun.*, 2021, **12**, 1–14.
- 77 X. Li, M. Zhang, S. Yuan and C. Lu, *ChemElectroChem*, 2020, **7**, 4289–4302.
- 78 X. Li, A. M. Colclasure, D. P. Finegan, D. Ren, Y. Shi, X. Feng, L. Cao, Y. Yang and K. Smith, Degradation mechanisms of high capacity 18650 cells containing Si-graphite anode and nickel-rich NMC cathode, *Electrochim. Acta*, 2019, **297**, 1109–1120.
- 79 J. S. Edge, S. O’Kane, R. Prosser, N. D. Kirkaldy, A. N. Patel, A. Hales, A. Ghosh, W. Ai, J. Chen, J. Yang, S. Li, M. C. Pang, L. Bravo Diaz, A. Tomaszewska, M. W. Marzook, K. N. Radhakrishnan, H. Wang, Y. Patel, B. Wu and G. J. Offer, Lithium ion battery degradation: what you need to know, *Phys. Chem. Chem. Phys.*, 2021, **23**, 8200–8221.
- 80 M. P. Bonkile, Y. Jiang, N. Kirkaldy, V. Sulzer, R. Timms, H. Wang, G. Offer and B. Wu, Coupled electrochemical-thermal-mechanical stress modelling in composite silicon/graphite lithium-ion battery electrodes, *J. Energy Storage*, 2023, **73**, 108609.
- 81 N. Kirkaldy, M. A. Samieian, G. J. Offer, M. Marinescu and Y. Patel, Lithium-Ion Battery Degradation: Measuring Rapid Loss of Active Silicon in Silicon-Graphite Composite Electrodes, *ACS Appl. Energy Mater.*, 2022, **5**, 13367–13376.
- 82 J. Guo, D. Dong, J. Wang, D. Liu, X. Yu, Y. Zheng, Z. Wen, W. Lei, Y. Deng, J. Wang, G. Hong and H. Shao, Silicon-Based Lithium Ion Battery Systems: State-of-the-Art from Half and Full Cell Viewpoint, *Adv. Funct. Mater.*, , DOI:10.1002/adfm.202102546.
- 83 T. M. M. Heenan, A. Jnawali, M. D. R. Kok, T. G. Tranter, C. Tan, A. Dimitrijevic, R. Jervis, D. J. L. Brett and P. R. Shearing, An Advanced Microstructural and Electrochemical Datasheet on 18650 Li-Ion Batteries with Nickel-Rich NMC811 Cathodes and Graphite-Silicon Anodes, *J. Electrochem. Soc.*, 2020, **167**,

-
- 140530.
- 84 X. J. S. Dahn J.R, Zheng T, Liu Y, Mechanisms for Lithium Insertion in Carbanaceous Materials, *Americican Assoc. Adv. Sci.*, 1995, **270**, 590–593.
- 85 R. Raccichini, A. Varzi, S. Passerini and B. Scrosati, The role of graphene for electrochemical energy storage, *Nat. Mater.*, 2015, **14**, 271–279.
- 86 M. Root, *The TAB Battery Book: An In-Depth Guide to Construction, Design, and Use*, 2010.
- 87 S. S. Zhang, A review on electrolyte additives for lithium-ion batteries, *J. Power Sources*, 2006, **162**, 1379–1394.
- 88 S. Chattopadhyay, A. L. Lipson, H. J. Karmel, J. D. Emery, T. T. Fister, P. A. Fenter, M. C. Hersam and M. J. Bedzyk, In situ X-ray study of the solid electrolyte interphase (SEI) formation on graphene as a model Li-ion battery anode, *Chem. Mater.*, 2012, **24**, 3038–3043.
- 89 M. Balasubramanian, H. S. Lee, X. Sun, X. Q. Yang, A. R. Moodenbaugh, J. McBreen, D. A. Fischer and Z. Fu, Formation of SEI on Cycled Lithium-Ion Battery Cathodes: Soft X-Ray Absorption Study, *Electrochem. Solid-State Lett.*, 2002, **5**, A22.
- 90 B. Michalak, B. B. Berkes, H. Sommer, T. Brezesinski and J. Janek, Electrochemical cross-talk leading to gas evolution and capacity fade in LiNi_{0.5}Mn_{1.5}O₄/graphite full-cells, *J. Phys. Chem. C*, 2017, **121**, 211–216.
- 91 A. L. Michan, B. S. Parimalam, M. Leskes, R. N. Kerber, T. Yoon, C. P. Grey and B. L. Lucht, Fluoroethylene carbonate and vinylene carbonate reduction: Understanding lithium-ion battery electrolyte additives and solid electrolyte interphase formation, *Chem. Mater.*, 2016, **28**, 8149–8159.
- 92 E. Peled, The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems—The Solid Electrolyte Interphase Model, *J. Electrochem. Soc.*, 1979, **126**, 2047–2051.
- 93 J. Xie and Y. C. Lu, A retrospective on lithium-ion batteries, *Nat. Commun.*, 2020, **11**, 9–12.

-
- 94 S. K. Heiskanen, J. Kim and B. L. Lucht, Generation and Evolution of the Solid Electrolyte Interphase of Lithium-Ion Batteries, *Joule*, 2019, **3**, 2322–2333.
- 95 K. Tasaki, A. Goldberg, J.-J. Lian, M. Walker, A. Timmons and S. J. Harris, Solubility of Lithium Salts Formed on the Lithium-Ion Battery Negative Electrode Surface in Organic Solvents, *J. Electrochem. Soc.*, 2009, **156**, A1019.
- 96 Y. Zhou, M. Su, X. Yu, Y. Zhang, J. G. Wang, X. Ren, R. Cao, W. Xu, D. R. Baer, Y. Du, O. Borodin, Y. Wang, X. L. Wang, K. Xu, Z. Xu, C. Wang and Z. Zhu, Real-time mass spectrometric characterization of the solid–electrolyte interphase of a lithium-ion battery, *Nat. Nanotechnol.*, 2020, **15**, 224–230.
- 97 M. Steinhauer, S. Risse, N. Wagner and K. A. Friedrich, Investigation of the Solid Electrolyte Interphase Formation at Graphite Anodes in Lithium-Ion Batteries with Electrochemical Impedance Spectroscopy, *Electrochim. Acta*, 2017, **228**, 652–658.
- 98 F. Zheng, M. Kotobuki, S. Song, M. O. Lai and L. Lu, Review on solid electrolytes for all-solid-state lithium-ion batteries, *J. Power Sources*, 2018, **389**, 198–213.
- 99 J. Janek and W. G. Zeier, Challenges in speeding up solid-state battery development, *Nat. Energy*, 2023, **8**, 230–240.
- 100 Y. Xiao, Y. Wang, S. H. Bo, J. C. Kim, L. J. Miara and G. Ceder, Understanding interface stability in solid-state batteries, *Nat. Rev. Mater.*, 2020, **5**, 105–126.
- 101 P. Arora and Z. Zhang, Battery separators, *Chem. Rev.*, 2004, **104**, 4419–4462.
- 102 X. Huang and J. Hitt, Lithium ion battery separators: Development and performance characterization of a composite membrane, *J. Memb. Sci.*, 2013, **425–426**, 163–168.
- 103 X. Huang, Separator technologies for lithium-ion batteries, *J. Solid State Electrochem.*, 2011, **15**, 649–662.
- 104 C. R. Birkel, M. R. Roberts, E. McTurk, P. G. Bruce and D. A. Howey, Degradation diagnostics for lithium ion cells, *J. Power Sources*, 2017, **341**, 373–386.
- 105 J. Wandt, A. T. S. Freiberg, A. Ogrodnik and H. A. Gasteiger, Singlet oxygen evolution from layered transition metal oxide cathode materials and its

-
- implications for lithium-ion batteries, *Mater. Today*, 2018, **21**, 825–833.
- 106 Y. Xi, Y. Liu, D. Zhang, S. Jin, R. Zhang and M. Jin, Comparative study of the electrochemical performance of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials for lithium ion batteries, *Solid State Ionics*, 2018, **327**, 27–31.
- 107 P. Rozier and J. M. Tarascon, Review—Li-Rich Layered Oxide Cathodes for Next-Generation Li-Ion Batteries: Chances and Challenges, *J. Electrochem. Soc.*, 2015, **162**, A2490–A2499.
- 108 R. Jung, M. Metzger, F. Maglia, C. Stinner and H. A. Gasteiger, Oxygen Release and Its Effect on the Cycling Stability of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) Cathode Materials for Li-Ion Batteries, *J. Electrochem. Soc.*, 2017, **164**, A1361–A1377.
- 109 C. Xu, P. J. Reeves, Q. Jacquet and C. P. Grey, Phase Behavior during Electrochemical Cycling of Ni-Rich Cathode Materials for Li-Ion Batteries, *Adv. Energy Mater.*, 2021, **11**, 1–12.
- 110 R. Jung, R. Morasch, P. Karayaylali, K. Phillips, F. Maglia, C. Stinner, Y. Shao-Horn and H. A. Gasteiger, Effect of ambient storage on the degradation of ni-rich positive electrode materials (NMC811) for li-ion batteries, *J. Electrochem. Soc.*, 2018, **165**, A132–A141.
- 111 R. T. Haasch, S. E. Trask and D. P. Abraham, Editorial: Lithium-bearing oxides for rechargeable Li-ion batteries, *Surf. Sci. Spectra*, 2019, **26**, 014002.
- 112 A. J. Naylor, E. Makkos, J. Maibach, N. Guerrini, A. Sobkowiak, E. Björklund, J. G. Lozano, A. S. Menon, R. Younesi, M. R. Roberts, K. Edström, S. Islam and P. G. Bruce, Depth-dependent oxygen redox activity in lithium-rich layered oxide cathodes, *J. Mater. Chem. A*, 2019, 25355–25368.
- 113 H. J. Noh, S. Youn, C. S. Yoon and Y. K. Sun, Comparison of the structural and electrochemical properties of layered $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ($x = 1/3, 0.5, 0.6, 0.7, 0.8$ and 0.85) cathode material for lithium-ion batteries, *J. Power Sources*, 2013, **233**, 121–130.
- 114 J. Xu, F. Lin, M. M. Doeff and W. Tong, A review of Ni-based layered oxides for rechargeable Li-ion batteries, *J. Mater. Chem. A*, 2017, **5**, 874–901.

-
- 115 L. Wu, K. W. Nam, X. Wang, Y. Zhou, J. C. Zheng, X. Q. Yang and Y. Zhu, Structural origin of overcharge-induced thermal instability of Ni-containing layered-cathodes for high-energy-density lithium batteries, *Chem. Mater.*, 2011, **23**, 3953–3960.
- 116 A. S. Menon, N. Shah, J. A. Gott, E. Fiamegkou, M. J. W. Ogley, G. J. P. Fajardo, N. Vaenas, I. Ellis, N. Ravichandran, P. Cloetens, D. Karpov, J. M. Warnett, P. Malliband, D. Walker, G. West, M. Loveridge and L. F. J. Piper, Quantifying Electrochemical Degradation in Single-Crystalline Postmortem Investigations, *Phys. Rev. Appl.*, 2024, **10**, 1.
- 117 J. Kim, H. Lee, H. Cha, M. Yoon, M. Park and J. Cho, Prospect and Reality of Ni-Rich Cathode for Commercialization, *Adv. Energy Mater.*, 2018, **8**, 1–25.
- 118 E. Hu, X. Wang, X. Yu and X. Q. Yang, Probing the Complexities of Structural Changes in Layered Oxide Cathode Materials for Li-Ion Batteries during Fast Charge-Discharge Cycling and Heating, *Acc. Chem. Res.*, 2018, **51**, 290–298.
- 119 Y. Su, Q. Zhang, L. Chen, L. Bao, Y. Lu, S. Chen and F. Wu, Stress accumulation in Ni-rich layered oxide cathodes: Origin, impact, and resolution, *J. Energy Chem.*, 2022, **65**, 236–253.
- 120 K. Kleiner, B. Strehle, A. R. Baker, S. J. Day, C. C. Tang, I. Buchberger, F. F. Chesneau, H. A. Gasteiger and M. Piana, Origin of High Capacity and Poor Cycling Stability of Li-Rich Layered Oxides: A Long-Duration in Situ Synchrotron Powder Diffraction Study, *Chem. Mater.*, 2018, **30**, 3656–3667.
- 121 R. Jung, P. Strobl, F. Maglia, C. Stinner and H. A. Gasteiger, Temperature dependence of oxygen release from LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622) cathode materials for Li-ion batteries, *J. Electrochem. Soc.*, 2018, **165**, A2869–A2879.
- 122 V. Charbonneau, A. Lasia and G. Brisard, Impedance studies of Li⁺ diffusion in nickel manganese cobalt oxide (NMC) during charge/discharge cycles, *J. Electroanal. Chem.*, , DOI:10.1016/j.jelechem.2020.113944.
- 123 A. T. S. Freiberg, M. K. Roos, J. Wandt, R. De Vivie-Riedle and H. A. Gasteiger, Singlet Oxygen Reactivity with Carbonate Solvents Used for Li-Ion Battery Electrolytes, *J. Phys. Chem. A*, 2018, **122**, 8828–8839.

-
- 124 H. Zhang, F. Omenya, P. Yan, L. Luo, M. S. Whittingham, C. Wang and G. Zhou, Rock-Salt Growth-Induced (003) Cracking in a Layered Positive Electrode for Li-Ion Batteries, *ACS Energy Lett.*, 2017, **2**, 2607–2615.
- 125 W. Liu, P. Oh, X. Liu, M. J. Lee, W. Cho, S. Chae, Y. Kim and J. Cho, Nickel-Rich Layered Lithium Transition-Metal Oxide for High-Energy Lithium-Ion Batteries, *Angew. Chemie - Int. Ed.*, 2015, **54**, 4440–4457.
- 126 L. Cai, Z. Liu, K. An and C. Liang, Probing Li-Ni cation disorder in $\text{Li}_{1-x}\text{Ni}_{1+x-y}\text{Al}_y\text{O}_2$ cathode materials by neutron diffraction, *J. Electrochem. Soc.*, 2012, **159**, 924–928.
- 127 M. Dixit, B. Markovsky, F. Schipper, D. Aurbach and D. T. Major, Origin of Structural Degradation during Cycling and Low Thermal Stability of Ni-Rich Layered Transition Metal-Based Electrode Materials, *J. Phys. Chem. C*, 2017, **121**, 22628–22636.
- 128 M. Metzger, C. Marino, J. Sicklinger, D. Haering and H. A. Gasteiger, Anodic oxidation of conductive carbon and ethylene carbonate in high-voltage Li-Ion batteries quantified by on-line electrochemical mass spectrometry, *J. Electrochem. Soc.*, 2015, **162**, A1123–A1134.
- 129 F. Wu, J. Tian, Y. Su, J. Wang, C. Zhang, L. Bao, T. He, J. Li and S. Chen, Effect of Ni^{2+} content on lithium/nickel disorder for Ni-rich cathode materials, *ACS Appl. Mater. Interfaces*, 2015, **7**, 7702–7708.
- 130 Y. Xia, J. Zheng, C. Wang and M. Gu, Designing principle for Ni-rich cathode materials with high energy density for practical applications, *Nano Energy*, 2018, **49**, 434–452.
- 131 K. Min, S. W. Seo, Y. Y. Song, H. S. Lee and E. Cho, A first-principles study of the preventive effects of Al and Mg doping on the degradation in $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials, *Phys. Chem. Chem. Phys.*, 2017, **19**, 1762–1769.
- 132 P. Keil, S. F. Schuster, J. Wilhelm, J. Travi, A. Hauser, R. C. Karl and A. Jossen, Calendar Aging of Lithium-Ion Batteries, *J. Electrochem. Soc.*, 2016, **163**, A1872–A1880.

-
- 133 R. Gauthier, A. Luscombe, T. Bond, M. Bauer, M. Johnson, J. Harlow, A. Louli and J. R. Dahn, How do Depth of Discharge, C-rate and Calendar Age Affect Capacity Retention, Impedance Growth, the Electrodes, and the Electrolyte in Li-Ion Cells?, *J. Electrochem. Soc.*, , DOI:10.1149/1945-7111/ac4b82.
- 134 K. Kalaga, M. T. F. Rodrigues, S. E. Trask, I. A. Shkrob and D. P. Abraham, Calendar-life versus cycle-life aging of lithium-ion cells with silicon-graphite composite electrodes, *Electrochim. Acta*, 2018, **280**, 221–228.
- 135 I. Zilberman, J. Sturm and A. Jossen, Reversible self-discharge and calendar aging of 18650 nickel-rich, silicon-graphite lithium-ion cells, *J. Power Sources*, 2019, **425**, 217–226.
- 136 B. Strehle, F. Friedrich and H. A. Gasteiger, A Comparative Study of Structural Changes during Long-Term Cycling of NCM-811 at Ambient and Elevated Temperatures, *J. Electrochem. Soc.*, 2021, **168**, 050512.
- 137 D. Werner, S. Paarmann and T. Wetzel, Calendar aging of li-ion cells—experimental investigation and empirical correlation, *Batteries*, , DOI:10.3390/batteries7020028.
- 138 K. Jalkanen, J. Karppinen, L. Skogström, T. Laurila, M. Nisula and K. Vuorilehto, Cycle aging of commercial NMC/graphite pouch cells at different temperatures, *Appl. Energy*, 2015, **154**, 160–172.
- 139 D. Dvorak, H. Popp, T. Bäuml, D. Simic and H. Kapeller, Arrhenius-Equation Based Approach for Modelling Lithium-Ion Battery Aging Effects, *ITI Symp.*
- 140 A. Zülke, Y. Li, P. Keil, R. Burrell, S. Belaisch, M. Nagarathinam, M. P. Mercer and H. E. Hoster, High-Energy Nickel-Cobalt-Aluminium Oxide (NCA) Cells on Idle: Anode- versus Cathode-Driven Side Reactions, *Batter. Supercaps*, 2021, **4**, 934–947.
- 141 I. Zilberman, S. Ludwig and A. Jossen, Cell-to-cell variation of calendar aging and reversible self-discharge in 18650 nickel-rich, silicon–graphite lithium-ion cells, *J. Energy Storage*, 2019, **26**, 100900.
- 142 M. Lewerenz, G. Fuchs, L. Becker and D. U. Sauer, Irreversible calendar aging and quantification of the reversible capacity loss caused by anode overhang, *J.*

-
- Energy Storage*, 2018, **18**, 149–159.
- 143 H. Zhang, H. Liu, L. F. J. Piper, M. S. Whittingham and G. Zhou, Oxygen Loss in Layered Oxide Cathodes for Li-Ion Batteries: Mechanisms, Effects, and Mitigation, *Chem. Rev.*, 2022, **122**, 5641–5681.
- 144 Y. S. Kang, S. Y. Park, K. Ito, Y. Kubo, Y. Shin, D. Y. Kim, D. H. Seo, S. Kim, J. H. Park, S. G. Doo, M. Koh, J. A. Seo and K. Park, Revealing the structural degradation mechanism of the Ni-rich cathode surface: How thick is the surface?, *J. Power Sources*, 2021, **490**, 229542.
- 145 P. Keil and A. Jossen, Calendar Aging of NCA Lithium-Ion Batteries Investigated by Differential Voltage Analysis and Coulomb Tracking, *J. Electrochem. Soc.*, 2017, **164**, A6066–A6074.
- 146 C. Y. Wang, T. Xu, S. Ge, G. Zhang, X. G. Yang and Y. Ji, A fast rechargeable lithium-ion battery at subfreezing temperatures, *J. Electrochem. Soc.*, 2016, **163**, A1944–A1950.
- 147 A. Tomaszewska, Z. Chu, X. Feng, S. O’Kane, X. Liu, J. Chen, C. Ji, E. Endler, R. Li, L. Liu, Y. Li, S. Zheng, S. Vetterlein, M. Gao, J. Du, M. Parkes, M. Ouyang, M. Marinescu, G. Offer and B. Wu, Lithium-ion battery fast charging: A review, *eTransportation*, 2019, **1**, 100011.
- 148 X. G. Yang, G. Zhang, S. Ge and C. Y. Wang, Fast charging of lithium-ion batteries at all temperatures, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 7266–7271.
- 149 J. Jiang and C. Zhang, *Fundamentals and Applications of Lithium-ion Batteries in Electric Drive Vehicles*, Wiley, 2015, vol. 6.
- 150 A. Abdollahi, X. Han, N. Raghunathan, B. Pattipati, B. Balasingam, K. R. Pattipati, Y. Bar-Shalom and B. Card, Optimal charging for general equivalent electrical battery model, and battery life management, *J. Energy Storage*, 2017, **9**, 47–58.
- 151 X. G. Yang and C. Y. Wang, Understanding the trilemma of fast charging, energy density and cycle life of lithium-ion batteries, *J. Power Sources*, 2018, **402**, 489–498.

-
- 152 K. Zaghib, M. Dontigny, A. Guerfi, P. Charest, I. Rodrigues, A. Mauger and C. M. Julien, Safe and fast-charging Li-ion battery with long shelf life for power applications, *J. Power Sources*, 2011, **196**, 3949–3954.
- 153 J. J. Chen, F. C. Yang, C. C. Lai, Y. S. Hwang and R. G. Lee, A high-efficiency multimode Li-Ion battery charger with variable current source and controlling previous-stage supply voltage, *IEEE Trans. Ind. Electron.*, 2009, **56**, 2469–2478.
- 154 P. H. L. Notten, J. H. G. O. H. Veld and J. R. G. Van Beek, Boostcharging Li-ion batteries: A challenging new charging concept, *J. Power Sources*, 2005, **145**, 89–94.
- 155 Y. H. Liu, C. H. Hsieh and Y. F. Luo, Search for an optimal five-step charging pattern for li-ion batteries using consecutive orthogonal arrays, *IEEE Trans. Energy Convers.*, 2011, **26**, 654–661.
- 156 T. T. Vo, X. Chen, W. Shen and A. Kapoor, New charging strategy for lithium-ion batteries based on the integration of Taguchi method and state of charge estimation, *J. Power Sources*, 2015, **273**, 413–422.
- 157 M. Abdel-Monem, K. Trad, N. Omar, O. Hegazy, P. Van den Bossche and J. Van Mierlo, Influence analysis of static and dynamic fast-charging current profiles on ageing performance of commercial lithium-ion batteries, *Energy*, 2017, **120**, 179–191.
- 158 J. Jaguemont, N. Omar, M. Abdel-Monem, P. Van den Bossche and J. Van Mierlo, Fast-charging investigation on high-power and high-energy density pouch cells with 3D-thermal model development, *Appl. Therm. Eng.*, 2018, **128**, 1282–1296.
- 159 C. Zou, X. Hu, Z. Wei and X. Tang, Electrothermal dynamics-conscious lithium-ion battery cell-level charging management via state-monitored predictive control, *Energy*, 2017, **141**, 250–259.
- 160 X. Wu, W. Shi and J. Du, Multi-objective optimal charging method for lithium-ion batteries, *Energies*, 2017, **10**, 1–18.
- 161 P. M. Attia, A. Grover, N. Jin, K. A. Severson, T. M. Markov, Y. Liao, M. H. Chen,

-
- B. Cheong, N. Perkins, Z. Yang, P. K. Herring, M. Aykol, S. J. Harris, R. D. Braatz, S. Ermon and W. C. Chueh, Closed-loop optimization of fast-charging protocols for batteries with machine learning, *Nature*, 2020, **578**, 397–402.
- 162 D. Wang, Y. Bao and J. Shi, Online lithium-ion battery internal resistance measurement application in state-of-charge estimation using the extended kalman filter, *Energies*, , DOI:10.3390/en10091284.
- 163 M. A. Hannan, M. S. H. Lipu, A. Hussain and A. Mohamed, A review of lithium-ion battery state of charge estimation and management system in electric vehicle applications: Challenges and recommendations, *Renew. Sustain. Energy Rev.*, 2017, **78**, 834–854.
- 164 D. Kim, K. Koo, J. J. Jeong, T. Goh and S. W. Kim, Second-order discrete-time sliding mode observer for state of charge determination based on a dynamic resistance li-ion battery model, *Energies*, 2013, **6**, 5538–5551.
- 165 P. Iurilli, C. Brivio and V. Wood, On the use of electrochemical impedance spectroscopy to characterize and model the aging phenomena of lithium-ion batteries: a critical review, *J. Power Sources*, 2021, **505**, 229860.
- 166 V. Vivier and M. E. Orazem, Impedance Analysis of Electrochemical Systems, *Chem. Rev.*, 2022, **122**, 11131–11168.
- 167 Q. A. Huang, Y. Shen, Y. Huang, L. Zhang and J. Zhang, Impedance Characteristics and Diagnoses of Automotive Lithium-Ion Batteries at 7.5% to 93.0% State of Charge, *Electrochim. Acta*, 2016, **219**, 751–765.
- 168 K. Märker, P. J. Reeves, C. Xu, K. J. Griffith and C. P. Grey, Evolution of Structure and Lithium Dynamics in $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) Cathodes during Electrochemical Cycling, *Chem. Mater.*, 2019, **31**, 2545–2554.
- 169 D. Di Lecce, R. Verrelli and J. Hassoun, Lithium-ion batteries for sustainable energy storage: Recent advances towards new cell configurations, *Green Chem.*, 2017, **19**, 3442–3467.
- 170 D. Di Lecce, D. Campanella and J. Hassoun, Insight on the Enhanced Reversibility of a Multimetal Layered Oxide for Sodium-Ion Battery, *J. Phys. Chem. C*, 2018, **122**, 23925–23933.

-
- 171 Y. C. Chien, H. Liu, A. S. Menon, W. R. Brant, D. Brandell and M. J. Lacey, Rapid determination of solid-state diffusion coefficients in Li-based batteries via intermittent current interruption method, *Nat. Commun.*, 2023, **14**, 35–37.
- 172 S. D. Kang and W. C. Chueh, Galvanostatic Intermittent Titration Technique Reinvented: Part I. A Critical Review, *J. Electrochem. Soc.*, 2021, **168**, 120504.
- 173 F. C. Walsh, The Overall Rates of Electrode Reactions: Faraday's Laws of Electrolysis, *Trans. IMF*, 1991, **69**, 155–157.
- 174 J. Xu, R. D. Deshpande, J. Pan, Y.-T. Cheng and V. S. Battaglia, Electrode Side Reactions, Capacity Loss and Mechanical Degradation in Lithium-Ion Batteries, *J. Electrochem. Soc.*, 2015, **162**, A2026–A2035.
- 175 D. Goswami, D. Yogi and K. Frank, *Energy Conversion*, CRC Press., 2007.
- 176 A. M. Crespi and P. M. Skarstad, Parasitic reactions and the balance of materials in lithium batteries for implantable medical devices, *J. Power Sources*, 1993, **43**, 119–125.
- 177 M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev and R. J. Staniewicz, Main aging mechanisms in Li ion batteries, *J. Power Sources*, 2005, **146**, 90–96.
- 178 H. Zhao, W. Y. A. Lam, L. Wang, H. Xu, W. A. Daoud and X. He, The significance of detecting imperceptible physical/chemical changes/reactions in lithium-ion batteries: a perspective, *Energy Environ. Sci.*, 2022, **15**, 2329–2355.
- 179 J. Wang, Y. Bai, M. Wu, J. Yin and W. F. Zhang, Preparation and electrochemical properties of TiO₂ hollow spheres as an anode material for lithium-ion batteries, *J. Power Sources*, 2009, **191**, 614–618.
- 180 T. F. Yi, C. Y. Li, Y. R. Zhu, J. Shu and R. S. Zhu, Comparison of structure and electrochemical properties for 5 v LiNi_{0.5}Mn_{1.5}O₄ and LiNi_{0.4}Cr_{0.2}Mn_{1.4}O₄ cathode materials, *J. Solid State Electrochem.*, 2009, **13**, 913–919.
- 181 M.-Q. Li, M.-Z. Qu, X.-Y. He and Z.-L. Yu, Electrochemical Performance of Si/Graphite/Carbon Composite Electrode in Mixed Electrolytes Containing LiBOB and LiPF₆, *J. Electrochem. Soc.*, 2009, **156**, A294.

-
- 182 J. J. Murray and J. E. A. Alderson, Precision cycling and coulombic efficiency measurements on Li/MoS₂ and Li,Al/FeS cells, *J. Power Sources*, 1989, **26**, 293–299.
- 183 A. J. Smith, J. C. Burns and J. R. Dahn, A high precision study of the coulombic efficiency of Li-Ion batteries, *Electrochem. Solid-State Lett.*, 2010, **13**, 177–180.
- 184 A. J. Smith, J. C. Burns, S. Trussler and J. R. Dahn, Precision Measurements of the Coulombic Efficiency of Lithium-Ion Batteries and of Electrode Materials for Lithium-Ion Batteries, *J. Electrochem. Soc.*, 2010, **157**, A196.
- 185 A. J. Smith, J. C. Burns, X. Zhao, D. Xiong and J. R. Dahn, A High Precision Coulometry Study of the SEI Growth in Li/Graphite Cells, *J. Electrochem. Soc.*, 2011, **158**, A447.
- 186 J. E. Harlow, D. A. Stevens, J. C. Burns, J. N. Reimers and J. R. Dahn, Ultra High Precision Study on High Capacity Cells for Large Scale Automotive Application, *J. Electrochem. Soc.*, 2013, **160**, A2306–A2310.
- 187 J. R. Dahn, J. C. Burns and D. A. Stevens, Importance of coulombic efficiency measurements in R & D efforts to obtain long-lived li-ion batteries, *Electrochem. Soc. Interface*, 2016, **25**, 75–78.
- 188 Z. Lin, T. Liu, X. Ai and C. Liang, Aligning academia and industry for unified battery performance metrics, *Nat. Commun.*, 2018, **9**, 8–12.
- 189 T. M. Bond, J. C. Burns, D. A. Stevens, H. M. Dahn and J. R. Dahn, Improving Precision and Accuracy in Coulombic Efficiency Measurements of Li-Ion Batteries, *J. Electrochem. Soc.*, 2013, **160**, A521–A527.
- 190 T. M. Bond, DALHOUSIE UNIVERSITY, 2012.
- 191 A. Zülke, Y. Li, P. Keil and H. Hoster, Communication—Why High-Precision Coulometry and Lithium Plating Studies on Commercial Lithium-Ion Cells Require Thermal Baths, *J. Electrochem. Soc.*, 2019, **166**, A2921–A2923.
- 192 J. Wilhelm, S. Seidlmayer, P. Keil, J. Schuster, A. Kriele, R. Gilles and A. Jossen, Cycling capacity recovery effect: A coulombic efficiency and post-mortem study, *J. Power Sources*, 2017, **365**, 327–338.

-
- 193 A. J. Smith, J. C. Burns, D. Xiong and J. R. Dahn, Interpreting High Precision Coulometry Results on Li-ion Cells, *J. Electrochem. Soc.*, 2011, **158**, A1136–A1142.
- 194 A. J. Smith, J. C. Burns and J. R. Dahn, High-precision differential capacity analysis of LiMn₂O₄/graphite cells, *Electrochem. Solid-State Lett.*, 2011, **14**, 12–15.
- 195 M. Winter, The solid electrolyte interphase - The most important and the least understood solid electrolyte in rechargeable Li batteries, *Zeitschrift fur Phys. Chemie*, 2009, **223**, 1395–1406.
- 196 P. Verma, P. Maire and P. Novák, A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries, *Electrochim. Acta*, 2010, **55**, 6332–6341.
- 197 S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure and D. L. Wood, The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling, *Carbon N. Y.*, 2016, **105**, 52–76.
- 198 L. D. Ellis, J. P. Allen, I. G. Hill and J. R. Dahn, High-Precision Coulometry Studies of the Impact of Temperature and Time on SEI Formation in Li-Ion Cells, *J. Electrochem. Soc.*, 2018, **165**, A1529–A1536.
- 199 J. C. Burns, A. Kassam, N. N. Sinha, L. E. Downie, L. Solnickova, B. M. Way and J. R. Dahn, Predicting and Extending the Lifetime of Li-Ion Batteries, *J. Electrochem. Soc.*, 2013, **160**, A1451–A1456.
- 200 J. C. Burns, D. A. Stevens and J. R. Dahn, In-Situ Detection of Lithium Plating Using High Precision Coulometry, *J. Electrochem. Soc.*, 2015, **162**, A959–A964.
- 201 R. Jung, R. Morasch, P. Karayaylali, K. Phillips, F. Maglia, C. Stinner, Y. Shao-Horn and H. A. Gasteiger, Effect of ambient storage on the degradation of ni-rich positive electrode materials (NMC811) for li-ion batteries, *J. Electrochem. Soc.*, 2018, **165**, A132–A141.
- 202 R. C. McNulty, E. Hampson, L. N. Cutler, C. P. Grey, W. M. Dose and L. R. Johnson, Understanding the limits of Li-NMC811 half-cells, *J. Mater. Chem. A*, 2023, **11**, 18302–18312.

-
- 203 M. Genovese, A. J. Louli, R. Weber, S. Hames and J. R. Dahn, Measuring the Coulombic Efficiency of Lithium Metal Cycling in Anode-Free Lithium Metal Batteries, *J. Electrochem. Soc.*, 2018, **165**, A3321–A3325.
- 204 Q. Li, D. Ning, D. Wong, K. An, Y. Tang, D. Zhou, G. Schuck, Z. Chen, N. Zhang and X. Liu, Improving the oxygen redox reversibility of Li-rich battery cathode materials via Coulombic repulsive interactions strategy, *Nat. Commun.*, 2022, **13**, 1–13.
- 205 R. Soares, A. Bessman, O. Wallmark, G. Lindbergh and P. Svens, An experimental setup with alternating current capability for evaluating large lithium-ion battery cells, *Batteries*, , DOI:10.3390/batteries4030038.
- 206 Understanding RTDs, <https://www.te.com/en/products/sensors/temperature-sensors/resources/understanding-rtds.html>, (accessed 3 June 2024).
- 207 Thermocouple Colour Codes & Tolerances, <https://tmseurope.co.uk/buy/thermocouple-rtd-colour-codes-tolerances.html>, (accessed 3 June 2024).
- 208 J. G. Zhu, Z. C. Sun, X. Z. Wei and H. F. Dai, A new lithium-ion battery internal temperature on-line estimate method based on electrochemical impedance spectroscopy measurement, *J. Power Sources*, 2015, **274**, 990–1004.
- 209 M. Abdel Monem, K. Trad, N. Omar, O. Hegazy, B. Mantels, G. Mulder, P. Van den Bossche and J. Van Mierlo, Lithium-ion batteries: Evaluation study of different charging methodologies based on aging process, *Appl. Energy*, 2015, **152**, 143–155.
- 210 Z. He, Z. Wang, H. Chen, Z. Huang, X. Li, H. Guo and R. Wang, Electrochemical performance of zirconium doped lithium rich layered $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_{2-x}$ oxide with porous hollow structure, *J. Power Sources*, 2015, **299**, 334–341.
- 211 S. J. Cooper, A. Bertei, D. P. Finegan and N. P. Brandon, Simulated impedance of diffusion in porous media, *Electrochim. Acta*, 2017, **251**, 681–689.
- 212 F. Single, B. Horstmann and A. Latz, Theory of Impedance Spectroscopy for Lithium Batteries, *J. Phys. Chem. C*, , DOI:10.1021/acs.jpcc.9b07389.

-
- 213 B. A. Mei, O. Munteshari, J. Lau, B. Dunn and L. Pilon, Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices, *J. Phys. Chem. C*, 2018, **122**, 194–206.
- 214 S. Wang, J. Zhang, O. Gharbi, V. Vivier, M. Gao and M. E. Orazem, Electrochemical impedance spectroscopy, *Nat. Rev. Methods Prim.*, , DOI:10.1038/s43586-021-00039-w.
- 215 V. Yufit, P. Shearing, R. W. Hamilton, P. D. Lee, M. Wu and N. P. Brandon, Investigation of lithium-ion polymer battery cell failure using X-ray computed tomography, *Electrochem. commun.*, 2011, **13**, 608–610.
- 216 R. Raccichini, M. Amores and G. Hinds, Critical review of the use of reference electrodes in li-ion batteries: A diagnostic perspective, *Batteries*, 2019, **5**, 1–24.
- 217 H. Brandstätter, I. Hanzu and M. Wilkening, Myth and Reality about the Origin of Inductive Loops in Impedance Spectra of Lithium-Ion Electrodes - A Critical Experimental Approach, *Electrochim. Acta*, 2016, **207**, 218–223.
- 218 W. M. Dose, C. Xu, C. P. Grey and M. F. L. De Volder, Effect of Anode Slippage on Cathode Cutoff Potential and Degradation Mechanisms in Ni-Rich Li-Ion Batteries, *Cell Reports Phys. Sci.*, 2020, **1**, 100253.
- 219 L. Zheng, J. Zhu, D. D. C. Lu, G. Wang and T. He, Incremental capacity analysis and differential voltage analysis based state of charge and capacity estimation for lithium-ion batteries, *Energy*, 2018, **150**, 759–769.
- 220 M. Dubarry and D. Anseán, Best practices for incremental capacity analysis, *Front. Energy Res.*, 2022, **10**, 1–18.
- 221 Y. Gao, J. Jiang, C. Zhang, W. Zhang and Y. Jiang, Aging mechanisms under different state-of-charge ranges and the multi-indicators system of state-of-health for lithium-ion battery with Li(NiMnCo)O₂ cathode, *J. Power Sources*, 2018, **400**, 641–651.
- 222 M. Varini, *Electrochemical characterization of different stages of lifetime*, 2020.
- 223 A. Weng, J. B. Siegel and A. Stefanopoulou, Differential voltage analysis for battery manufacturing process control, *Front. Energy Res.*, 2023, **11**, 1–18.

-
- 224 M. E. Wojtala, A. A. Zülke, R. Burrell, M. Nagarathinam, G. Li, H. E. Hoster, D. A. Howey and M. P. Mercer, Entropy Profiling for the Diagnosis of NCA/Gr-SiO_x Li-Ion Battery Health, *J. Electrochem. Soc.*, 2022, **169**, 100527.
- 225 J. Sturm, A. Rheinfeld, I. Zilberman, F. B. Spingler, S. Kosch, F. Frie and A. Jossen, Modeling and simulation of inhomogeneities in a 18650 nickel-rich, silicon-graphite lithium-ion cell during fast charging, *J. Power Sources*, 2019, **412**, 204–223.
- 226 J. Z. Olson, C. M. López and E. J. F. Dickinson, Differential Analysis of Galvanostatic Cycle Data from Li-Ion Batteries: Interpretative Insights and Graphical Heuristics, *Chem. Mater.*, 2023, **35**, 1487–1513.
- 227 P. Mohtat, S. Lee, V. Sulzer, J. B. Siegel and A. G. Stefanopoulou, Differential Expansion and Voltage Model for Li-ion Batteries at Practical Charging Rates, *J. Electrochem. Soc.*, 2020, **167**, 110561.
- 228 A. Eddahech, O. Briat and J. M. Vinassa, Determination of lithium-ion battery state-of-health based on constant-voltage charge phase, *J. Power Sources*, 2014, **258**, 218–227.
- 229 D. Li, H. Li, D. Danilov, L. Gao, J. Zhou, R. A. Eichel, Y. Yang and P. H. L. Notten, Temperature-dependent cycling performance and ageing mechanisms of C6/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ batteries, *J. Power Sources*, 2018, **396**, 444–452.
- 230 R. F. Ziesche, T. M. M. Heenan, P. Kumari, J. Williams, W. Li, M. E. Curd, T. L. Burnett, I. Robinson, D. J. L. Brett, M. J. Ehrhardt, P. D. Quinn, L. B. Mehdi, P. J. Withers, M. M. Britton, N. D. Browning and P. R. Shearing, Multi-Dimensional Characterization of Battery Materials, *Adv. Energy Mater.*, 2023, **2300103**, 1–20.
- 231 R. F. Ziesche, N. Kardjilov, W. Kockelmann, D. J. L. Brett and P. R. Shearing, Neutron imaging of lithium batteries, *Joule*, 2022, **6**, 35–52.
- 232 T. E. Ashton, P. J. Baker, C. Sotelo-Vazquez, C. J. M. Footer, K. M. Kojima, T. Matsukawa, T. Kamiyama and J. A. Darr, Stoichiometrically driven disorder and local diffusion in NMC cathodes, *J. Mater. Chem. A*, 2021, **9**, 10477–10486.
- 233 L. Geng, J. Liu, D. L. Wood, Y. Qin, W. Lu, C. J. Jafra, Y. Bai and I. Belharouak,

-
- Probing Thermal Stability of Li-Ion Battery Ni-Rich Layered Oxide Cathodes by means of Operando Gas Analysis and Neutron Diffraction, *ACS Appl. Energy Mater.*, 2020, **3**, 7058–7065.
- 234 M. Avdeev and J. R. Hester, ECHIDNA: A decade of high-resolution neutron powder diffraction at OPAL, *J. Appl. Crystallogr.*, 2018, **51**, 1597–1604.
- 235 T. F. Der Albert-ludwigs-universität and M. Drews, Anode Materials and Processing Technologies for Modern Lithium-Ion Battery Cell Concepts.
- 236 A. V. Llewellyn, A. Matruglio, D. J. L. Brett, R. Jervis and P. R. Shearing, Using in-situ laboratory and synchrotron-based x-ray diffraction for lithium-ion batteries characterization: A review on recent developments, *Condens. Matter*, 2020, **5**, 1–28.
- 237 L. de Biasi, A. Schiele, M. Roca-Ayats, G. Garcia, T. Brezesinski, P. Hartmann and J. Janek, Phase Transformation Behavior and Stability of LiNiO₂ Cathode Material for Li-Ion Batteries Obtained from In Situ Gas Analysis and Operando X-Ray Diffraction, *ChemSusChem*, 2019, **12**, 2240–2250.
- 238 I. Buchberger, S. Seidlmayer, A. Pokharel, M. Piana, J. Hattendorff, P. Kudejova, R. Gilles and H. A. Gasteiger, Aging Analysis of Graphite/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ Cells Using XRD, PGAA, and AC Impedance, *J. Electrochem. Soc.*, 2015, **162**, A2737–A2746.
- 239 D. Matras, T. E. Ashton, H. Dong, M. Mirolo, I. Martens, J. Drnec, J. A. Darr, P. D. Quinn, S. D. M. Jacques, A. M. Beale and A. Vamvakeros, Emerging chemical heterogeneities in a commercial 18650 NCA Li-ion battery during early cycling revealed by synchrotron X-ray diffraction tomography, *J. Power Sources*, 2022, **539**, 231589.
- 240 L. Romano Brandt, J. J. Marie, T. Moxham, D. P. Förstermann, E. Salvati, C. Besnard, C. Papadaki, Z. Wang, P. G. Bruce and A. M. Korsunsky, Synchrotron X-ray quantitative evaluation of transient deformation and damage phenomena in a single nickel-rich cathode particle, *Energy Environ. Sci.*, 2020, **13**, 3556–3566.
- 241 M. J. Brand, S. F. Schuster, T. Bach, E. Fleder, M. Stelz, S. Gläser, J. Müller,

-
- G. Sextl and A. Jossen, Effects of vibrations and shocks on lithium-ion cells, *J. Power Sources*, 2015, **288**, 62–69.
- 242 K. Y. Oh, J. B. Siegel, L. Secondo, S. U. Kim, N. A. Samad, J. Qin, D. Anderson, K. Garikipati, A. Knobloch, B. I. Epureanu, C. W. Monroe and A. Stefanopoulou, Rate dependence of swelling in lithium-ion cells, *J. Power Sources*, 2014, **267**, 197–202.
- 243 L. Somerville, J. Bareño, S. Trask, P. Jennings, A. McGordon, C. Lyness and I. Bloom, The effect of charging rate on the graphite electrode of commercial lithium-ion cells: A post-mortem study, *J. Power Sources*, 2016, **335**, 189–196.
- 244 M. Lewerenz, A. Warnecke and D. U. Sauer, Post-mortem analysis on LiFePO₄|Graphite cells describing the evolution & composition of covering layer on anode and their impact on cell performance, *J. Power Sources*, 2017, **369**, 122–132.
- 245 K. Dai, Z. Wang, G. Ai, H. Zhao, W. Yuan, X. Song, V. Battaglia, C. Sun, K. Wu and G. Liu, The transformation of graphite electrode materials in lithium-ion batteries after cycling, *J. Power Sources*, 2015, **298**, 349–354.
- 246 B. P. Matadi, S. Geniès, A. Delaille, T. Waldmann, M. Kasper, M. Wohlfahrt-Mehrens, F. Aguesse, E. Bekaert, I. Jiménez-Gordon, L. Daniel, X. Fleury, M. Bardet, J.-F. Martin and Y. Bultel, Effects of Biphenyl Polymerization on Lithium Deposition in Commercial Graphite/NMC Lithium-Ion Pouch-Cells during Calendar Aging at High Temperature, *J. Electrochem. Soc.*, 2017, **164**, A1089–A1097.
- 247 A. Pfrang, A. Kersys, A. Kriston, D. U. Sauer, C. Rahe, S. Käbitz and E. Figgemeier, Geometrical Inhomogeneities as Cause of Mechanical Failure in Commercial 18650 Lithium Ion Cells, *J. Electrochem. Soc.*, 2019, **166**, A3745–A3752.
- 248 M. Spielbauer, J. Soellner, P. Berg, K. Koch, P. Keil, C. Rosenmüller, O. Bohlen and A. Jossen, Experimental investigation of the impact of mechanical deformation on aging, safety and electrical behavior of 18650 lithium-ion battery cells, *J. Energy Storage*, 2022, **55**, 105564.

-
- 249 R. Weber, M. Genovese, A. J. Louli, S. Hames, C. Martin, I. G. Hill and J. R. Dahn, Long cycle life and dendrite-free lithium morphology in anode-free lithium pouch cells enabled by a dual-salt liquid electrolyte, *Nat. Energy*, 2019, **4**, 683–689.
- 250 D. S. Ko, J. H. Park, S. Park, Y. N. Ham, S. J. Ahn, J. H. Park, H. N. Han, E. Lee, W. S. Jeon and C. Jung, Microstructural visualization of compositional changes induced by transition metal dissolution in Ni-rich layered cathode materials by high-resolution particle analysis, *Nano Energy*, 2019, **56**, 434–442.
- 251 L. Hartmann, L. Reuter, L. Wallisch, A. Beiersdorfer, A. Adam, D. Goldbach, T. Teufl, P. Lamp, H. Gasteiger and J. Wandt, Depletion of Electrolyte Salt Upon Calendaric Aging of Lithium-Ion Batteries and its Effect on Cell Performance, *J. Electrochem. Soc.*, , DOI:10.1149/1945-7111/ad4821.
- 252 H. Xia, L. Lu, Y. S. Meng and G. Ceder, Phase Transitions and High-Voltage Electrochemical Behavior of LiCoO₂ Thin Films Grown by Pulsed Laser Deposition, *J. Electrochem. Soc.*, 2007, **154**, A337.
- 253 J. Chen, M. N. Marlow, Q. Jiang and B. Wu, Peak-tracking method to quantify degradation modes in lithium-ion batteries via differential voltage and incremental capacity, *J. Energy Storage*, 2022, **45**, 103669.
- 254 Z. Li, H. Yi, W. Ding, H. Ren, Y. Du, M. Shang, W. Zhao, H. Chen, L. Zhou, H. Lin, Q. Zhao and F. Pan, Revealing the Accelerated Capacity Decay of a High-Voltage LiCoO₂ upon Harsh Charging Procedure, *Adv. Funct. Mater.*, 2024, **34**, 1–10.
- 255 L. Spitthoff, P. J. S. Vie, M. S. Wahl, J. Wind and O. S. Burheim, Incremental capacity analysis (dQ/dV) as a tool for analysing the effect of ambient temperature and mechanical clamping on degradation, *J. Electroanal. Chem.*, 2023, **944**, 117627.
- 256 J. Vetter, P. Novák, M. R. Wagner, C. Veit, K. C. Möller, J. O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler and A. Hammouche, Ageing mechanisms in lithium-ion batteries, *J. Power Sources*, 2005, **147**, 269–281.
- 257 M. Kasper, M. Moertelmaier, M. Ragulskis, N. Al-Zubaidi R-Smith, J. Angerer,

-
- M. Aufreiter, A. Romero, J. Krummacher, J. Xu, D. E. Root and F. Kienberger, Calibrated Electrochemical Impedance Spectroscopy and Time-Domain Measurements of a 7 kWh Automotive Lithium-Ion Battery Module with 396 Cylindrical Cells, *Batter. Supercaps*, , DOI:10.1002/batt.202200415.
- 258 E. Teliz, C. F. Zinola and V. Díaz, Identification and quantification of ageing mechanisms in Li-ion batteries by Electrochemical impedance spectroscopy., *Electrochim. Acta*, , DOI:10.1016/j.electacta.2022.140801.
- 259 N. Ogihara, Y. Itou, T. Sasaki and Y. Takeuchi, Impedance spectroscopy characterization of porous electrodes under different electrode thickness using a symmetric cell for high-performance lithium-ion batteries, *J. Phys. Chem. C*, 2015, **119**, 4612–4619.
- 260 A. W. Rowe, J. Camardese, E. McCalla and J. R. Dahn, High Precision Coulometry Studies of Single-Phase Layered Compositions in the Li-Mn-Ni-O System, *J. Electrochem. Soc.*, 2014, **161**, A1189–A1193.
- 261 K. Wang, Y. Xu, H. Wu, R. Yuan, M. Zong, Y. Li, V. Dravid, W. Ai and J. Wu, A hybrid lithium storage mechanism of hard carbon enhances its performance as anodes for lithium-ion batteries, *Carbon N. Y.*, 2021, **178**, 443–450.
- 262 K. H. Chen, V. Goel, M. J. Namkoong, M. Wied, S. Müller, V. Wood, J. Sakamoto, K. Thornton and N. P. Dasgupta, Enabling 6C Fast Charging of Li-Ion Batteries with Graphite/Hard Carbon Hybrid Anodes, *Adv. Energy Mater.*, 2021, **11**, 1–12.
- 263 B. Wu, T. Liu, Q. Xia and X. Wu, Hard Carbon with Nano-Graphite Domain as High Performance Anode Material for Lithium-Ion Batteries, *J. Electrochem. Soc.*, 2013, **160**, A1720–A1724.
- 264 H. Maleki and J. N. Howard, Internal short circuit in Li-ion cells, *J. Power Sources*, 2009, **191**, 568–574.
- 265 M. D. L. Garayt, M. B. Johnson, L. Laidlaw, M. A. McArthur, S. Trussler, J. E. Harlow, J. R. Dahn and C. Yang, A Guide to Making Highly Reproducible Li-Ion Single-Layer Pouch Cells for Academic Researchers, *J. Electrochem. Soc.*, 2023, **170**, 080516.

-
- 266 T. Roth, L. Streck, A. Graule, P. Niehoff and A. Jossen, Relaxation Effects in Self-Discharge Measurements of Lithium-Ion Batteries, *J. Electrochem. Soc.*, 2023, **170**, 020502.
- 267 M. Lewerenz and D. U. Sauer, Evaluation of cyclic aging tests of prismatic automotive LiNiMnCoO₂-Graphite cells considering influence of homogeneity and anode overhang, *J. Energy Storage*, 2018, **18**, 421–434.
- 268 B. Gyenes, D. A. Stevens, V. L. Chevrier and J. R. Dahn, Understanding Anomalous Behavior in Coulombic Efficiency Measurements on Li-Ion Batteries, *J. Electrochem. Soc.*, 2015, **162**, A278–A283.
- 269 A. Eldesoky, M. Bauer, T. Bond, N. Kowalski, J. Corsten, D. Rathore, R. Dressler and J. R. Dahn, Long-Term Study on the Impact of Depth of Discharge, C-Rate, Voltage, and Temperature on the Lifetime of Single-Crystal NMC811/Artificial Graphite Pouch Cells, *J. Electrochem. Soc.*, 2022, **169**, 100531.
- 270 X. Ma, J. E. Harlow, J. Li, L. Ma, D. S. Hall, S. Buteau, M. Genovese, M. Cormier and J. R. Dahn, Editors' Choice—Hindering Rollover Failure of Li[Ni 0.5 Mn 0.3 Co 0.2]O₂ /Graphite Pouch Cells during Long-Term Cycling, *J. Electrochem. Soc.*, 2019, **166**, A711–A724.
- 271 K. Xu, Electrolytes and interphases in Li-ion batteries and beyond, *Chem. Rev.*, 2014, **114**, 11503–11618.
- 272 J. Kalhoff, G. G. Eshetu, D. Bresser and S. Passerini, Safer electrolytes for lithium-ion batteries: State of the art and perspectives, *ChemSusChem*, 2015, **8**, 2154–2175.
- 273 P. A. K. Jun Li, Edward Murphy, Jack Winnick, The effects of pulse charging on cycling characteristics of commercial lithium-ion batteries, *J. Power Sources*, 2001, **102**, 302–309.
- 274 C. Qiu, G. He, W. Shi, M. Zou and C. Liu, The polarization characteristics of lithium-ion batteries under cyclic charge and discharge, *J. Solid State Electrochem.*, 2019, **23**, 1887–1902.
- 275 T. H. Dubaniewicz, T. L. Barone, C. B. Brown and R. A. Thomas, Comparison of thermal runaway pressures within sealed enclosures for nickel manganese

-
- cobalt and iron phosphate cathode lithium-ion cells, *J. Loss Prev. Process Ind.*, 2022, **76**, 104739.
- 276 A. Jnawali, M. D. R. Kok, F. Iacoviello, D. J. L. Brett and P. R. Shearing, Examining the effects of silicon based additives on the long-term cycling capabilities of cylindrical cells, *J. Power Sources*, 2024, **591**, 233851.
- 277 C.-H. Chen, F. Brosa Planella, K. O'Regan, D. Gastol, W. D. Widanage and E. Kendrick, Development of Experimental Techniques for Parameterization of Multi-scale Lithium-ion Battery Models, *J. Electrochem. Soc.*, 2020, **167**, 080534.
- 278 C. Busà, M. Belekoukia and M. J. Loveridge, The effects of ambient storage conditions on the structural and electrochemical properties of NMC-811 cathodes for Li-ion batteries, *Electrochim. Acta*, , DOI:10.1016/j.electacta.2020.137358.
- 279 D. Anseán, G. Baure, M. González, I. Cameán, A. B. García and M. Dubarry, Mechanistic investigation of silicon-graphite/LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ commercial cells for non-intrusive diagnosis and prognosis, *J. Power Sources*, , DOI:10.1016/j.jpowsour.2020.227882.
- 280 H. Pegel, O. von Kessel, P. Heugel, T. Deich, J. Tübke, K. P. Birke and D. U. Sauer, Volume and thickness change of NMC811|SiO_x-graphite large-format lithium-ion cells: from pouch cell to active material level, *J. Power Sources*, 2022, **537**, 231443.
- 281 I. Bloom, A. N. Jansen, D. P. Abraham, J. Knuth, S. A. Jones, V. S. Battaglia and G. L. Henriksen, Differential voltage analyses of high-power, lithium-ion cells 1. Technique and application, *J. Power Sources*, 2005, **139**, 295–303.
- 282 M. Schindler, J. Sturm, S. Ludwig, A. Durdal and A. Jossen, Comprehensive Analysis of the Aging Behavior of Nickel-Rich, Silicon-Graphite Lithium-Ion Cells Subject to Varying Temperature and Charging Profiles, *J. Electrochem. Soc.*, 2021, **168**, 060522.
- 283 B. Epling, B. Rumberg, H. Jahnke, I. Stradtman and A. Kwade, Investigation of significant capacity recovery effects due to long rest periods during high

-
- current cyclic aging tests in automotive lithium ion cells and their influence on lifetime, *J. Energy Storage*, 2019, **22**, 249–256.
- 284 M. Schindler, J. Sturm, S. Ludwig, J. Schmitt and A. Jossen, Evolution of initial cell-to-cell variations during a three-year production cycle, *eTransportation*, 2021, **8**, 100102.
- 285 C. Xu, K. Märker, J. Lee, A. Mahadevegowda, P. J. Reeves, S. J. Day, M. F. Groh, S. P. Emge, C. Ducati, B. Layla Mehdi, C. C. Tang and C. P. Grey, Bulk fatigue induced by surface reconstruction in layered Ni-rich cathodes for Li-ion batteries, *Nat. Mater.*, 2021, **20**, 84–92.
- 286 F. Friedrich, B. Strehle, A. T. S. Freiberg, K. Kleiner, S. J. Day, C. Erk, M. Piana and H. A. Gasteiger, Editors' Choice—Capacity Fading Mechanisms of NCM-811 Cathodes in Lithium-Ion Batteries Studied by X-ray Diffraction and Other Diagnostics, *J. Electrochem. Soc.*, 2019, **166**, A3760–A3774.
- 287 J. P. Schmidt, P. Berg, M. Schönleber, A. Weber and E. Ivers-Tiffée, The distribution of relaxation times as basis for generalized time-domain models for Li-ion batteries, *J. Power Sources*, 2013, **221**, 70–77.
- 288 A. Barai, K. Uddin, W. D. Widanage, A. McGordon and P. Jennings, A study of the influence of measurement timescale on internal resistance characterisation methodologies for lithium-ion cells, *Sci. Rep.*, 2018, **8**, 1–13.
- 289 J. Landesfeind, D. Pritzl and H. A. Gasteiger, An analysis protocol for three-electrode Li-ion battery impedance spectra: Part I. Analysis of a high-voltage positive electrode, *J. Electrochem. Soc.*, 2017, **164**, A1773–A1783.
- 290 B. Lu, Y. Song, Q. Zhang, J. Pan, Y. T. Cheng and J. Zhang, Voltage hysteresis of lithium ion batteries caused by mechanical stress, *Phys. Chem. Chem. Phys.*, 2016, **18**, 4721–4727.
- 291 L. Stolz, M. Gaberšček, M. Winter and J. Kasnatscheew, Different Efforts but Similar Insights in Battery R&D: Electrochemical Impedance Spectroscopy vs Galvanostatic (Constant Current) Technique, *Chem. Mater.*, 2022, **34**, 10272–10278.
- 292 N. Meddings, M. Heinrich, F. Overney, J. S. Lee, V. Ruiz, E. Napolitano, S. Seitz,

-
- G. Hinds, R. Raccichini, M. Gaberšček and J. Park, Application of electrochemical impedance spectroscopy to commercial Li-ion cells: A review, *J. Power Sources*, , DOI:10.1016/j.jpowsour.2020.228742.
- 293 Y. Che, X. Hu, X. Lin, J. Guo and R. Teodorescu, Health prognostics for lithium-ion batteries: mechanisms, methods, and prospects, *Energy Environ. Sci.*, 2023, **16**, 338–371.
- 294 T. R. Tanim, Z. Yang, A. M. Colclasure, P. R. Chinnam, P. Gasper, Y. Lin, L. Yu, P. J. Weddle, J. Wen, E. J. Dufek, I. Bloom, K. Smith, C. C. Dickerson, M. C. Evans, Y. Tsai, A. R. Dunlop, S. E. Trask, B. J. Polzin and A. N. Jansen, Extended cycle life implications of fast charging for lithium-ion battery cathode, *Energy Storage Mater.*, 2021, **41**, 656–666.
- 295 A. Eldesoky, E. R. Logan, A. J. Louli, W. Song, R. Weber, S. Hy, R. Petibon, J. E. Harlow, S. Azam, E. Zsoldos and J. R. Dahn, Impact of Graphite Materials on the Lifetime of NMC811/Graphite Pouch Cells: Part II. Long-Term Cycling, Stack Pressure Growth, Isothermal Microcalorimetry, and Lifetime Projection, *J. Electrochem. Soc.*, 2022, **169**, 010501.
- 296 J. E. Harlow, X. Ma, J. Li, E. Logan, Y. Liu, N. Zhang, L. Ma, S. L. Glazier, M. M. E. Cormier, M. Genovese, S. Buteau, A. Cameron, J. E. Stark and J. R. Dahn, A Wide Range of Testing Results on an Excellent Lithium-Ion Cell Chemistry to be used as Benchmarks for New Battery Technologies, *J. Electrochem. Soc.*, 2019, **166**, A3031–A3044.
- 297 M. Petzl, M. Kasper and M. A. Danzer, Lithium plating in a commercial lithium-ion battery – A low-temperature aging study, *J. Power Sources*, 2015, **275**, 799–807.
- 298 S. Solchenbach, X. Huang, D. Pritzl, J. Landesfeind and H. A. Gasteiger, Monitoring SEI Formation on Graphite Electrodes in Lithium-Ion Cells by Impedance Spectroscopy, *J. Electrochem. Soc.*, 2021, **168**, 110503.
- 299 B. Li, Y. Chao, M. Li, Y. Xiao, R. Li, K. Yang, X. Cui, G. Xu, L. Li, C. Yang, Y. Yu, D. P. Wilkinson and J. Zhang, *A Review of Solid Electrolyte Interphase (SEI) and Dendrite Formation in Lithium Batteries*, Springer Nature Singapore, 2023, vol. 6.

-
- 300 W. Lv, C. Zhu, J. Chen, C. Ou, Q. Zhang and S. Zhong, High performance of low-temperature electrolyte for lithium-ion batteries using mixed additives, *Chem. Eng. J.*, 2021, **418**, 129400.
- 301 W. Wang, T. Yang, S. Li, W. Fan, X. Zhao, C. Fan, L. Yu, S. Zhou, X. Zuo, R. Zeng and J. Nan, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) as an ionic liquid-type electrolyte additive to enhance the low-temperature performance of LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂/graphite batteries, *Electrochim. Acta*, 2019, **317**, 146–154.
- 302 S. S. Zhang, K. Xu and T. R. Jow, Electrochemical impedance study on the low temperature of Li-ion batteries, *Electrochim. Acta*, 2004, **49**, 1057–1061.
- 303 T. Waldmann, B. I. Hogg and M. Wohlfahrt-Mehrens, Li plating as unwanted side reaction in commercial Li-ion cells – A review, *J. Power Sources*, 2018, **384**, 107–124.
- 304 J. Fan, On the discharge capability and its limiting factors of commercial 18650 Li-ion cell at low temperatures, *J. Power Sources*, 2003, **117**, 170–178.
- 305 Y. Zhang, C. Y. Wang and X. Tang, Cycling degradation of an automotive LiFePO₄ lithium-ion battery, *J. Power Sources*, 2011, **196**, 1513–1520.
- 306 R. D. Deshpande, P. Ridgway, Y. Fu, W. Zhang, J. Cai and V. Battaglia, The Limited Effect of VC in Graphite/NMC Cells, *J. Electrochem. Soc.*, 2015, **162**, A330–A338.
- 307 J. Li, S. L. Glazier, K. Nelson, X. Ma, J. Harlow, J. Paulsen and J. R. Dahn, Effect of Choices of Positive Electrode Material, Electrolyte, Upper Cut-Off Voltage and Testing Temperature on the Life Time of Lithium-Ion Cells, *J. Electrochem. Soc.*, 2018, **165**, A3195–A3204.
- 308 D. Hu, G. Chen, J. Tian, N. Li, L. Chen, Y. Su, T. Song, Y. Lu, D. Cao, S. Chen and F. Wu, Unrevealing the effects of low temperature on cycling life of 21700-type cylindrical Li-ion batteries, *J. Energy Chem.*, 2021, **60**, 104–110.
- 309 K. Xu, Nonaqueous liquid electrolytes for lithium-based rechargeable batteries, *Chem. Rev.*, 2004, **104**, 4303–4417.
- 310 M. Feinauer, M. Wohlfahrt-Mehrens, M. Hölzle and T. Waldmann, Temperature-

-
- driven path dependence in Li-ion battery cyclic aging, *J. Power Sources*, , DOI:10.1016/j.jpowsour.2023.233948.
- 311 H. Rouhi, E. Karola, R. Serna-Guerrero and A. Santasalo-Aarnio, Voltage behavior in lithium-ion batteries after electrochemical discharge and its implications on the safety of recycling processes, *J. Energy Storage*, 2021, **35**, 102323.
- 312 Q. Liu, S. Li, S. Wang, X. Zhang, S. Zhou, Y. Bai, J. Zheng and X. Lu, Kinetically Determined Phase Transition from Stage II (LiC₁₂) to Stage I (LiC₆) in a Graphite Anode for Li-Ion Batteries, *J. Phys. Chem. Lett.*, 2018, **9**, 5567–5573.
- 313 R. Lin, S. M. Bak, Y. Shin, R. Zhang, C. Wang, K. Kisslinger, M. Ge, X. Huang, Z. Shadike, A. Pattammattel, H. Yan, Y. Chu, J. Wu, W. Yang, M. S. Whittingham, H. L. Xin and X. Q. Yang, Hierarchical nickel valence gradient stabilizes high-nickel content layered cathode materials, *Nat. Commun.*, 2021, **12**, 1–10.
- 314 B. L. D. Rinkel, D. S. Hall, I. Temprano and C. P. Grey, Electrolyte oxidation pathways in lithium-ion batteries, *J. Am. Chem. Soc.*, 2020, **142**, 15058–15074.
- 315 B. L. D. Rinkel, J. P. Vivek, N. Garcia-Araez and C. P. Grey, Two electrolyte decomposition pathways at nickel-rich cathode surfaces in lithium-ion batteries, *Energy Environ. Sci.*, 2022, **15**, 3416–3438.
- 316 E. Björklund, C. Xu, W. M. Dose, C. G. Sole, P. K. Thakur, T. L. Lee, M. F. L. De Volder, C. P. Grey and R. S. Weatherup, Cycle-Induced Interfacial Degradation and Transition-Metal Cross-Over in LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂-Graphite Cells, *Chem. Mater.*, 2022, **34**, 2034–2048.
- 317 H. S. Magar, R. Y. A. Hassan and A. Mulchandani, Electrochemical impedance spectroscopy (Eis): Principles, construction, and biosensing applications, *Sensors*, , DOI:10.3390/s21196578.
- 318 Y. Sun, S. Zhang, J. Qi and Z. Su, Calendar degradation of Li-ion batteries under high storage temperature based on electrochemical impedance spectroscopy, *Microelectron. Reliab.*, 2021, **126**, 114316.
- 319 B. W. Sheldon and A. Tokranov, Internal stress due to solvent co-intercalation

-
- in graphite electrodes for Li ion batteries, *Extrem. Mech. Lett.*, 2016, **9**, 379–385.
- 320 E. Sahraei, J. Campbell and T. Wierzbicki, Modeling and short circuit detection of 18650 Li-ion cells under mechanical abuse conditions, *J. Power Sources*, 2012, **220**, 360–372.
- 321 H. Maleki, G. Deng, I. Kerzhner-Haller, A. Anani and J. N. Howard, Thermal Stability Studies of Binder Materials in Anodes for Lithium-Ion Batteries, *J. Electrochem. Soc.*, 2000, **147**, 4470.
- 322 L. Fransson, T. Eriksson, K. Edström, T. Gustafsson and J. O. Thomas, Influence of carbon black and binder on Li-ion batteries, *J. Power Sources*, 2001, **101**, 1–9.
- 323 M. D. R. Kok, A. Jnawali, T. M. M. Heenan, T. G. Tranter, D. J. L. Brett, P. R. Shearing and J. B. Robinson, Tracking the Lifecycle of a 21700 Cell: A 4D Tomography and Digital Disassembly Study, *J. Electrochem. Soc.*, 2023, **170**, 090502.
- 324 M. Spielbauer, M. Steinhardt, J. Singer, A. Aufschläger, O. Bohlen and A. Jossen, Influence of Breathing and Swelling on the Jelly-Roll Case Gap of Cylindrical Lithium-Ion Battery Cells, *Batteries*, 2023, **9**, 1–13.
- 325 R. Xu, H. Sun, L. S. de Vasconcelos and K. Zhao, Mechanical and Structural Degradation of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ Cathode in Li-Ion Batteries: An Experimental Study, *J. Electrochem. Soc.*, 2017, **164**, A3333–A3341.
- 326 Z. Zhang, S. Said, A. J. Lovett, R. Jervis, P. R. Shearing, D. J. L. Brett and T. S. Miller, The Influence of Cathode Degradation Products on the Anode Interface in Lithium-Ion Batteries, *ACS Nano*, , DOI:10.1021/acsnano.3c10208.
- 327 J. H. Ryu, J. W. Kim, Y. E. Sung and S. M. Oh, Failure modes of silicon powder negative electrode in lithium secondary batteries, *Electrochem. Solid-State Lett.*, , DOI:10.1149/1.1792242.
- 328 A. Mikheenkova, A. J. Smith, K. B. Frenander, Y. Tesfamhret, N. R. Chowdhury, C.-W. Tai, T. Thiringer, R. W. Lindström, M. Hahlin and M. J. Lacey, Ageing of High Energy Density Automotive Li-Ion Batteries: The Effect of Temperature and

-
- State-of-Charge, *J. Electrochem. Soc.*, 2023, **170**, 080503.
- 329 B. Stiaszny, J. C. Ziegler, E. E. Krauß, M. Zhang, J. P. Schmidt and E. Ivers-Tiffée, Electrochemical characterization and post-mortem analysis of aged LiMn₂O₄-NMC/graphite lithium ion batteries part II: Calendar aging, *J. Power Sources*, 2014, **258**, 61–75.
- 330 T. Waldmann, M. Wilka, M. Kasper, M. Fleischhammer and M. Wohlfahrt-Mehrens, Temperature dependent ageing mechanisms in Lithium-ion batteries - A Post-Mortem study, *J. Power Sources*, 2014, **262**, 129–135.
- 331 M. Dubarry, N. Qin and P. Brooker, Calendar aging of commercial Li-ion cells of different chemistries – A review, *Curr. Opin. Electrochem.*, 2018, **9**, 106–113.
- 332 C. Roy, B. Sebok, S. B. Scott, E. M. Fiordaliso, J. E. Sørensen, A. Bodin, D. B. Trimarco, C. D. Damsgaard, P. C. K. Vesborg, O. Hansen, I. E. L. Stephens, J. Kibsgaard and I. Chorkendorff, Impact of nanoparticle size and lattice oxygen on water oxidation on NiFeOxHy, *Nat. Catal.*, 2018, **1**, 820–829.
- 333 S. Tan, Z. Shadike, J. Li, X. Wang, Y. Yang, R. Lin, A. Cresce, J. Hu, A. Hunt, I. Waluyo, L. Ma, F. Monaco, P. Cloetens, J. Xiao, Y. Liu, X. Q. Yang, K. Xu and E. Hu, Additive engineering for robust interphases to stabilize high-Ni layered structures at ultra-high voltage of 4.8 V, *Nat. Energy*, 2022, **7**, 484–494.
- 334 M. Yue, C. Aiken, J. Deshmukh, M. D. L. Garayt, M. Johnson, J. R. Dahn and C. Yang, Improved Elevated Temperature Performance of LiFePO₄/Graphite Cell by Blending NMC640 in Cathode, *J. Electrochem. Soc.*, 2023, **170**, 110532.

List of Publications and Conferences

Publications

- Leach et al., 2022, *Frontiers in Chemical Engineering*, 3, p.794194
- Heenan et al., 2020, *Advanced Energy Materials*, 10(47), p.2002655.
- Heenan et al., 2020, *Journal of the Electrochemical Society*, 167(14), p.140530.
- Heenan et al., 2020, *Data in Brief*, 32, p.106033.

In preparation

- Dimitrijevic et al., “Predicting fade behaviour using High-Precision Coulometry”
- Dimitrijevic et al., “Degradation effects of variable current protocols on commercial cells”
- Majherova et al., “Revealing how silicon oxide accelerates calendar ageing of commercial 21700 nickel-rich lithium-ion cells”

Conference presentations:

- London Energy Materials and Devices Hub 2019, UCL, UK. Organising committee and poster presentation
- Materials for Clean Energy Conference 2019, National Physical Laboratory, UK. Poster presentation
- STFC Early Career Researchers Conference 2019, Abingdon, UK. Poster presentation
- European Space Power Conference 2023, Elche, Spain. Oral presentation

8 Appendix

8.1 Appendices of Chapter 4

Figure 8-1 represent the full Nyquist spectra (1 MHz to 10 mHz) of all cell from the LCO/HC, LCO/Graphite and NMC/Graphite cells dataset. Observable are the induction tails which show already present variations despite being at BoL. This is due to cables, setup abd various interconnections within the cells.

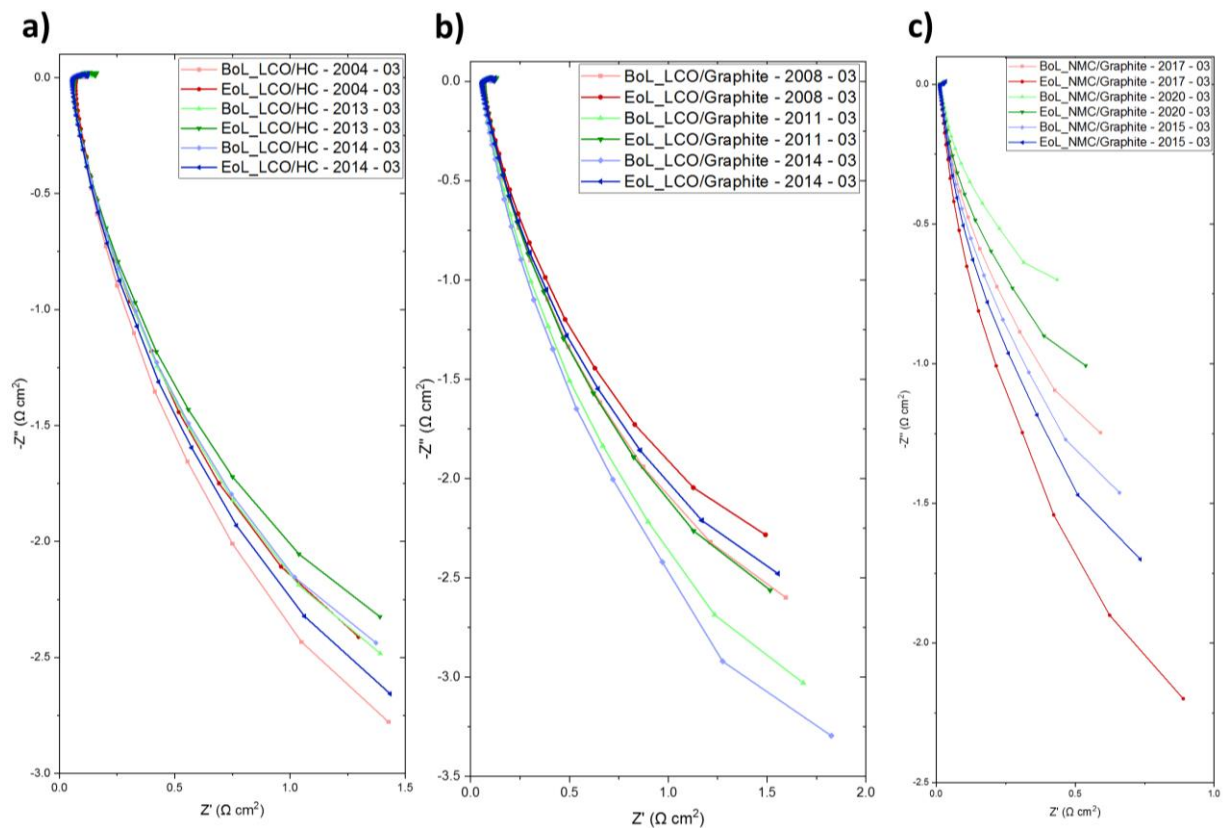


Figure 8-1. Nyquist spectra of BoL and EoL at 50% SoC of a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite cells.

Figure 8-2 displays the CE of all cells, with consideration of the very first cycle. This shows significant CE readjustment, as the initial cycle is a discharge first, from the SoC as received, and not displayed here.

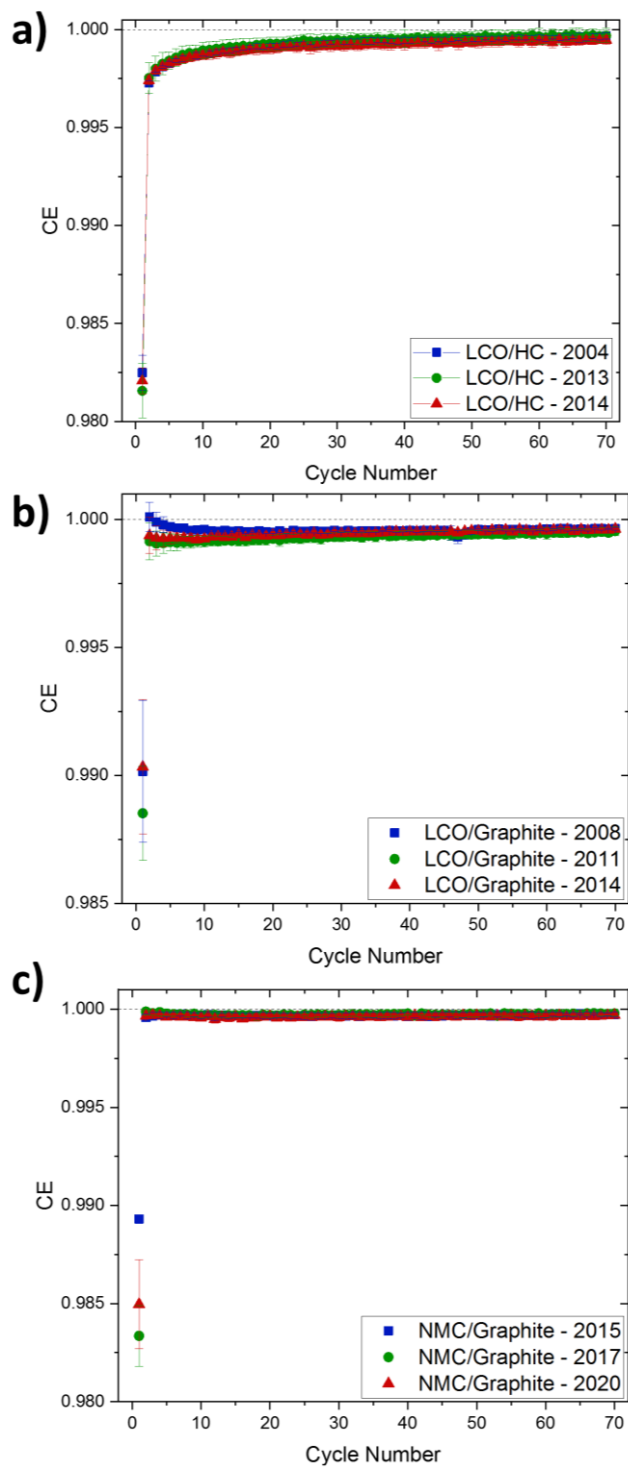


Figure 8-2. Coulombic efficiency values with consideration of the first cycle for each batch on average for a) LCO/HC, b) LCO/Graphite and c) NMC/Graphite cells.

8.2 Appendices of Chapter 5

Figure 8-3 represents the dV/dQ plots that were used to calculate the various “Q” intervals between key peaks of the DVA.

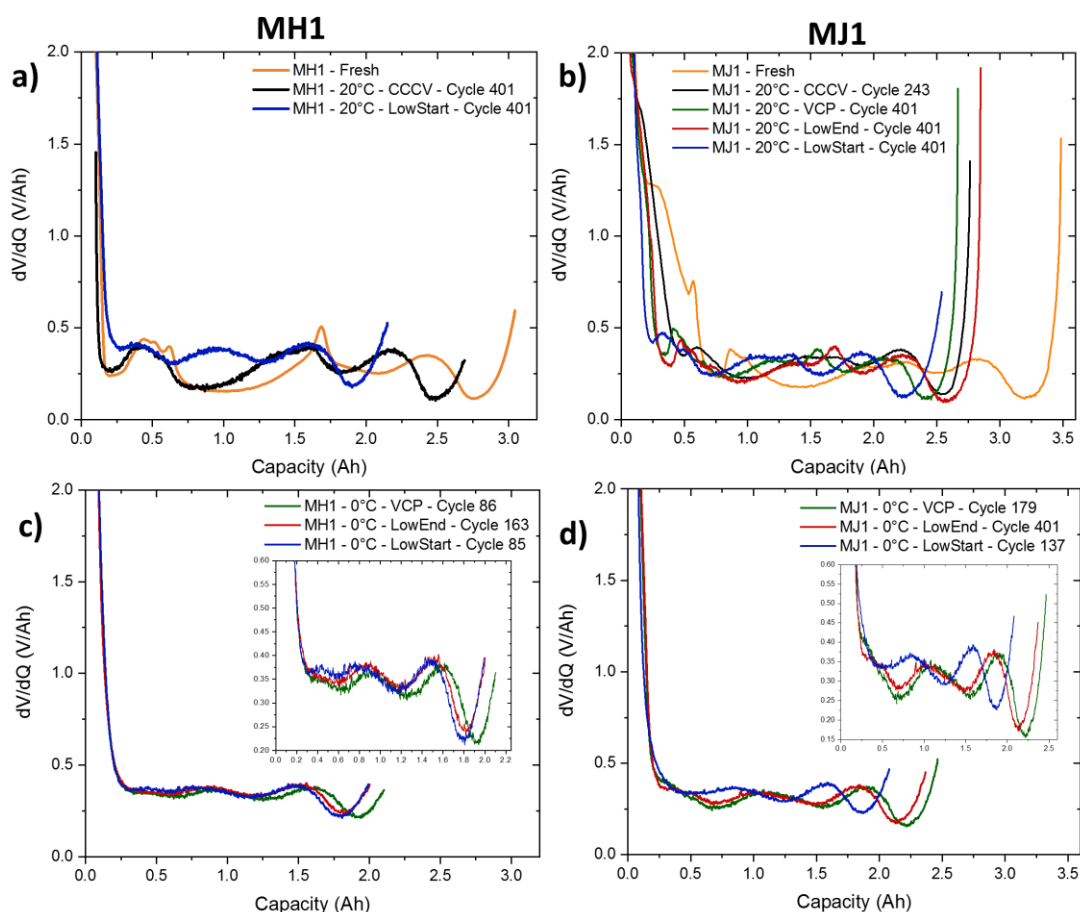


Figure 8-3. dV/dQ plots for MH1 cells at a) 20°C and c) 0°C respectively, and MJ1 cells at b) 20°C and d) 0°C respectively.

Figure 8-4 displays part of the TEM/EELS cathode investigation work carried out in collaboration with the University of Cambridge by May Ching Lai. More prevalent intragranular cracks were identified in the primary NMC particles within the LowStart material, one of which is shown in a), compared to its LowEnd counterpart. Moreover, b) evidences the presence of RSL closer to said crack, where the interlayer spacing within the rock-salt phase is observed to be approximately 2.5 Å, indicative of a high degree of structural distortion. Conversely, moving towards the bulk region, the interlayer spacing increases to 4.9 Å, suggesting the presence of a well-ordered layered structure characteristic of NMC materials in their pristine state. Furthermore,

Electron Energy Loss Spectroscopy (EELS) signals of the c) Oxygen K-edge and d) Nickel L₃/L₂ edges, typically indicates a change in the oxidation state of the transition metals, such as nickel, and oxygen bond characteristics. Specifically, the observed shift likely corresponds to the reduction of Ni³⁺ to Ni²⁺, and a slightly more prominent shift has been observed for the LowStart material as opposed to the LowEnd counterpart. This reduction is correlated to RSL formation and subsequent Oxygen release, as discussed previously. Hence, despite the prominent degradation evidenced on the anode side, degradation at the cathode is still present, and appears to be more prominent as well for the LowStart cells, where the time spent at high voltage was prominent.

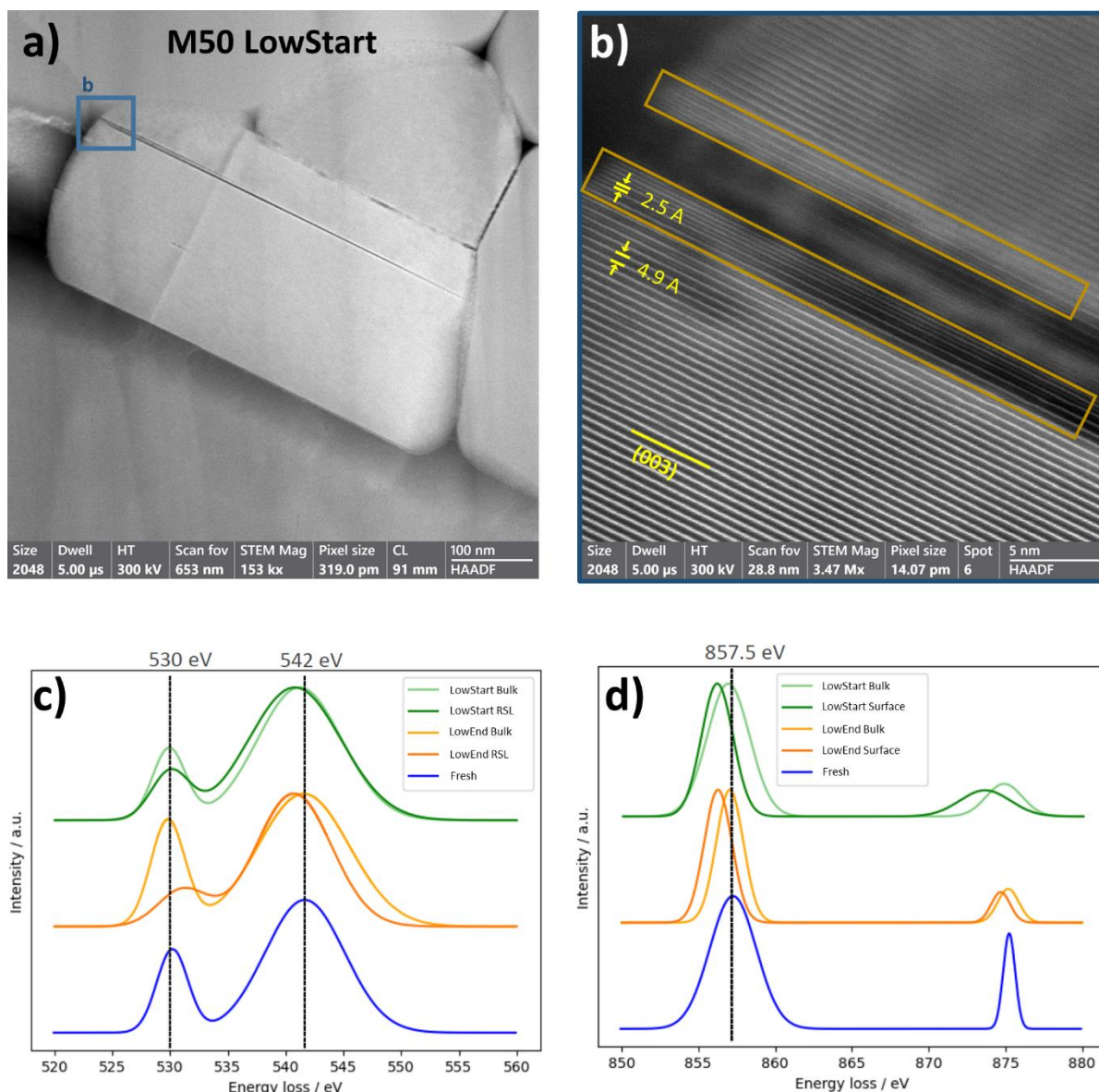


Figure 8-4. LowStart_02 cathode sample a) microgram showing formation of intragranular crack in a primary particle and b) inset showing structural changes from layered structure to RSL (yellow rectangle) towards the crack region. c) and d) represent the average core-loss EELS spectra of LowStart_02, LowEnd_02 and Fresh arranged from top to bottom where the fine structure EELS is shown for c) the Oxygen K-edge and d) the Nickel L_3/L_2 edges. Vertical dashed lines indicate relevant, expected peak positions and are shown as a guidance to the eye. Data gathered by May Ching Lai from Cambridge University.

8.3 Appendices of Chapter 6

Figure 8-5 displays the original intensity NPD data of the cells at all SoCs, as well as their individual plot with refinements and residuals.

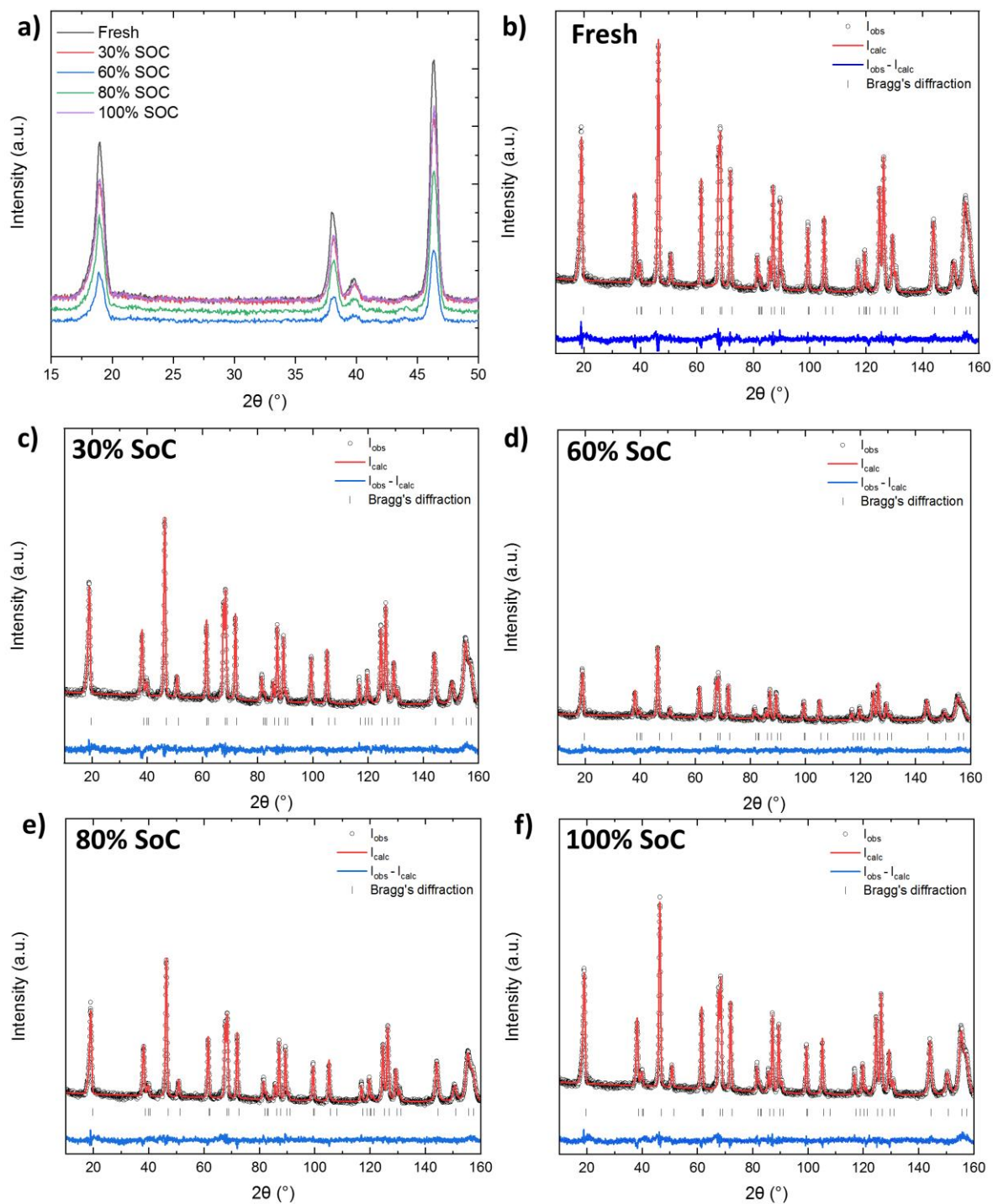


Figure 8-5. NPD data of a) all cells, and refined data and residuals for b) fresh, c) 30% SoC, d) 60% SoC, e) 80% SoC and f) 100% SoC of the 25°C and 52 weeks batch.