

Imperial College London

Department of Mechanical Engineering

DEVELOPMENT OF NEW ON-BOARD BATTERY DIAGNOSIS/PROGNOSIS TOOLS FOR EXTENDING LIFETIME AND MITIGATING FAILURE

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PhD Thesis

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DECLARATION OF ORIGINALITY

I hereby declare that this thesis and the work presented herein is my own work except where appropriately referenced or acknowledged.

Yu Merla

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ABSTRACT

Lithium-ion batteries age over their lifetime of operation through various complex degradation mechanisms. In order to maximise battery performance and lifetime, the industrial standard method of measuring the state of health (SOH) by capacity and power fade is no longer good enough. In this thesis, Differential Thermal Voltammetry (DTV) is introduced as a new *in-situ* diagnosis/prognosis tool that is capable of a more sophisticated diagnosis of SOH, and is application ready with minimal installation costs.

DTV uses only cell voltage and surface temperature measurements to infer detailed SOH information. The method was validated through various accelerated ageing experiments carried out on commercial lithium-ion pouch cells as well as through industrial collaborations.

DTV was demonstrated for use as a diagnostic tool on a cell level for tracking battery degradation throughout its operation, for screening 2nd life batteries to estimate the degradation state/history, and for estimating the state-of-charge (SOC) of lithium iron phosphate cells during partial charge/discharges.

In anticipation of an EV application, the technique was tested for its capabilities in a battery pack. DTV was able to correctly identify aged cells within a pack in a quantitative manner validating its capability embedded within a battery management system (BMS).

Through an industrial collaboration, DTV demonstrated its use as a prognosis tool for forecasting cell failure in a commercial BMS mounted on a high-power battery pack used in a motorsport application.

The concept of adaptive operation through DTV analysis was explored which resulted in a slower rate of degradation.

Given the application opportunities validated through experiments, this research aims to provide an alternative tool for battery diagnosis/prognosis in a real-world application.

ACKNOWLEDGEMENT

First and foremost, I wish to express my deepest gratitude to my supervisor, Dr Gregory Offer, for his continuous guidance, contribution and engagement in my PhD research. His trust in me and enthusiasm in our research made my time as a PhD student fruitful and enjoyable.

I must also thank my supervisors, Dr Billy Wu and Dr Vladimir Yufit, for their countless technical insights and involvement. My supervisors have been invaluable to my PhD and without them, our research would not have been as productive.

I would like to extend my gratitude to Toshio Shibagaki-san for his contributions to the DTV technique used in LFP cells and to Dr Moshiel Biton and Dr Farid Tariq for their time and effort during the *in-operando* tomography project of silicon half-cells.

I would like to thank all past and present members of the research group for providing a wonderful working environment. I wish to extend particular thanks to Ian C, Krishna, Alex, Monica, Yan, Yatish, Wasim, Ian H, Harini and Dan for their practical and friendly support.

In addition, I wish to thank Prof. Ricardo Martinez-Botas and my funding bodies, Climate-KIC and Innovate UK, for providing me with this PhD opportunity.

I would also like to thank all my friends who pulled me through all these years and gave me a life outside research. A particular mention to Jay who lived with me as a friend/brother for the past 8 years ever since being randomly selected as my roommate in halls in first year undergrad. I want to thank all my previous housemates Kieron, Chris D, Niko, Toriche, Jack, James, Paddy and Kitty for providing awesome houses. All members of Imperial College Canoe Club for the fantastic adventures around the globe. Jarith crews Kuru, Ash, Shaan and Gary for the epic gaming weekends. Aki and Kato for the bouldering breaks. Sharon for all the food adventures around London. And Aeri for her love, understanding and emotional support.

Finally, I wish to extend my gratitude to my parents, my sisters, my grandparents and all my family members for their continuous love and support.

PROJECT OUTPUTS

PATENT

“New method for battery degradation tracking” – [Yu Merla](#), Billy Wu, Vladimir Yufit and Gregory J. Offer. Filed to the UK patent office on 24th March 2016 (PATENT APPLICATION NUMBER 1605060.1). Imperial Innovations.

ACADEMIC JOURNAL PUBLICATIONS

“An easy to parameterise physics-informed battery model and its application towards lithium-ion battery cell design, diagnosis and degradation” - [Yu Merla](#), Billy Wu, Vladimir Yufit, Ricardo F. Martinez-Botas and Gregory J. Offer. In preparation.

“Tracking degradation in lithium iron phosphate batteries using differential thermal voltammetry” - Toshio Shibagaki, [Yu Merla](#), Gregory J Offer. *Journal of Power Sources*. Under review.

“Extending battery life : A low-cost practical diagnostic technique for lithium-ion batteries” - [Yu Merla](#), Billy Wu, Vladimir Yufit, Nigel P. Brandon, Ricardo F. Martinez-Botas and Gregory J. Offer. *Journal of Power Sources*. 331 (2016) 224–231.
doi:10.1016/j.jpowsour.2016.09.008.

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“In-operando X-ray tomography study of lithiation induced delamination of Si based anodes for lithium-ion batteries” - Farid Tariq, Vladimir Yufit, David S. Eastwood, Yu Merla, Moshiel Biton, Billy Wu, Zhangwei Chen, Kathrin Freedman, Gregory Offer, Emanuel Peled, Peter D. Lee, Diana Golodnitsky and Nigel P. Brandon. *ECS Electrochemistry Letters*. 3 (2014) A76eA78. doi.org/10.1149/2.0081407eel.

CONFERENCE PRESENTATIONS

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“Detecting, diagnosing and controlling degradation in lithium ion battery packs” – Yu Merla, Ian Hunt, Yan Zhao, Marie-Therese v. Srbik, Monica Marinescu, Vladimir Yufit, Billy Wu, Ricardo Martinez-Botas, Nigel Brandon, Gregory J Offer. 67th Annual Meeting of the International Society of Electrochemistry (*ISE 2016*). The Hague, The Netherlands. 2016.

“Differential thermal voltammetry for tracking of degradation in lithium-ion batteries” - Yu Merla, Billy Wu, Vladimir Yufit, Ricardo F. Martinez-Botas, Nigel P. Brandon, Gregory J. Offer. 226th Meeting of the Electrochemical Society (*ECS 2014*). Cancun, Mexico. 2014

“Differential thermal voltammetry for tracking of degradation in lithium-ion batteries” - Yu Merla, Billy Wu, Vladimir Yufit, Ricardo F. Martinez-Botas, Nigel P. Brandon, Gregory J. Offer. 11th Symposium on Fuel Cell and Battery Modeling and Experimental Validation (*ModVal11*). Winterthur, Switzerland. 2014.

POSTERS

“Making Batteries Last Longer: A low-cost practical diagnosis technique for lithium-ion batteries” – Yu Merla, Billy Wu, Vladimir Yufit, Ricardo F. Martinez-Botas, Nigel P. Brandon, Gregory J. Offer. Advanced Battery Power Conference (*Batterietagung 2016*). Münster, Germany. 2016.

“Still Alive? Differential thermal voltammetry for tracking of degradation in lithium-ion batteries” - Yu Merla, Billy Wu, Vladimir Yufit, Ricardo F. Martinez-Botas, Nigel P. Brandon, Gregory J. Offer. Early Career Researchers Conference 2015 (*STFC 2015*). Abingdon, UK. 2015

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LIST OF SYMBOLS

Symbol	Unit	Name
A	-	Pre-exponent factor
C	F	Capacitance
DF	-	Degradation factor
E	V	Electrode potential
E_a	J/mol	Activation energy
E_{eq}	V	Equilibrium potential
F	C	Faraday constant
G	J	Gibb's free energy
j	A/m ²	Electrode current density
j_0	A/m ²	exchange current density
k	W/mK	Thermal conductivity
k_r	-	Rate constant
k_{wt}	-	Warning threshold coefficient
n	-	Number of electrons passed
OCV	V	Open circuit voltage
P	Pa	Pressure
$\dot{q}_x''$	W/m ²	Heat flux
R	Ω	Resistance
R_g	J/molK	Universal gas constant
S	J/K	Entropy
SOC	-	State of charge
SOH	-	State of health
t	s	Time
T	K	Temperature
V	V	Voltage
wt	-	Warning threshold

α_a	-	anodic charge transfer coefficient
α_c	-	cathodic charge transfer coefficient
η	V	Overpotential

ACRONYMS

ARC	Accelerating rate calorimetry
BEV	Battery electric vehicle
BMS	Battery management system
CAES	Compressed air energy storage
CC	Constant current
CPE	Constant phase element
CV	Constant voltage
DEC	Diethyl carbonate
DF	Degradation factor
DHFV	Differential heat flux voltammetry
DMC	Dimethyl carbonate
DTV	Differential thermal voltammetry
DV	Differential voltage
EC	Ethyl carbonate
EC	Electrochemical calorimetry
ECM	Equivalent circuit model
EIS	Electrochemical impedance spectroscopy
EMC	Ethylmethyl carbonate
EV	Electric vehicle
FOI	Features of interest
FRD	Faradic rate degradation
GHG	Greenhouse gas
GPE	Gel polymer electrolyte
HF	Heat flux
ICA	Incremental capacity analysis (dQ/dV)
IEA	International Energy Agency
IRENA	International Renewable Energy Agency
LAM	Loss of active material

LCO	Lithium cobalt oxide
LCP	Lithium cobalt phosphate
LF	Low frequency (approx. 1~100Hz)
LFP	Lithium ion phosphate
LFSF	Lithium iron fluorosulfate
LLI	Loss of lithium inventory
LMO	Lithium manganese oxide
LTO	Lithium titanate
LTS	Lithium titanium sulphide
MAD	Mean of absolute deviation
MF	Medium frequency (approx. 100~1000Hz)
NaS	Sodium sulphur battery
NCA	Nickel cobalt aluminium oxide
NCM	Nickel manganese cobalt
OCV	Open circuit voltage
ORI	Ohmic resistance increase
PC	Propylene carbonate
PEM	Potentiometric entropy measurement
PHEV	Plug-in hybrid electric vehicle
PVdF	Poly(vinylidene fluoride)
RC pair	Resistor-capacitor pair
RMS	Root mean squared
RUL	Remaining useful life
SEI	Solid electrolyte interphase
SEM	Scanning electron microscope
SOC	State of charge
SOF	State of function
SOH	State of health
SRCV	Slow-rate cyclic voltammetry
UAV	Unmanned air vehicle

VC	Vinylene carbonate
VEC	Vinyl ethylene carbonate
<i>wt</i>	Warning threshold
XRD	X-ray diffraction

Chapter 1. INTRODUCTION

1.1. WHY DO WE NEED BATTERIES?

Batteries are used in numerous applications and have become a crucial form of energy storage device in recent years. Notable applications are illustrated in Figure 1 which describes how batteries support our lives in many aspects such as transport, communication, entertainment and security.



Figure 1. Various applications of a battery

Batteries have become the preferred mode of energy storage for number of different reasons. One of the main factor is their high energy and power densities in terms of both volume and weight. Currently, portable electronics take the biggest proportion of the available worldwide battery capacity but this is set to change by around 2023 with the growth of the electric vehicle

(EV) market which is necessary to reduce greenhouse gas (GHG) emissions. Figure 2 provided by Bloomberg New Energy Finance, illustrates the forecast [1].

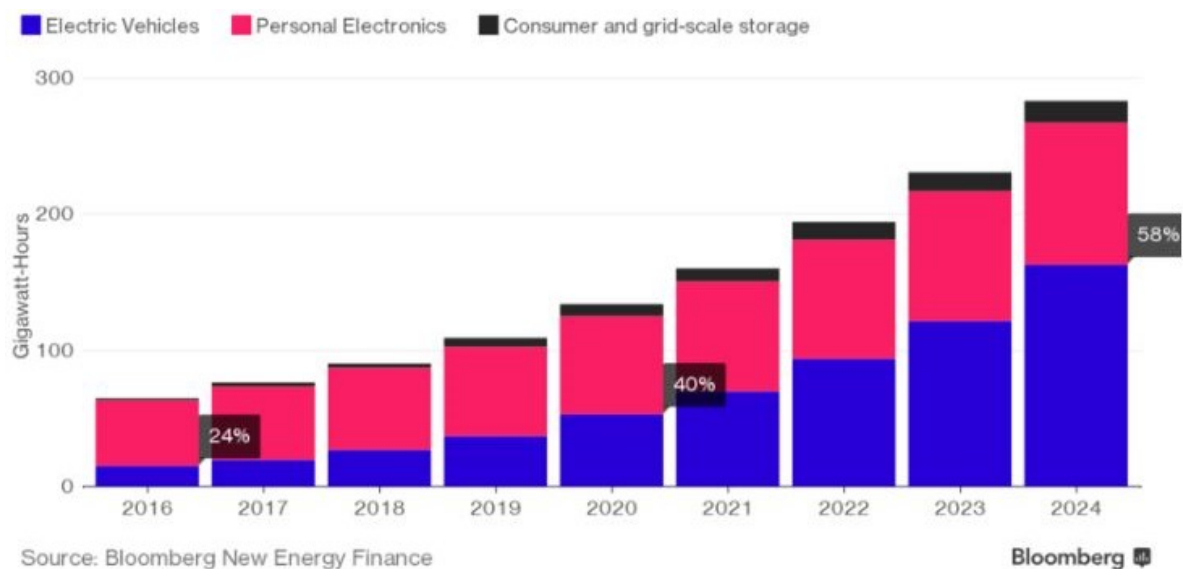


Figure 2. GWh usage of worldwide lithium-ion batteries. Currently, personal electronics dominate the usage however EVs are forecast to surpass electronics [1].

Global sales of EVs have been rapidly increasing over the last few years with over 750'000 plug-in electric cars sold just in 2016 [2]. Electric cars include battery electric vehicles (BEVs) and plug-in hybrid electric vehicles (PHEVs). This is a phenomenal transition considering that the sales were around 6000 units in 2010 [3]. As illustrated in Figure 3, the International Energy Agency (IEA) reports that EV sales grew by 40% between 2014-2015 followed by 70% between 2015-2016 which now puts over 2 million electric cars in circulation [2].

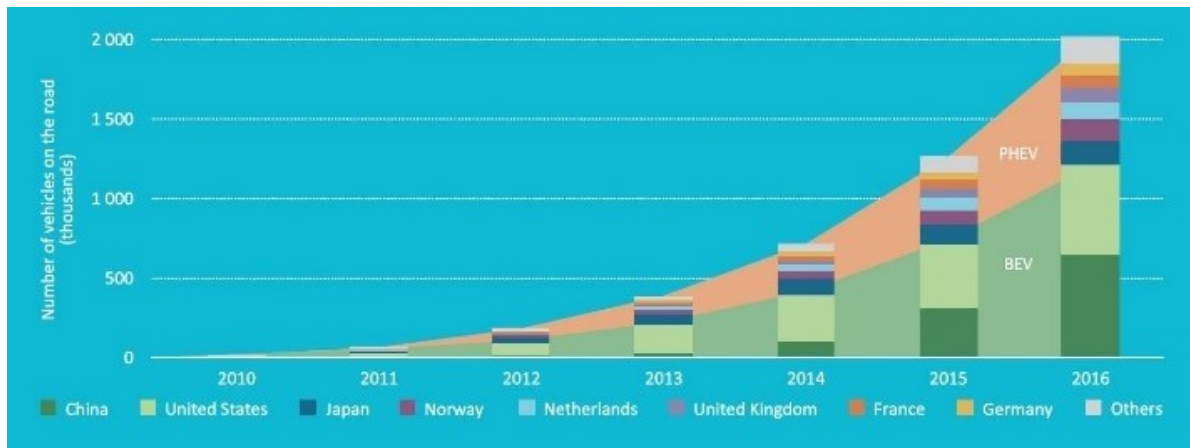


Figure 3. Evolution of the electric car stock (BEV and PHEV) between 2010 and 2016 [2].

It should be noted that passenger cars are not the only type of vehicle to see recent electrification. Notably there are more than 200 million electric two-wheelers and about 170,000 electric buses worldwide [4]. Electric light-duty vehicles have also become more visible in recent years as well as announcements of electric heavy-duty vehicles by some manufacturers.

This growth is the result (and the cause) of improvements in battery cost and capacity. The volumetric energy density of lithium-ion batteries based on industrial-wide trend is said to have increased from 60 Wh/L in 2008 to 295 Wh/L in 2015 [5]. It is difficult to get a complete view on the cost of a battery pack today as most automotive manufacturers do not disclose this information. McKinsey & Company recently released a report [3] stating that battery pack costs are now below \$230/kWh which is almost 80% cost reduction since 2010 at \$1000/kWh. Figure 4 describes how the average battery pack price has decreased over the last 6 years and how this has helped the EU and China to greatly increase their EV sales.

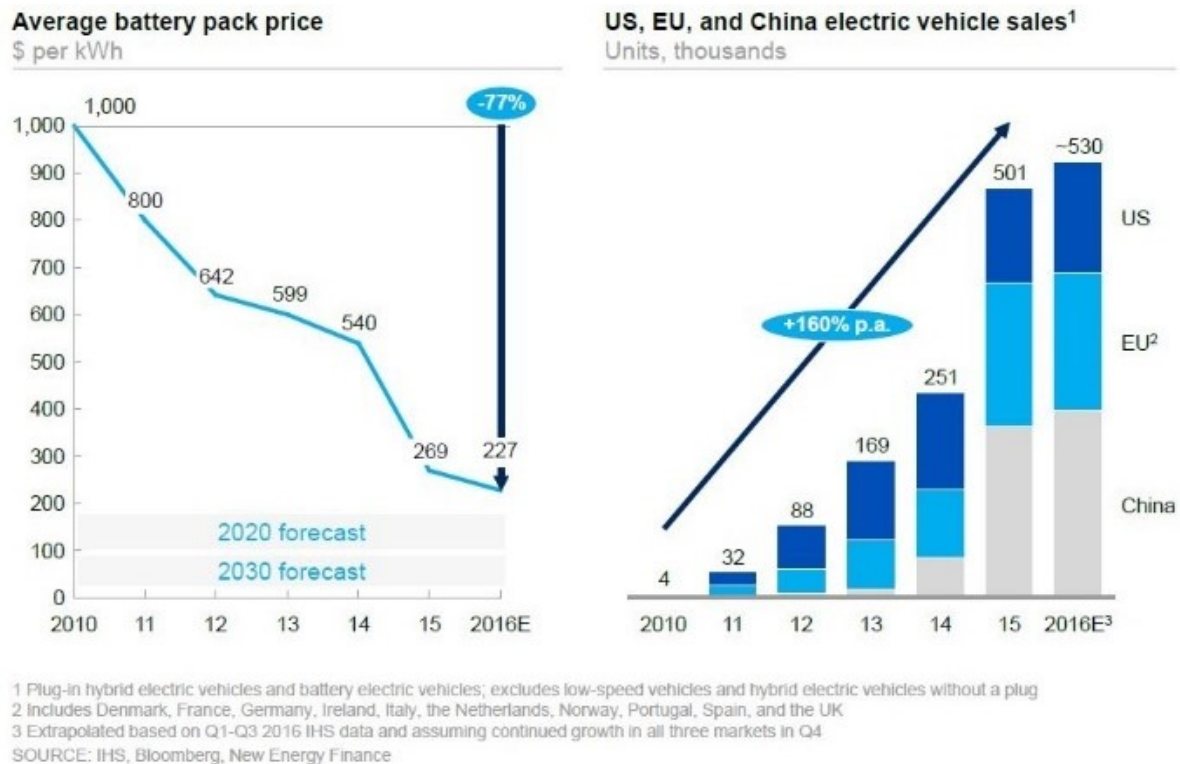


Figure 4. Rapid decrease in average battery pack price (left) which has helped EU and China to greatly increase their EV sales in recent years (right) [3].

What is interesting here is that the rate of decrease in battery pack price has always surpassed expectations in the last few years. For example, already in 2014, the cost was below the average projected cost for 2020 [6].

By 2016, the annual market share of EVs rose above 1% in seven countries [4] where Norway has a staggering 23% followed by the Netherlands at almost 10% and Sweden at around 4%.

The remaining four countries are France, United Kingdom, China and Denmark.

Actual EV sales on the other hand is dominated by China with almost 350,000 units in 2016 followed by the United States with more than 150,000 units and Norway at around 50,000 units [2]. Figure 5 illustrates the statistics provided by the IEA. China currently has approximately 650,000 electric cars alone as well as 350,000 electric buses and 200 million electric two-wheelers.

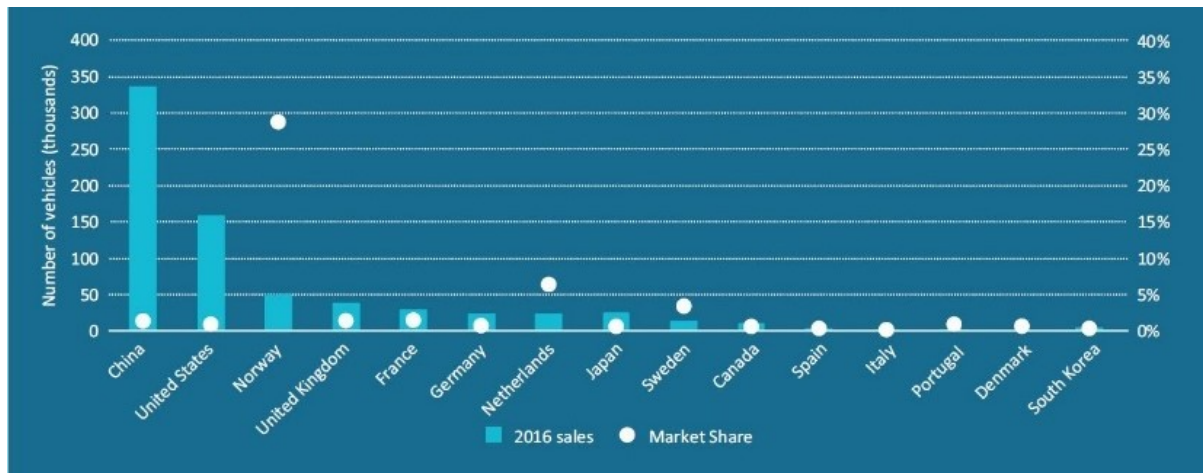
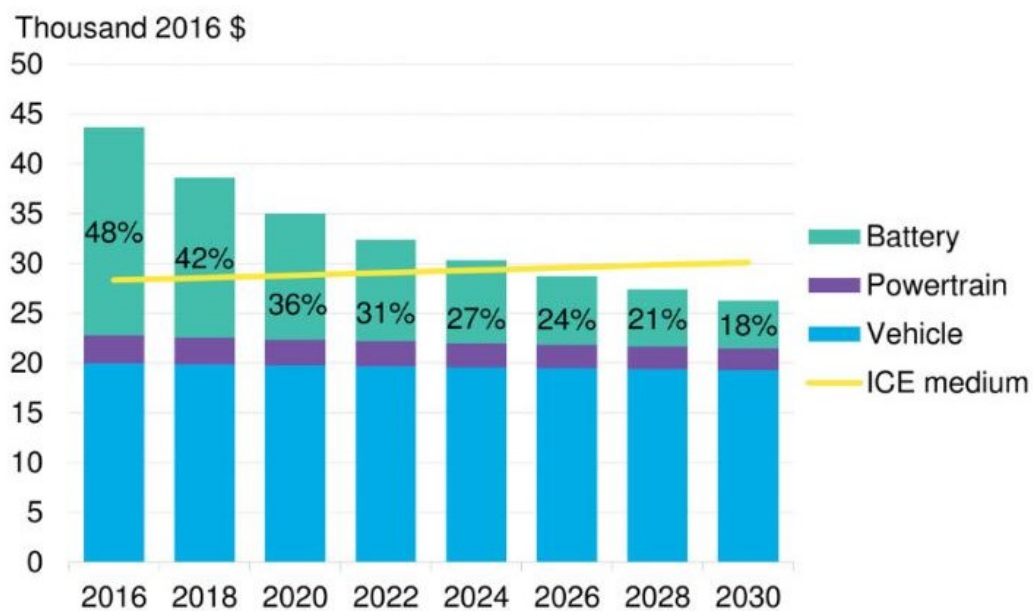


Figure 5. EV sales and market share in selected countries, 2016 [2].

The two key factors limiting the consumers buying an electric vehicle today is its cost and range relative to internal combustion engine (ICE) vehicles. McKinsey & Company predicts the EV battery pack cost to drop below \$190/kWh by 2020 and speculates below \$100/kWh by 2030 [3]. Bloomberg New Energy Finance also suggests a price parity with ICE vehicles in 2025 pre-tax retail price as presented in Figure 6 which should greatly impact on EV sales [7].



Source: Bloomberg New Energy Finance

Note: Estimated pre-tax retail prices

Figure 6. EV vs. ICE U.S. medium segment vehicle price estimates [7]

Grid and home level energy storage should also be considered for lithium-ion battery usage despite the relatively small fractional usage as seen in Figure 2. Pumped hydro storage has been the sole significant technology for over a century in grid-level energy storage but that is slowly beginning to change where batteries are now accepted as a viable alternative [8]. Given the improved and cheaper renewable energy generation from solar and wind, lithium-ion batteries are increasingly favourable as a storage device to redistribute energy to balance supply and demand [4]. Amongst other available non-pumped hydro technologies, lithium-ion battery is dominating in terms of annual shares and installation as depicted in Figure 7 and Figure 8 [2].

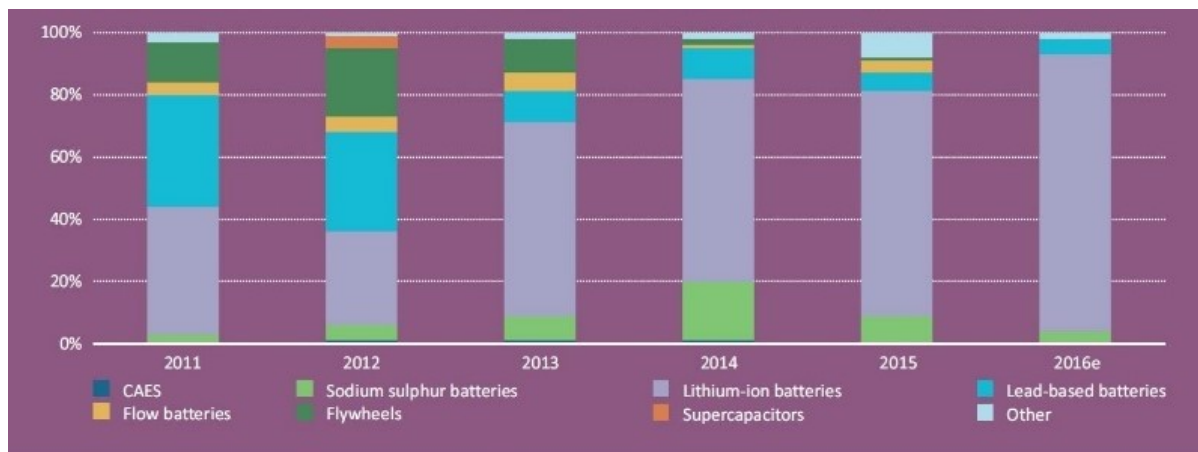


Figure 7. Annual shares in non-pumped hydro storage technology additions [2]. CAES stands for compressed air energy storage.

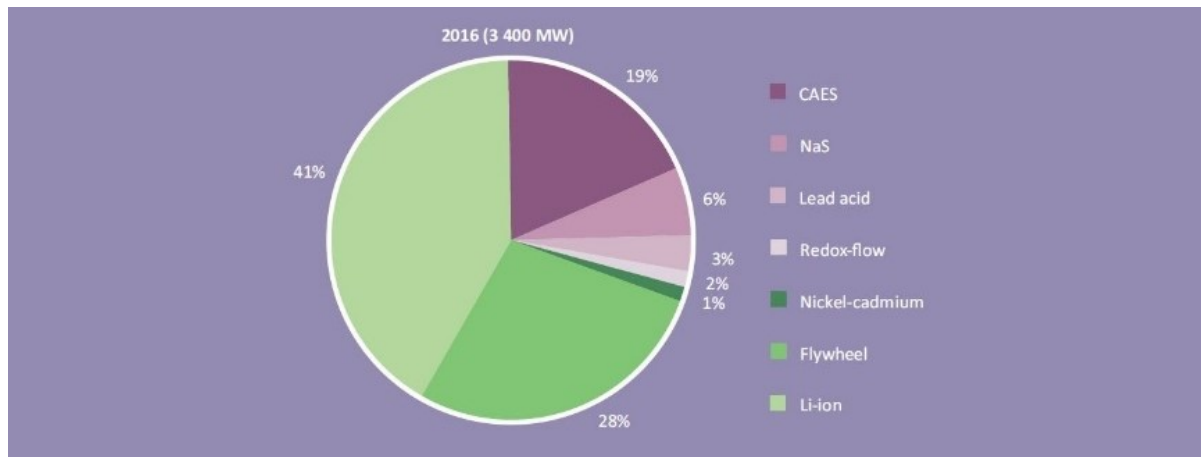


Figure 8. Installed non-pumped hydro storage in 2016 [2]. CAES stands for compressed air energy storage and NaS for sodium sulphur batteries.

With the increasing demands from personal electronics, EVs and grid-level storages, it is said that our worldwide battery power capacity has to increase an additional 21GW by 2025 from the current 1GW [2]. The International Renewable Energy Agency (IRENA) forecasts the worldwide battery power capacity and annual revenue to 2023 in Figure 9.

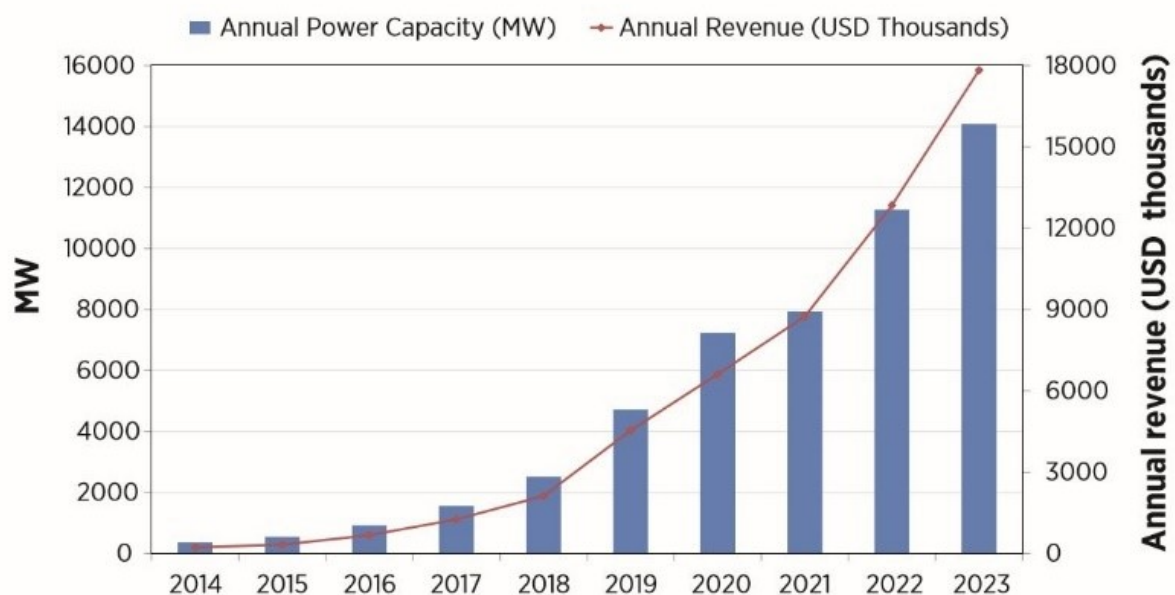


Figure 9. Worldwide forecast of battery power capacity and annual revenue for utility-scale applications [8].

The next natural question here is that who is going to produce so many batteries? The short answer is China [1]. Elon Musk states that his Gigafactory will be able to produce 35 GWh of

batteries a year when completed in 2018. In contrast, China is already producing the majority of the batteries and have announced that they will be producing 120 GWh annually by 2021. This forecast is visualised in Figure 10.

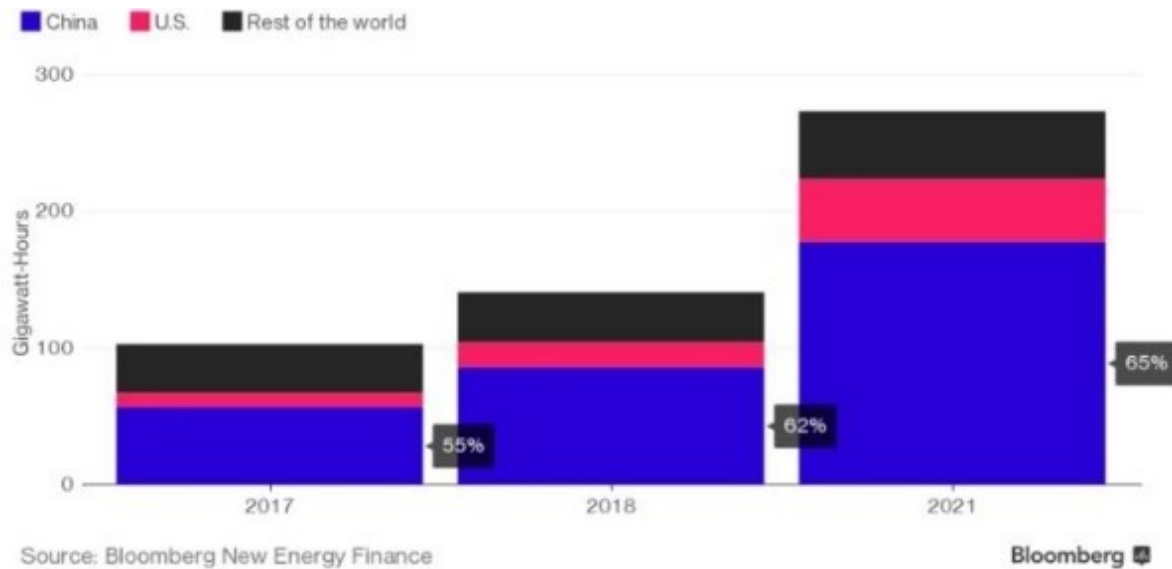


Figure 10. Annual worldwide lithium-ion battery production forecast in GWh [1].

In anticipation of this immense increase in battery demand, it is our duty, as battery researchers, to further reduce battery (pack) costs and improve performance to meet future targets.

It should also be noted that it is crucial to increase the availability of charging infrastructure and reinforce policy changes that will financially favour consumers to use EVs instead of ICE vehicles for GHG emission targets. However, this is regarded as outside the scope of this PhD.

1.2. THESIS AIM

There are many ways to reduce the costs of a battery. One way is to increase the level of understanding of a given battery so that the engineers can reduce the safety factor and avoid over-engineering the battery to meet system requirements with enough confidence. Another way is to promote the use of second life batteries to avoid purchasing fresh batteries where

possible. It is also possible to reduce the material costs through more efficient material extraction or substitution with cheaper materials. The costs of manufacture can be reduced by automating as much of the process as possible and/or developing a more cost-effective assembly procedure.

Battery performance can be improved internally through materials and design or externally through system design and adaptive operation to match external and internal conditions. When introducing a new technology, it is important to consider the impact on costs and various performance parameters. Even if a new technology doubles the energy density, it may not be favourable if it increases the cost or decreases the cycle life considerably.

Given the timeframe of the PhD and the engineering focus, I have focussed on the following:

- Expand the knowledge of lithium-ion batteries in terms of how its internal state affects the performance. Do this for the two of the most common battery chemistries: graphite-nickel cobalt manganese (NCM) & graphite-lithium iron phosphate (LFP) cells. It is important to explore both cell-level and pack-level performances to cover various applications (e.g. smartphone vs. EV).
- Develop a new diagnosis technique that can measure the battery internal state in detail while minimising equipment/installation costs and complexity to make it readily suitable for an on-board usage in the most relevant applications such as portable electronics and EVs. This should ideally be usable for both tracking the state-of-health (SOH) of a battery in operation as well as a factory acceptance test (FAT) for industries to screen 2nd life batteries.
- Develop a way to interpret and use the results from such diagnosis to adaptively control the battery operation to maximise cycle life.
- Develop prognosis capabilities from the technique to predict and mitigate any potential upcoming battery failures.

1.3. RESEARCH QUESTIONS AND HYPOTHESIS

Good research questions come from good hypotheses. A gap exists in the science in terms of a low-cost application-ready battery diagnosis/prognosis method that can increase operation lifetime and mitigate failure (to be discussed in detail in the next chapter). The hypothesis is that temperature and voltage measurements of a battery in operation can provide a wealth of information if analysed appropriately. The following research questions are:

- Can temperature and voltage measurement give enough information alone to identify the complex internal state of a battery in detail?
- Can such information be used to minimise degradation of a battery?
- Can such information be used for predicting future battery failures?
- Can such a technique be installed at a low-cost?
- Can the technique be upscaled to pack application?
- Can the technique provide similar information for various chemistries?

It should be noted that these are the overall research questions and many more research sub-questions were addressed throughout the various experiments (to be identified in later chapters).

1.4. THESIS STRUCTURE

The thesis will continue from here with a detailed literature review identifying the gap mentioned above followed by stages of experiments carried out in roughly chronological order to answer the overall research questions. The detailed structure is as follows:

Chapter 1: Introduction

- Sets the scene with a market review on the current situation and future projections of the battery economy. Lays out the thesis aim, hypothesis and key research questions.

Chapter 2: Literature review

- A focused literature review on the past, present and future of battery technology identifying the gap in research.

Chapter 3: DTV concept and cell-level application

- Introduces the concept of the novel diagnosis technique and presents findings from accelerated aging experiments on NCM cells to validate its use as a diagnosis method on a cell level.
- Presents the use of the technique as a 2nd life battery screening tool for diagnosing cells with unknown history.

Chapter 4: Pack application, DHFV and prognosis

- Presents the capability of the technique in a battery pack and how it can be used to identify aged cells and predict upcoming fail cells at a low-cost while maintaining robustness of the method.
- Also, explores a complimentary technique using heat flux instead of temperature.

Chapter 5: IR-decoupled DTV and adaptive operation

- Presents an additional upgrade to the technique to decouple information to help analyse the results in a greater detail.
- Simultaneously presents a new technique that can obtain the open circuit voltage (OCV) curve and the overall internal impedance of the cell in a normal charging time (~1 hour).
- Presents how the upgraded technique can be used to adaptively change the operating condition of the battery to slow down certain degradation mechanisms.

Chapter 6: LFP application and SOH estimation

- Presents results from accelerated aging experiment on LFP cells to validate the use of the technique on another common battery chemistry and expand its use as a capacity estimation tool from a partial charge/discharge.

Chapters 3, 4, and 6 contain work from academic journal publications published in the Journal of Power Sources by Elsevier of which I am the author of [9–11]. I would like to acknowledge that Elsevier holds the copyright to these publications and I, as an author, have the rights to insert and/or reproduce the said publications for my personal use in the form of a thesis which is to be published strictly for non-commercial use [12]. Entries in these chapters may be, in full or in part, included verbatim from the said publications.

Chapter 5 contains new developments and additional features/applications for the DTV technique from a patent of which I am one of the inventors [13]. If any commercial application is derived from this work, please consult Imperial Innovations.

I would like to note that I carried out the research presented in these chapters in full under the guidance of my supervisors unless otherwise stated.

The DTV concept was initially published in [14] by Wu et al. of which I am the co-author of where my contribution was the experimental validation.

For Chapter 6, I would like to acknowledge that Toshio Shibagaki-san carried out all the laboratory experiments and data computation presented. I contributed to this work as a supervisor during the entirety of his research as well as wrote the MATLAB codes for data processing. The results analysis was carried out collectively by all authors.

Chapter 2. LITERATURE REVIEW

This chapter presents a concise and relevant literature review on the current state of lithium-ion batteries as well as their degradation mechanisms and diagnosis techniques. The review will focus on identifying the gaps in the literature which led to this research.

2.1. WHY USE A LITHIUM ION BATTERY?

Amongst many selections of electrochemical cells, lithium-ion batteries are currently the most common sustainable energy storage method for commercial applications due to the relative maturity of technology, the existing size of the industry, a good balance between energy and power densities, and acceptable cost for many applications. In EV applications, high gravimetric power and energy densities are crucial for acceleration and range respectively. In space-limited applications such as portable electronics, high volumetric energy density is needed. Figure 11 maps the gravimetric energy and power densities of various electrochemical cells. However, it should be noted that solid-state, Li-S and Li-O₂ batteries are not mature technologies, and hence lithium-ion batteries are currently the best available for commercial application.

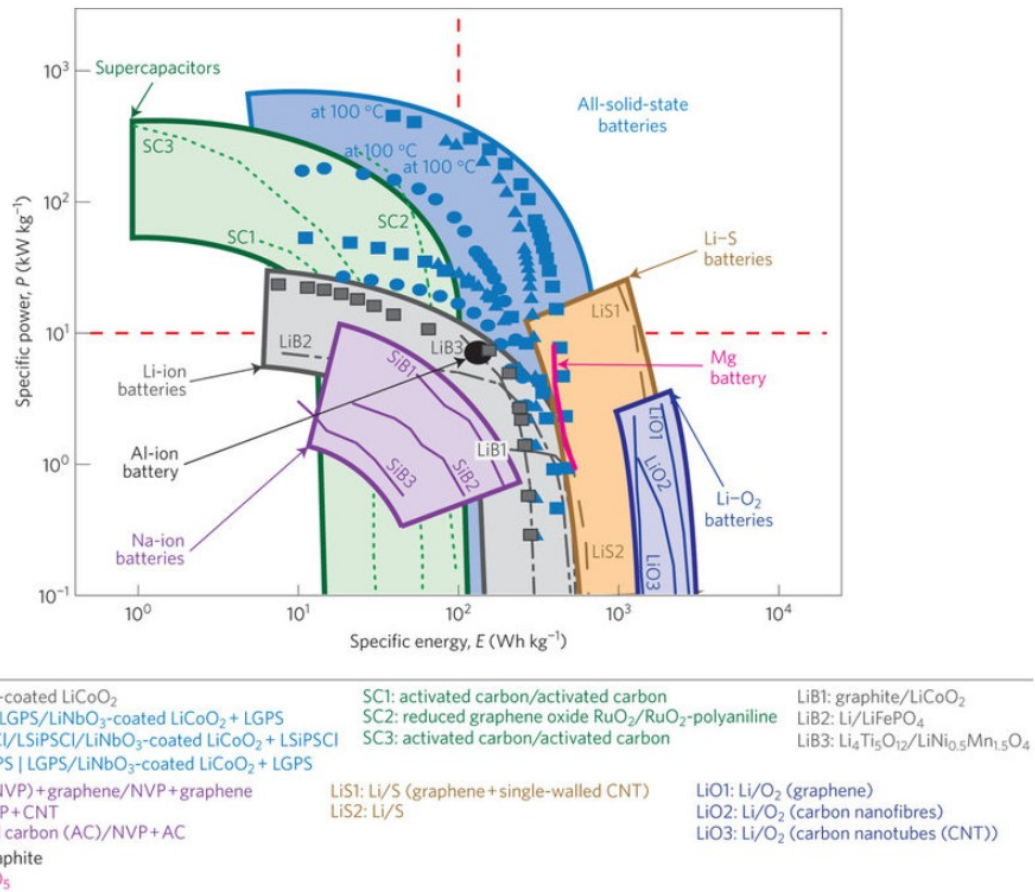


Figure 11. Ragone plot describing the gravimetric energy and power densities of various conventional and new electrochemical cells. Source: [15].

2.2. WHAT IS A LITHIUM ION BATTERY?

Lithium ion batteries are made from 5 main components. A positive electrode and a negative electrode sandwich an electrically insulating separator immersed in an ion-conducting electrolyte where the outer electrode surfaces are adhered to current collectors. The positive and negative electrodes are often referred to as the cathode and the anode of the cell respectively (despite the fact that by definition they change from cathode to anode between charge and discharge) and are made from porous materials. Figure 12 depicts the internal configuration for a cylindrical cell. There are also other inactive components that make up the battery such as binders and conductive agents in the electrodes, and salts and additives in the electrolyte.

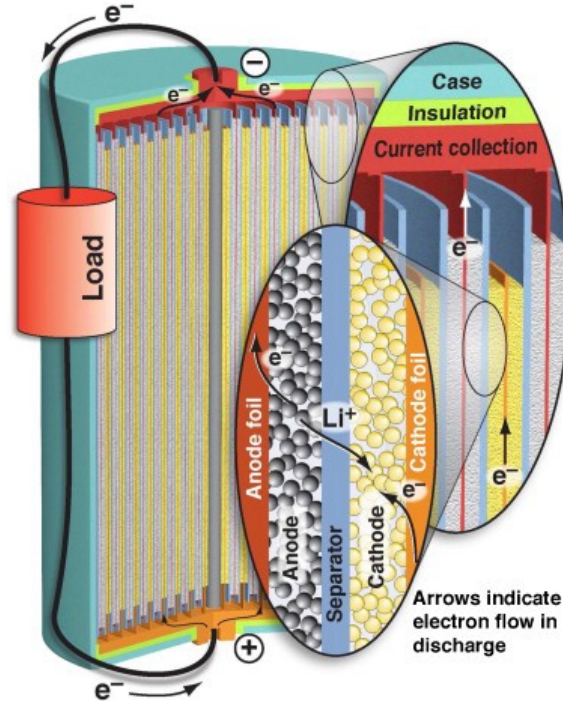
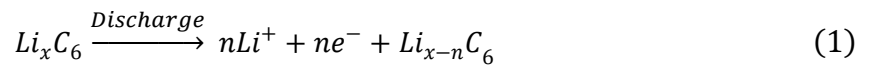
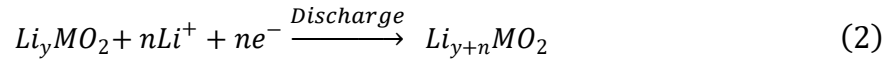


Figure 12. Internal illustration of a cylindrical cell on an electrode- and particle-level. Source: [16].

When the cell is fully charged, all the cyclable lithium is stored in the porous anode which is commonly made of graphitic carbon. The different thermodynamic potential of the anode and the cathode creates the potential difference measured between the two terminals. When a load is applied to the terminals, reactions occur at the electrode-electrolyte interface where the lithium splits into lithium ions and electrons, with the opposite occurring at the other electrode. The electrochemical reaction for a conventional graphitic carbon anode is as follows:



It is thermodynamically favourable for the lithium ion to diffuse through the electrolyte and separator to the cathode due to the lithium concentration gradient. The electrons in turn will conduct through the external circuit providing the electrical work. This occurs through the current collectors as electrons cannot conduct through the electrically insulating separator. The lithium ions at the cathode combine with the electrons and the cathode material to form a lithium rich cathode material. The electrochemical reaction for a typical lithium metal oxide cathode is as follows:



The whole process is reversed when the cell is charging where the lithium is extracted from the cathode at its electrolyte interface and the ions diffuse to the anode surface where it is inserted back.

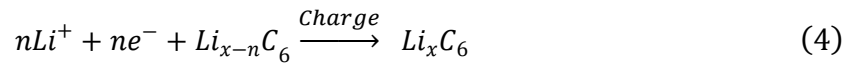
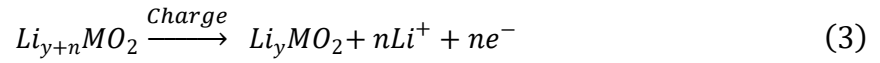


Figure 13 illustrates how the lithium-ions shuttle back and forth during operation between the layered electrodes as intercalated lithium.

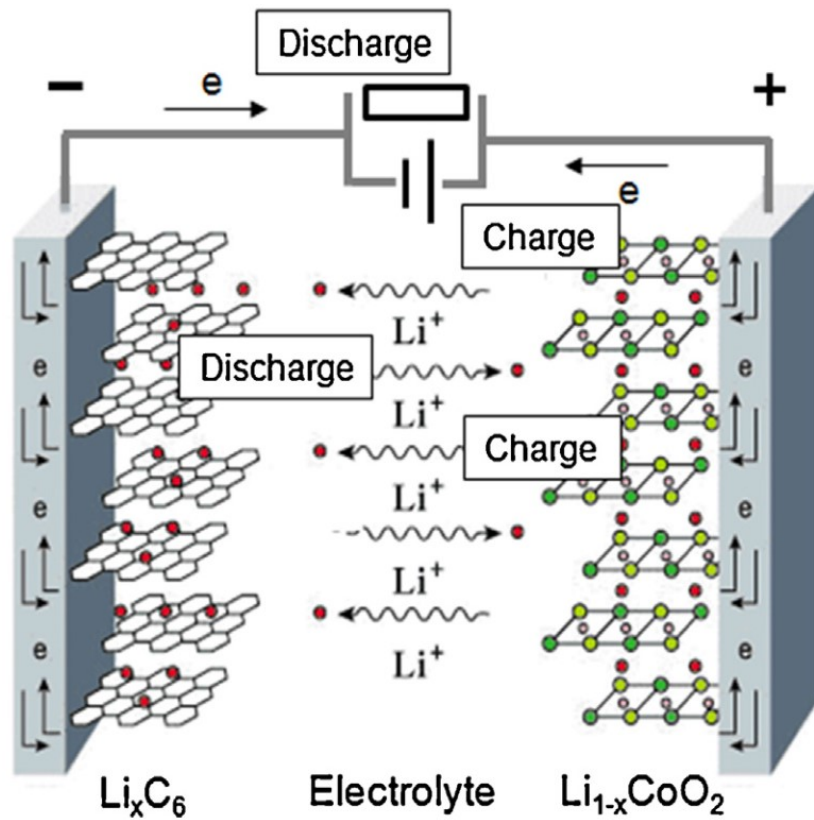


Figure 13. Illustration of movement of lithium-ions during charge and discharge for a typical graphite - lithium cobalt oxide cell. Source: [17].

During discharge, the depletion of lithium at the negative electrode-electrolyte interface creates a lithium concentration gradient in the electrode particles. This gradient drives the lithium to diffuse from the bulk to the surface as this is the lowest energy state. The diffusion process in a typical graphitic anode at a room temperature is said to take roughly 20-40 minutes of relaxation phase to equilibrate after load [18]. Therefore, solid state diffusion has a strong impact on power capabilities of a cell as this defines how fast the lithium can be extracted/inserted while maintaining an operational cell voltage. This is strongly dependant on many parameters notably the temperature and current rate.

The capacity of the cell is defined by how much lithium can be stored in an electrode. This suggests that increasing the volume fraction of electrode material and/or increasing its energy density can increase the capacity of a lithium-ion battery. It is to be noted that the capacity of the cell is defined by the electrode with the smaller capacity.

Typically, a commercial lithium-ion battery stores lithium using intercalation electrodes however much research is also carried out on conversion electrodes for their higher theoretical specific capacity as demonstrated in Figure 14. The following sections will focus on literature related to intercalation electrodes as they are more relevant for immediate real world applications.

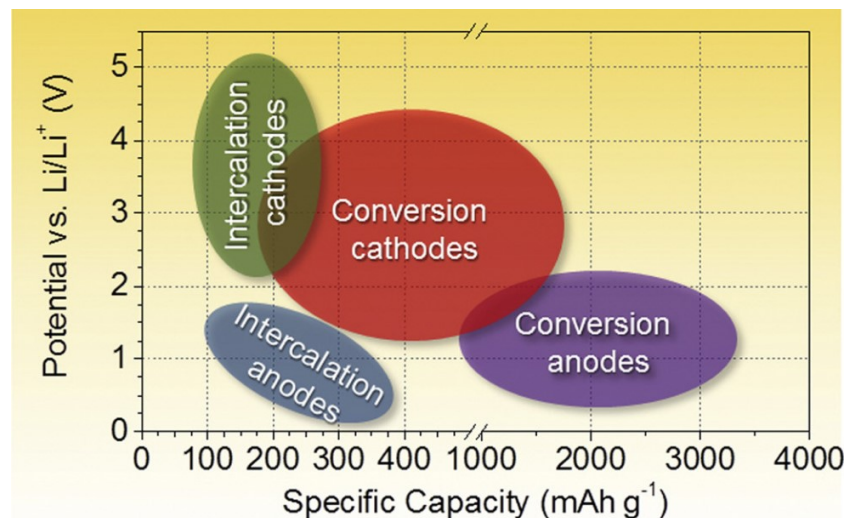


Figure 14. An overview of potentials and specific capacities of electrode types. Source: [19].

2.3. INTERNAL COMPONENTS

2.3.1. CATHODE

Modern intercalation cathodes are made from transition metal oxides, metal chalcogenides, and polyanion compounds [19]. The material is required to reversibly store and release lithium for it to function as an electrode. An ideal cathode material should have a high potential and rate capabilities for increased power; high specific capacity and coulombic efficiency for more stored energy; long cycle life; high safety; and low cost of material and production. It is clearly very difficult to achieve all criteria and many battery researchers focus solely on improving the material. Figure 15 presents the potentials and specific capacities of some conventional intercalation cathode materials where the acronyms represent lithium cobalt phosphate (LCP), lithium cobalt oxide (LCO), nickel cobalt manganese oxide (NCM), nickel cobalt aluminium oxide (NCA), lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium iron fluorosulfate (LFSF), and lithium titanium sulphide (LTS).

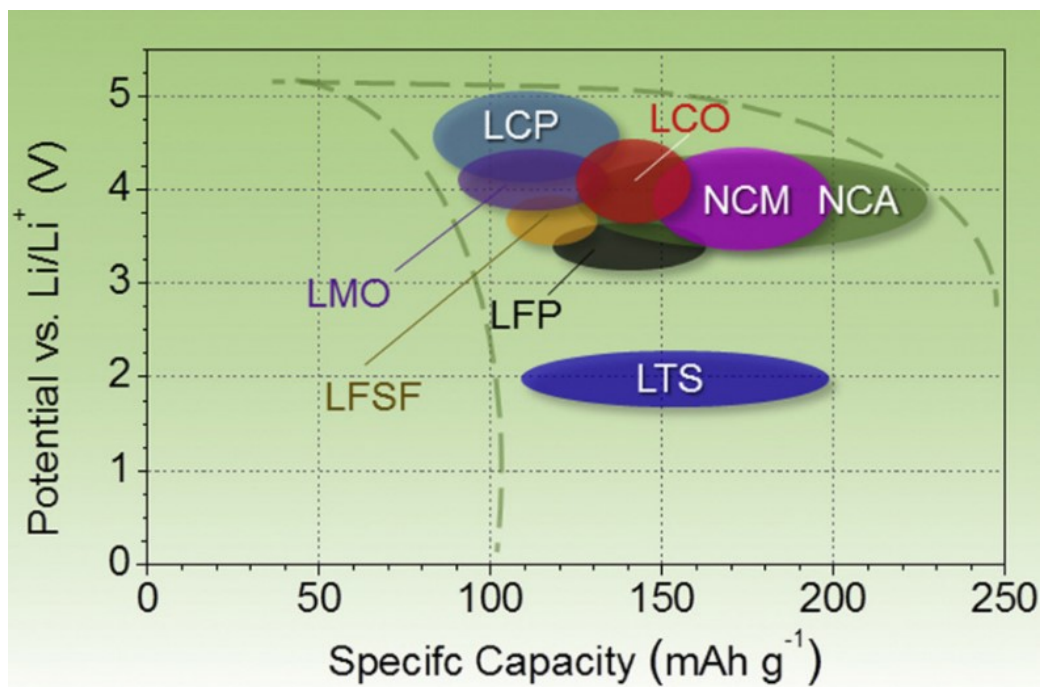


Figure 15. An overview of potentials and specific capacities of common intercalation cathodes. Source: [19].

As depicted in Figure 16, these intercalation materials are often made from one of the four crystalline structures: layered, spinel, olivine and tavorite.

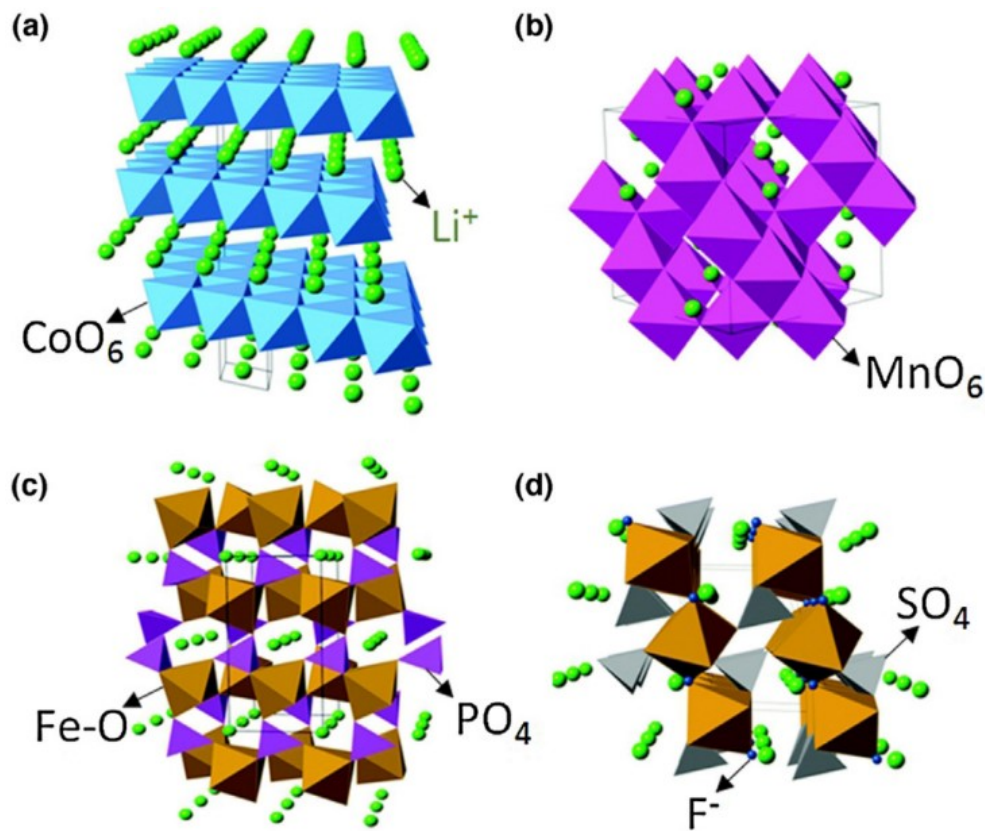


Figure 16. Four typical crystalline structures of intercalation cathodes: (a) layered LCO, (b) spinel LMO, (c) olivine LFP, and (d) tavorite LFSF. Green spheres represent stored lithium and the various prisms represent the cathode material.

Source: [19].

LCO is said to be the first transition metal oxide cathode to be introduced [20] as well as the most commercially successful cell chemistry still used by the majority of commercial lithium-ion cells today. LCO has great specific capacity and volumetric capacity amongst other advantages [21]. However, it comes with the downside of high cobalt cost [22] and low thermal stability. Nickel can substitute cobalt with lower costs while maintaining similar theoretical specific capacity but also has a very low thermal stability [23]. This problem can be improved by adding small amounts of aluminium [24] which lead to the growth in popularity of NCA cells (e.g. Panasonic cells used in TESLA).

LMO is also an attractive chemistry for the lower cost of manganese relative to cobalt [25] and low toxicity, however it suffers from low structural stability especially at elevated temperatures. To increase the structural stability, nickel and cobalt can be added to form NCM cathodes [26,27]. Typically, the stoichiometric composition of the transition metals is equal at $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, however in recent times, nickel-rich NCM cathodes, $\text{LiNi}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18}\text{O}_2$, have been reported to increase capacity [28]. The core of the electrode particle is nickel rich to store more lithium and the surface has more manganese for better thermal stability.

Researchers have developed polyanions as alternative cathode compounds which contain large $(\text{XO}_4)^{3-}$ polyanions ($\text{X} = \text{S}, \text{P}, \text{Si}, \text{As}, \text{Mo}, \text{W}$) to increase redox potential as well as structural stability [29]. LFP is the most common cell chemistry for this type of compound and is widely available commercially. Its olivine structure is said to have excellent structural stability and high rate capability but suffers from relatively low average voltage and conductivity.

LTS is a representative metal chalcogenide cathode with 1000+ cycle life and high gravimetric energy density [30]. Despite its advantages, the cell chemistry is not as common for its low voltage.

Table 1 summarises the characteristics of the discussed intercalation cathode materials.

Table 1. Properties of representative commercial intercalation cathode materials. Specific capacity represented in [theoretical/experimental/commercial] and Volumetric capacity in [theoretical/commercial]. Adapted from [19].

Crystal structure	Material	Specific capacity	Volumetric capacity	Average voltage	Comments
Units	-	mAh g ⁻¹	mAh cm ⁻³	V	-
Layered	LTS	225/210 [31]	697	1.9	High gravimetric energy density and long cycle life. Low voltage [30].
	LCO	274/148 [32]/145	1363/550	3.8	Very common. High material cost. Low thermal stability [22].
	NCM	280/160 [33]/170	1333/600	3.7	Better thermal stability and lower cost than LCO [27].
	NCA	279/199 [34]/200	1284/700	3.7	Higher specific capacity. Low thermal stability [35,36].
Spinel	LMO	148/120 [37]	596	4.1	Low material cost and less toxic than Co & Ni. Low thermal stability . [38,39]
Olivine	LFP	170/165 [40]	589	3.4	High thermal stability. Low voltage. [41]

2.3.2. ANODE

An ideal anode should have all the positive characteristics described previously for the cathode such as low cost, high capacity and cycle life. The only difference is that it should have a lower potential to increase the potential difference between the two electrodes for a higher power (it should be noted that rate capability and electrical/ionic conductivities are also important for power). Figure 17 maps the different anode materials according to their specific capacities and potentials. Carbon and lithium titanate (LTO) are intercalation anodes and the remaining are conversion anodes. Anodes are often used with excess capacity with respect to the cathode in a cell for its higher specific capacity and to minimise anode overcharge.

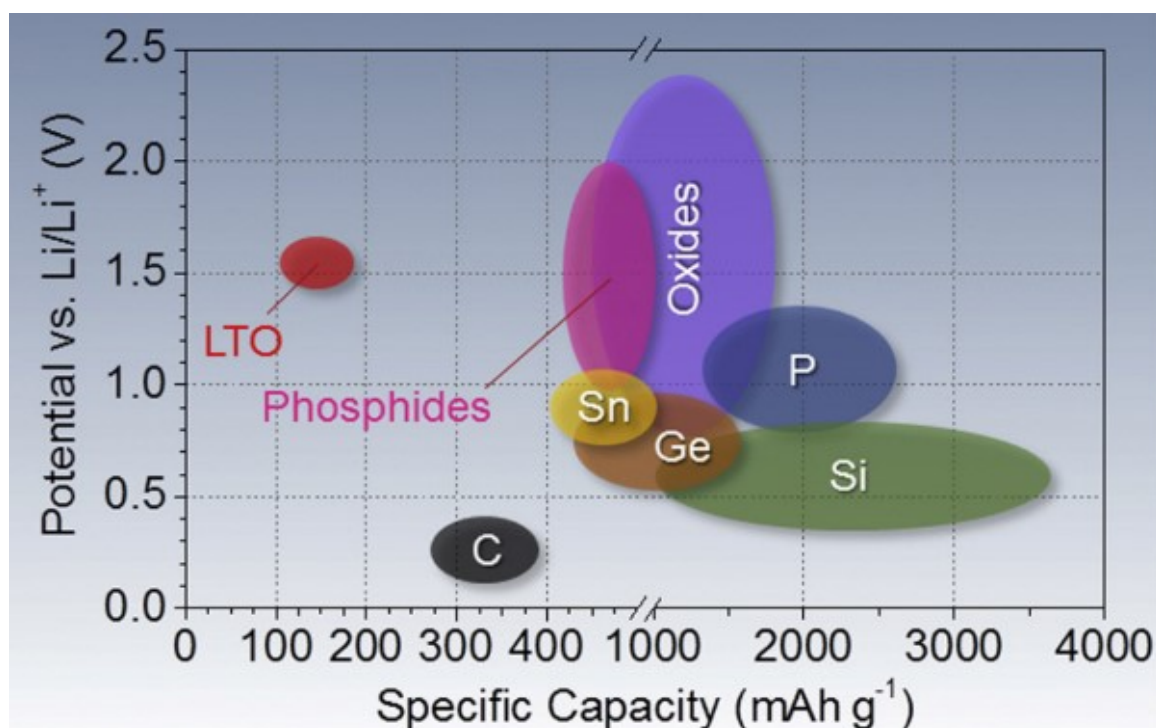


Figure 17. An overview of potentials and specific capacities of common anodes. Source: [19].

In the early years of lithium-ion battery research, lithium metal was used as the anode which has a very high specific capacity and low potential. However, new anode materials were developed as lithium metal anode are susceptible to dendrite growth which can lead to internal short circuit followed by catastrophic failure [42].

Carbon is currently the most common and commercially viable option for the anode. It is often made from graphite where the lithium is intercalated between the sheets of carbon as depicted in Figure 18a. Carbon has most of the positive characteristics required for an anode: low cost due to its material abundance; high specific capacity; high power due to its high lithium diffusivity, electrical conductivity and low delithiation potential; and high cycle life due to its mechanical stability and low volume expansion [19,43]. The notable disadvantage is its low volumetric capacity. Other forms of carbonaceous anodes have been explored by micro-, nano-structuring the material. It is demonstrated that nano-voids and defects create additional lithium capacity and raise the specific capacity of the anode above the theoretical 372 mAh g^{-1}

[43–46]. These examples include carbon nanofibers (450 mAhg^{-1}) [47], graphene (960 mAh^{-1}) [48], carbon nanotubes (1100 mAhg^{-1}) [49], and porous carbon ($800\text{--}1100 \text{ mAhg}^{-1}$) [50].

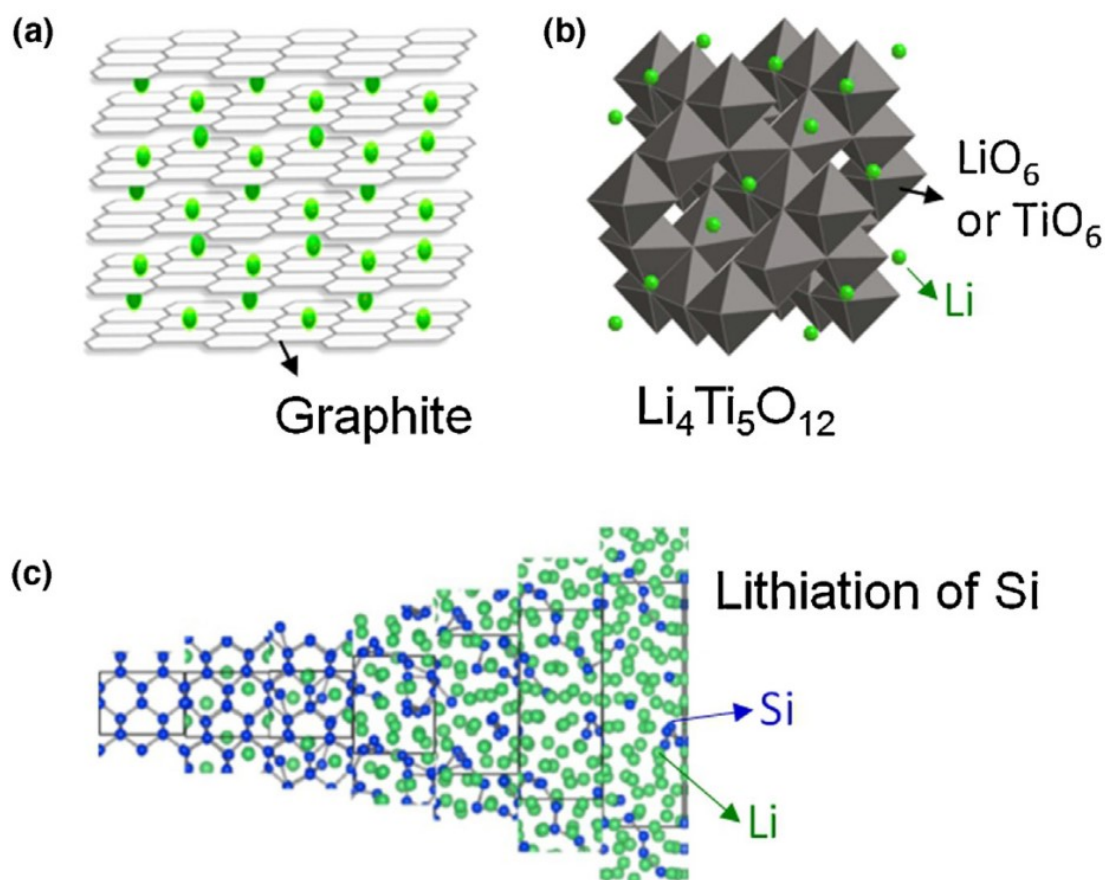


Figure 18. Crystalline structure of representative anode materials. (a) graphite [51], (b) LTO [52], and (c) silicon [53]. The green spheres represent lithium. Adapted from [19].

LTO has also seen a commercial success for its excellent safety, thermal stability and cycle life as well as its relatively high volumetric capacity [41]. Depending on the application, the benefits outweigh the disadvantages of high titanium cost [54], lower cell potential, and specific capacity. The crystal structure is depicted in Figure 18b. Its high thermal stability and cycle life are said to come from its negligible volumetric expansion upon lithiation [55–57] which minimises the mechanical strain on the material. Additionally, its high working potential suggests higher thermodynamic stability with the electrolyte minimising irreversible surface reactions and dendrite growth at the interface.

Silicon should be mentioned as a representative conversion anode material for its increasing attention in research [58–60]. Conversion anodes are said to have significantly higher specific capacity and volumetric capacity but suffer from large volume expansions which lead to low cycle life. As depicted in Figure 18c, silicon electrochemically alloys with lithium to form a compound phase at low potential. It is also to be noted that silicon is very cheap due to its high abundance on earth [61]. Small amounts of silicon (e.g. 10%) can be mixed in graphite to form an electrode material with higher specific capacity than graphite alone while minimising detrimental volume expansion [62].

Table 2 summarises the anode characteristics.

Table 2. Properties of representative anode materials. Adapted from [19,61].

Material	Specific capacity	Volumetric capacity	Delithiation potential	Volume expansion	Comments
Units	mAhg⁻¹	mAhcm⁻³	V vs. Li	%	-
Li-metal	3860	2280 [42]	-	-	Unsafe due to dendrite growth. Poor coulombic efficiency. Very high specific capacity and lowest potential vs. Li
Graphite	372	330-430	0.1 0.14, 0.23	10%	Remains most commercially viable. Low cost, moderate energy and power density, and cycle life. Low volumetric capacity.
LTO	175	600	1.58	0.20%	High power and cycle life application. Low energy and higher material cost (Ti).
Si	4200	9786 [63,64]	0.31, 0.47	270%	Low cost, extremely high gravimetric and volumetric capacity. Low cycle life due to large expansion upon lithiation.

2.3.3. ELECTROLYTE

The function of the electrolyte is to allow lithium-ion diffusion from one electrode to the other while inhibiting electron transport. For this purpose, the electrolyte should be a good ionic

conductor and an electrical insulator. An ideal electrolyte should have high lithium salt solubility, low toxicity, low flammability, and low cost. For prolonged lifetime, it is crucial for the electrolyte to be electrochemically stable within the expected voltage and temperature window of cell operation and inert to other internal components. For this reason, the choice of electrolyte is often dictated by the electrode materials in use.

Electrolyte can come in many forms where liquid electrolytes made from lithium salts dissolved in either aqueous or aprotic solvents are the most commonly used electrolytes today. Lithium hexafluorophosphate (LiPF_6) with ethylene carbonate (EC)/linear carbonate mixture is said to be the most popular combination used in lithium-ion batteries [65].

Propylene carbonate (PC) has attracted much attention over the years for its ability to dissolve various types of lithium salts i.e. its high dielectric constant (ϵ). Its low melting point (T_m) and high boiling point (T_b) meant that it can maintain its liquid phase for normal battery operation and its low viscosity (η) facilitates lithium-ion diffusion. Its high flash point (T_f) suggests low flammability. However, PC suffers from low cycling efficiency and the formation of lithium dendrites and isolated particles which can pose a serious safety hazard through internal short circuit [66,67].

EC has similar/better properties than PC except for its high melting point of 36.4°C which makes it useless as it will be solid at room temperature. To overcome this issue EC is blended with linear carbonates such as diethyl carbonate (DEC) [68–70], dimethyl carbonate (DMC) [71,72] and ethylmethyl carbonate (EMC) [73].

Table 3 summarises the properties of the mentioned solvents.

Table 3. Properties of organic solvents used in lithium-ion battery electrolytes. Adapted from [65]

Solvent	$T_m/^\circ\text{C}$	$T_b/^\circ\text{C}$	$T_f/^\circ\text{C}$	$\eta/\text{cP @ } 25^\circ\text{C}$	$\epsilon @ 25^\circ\text{C}$
PC	-48.8	242	132	2.53	64.92
EC	36.4	248	160	1.90 (@ 40°C)	89.78
DEC	-74.3	126	31	0.75	2.805

DMC	4.6	91	18	0.59 (@20°C)	3.107
EMC	-53	110	-	0.65	2.958

LiPF₆ is a commercially successful lithium salt used in electrolytes for its good balance of properties such as its ability to dissolve and dissociate in aprotic solvents, mobility of lithium cations in the electrolyte and inertness of anion to other internal components [65,74,75]. Other salts such as lithium perchlorate (LiClO₄) [76,77], lithium hexafluoroarsenate (LiAsF₆) [78–80], lithium tetrafluoroborate (LiBF₄) [81,82] and lithium triflate (LiTf) [83] are also interests of research however not as popular for one or more weaknesses.

Gel polymer electrolytes (GPE) have also seen commercial success. The advantages of GPEs are their enhanced mechanical integrity [84,85] which simplifies battery processing and increases resistance towards internal short circuit and electrolyte leakage as well as their non-combustible reaction products at the electrode interface [86]. GPEs are prepared by wetting polymer electrolyte hosts with conventional electrolyte solutions. This allows the polymer electrolyte to maintain similar electrochemical performance to the liquid electrolytes. GPE hosts include poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF) and PVdF-hexafluoro propylene.

Solid polymer electrolytes (SPE) are being researched for their even higher mechanical stability suggesting the possibility of ultrathin/flexible batteries. However, they are not yet suitable for commercialisation of large cells due to their poor ionic conductivity [65,87].

2.3.4. SEPARATOR

The separator is sandwiched in between the anode and the cathode to prevent any physical contact of the two electrodes. For this purpose, a separator must be an excellent electrical insulator and have a high mechanical integrity to cope with any possible mechanical and thermal abuse. It must also allow the electrolyte to transport lithium-ions across it and be

unreactive with other internal components. It is often made from a polymeric mesh as this meets the requirements while being low cost, light and easy to manufacture.

Polyethylene (PE) and polypropylene (PP) are common materials used for the separator. The two materials can be combined to form a PP-PE-PP tri-layer which has been presented as shutdown separator [88]. PE has a melting point of 130°C where the pores of the mesh would close when the cell reaches such dangerously high temperature for any reason. PP on the other hand has a higher melting point which allows the separator to still hold its mechanical integrity [89]. The idea is that this will “shut down” any lithium-ion diffusion across the separator preventing further heat generation.

2.3.5. CURRENT COLLECTOR

Electrode materials are adhered to current collectors to transport electrons to the external circuit as well as providing mechanical integrity to the cell. For this purpose, a current collector must be an excellent electrical conductor, mechanically rigid, low mass, volume and electrochemically unreactive with other internal components.

Copper is used as the anode current collector for its high conductivity and relative low cost however it is not suitable for the cathode as copper corrodes at potentials $> 2 \text{ V (vs Li+)}$ [90]. Aluminium is typically used instead as the cathode current collector for its suitable properties including its corrosion resistance of up to 4.5 V (vs. Li+) [91].

2.4. OPERATING CONDITIONS OF A BATTERY

The performance of a lithium-ion battery is heavily dependent on its operating (and storage) conditions. It is important to understand the relationships between battery performance, such as energy and power capabilities, cycle life and safety, with operating conditions such as temperature, voltage and current. With this knowledge, the battery operation can be controlled accordingly to maximise its full potential.

2.4.1. VOLTAGE

A lithium-ion battery will always have lower and upper voltage limits provided by the manufacturer for safe operation. This voltage window is dictated by the combination of the positive and negative electrode materials used. The cell potential is the potential difference between the cathode and the anode. The cell voltage should not go below its lower voltage limit to avoid the oxidation of the copper current collector at the anode [90] (note that low cell voltage implies high anode voltage and low cathode voltage). The cell voltage should not go above its upper limit to avoid the formation of lithium dendrites. High cell voltage implies low anode voltage and when the electrode voltage is too low, it becomes thermodynamically more favourable to plate the lithium on the electrode surface rather than intercalating into the graphite layers [92]. The serious hazards of dendrite formation will be discussed in detail later in this chapter.

Voltage limits are usually controlled by a battery management system (BMS) where it forces the cell to stop charging/discharging when the upper/lower voltage limits are reached (e.g. a smartphone turning off when battery reaches 0% SOC). In a pack application, cell balancing can be carried out to move charge between cells to avoid one cell reaching the voltage cut-off earlier than the rest of the cells in the pack.

Figure 19 summarises the safe operating window of a lithium-ion battery in terms of voltage and temperature.

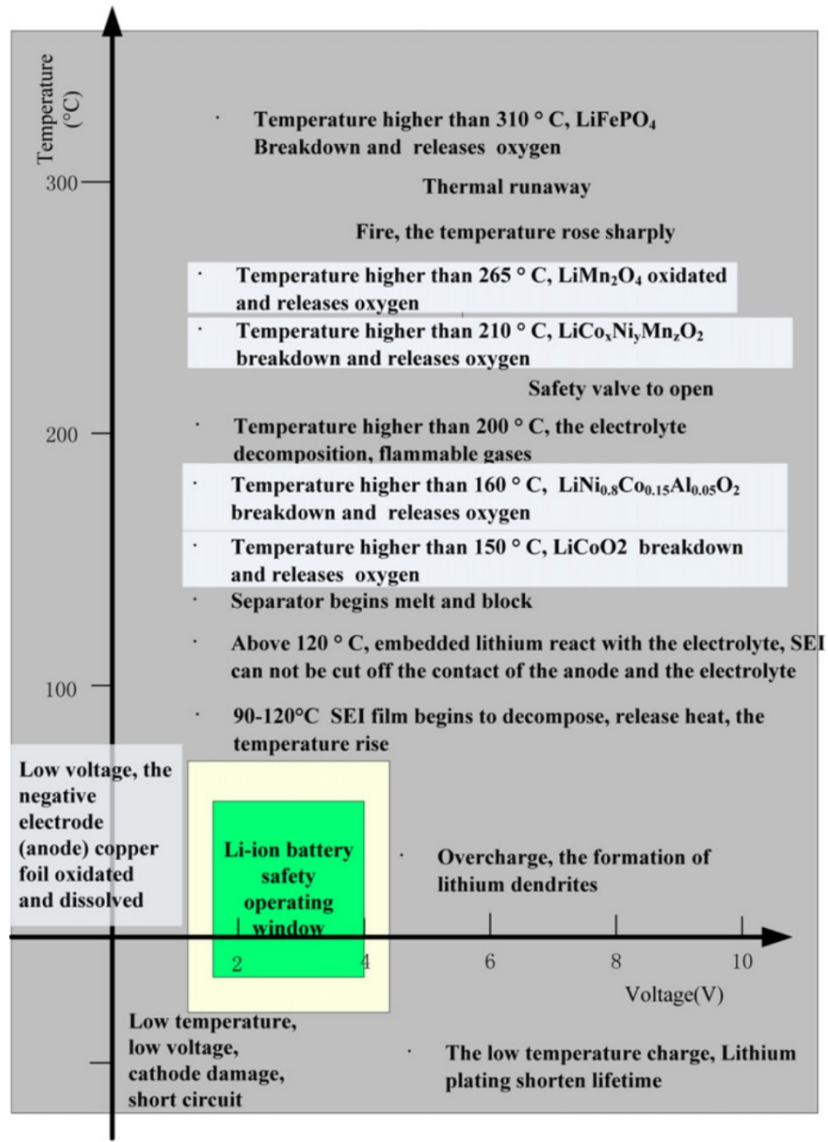


Figure 19. Safety operation map of a lithium-ion battery in terms of temperature and voltage. Green window is safe; yellow is approaching the limits; and grey is unsafe. Source [92].

2.4.2. TEMPERATURE

Temperature of the cell affects the internal reaction rates as provided by the Arrhenius equation [93]:

$$k_r = Ae^{-\frac{E_a}{R_g T}} \quad (5)$$

Where k_r is the rate constant, T is the absolute temperature, A is the pre-exponent factor, E_a is the activation energy for the reaction, and R_g is the universal gas constant. In turn, reaction rates

define the impedance of the cell which is the phase-dependent resistance. This suggests that higher temperature provides higher reaction rates and lower cell impedance. This then allows for higher power due to the increased rate capability i.e. how fast lithium can be extracted, diffused, and inserted. This has been experimentally validated by measuring the cell impedance at various temperatures [94].

The overpotential of a cell, η , is defined as the drop/rise in cell potential, E , from its thermodynamic potential, E_{eq} , during discharge/charge.

$$E - E_{eq} = \eta \quad (6)$$

The overpotential is related to the resistance of the cell which suggests that a higher temperature will result in a smaller overpotential [93]. This means that the cell will hit the cut off voltage at a later point increasing its useable capacity.

However, operation at a higher temperature is a double-edged sword in the sense that the increased reaction kinetics also increase the rate of degradation through irreversible reactions hence lowering its cycle life [90]. As summarised in Figure 19, electrolyte decomposition and cathode breakdown may occur at very high temperatures which can lead to catastrophic failure. Cell temperature can be controlled by a thermal management system such as air cooling, liquid cooling [95], phase changing materials [96] and Peltier elements [97]

Operation at low temperature can also be detrimental where charging at such temperature induces lithium plating due to the low solid diffusion rate of the anode unable to catch up with the rate of lithium insertion [98]. If the cell temperature is lower than the melting point of the electrolyte solvent, it may solidify and its low ionic conductivity will reduce its power to null [65]. Heating systems, although less common, may be required in colder climates where resistive heating can be used to heat up the cell to a suitable temperature before start up.

2.4.3. CURRENT

As power is a direct function of current, it is ideal for a cell to have the ability to draw high currents. The Butler-Volmer equation defines that the electrode current is dependent on the electrode potential taking into consideration that both anodic and cathodic reactions occur on the same electrode [93],

$$j = j_0 \cdot \left\{ \exp \left[\frac{\alpha_a n F}{RT} (E - E_{eq}) \right] - \exp \left[-\frac{\alpha_c n F}{RT} (E - E_{eq}) \right] \right\} \quad (7)$$

Where:

- j = electrode current density, A/m² (defined as $i = I/A$)
- j_0 = exchange current density, A/m²
- E = electrode potential, V
- E_{eq} = equilibrium potential, V
- T = absolute temperature, K
- n = number of electrons involved in the electrode reaction
- F = Faraday constant
- R = universal gas constant
- α_c = cathodic charge transfer coefficient, dimensionless (between 0 and 1)
- α_a = anodic charge transfer coefficient, dimensionless (between 0 and 1)

The exchange current density can be considered as the background current in both directions from anodic and cathodic reactions within an electrode resulting in zero net electrolysis and overpotential. The first exponential term in the equation corresponds to the contribution from the anodic reactions and the second to the cathodic reactions.

This suggests that a higher current requires a higher overpotential hence the voltage cut-off will be reached sooner than if the cell was loaded at a lower current. This means that a higher current sacrifices energy for extra power.

Note how this equation also demonstrates that a smaller overpotential is required at a higher temperature for a given current density.

High current is also associated with a number of degradation mechanisms such as lithium plating, passivation layer growth and mechanical fracture of the electrodes which will be described in detail in the following section. It should also be noted that a higher current operation is associated with increased heat generation so cooling must take place appropriately.

High cell current can be mitigated by placing cells in parallel to share the current [99,100] as well as hybridising it with a high power supercapacitor to shave off the peak currents [101].

Many calendar ageing experiments have been carried out to examine the effects of various V , I and T range on cycle life [102–105].

2.5. DEGRADATION IN LITHIUM-ION BATTERIES

Lithium-ion batteries age during a lifetime of operation by various degradation mechanisms. Some mechanisms may be more detrimental than others and there is often a complex combination of several mechanisms. Each mechanism will have likely causes, effects and mitigation possibilities. This section hopes to lay out the key degradation mechanisms known today and discuss what can be done to minimise them. Figure 20 illustrates some of the mechanisms going to be discussed.

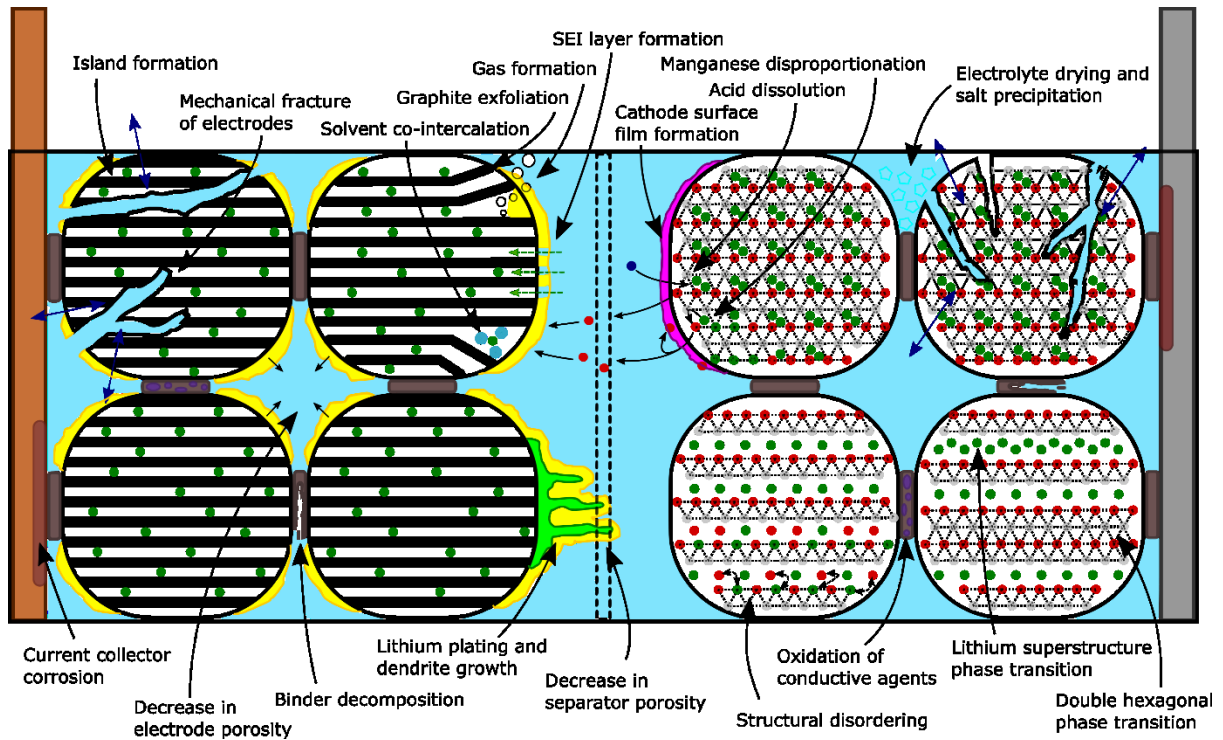


Figure 20. Illustration of key degradation mechanisms in lithium-ion batteries. Graphitic carbon on the left and lithium metal oxide cathode on the right. Green represents lithium. Source: [9].

2.5.1. SOLID ELECTROLYTE INTERFACE LAYER FORMATION

Solid electrolyte interface (SEI) layer formation is possibly the most notable degradation mechanism in a lithium-ion battery. The low potential of the carbon anode is often outside the electrochemically stable potential window of the electrolyte [106]. Upon the first charging cycle of the cell, SEI forms at the anode-electrolyte interface as a passivation layer through surface reactions. Figure 21 illustrates the operating voltage windows of various electrodes and how the SEI forms as a passivation layer at the graphite-electrolyte interface. It can be noticed that LTO anode is within the stable voltage domain of the electrolyte hence it has a negligible SEI layer formation which is believed to be the advantage of this material [19].

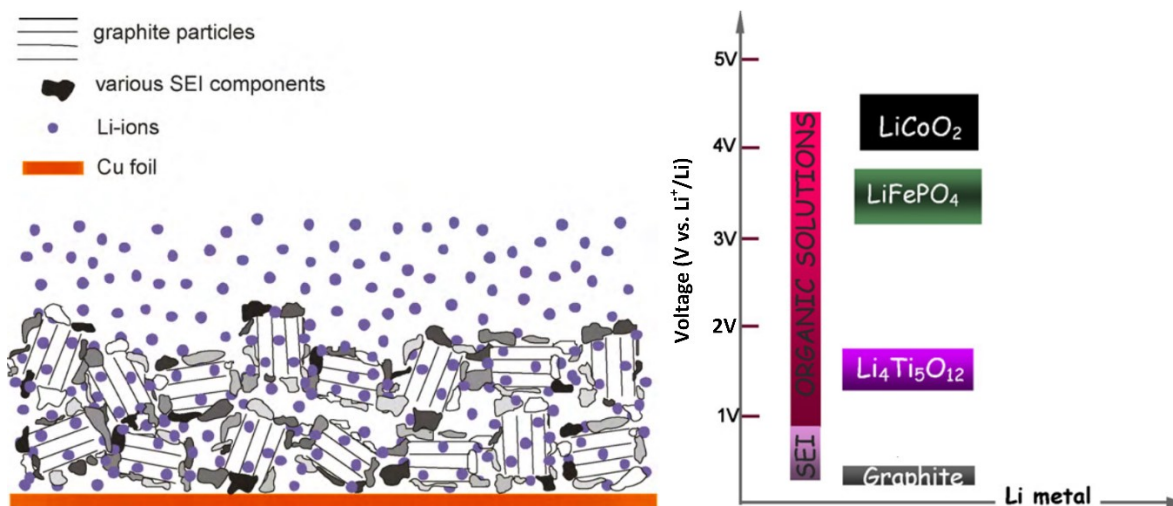


Figure 21. Illustration of SEI forming at the graphite anode-electrolyte interphase (left). Source: [107]. Operating voltage window of graphite, LTO, LFP, and LCO electrodes with the stability domain of a common liquid electrolyte (right). Adapted from [106].

Peled et al. showed that the SEI consists of organic products which result from partial and complete reduction of the electrolyte solvent [108]. SEI may also consist of inorganic products which are typically from lithium salt degradation. Verma et al. provides a review on all the reported SEI compositions found through various experimentations [107]. This suggests that the formation of SEI irreversibly consumes cyclable lithium leading to a capacity fade.

The purpose of the SEI is to prevent further reduction at the anode surface hence a perfect SEI must be impermeable to the electrolyte while allowing the diffusion of lithium-ions. SEI layers are typically tens of nanometres thick and contribute to additional impedance of the cell at roughly 10 to 100 Ωcm^2 as the lithium-ions must diffuse through the layer [108]. Figure 22 is a scanning electron microscope (SEM) image of a graphite electrode before and after its first cycle. SEI layer is visible as surface films on the graphite electrode particles after the first cycle.

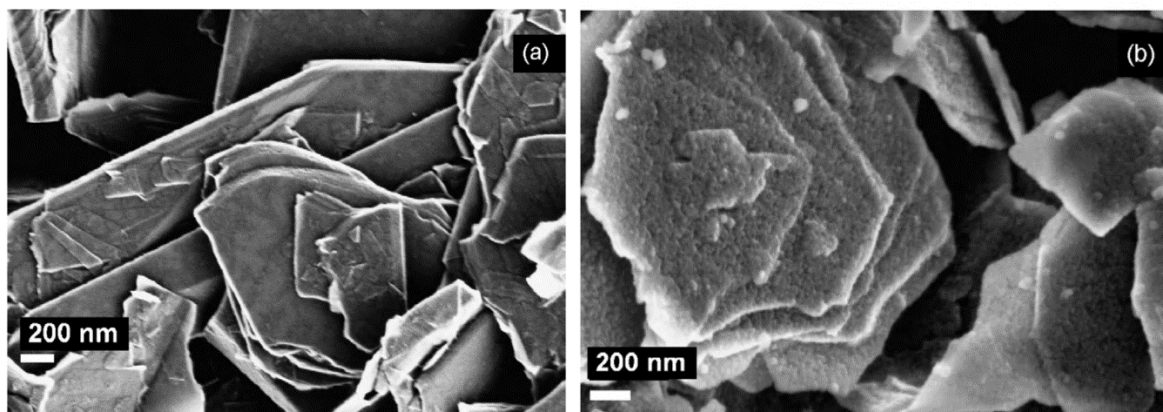


Figure 22. SEM images of composite graphite electrode. (a) pristine electrode and (b) after one cycle vs. lithium metal.

Notice the presence of the surface film after the cycle. Source [107].

The SEI layer continues to grow throughout the lifetime of the cell. This is because, as the cell is cycled, the lithium-ions diffusing through the SEI can expose fresh electrode surfaces to the electrolyte again where more SEI will form [109]. Volume expansion of the electrode through lithium intercalation also has the same effect where small cracks can form in the SEI.

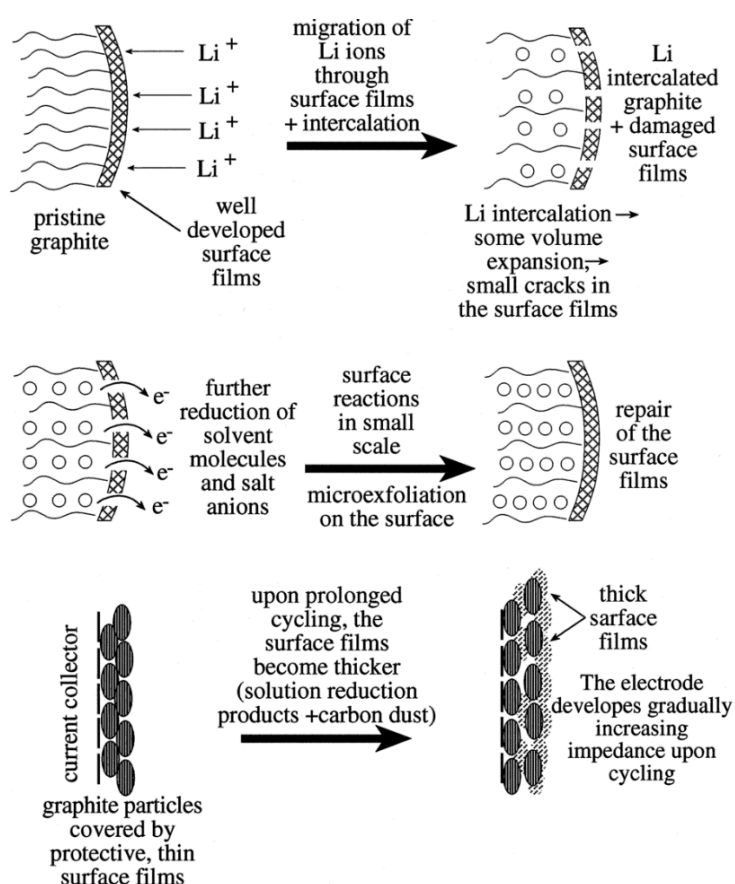


Figure 23. Illustration of how cycling promotes further SEI layer growth. Source: [109].

This phenomenon makes the SEI grow thicker as illustrated in Figure 23. This results in both power and capacity fade through increased cell impedance and lithium consumption.

This degradation mechanism is said to accelerate at higher cell potential, i.e. lower anode potential, due to the increased thermodynamic instability to the electrolyte and at high temperatures due to faster reaction kinetics [110,111].

Electrolyte additives, such as vinylene carbonate (VC) and vinyl ethylene carbonate (VEC), have been extensively studied to reduce the rate of SEI layer growth [65,112–115]. It is also suggested that SEI layer growth gradually slows down as the layer thickens due to increased diffusion for the electrolyte to reach the electrode surface [116].

2.5.2. ELECTROLYTE DECOMPOSITION

Electrolyte in a lithium-ion battery is often made from a mixture of lithium salt and aprotic solvents. Electrolyte is said to decompose at high temperatures where irreversible reactions can occur between the solute and the solvent at $> 60^{\circ}\text{C}$ [65].

As discussed for the SEI layer formation, the electrolyte is electrochemically unstable with the graphite electrode inducing electrolyte decomposition through side reactions. Jalkanen et al. has reported severe drying of the electrolyte for cells cycled at elevated temperatures [117]. It is suggested that this drying is due to the electrolyte being consumed through side reactions leaving salt precipitates.

Overall, the decomposition of electrolyte lowers the ionic conductivity of the electrolyte phase lowering the power capabilities. The reaction may also consume lithium which will contribute to capacity fade.

2.5.3. GRAPHITE EXFOLIATION (GAS FORMATION & SOLVENT CO-INTERCALATION)

Graphite exfoliation is when the graphite layers get peeled or cracked losing the ability to intercalate lithium in that region. This results in loss of capacity at the anode and is hypothesised to occur through two mechanisms.

Winter et al. proposed that the solvent of the electrolyte can in some cases co-intercalate along with the lithium ion. This is followed by a subsequent solvent decomposition leading to an irreversible loss of ability to intercalate lithium at the exfoliated region and hence a loss in capacity [44]. This is particularly problematic in PC electrolytes used with graphitic electrodes [118]. Figure 24 illustrates the graphite exfoliation mechanism through solvent co-intercalation.

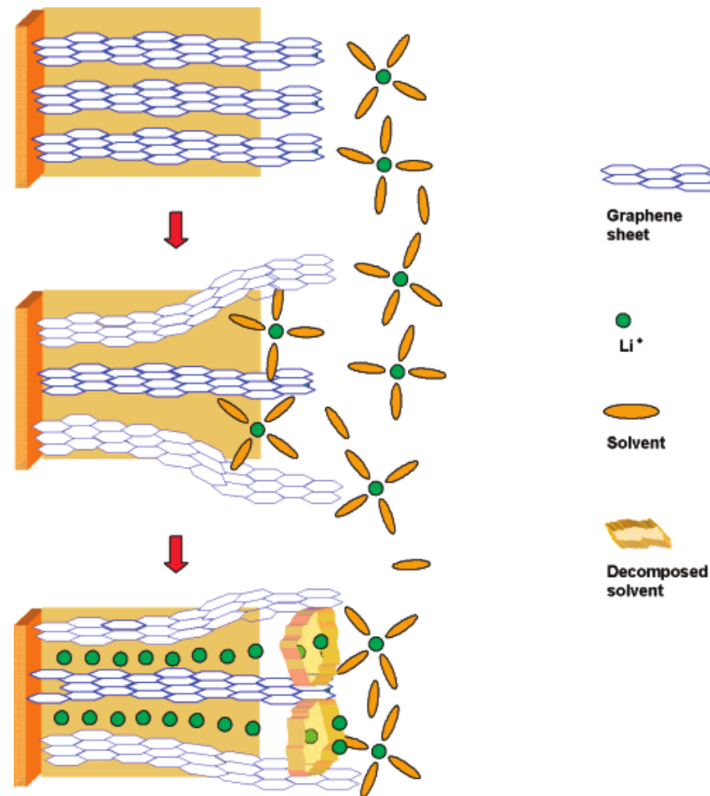


Figure 24. Illustration of graphite exfoliation mechanism by solvent co-intercalation. Source: [65].

The second proposed mechanism by Aurbach is the gas formation [119]. Aurbach suggests that PC electrolyte is reduced at the crevices at the edge of the graphene layers. As a result, propylene gas is formed and builds up pressure inducing exfoliation. In turn, this exfoliation exposes new fresh electrode surfaces promoting SEI layer formation. Gas formation can also be dangerous at high levels as the pressure build up may eventually cause rupture of cell casing leading to oxidation of lithium [65].

Graphite exfoliation can be minimised by electrolyte additives to stabilise the passivating film. VC [113], VEC [115], CO₂, N₂O [120] and lithium salicylatoborate [121] have been demonstrated as electrolyte additives to reduce graphite exfoliation.

2.5.4. MECHANICAL FRACTURE OF ELECTRODES

With enough mechanical stress, electrodes may result in fractures where freshly revealed surfaces will react with the electrolyte to form SEI.

The cause of the fracture can be from external or internal mechanical abuse. Examples of external abuse may be dropping the battery from a height, bending or compressing the cell [122], and applying a dent on its surface [123]. Internal abuse can occur through mechanical stress and strain applied to the electrode through volume expansion/contraction during lithium insertion/extraction. This is particularly severe in silicon anodes due to its large volume expansion upon lithiation (~400%) as well as other alloying anodes [59,124]. It is also said that mechanical fractures occur more readily at lower temperatures as the material becomes more brittle [125]. This phenomenon is demonstrated by SEM images of cycled graphite anode at various temperature and current conditions in Figure 25.

The crack can propagate as the cell is continuously cycled until a piece of electrode completely detaches itself as an isolated material. If the fractured piece of an electrode loses electrical contact to the current collector, this active material is lost including any lithium that may be left inside (this phenomenon is also referred to as an island formation).

The rate of crack propagation can be reduced by minimising graphite exfoliation; lowering the volumetric expansion of the electrode by mixing with other materials, such as adding carbon to silicon electrodes [126,127]; lowering the mechanical strain by using smaller particles [43,128]; and using special microstructures like nanotubes to strengthen its mechanical properties [49,129,130].

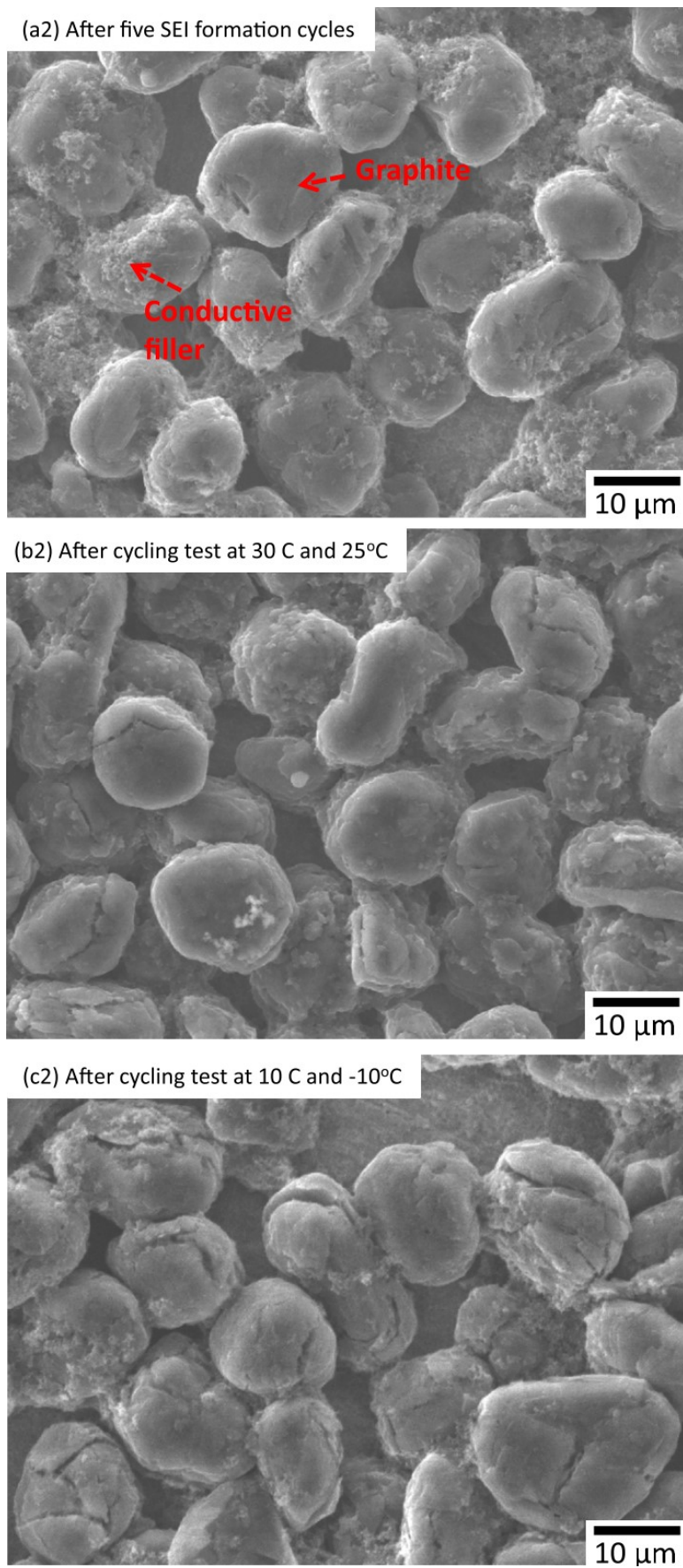


Figure 25. SEM images of graphite particles cycled at different current and temperature conditions. Source: [125].

2.5.5. CHANGES IN ELECTRODE/SEPARATOR POROSITY

The electrodes are made of porous materials so that the electrolyte can diffuse inside to maximise the electrode-electrolyte interfacial area. The separator also consists of pores to allow the electrolyte to have a continuous path of lithium-ion transport between the two electrodes. On a longer timescale, the growing SEI layer can slowly fill the pores and lower the electrode/separator porosity. This has a negative effect on the battery power capability as the electrode-electrolyte contact area is reduced as well as the ionic conductivity in the electrolyte phase due to its narrow and tortuous pathways for lithium-ion transport [131].

The polymer separator may also lose porosity under mechanical compression. With enough stress, the separator can irreversibly deform resulting in loss of porosity [132].

On the other hand, Rubino et al. has suggested that an increase in porosity can also have adverse effects on battery performance [133]. This can occur due to the swelling of electrodes under low cell stack pressure. The argument is that the increase in porosity will reveal more electrode surfaces to the electrolyte which leads to SEI layer formation consuming lithium. As the porosity continues to increase the electrical contact between the electrode particles will decrease and eventually may become isolated losing further capacity.

2.5.6. METALLIC LITHIUM PLATING/DENDRITIC GROWTH

During battery charge, metallic lithium may be deposited on the anode surface if the lithium-ion fails to intercalate into the anode. The exposed lithium metal will react with the electrolyte to form an SEI layer irreversibly consuming lithium as well as increasing the cell impedance [134,135]. This can occur when the lithium concentration at the anode surface is very high and it is thermodynamically more favourable for the lithium-ion to form metallic lithium on the surface rather than intercalating into the anode [136]. This occurrence is because the potential of lithiated carbon is very close to that of metallic lithium. This degradation mechanism can be due to overcharging the anode or the rate of lithium diffusion and/or the rate of charge transfer at the electrode surface being unable to keep up with the rate of lithium insertion [137]. Figure

26 illustrates this phenomenon and Figure 27 shows a laser scanning microscope image of lithium plating on a graphite electrode. In order to avoid anode overcharge, the electrode is almost always placed in excess in terms of lithium capacity. Lithium plating is enhanced at higher charging currents and lower temperature i.e. lower rate of lithium diffusion [98]. Although lithium plating is more commonly known to occur at low temperatures, Jalkanen et al. have experimentally observed that it can also occur at elevated temperatures $> 45^{\circ}\text{C}$ [117].

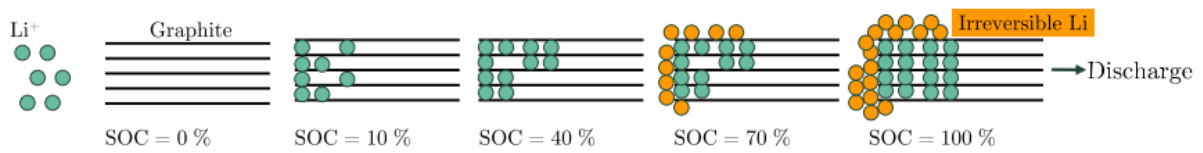


Figure 26. Illustration of lithium plating on the graphite anode surface during charge at low temperature. Adapted from [138].

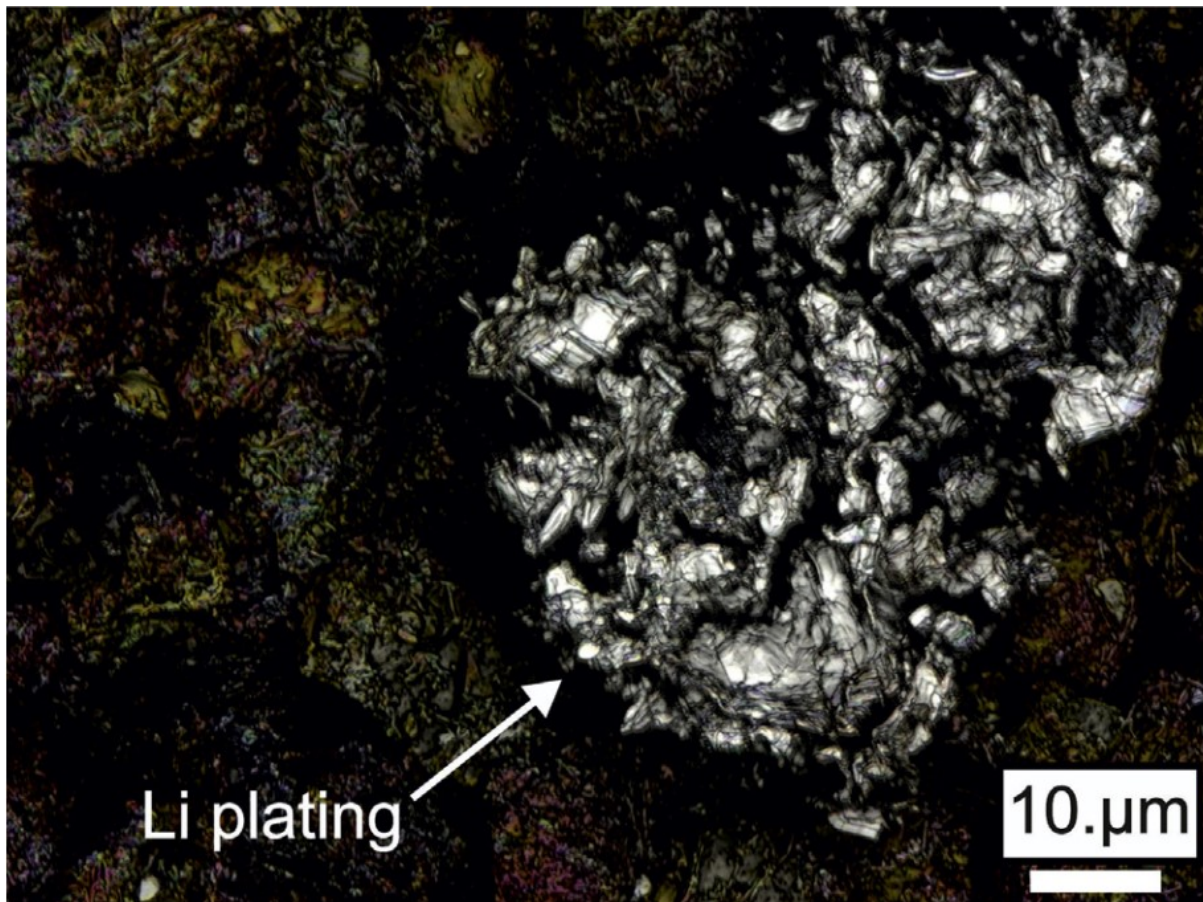


Figure 27. Laser scanning microscope image of lithium plating on a graphite electrode surface. Source: [98].

The deposited lithium metal can grow to form dendrites at the surface which poses a severe safety hazard to battery operation. If the dendrite continues to grow and pierces the separator, it may form an internal short circuit by coming into electrical contact with the positive electrode. This will cause large internal current to flow generating large amounts of heat. As the temperature increases uncontrollably, a catastrophic failure called a thermal runaway can occur (this failure mechanism to be reviewed in detail later). Figure 28 shows a 3D image of a lithium dendrite microstructure on a lithium metal electrode.

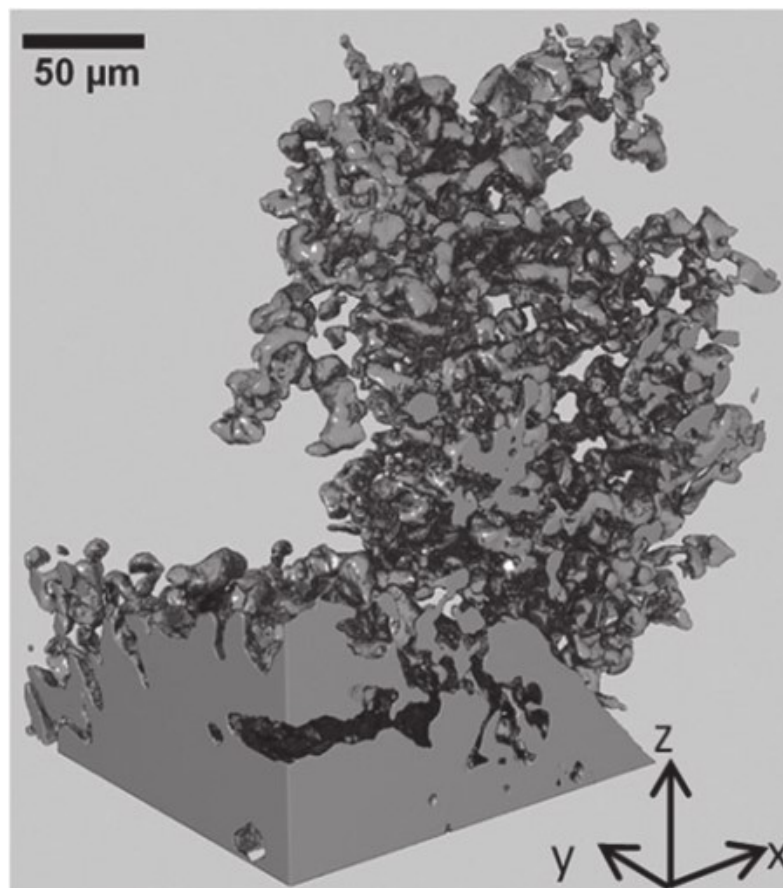


Figure 28. X-ray phase contrast imaging of a lithium microstructure growing from a lithium metal electrode surface during Galvanostatic cycling. Source: [139].

For this reason, it is critical to prevent lithium plating. This degradation mechanism may be reduced by avoiding charge at low temperatures and high currents. With increasing demand for fast-charging capabilities, engineers must take care to ensure that the rate of lithium diffusion and charge transfer are always faster than the rate of lithium insertion. LTO electrodes are

generally considered to be free from this degradation mechanism due to its high anode potential compared to the potential of lithium metal [19].

Dangers of lithium dendrite growing towards the positive electrode can also be mitigated by using a porous copper current collector (also referred to as a copper foam) [140–142]. The graphite anode material is adhered on the copper surface within the pores. Not only this increases the electrode-current collector contact area, the dendrite growth can be directed to grow into the pores rather than toward the separator and the cathode.

2.5.7. *STRUCTURAL DISORDERING*

Structural disordering is a degradation mechanism more relevant in the layered lithium metal oxide structures such as LNO. Divalent nickel ions have a tendency to substitute lithium ions in the layered structure [90]. This substitution consumes cyclable lithium and lowers the lithium diffusion of the material by blocking its pathway leading to both capacity and power loss. Partial substitution of nickel by cobalt has proven to reduce this cationic structural disorder [143].

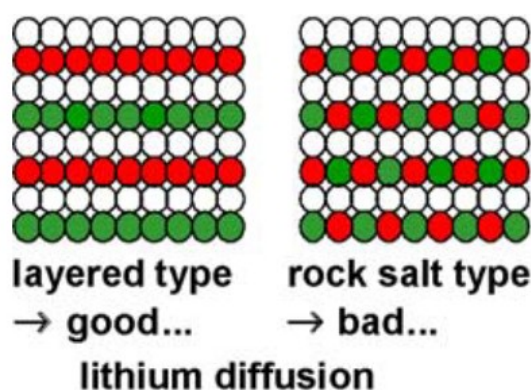


Figure 29. Illustration of structural disordering in a layered lithium metal oxide electrode. Green is lithium, red is transition metal such as nickel, and white is oxygen. Source: [90].

2.5.8. *METAL DISSOLUTION*

Spinel structures such as LMO and NCM can release manganese-ions to the electrolyte through chemical dissolution especially at elevated temperatures [144,145]. This is problematic for two reasons: the lost manganese is replaced by lithium (capacity loss) [146]; and the manganese-

ions can reprecipitate at the cathode surface or travel and deposit to the anode surface through parasitic reactions with the electrolyte (increased impedance -> power loss) [147]. Manganese dissolution can occur at both low and high voltages. The dissolution mechanism is different for each case where manganese disproportionation occurs at low potential and acid dissolution catalysed by HF occurs at high potential [90]. HF is a by-product of LiPF_6 and water. Figure 30 provides an illustration of the mechanisms.

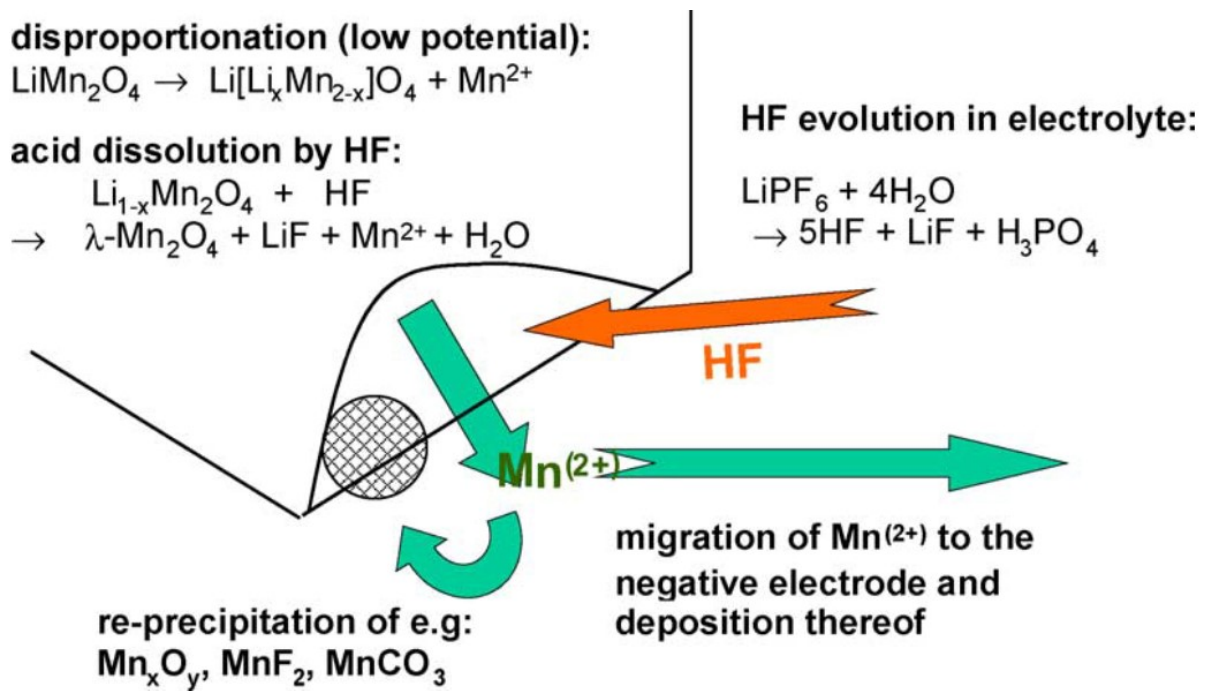


Figure 30. Illustration of metal dissolution mechanisms in a LMO spinel electrode. Source: [90].

It has been shown that Al_2O_3 coating on the spinel cathode surface reduces manganese dissolution [148].

2.5.9. CURRENT COLLECTOR CORROSION

As briefly discussed previously, copper can oxidise at $> 2 \text{ V (vs. Li}^+)$ [90] and aluminium at $> 4.5 \text{ V (vs. Li}^+)$ [91]. This means that corrosion of current collectors can occur at high anode/cathode potentials. Over-discharging will raise the anode voltage promoting copper current collector corrosion and overcharging will raise the cathode voltage promoting aluminium current collector corrosion [90]. The corrosion product exhibit poor electric conductivity lowering the

power capability of the cell. Capacity is also lost if the current collector loses electrical contact and forms isolated electrode materials. Additionally, this may create inhomogeneous current distribution in the electrode possibly promoting lithium plating by high local current flow during charge.

2.5.10. BINDER DECOMPOSITION

Electrode particles are held together and adhered to the current collector using some form of binder such as those based on carboxymethyl cellulose (CMC) and PVdF [149,150]. The binders can break apart under mechanical stress for example through expansion and contraction of the electrodes during cycling. This lowers the electrical contact of the electrode particles to each other and/or the current collector increasing its impedance. There is also a possibility of island formation if a piece of an electrode is completely detached lowering its capacity. Binder-free electrodes have been explored using nanostructures which will eliminate this degradation mechanism [151,152].

2.5.11. LOSS OF CONDUCTIVE ADDITIVES

Non-carbonaceous electrodes, such as LFP or LTO, may be mixed with small amounts of conductive fillers to increase its electrical conductivity hence power. These conductive fillers are often made from carbon in the form of graphite [125], graphene [153] or carbon nanotubes [154] etc. These additives maybe lost through operation lowering electrode conductivity and power.

2.5.12. STOICHIOMETRIC DRIFT

Stoichiometric drift is an effect of degradation rather than a mechanism. Electrode stoichiometry has a certain alignment from cell assembly which determines the recommended upper and lower voltage of operation [155,156]. As the cell degrades through various mechanisms, the electrode stoichiometry can become misaligned [157]. This phenomenon is referred to as the stoichiometric drift. This misalignment can suggest that the cell may be

overcharged or over discharged at its initial recommended limits. Figure 31 illustrates the phenomenon. Overcharge/discharge will accelerate further degradation mechanisms as listed above and in turn will generate a larger stoichiometric drift creating a positive feedback of accelerated degradation. Due to this reason, it is ideal to track such misalignment to avoid electrode overcharge/discharge.

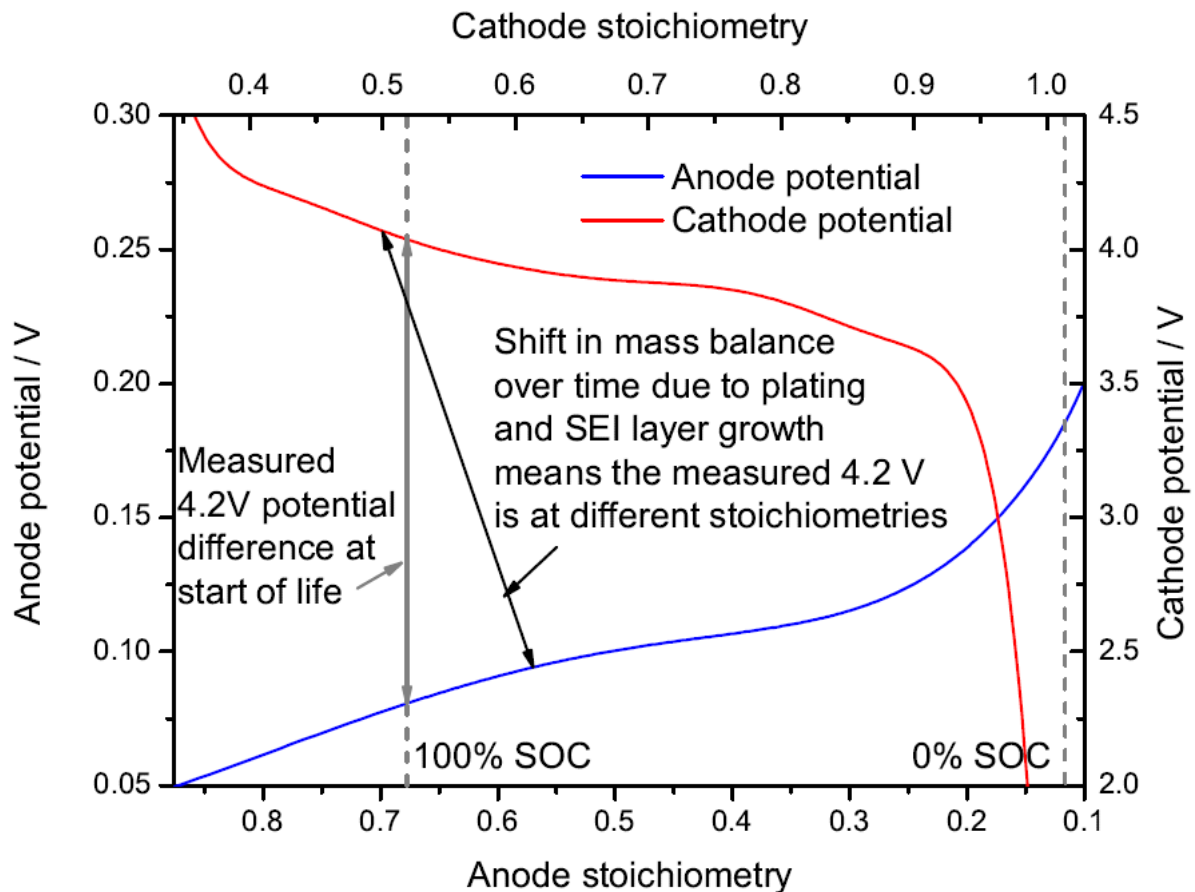


Figure 31. Illustration of stoichiometric misalignment aka stoichiometric drift. Notice how the cathode is overcharged at 4.2 V after stoichiometric drift. Source: [158].

2.5.13. THERMAL RUNAWAY

Thermal runaway is a dangerous and destructive mechanism that leads a lithium-ion battery to a catastrophic failure. When the battery reaches a certain threshold temperature (dependent on the cathode material used), the cathode begins to breakdown releasing oxygen and generating heat through a self-sustaining exothermic reaction known as thermal runaway [92,159]. Once the temperature hits this threshold there is no way to stop the thermal runaway until

destruction of the cell. The heat generation will continue where the electrolyte is eventually ignited and burst into flames. The different degradation stages leading up to thermal runaway are described in Figure 32 which was generated through an accelerating rate calorimetry (ARC) test where the heat generation of the cell is measured as the cell temperature is increased.

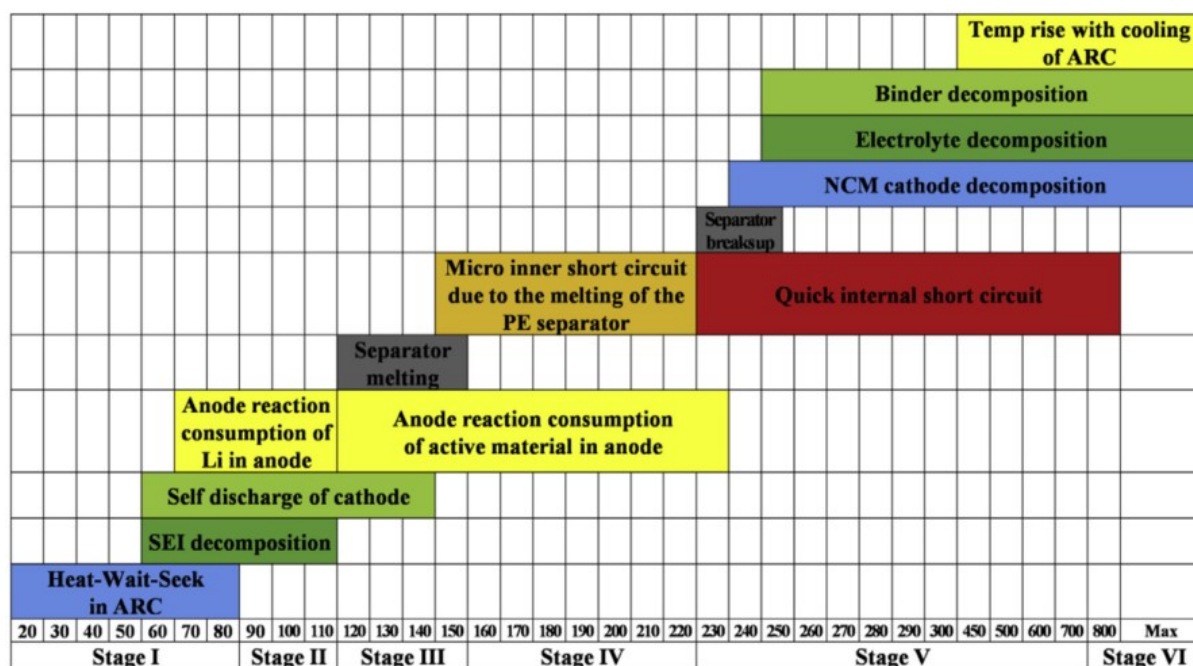


Figure 32. Different temperature stages leading to thermal runaway using an ARC test. X-axis is temperature (°C).

Source: [160].

The threshold temperature for thermal runaway is dependent on the thermal stability of the cathode material as illustrated previously in Figure 19. Within the chemistries discussed in this review, LCO has the lowest thermal stability where cathode breakdown can start as low as 150°C and LFP with the highest at 310°C [19]. The thermal stability of LCO can be improved by doping magnesium or aluminium into the electrode [19,24]. As briefly discussed, the shutdown separator can act as an emergency irreversible shutdown of battery operation to avoid further heat generation by disallowing lithium-ion transport between the electrodes [161]. This mechanism is the reason why internal short circuit can be so hazardous. The large internal current flow will cause a sharp rise in temperature which could lead to thermal runaway.

Examples of thermal runaway in recent commercial applications would be the Samsung Galaxy Note 7 and Boeing 787 Dreamliner (Figure 33) [162,163]. Following their battery failures, Samsung stressed the importance of battery safety check and the need for a re-assessment of characterisation methods.

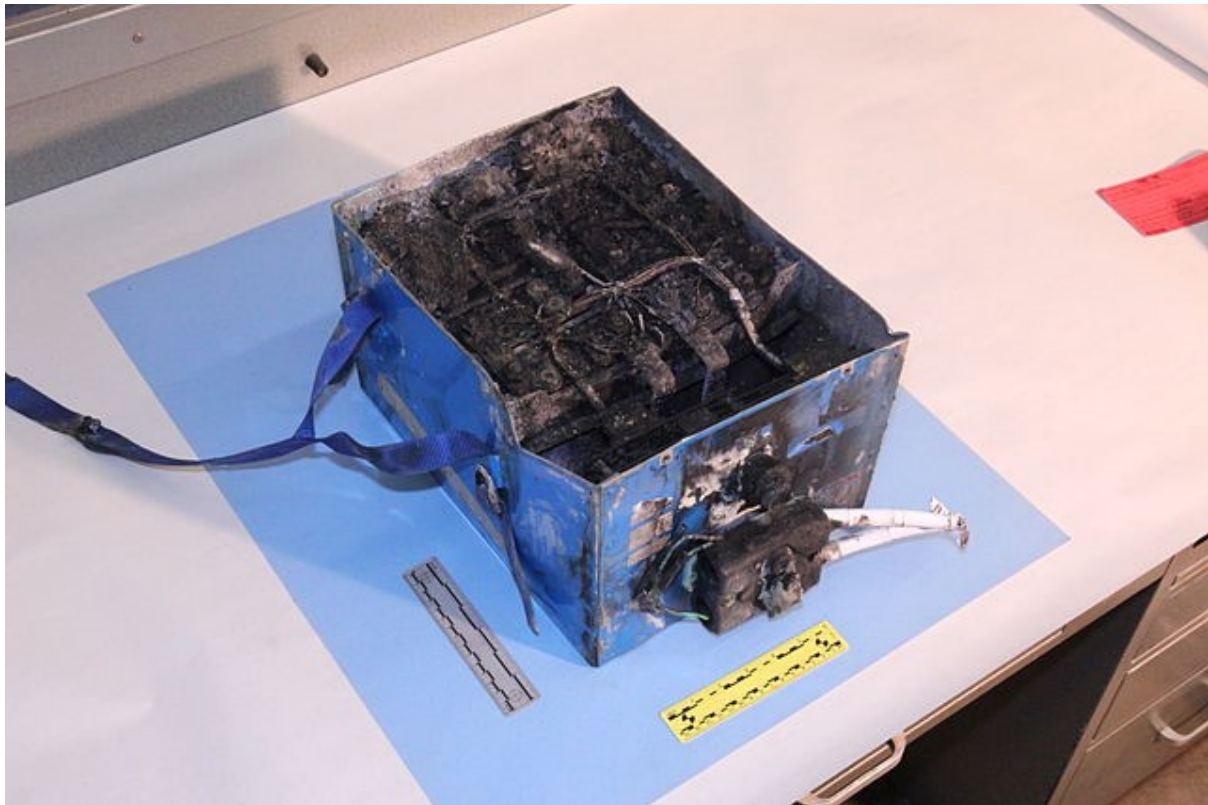


Figure 33. Heavily burnt battery pack from Boeing 787 Dreamliner following a thermal runaway. Source: [164].

2.6. MEASUREMENT OF DEGRADATION

In order to avoid battery failure and ensure a long/safe operation, it is critical to have a suitable system for the measurement of battery degradation. Below sections provide the current industrial standard measurements as well as more recent ideas.

2.6.1. CAPACITY LOSS & POWER LOSS

The two important parameters in a battery are ultimately its capacity and power. Capacity loss and power loss (also referred to as capacity fade and power fade) are the simplest approach of quantifying battery degradation. It is a measurement of how much capacity in Ah or power in

Wh the battery has lost in comparison to how much it had at its beginning of life. This is a very basic measurement of degradation as it provides no further information than the essential battery performance capability.

2.6.2. *SOH, SOF, RUL, EOL, BOL*

State-of-health (SOH) is the quantitative measurement (usually represented in percentages) of how much the cell has degraded with respect to its fresh state. There is no fixed definition for the SOH however the current industrial standard would simply be the capacity loss [165]. Again, there is no standardised measurement procedure for capacity. The most common method seems to be a constant current 1 C discharge at room temperature from the upper voltage limit of the cell to its lower voltage limit. The unit “C” represents the C-rate of the cell which is a unit describing the current with respect to the cell capacity. For example, a 1C discharge of a 5 Ah cell would be 5 A and a 2 C discharge of the same cell should be about 10 A. Due to the lack of standardised measurement, every mention of capacity should include exactly how the parameter was measured each time.

$$SOH(t) = \frac{\text{actual cell capacity } (t)}{\text{fresh cell capacity}_{t=0}} \quad (8)$$

State-of-function (SOF) and remaining-useful-life (RUL) are less common yet still employed measurements of degradation [166–169]. SOF determines the battery’s ability to deliver a certain amount of energy or power under given operating conditions. RUL defines the amount of overall operational lifetime left of the cell.

Beginning-of-life (BOL) is defined as the fresh state of the cell i.e. 100% SOH. End-of-life (EOL) marks the end of a battery operation after significant ageing. EOL is often defined at 20% capacity loss or 80% SOH.

2.6.3. DEGRADATION MODES

In non-demanding operations, the above measurements of degradation may suffice. However, these measurements only give limited information. Batteries used in an aggressive and performance demanding operation will require a more sophisticated approach. Dubarry et al. have introduced the concept of degradation modes for tracking battery SOH in greater detail [170].

The degradation modes can be categorised into four broad terms: loss of lithium inventory (LLI), loss of active material (LAM); ohmic resistance increase (ORI); and faradaic rate degradation (FRD). LAM is further categorised into LAM in the positive and negative electrode (PE/NE) while it is lithiated and delithiated (*li/de*): $LAM_{PE,li}$, $LAM_{PE,de}$, $LAM_{NE,li}$, $LAM_{NE,de}$. LLI and LAM define where and in what state the capacity was lost (Figure 34); ORI represents high frequency impedance rise hence power loss (Figure 35a); and FRD represents loss in kinetic performance (Figure 35b) i.e. lower frequency impedance rise. The various modes represent different effects on the half-cell voltage curves and their electrode stoichiometric alignment.

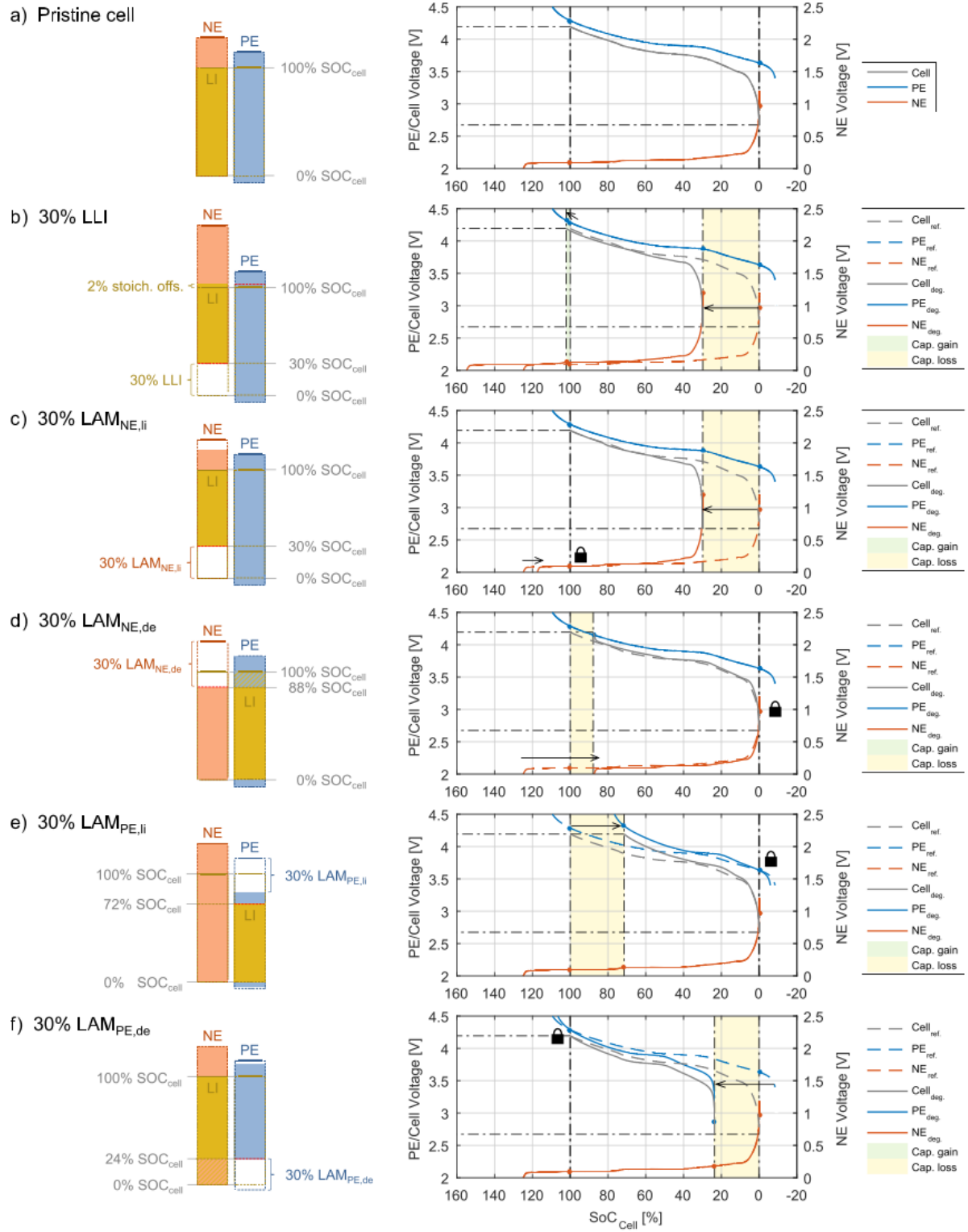


Figure 34. Illustration of capacity loss due to LLI and LAM (left) and its effect on half-cell voltage curves (right). Notice the stoichiometric misalignment in all cases of degradation modes. Source: [171].

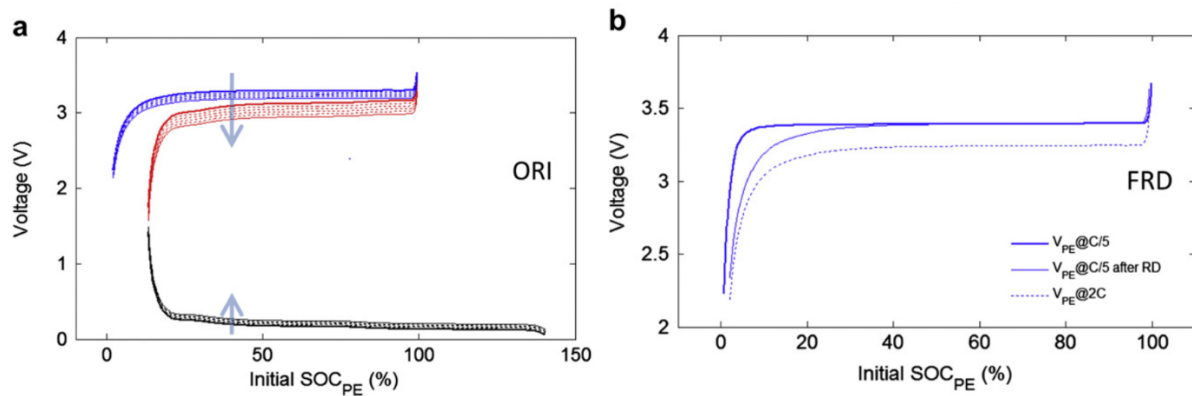


Figure 35. Illustration of (a) ORI and (b) FRD effects on half-cell/full cell voltages upon degradation. Source: [170].

Each of these degradation mode gives more insight into the battery SOH than the conventional capacity and power loss. In Figure 36, Birkel et al. provide a useful correlation between degradation causes, mechanisms, and modes (LLI and LAM) as well as their final effect on capacity and power [171].

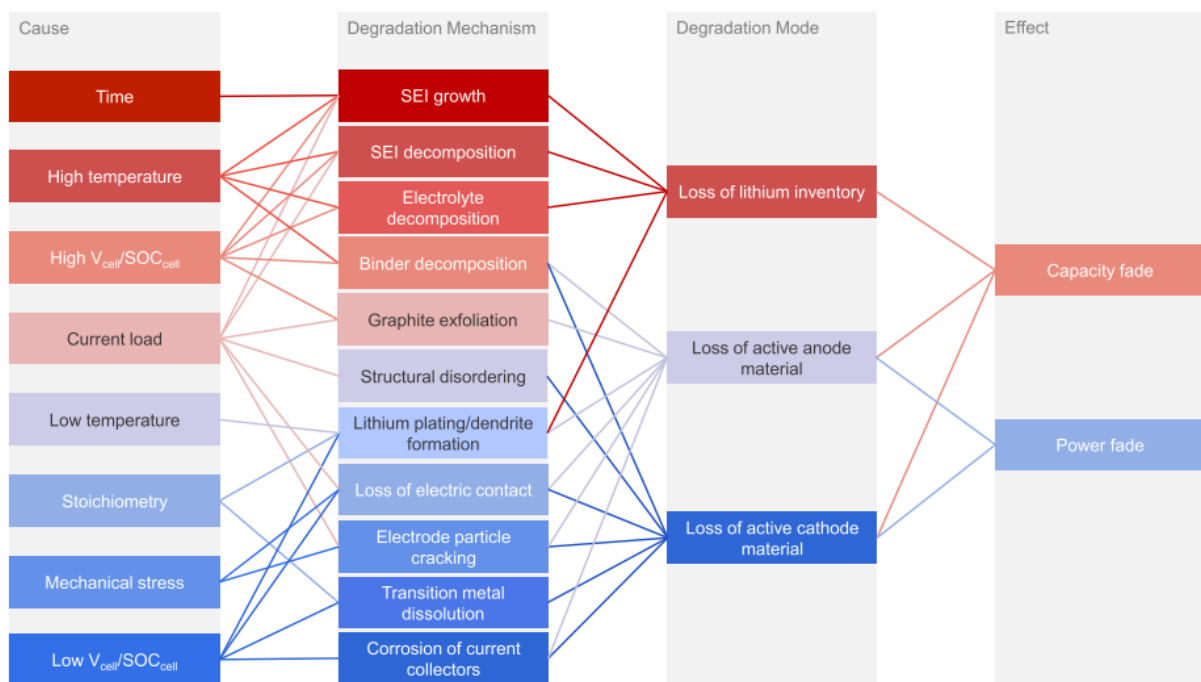


Figure 36. Degradation map starting from possible cause to degradation mechanism to degradation mode (LLI and LAM) and finally to effect. Although the link is not made in this figure, LLI in the electrolyte will lower the ionic conductivity hence there will be power fade. Source: [171].

2.7. IN-SITU DIAGNOSIS

To make the link between degradation mechanisms and degradation modes, a diagnosis is required through battery characterisation test(s). Broadly there are two types of diagnosis methods: *in-situ* and *ex-situ*.

Ex-situ methods require dismantling of the cell with often irreversible damage and contamination. X-ray techniques, optical techniques, and electron microscopies are common diagnosis methods generally carried out *ex-situ* for commercial lithium-ion batteries. These methods can often give detailed information on the internal state of the cell. However, as *ex-situ* methods come with the cost of irreversible dismantling, they are not suitable for real world applications but find their use in laboratory scale research and post-mortem analysis. For the purpose of this research, this review will focus on *in-situ* methods however [172] provides a useful review on the recent development of common *ex-situ* methods. It should be noted that these methods can be carried out *in-situ* in special conditions often involving purpose-built cells [58,124,173,174].

In-situ methods however do not require the disassembly of the cell which makes it suitable for tracking SOH and degradation. There are experiment-based techniques and model-based techniques. Model-based techniques can be useful but often require high computational capabilities. These techniques are outside the scope of this thesis however detailed reviews can be found in [175,176].

While there are many experiment-based *in-situ* diagnosis techniques, only a few have the ability to be carried out *in-operando*. *In-operando* diagnosis means that the cell can be characterised during a “normal” operation of a battery in application such as during a dynamic discharge (drive cycle) and constant power/current charging. The strength of these techniques is the fact that it does not require a separate specific characterisation cycle which may often require additional hardware.

2.7.1. COULOMB COUNTING

Coulomb counting, also known as Ah counting, is the simplest way to measure the capacity of the cell. The method works by counting the coulomb (Ah) throughput of the cell during a charge or discharge cycle. To measure the total capacity of the cell, coulomb counting is often carried out under a constant current discharge from the upper voltage limit of the cell to the lower voltage limit. In order to determine the capacity fade hence the industrial measurement of SOH, the actual cell capacity can be compared with the cell capacity previously measured when the cell was fresh using the same test conditions including its temperature [165].

Coulomb counting is also used as a simple form of SOC estimator however it struggles to maintain its accuracy as capacity fades [177,178]. The estimation technique also requires accurate cell current readings and initial SOC value.

2.7.2. INCREMENTAL CAPACITY ANALYSIS

Incremental capacity analysis (ICA) is a method where the differential capacity (dQ) and voltage (dV) are measured through constant current charge or discharge. The dQ/dV value is then plotted against cell potential to give a curve which looks like the example given in Figure 37a. A high dQ/dV magnitude means that there is a significant amount of capacity stored at that potential. This suggests that each peak in the ICA curve represents an electrode phase where only the lithium concentration in the electrode material is changing. Typically, electrode materials go under one or more phase transitions within the voltage window of battery operation. When the curve moves from a peak to the next peak, this is when one of the electrode phases is no longer thermodynamically stable at the given lithium concentration and undergoes a structural change. As the new material structure has a different standard electrode potential, there is a rapid change in potential. Therefore, the movement between peaks represents a phase transition.

Dubarry et al. suggests that the ICA results measured in a full cell are always a combination of different contributions from the anode and the cathode [179]. For this reason, each peak

represents a particular combination of anode and cathode phases and the movement of peak to another peak is when one of the electrode undergoes a phase transition. This concept is illustrated in Figure 37b.

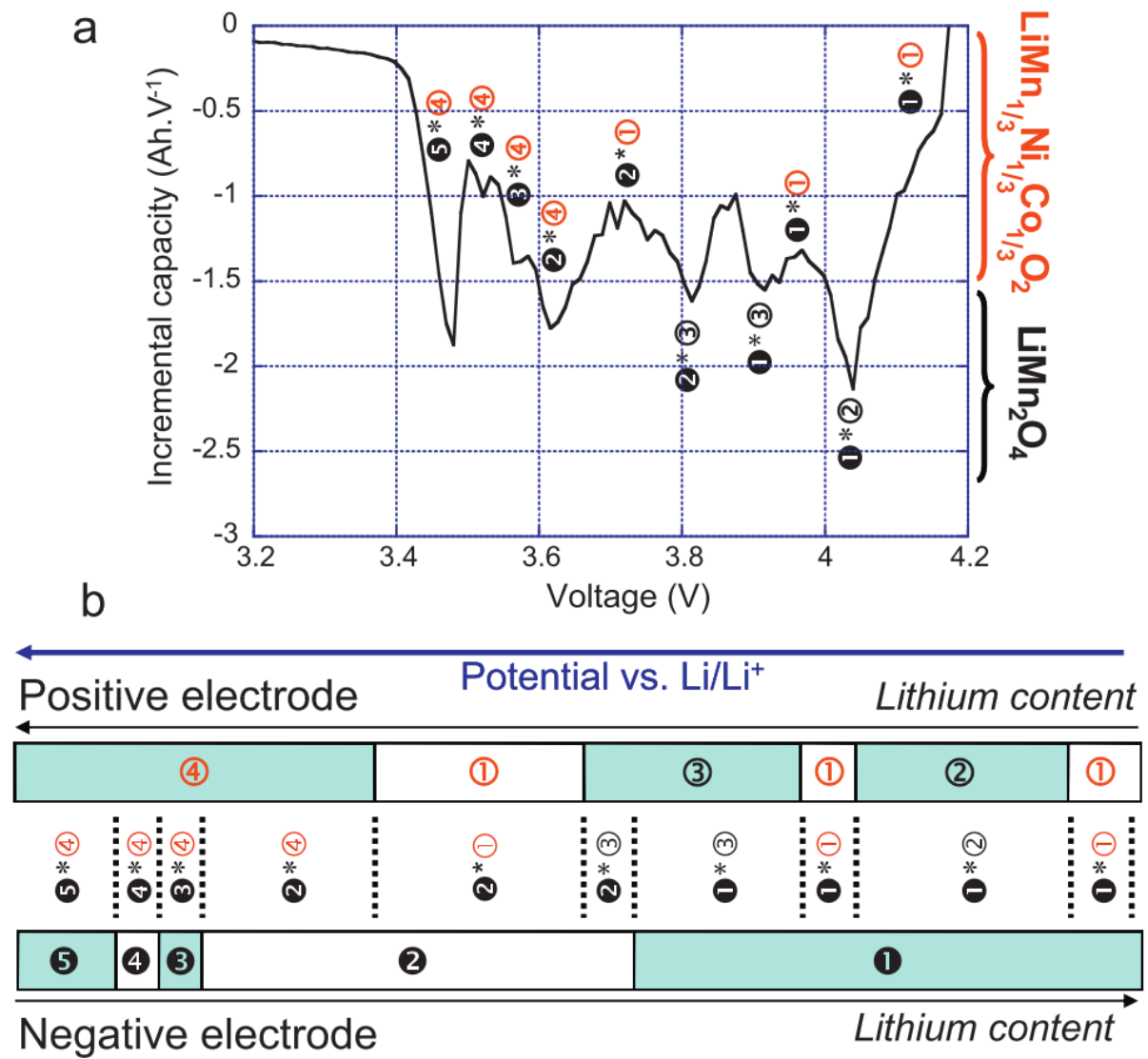


Figure 37. (a) ICA curve of a graphite – NCM & LMO cell generated through C/25 discharge. ICA peaks are labelled according to (b) the phase combination schematic. Top bar represents cathode phases (NCM & LMO). Bottom bar represents anode phases (graphite). Each ICA peak represents a combination of anode and cathode phases. Source: [180].

Referring back to Figure 34, different degradation modes will affect the full cell voltage curve differently. As ICA is carried out at a constant current in these cases, the dQ term of dQ/dV is a constant. This suggests that an ICA curve is a representation of the full cell differential voltage,

i.e. $1/dV$. It has been suggested that SOH can be estimated by identifying and tracking the features of interest (FOI) of the ICA curve [181,182]. Dubarry et al. proposed that the evolution of FOI can give indications on the degradation modes such as LLI and LAM as simulated in Figure 38 [183,184]. Birkel et al. took a similar approach to use an OCV model to diagnose the degradation modes from experimental OCV data [171].

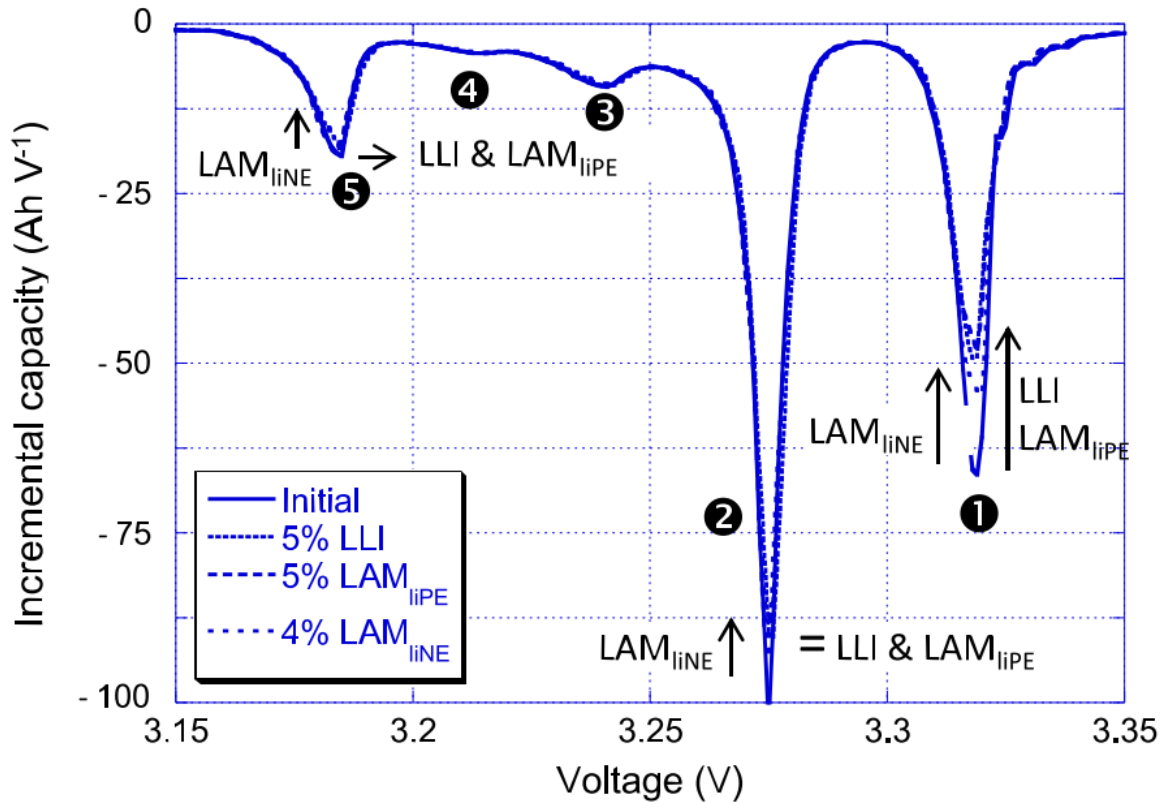


Figure 38. Simulated ICA peak evolution for various degradation modes. [183].

The benefit of the ICA is the potential for the SOH estimation through tracking curve FOI. It also provides information on the electrochemical performance of the cell i.e. how much capacity is stored at what potential. The downside of the method is in its requirement for individual cell current measurement. Current distribution is not homogeneous in a parallel battery pack [100,185,186] which suggests that a current measurement is required for every parallel string in the pack to carry out ICA. Current measurement per cell is unrealistic due to the extra cost, volume and wasted energy.

Another disadvantage of this technique is the dependency on cell temperature. As previously mentioned, the potential of an electrode at a given current depends on its temperature. In order to have an accurate, coherent measurement throughout the characterisation cycle, an isothermal condition is required for the cell which may be difficult to achieve even with a thermal management system.

2.7.3. DIFFERENTIAL VOLTAGE

Differential voltage (DV) is essentially the inverse of ICA where the dV/dQ is plotted against cell capacity. The two techniques are carried out in the exact same manner but the data is plotted differently. The plateaus in ICA will appear as peaks in DV and vice versa. DV may be favoured over ICA when the curve FOI, such as a peak, is easier to track than the equivalent FOI in ICA. Wang et al. used the points of inflection of a DV curve as FOI to estimate battery capacity [187] and Bercibar et al. used peak-to-asymptote distance to estimate the SOH (

Figure 39) [188].

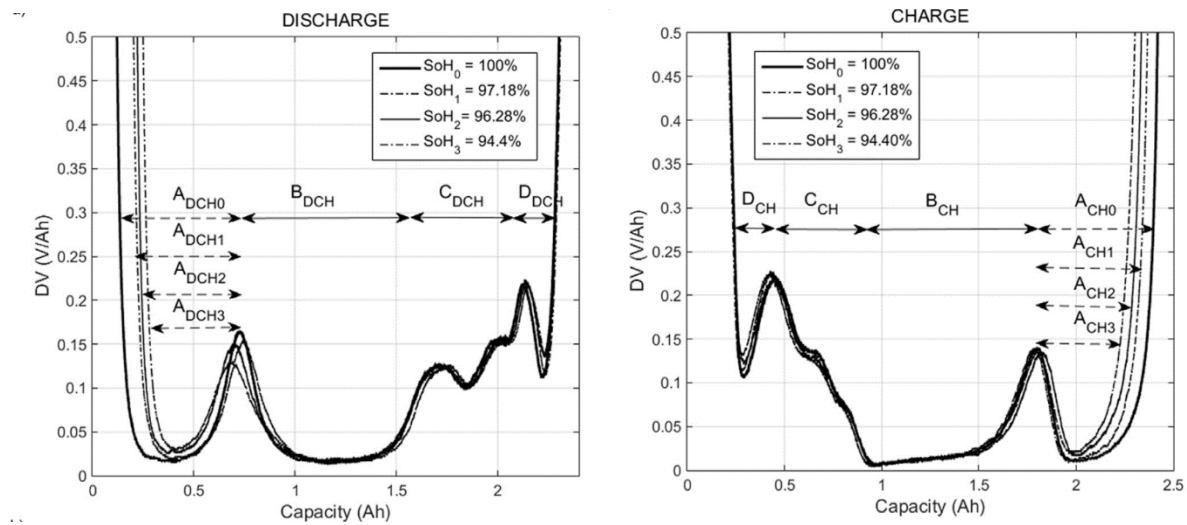


Figure 39. DV curve results for a commercial graphite-LFP cell at various stages of capacity loss. Discharge DV (left) and charge DV (right). Source: [188].

2.7.4. SLOW-RATE CYCLIC VOLTAMMETRY

Slow-rate cyclic voltammetry (SRCV) is a technique where the cell is scanned through the full operating potential window at a slow voltage ramp rate such as $100\mu\text{V/s}$ and the current response is measured (Figure 40a). The technique is also referred to as linear sweep voltammetry or voltage scanning. The resulting information is similar to ICA. When current response is plotted against cell voltage, the SRCV curve will give indications on where the phase transitions are occurring in the cell (Figure 40b) [17,189,190]. The evolution in curve FOI can give indications on cell SOH. SRCV is a useful method with simple computation however it requires current measurements for individual cells and it takes several hours to complete due to its slow scan rate. It is important to keep the scan rate slow so that the peak current does not exceed the recommended maximum current for the cell. The main disadvantages are that the operating mode is highly unlikely to ever occur naturally in an application as well as the isothermal condition requirement for the same reason as mentioned previously.

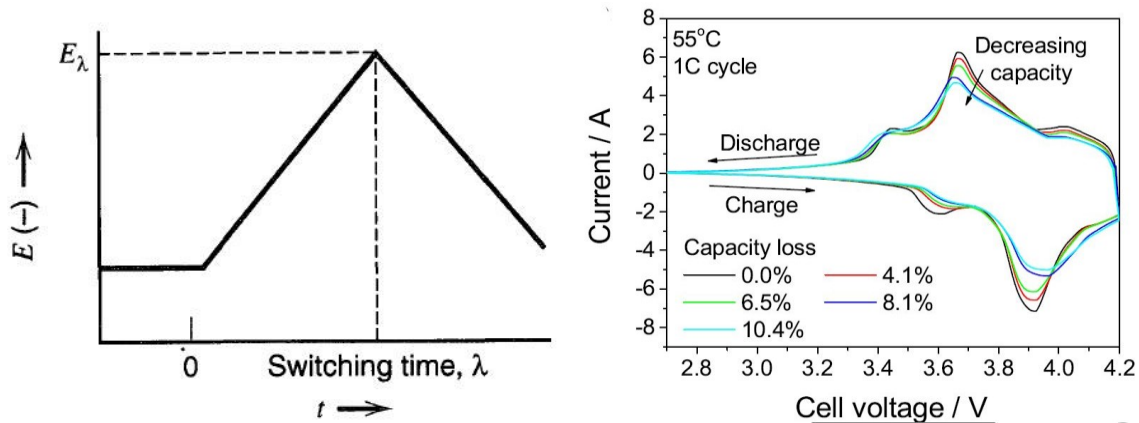


Figure 40. Cyclic potential sweep for SRCV (left) [93]. SRCV curve at various stages of capacity loss. Scanned at $150\mu\text{V/s}$ (right).

2.7.5. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Electrochemical impedance spectroscopy (EIS) is carried out by applying sine waves of current or voltage on the cell and by measuring the impedance response at various wave frequencies. This will result in an impedance curve plotted on a Nyquist plot (Figure 41). The impedance

curve can then be fitted onto a suitable equivalent circuit model (ECM) using a fitting software where the cell can be parameterised into individual characteristics. Figure 42 is a typical representation of a lithium-ion battery. Cathode charge-transfer resistance often represents solid state mass diffusion process using a Warbourg element [104].

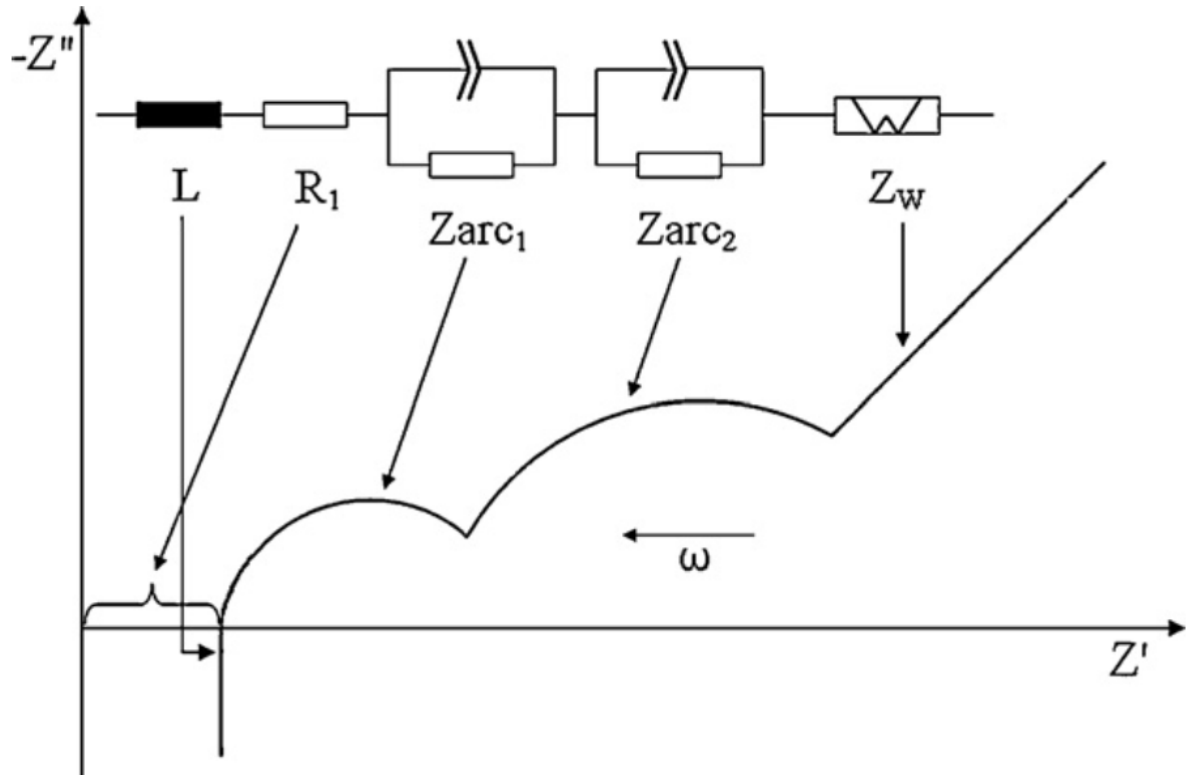


Figure 41. Typical impedance spectrum of a lithium-ion battery. Each feature in the spectrum is attributed to a parameter in an ECM. Source: [191].

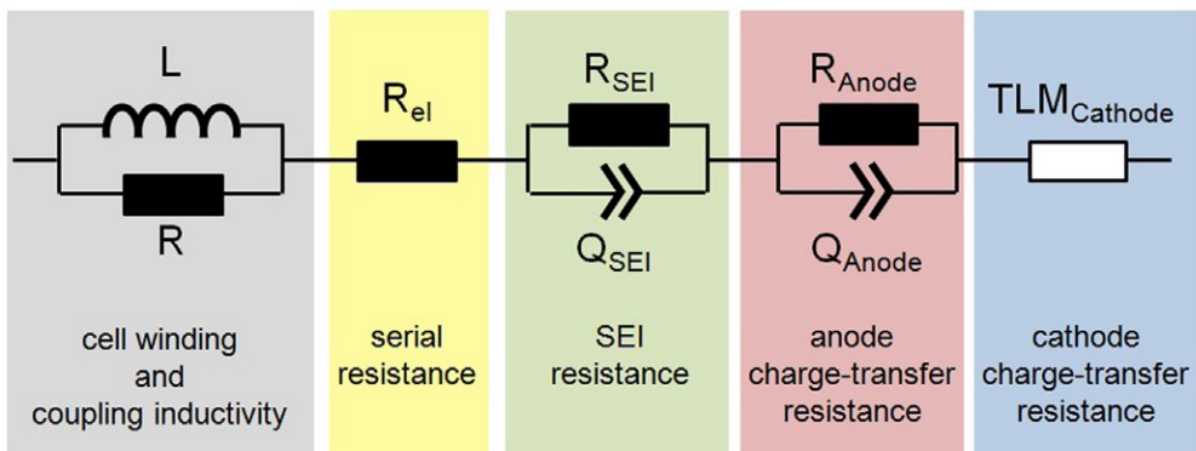


Figure 42. ECM parameter representation of a lithium-ion battery. Source: [189].

EIS is useful for determining decoupled parameters however this method requires impedance measurements and a complex computation. EIS is not used for on-board analysis due to these reasons. However, Howey et al. have recently introduced an in-operando alternative for EV application where the impedance is measured through motor controller excitation [192]. It is also to be noted that all the in-situ diagnosis methods described above require isothermal conditions to get an accurate result which is difficult to obtain in real application.

2.7.6. POTENTIOMETRIC ENTROPY MEASUREMENT

Potentiometric entropy measurement (PEM), also referred to as electrochemical thermodynamics measurement, is a method which measures the entropy changes in a cell. This is carried out by observing the OCV variation with temperature at various SOC. Figure 43 describes a typical PEM procedure where the OCV of the cell is measured at various controlled temperatures ensuring cell equilibrium each time by resting for several minutes. The OCV is plotted against temperature, T , where the slope of the line gives information about its entropy changes, ΔS , through the following equation [193]:

$$\Delta S(SOC) = -nF \left(\frac{\partial}{\partial T} OCV(SOC, T) \right)_{SOC} \quad (9)$$

F is the Faraday constant and n is the charge number (= 1 for lithium-ion batteries). The cell is then discharged (or charged) a small amount to increment its SOC and then the temperature procedure is repeated. Finally, the entropy changes can be plotted against the SOC to get a full spectrum as presented in Figure 43.

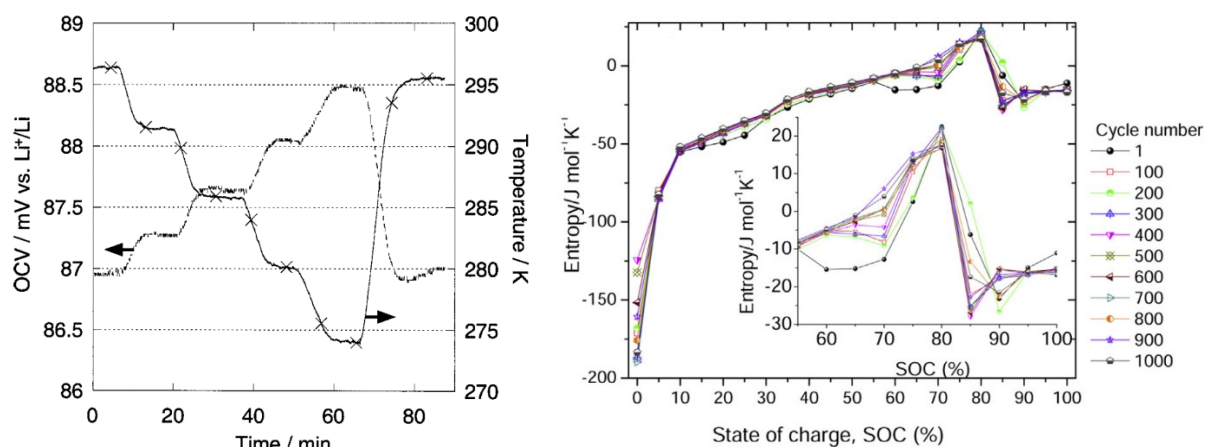


Figure 43. A typical PEM protocol for measuring temperature dependent OCV at a particular SOC (left) [194]. Final entropy spectrum at various SOC (right) [195].

Entropy information gives indication about thermal and structural properties of a cell which in turn may be used to track the cell SOH. The disadvantage of this technique is the several hours (or days) required to complete the test as the cell needs to reach its equilibrium at each OCV measurement. Zhang et al. has recently presented a faster alternative using continuous entropy measurement with baseline corrections which allows the test to be completed within hours however it suffers a large relative error (>100%) [196].

2.7.7. ELECTROCHEMICAL CALORIMETRY

Electrochemical calorimetry (EC) is a technique used to measure the heat flow of a cell under slow charge and discharge cycle inside an isothermal calorimeter. The heat flow of the cell provides its thermal power characteristics which in turn can give information about its chemical reactions and phase transitions. Krause et al. defines the total heat flow of a cell to be the sum of heat generations from the reversible reactions, parasitic reactions and cell polarisation [197]. Together with a high precision coulomb counting, the three heat generation terms can be decoupled to track the parasitic power of the cell per cycle.

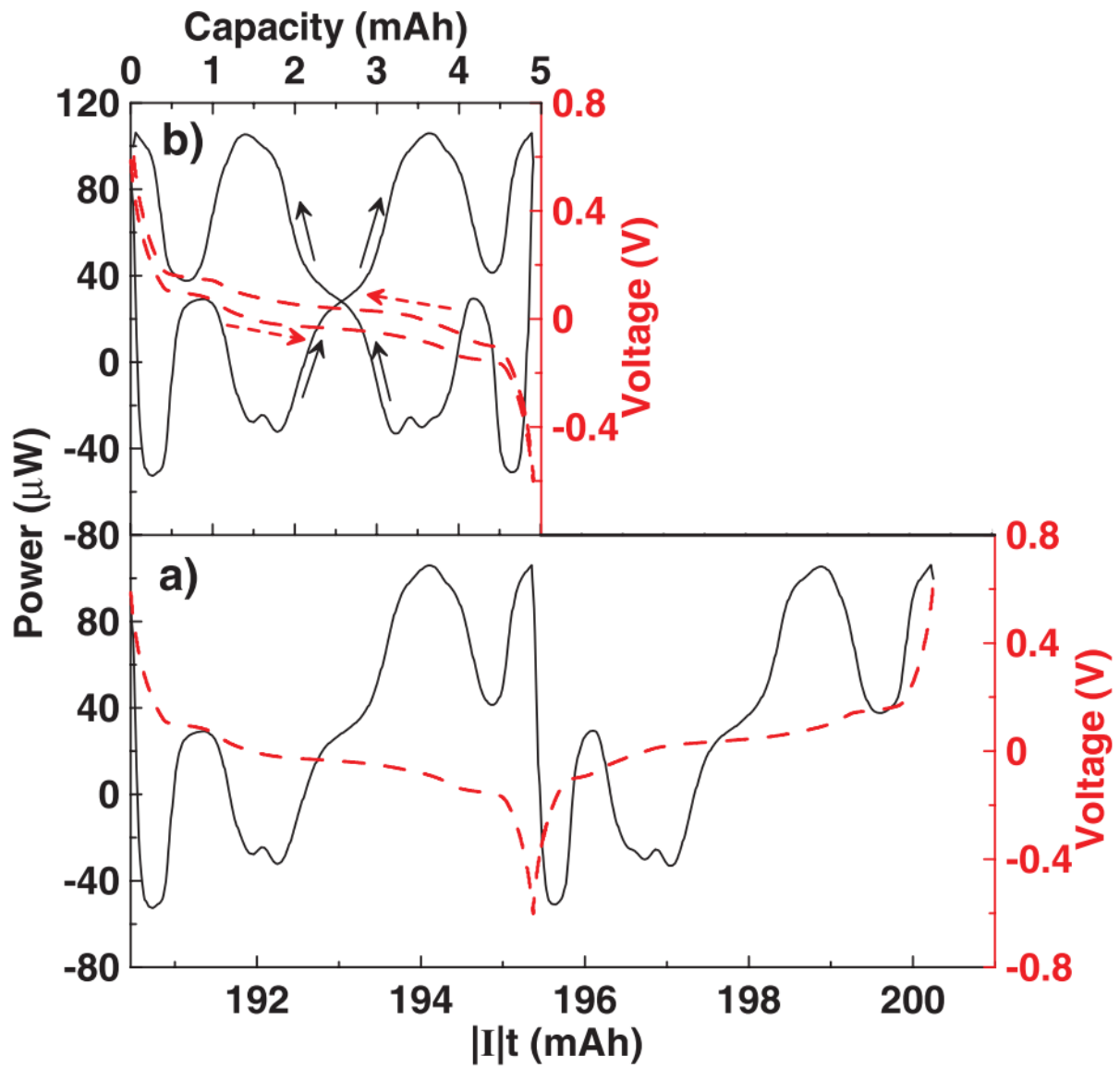


Figure 44. Thermal power and cell potential vs cumulative capacity (a) and discharge capacity (b) of a cycled lithium-ion cell. Source: [197].

Downie et al. used the technique to identify lithium plating and stripping in a graphite electrode [135]. Krause et al. presented a characterisation of electrolyte stability at various potential windows in a separate publication [198]. The results are shown in Figure 45 where they demonstrated that cycling between 3.8 V – 4.0 V has less parasitic power hence irreversible damage than cycling between 4.0 V – 4.2 V.

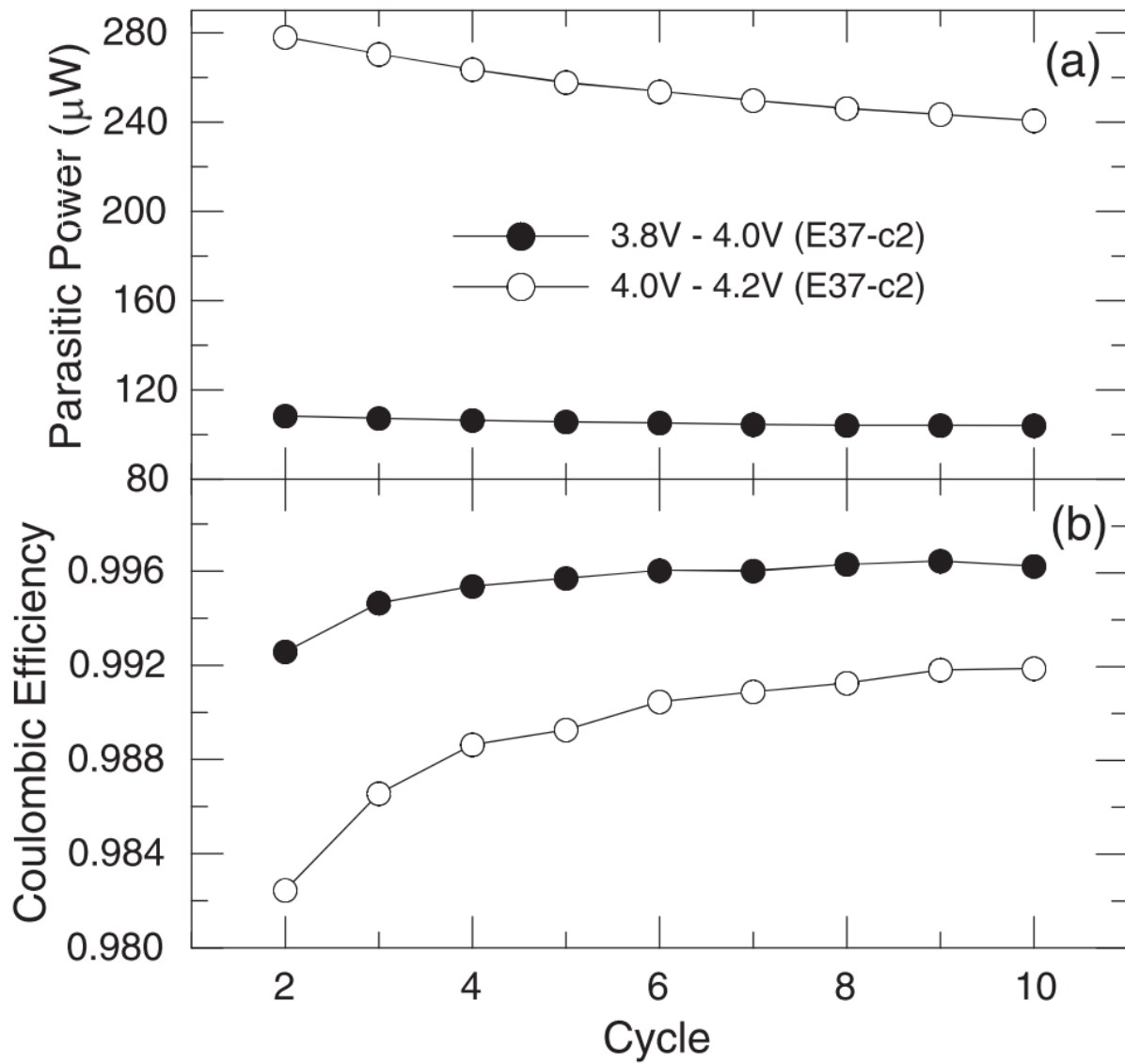


Figure 45. Parasitic thermal power (a) and coulombic efficiency (b) of a lithium-ion battery cycled at different potential windows. Source: [198].

EC is useful for tracking the parasitic power in a lithium-ion cell however requires expensive equipment and must be carried out inside a calorimeter making it unsuitable for an on-board application.

2.8. INTERIM CONCLUSION

To meet future energy storage demands, better performance and long cycle life are required from lithium-ion batteries. Many researchers are studying novel battery materials to tackle this problem however these battery chemistries currently have some sort of major drawback

preventing commercialisation for some applications which may take years or decades to solve if ever. Until then, a more immediate solution is required.

The literature review has shown that batteries have limited lifetime with complex degradation mechanisms. The industrial standard capacity loss and power loss are not detailed enough to understand the battery SOH. As such, degradation modes have been recently introduced as an alternative.

To track the battery SOH in a real-world application, such as in EVs and smartphones, low cost *in-situ* characterisation methods are required. To maintain a low cost, the technique must work *in-operando* to avoid additional hardware and expensive measurements such as individual cell current and impedance must be avoided.

Table 4 summarises the mentioned in-situ techniques and demonstrates a clear gap in the availability of a method suitable for on-board application. To address this issue, a new *in-situ in-operando* technique called the differential thermal voltammetry (DTV) is introduced and developed through this PhD research.

Table 4. Summary of various experimental in-situ diagnosis techniques. Disadvantages as an on-board application are in red.

Technique	In-operando	Measurements	Isothermal requirement	Comments
Coulomb counting	Yes	Current	Yes	Simple computation. Limited information.
ICA	Yes	Current, voltage	Yes	SOH tracking opportunity through phase transition information.
DV	Yes	Current, voltage	Yes	Same as ICA.
SRCV	No	Current, voltage	Yes	Same as ICA. Takes several hours.
EIS	No	Impedance	Yes	Decoupled parametrisation of ECM. High computational requirement.
PEM	No	Voltage, temperature	n.a.	Entropy information. Takes hours if not days. Requires temperature control.
EC	No	Voltage, heat flow	Yes	For tracking parasitic power. Requires calorimeter. Expensive.
DTV	Yes	Voltage, temperature	No	Same as ICA with additional entropy information.

Chapter 3. DTV CONCEPT AND CELL-LEVEL APPLICATION

3.1. INTRODUCTION

The literature review identified that a new *in-situ* diagnosis method for lithium-ion batteries aimed at real world application is required for understanding and measuring battery degradation mechanisms. This chapter introduces the concept of the new technique called differential thermal voltammetry (DTV) as a SOH estimator for lithium-ion cells.

Accelerated ageing experiments were carried out on 5Ah commercial NCM cells operated and stored at different temperature and loading conditions. The cells were analysed regularly with various existing *in-situ* diagnosis methods and the novel DTV technique to track their SOH. The diagnosis results were used collectively to understand the degradation mechanisms inside the cells. The DTV spectra were decoupled into individual peaks, which each represent a combination of phases in the negative and positive electrode. The peak parameters were used to quantitatively analyse the battery SOH.

In order to validate its use also as a screening tool for 2nd life batteries, a different cell of the same chemistry with unknown degradation history was analysed to explore how DTV is able to identify what conditions unknown cells are in.

3.2. DTV CONCEPT

The beauty of the DTV technique is that it is low cost and simple to carry out with minimal measurements. The only two measurements this technique requires are surface cell temperature and voltage readings. Temperature can be measured using simple thermocouples or a thermal imaging camera. It is to be noted that these measurements are already taken in most applications including EVs to monitor safety and SOC respectively which suggests that the initial installation costs for this technique should be minimal if no additional measurement hardware is needed.

To carry out the analysis, the time differentials of both parameters are calculated: dT/dt & dV/dt . The differential of the temperature is divided by the differential of the voltage to obtain what is called the DTV parameter as written in **Error! Reference source not found.0**.

$$DTV = \frac{dT}{dt} / \frac{dV}{dt} = \frac{dT}{dV} \quad (10)$$

This is then plotted against the voltage to obtain the DTV curve as depicted in Figure 46 (top right subfigure).

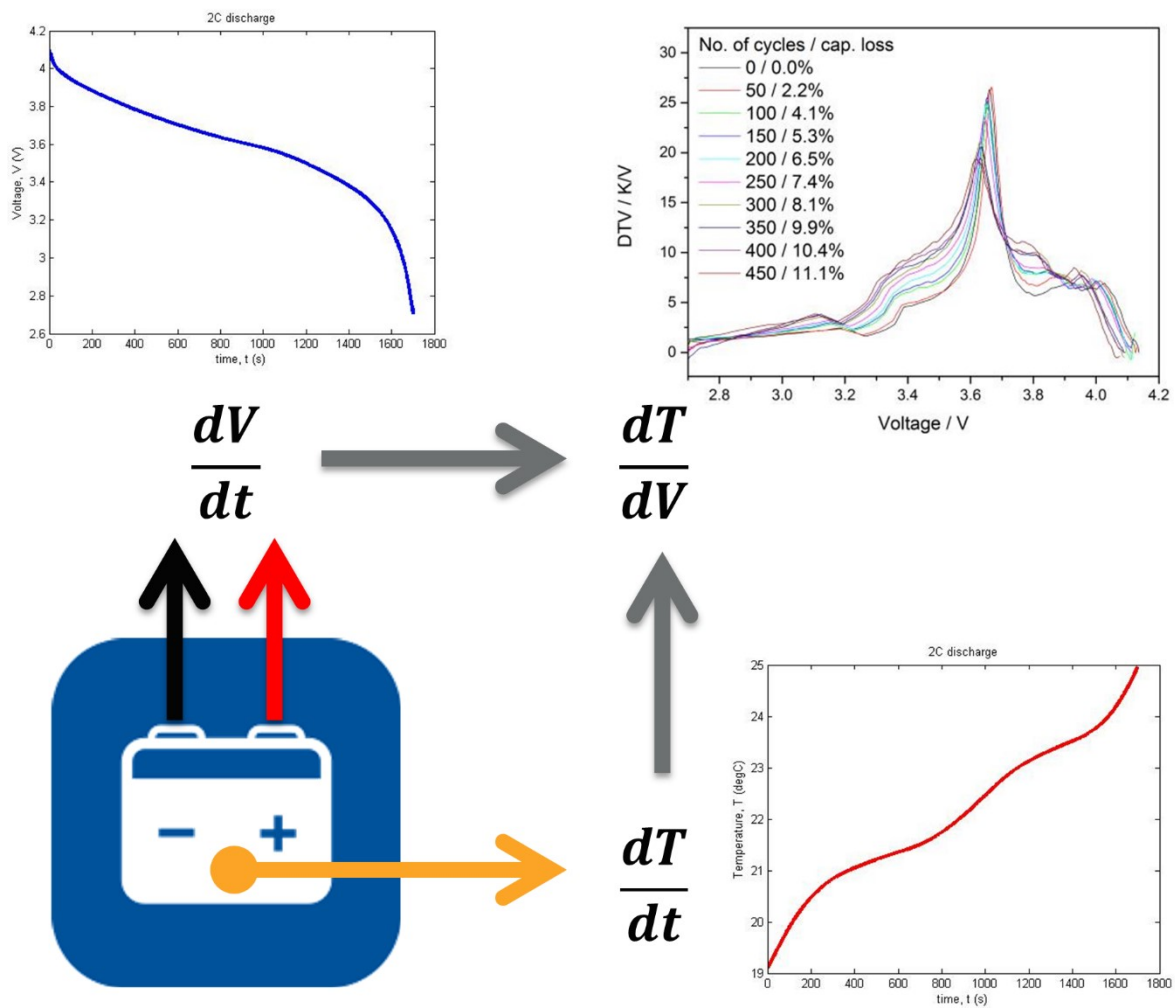


Figure 46. Illustrative description of the DTV technique. Subfigures contain a voltage (top left) and a temperature curve (bottom right) of a NCM cell during a 2C (10A) constant current discharge; and evolution of the DTV curve through various stages of capacity loss (top right). Figure data source: [14].

Theoretically, the DTV curve describes the entropic characteristic of the cell at various cell SOC's. During a reversible electrochemical reaction, the energy dissipated in a cell can be described through the free energy equation [93]:

$$\Delta G = -nFE \quad (11)$$

Where ΔG is the Gibbs free energy change per atom of lithium reacted, n is the number of electrons passed, F is the Faraday constant, and E is the reversible potential difference. The entropy change in a cell reaction, ΔS , at a constant pressure, P , is described by the temperature dependence of ΔG [93]:

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad (12)$$

And combining the above two equations gives the following relationship of $\partial E/\partial T$ to the entropy change in a cell:

$$\Delta S = nF \left(\frac{\partial E}{\partial T}\right)_P \quad (13)$$

The $\partial E/\partial T$ term is associated with the inverse of dT/dV in the DTV analysis. This suggests that a peak in the DTV curve, i.e. a high dT/dV , represents a low $\partial E/\partial T$ term hence small change in entropy at that cell potential. Similarly, a plateau or the peak-to-peak transition region on the DTV curve represents a high $\partial E/\partial T$ term hence large change in entropy at that cell potential.

What this means physically is that at a DTV peak i.e. during low entropy changes, the electrode phase is quasi-static. Only the lithium concentration is changing in the electrodes. When moving from peak to peak i.e. through high entropy changes, the electrode phase is undergoing a rapid transition. At a critical lithium concentration, the electrode structure is no longer thermodynamically stable and transitions phase. Phase change is also associated with rapid voltage change as the new electrode phase has a different standard electrode potential.

Reynier et al. [194] demonstrated that entropy profiles have sharp features at stage transitions in well graphitized material. Maher and Yazami [195] later stated that for a graphite negative electrode and LCO positive electrode cell, the entropy profile undergoes significant changes at specific OCPs/SOCs under cycling and that these entropic changes can be attributed to degradation in specific electrodes. They concluded in their work that entropic changes at high potential (OCP value of 4.075 V, 4.05 V and 3.95 V) are due to the crystal structure transformation of LCO positive electrodes and low potential staging phenomena in graphitic negative electrodes.

It can be seen that the DTV curve evolves as the capacity fades. These peaks can act as “footprints” of the cell SOH and it is possible to track the cell degradation by observing how these peaks change in terms of position, width and height. A deeper insight into this peak analysis concept will be explored later in this chapter.

The DTV technique is suggested as a complimentary method to the conventional ICA and SRCV techniques. These conventional techniques also provide useful information however require individual cell current measurement which is too costly to carry out in reality for battery packs with a number of parallel strings.

Similar to SRCV and ICM, the peaks in the profile represent stages of lithium (de)intercalation in the full cell which affect the amount of enthalpic and entropic heat generated/absorbed for a given voltage window. Peak evolutions in DTV under capacity fade can provide complementary information on specific degradation mechanisms to that of dQ/dV , as shown later in this chapter.

DTV has a number of unique advantages compared to the existing in-situ methods. Crucially DTV includes the additional entropic information that cannot be obtained directly through EIS, SRCV or ICM as seen in the results of this chapter. DTV also does not require the isothermal conditions which are normally required in the other methods to obtain accurate diagnosis, instead it relies upon the cell temperature changing during discharge/charge. The DTV method

combined with the OCV extrapolation technique (described later) is inherently temperature correcting as the results take temperature change into account.

3.3. RESEARCH QUESTIONS

In this series of experiments, the aim is to answer the first key research question for application with NCM cells:

- Can temperature and voltage measurement give enough information alone to identify the complex internal state of a battery in detail?

This work package also aims to address the following sub-questions:

- Can DTV provide similar, if not more, information as ICA & SRCV?
- Do the cells age differently depending on the method of ageing and can DTV identify the difference?
- How do the expected dominating degradation mechanisms show in the DTV curve evolutions?
- Can DTV be used as a 2nd life screening tool to diagnose the SOH of cells with unknown history?
- Can DTV be used to look at degradation distribution depending on the physical position of the cell? (i.e. middle vs. near cell tabs)

3.4. EXPERIMENTAL

3.4.1. CONTROLLED ACCELERATED AGEING

In order to validate the concept, accelerated ageing experiments were carried out on commercial 5Ah lithium-ion polymer cells manufactured by Dow Kokam (model SLPB11543140H5). See appendix entry A1 for full cell specifications as provided by the manufacturer. The cells used in this study contained a carbon negative electrode and NCM positive electrode of which the exact stoichiometric composition is unknown. The cells were

stored at 10°C before use and then operated at different temperatures and different load profiles as shown in Table 5 to accelerate ageing and identify what diagnosis result is seen from cells aged with different expected degradation mechanisms [90].

Table 5. Accelerated ageing experiment for NCM cells [9].

Cell	Load	Temperature
1	Held at constant 4.2 V (trickle charge)	55°C
2	5 A (≈ 1 C) cycling	55°C
3	5 A (≈ 1 C) cycling	Ambient

For the cells operated or stored at high temperature, they were placed inside a thermal chamber (ESCO Isotherm 32L) under forced air convection at 55°C. The cells were characterised at room temperature of 20°C $\pm$ 2°C every 50 cycles using 4 diagnosis methods: EIS, SRCV, ICM and DTV.

Load cycling consisted of 1 C charge followed by constant voltage charge with cut-off current at 250 mA and 10-minute relaxation phase then 1 C discharge and 10 minutes relaxation phase.

For detailed specifications on the ageing and characterisation procedures as well as a full list of apparatus, please refer to the appendix entry A2.

3.4.2. DATA PROCESSING

In order to obtain useable information, the temperature measurements had to be smoothed appropriately as the temperature rise measured between each recording was considerably noisy. Smoothing was carried out with a combination of Savitsky-Golay filter and moving average. The two methods combined were chosen to increase the signal-to-noise ratio of the data without significantly diverting from the original curve. Moving average was used to eliminate the majority of measurement noise and Savitsky-Golay filter to finely smooth the data while maintaining the curve characteristic. The smoothed data was compared to the raw dataset to check whether it accurately followed the original curve characteristics. This was done by

ensuring that the median of the absolute deviations of recorded dataset about the smoothed line is below $< 0.3\%$.

It should be noted that this smoothing method was revised in proceeding experiments described in later chapters for optimised smoothing. The effect of smoothing parameters on the DTV analysis is explored in detail in 4.3.2 using the final smoothing method.

It is important to understand the errors associated with the measurements and what effect it may have on the results. As an example, the Bio-Logic battery cycler system has a voltage measurement accuracy of $\pm 0.3\text{mV}$ and a temperature measurement accuracy of around $\pm 2^\circ\text{C}$ with the K-type thermocouples. Caution must be taken whenever interpreting results within the error margin. Thankfully, the DTV analysis is looking in the voltage resolution of at least an order of magnitude greater than the measurement accuracy. However, the temperature measurement has a relatively significant error. It is estimated that this $\pm 2^\circ\text{C}$ accuracy is mostly referring to possible static offsets as temperature readings observed through experiments seem to have approximately $\pm 0.05^\circ\text{C}$ transient error which is an acceptable error margin for the upcoming analysis. Any effect from transient error is minimised by using a high sampling rate and data smoothing. Static offset is overcome by using the same calibrated equipment for the entire experiment.

3.4.3. VALIDATION OF METHOD ON A CELL WITH UNKNOWN HISTORY

In order to validate the use of DTV as a 2nd life battery screening tool, the method was also applied to a fresh and an aged 25 Ah large form factor pouch lithium-ion cells of unknown degradation history. The tested 25 Ah cells were made by the same manufacturer and with the same cell chemistry as the 5 Ah cell.

It is known that a cell may have a temperature variation depending on the internal configuration of the cell [199]. In addition to surface thermocouples, the cell temperature was

monitored using a thermal imaging camera (model A655sc by FLIR Systems) to see if there was a difference in the DTV diagnosis depending on the physical position of temperature measurement, i.e. to see if spatially unequal degradation had occurred.

The cell surface, including tab connections were spray painted black and placed inside a painted box to give uniform infrared emissivity for thermal imaging camera measurement, and the thermal imaging camera temperature was checked against the thermocouples.

3.5. RESULTS AND DISCUSSION PART 1: TRACKED AGEING OF 5AH CELLS

3.5.1. *CAPACITY FADE*

The capacity fade of the cells, shown in Figure 47, were taken from the loss of Ah compared to the Ah measured when the cell was fresh. The capacity was determined from a slow rate voltage scan of $-150 \mu\text{V/s}$ between 4.2 V and 2.7 V. The tests were carried out on all 3 cells at every 50 cycles. The change in the results between 300 and 350 cycles were likely to be due to the fact that the ambient lab temperature had dropped from 20°C to 18°C for the characterisation tests. The temperature in the thermal chambers was not affected, and therefore the actual degradation experiments were not affected, hence the return to trend once the next characterisation tests were performed at the correct temperature.

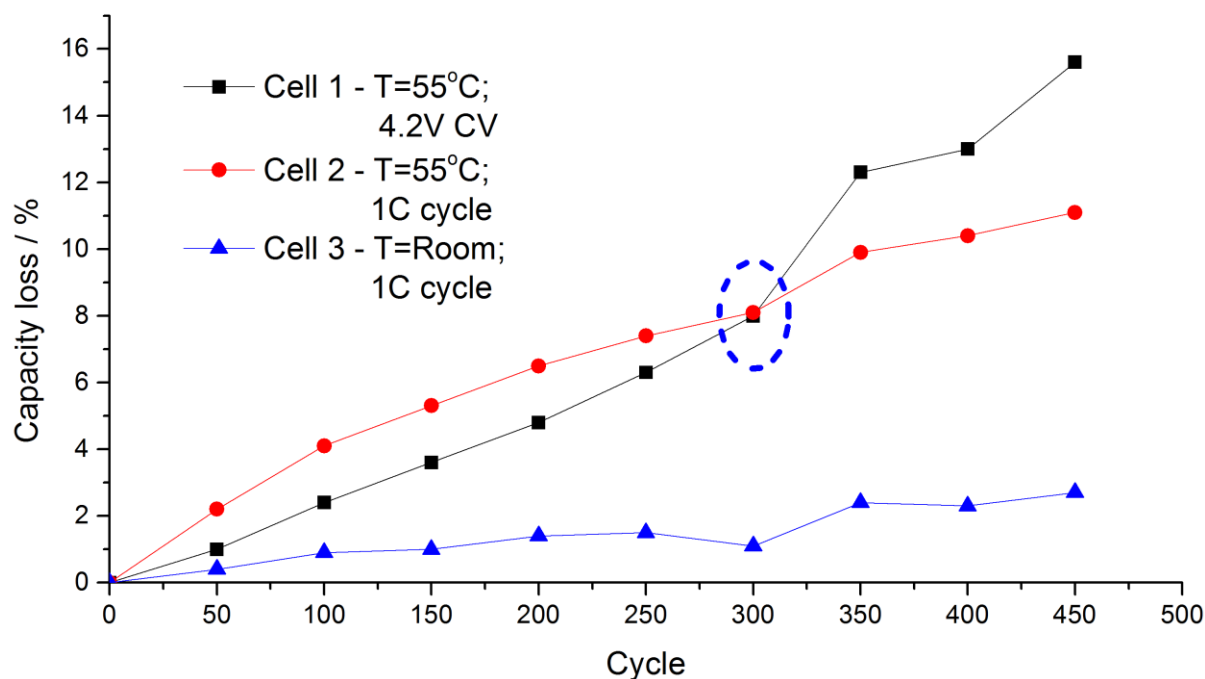


Figure 47. Capacity loss measurement of the three cells under accelerated degradation. Note cycle number 300 where two cells have approximately 8% capacity loss but the cells will behave differently in the future. Adapted from [9].

As seen from the capacity loss curves, the cell 2 (1 C cycling at high temperature) initially shows higher capacity loss which decreases over time. Based upon [107,200,201], the cycled cell is likely to experience an initial fast rate of SEI growth due to the exposure of fresh electrode surface to the electrolyte as a result of cracks in the surface film caused by cycling [109]. However, the rate of degradation is expected to slow down as the SEI layer thickened [116] which matches the capacity loss behaviour.

The cell 1 on the other hand (held at high potential & temperature) initially shows a slow rate of capacity loss which increases over time. Based upon [106,202,203], the cell held at high potential is expected to also experience SEI layer growth (but not as much as the cycled cell) caused by the low negative electrode potential and the high temperature (i.e. faster reaction kinetics and diffusion). The gradual increase in the rate of capacity loss may be hypothesised that the cathode is degrading as the cell spends all its time at its highest potential limit recommended by the manufacturer.

The cell 3 (1 C cycling at ambient temperature) shows very little capacity loss relative to the other cells as suggested due to lower reaction kinetics at lower temperatures [90].

Further discussion will focus on analysing the two cells held at higher temperature (cell 1 and cell 2) due to their significant degradation.

The interesting point to note here is at cycle 300 when the capacity losses in cell 1 and cell 2 are approximately the same. In the eyes of the industrial standard measurement of SOH, which is simply the capacity fade, these two cells look identical. However, it is clear that these cells have had a different ageing history and will behave differently in the future where one cell may fail sooner than the other if the ageing conditions continued as it is. This result highlights the need for a different approach on defining the SOH in an on-board application which is addressed by the DTV technique in this work.

3.5.2. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

The impedance of the cells was measured every 50 cycles using a 4 channel Bio-logic VSP with a 5 A booster. The EIS tests were carried out at 5A constant current load and AC amplitude of 0.2A root mean squared (RMS) at between 2kHz and 1Hz with 6 measurements per decade at different voltages from 4.2V to 2.7V at ambient temperature under fan forced convection to avoid different impedance responses [204]. EIS measurements were recorded sufficiently fast so that there was no significant change in SOC during the experiments. The resulting impedance spectra were fitted with an equivalent circuit model (ECM) as shown in Figure 48a using the software ZView (Scribner).

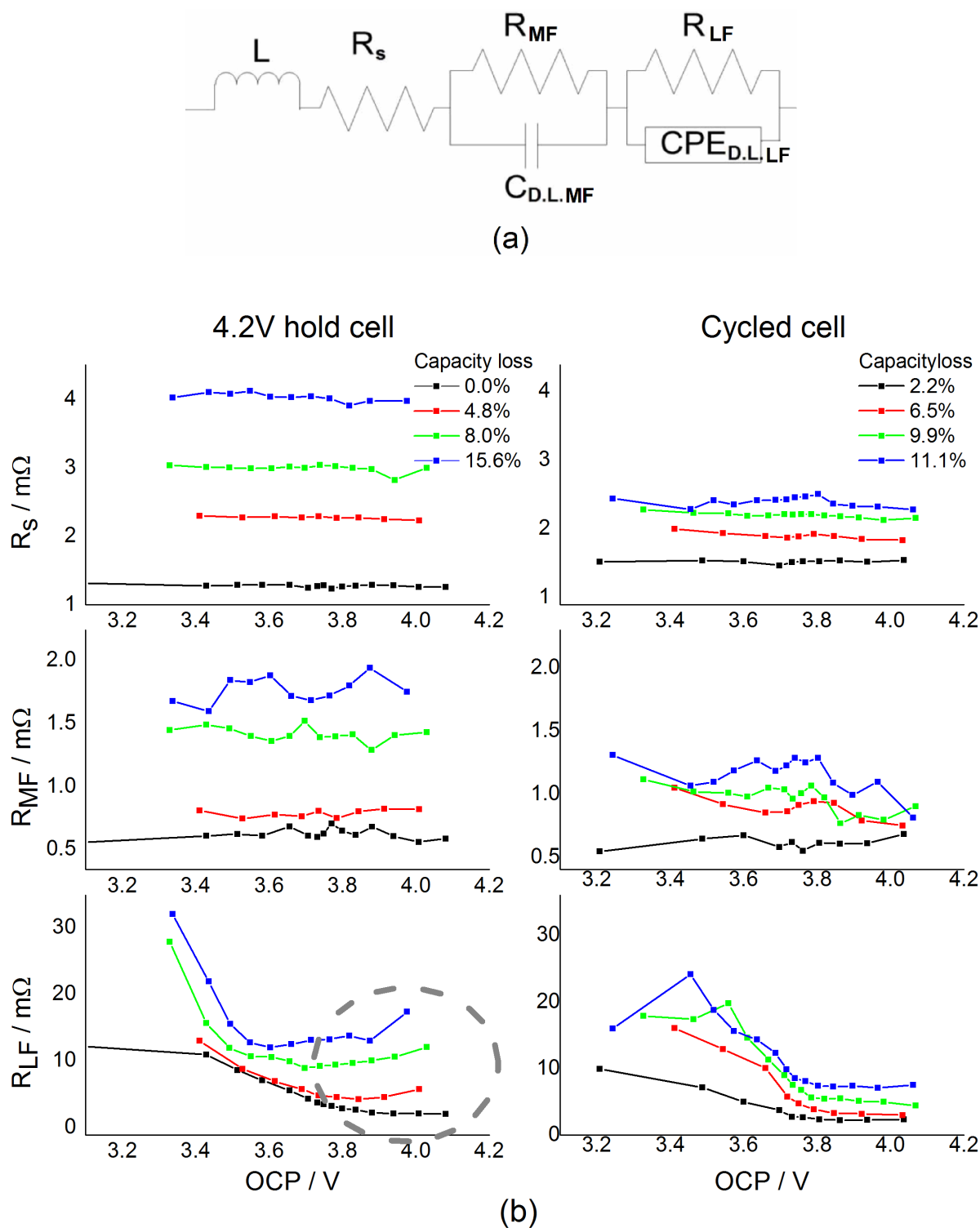


Figure 48. (a) Equivalent circuit model used. CPE = constant phase element. (b) Resistance parameters determined from impedance curve fitting at various stages of capacity fade. From top to bottom: series resistance, medium frequency (MF) resistance and low frequency (LF) resistance. Cell held at high potential (left) and cycled cell (right). Adapted from [9].

Figure 48b shows the resistance parameter values of cells 1 and 2 at various stages of capacity loss. It describes the progression of three resistance components: series, medium and low

frequency. Medium frequency (MF) resistor-capacitor (RC) pair is often associated with lithium ion transport at the SEI layer and low frequency (LF) RC pair with lumped charge transfer at both the electrode/electrolyte interfaces [205,206].

A steady increase in all resistance parameters can be seen in both cells. The cause of this impedance rise is a combination of various degradation mechanisms [90]. It is observed that the series resistance in the cell held at 4.2V is greater than the cycled cell. This is hypothesised to be a result of the reduction of the ionic conductivity of the electrolyte due to electrolyte decomposition at higher voltages.

It is noticed that the mid-frequency resistance, often attributed to the SEI layer, initially shows a greater increase in the cycled cell for the reason mentioned in the previous section. However, from approximately 8% capacity fade (i.e. cycle 300), the cell held at 4.2V now shows a rapid increase which could be hypothesised as the transition metals released from the cathode depositing at the anode surface to form more SEI.

The low-frequency resistance, often attributed to the charge transfer resistance, has an interesting observation for the cell held at 4.2V where the higher voltage region is increasing which is entirely unobserved in the cycled cell (highlighted by the grey dashed circle in Figure 48b). Wu has presented the decoupled charge transfer coefficients per electrode for the same cell chemistry [158] which suggested that the coefficient of the cathode is higher at higher cell voltage and *vice versa* for the anode. As the charge transfer resistance is a direct function of the coefficient, it can be hypothesised that this increase in resistance at higher cell potential can be attributed to the cathode degradation. This matches the initial expectation that high voltage storage gradually promotes cathode degradation through metal dissolution.

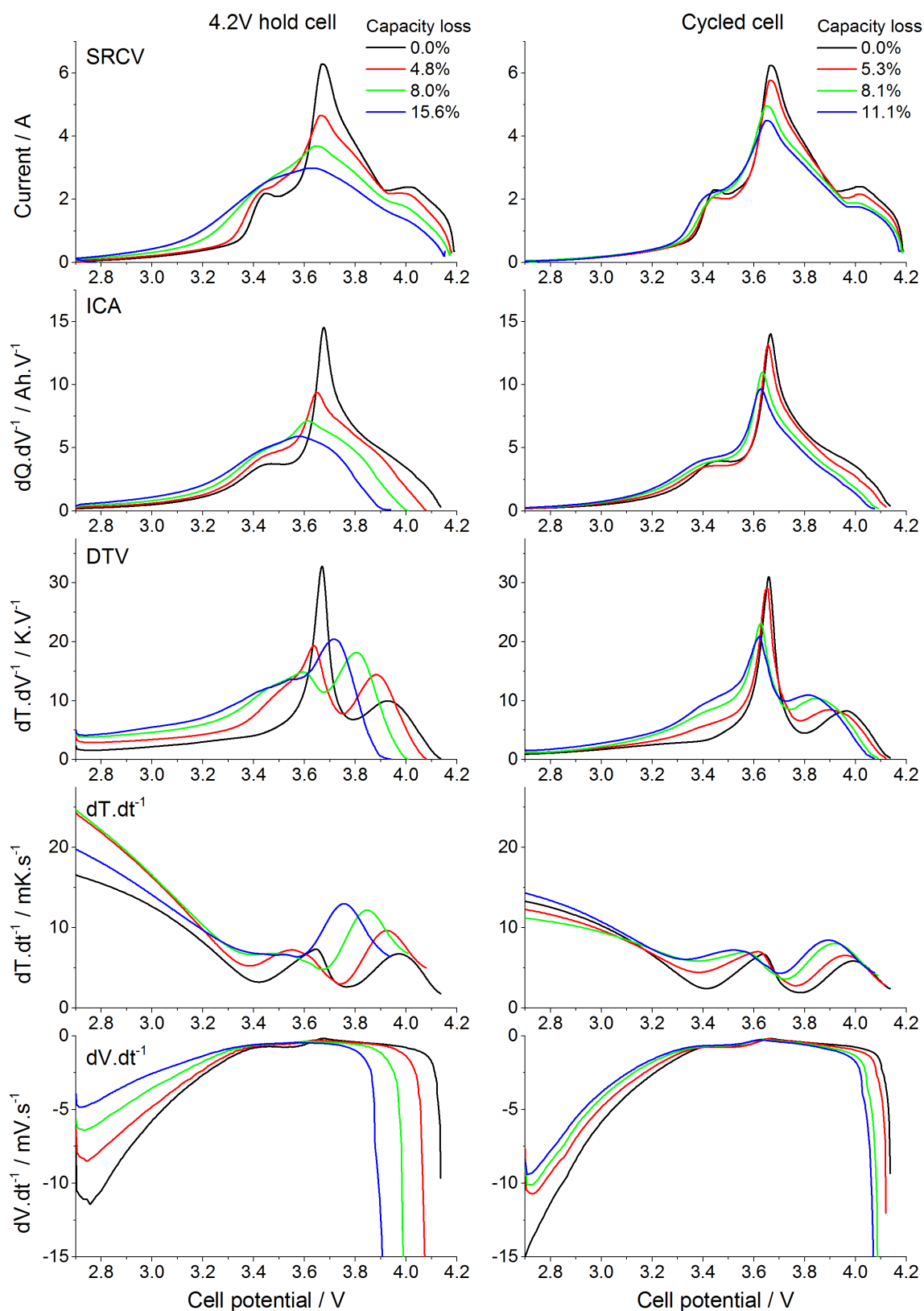


Figure 49. SRCV, ICA, DTV, dT/dt and dV/dt results for the two cells at different stages of capacity fade. Cell held at 4.2V on the left. Cycled cell on the right. SRCV at $-150\mu V/s$. ICM, DTV, dT/dt and dV/dt carried out simultaneously at 2C discharge. Adapted from [9].

3.5.3. SRCV, ICA AND DTV

Figure 49 shows the results from SRCV, ICA and DTV for the two cells as well as the decoupled dT/dt and dV/dt . SRCV was carried out at a voltage scan of $-150 \mu\text{V/s}$ between 4.2 V and 2.7 V. ICA and DTV were carried out simultaneously at 10 A (2 C) constant current discharge at room temperature. 2 C was chosen in this case as a suitable balance between speed of testing and clarity of entropic contribution within mixed heat generation of enthalpy and entropy [14].

It can be seen that SRCV and ICA generate curves with similar peak positions and shapes. It can be noted that the peak position of ICA (and DTV) results are shifted towards lower potential compared to SRCV. This is due to the greater overpotentials as result of higher testing currents. The term overpotential is used in this thesis to describe the difference in the observed voltage from the thermodynamic potential of the cell. The SRCV result shown here was obtained in 180 minutes whereas the ICM and DTV took 30 minutes. It is possible to see from these results that ICA (and DTV) can give information comparable to SRCV in a reduced measurement time.

ICA, aka dQ/dV method, is carried out at a constant current hence the term " dQ/dt " is a constant. This means that dQ/dV is essentially showing information on the differential voltage, dV/dt , alone. The differential of temperature, dT , provides information on the enthalpic and entropic behaviour of the cell and is not constant through charge/discharge as seen in Figure 49. It can already be observed that the cells have different behaviour at similar stages of capacity loss depending on its ageing history. Hence, it can be said that DTV provides similar information as ICA with the addition of the thermal information about the cell.

3.5.4. DTV PEAK FITTING AND ANALYSIS

Evolution of peaks as a result of degradation is clearly visible qualitatively. However, in order for a BMS to analyse the results to interpret and make informed decisions, this change needs to be quantified and identifiable by code running in a microcontroller.

In order to analyse the result quantitatively, the DTV curve was decoupled into 4 peaks using the open code “peakfit.m” on MATLAB [207,208]. Figure 50 shows an example decoupling of peaks. Using the MATLAB code, the peaks were set to be Lorentzian for the best accuracy of fit and quantitative information for individual peaks was obtained for analysis such as: peak position, height and width. The width was calculated at the half height of the peak.

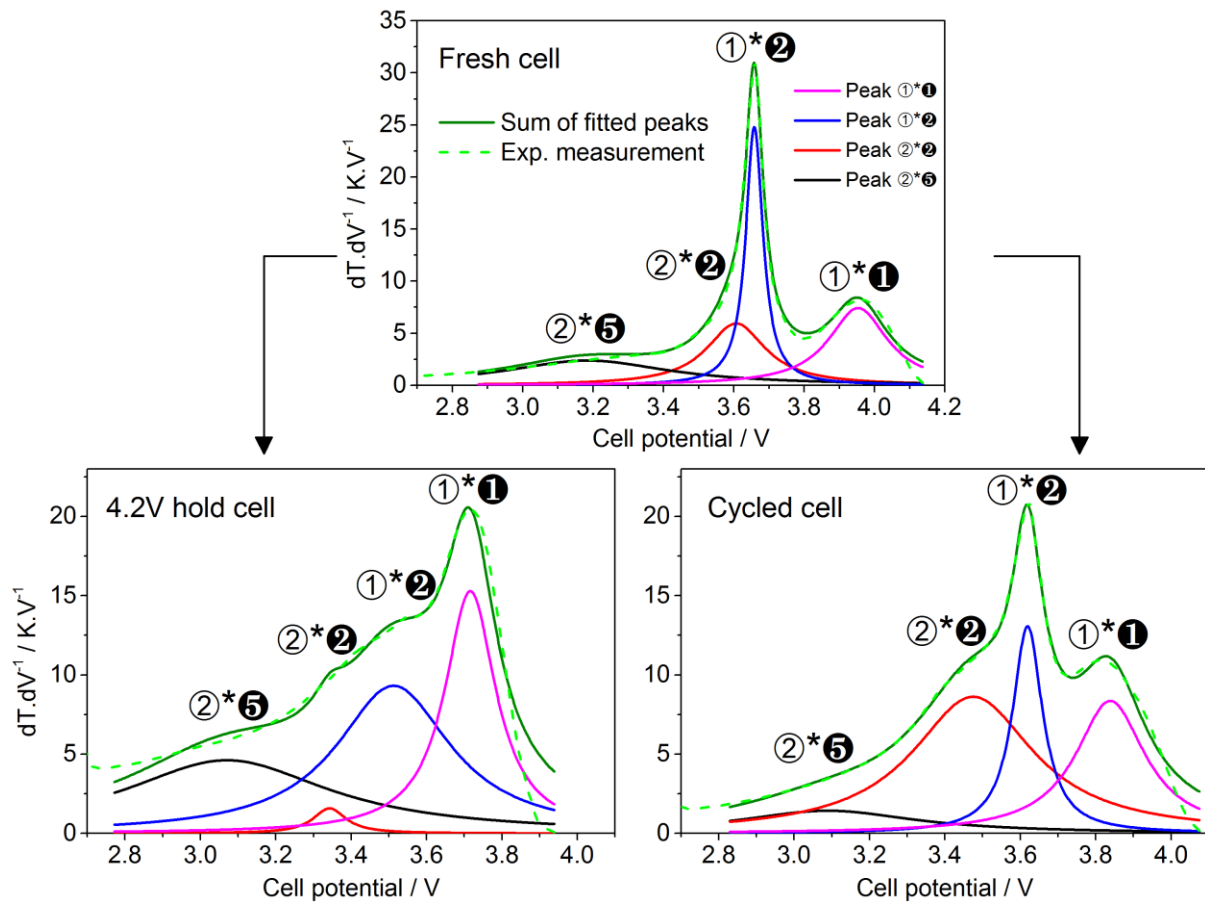


Figure 50. Peak fitting using MATLAB. DTV results for a fresh cell and aged 5Ah cells. Adapted from [9]. Refer to Table 6 and Table 7 for definition of peak numbering.

For DTV to be implemented in a BMS, this peak fitting algorithm is rather computationally intensive. It is to be noted that a simpler, less computationally intensive fitting method is developed and presented in later chapters.

Dubarry et al. [180] has shown that each peak in a dQ/dV curve represents a particular phase of the negative and positive electrodes combined. A peak is where there is a significant

temperature generation within a small voltage change. This suggests that each DTV peak represents a combination of the two electrode phases where only the lithium concentration is changing within the electrodes. When moving from a peak to another peak this is where there is a large voltage change within a short time. This represents the point where one of the electrode's structure goes under a rapid structural change shifting to a different standard electrode potential.

As presented in Table 6, Aurbach et al. [118] states that there are five stages of lithium intercalation where phase transitions occur in between (labelled in this paper as ① to ⑤):

Table 6. Lithium intercalation stages of graphite negative electrode. Adapted from [118].

①	LiC_6
②	$\text{Li}_{0.5}\text{C}_6$
③	$\text{Li}_{0.222}\text{C}_6$
④	$\text{Li}_{0.166}\text{C}_6$
⑤	$\text{Li}_{0.083}\text{C}_6$

Based on [209–211], there is a transition over two hexagonal phases for an NMC positive electrode below 4.2 V (labelled ① and ②). Despite the exact composition of the NMC electrode being unknown, assuming an equal mole ratio, the two hexagonal phases can be described as presented in Table 7.

Table 7. Hexagonal phases of a NCM positive electrode. Adapted from [211].

①	$\text{Li}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$
②	$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$

Following Dubarry's approach, each peak in DTV (and ICA) can be attributed to particular phases for the combined cell as illustrated in Figure 51. Peaks ②*③ and ②*④ are not shown/visible in the results. This is expected as the entropic heat generation of lithium

intercalation stages ③ and ④ are very small compared to the other stages [118]. Hence the two peaks are masked by the surrounding peaks and would require more precise measurements to be resolved.

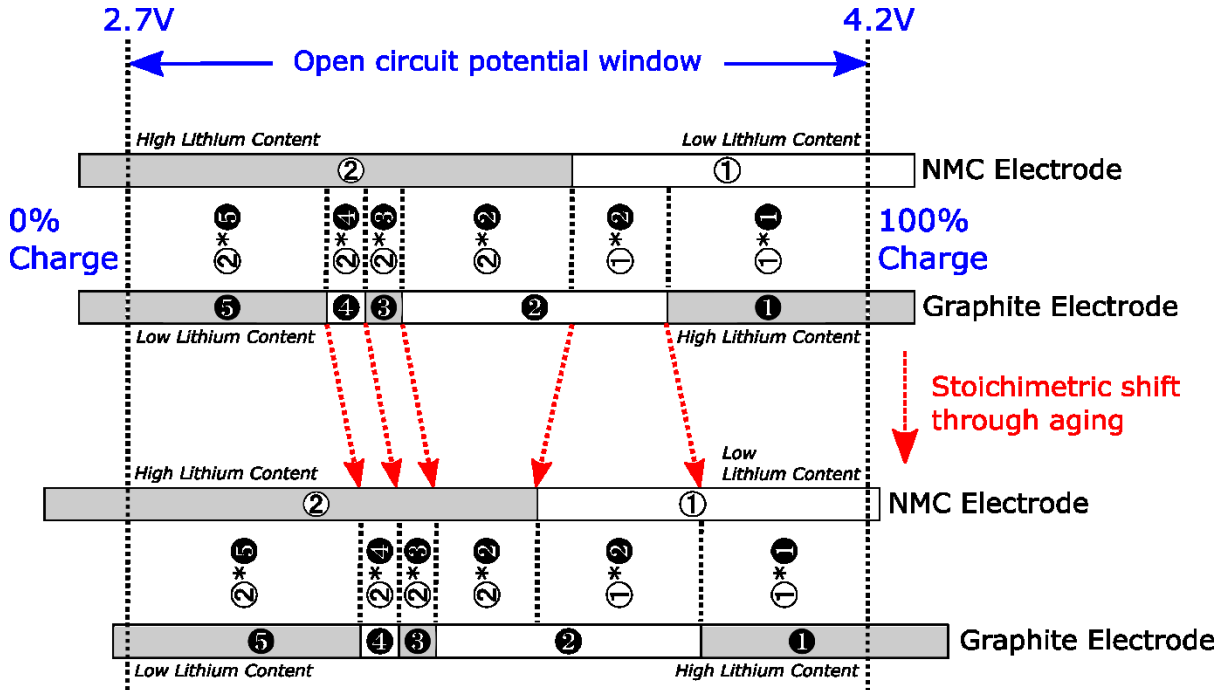


Figure 51. Schematic of combined phase transitions in graphitic carbon negative electrode and NMC positive electrode.

Figure modified from [29] with different positive electrode chemistry and addition of effect of stoichiometric drift through ageing. Adapted from [9].

The peaks with greatest change in the peak parameters are of particular interest to diagnose the degraded cells. In this case, this is peak ①*① and ①*②. It should be noted that peak ①*① is hardly distinguishable in either the SRCV or ICA techniques as it is masked by the peak next to it. Figure 52 describes the peak evolution of the two cells.

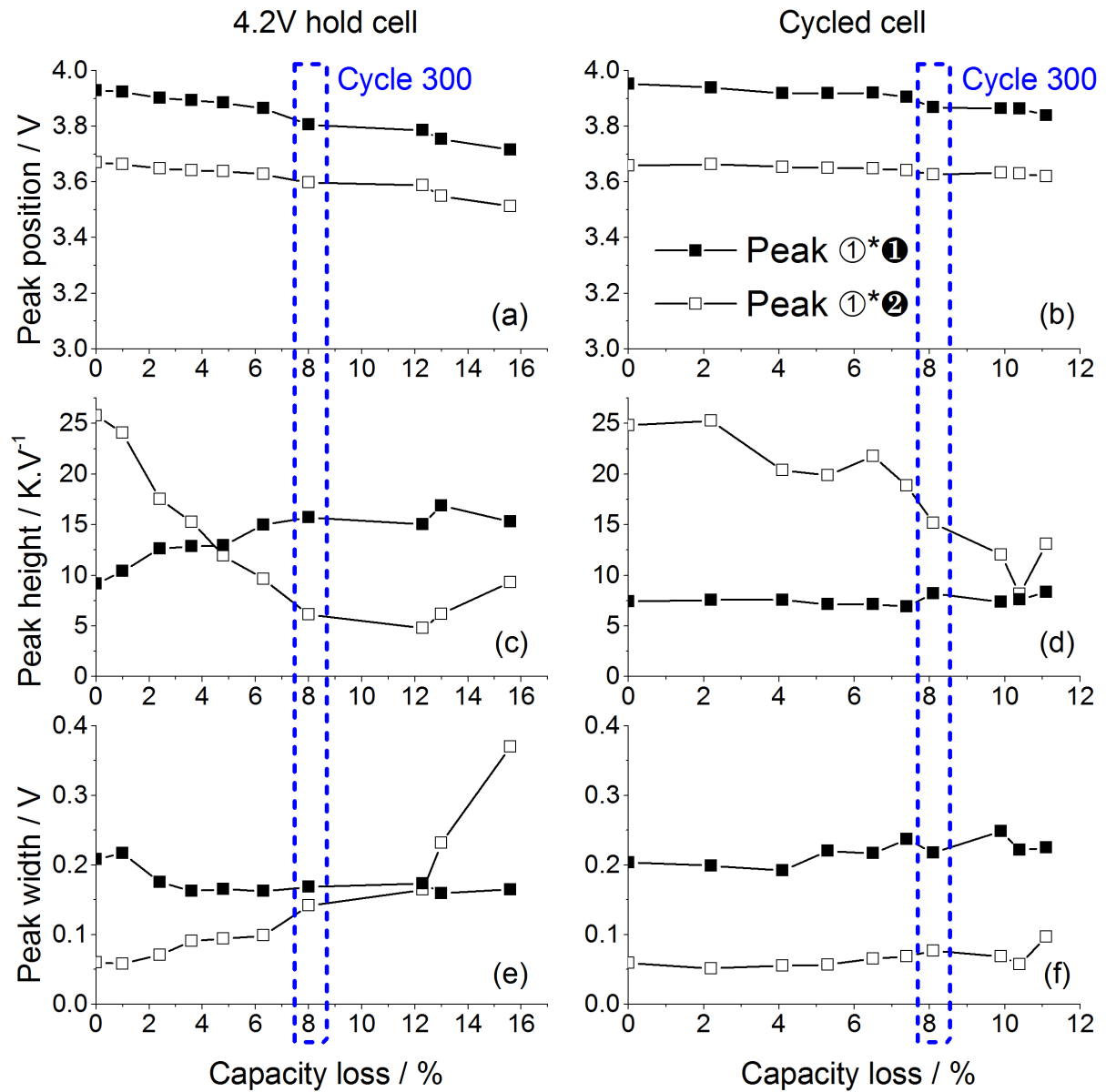


Figure 52. Peak parameter evolutions for the two cells stored at high temperature. Cell stored at high potential on the left. Cycled cell displayed on the right. Peak position (a-b), peak height (c-d) and peak width (e-f) are shown. Adapted from [9].

It is necessary to identify what these changes in the peak parameters represent in terms of battery SOH. Possible interpretations of various peak parameter changes:

- Changes in the peak position can be explained by increases in the overpotential of the cell caused by increasing impedance [212] as well as a shift in electrode stoichiometry (as illustrated in Figure 51 and effect described in 2.5.12). N.B. In Chapter 5, a new

complimentary method is presented which allows to decouple the overpotential from the stoichiometric drift.

- Increase in peak height can be from the increase in heat generation as a result of increased impedance.
- Decrease in peak height can be a result of the widening of the peak as the area under the peak is associated with the power capacity of the combined phases. This correlation comes from the fact that the area under a peak represents how much heat was generated in the combined phases and heat generation is associated with power. If the peak is initially negative (seen in results introduced in later chapters) approaching $dT/dV = 0$, this could also be a result of higher enthalpic heat generation due to increased impedance.
- Widening of a peak can be explained by the increased lithium concentration inhomogeneity within an electrode. For example, as the solid diffusion performance degrades, a greater lithium concentration gradient is generated in an electrode especially at higher current. This suggests that at a particular cell potential, the various electrode regions could be at different SOC hence widening the peak [18]. Additionally, it can be a result of stoichiometric drift as described in Figure 51.
- Narrowing of a peak is associated with stoichiometric drift as described in Figure 51 as well as an unbalanced loss of active materials between the two electrodes.

It is to be noted that the interpretation of DTV results is not limited to the points above and should be compared against the literature and/or other characterisation methods to validate a hypothesis.

Going back to cycle 300, the crucial part to note here is that DTV is able to quantitatively identify differences between the two cells (highlighted by the blue dashed boxes in Figure 52) which was not possible with the conventional method of capacity fade (~8%). DTV can now tell you that these two cells have aged differently and one cell, in this case the cell held at 4.2V, will

fail earlier than the other cell, which is a vital information. Based on this diagnosis, the BMS may make a decision to operate the cells differently to minimise the onset of accelerated degradation or warn the user to replace dangerous or failing cells.

3.5.5. COLLECTIVE DIAGNOSIS OF INDIVIDUAL CELLS

It is difficult, if not impossible, to come to a confident diagnosis about a cell's SOH with just one characterisation technique. As mentioned earlier, it is important to validate a hypothesis by collectively analysing the cell using results from various methods and/or literature. It should be reiterated that EIS, ICA and SRCV are mainly for lab-scale research and not typically suitable for on-board application due to their measurement requirement as described in the literature review. This suggests that capacity loss and DTV may be the only available information in a real-world application.

Cell Held at High Potential

As initially mentioned in section 3.5.1, the literature suggests a gradual SEI layer growth due to electrolyte decomposition. This is validated by the relatively slow capacity fade, SEI resistance increase from the EIS and shift in DTV peak positions.

As the cell degrades and consumes cyclable lithium, there will be a shift in electrode stoichiometry. The stoichiometric drift in the electrode narrows the real safe operating potential in comparison to the safe operating potential recommended by the manufacturers [213]. As the negative electrode stoichiometry shifts to lower lithium content, the positive electrode becomes increasingly overcharged at 4.2V [157] (despite the cell being at the higher limit of the recommended operating voltage) promoting cathode material decomposition and metal dissolution [214,215]. This will in turn cause more stoichiometric drift generating a positive feedback of accelerating degradation which highlights the necessity of an early identification of such processes occurring. The accelerating rate of degradation is seen by the capacity loss however this observation is not possible to identify more details from capacity loss alone. EIS suggests cathode degradation by the increasing charge transfer resistance at higher

cell voltage. Finally, DTV validates the hypothesis of a continuous stoichiometric drift by the evolution of its peak width. Referring to Figure 51 and Figure 52, the increase in width of peak ①*② and decrease in peak ①*① is a characteristic of the misbalancing of electrode stoichiometry.

This is then expected to lead to accelerating SEI layer growth due to metal deposition on the negative electrode as also seen from the capacity loss and EIS results [90,216]. This is also reflected in the DTV results by the increase in height of peak ①*① i.e. increasing rate of heat generation during the (de)intercalation stages at high cell potential due to the increased impedance. Note how the peak ①*② height eventually also begins to rise as the positive-electrode impedance increases.

Cycled Cell

As initially mentioned in section 3.5.1, the literature suggests a rapid SEI layer growth due to cycling which saturates over time. This phenomenon is observed by the capacity loss as well as the SEI resistance change from EIS. DTV results validates a gradual increase in impedance from the peak positions. This supports the hypothesis that the degradation process slows down as SEI grows thicker [202].

As the cell is continuously cycled (and the cathode does not spend much time at a high potential), a slower stoichiometric drift is expected. The flat charge transfer resistance at higher cell potential suggests this is true. Finally, DTV is able to validate that there is negligible stoichiometric drift as the peak width remain almost unchanged. This also suggests that the concentration gradient inside the electrodes hence diffusion properties at these cell potential windows also undergo little degradation to this point.

3.6. RESULTS AND DISCUSSION PART 2: SCREENING OF 25Ah CELLS OF UNKNOWN HISTORY

Using the results obtained from the 5Ah data, another cell with unknown degradation history was examined to validate the application of DTV as a screening tool for 2nd life batteries. A fresh and aged 25Ah lithium-ion cell with the same cell chemistry and manufacturer as the 5Ah cells were used. Please refer to appendix entry A3 for detailed technical specification of the 25Ah cell.

The capacity fade of the aged cell was first determined as presented in Figure 53. A 0.8 C slow CC discharge (20 A) has shown a 35.6% capacity fade compared to the fresh cell, and a significant rise in overpotential.

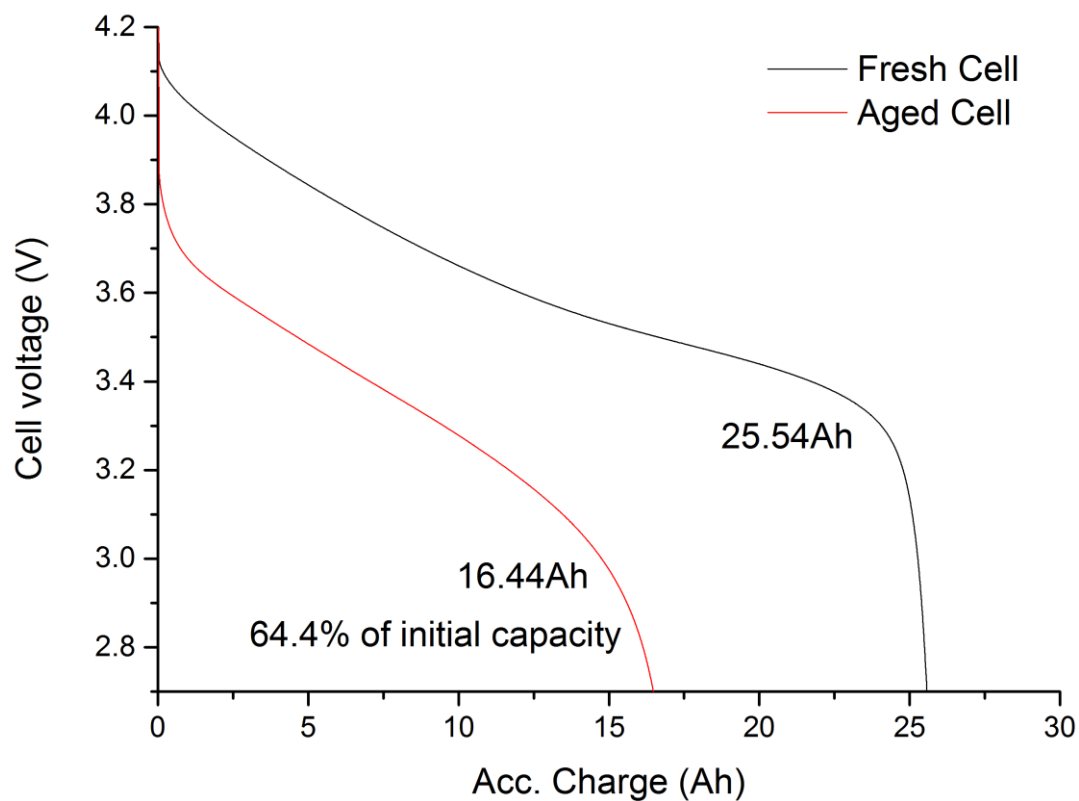


Figure 53. 0.8C constant current discharge voltage curves.

DTV at 1 C was carried out while monitoring the cell surface temperature with a thermal imaging camera, FLIR, as presented in Figure 54. The 25Ah cell was ideal for this test due to its

large imaging surface area. Figure 55 shows the DTV results for the fresh and aged cell with decoupled peaks.

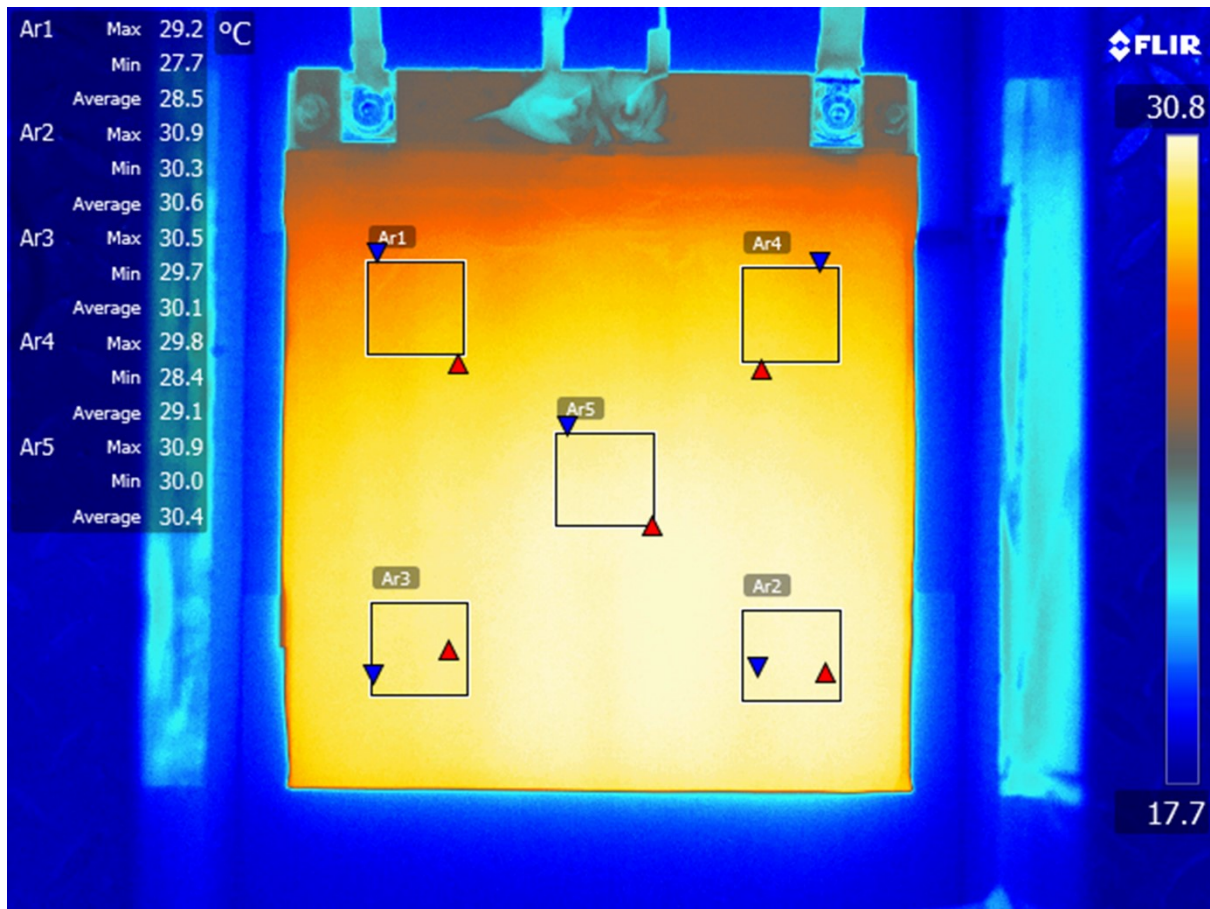


Figure 54. Thermal imaging of 25Ah NCM cell under 1C discharge for DTV analysis. Various regions of the cell surface were analysed separately to check for spatial degradation distribution.

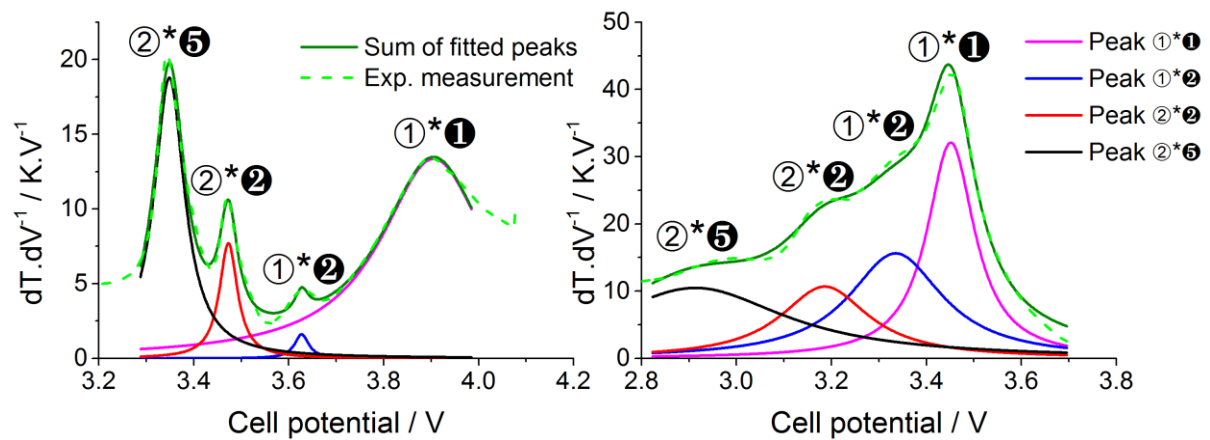


Figure 55. DTV results for 25Ah fresh cell (left) and aged cell (right). Adapted from [9].

The DTV results were checked for different locations on the cell surface however there were no significant differences in the results in this case. Therefore, either the cell was uniformly degraded spatially, or the DTV technique with a thermal imaging camera may not be suitable for detecting all types of spatially unequal degradation. DTV peak heights were smaller towards the cell tabs due to passive cell tab cooling and also smaller on the negative electrode side as the copper current collector is a better thermal conductor than aluminium on the positive electrode side.

The results suggest that the DTV spectrum for the aged cell has a striking resemblance to that of the 5Ah cell held at high potential (Figure 50). Both cells show 4 distinct peaks. The “fresh cell” DTV curve does not look similar to the 5Ah fresh cell however this is expected as the storage condition and time prior to experiment was unknown.

The peaks can be decoupled and quantified using the same MATLAB method and the peak change can be calculated. Focusing on the same two peaks again for comparison with the 5Ah data, Figure 56 shows the peak parameters for the fresh and aged cell.

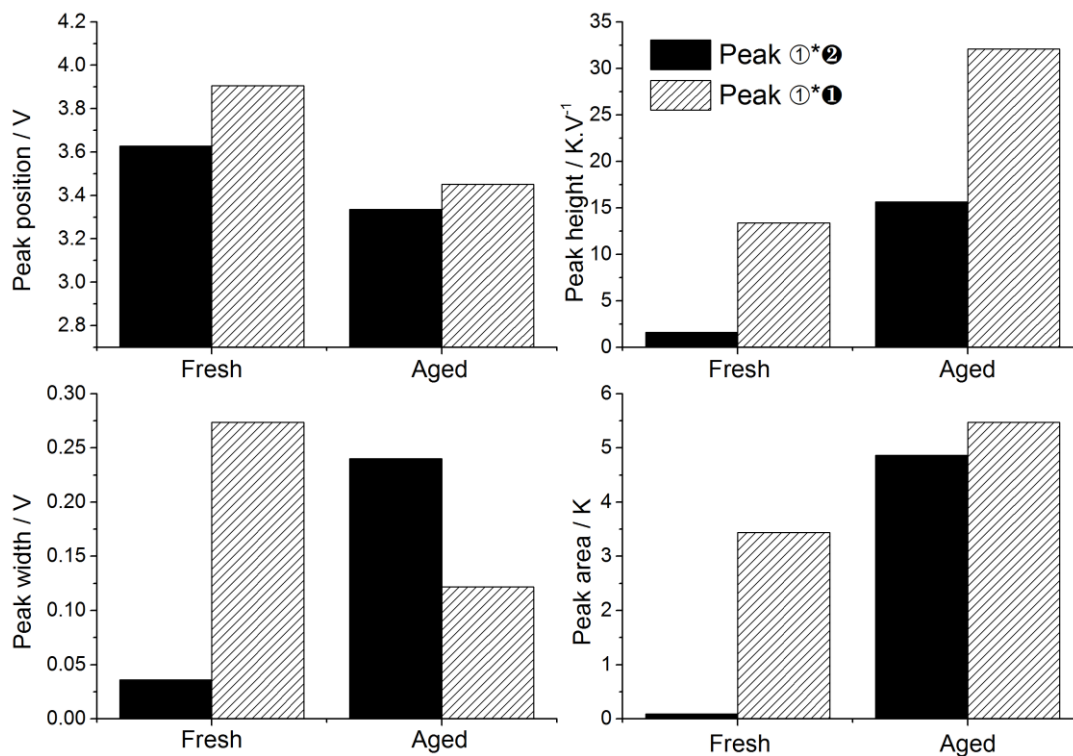


Figure 56. Peak parameters for fresh and aged 25Ah cell. Adapted from [9].

Peak positions dramatically shift to lower potentials. This gives information on the significant rise of the cell impedance. At this point, this power fade could be a result of combination of various degradation mechanisms and it is hard to pinpoint a dominating mode.

Focusing on peak width, peak ①*① has decreased and peak ①*② has increased. The change is so significant that peak ①*② has become wider than peak ①*①. This is the same observation as for the 5Ah cell held at high potential and infers the existence of major electrode stoichiometric drift. From this result, it can be hypothesised that the impedance rise seen through peak position is likely to be due to severe SEI layer growth.

For peak height, both see significant increases where peak ①*① has a greater change. This can be explained by the increased impedance at higher cell potentials due to the increase in charge transfer resistance at such voltage region which is characteristic of a stoichiometric drift. The profile of this impedance rise suggests high heat generation, i.e. peak height, for peak ①*① and less for peak ①*② which matches the result suggesting significant degradation at the positive electrode.

Having analysed the DTV peaks quantitatively, it can be interpreted that the 25 Ah aged cell has reached a similar state as the 5 Ah cell held at high potential. Through individual peak parameter observation, it can be estimated that there is a substantial electrode stoichiometric drift through SEI layer growth and significant degradation at the positive electrode. It is difficult to predict the operational history from 2 data sets. However regardless of how it was aged it is possible to suggest unequivocally using the DTV diagnostic technique that the performance of the aged cell is limited mostly by the positive electrode and therefore should not be charged up to 4.2V any longer.

3.7. INTERIM CONCLUSION

DTV method has been demonstrated to be useful in diagnosing the SOH of a lithium ion battery with far more fidelity than common capacity fade measurements, using cost-effective thermocouples under natural convection on a lab bench environment.

The method has been presented in this paper as a battery diagnosis method to compliment SRCV and ICA. It is faster than SRCV and provides similar results as ICA but with the additional thermal behaviour. DTV is also simple to compute unlike parameterising an equivalent circuit model from EIS data. The use of a thermal imaging camera was also demonstrated.

Three cells (graphitic carbon negative electrode - NCM positive electrode) were placed under different accelerated ageing experiments including high temperature, cycling and high potential hold. The cells were analysed regularly to track specific degradation modes. DTV peaks, representing (de)intercalation stages of lithium in both electrodes, were decoupled using MATLAB to quantitatively analyse the peak evolutions over various stages of capacity loss.

DTV quantitatively identified the difference between the aged cells where it was not possible to tell by the industrial standard method of looking at the capacity fade alone. DTV was able to support in-depth hypotheses for the SOH of the degraded cells collectively with the other mentioned methods.

The DTV information obtained from the controlled degradation experiment was then applied to an aged cell of unknown history. DTV was able to present a diagnosis for the cell no longer relying on collective information from other methods and demonstrated as a screening tool for 2nd life batteries. Spatial differences in degradation were investigated, however, none were observed suggesting either they did not occur or the technique could not detect them.

Chapter 4. PACK APPLICATION, DHFV AND PROGNOSIS

4.1. INTRODUCTION

DTV was presented as a suitable diagnosis method for use in real-world applications, however the previous validation experiments were all carried out on individual cells under natural convection thermal boundary conditions. In high power applications, such as in electric vehicles, the cells would be connected in a pack with a thermal management system to maintain the cells at safe operating temperature. In addition, the NCM experiment was only validated for constant current discharge which meant that the diagnosis required a dedicated discharge cycle, which is uncommon in many applications.

In this chapter, DTV experiments have been carried out on a battery pack made from four commercial lithium polymer cells in parallel placed under forced air surface cooling to emulate an electric vehicle application. One cell was deliberately aged prior to the experiments to demonstrate how the technique could diagnose unequal degradation. The test was performed at both constant current charge and discharge to demonstrate its use under charging conditions. The technique could be particularly useful under charge when constant current or constant power is common, this therefore should be of significant interest to all lithium-ion battery users.

Differential heat flux voltammetry (DHFV), or dHF/dV , is also introduced as a complementary method when dT/dt is too small to measure accurately under strong cooling conditions.

Measurements are achieved using low-cost thermocouples and a single voltage measurement at a frequency of 1Hz, demonstrating the feasibility of implementing this approach on real world battery management systems.

Lastly, this chapter presents a research collaboration work with an industry partner where the prognosis capability of the DTV technique was validated and implemented in a commercial BMS for the first time. Provided with data from a high-power battery pack used in a motorsport

application, the aim was to predict the cell which had failed from charge data several drive cycles before the actual failure.

4.2. RESEARCH QUESTIONS

In this series of experiments, the aim is to answer the key research questions for DTV development:

- Can DTV be upscaled to pack application?
- Can DTV be used for predicting future battery failures?

This work package also aims to address the following sub-questions:

- Can DTV provide similar, if not more, information as ICA in a pack environment?
- How is the power distributed in a parallel pack of cells with unequal SOH?
- Does an aged cell in a parallel pack lower the performance of other healthier cells?
- Does DTV work under *quasi*-constant current application, for example, in a parallel pack with unequal current distribution?
- Does DTV work under charge for NCM cells?
- Does DTV work for slower C-rates? ($<1C$)
- Can heat flux be used instead of temperature to infer the same information?
- Can DTV be implemented in a commercial BMS?

4.3. METHODS

4.3.1. BATTERY TESTING

The experiment was performed using a battery pack made from four commercial 5Ah lithium-polymer pouch cells connected in parallel. The same product model from Chapter 3 was used (Dow Kokam, model SLPB11543140H5) where each cell consists of a carbon graphite negative electrode and a NCM positive electrode. Please refer to appendix entry A1 for technical details and specifications provided by the manufacturer.

Heat flux sensors with K-type thermocouples (OMEGA HFS-4) were placed on the surface at the centre of the cells. Shunt resistors (RS 810-3273 rated at 0.5 m Ω) were placed in series with each cell to measure the current across every individual cell. It should be noted, that current measurements were taken in order to compare the DTV technique to ICA and to understand how the current is distributed to cells in parallel, but the current measurement is not required for, and was not used for the DTV calculation. One deliberately aged cell and three fresh cells were placed together in the pack to determine whether the diagnosis methods could correctly determine the SOH of the individual cells. The aged cell was previously stored at 55°C at 4.2V for approximately 15 days. The characteristics of this cell can be estimated to be similar to the aged cell held at high potential analysed in section 3.5.5 which is the same product model aged in the same condition. The pack was prepared in a way to minimise differences in external resistance such as equal cable lengths, fastening torque (8 Nm) and cleaned contact surfaces. Larger cables were used to handle the higher currents.

During the experiments, the pack was placed inside an incubator (Binder KB-23) with forced air convection flowing over the cell surfaces (as illustrated in Figure 57) while keeping the incubator door open to emulate a surface cooling system to recreate real conditions such as those in electric vehicles. A Maccor Battery Tester series 4000 was used for measurements and loading during pack experiments whereas a Bio-Logic BCS-815 was used for individual cell experiments. Pico TC-08 was used for heat flux sensor measurements and Yokogawa MX100 for shunt resistor measurements. A photo of the pack is presented in Figure 58.

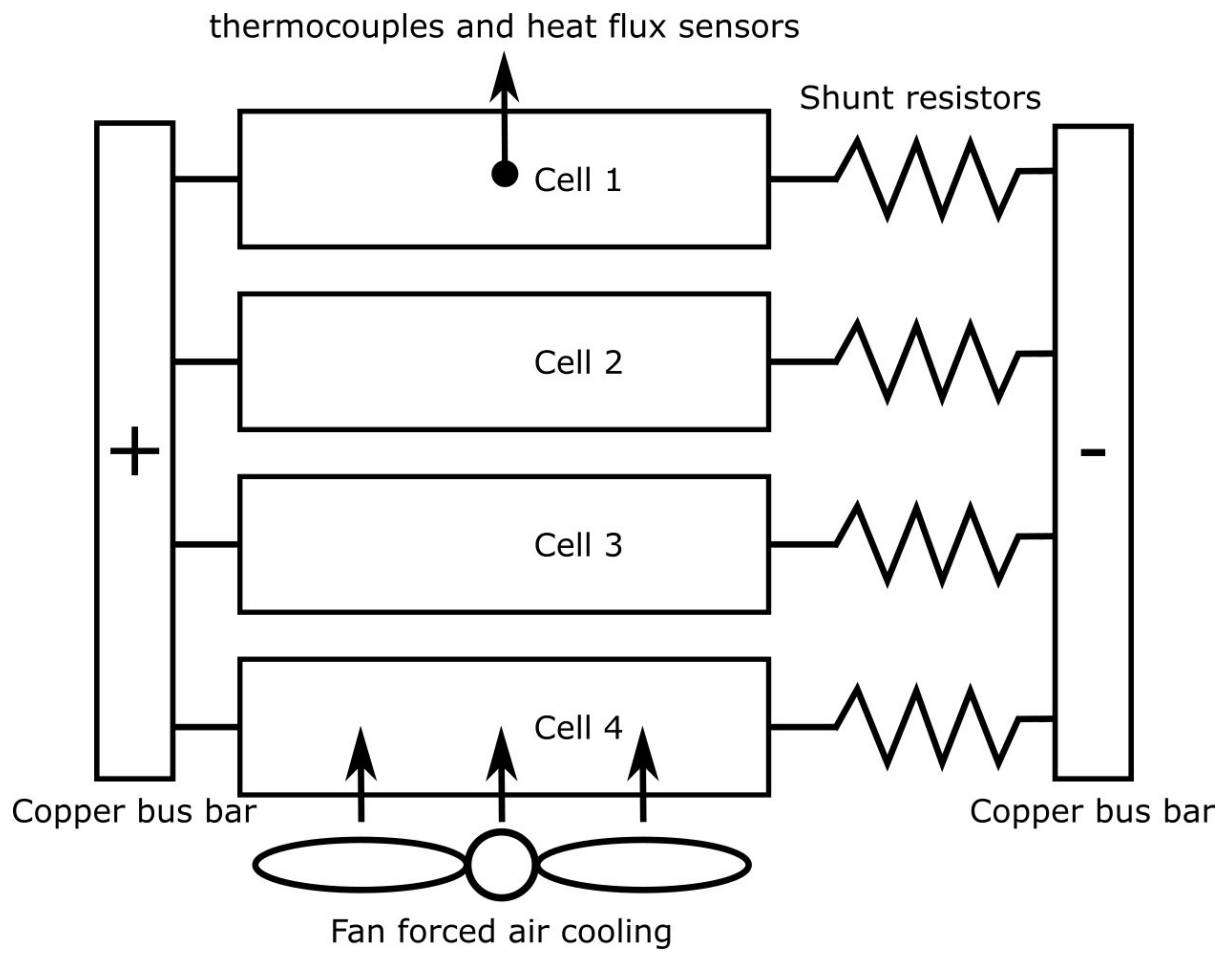


Figure 57. Experimental pack diagram. Source: [10].

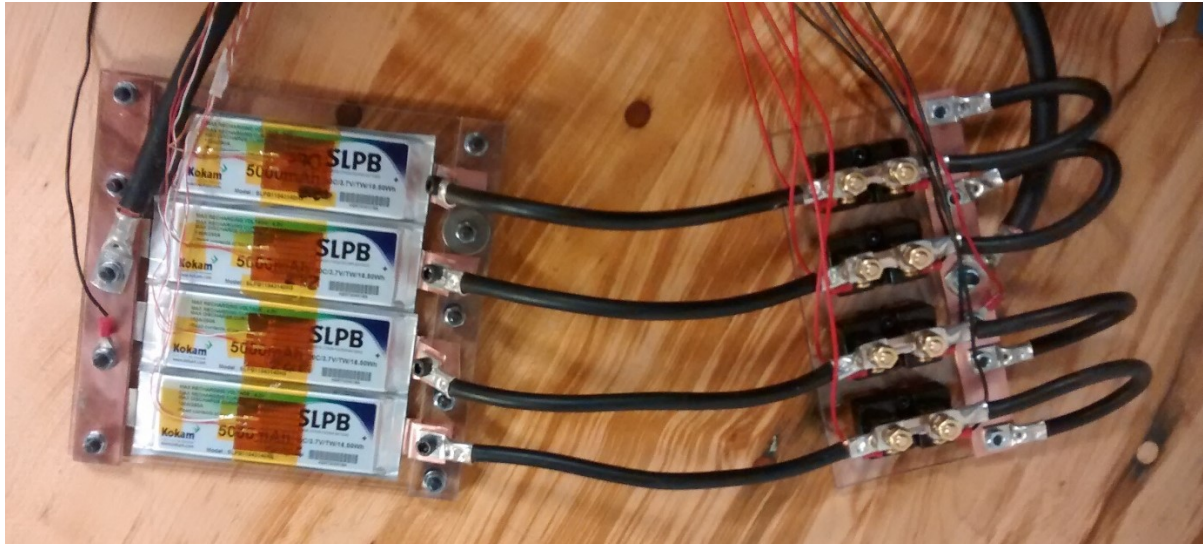


Figure 58. Experimental pack photo. The orange square patch on each cell surface is the heat flux sensor with an embedded thermocouple. The block on the right consists of the four shunt resistors.

The pack experiment was carried out at 2C constant current charge and discharge to diagnose the individual cells simultaneously in the pack using DTV, DHFV and ICA. The same experiment was repeated for 0.5C to demonstrate the use of the technique under both fast and slow charging/discharging conditions. The 0.5C results are attached in the appendix entry A4 effectively demonstrating the same results as 2C. Then the cells were individually characterised through constant current discharges at 2C to determine their SOH through capacity fade.

Detailed condition of test is described in Table 8.

Table 8. Pack experiment details. Adapted from [10].

	Loading condition	Cut-off voltage	Initial condition
Pack discharge	2C constant current	2.7V	CCCV charging at 1C to 4.2V until $I < 0.25A$ followed by 1h rest
Pack charge	2C constant current	4.2V	CCCV discharging at 1C to 2.7V until $I > -0.25A$ followed by 1h rest
Cell discharges	2C constant current	2.7V	CCCV charging at 1C to 4.2V until $I < 0.1A$ followed by 1h rest

4.3.2. DATA PROCESSING

Depending on the noise of data acquisition, it is necessary to smooth the raw data before evaluation. In this experiment, a repeated moving average was used to smooth the temperature or heat flux data. The smoothing method was revised since the work presented in 3.4.2 (using a combination of moving average and Savitsky-Golay filter) as this new method proved to be more stable for increasing the signal-to-noise ratio while maintaining the original curve characteristics.

A study was carried out to determine the optimum smoothing span. When the data span used for the moving average is too small, the results are too noisy to determine the features. It is also important to avoid over-smoothing as this loses the original characteristics of the curve. Figure 59 illustrates the effect of smoothing the temperature data on the final DTV curve. 0.25%, 0.50%, and 1.00% are mentioned here as examples of various data span percentages used during the moving average smoothing. If the data consists of 5000 data points and a 1.00% span is used, the moving average will use 50 points surrounding a point to compute its smoothed value. Table 9 summarises the dependence of smoothing span on DTV analysis such as peak position, width, and height. It can be seen from the figure alone that the smoothed temperature curve is starting to diverge from its raw measurement at 1.00% span. On the other hand, 0.25% remains noisy and returns too many peaks which are likely to be artefacts arising from low signal-to-noise ratio.

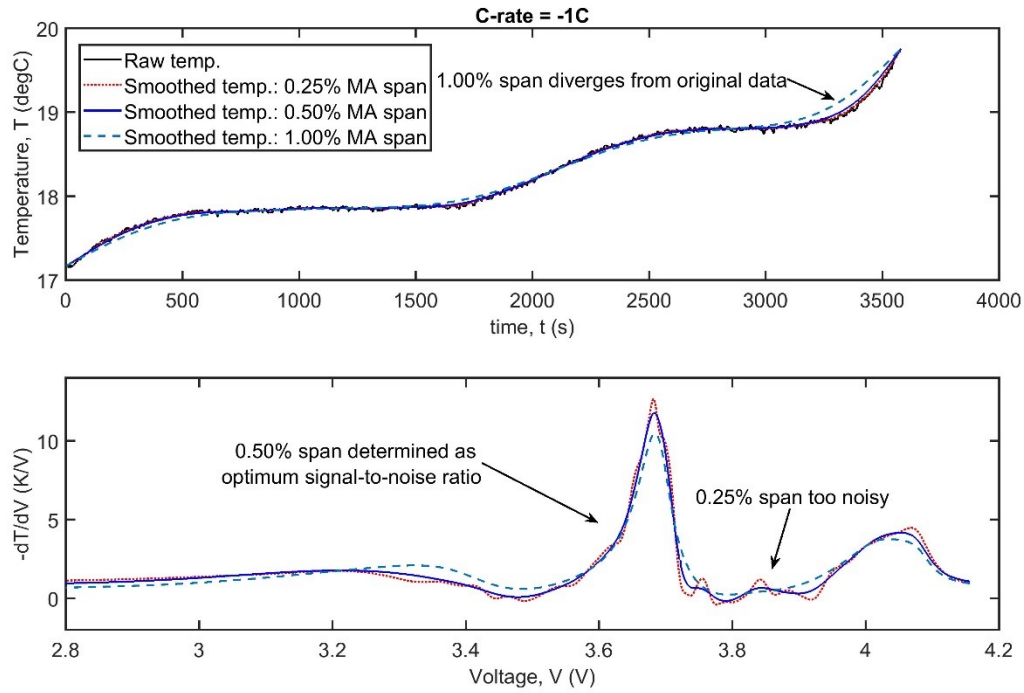


Figure 59. Effect of smoothing temperature data with various moving average span on DTV curve.

Table 9. Effect of smoothing temperature data with different moving average span on DTV peak analysis.

Moving average span	Median of absolute deviation	Peak ①*① position	Peak ①*① width	Peak ①*① height	Peak ①*② position	Peak ①*② width	Peak ①*② height
%	%	V	V	K/V	V	V	K/V
0.25	0.06	4.068	0.134	4.483	3.682	0.064	12.659
0.50	0.08	4.052	0.139	4.176	3.683	0.063	11.782
1.00	0.18	4.034	0.152	3.760	3.684	0.066	10.480

In order to capture the results with the optimum signal-to-noise ratio, the median of the absolute deviation was kept below 0.1% for temperature and 7.5% for heat flux. As changing the smoothing parameters can have an effect on peak analysis, the smoothing conditions were kept identical for the 4 cells for a particular loading (charge or discharge) and diagnosis (DTV or DHFV). Peak fitting errors were kept to a maximum of 3.3%.

4.3.3. DIFFERENTIAL HEAT FLUX VOLTAMMETRY

DHFV is introduced as a complimentary technique to the usual DTV to achieve a similar information about the battery SOH. DTV infers information from the change in the surface

temperature and voltage of cell. With the use of an active cooling system to emulate real battery packs in application, it may be possible that this change in temperature would be too small to obtain a good signal-to-noise ratio especially under strong cooling. The alternative method here is to use heat flux instead of temperature. As heat flux (HF) is the rate of heat flow through a surface per unit time as described by Fourier's law:

$$HF = \dot{q}_x'' = -k \frac{dT(x)}{dx} \quad (14)$$

Where $T(x)$ is the temperature profile in a material and k is its thermal conductivity. This suggests that heat flux can be used in place of temperature to obtain the same information of heat generation of the cell.

DHFV is derived in the manner as DTV as follows:

$$DHFV = \frac{d\dot{q}_x''}{dt} \bigg/ \frac{dV}{dt} = \frac{d\dot{q}_x''}{dV} \quad (15)$$

The advantage of this technique is that it can be used when dT is difficult to measure due to strong cooling. The obvious disadvantage is however cost as a heat flux sensor costs roughly a hundred times more than a thermocouple (few hundred GBP vs. few GBP).

4.4. RESULTS

Figure 60 shows pack experimental results for 2C (40A) discharge. In an ideal battery pack, each cell is expected to provide 10A. However, Figure 60a shows that the current paths between the four cells are heterogeneous. The three fresh cells have relatively similar current profile whereas the aged cell performs very differently. This aged cell initially contributes less power from the pack due to its higher impedance hence overpotential. As the pack is further discharged and the charge transfer and diffusion resistances increase in the fresh cells, the aged cell now has a lower impedance and begins to contribute more of the pack power. The aged cell current peaks at 2.86C (14.3A). Operating at higher currents accelerates degradation

mechanisms such as lithium plating on charge and electrolyte decomposition by higher heat generation [90,213]. Hence it is crucial for a battery management system to be able to correctly identify unhealthy cells to be replaced at an early stage.

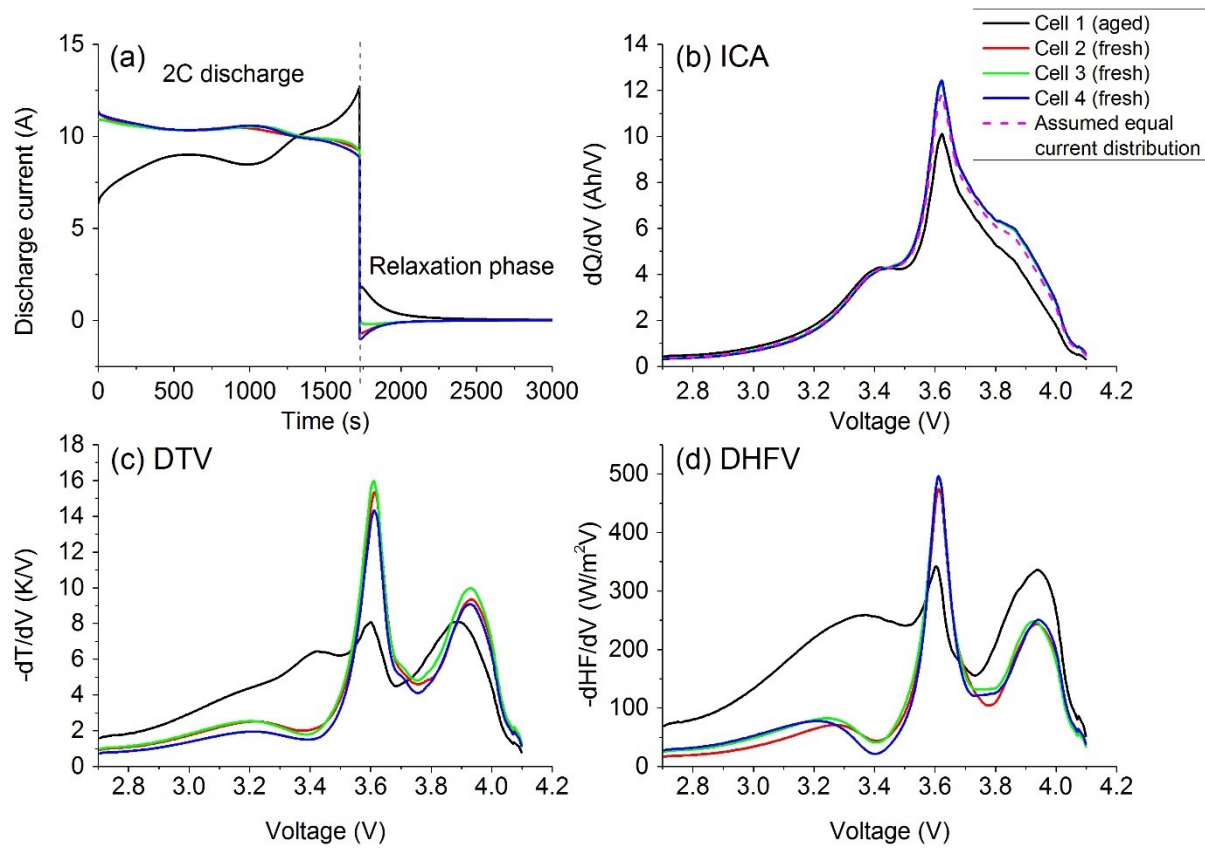


Figure 60. Pack analysis under 2C constant current discharge. (a) Cell current. (b) Incremental capacity method. (c) Differential thermal voltammetry. (d) Differential heat flux voltammetry. Source: [10].

This heterogeneous current distribution, where certain cells are loaded at a higher current than otherwise split equally at a particular stage of the pack discharge, is analogous to the performance of a cell with a thermal gradient between its layers. Hunt et al. [97] carried out an accelerated aging experiment comparing two types of thermal gradients inside a layered pouch cell to see if one gradient was more detrimental to the cell's health than the other. The two thermal gradients explored were across layer surface and through the layers. The two gradients were generated using tab cooling and surface cooling respectively as illustrated in Figure 61.

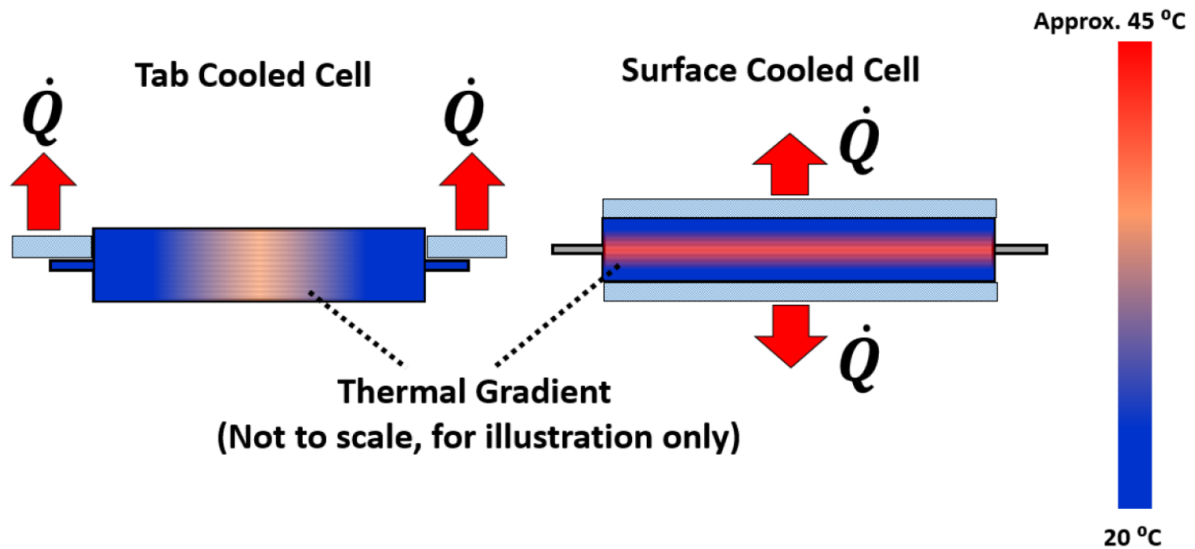


Figure 61. Thermal gradient across the layer surface generated by tab cooling (left); and thermal gradient through the layers generated by surface cooling (right). Source: [97].

The finding from this work was that surface cooling, i.e. thermal gradient through the layers, significantly accelerated the power fade of the cell relative to tab cooling. In the tab cooled cell, each layer essentially behaves the same electrochemically as the thermal gradient is across the surface. Whereas in the surface cooled cell, the layers near the surface are cool and the middle layer is hot. As impedance is a direct function of temperature, the hottest layer in the middle has the lowest impedance hence is initially loaded at a higher current than the other layers. As the layer is discharged and its impedance increases, the adjacent layers with now the lowest impedance will have a higher current. Thus, there is a domino effect where each layer inside the cell peaks at a higher current than if split equally at different stages of the cell discharge accelerating its degradation.

Figure 60a also shows internal current during relaxation. At the end of discharge, the cells were at different OCVs and therefore after removal of load the aged cell recharges the fresh cells for an appreciable length of time. This further loads the cells and over time can get worse and could lead to additional degradation. It was shown in previous work that for a noisy load, this redistribution effect can be continuous and significant, leading to the net current throughput

through the cells being significantly higher than otherwise [217], which again could lead to additional degradation.

In Figure 60b, the ICA plot, calculated by dQ/dV , shows a small difference between the aged and the fresh cells as the different current profiles result in different dQ terms. The critical part to note here is that in a parallel pack, the cells have the same voltages and, as discussed earlier, current measurement per cell is too costly in real application especially for packs with a number of parallel strings. This suggests that the BMS is left with no choice but to assume equal current distribution hence all the cells would have the same “ dQ/dV ” result as demonstrated by the pink dashed line in Figure 60b. This means that ICA cannot identify the aged cell in a parallel pack highlighting the need for an alternative diagnosis method.

Figure 60c and Figure 60d show DTV and DHFV results respectively. The notable differences can be immediately observed between the aged cell and the fresh cells.

The peak in the dT/dV , or the plateau in the voltage curve, represents a combination of different contributions from the positive and the negative electrode phase. It corresponds to a region where an electrode phase is not changing, but the concentration of lithium in that phase is increasing or decreasing [182,218]. Then, at some critical concentration the lattice structure of the material becomes unstable, and the material undergoes a phase change to a new lattice structure which is more stable at the given concentration of lithium. At this point the voltage shifts dramatically, and hence the phase change is associated with moving from one peak to another.

Peak fitting analysis of the results are carried out using peakfit.m script [207] in MATLAB where the differences in the peak parameters such as the peak position and width can give information on the cell's state-of-health [9,170]. Figure 62a and Figure 62b demonstrate example peak fittings of DTV curves where each peak has been labelled accordingly for a combination of NCM electrode phase (①-②) [209–211] and a graphitic carbon phase (①-⑤) [219]. The schematic

above the plot illustrates this concept of combined electrode phases corresponding to regions of voltage plateaus, and hence peaks in the dT/dV measurement.

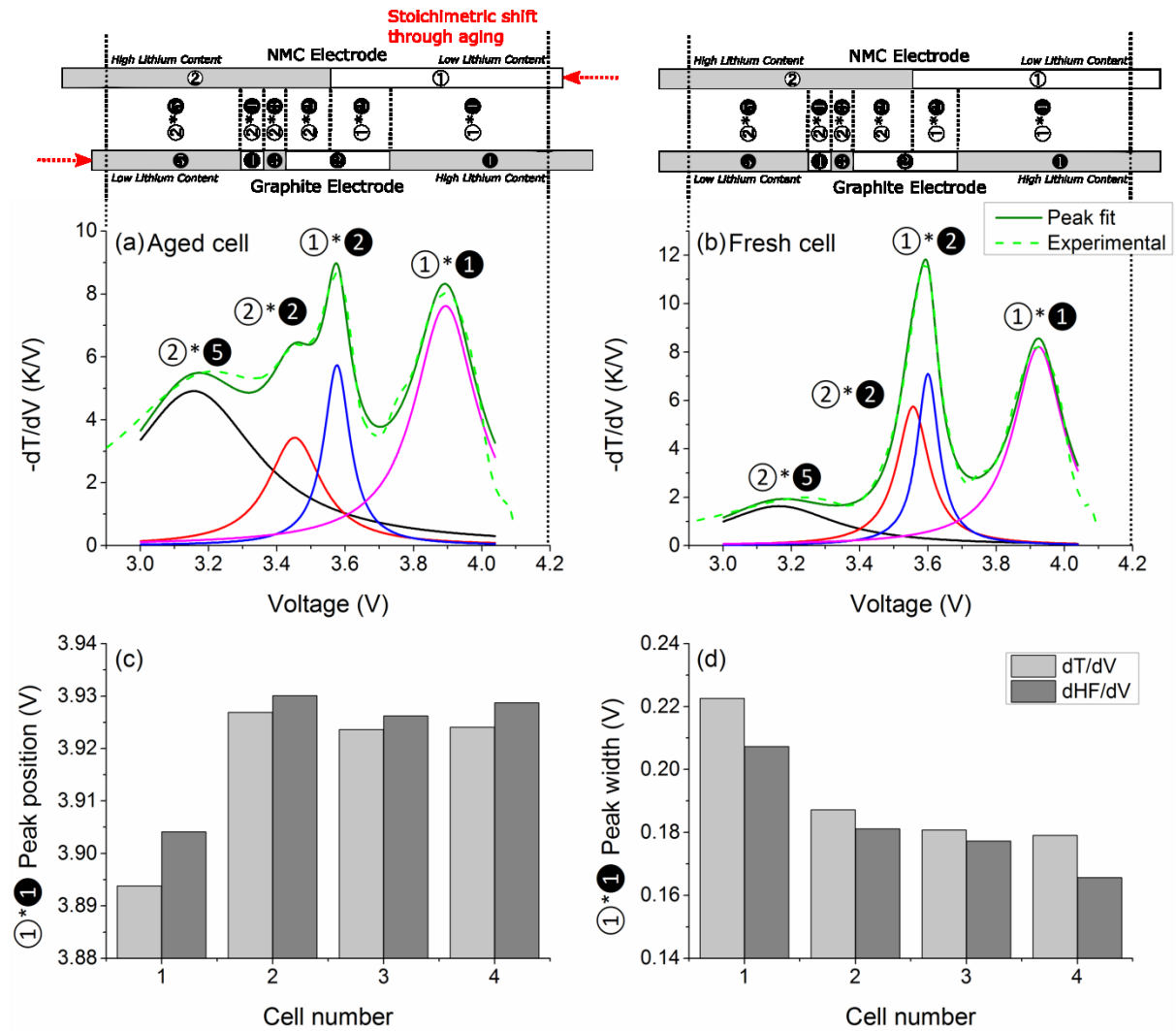


Figure 62. Peak fitting of differential thermal and heat flux voltammetry results for 2C constant current discharge. Example peak fittings for cell 1 (a) and cell 4 (b). Schematics of combined phases are shown above. Schematic modified from [180]. Peak position (c) and peak width (d). Source: [10].

It can be seen in Figure 62c and Figure 62d that the aged cell has a lower $\textcircled{1}^* \textcircled{1}$ peak potential and a wider peak width than the fresh cells for both DTV and DHFV. Peak width is taken as the width of the peak at its half height. As illustrated above Figure 62a, degradation in the cell can result in stoichiometric drift which will change the peak parameters such as position and width.

Using this method, it is possible to quantitatively diagnose the cell SOH and determine that cell 1 has significantly aged compared to the remaining fresh cells.

It can also be confirmed from this diagnosis that, if necessary, it is sufficient to analyse only peak ①*①, which is the first peak during discharge at approximately 3.9V. In Figure 62a and Figure 62b, it is observed that there is minimal overlap of the peaks above 3.8V. This suggests that DTV does not need to be carried out through the entire potential range of the cell which will further reduce the time of diagnosis i.e. it may be sufficient to discharge from 4.2V to 3.8V to identify the aged cell.

In practice if the peak position of a particular cell is significantly shifted to a lower potential and/or the peak width is wider than the rest of the cells in a pack, it can be assumed that the pack has unequal current distribution.

In many real applications, such as in EVs, it would be much more practical to be able to conduct the diagnosis under a constant current charge. This would enable the diagnosis to be carried out when the EV is left to charge and no dedicated charging or discharging profile is required.

Figure 63 shows results for a 2C (40A) charge, typical charging rates for a fast charge for an electric vehicle. The resulting curves look different from discharge results due to the differences in power performance and entropic heat generation. However, the aged cell can still be identified for both DTV and DHFV. The negative peak in Figure 63c and Figure 63d appears from the negative dT/dt when the heat transfer from cooling dominates over the enthalpic and entropic heat generation, and where the entropic heat generation term likely became close to zero or even negative. This happens as a reversible exothermic reaction become endothermic in its reverse reaction. That is to say heat generation during discharge is heat absorbing during charge for such entropic reactions.

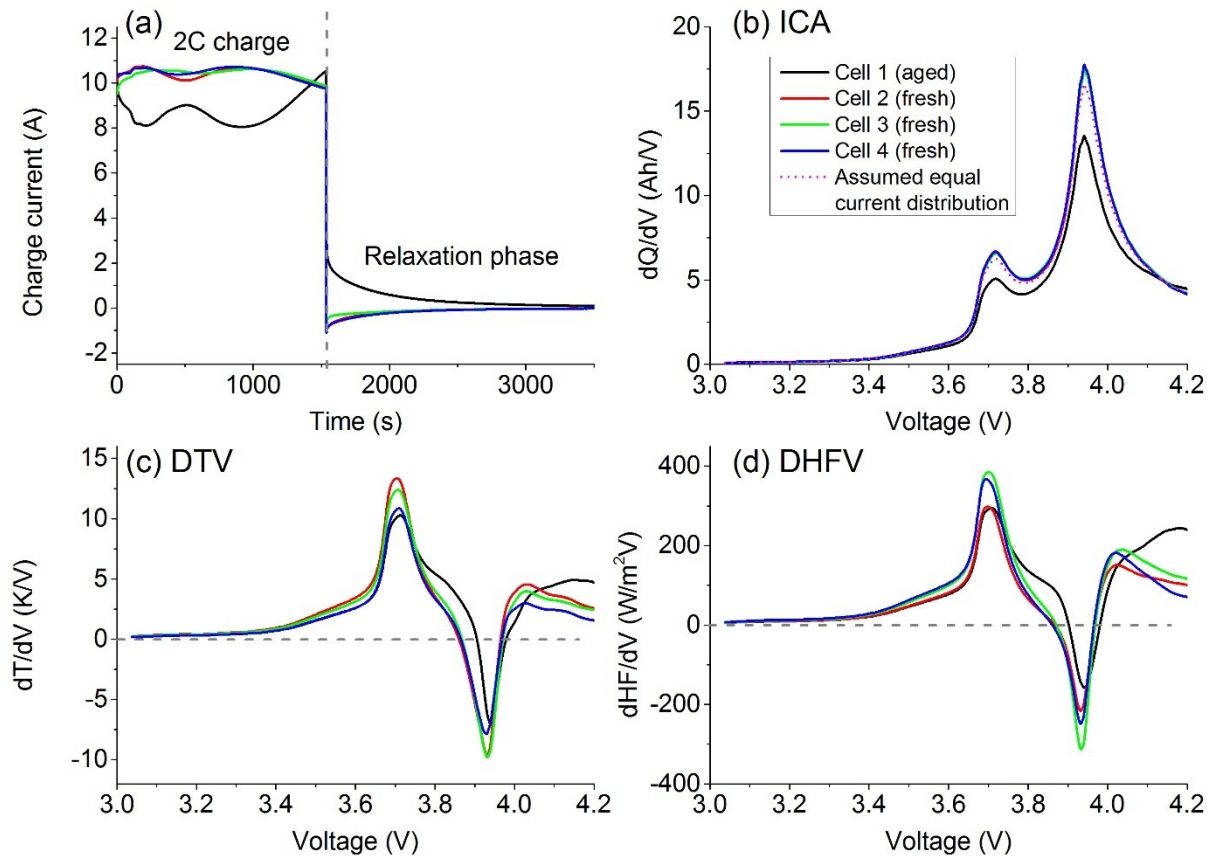


Figure 63. Pack analysis under 2C constant current charge. (a) Cell current. (b) Incremental capacity method. (c) Differential thermal voltammetry. (d) Differential heat flux voltammetry. Source: [10].

Figure 64a shows the DTV result during 2C charge with a zoomed in figure on the negative peak. The negative peak here represents peak ①*② which is negative due to the negative dT/dt term. The notable and interesting difference with the DTV analysis during charge is the presence of two $dT/dV = 0$ transitions. dT/dV approaches zero as dV/dt is significantly higher than dT/dt i.e. a significant change in voltage while temperature remains almost unchanged. As mentioned before the phase transition is associated with a considerable change in voltage therefore as the crystallographic structure changes, the cell potential at $dT/dV = 0$, or a minima between two peaks, can be used as a footprint to track phase transition points hence electrode stoichiometry.

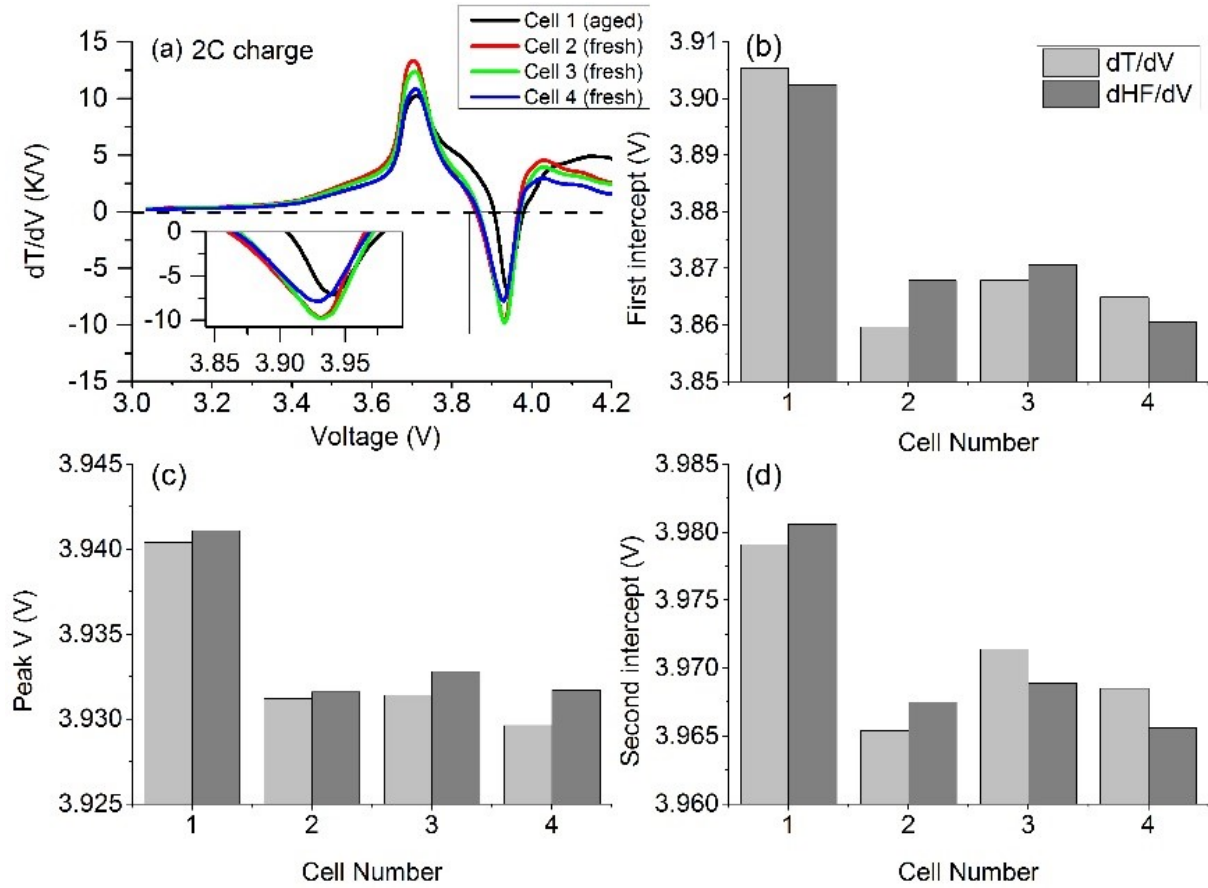


Figure 64. Peak analysis of differential thermal and heat flux voltammetry results for 2C constant current charge. (a) Zoomed in differential thermal voltammetry result. Starting potential (b), peak potential (c) and end potential (d) for the positive peak are shown here. Source: [10].

Figure 64b, c and d demonstrate the potential at the initial x-axis intersect (i.e. $dT/dV = 0$ and $dHF/dV = 0$), the potential at the lowest point of the peak and second x-axis intersect respectively. It can be seen from all three parameters that the aged cell has a notably higher potential than the fresh cells for both DTV and DHFV because of a combination of increase in resistance and stoichiometric shift in the electrodes. When the phase transition occurs at $dT/dV = 0$, it is particularly useful for tracking the degradation as it requires less computations and peak fitting is unnecessary. In practice, it is recommended to use the potential at the initial x-axis intersect as the change is larger and hence is less sensitive to the inaccuracies in the voltage measurements. Here the use of DTV and DHFV has been demonstrated for an on-board identification of aged cells in a battery pack under thermal management during charge.

The pack is then dismantled and characterisation tests are carried out on the individual cells to prove the correct cell had been identified. The experimental setup is exactly the same but the cells are loaded individually. Constant current discharges at 2C is performed, and their capacity is shown in Table 10.

Table 10. Discharge capacity of individual cells at various C-rates. Adapted from [10].

	2C discharge capacity (Ah)
Cell 1 (aged)	4.39
Cell 2 (fresh)	4.83
Cell 3 (fresh)	4.83
Cell 4 (fresh)	4.82
Sum of individual	18.87
Pack capacity	18.89

The results clearly show that cell 1 is the aged cell with 91% of its initial capacity at 2C discharge, in agreement with the DTV and DHFV diagnosis. Pack capacity and sum of individual cell capacities are compared to see if the presence of an aged cell affects the performance of the other fresh cells in a parallel pack. The results show a negligible difference between the two capacity measurements ($\sim 0.1\%$) suggesting that the aged cell does not lower the performance of the individual cells in a parallel pack. This is later validated separately by [220]. The marginal higher capacity as a pack may be hypothesised from the fact that the cells are hotter during a pack application due to its proximity to other active cells lowering their impedance hence hitting the cut-off voltage later. It should be clarified that the higher peak currents of each cells from the inhomogeneous current distribution means that the aged cell should still be identified and replaced as soon as possible to minimise accelerated degradation.

4.5. DISCUSSION

Existing BMS are typically very simple, and have been designed to meet minimum specifications for safety and monitoring, to prevent over-heating and over charging/discharging. The measurements they take are then typically compared to empirically validated equivalent circuit models in order to estimate SOC or state-of-power (SOP). SOH prediction is typically based upon energy throughput models or simple recalibration of the capacity after a complete charge or discharge [169,182,221]. As mentioned in Chapter 3, it is possible for cells that have been aged in different ways to have the same capacity fade, and even power fade, and standard techniques are not capable of diagnosing the differences. In addition, if cells are in parallel with each other, unless the individual currents are measured, it is not currently possible to identify differences in SOH between the cells quickly and easily. Other more advanced techniques such as EIS require additional hardware to be implemented which comes at a cost. EIS is also highly sensitive to temperature, which although making them useful for internal temperature estimation, makes them impractical for SOH diagnosis in most cases [199,204,222]. ICA is probably the most useful of the existing techniques, although it requires accurate current measurement for each cell, which can be impractical for cells in parallel. Again, this technique is sensitive to temperature affecting the peak positions due to the exponential relationship between impedance and temperature. There is therefore a need for a more sophisticated technique that can be used to diagnose the SOH of individual cells even when they are in parallel and in a noisy temperature changing environment. In order to be used in real world applications a diagnostic technique must also be low cost which means it must use a limited number of cheap sensors and require minimal computational power and memory monitored at low frequencies.

It is accepted that pack design can give rise to inhomogeneity in both current and temperature between cells [217]. The unequal and changing current in the cells as observed in Figure 60a and Figure 63a is a result of differences in internal impedance and external resistance. The difference in internal impedance will depend on the cell's SOH, SOC, temperature and

manufacturing inequalities [199,204]. The difference in external resistance arises from different contact resistances, wire length and cell's proximity to the loading point on the copper bus bar [205]. The unequal temperature is then caused by the differences in internal current, impedance and thermal boundary conditions. This can lead to both negative and positive feedback during operation. For a diagnosis technique to be suitable for implementation in a pack application, it must also be insensitive to these effects.

In this chapter the slight differences observed between the three fresh cells are likely to be a combination of manufacturing inequalities, differences in contact resistances and thermal boundary condition. As illustrated in Figure 57, cell 4 is closest to the cooling fan than cell 3 followed by cell 2 and cell 1. However, the differences in performance between cells 4, 3 and 2, are minimal and confirm that almost equal cooling for all cells was achieved. In the same way, the external resistances were balanced so they were insignificant compared to the differences between the cell impedances. For optimal thermal diagnosis, it is ideal to have homogeneous thermal boundary conditions i.e. equal cooling for all cells in a pack.

In real application, such as in electric vehicles, where there are many more cells to be measured, the diagnosis may be challenging in the presence of noise and small inconsistencies between healthy cells as discussed above. In such cases data mining techniques can be used to evaluate changes from healthy to faulty cells in order to maintain diagnosis performance on a BMS [223].

Despite the changing currents between the cells, and active cooling, the aged cell was correctly identified and meaningful information was obtained as seen in both Figure 62 and Figure 64.

The results are comparable to the single cell test under natural convection carried out in Chapter 3 [9]. This work also demonstrates the use of the technique under charge for the first time, and the use of heat flux measurement instead of temperature. However, the heat flux sensors required for DHFV cost significantly more than regular thermocouples required for DTV. Therefore, the use of DHFV is only suggested when accurate dT/dt is difficult to measure in applications with high cooling requirements.

Due to the simple requirements of measurements and computation, this method should be applicable to various real systems such as smartphones, laptops, electric vehicles and grid level storage, all at a low cost. The importance of its application is to monitor the detailed SOH of the battery system and then to adapt its operating conditions for the given diagnosis to maximise its lifetime and prevent catastrophic failure. This is especially required for pack applications where the lifetime of the whole system is limited by its weakest cell.

4.6. INDUSTRY COLLABORATION: PROGNOSIS OF FAIL CELLS IN A BATTERY PACK

One of the key objectives of the DTV technique is to develop and validate a prognosis capability where it allows the BMS to quantitatively determine that one or more cells within a pack are likely to fail in the near future.

A collaborative project was carried out with an industry partner, who will remain anonymous for contractual reasons, to test this feature on high power battery packs used in a motorsport application. The battery packs were experiencing an issue where after a number of drive cycles, a seemingly random cell would fail in a particular manner. The failing cell was only noticed during the failure and remained undetected until it was too late.

The battery pack consists of over a hundred cells in series where individual cell voltages and surface temperatures are measured at 1Hz or faster. The aim of this research collaboration was to use the DTV technique on the battery pack charging data to predict the failing cell before the actual failure. Once such cells are flagged by the algorithm, the industry partner could make an informed decision on whether to replace the cell or keep the pack going depending on cost benefits.

By analysing the failure mode, it was hypothesised that the failure was linked with an increase in series resistance. As previously mentioned, DTV peak positions can be correlated to the internal impedance of the cell. The prognosis algorithm was written in MATLAB and Simulink to determine the peak position of each cell and flag an outlier as a potential future failing cell.

The outlier needed to be quantified so that the BMS could determine the cell as an outlier. The outlier was defined by a degradation factor (DF) which is the difference between the peak position of the cell and the warning threshold, wt . The warning threshold was in turn calculated from the mean of absolute deviation (MAD) and the user-defined warning threshold coefficient, k_{wt} :

$$MAD = \text{mean}(|DTV \text{ peak position} - \text{mean}(DTV \text{ peak position})|) \quad (16)$$

$$wt = k_{wt} \times MAD \quad (17)$$

$$DF = DTV \text{ peak position} - wt \quad (18)$$

It was determined that a k_{wt} of 2 is optimal for prognosis of the failing cell for this pack design/configuration and this value was used for all data in this project. This value could be decreased to be give more conservative warnings and vice versa. A positive DF is flagged as a caution for future failing cells and the larger the DF, the more likely and/or imminent the failure.

Figure 65 presents an example analysis of the battery pack from a constant current charging event. It is known that cell number 132 would fail after several more drive cycles and the DTV peak position outlier method correctly identified the cell validating its use as a prognosis tool.

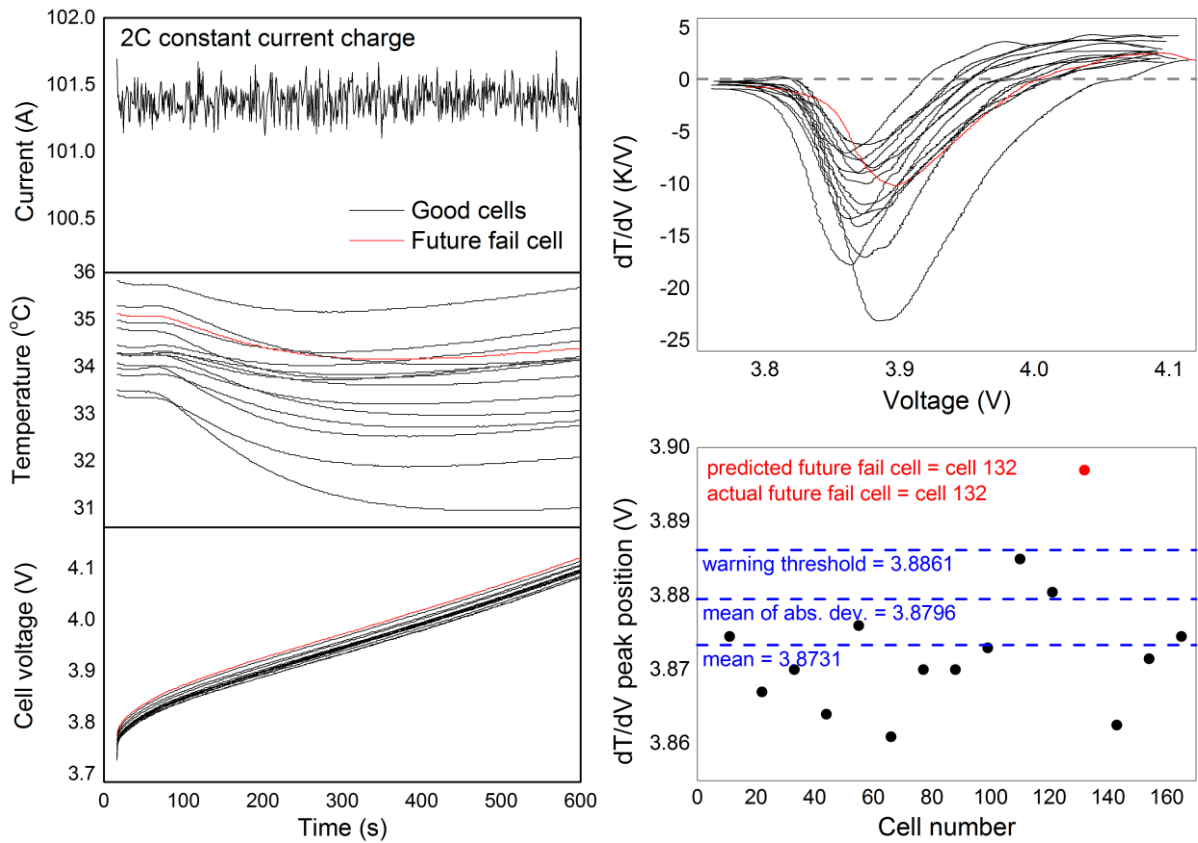


Figure 65. Example DTV prognosis result for a high-power battery pack from a constant current charge data. Current, temperature and voltage data (left). Note that all cells are connected in series hence have the same current. DTV curve (top right) and DTV peak position analysis (bottom right). Warning threshold coefficient of 2 was used.

This validated algorithm is now installed and used in the BMS proving its use in a commercial battery pack.

4.7. INTERIM CONCLUSION

In this chapter, DTV diagnosis methods were performed on a pack of commercially available lithium-ion batteries. Four cells were placed in parallel where one of them was deliberately aged prior to the experiment. The pack was placed under forced air cooling to emulate a thermal management system in a real-world application and tested under a 2C charge and discharge.

DTV and DHFV both correctly identified the aged cell within the pack for both charge and discharge with unknown, changing and different currents between the cells. The methods

quantitatively measured an advanced state-of-health parameter through diagnosing stoichiometric shift between the two electrodes. DHFV was demonstrated to provide a complimentary diagnosis method using heat flux instead of temperature during strong cooling conditions.

The current from each cell was recorded, but not used, and showed unequal current distributions caused by the presence of the aged cell, which could lead to accelerated degradation due to the higher transient local currents and temperature inhomogeneities. Therefore, it is crucial to quickly identify aged cells so they can be replaced to maximise overall pack lifetime and performance.

DTV is more suitable as a diagnosis method for real-world applications compared to other common methods such as SRCV, EIS and ICA. This is because the method only requires a single surface temperature per cell and voltage measurement which are normally already available in modern applications for monitoring safety and SOC respectively. It does not require additional hardware like EIS, individual cell current measurement like ICA, or very slow and specific load profiles like SRCV. The installation cost in most cases should be minimal if the correct sensors are already in place, and it should be possible to handle the simple computation within most existing battery management systems.

In this chapter, the use of DTV and DHFV has been demonstrated in a pack condition under slow and fast constant current charges and thermal management which means the diagnosis can be carried whenever a smartphone or an electric vehicle is left to charge.

It was also found that the presence of an aged cell in a parallel pack does not limit the performance of the other cells by comparing the pack capacity and the sum of individual cell capacities.

Through industry collaboration, the use of DTV has been validated as a prognosis tool to forecast failing cells in a high-power battery pack used in a motorsport application. Outliers in

the DTV peak position during a constant current charge were used to determine the degradation factor. This DTV outlier method can now be used by a BMS to quantitatively identify an outlier with different levels of caution. The algorithm has been implemented in their BMS demonstrating its use in a commercial battery pack.

Chapter 5. IR-DECOUPLED DTV AND ADAPTIVE OPERATION

5.1. INTRODUCTION

In the previous chapters, DTV has been demonstrated as a low-cost on-board diagnosis for both cell-level and pack-level application. The technique has also been proven to work as a prognosis tool for mitigating failure in a commercial high-power battery pack. The next key question is whether the DTV diagnosis results can be used to optimise the operation of the cell accordingly to prevent the onset of accelerating degradation and extend lifetime.

Lithium-ion batteries are known to degrade faster at their potential extremes [90]. Current battery applications use agnostic derating where the cells are limited to operate between a preselected fixed voltage ranges to minimise degradation accelerated at high and/or low voltage. This is clearly not effectively utilising the available power/energy in a cell. For example, batteries in a Chevrolet Volt are limited between 30% and 80% SOC and Nissan LEAF model 2013 is limited up to 80%. For electric vehicle applications, especially in motorsport where the vehicle needs to be pushed to its extremes, a more intelligent derating system is critical.

In this chapter, a novel adaptive derating method is introduced using the cell diagnosis results obtained through DTV. This method aims to be better than agnostic derating methods used today: capacity use is maximised while keeping the degradation rate to a minimum.

Additionally, two new features for the DTV technique are introduced to optimise the SOH diagnosis capabilities to better understand how the adaptive derating should be applied. The first feature is an in-operando open circuit voltage (OCV) estimation during a constant current charge to IR correct diagnosis results such as from ICA and DTV. The second feature is an alternative peak fitting method that requires less computational power and complexity to facilitate the transition from a desktop application to commercial BMS.

An accelerated ageing experiment is carried out on commercial lithium polymer cells to validate the application of the DTV-based adaptive derating to extend lifetime together with the use of the new OCV estimation and peak fitting techniques.

5.2. RESEARCH QUESTIONS

In this series of experiments, the aim is to answer the key research questions for DTV development:

- Can DTV information be used to minimise degradation of a battery?

This work package also aims to address the following sub-questions:

- Is there a way to estimate the OCV accurately during a “normal” charging/discharging time?
- Can contributions from overpotential effects and stoichiometric drift be decoupled in DTV analysis?
- Is there a less computationally intensive and complex way to determine DTV peak parameters?
- Can the quantitative stoichiometric drift values be used to adaptively de-rate the cell operation to mitigate the onset of accelerated degradation?

5.3. IN-OPERANDO OCV ESTIMATION

Acquiring the OCV curve of the cell can be useful in many applications as this measurement of the thermodynamic potential isolates the effect of overpotentials. It was previously discussed that DTV peak position is defined by the combined contributions from the overpotentials and stoichiometric drift. If there is a way to decouple the two effects, the diagnosis can look at the stoichiometric drift and the total impedance of the cell separately allowing for a more detailed insight into the battery SOH.

The OCV is defined as the cell potential at thermodynamic equilibrium with no load. That is to say there should be zero lithium concentration gradient in the solid phase. As seen in Chapter 4

Figure 63, the cells require some time after the load has been cut-off to saturate and reach equilibrium i.e. its OCV. Zinth et al. suggests in their paper that the graphite anode of a lithium-ion battery requires 20-40 minutes at 25°C for the relaxation phase [18].

There are currently two commonly used methods of measuring the OCV curve of a cell. The critical disadvantage of these techniques is that they naturally both take several hours if not days to complete. The first method is the slow discharge. By discharging the cell extremely slowly e.g. at C/25 (or in 25 hours), the cell is assumed to be at a *quasi-equilibrium* state and the measured cell potential is approximated to be the OCV. The advantage is in its simple procedure however with the drawback that the measurement is not at the real equilibrium. The second method is the galvanostatic intermittent titration technique (GITT) where the cell is pulse discharged for a short period of time followed by a relaxation phase until the cell reaches equilibrium to measure the OCV at that SOC [224]. The cell is then pulse discharged again to increment its SOC and the procedure is repeated until the cell is completely discharged. An illustration of this technique is presented in Figure 66. The advantage of this method is the measurement of real OCV however comes with the downside that the OCV points across the cell SOC need to be interpolated to get a full curve.

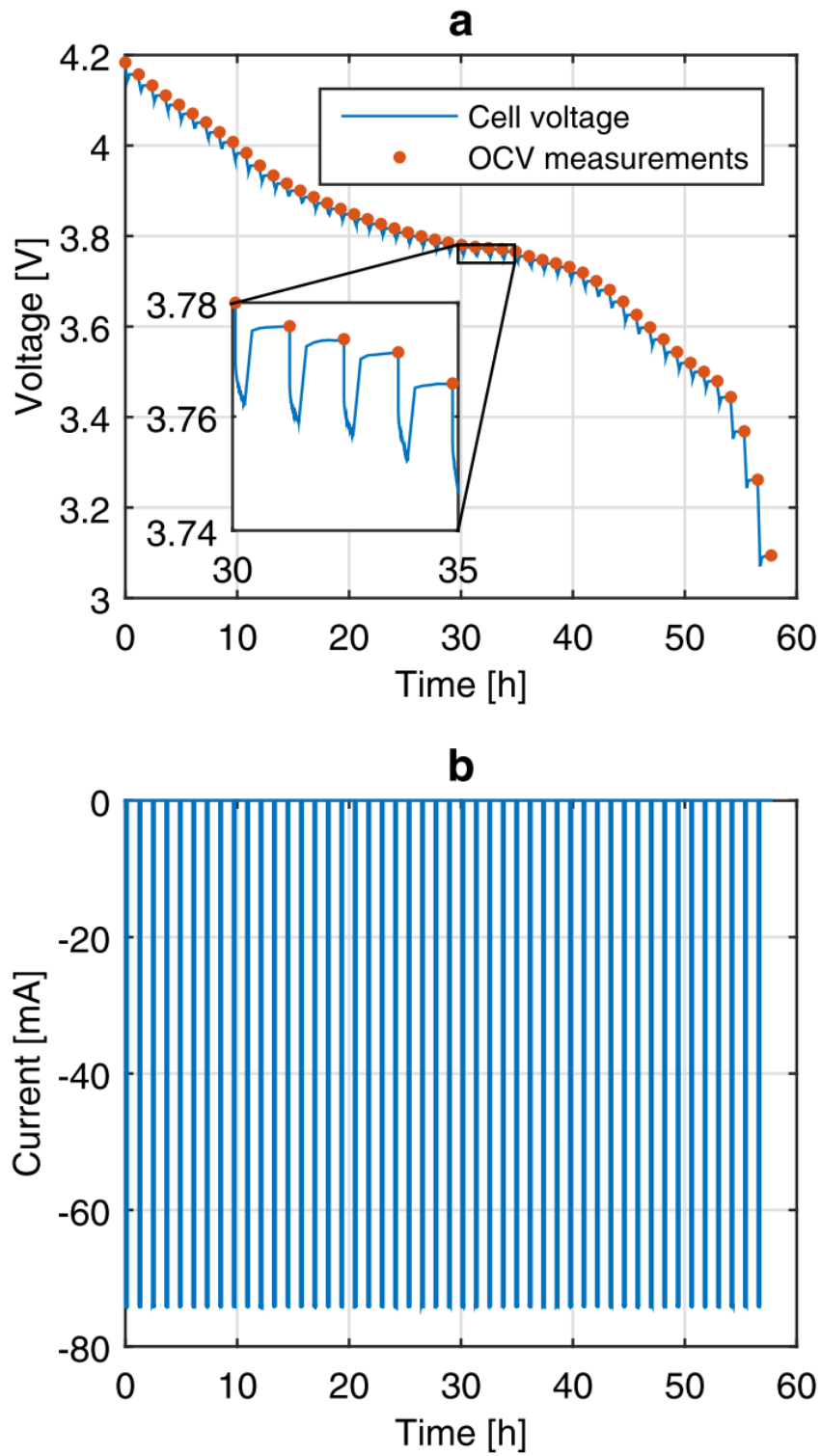


Figure 66. Illustration of GITT on a commercial lithium-ion battery. Voltage profile with OCV measurements (top) and pulse discharge current profile (bottom). Notice how the procedure took approximately 60 hours. Source: [155].

The loading profiles of the two methods are not suitable for a simultaneous DTV analysis. The slow discharge method is too low power to measure significant heat generation and the GITT

produces cyclic temperature profile as it heats up during the short discharge and cools back down to room temperature during the long relaxation phase which essentially results in a discontinuous dT/dV curve.

A variant of the GITT method is proposed where the OCV is extrapolated from the first few seconds of the relaxation phase. The benefit of this method is the significant decrease in required test time. Given the few seconds of rest phase instead of minutes/hours, the OCV measurements can be obtained by only adding a couple of seconds for each data point to a constant current loading. Hence this method allows for the determination of OCV and internal resistance profile across the cell SOC in a normal charging/discharging time e.g. in an hour. The added benefit of this method is that a DTV can be carried out at the same time. Despite the few seconds of rest, a continuous dT/dV curve is obtainable due to the large thermal inertia of the cell. This means that a DTV analysis can be carried out with respect to the cell OCV allowing for a SOH diagnosis independent of cell current and resistance.

The intermittent constant current charge technique consists of a constant current charging phase and a short rest phase both of which can easily be carried out by existing systems such as consumer electronics and electric vehicles etc. The rest phase is set to occur every few minutes (depending on charging current) where the rest phase itself lasts a few seconds. For example, 4s of rest every 100s of 1C charging. The cell potential will approach its OCV following mass diffusion however this process can take hours to reach saturation. The proposed technique is to take the first few seconds of potential profile at rest, and fit it to a power equation to extrapolate the final OCV. This way the OCV can be estimated during “normal” charging and DTV analysis can be carried out at the same time. The computation is aimed to be simple enough to be handled by existing BMS.

A power equation, $ax^b + c$, is used as a simplification of the exact representation of the diffusion process to minimise computation time and requirement. The selection process for the curve fitting equation is carried out by comparing the goodness of fit in MATLAB's curve fitting

toolbox. Various equations are used to fit the rest profiles of commercial 5Ah lithium-ion cells. An example result of the curve fitting is illustrated in Figure 67. The cells are the same product model as the ones presented in the previous chapters.

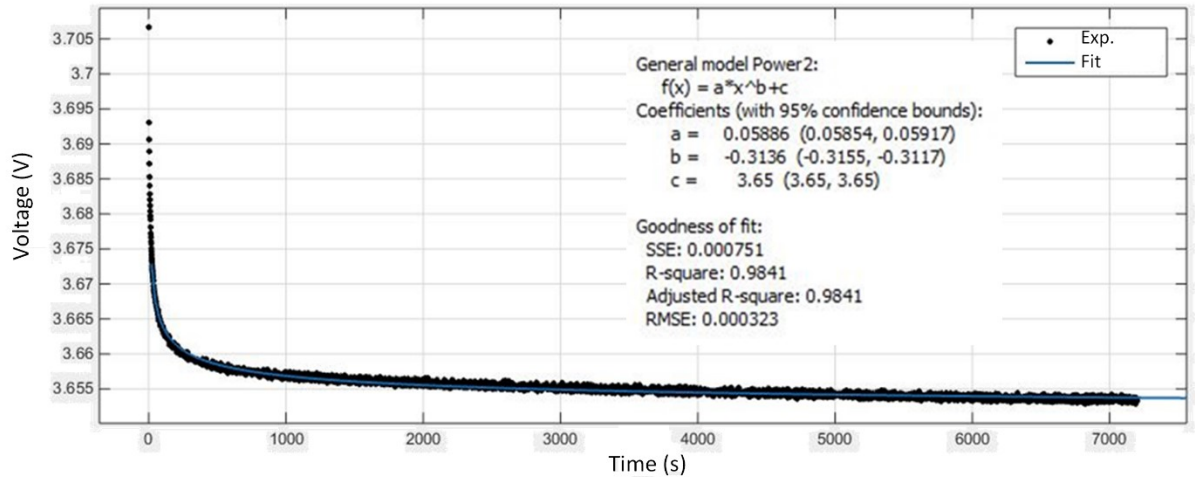


Figure 67. Curve fitting the rest profile to a power equation in MATLAB curve fitting toolbox. Notice the high goodness of fit.

In order to validate this technique as an in-operando OCV estimation technique, the cells are charged with 2 hours rest every 100 seconds of charge at various C-rates. Assuming 2 hours is enough to reach saturation (i.e. OCV), the estimated OCV is extrapolated from the initial 3.5 seconds of rest data and compared to the actual value after 2 hours. The relaxation phase used for the OCV extrapolation (i.e. the first 3.5 seconds in this case) should be sampled at 20Hz or higher to get enough data points for an accurate estimation. The other times may be sampled at a lower frequency to minimise memory requirements.

The method also needs to be accurate for cells at various SOH for it to be used with DTV as a degradation tracking tool. To validate this capability, a fresh and an aged cell are taken and tested for the accuracy of OCV estimation. The aged cell was stored in an incubator at 60°C at 4.2V for 20 days. The two results are presented in Figure 68 and Figure 69.

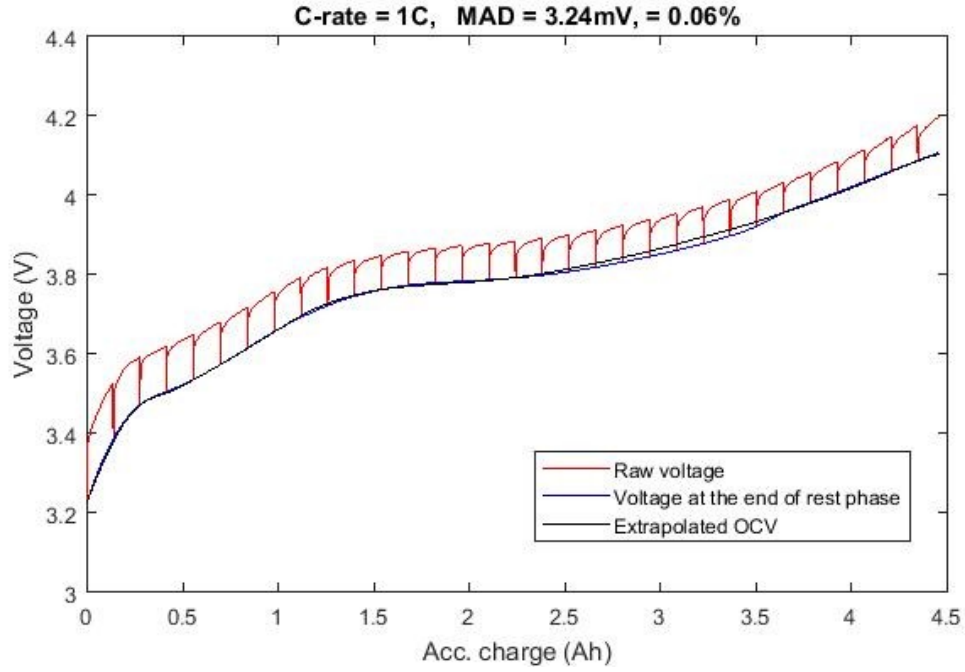


Figure 68. OCV extrapolation test for a fresh Kokam cell. 100 seconds of 1C charge followed by 2 hours of rest (red). Voltage at the end of rest phase is assumed to be OCV (blue). Extrapolated OCV only uses the first 3.5 seconds of the relaxation phase data (black).

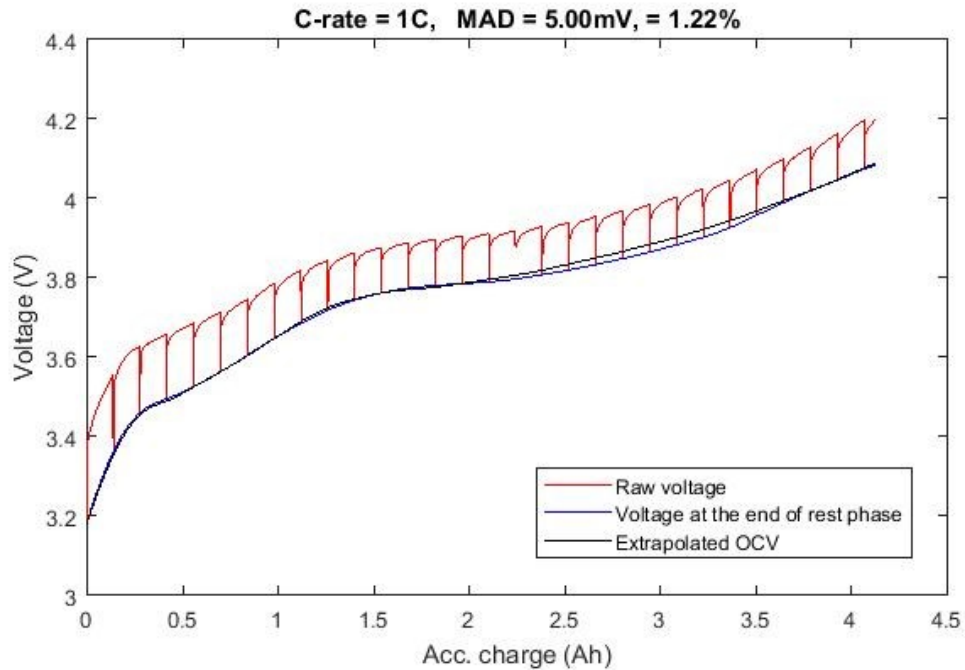


Figure 69. OCV extrapolation test for an aged Kokam cell. 100 seconds of 1C charge followed by 2 hours of rest (red). Voltage at the end of rest phase is assumed to be OCV (blue). Extrapolated OCV only uses the first 3.5 seconds of the relaxation phase data (black). The cell was aged for 20 days at 4.2V at 60°C.

The results show a close correlation between the real OCV and its estimation with a MAD less than 5 mV for both fresh and aged cell. It should be noted that there is a slight increase in deviation around 3.8 V thus the user should be cautious when interpreting the extrapolated OCV around this voltage region. It was found through trial and error that data points between 1.5 to 3.5 seconds should be used for fitting the power equation to get the best accuracy of estimation. It is assumed that it is better to skip the first 1.5 seconds as this region of the relaxation phase is dominated by the effects of higher frequency impedance, such as the series resistance and charge transfer resistance, which does not represent the voltage saturation from diffusion.

By measuring the cell surface temperature during this in-operando OCV estimation, it is now possible to carry out the DTV analysis based on the cell OCV instead of the cell potential. An example result for a 1C intermittent charging is presented in Figure 70.

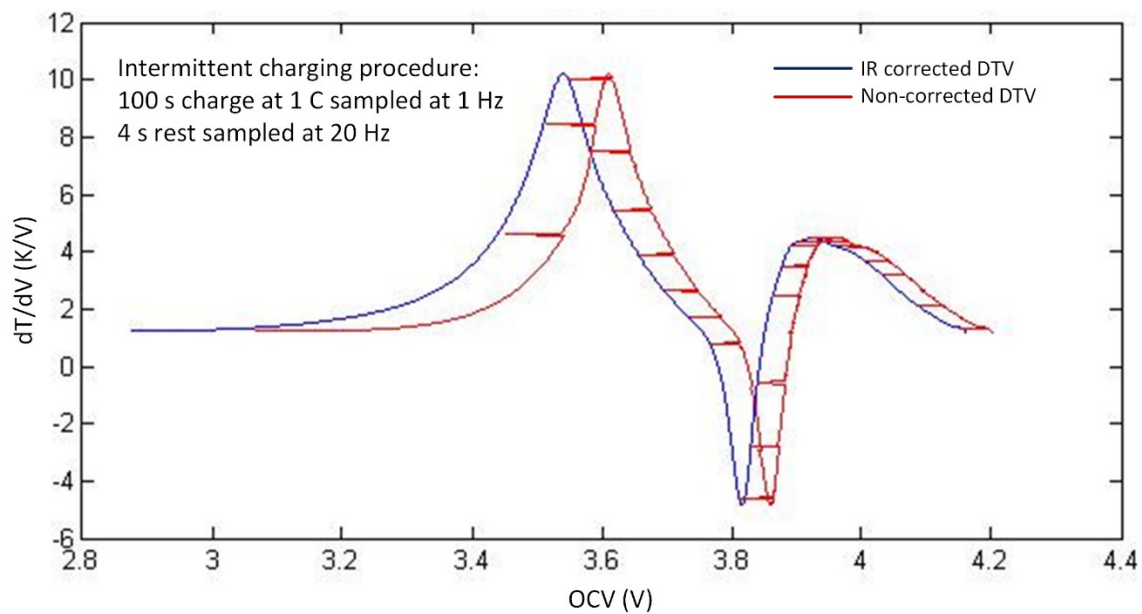


Figure 70. IR corrected DTV using in-operando OCV estimation. Notice how the peak parameters are now decoupled from impedance effects. The horizontal spikes on the non-corrected DTV (red curve) comes from the voltage relaxation phase of the intermittent charging procedure

The DTV curve and its peak parameters are now decoupled from impedance effects. It is observed that the peak positions shift to a lower potential as the overpotential during charge is

subtracted. The evolution of peak position through degradation analysed this way can now be attributed to the stoichiometric drift alone.

5.4. SIMPLIFIED PEAK TRACKING METHOD

An industrial collaboration with a BMS company (Innovate UK funded project with Dukosi Ltd) proved that the bottleneck of the DTV algorithm is in its advanced peak fitting which is too complex to implement in a commercial BMS. On top of this complexity, the original fitting algorithm did not support negative peaks seen in DTV under charge. This issue is addressed through a new peak tracking method that requires less computational complexity and requirement.

Instead of fitting individual peaks, the DTV curve is first screened for any maxima and minima by looking at where the derivative of dT/dV is equal to 0. Any maxima above $dT/dV = 0$ and minima below $dT/dV = 0$ is assumed to be a peak position. The peak height is calculated from the value of dT/dV at such peak position. Finally, the peak width is calculated by the voltage distance between the two half height points along the curve.

Naturally this method is not as accurate as fitting individual peaks however it significantly reduces computational complexity and is capable of tracking negative peaks making it more suitable for BMS application with limited specs. As the peak width is calculated by the points on the total DTV curve instead of a fitted single peak, it is possible that the width is unmeasurable if the DTV curve does not reach the half height value.

An example result of the simplified peak tracking method is presented in Figure 71.

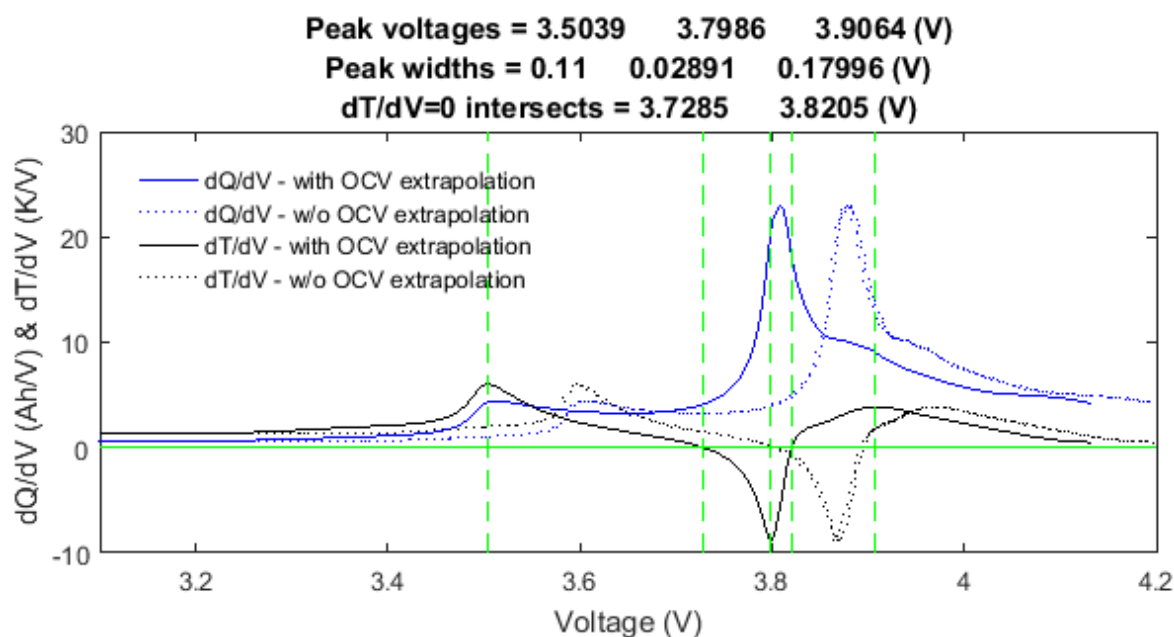


Figure 71. Simplified peak tracking results on a fresh cell. DTV by 1 C intermittent charging (100 s charge and 4 s rest).

Vertical dashed green lines represent position of DTV peaks and $dT/dV = 0$ intersect.

The position of x-axis intersection i.e. $dT/dV = 0$ is also recorded as a possible tracking parameter. As presented in Chapter 4, this zero-intersect may be used to identify aged cells.

5.5. ADAPTIVE DERATING

It has been discussed that the peak position is a combination of IR effects, i.e. overpotential, and stoichiometric drift. The addition of the in-operando OCV estimation allows for the decoupling of the two. The IR corrected DTV curve can be analysed for stoichiometric drift between the combined electrodes throughout battery lifetime using the same peak evolution analysis technique as presented in the previous chapters. The quantitative shift in stoichiometry can be used in turn to determine a derating method to minimise cathode over charge hence minimise further degradation to ultimately increase cell lifetime and maximise its available energy.

To put it into context, an NCM cell has a maximum operating voltage of 4.2 V at the beginning of its life. As the cell is aged and the stoichiometry is shifted, the new maximum operating voltage may decrease to 4.15 V to avoid cathode overcharge. The argument is that the little amount of capacity between 4.15 V and 4.2 V is not worth accessing considering the extra degradation that

will be incurred and hence the cell will last longer providing a greater total lifetime energy throughput.

In order to validate the concept of adaptive derating, an accelerated ageing experiment similar to that of [9] presented in Chapter 3 is carried out with the new in-operando OCV extrapolation and simplified peak tracking to quantitatively measure the stoichiometric drift.

5.5.1. EXPERIMENTAL SETUP

5Ah commercial lithium-ion pouch cells provided by Dow Kokam (model SLPB11543140H5) were used for the following experiment. The cell consists of a graphitic carbon anode and a NCM cathode. Please refer to appendix entry A1 for detailed technical specifications as provided by the manufacturer.

Four cells were used in this accelerated ageing experiment where two cells were cycled at 2 C and the other two cells were held at 4.2 V (100% SOC). The cycling procedure does not contain CV mode or relaxation phase. All cells were placed inside an incubator (Binder KB-23) at 55°C to speed up the ageing process. Between the two cells with the same ageing condition, one was adaptively de-rated every 100 hours whereas the other one was not. This was to see if the adaptive derating could slow down the rate of degradation. The ageing setup is summarised in Table 11.

Table 11. Summary of accelerated ageing conditions for adaptive derating concept validation.

	Ageing method	Temperature	Adaptive derating
Cell 1	2 C cycling	55 °C	No
Cell 2	2 C cycling	55 °C	Yes
Cell 3	4.2 V hold	55 °C	No
Cell 4	4.2 V hold	55 °C	Yes

A characterisation procedure was carried out every 100 hours of controlled degradation (approximately 100+ cycles). The procedure is as follows:

- The cells were cooled down to 20 °C using the incubator.
- Pre-cycled 10 times at 1 C to equilibrate the cell performance.
- Pulse discharge and charge were carried out at 2C to get IR corrected DTV results using the in-operando OCV estimation technique.
- Cells 2 and 4 were then adaptively de-rated for the next period of accelerated ageing according to the stoichiometric drift measured through the simplified peak tracking method.

The pulse discharge and charge were carried out by repeating 30 s of 2 C loading and 4 s of relaxation. OCV was extrapolated at a faster interval than mentioned previously for 1 C loading as the current is higher hence the SOC increments faster. Bio-Logic BCS-815 was used for both the ageing and characterisation process.

5.5.2. RESULTS AND DISCUSSION

Once the IR-corrected DTV is determined, the results are used to quantify the stoichiometric drift. In this case, the position of the peak at approximately 3.5 V was selected as the tracking parameter to quantitatively measure the stoichiometric drift in the cells. This peak was chosen as the other two peaks at roughly 3.8 V and 3.9 V are close to the region where the extrapolated OCV value visibly deviates from the actual OCV (refer to Figure 68 & Figure 69).

The accelerated ageing is carried out for 800 hours (approximately 32 days) where the cells are characterised 9 times in total including the initial characterisation when the cell is fresh. The results of the experiment are presented in Figure 72. Note how the upper voltage limit is unchanged for the cells without adaptive derating. The capacity loss is calculated relative to the capacity after the first ageing process as the cells are aged with the same upper voltage until then suggesting that any difference up until this point is due to manufacturing inequalities.

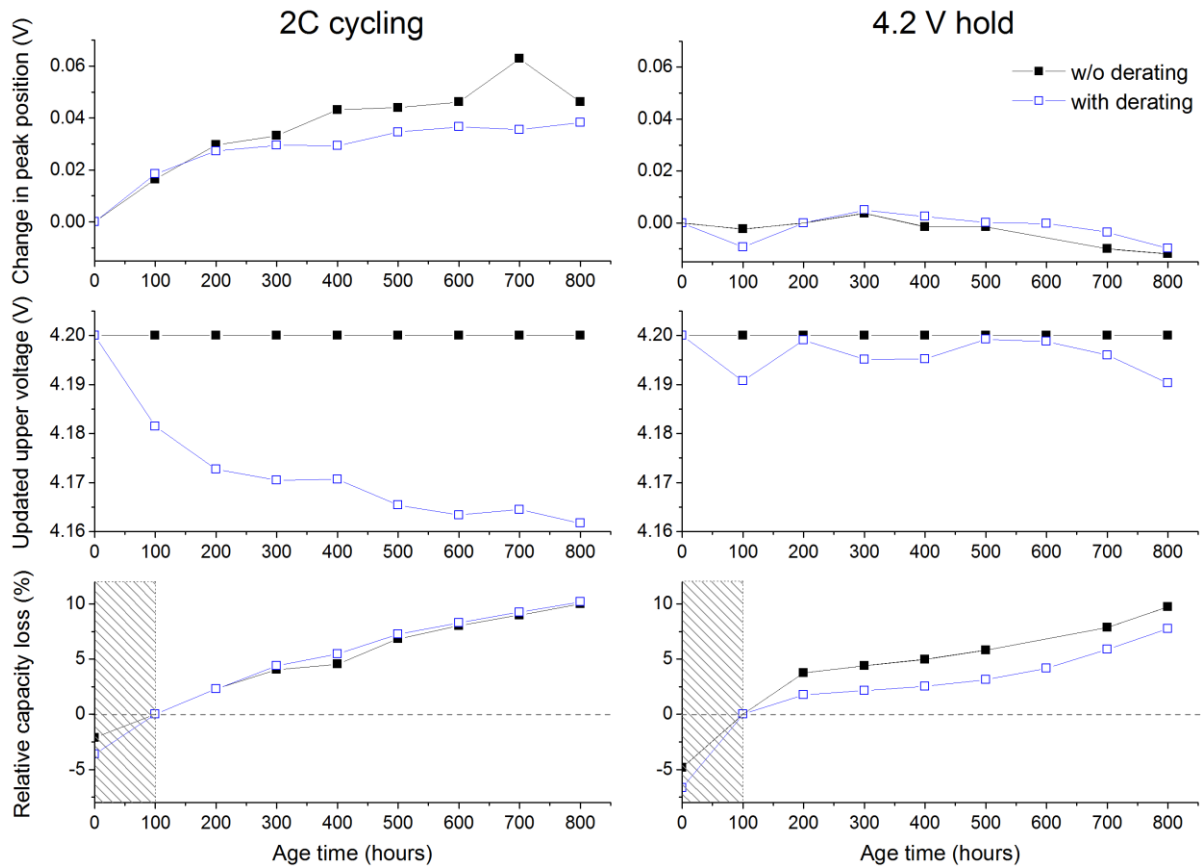


Figure 72. Accelerated ageing experiment with and without adaptive derating. Ageing by 2 C cycling on the left column and ageing by 4.2 V hold on the right, Change in peak position relative to the fresh cell (top). Updated upper voltage of operation (middle). Relative capacity loss (bottom).

Looking at the 2 C cycling results, a stoichiometric drift is observed by the shift in IR decoupled DTV peak which gradually slows down as the cell is continuously aged. This matches the findings from Chapter 3 as the expected dominating degradation mechanism in this cell is a rapid SEI layer growth which gradually saturates as the layer thickens. Formation of the SEI consumes cyclable lithium (LLI) which shifts the stoichiometry in a direction so that the combined phase alignment moves to a more positive cell potential [170]. The cell with adaptive derating has an updated upper voltage limit of roughly 4.16 V by 15% total capacity fade. Up to this point, the relative capacity loss does not show any difference with adaptive derating. However, it is evident through the change in peak position that the adaptive derating is slowing down the stoichiometric drift. It may be that the benefit of the extended lifetime would become more visible closer to the end of its life where the degradation becomes cathode dominated.

The cells held at 4.2 V show completely different results. The change in peak position is observed to be smaller and becomes negative at times. From the previous section in Chapter 3, the expected dominating degradation mechanisms in such a cell is the electrolyte decomposition (LLI) and metal dissolution at the de-lithiated positive electrode (LAM_{dePE}). LLI shifts the peak position to a more positive potential whereas the LAM_{dePE} is suggested to shift in the opposite direction [9,170]. It can be hypothesized that the movement of the peak position is continuously being cancelled out by the two degradation mechanisms which would suggest that peak position is not the optimal measure of stoichiometric drift for this combination of degradation mechanisms. Other tracking parameters such as the peak width should be explored in the future. There seems to be a capacity retention between hours 100 and 200 where the cell is de-rated at around 4.19 V however it is difficult to justify the validity of the technique through this ageing condition.

Ideally, the cells should be aged until the onset of accelerated degradation is observed towards its end of life to further validate this concept of battery life extension through adaptive de-rating. One of the issues with the above experiment is the slow stoichiometric drift as the concept relies on slowing down degradation by minimising and compensating for this electrode misalignment. Perhaps a future experiment should use lithium plating as an expected dominating degradation mechanism as this is known to have severe effects on electrode balance.

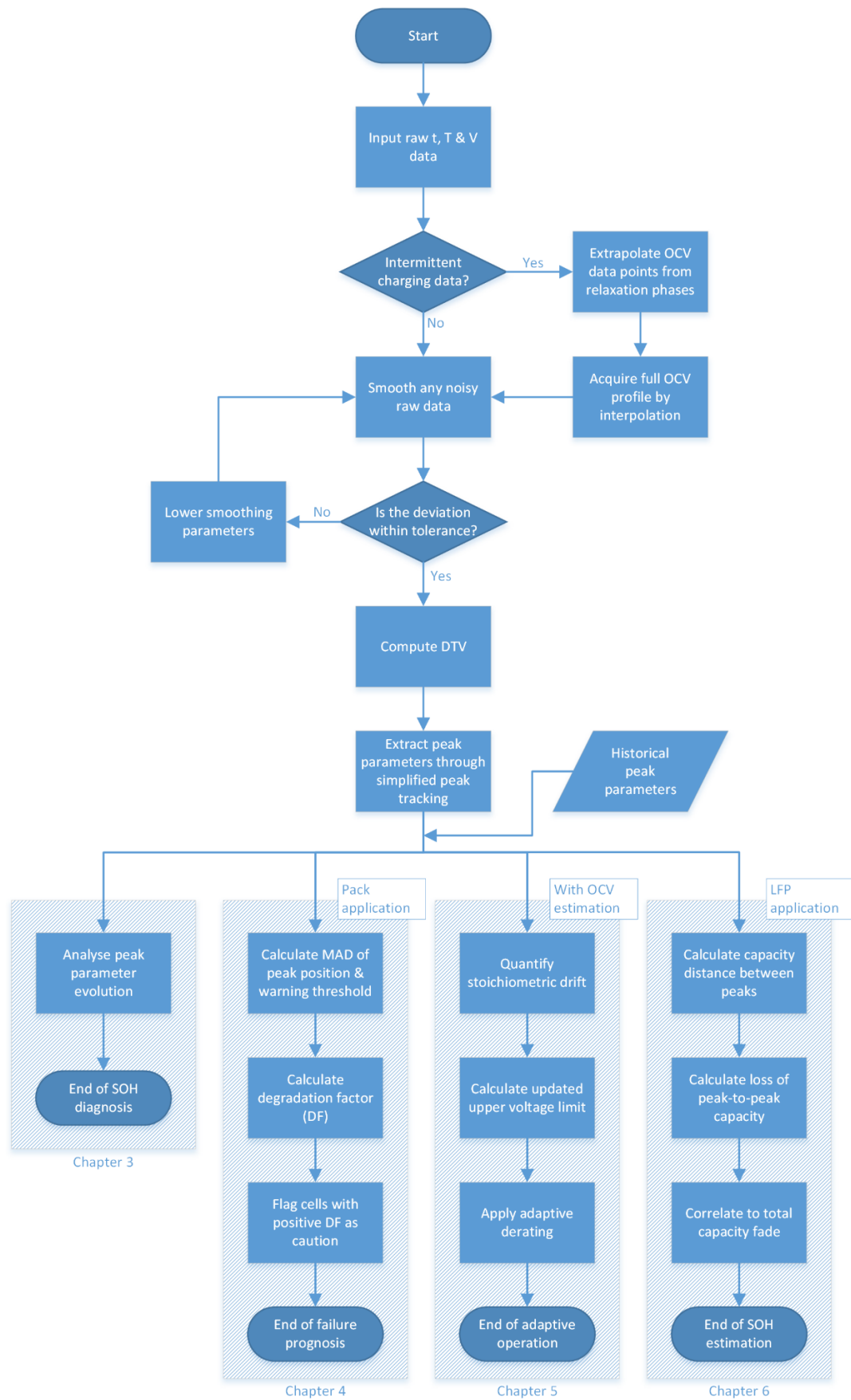


Figure 73. Flow chart of the DTV algorithm. Each application is presented in a separate chapter of the thesis.

5.6. DTV ALGORITHM FLOW CHART

To this point, the DTV technique has been continuously revised and optimised for SOH diagnosis, failure prediction and adaptive operation. The algorithm is written and developed as a MATLAB script and it has been translated into a Simulink model as well as C and C# in various projects such as industrial collaborations and internal research purposes. Figure 73 aims to illustrate the algorithm process through a flow chart for better understanding and reproducibility.

5.7. INTERIM CONCLUSION

In this chapter, two new features for the DTV technique were introduced to optimise the SOH diagnosis capability.

A GITT based in-operando OCV estimation technique was developed to extrapolate the OCV information of the cell while simultaneously carrying out DTV under a “normal” charging/discharging condition. The technique uses a second order power equation to fit the voltage response between 1.5s to 4s during the relaxation phase. The fitted equation is then used to extrapolate the voltage at equilibrium i.e. its OCV. The method proved to have an accuracy of 5 mV for both fresh and aged cells validating its use while tracking cell SOH. DTV together with this method allows for the decoupling of the IR effects from the peak analysis suggesting that a more detailed SOH diagnosis was possible.

An industrial collaboration highlighted that the original advanced peak fitting method was not ideal for BMS implementation due to its complexity. Furthermore, this fitting algorithm was not capable of fitting negative peaks which is necessary in analysing DTV under charge. A simplified peak tracking method was introduced to handle both issues. The new method screens the total DTV curve for any maxima/minima and assumes peak position at these locations.

Utilising the new methods, an IR corrected DTV is proposed to adapt the cell operation to extend cell lifetime. The concept is to intermittently quantify the stoichiometric drift of the cell

and adaptively de-rate the upper voltage of cell operation to slow down accelerated degradation by cathode over-charge while maximising available capacity.

An accelerated ageing experiment was carried out on commercial lithium-ion cells held at 55°C with and without adaptive de-rating. For cells cycled at 2 C, the stoichiometric drift was observed to slow down with adaptive derating. Cells held at 4.2 V proved to be difficult to analyse as the two dominating degradation mechanisms are hypothesised to shift the stoichiometry in opposite directions potentially cancelling each other out. More experimentation is required to fully validate its use for extending battery lifetime.

A flow chart of the DTV technique is also created to illustrate the DTV algorithm and facilitate future developments and translation into other formats.

Chapter 6. LFP APPLICATION AND SOH ESTIMATION

6.1. INTRODUCTION

In the previous chapters, the use of the DTV technique was developed and validated for NCM cells. DTV has the advantage of not requiring current and works for multiple cells in parallel, and is less sensitive to temperature as a noise factor.

Lithium iron phosphate (LFP) is also a commercially successful battery chemistry because of its high energy, power densities and stability in high temperature environments [92].

The degradation in LFP cells has already been extensively studied previously [170,181]. In particular, Dubarry et al. showed using ICA that LLI was the main consequence of SEI layer growth consuming lithium and that this was the most important degradation mechanism [212]. Kassem et al. also showed that LFP battery stored at high temperature (45 °C or 60 °C) exhibited capacity fade which was mainly caused by cyclable lithium loss (i.e. LLI) [225]. Ouyang et al. suggested that each peak in the ICA curve corresponded to different phases of the transition process [226].

An important feature and a key difference of LFP cells are their hysteresis, the asymmetric behaviour between charge and discharge caused by the phase change of the LFP material [227]. Despite this, Berecibar et al. [188] showed that the peaks in ICA can be used as markers for SOC and hence SOH diagnosis can be carried out without requiring a complete charge/discharge which otherwise is necessary to return the cell to a point where the voltage can be directly correlated to SOC (i.e. close to 100% or 0% SOC).

In this chapter, the application of DTV to LFP cells is reported for the first time, and the research demonstrates that the technique is capable of diagnosing degradation in a similar way to ICA. LFP batteries were placed under accelerated aging experiments and diagnosed using the DTV

method in order to validate its application for this particular chemistry. Whether DTV can be used to diagnose SOH and if the peaks in DTV can be used as SOC markers, in the same way as ICA, is also considered. In addition, the influence of the charging and discharging rate on the DTV method is also considered.

6.2. RESEARCH QUESTIONS

In this series of experiments, the aim is to answer the key research questions for DTV development:

- Can DTV provide similar information for other intercalation chemistries such as LFP cells?

This work package also aims to address the following sub-questions specific to the LFP chemistry:

- How do the aging mechanisms differ from NCM cells under similar ageing conditions?
- How does the direction of loading (i.e. charge/discharge) affect the DTV diagnosis?
- How does the rate of charge/discharge affect the DTV diagnosis?
- Can DTV fingerprints, e.g. peak position, be used as SOC markers?
- Can DTV fingerprints, e.g. peak position, be used for SOH estimation?
- How does the total impedance evolve as the cell ages?

6.3. EXPERIMENTAL METHOD

6.3.1. CHARACTERISATION TEST

The experiments were performed using commercial 20Ah lithium-ion pouch cells (A123 SYSTEMS, model AMP20M1HD-A) where the cell consists of a carbon graphite negative electrode and a lithium iron phosphate (LiFePO_4) positive electrode. Please refer to appendix entry A5 for detailed specifications as provided by the manufacturer.

The characterisation tests were conducted at 20 °C inside an incubator (Binder KB-23) every 4 days using two diagnosis methods. Pulse loading with open circuit voltage (OCV) extrapolation, was carried out to obtain the OCV curve and total differential resistance. Constant current charging and discharging was carried out to obtain the ICA and DTV analysis simultaneously. It should be noted that it is particularly important both procedures were carried out for both charge and discharge as LFP cells demonstrate resistance as well as voltage hysteresis.

K-type thermocouples were placed on the cell surface between the cell tabs for temperature measurement using a Picologger (model USB TC-08) to log the thermocouple readings. Maccor battery cycler (model Series 4000) was used for loading and measurement.

6.3.2. CONTROLLED ACCELERATED AGING

In order to validate the DTV method under various aging process, two accelerated aging load profiles were carried out on the LFP cells as shown in Table 12. The same incubator (Binder KB-23) was used to maintain the cells at 45 °C under forced air convection.

Cell 1 was held at 3.65V at 45°C equivalent to a trickle charge at maximum SOC. Cell 2 was cycled at 1C charge with a cut-off voltage of 3.65 V and 6C discharge with cut-off voltage 2.00 V with no constant voltage or relaxation phase at either end. Similar ageing conditions to the accelerated ageing experiment of NCM cells presented in Chapter 3 (100% SOC hold and cycling) were used so that the effect of the different cathode chemistry on the degradation mechanisms can be observed.

Table 12. Accelerated aging specifications for LFP cells. Source: [11].

Cell	Load	Temperature
1	Held at constant 3.65V (100% SOC)	45°C
2	Cycling at 1C (20A) charge, 6C (120A) discharge	45°C

6.3.3. DATA PROCESSING

In order to obtain useful information, the temperature measurements had to be smoothed appropriately as the data is often noisy. Smoothing was carried out carefully by using repeated

moving average as described in 4.3.2. The smoothed data was compared back to the original temperature data to make sure it did not deviate significantly from the original curve shape and characteristic.

6.3.4. PULSE LOADING WITH OCV EXTRAPOLATION METHOD

As mentioned, pulse loading was carried out to determine the total overpotential and the OCV during charge and discharge. Conventionally this is done by loading the cell with a short pulse to increment its SOC and then rested for few hours to reach thermodynamic equilibrium. While this provides useful information, the method can take hours if not days to complete.

In this work, the pulse loadings were carried out using 10 A constant current (0.5 C) discharge pulse for 60 seconds followed by 6 seconds of rest from 3.65 V to 2.0 V at approximately 20 °C. The same procedure was repeated for charge to observe the difference in performance.

6.4. RESULTS

6.4.1. CAPACITY FADE

The capacity fade of the cells, presented in Figure 74, is taken from the loss of Ah compared to the Ah measured when the cell was fresh. The capacity is determined through a 0.5C discharge between 3.65 V and 2.0 V followed by a constant voltage hold with a 0.1 A current cut-off. The tests are carried out on both cells every 4 days. In order to stabilize the cell condition after accelerated degradation, 3 charge/discharge pre-cycles are conducted before each characterization. Kassem et al, employed a similar process [228].

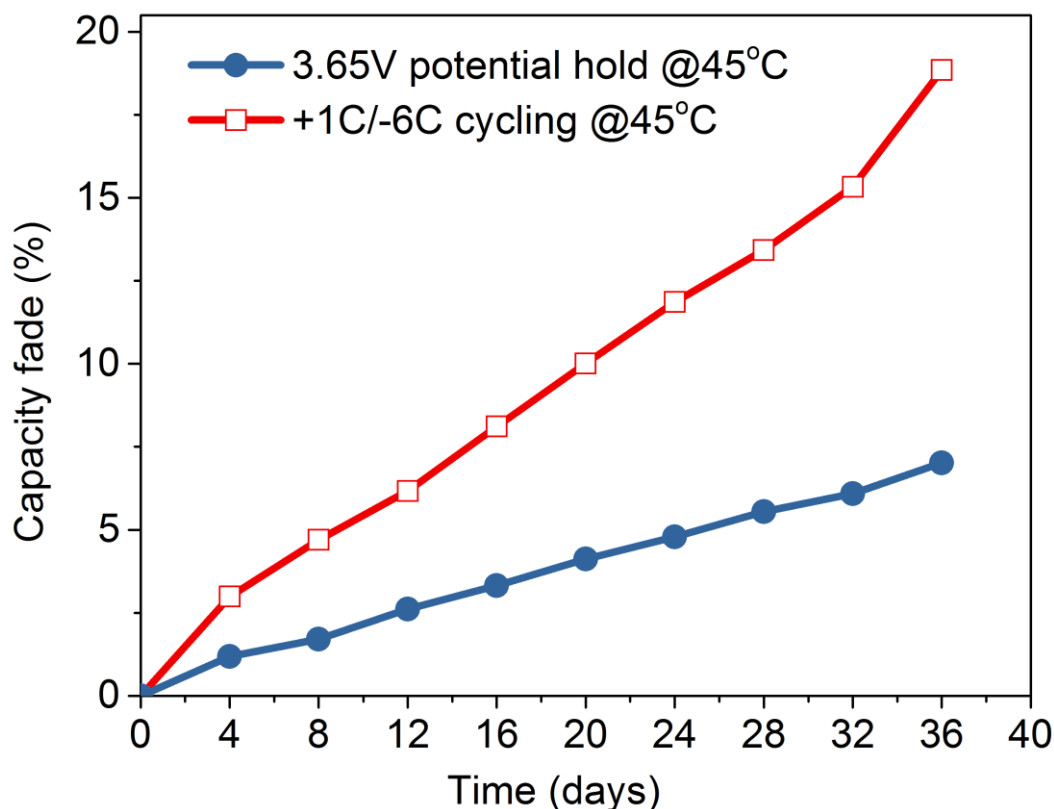


Figure 74. Capacity loss measurement of the 2 cells after accelerated degradation (0.5C discharge and constant voltage hold at 2V until current has decayed to 1%). Adapted from [11].

As seen from the capacity loss, the cycled cell shows more than two times as much capacity loss as the cell held at high potential. This could be since during the cycling process, SEI cracking can occur leading to a faster rate of SEI growth on the newly exposed electrode surfaces. Due to this process, more lithium is consumed by forming the new SEI [9,109,229].

This is a different observation from the NCM experiment where the high potential hold cell experienced a faster capacity loss towards the second half of the ageing procedure. This can be hypothesised by the difference in the positive electrode chemistry. LFP cathodes are known to be more stable than NCM cathodes where manganese dissolution is prevalent at high potentials [90]. In the NCM cell, it was suggested that the cathode was overcharged as the electrode stoichiometry gradually shifted causing manganese dissolution and subsequent metal deposition on the SEI [9]. This degradation process further accelerated the stoichiometric drift creating a positive feedback of accelerated degradation. In the LFP cell, it can be hypothesized

that the manganese dissolution is absent due to its different chemistry and consequently the rate of degradation should not accelerate.

In addition, it should be noted that the cycled cell is discharged at a higher rate (6C) than the cycled cell in the NCM experiment (1C). The results are that the surface temperature of the cycled cell almost reaches 60 °C during the cycling process inside the incubator, whilst the high potential cell remains close to 45 °C. According to Kassem et al, capacity loss is faster for cells stored at 60 °C compared to 40 °C [228,229]. Moreover, according to [90], high cycling rate enhances capacity fade rather than high SOC which matches the results.

6.4.2. INTERNAL RESISTANCE

The internal resistances of the cells are measured using pulse charge and discharge with the OCV extrapolation method.

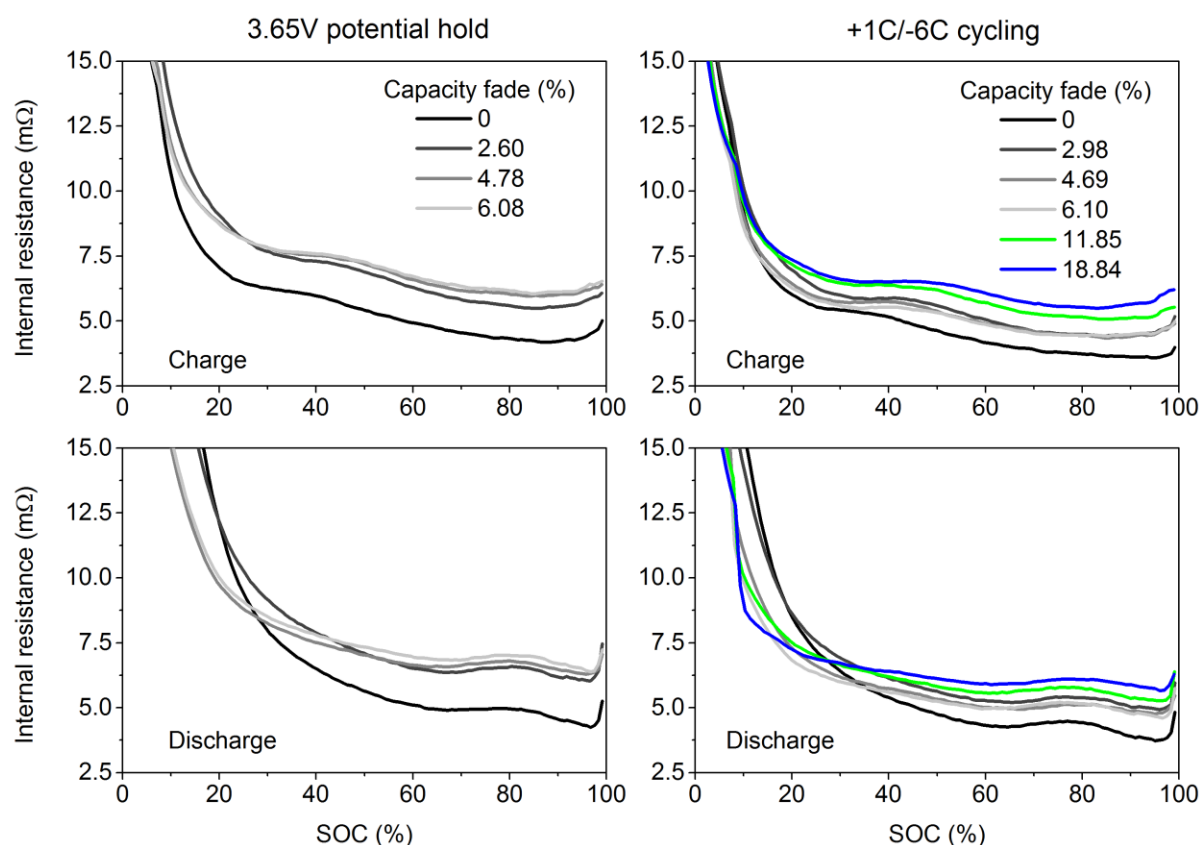


Figure 75. Internal resistance calculated from OCV Extrapolation for the 2 cells at characterisation cycles with roughly equivalent capacity fade after accelerated degradation for both charge and discharge (illustrated by black/grey lines).

Adapted from [11].

Figure 75 shows the internal resistance of these two cells at various stages of accelerated aging process. It indicates the progression of total internal resistances across its SOC. It can be observed that the internal resistance rapidly increases below 20 % SOC when charging and between 20-40% when discharging. It can be interpreted that this change corresponds to the increasing charge transfer and diffusion resistances at lower SOC. A steady increase in all resistance parameters can be seen in both cells. The main cause of this resistance rise has previously been attributed to a decrease in the charge-transfer kinetics and other interfacial contributions [228].

The power fade of the high potential cell is slightly higher than the cycle cell for the same capacity fade. This suggests that there is a specific degradation mechanism that increases the internal impedance without consuming cyclable lithium or active material. This could be due to

several degradation mechanisms such as electrolyte decomposition, oxidation of conductive agents and/or binder decomposition etc. To confirm such hypotheses or not, any further analysis requires the use of ICA or DTV.

6.4.3. DIFFERENTIAL THERMAL VOLTAMMETRY

Figure 76 shows the results from DTV for the two cells. The peaks represent regions on the (dis)charge curve where the voltage is not changing rapidly, but significant heat is generated. A transition between peaks is typically a result of the voltage changing rapidly, and is indicative of one of the electrodes undergoing a phase transition, similarly to ICA. As introduced in Chapter 4, a significant difference between ICA and DTV is that negative peaks are possible, as the temperature can also decrease if the entropic heat absorption from an endothermic reaction in an electrode is significantly larger than the enthalpic heat generation at that current. Negative peaks will disappear and become positive as the current increases, as the entropic heat scales linearly with current whilst enthalpic heat scales by the square of current [156,230,231]. It should also be mentioned that a negative peak which arises from dominating entropic heat absorption flips positive when the direction of the current is changed as the endothermic reaction will become exothermic in a reverse reaction.

For LFP cells it is likely that the peak changes are specific to the graphite anode, as the LFP cathode undergoes a single continuous phase transition throughout the entire charge/discharge [106]. DTV is carried out at 10 A (0.5 C) and 40 A (2 C) constant current charge/discharge between 3.65 V and 2.0 V at approximately 20 °C. 0.5 C and 2 C are chosen in this work to represent slow and fast charging applications. Ideally the current should not be lower than 0.5C to have measurable heat generation and no higher than 3C to avoid enthalpic heat masking the entropic heat generation.

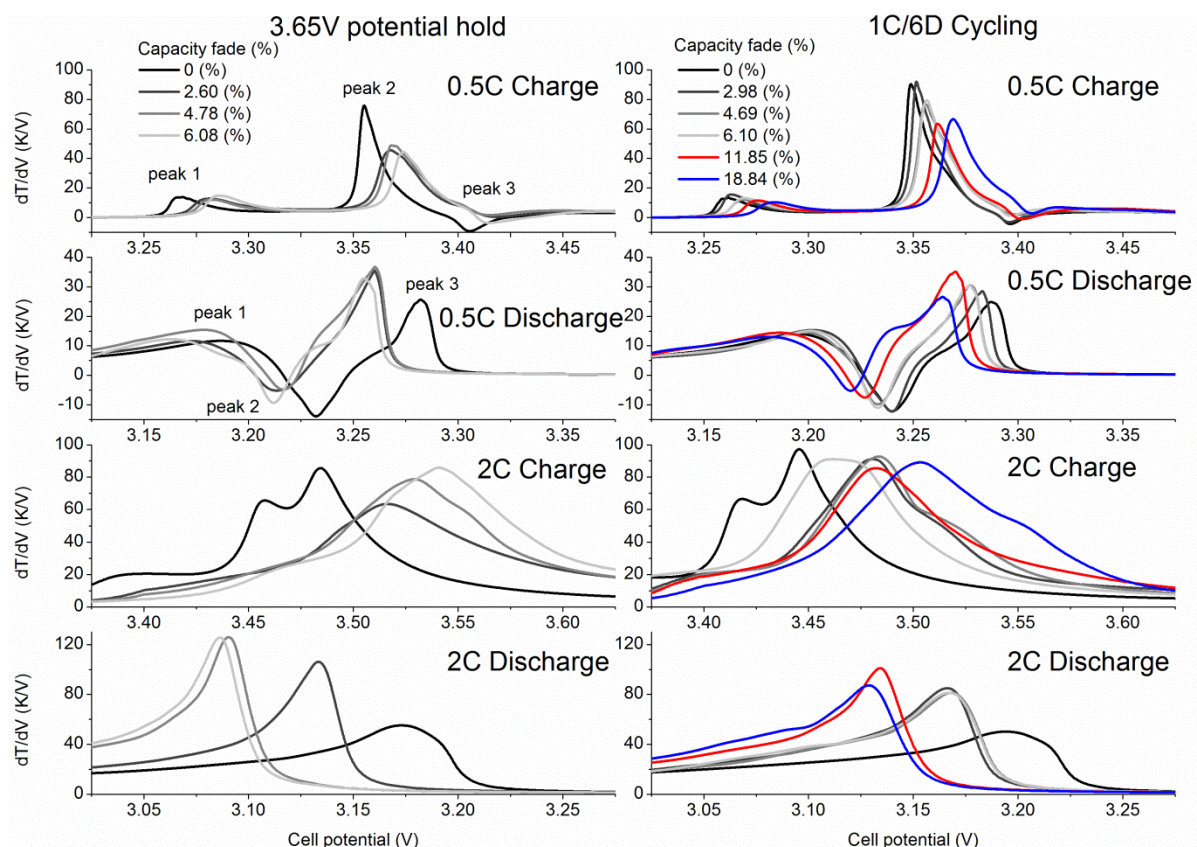


Figure 76. DTV results for the two cells at different C rates and various stages of the ageing process. Adapted from [11].

It can be seen that DTV at 0.5C generates curves with several peaks including a negative peak which comes from the endothermic entropic heat. As observed by peak 2 and 3, the negative peak, which arises from the dominating reversible heat absorption, flips positive in a reverse reaction.

On the other hand, DTV at 2C generates curves with just one maxima except for the fresh cell under charge. In this case, the several peaks which can be seen at 0.5 C merge at 2 C rate as concentration and thermal gradients combined with current heterogeneities can result in different regions of the cell undergoing transitions at different times, broadening the peaks leading to phase overlaps. This phenomenon is presented by Zinth et al. [18] who conducted an *in-situ* neutron diffraction experiment on a graphite anode of a lithium-ion battery during discharge followed by a relaxation phase. The illustration of this phase overlap phenomenon is presented in Figure 77. Notice the increased phase overlaps for the high current scenario.

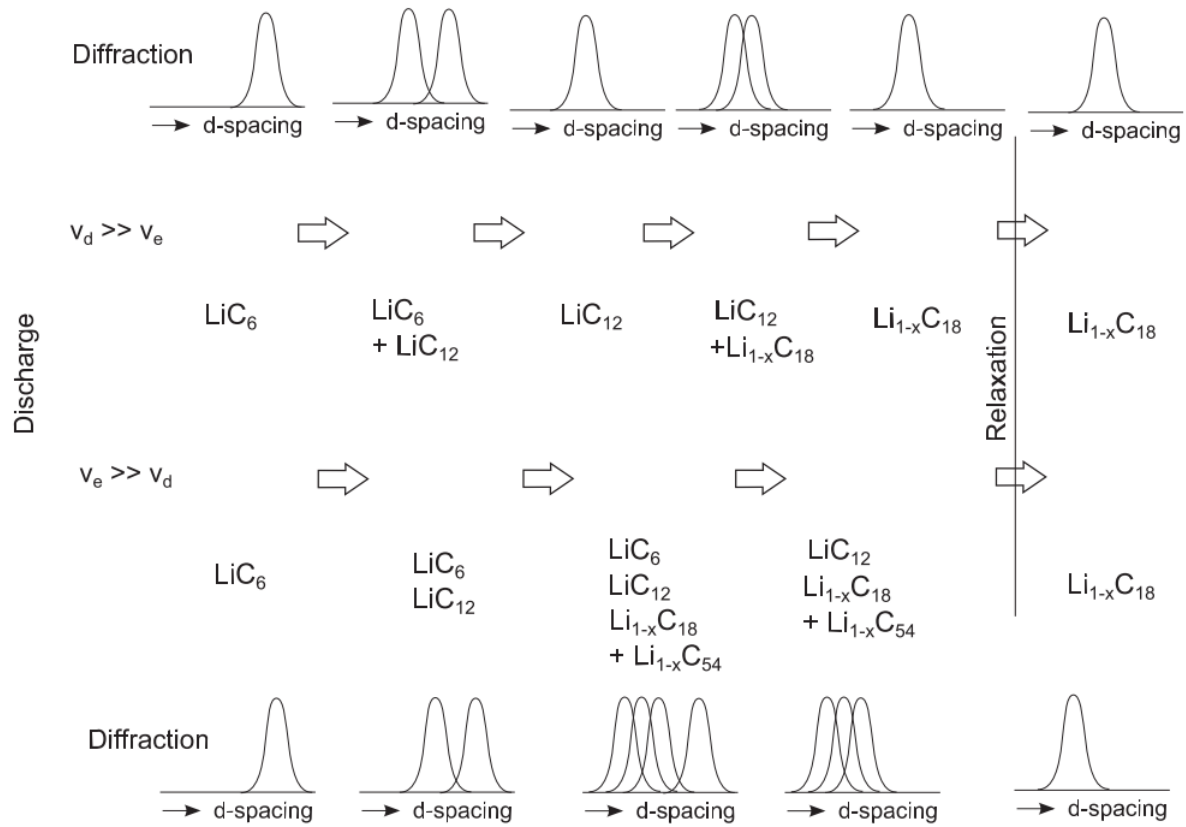


Figure 77. Illustration of lithium-intercalated graphite phase distributions during a cell discharge followed by a relaxation phase. Top half represents a scenario where the lithium diffusion (v_d) is much faster than the rate of extraction (v_e) i.e. low current. Bottom half represents the opposite case where $v_e \gg v_d$ i.e. high current. Source: [18].

It can be noted that the peak position shifts towards higher potential at charge and lower potential at discharge as the cell ages. This is due to the greater overpotential as a result of the increasing internal resistance caused by degradation. These results match with the increase in the internal resistance calculated by the OCV extrapolation method. The term overpotential is used in this thesis to describe the difference in the observed voltage from the thermodynamic potential of the cell.

For a real in-operando diagnostic technique a full spectra analysis is unlikely to be possible or necessary. Instead is desirable to determine and analyse peak parameters, and then compare how simple measures such as peak height, position or width correlate with degradation. Figure 78 and Figure 79 show the evolution of the peak parameters for the largest positive peak for the

two cells at different C rates under both charge/discharge. The peak parameters are calculated using the faster, less computationally intensive peak fitting algorithm introduced in 0.

The largest positive peak is chosen as it has the clearest and most consistent shift. In this case, the tracked peak represents graphite anode phase $\text{Li}_{0.5}\text{C}_6$ for charge and LiC_6 for discharge (note that the LFP cathode goes under a continuous phase transition throughout the charge/discharge cycle as mentioned earlier). It can be said that DTV peak parameters could be tracked and fitted to models and theory in the same way as ICA, as reported by Berecibar et al. [188].

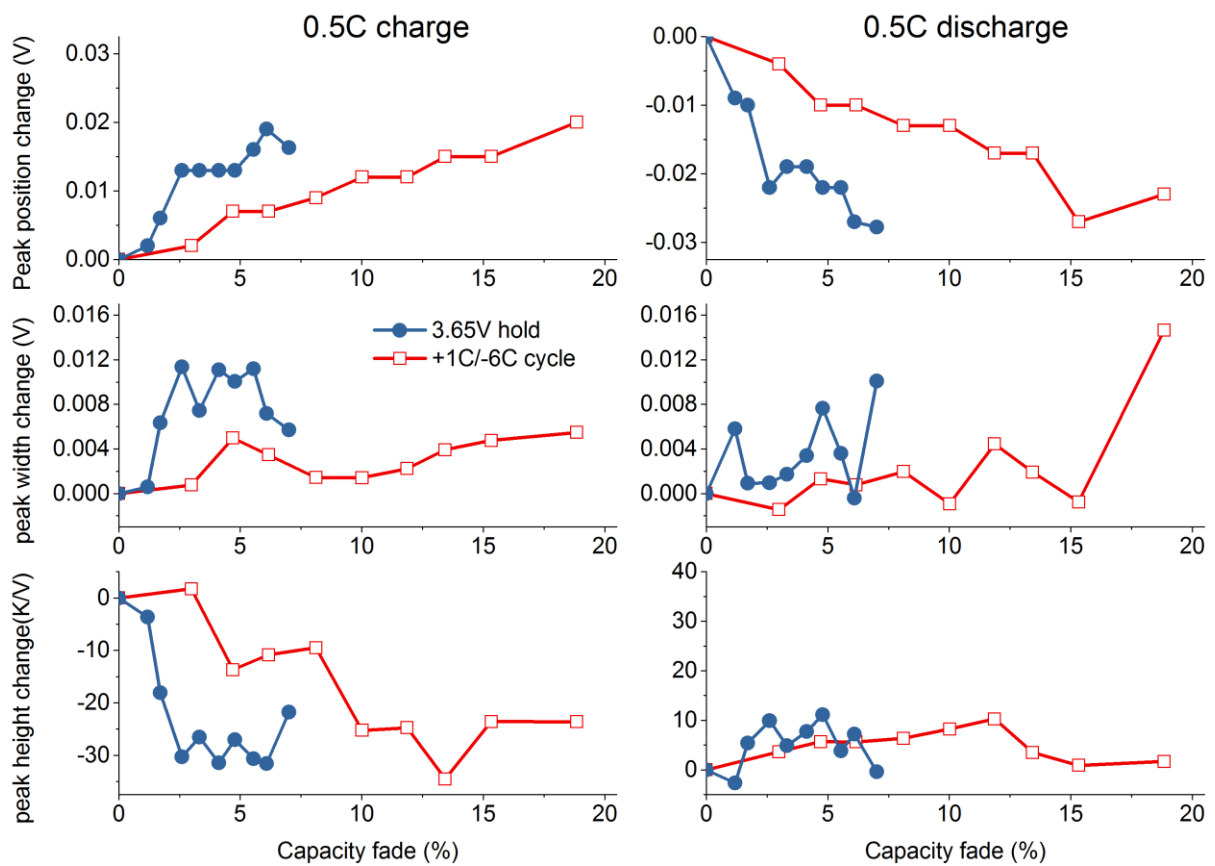


Figure 78. Peak parameters measured at 0.5C and 0.5D at approximately 20 °C at various stages of the ageing process.

Adapted from [11].

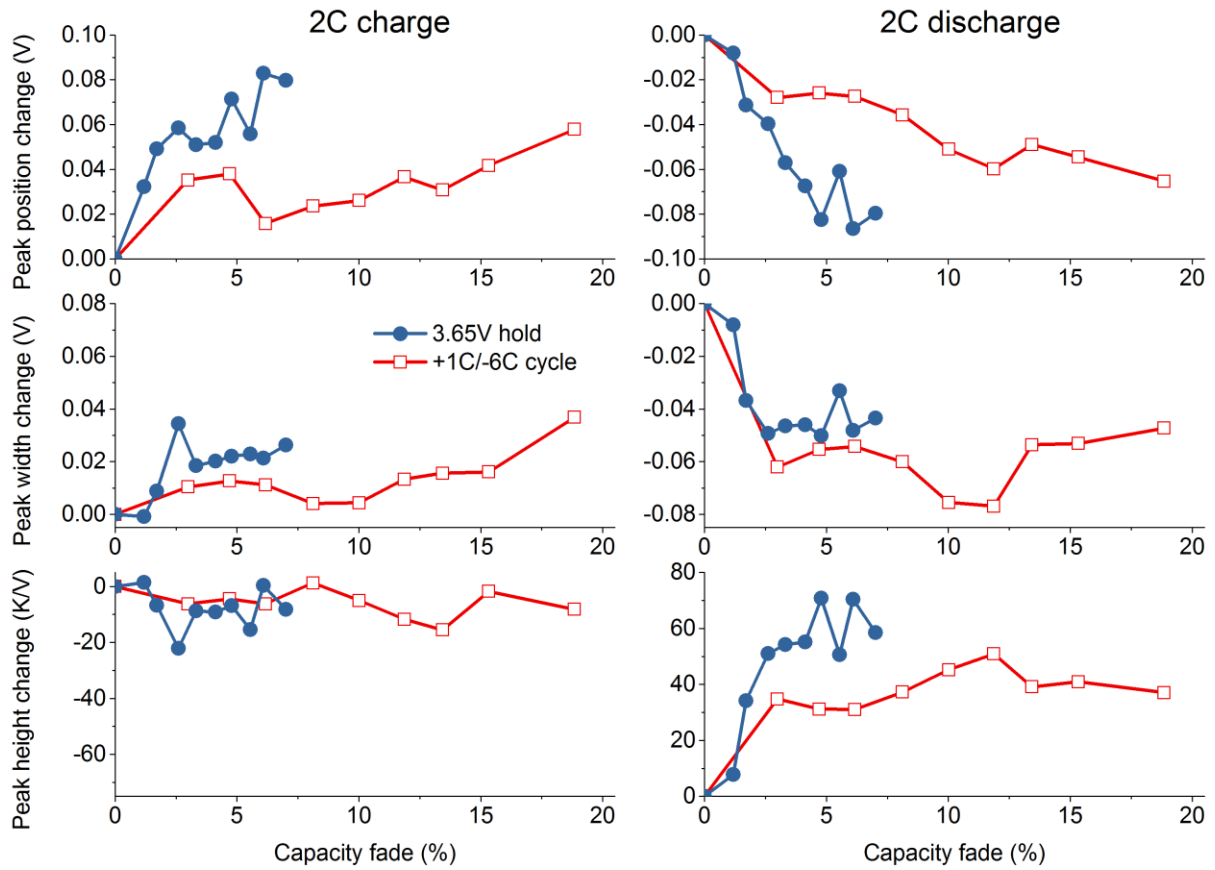


Figure 79. Peak parameter evolutions measured at 2C and 2D at approximately 20 °C at various stages of the ageing process. Adapted from [11].

The peak positions show a steady shift to higher/lower potentials which can be explained by the greater overpotential of the cells during charge/discharge due to the increasing cell impedance which is consistent with the internal resistance results shown in Figure 75.

As mentioned previously, the peaks broaden and can overlap as a result of concentration and thermal gradients within the electrode. It is discussed that this phase overlap increases as the lithium diffusion fails to keep up with the rate of lithium extraction. Degradation in diffusion resistances and reaction kinetics can enhance this phenomenon. Increase in peak width as seen during charging DTV, provides indication of this aging process in both cells. As the area underneath a peak correlates to the power capacity (or how much heat is generated) within the combined electrode phases, the height of such peaks are in turn seen to change.

It is observed that the cell held at 3.65V experiences a faster rate of increase in its diffusion resistance compared to the cycled cell for a particular capacity loss. This result matches with the capacity loss and total impedance measurements which suggested that the power fade in this cell is faster for a given capacity fade. DTV now suggests that this power fade is a result of slower lithium diffusion. The hypothesis for the degradation mechanism can now be narrowed down to mechanisms that slow down lithium diffusion in the solid phase; increases the lithium concentration gradient within the electrode; does not consume as much lithium inventory and/or active materials compared to SEI layer growth through cycling; and occurs by holding the cell at a high potential. Given the clues, it can be hypothesised that the cell has experienced a possible combination of electrode structural disordering, current collector corrosion, oxidation of conductive agents and/or binder decomposition as well as electrolyte decomposition from high temperature & voltage storage.

Increasing peak heights can be considered to be due to the increase in resistance, generating more heat. As the peak width is measured at its half-height, such peaks narrow as the cell degrades. It can be inferred from this result that there may be a greater concentration gradient in the electrodes during a charge process and that more entropic heat is generated during a discharge process. This suggests that lithium diffusion is slower during charge which correlates to the rate capabilities of the LFP cell as provided by the cell manufacturer who recommends 60 A as a maximum continuous charge current at 25°C and 200 A for discharge [232]. The different patterns in behaviour during charge and discharge demonstrate that different information can be inferred from each loading.

The cycled cell sees a narrower peak width compared to the high potential hold cell as well as an increasing peak height. This suggests that there has been an increase in the higher frequency impedance without a significant increase in lithium diffusion resistance hence concentration gradient. As the cell was cycled, this degradation can be predominantly attributed to SEI layer growth which matches the finding of the NCM cycled cell using the same anode chemistry [9].

Upon 2C, the peak heights are observed to be more positive as the enthalpic heat generation dominates. For 2C discharging, the entropic heat from peak 2 is positive and hence the increase in enthalpic heat as the cell resistance increases is far more apparent, hence the peak height increases as the cell ages. These results correlate well with the increase in internal resistance. Thus, at 2C, the peak position and peak height are both strongly correlated to increasing resistance. This conclusion is also consistent with the conclusions from Chapter 3 [9].

6.4.4. COMPARING CAPACITY FADE TO PEAK PARAMETERS

Berecibar et al. [188] reported that phase transitions could be used as markers for SOC during the charge/discharge curves for LFP and that it was therefore possible to diagnose SOH for partial cycles. In order to test if this is possible for DTV, the peak-to-peak capacity is compared against total capacity for the charge and discharge at 0.5C as shown in Figure 80, and the relative decrease in peak-to-peak capacity compared to total capacity is shown in Figure 81.

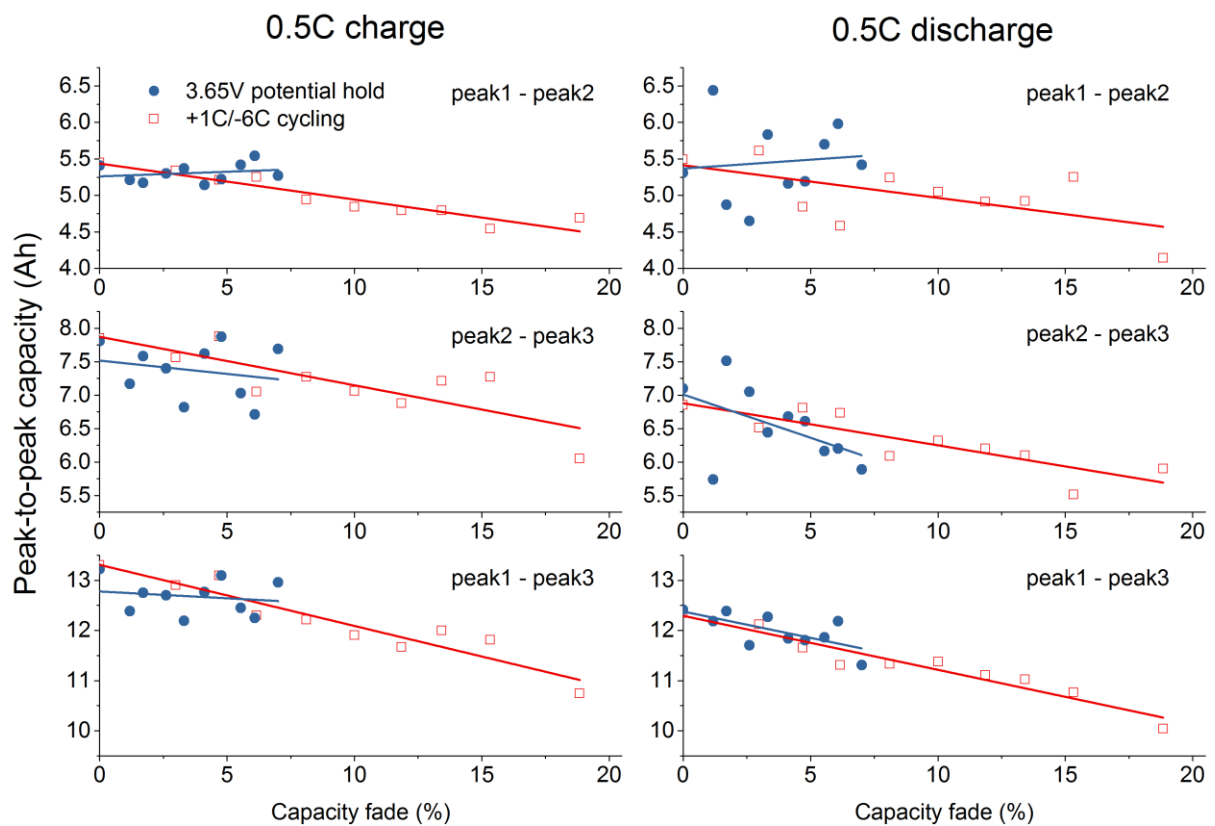


Figure 80. Peak-to-peak capacity compared to total capacity at 0.5C charge and discharge at approximately 20 °C at various stages of the ageing process. Adapted from [11].

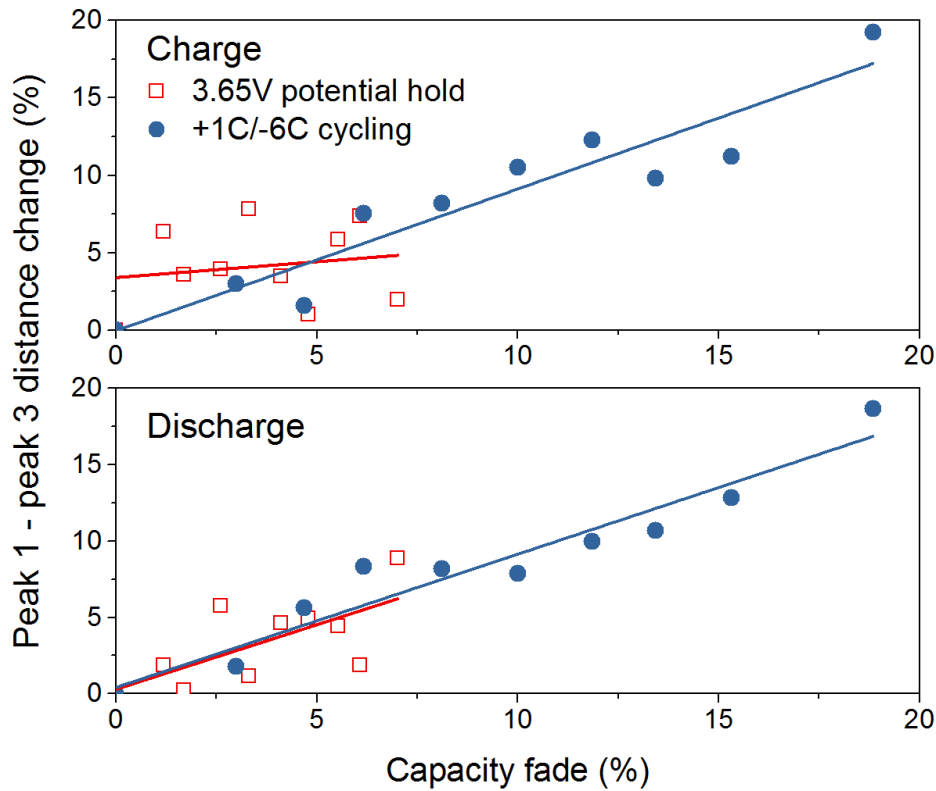


Figure 81. Relative change in peak-to-peak capacity compared to relative change in total capacity at 0.5C charge and discharge at approximately 20 °C at various stages of the ageing process. Adapted from [11].

It can clearly be seen that there is a direct correlation between the peak-to-peak capacity and total capacity for the cycled cell, suggesting that the peak position parameter could be used for SOH diagnosis in an application. There is a weaker correlation for the cell held at high potential during charge DTV, the result appears too noisy to infer significant information. Given the results, it is suggested to use a 0.5C discharge from 3.30V to 3.15V avoiding the necessity to charge/discharge to the cell extremes.

6.5. INTERIM CONCLUSION

Lithium iron phosphate batteries were aged in two ways, by holding at a high potential corresponding to 100% SOC and cycling at +1C/-6C at elevated temperature of 45 °C. In both cases, DTV was capable of diagnosing degradation in a similar way to ICA. It was possible to directly correlate peak parameters with capacity fade, resistance increase and inhomogeneous

electrode performance suggesting that the technique could be used for SOH estimation in real applications of LFP batteries.

The cycled cell had experienced SEI layer growth due to continuous cycling similar to the NCM cell in Chapter 3. The cell held at 3.65V on the other hand was seen to have had less capacity loss but more power fade and phase overlaps from concentration gradient. The hypothesis is that the cell had experienced a combination of degradation mechanisms that slows lithium diffusion without consuming as much lithium inventory and/or active material as the cycling cell. The lack of accelerating degradation as opposed to the NCM cell may be due to the difference in the cathode material. The absence of manganese in LFP prevents metal dissolution and subsequent deposition on the anode surface.

In this work, the cells were analysed using DTV at 0.5 C and 2 C to emulate slow and fast charging applications. Useful information was obtained from both currents however a significant phase overlap was observed at 2 C due to the increased concentration gradient as the lithium diffusion is slower than the rate of lithium extraction.

DTV analysis was carried out at both charge and discharge to see if there was any difference in the diagnosis which is of particular interest for LFP cells due to the presence of voltage hysteresis. It was observed that there are increased phase overlaps during charge which suggests that lithium diffusion is slower during charge than discharge. This result matches with the rate capabilities of the LFP cell where the maximum charge/discharge continuous current at 25°C is 60 A/200 A respectively.

There was good correlation between the peak-to-peak capacity and total capacity fade for the cell cycled at elevated temperature, suggesting that complete charge or discharge (i.e. returning close to 100% or 0% outside the hysteresis region) would not be necessary to estimate SOC or SOH for cells used in this way. The results suggest that a 0.5 C discharge between 3.30V and 3.15V is optimal for capacity estimation.

FUTURE WORKS

The introduction and development of the DTV technique demonstrated several on-board applications such as for SOH diagnosis, failure prognosis, adaptive operation and SOH estimation. This research hopes to lead into further works to validate and/or optimise its existing applications as well as introducing new ones.

Given the limited timeframe of a PhD, there were a few concepts that were partially explored which should be of interest to continue:

- Extending cell lifetime by adaptive operation based on DTV results should be explored further. Potentially repeat experiment with lithium plating by cycling the cell in a cold environment ($\sim 5^{\circ}\text{C}$) for rapid stoichiometric drift.
- Spatial degradation and its DTV diagnosis capabilities using multiple thermocouples or imaging camera on a single cell. The cell should be placed in a controlled ageing condition which would stress certain regions of the cell differently such as using Peltier elements to induce a thermal gradient across the electrode surface.

There are also a number of other upcoming/ongoing research carried out by other members of the group to explore new applications:

- Implementation of DTV on an in-house battery pack to demonstrate its use in a BMS. The DTV algorithm has successfully been installed on a Raspberry Pi unit attached to a battery pack made by our research team.
- Use of DTV on non-intercalation chemistries such as lithium-sulphur cells.
- Use of DTV on other energy storage devices such as lithium-ion capacitors.
- Using DTV to diagnose cells under micro-cycling and subsequent adaptive operation to maximise cell lifetime while maintaining energy throughput.

- Combination of DTV with a thermally coupled model to simulate DTV results under various cell conditions.

Advancements in all areas should greatly increase the value in the diagnosis/prognosis technique bringing more opportunities for not only academic but also commercial applications.

CONCLUSION

In anticipation of future demand for higher battery performance and lower costs, a novel *in-situ* diagnosis method called differential thermal voltammetry (DTV) has been presented. The literature review demonstrated a clear gap and demand for a diagnosis technique suitable for on-board application which is capable of identifying more than just the conventional capacity and power fade. The unique benefit of DTV is that it has a low computational requirement and only needs voltage and surface temperature measurements to carry out a detailed SOH characterisation. This suggests that the technique can be installed at a low cost with minimal additional hardware and/or software capabilities making it application ready.

The DTV concept was first validated on a cell level through an accelerated ageing experiment carried out on commercial lithium-ion pouch cells (graphite – NCM). The cells were stored at 55°C inside an incubator. One cell was cycled at 1 C and the other held at 100% SOC (4.2 V). Characterisation tests were carried out regularly to track the SOH evolution of the cells. DTV results provided cell information as good as SRCV and ICA with the added information from the entropic heat generation. It is said that each DTV peak plotted against the cell voltage represents a combination of phases from the positive and the negative electrode. Tracking the evolution of the peak parameters such as position, height and width allows for an in-depth analysis of the internal state of the battery. When the cycled cell and the high potential hold cell looked identical in terms of capacity fade, which is the industrial standard measurement of SOH, DTV was able to tell the difference in degradation. DTV determined that one cell has aged differently from the other and that one cell is more likely to fail earlier than the other which can be a critical information for safety.

DTV was then used to diagnose two cells of unknown degradation history to test its capability as a screening tool for 2nd life batteries. Results identified that one cell has aged significantly in a

similar manner to the cell held at high potential in the previous experiment suggesting that it should not be operated at high potentials to minimise rapid degradation through cathode overcharge.

Market research showed that the majority of the global lithium-ion battery capacity is going to be used in EV applications within the next decade. This suggests that a battery diagnosis method has be easily up-scaled to pack application with minimal costs. A parallel battery pack was made from four commercial lithium-ion cells where one of them was aged prior to the experiment in a controlled environment. DTV was carried out on the pack, that is to say on all four cells simultaneously, under forced air convection to emulate real world application with a thermal management system. The technique correctly and quantitatively identified the aged cell within the parallel pack under both charge and discharge validating its use in a pack on-board a BMS. It is to be noted that ICA (dQ/dV) was unable to identify the aged cell in this case as the voltage across each cell was the same and individual cell current would not typically be measured due to high costs. Even if current was used the aged cell was harder to diagnose using ICA than DTV. It was also demonstrated through this experiment that the presence of an aged cell in a parallel pack does not lower the performance of the other fresh cells in terms of useable capacity however it does increase the peak current on all cells accelerating degradation. Hence it is important to identify such aged cells as soon as possible to adapt their operation or replace the cells.

The prognosis capability of the DTV technique was tested through an industrial collaboration. DTV was carried out on high-power battery packs used in a motorsport application. The packs had suffered from cells failing unexpectedly in a particular manner after a certain number of drive cycles. The aim was to predict which cell(s) are likely to fail from charging cycles before the actual failure. By measuring the outliers in DTV peak position, degradation factors were determined per cell which successfully managed to forecast cells that would fail in the next few

drive cycles. This work demonstrated and validated the use of the technique as a prognosis for failure mitigation in a commercial BMS.

In order to decouple the overpotential and stoichiometric drift information from the DTV peak analysis, an in-operando OCV estimation technique was developed. The pulse loading profile was based on GITT but with a few seconds of rest rather than hours to wait for complete equilibrium. The OCV is extrapolated from the short voltage response data of the relaxation phase by fitting a 2nd order power equation. The method proved to be accurate to 5mV for both fresh and aged cells at 1C. This OCV extrapolation technique allows DTV to be carried out while estimating the OCV simultaneously.

Using the new OCV-based DTV technique, another accelerated ageing experiment was carried out where some cells were adaptively operated depending on the DTV results in aims of extending cell lifetime and slowing down degradation. The cells were aged by cycling or holding at 100% SOC. Each ageing condition had a cell with and without adaptive operation. The concept was to quantitatively measure the stoichiometric drift of the cell through DTV diagnosis and periodically de-rate the upper operational voltage limit by that amount to minimise cathode overcharge which leads to further stoichiometric drift. For the cycled cell, the adaptive de-rating was seen to slow down the shift in electrode stoichiometry. The cell held at 100% SOC did not demonstrate any visible benefit of the adaptive derating. It was hypothesised that the stoichiometric drift may have been cancelled out by the two dominating degradation mechanisms shifting the electrode stoichiometry in opposite directions.

The application of the DTV technique was extended to LFP cells to demonstrate its use in other intercalation chemistries. Accelerated ageing experiments were carried out while tracking the SOH through the OCV-based DTV. Despite using similar ageing conditions to the first NCM experiment, the cells showed different ageing processes specific to the chemistry. DTV demonstrated the ability to diagnose the different performances of the cell under charge vs. discharge. Finally, the DTV peak positions were used as SOC markers and its use as a SOH

estimator was validated. The estimation allowed the DTV to correlate the total capacity fade of the cell from a partial charge/discharge without going to the voltage extremes.

Overall, this collection of research works has expanded the understanding of lithium-ion batteries in terms of how they degrade depending on ageing conditions and what is to be done to mitigate failure and accelerated degradation. DTV can grow as a SOH diagnosis/prognosis tool by continuing to expand this library of battery degradation. The research hopes to have presented a significant step forward in on-board characterisation technique for lithium-ion batteries and support the increasing demands in electric vehicles, grid-level energy storage and personal electronics.

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APPENDICES

A1. 5Ah NCM CELL TECHNICAL DETAILS

Table 13. Kokam NCM cell technical specification [233]

Brand Name	Kokam
Model Number	SLPB11543140H5
Type	Lithium Polymer
Size	142.5*43.5*11.7mm
Weight	132g
Form	Pouch
Nominal Voltage	3.7V
Nominal Capacity	5Ah
Max Charge	10A
Max Discharge	150A
Max Allowable Charge Voltage	4.2V
Storage Temp. Range	25 to 40°C for 3 months @ 50% SOC 40 to 60°C for a week @ 50% SOC
Operating Temp. Range	0 to 45°C charge -20 to 55°C discharge

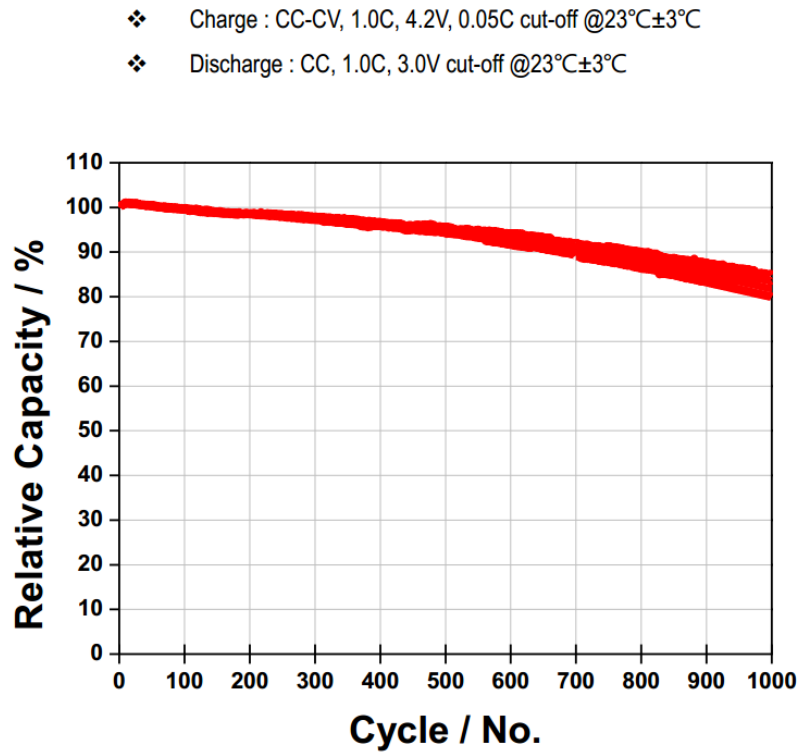


Figure 82. Kokam SLPB11543140H5 cycle characteristics [233].

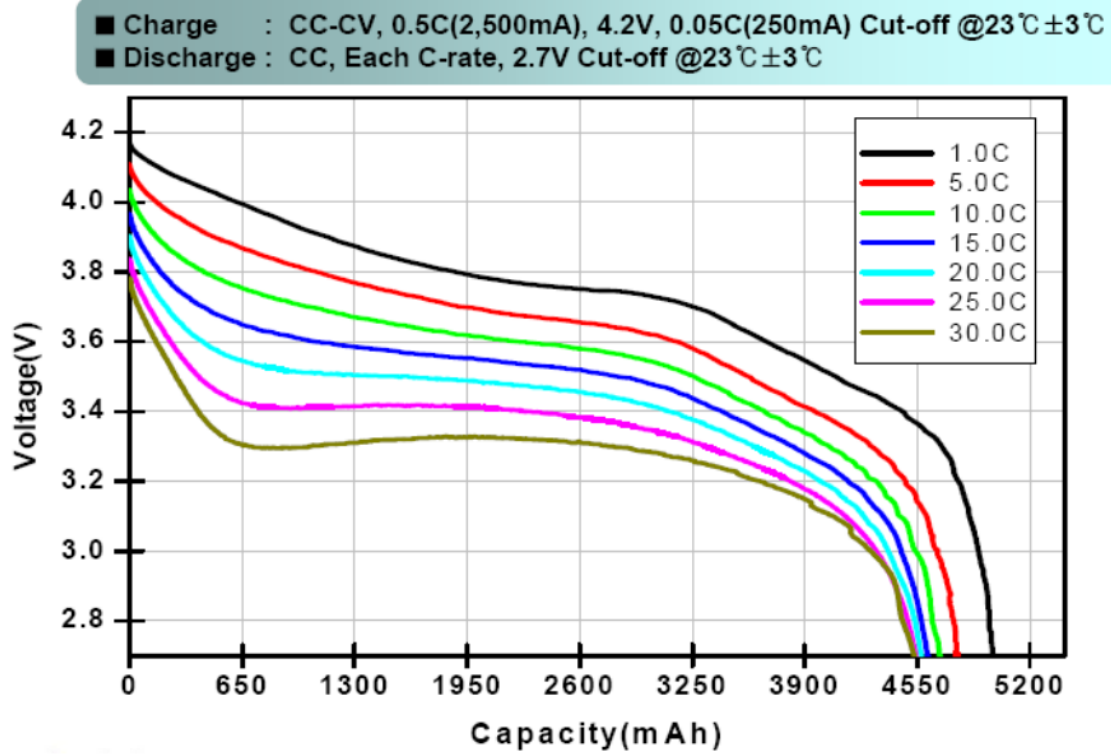


Figure 83. Kokam SLPB11543140H5 discharge curves [233].

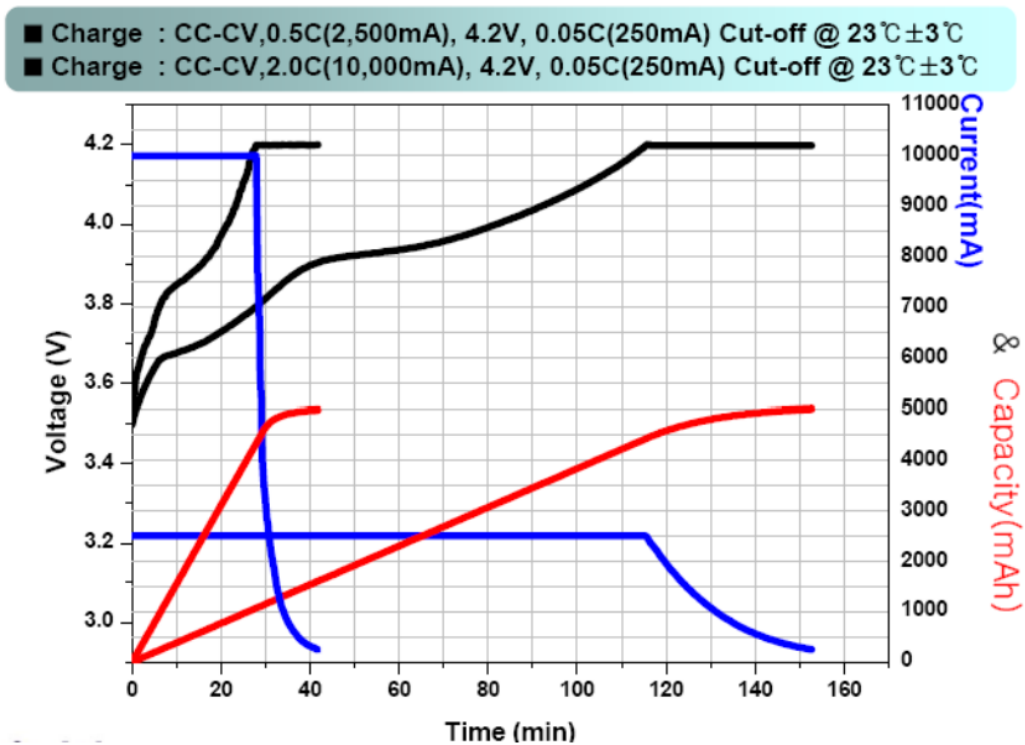


Figure 84. Kokam SLPB11543140H5 charge characteristics [233].

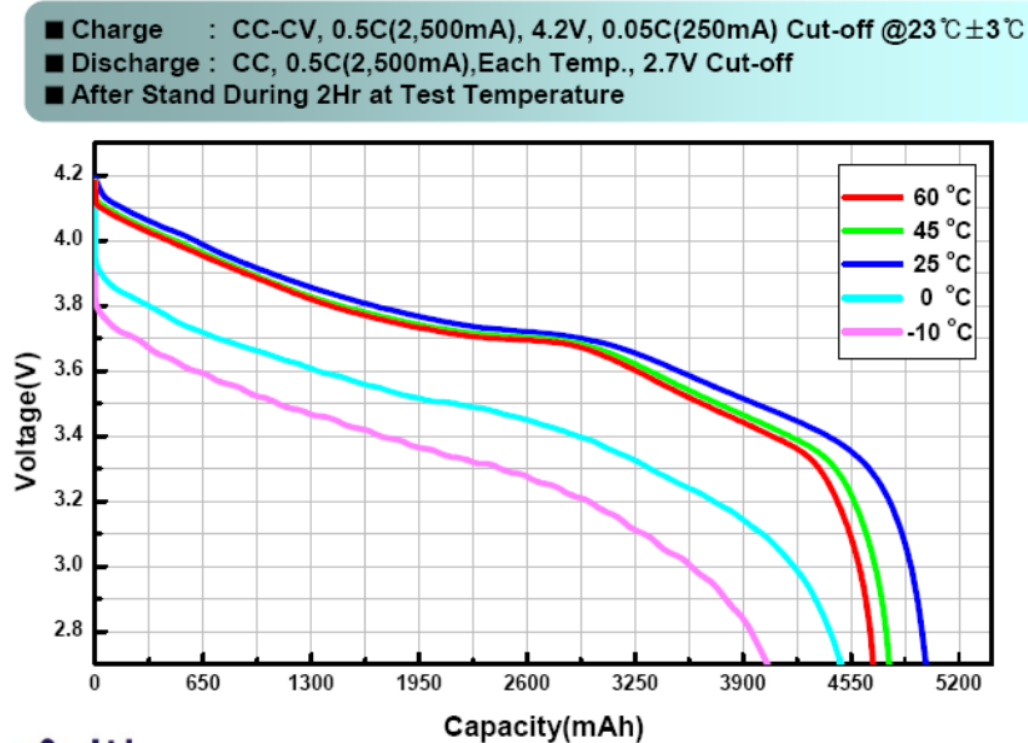


Figure 85. Kokam SLPB11543140H5 discharge characteristics for various operating temperatures [233].

A2. ACCELERATED AGEING EXPERIMENT TEST PROCEDURES FOR NCM CELLS

APPARATUS:

Name	Quantity	Purpose
Kokam 5Ah cell	3	
Maccor	1	Loading; measurements; data logging
Bio-Logic	1	EIS; measurements; data logging
Incubator	1	Storage temperature control
Fire-resistant tiles	2	Fire protection
T-type thermocouples	16	T measurement
Insulated cell box	1	Electrical insulation; ambient storage
Kapton tape	As appropriate	Thermocouple fixture
Test leads	As appropriate	Electrical connection

PREPARATION:

- Acquire all appropriate apparatus.
- Prepare all electrical connections and measurement devices.
- Write load cycles, data logging and various test procedure for Maccor (load cycle, SRCV, DTV) and potentiostat (EIS)
- Test all procedures on a used cell, during the day, to ensure it is safe, before starting full overnight testing
- Prepare containment & extraction measures for cell venting/fire.

PROCEDURE:

1. Prepare cables.
2. Place 2 Kokam cells in the incubator and 1 in the insulated box. Cells inside the incubator should be placed on fire-resistant ceramic plates.

3. Attach sense and working electrodes on the Kokam cells. Place sense electrodes closer to cell.
4. Attach thermocouples to each Kokam cells with Kapton tape.
5. Connect the cells to Biologic.
6. Run EIS. See below for details. EIS is to check where the degradation correlates to.
7. Connect the cells to Maccor.
8. Take capacity measurement. This process includes DTV. See below for details.
9. Run SRCV. See below for details.
10. Heat incubator to 55°C.
11. Wait 10 mins after cell surface temperatures reach 55 °C.
12. Run appropriate load cycles. See below.
13. After 50 cycles, turn incubator off; open door.
14. Wait 10 mins after cell surface temperatures reach ambient.
15. Repeat from step 6 until cells have degraded to 75% of its original capacity.

LOAD CYCLE DETAILS

Cell No.	1	2	3
C-rate	0	1	1
Current, I (A)	0	5	5
Voltage (V)	4.2V constant [110,111]	4.2V to 3.0V	4.2V to 3.0V
Temperature	55 °C	55 °C	Room
Charge	n.a. (CV @ 4.2V)	CC at 5A; 4.2V cut-off; CV at 4.2V; Cut-off at I<0.25A Rest for 20 mins	CC at 5A; 4.2V cut-off; CV at 4.2V Cut-off at I<0.25A Rest for 20 mins

Discharge	n.a.	CC at 5A; 3.0V cut-off Rest for 20 mins	CC at 5A; 3.0V cut-off Rest for 20 mins
Cut-off Temp.	60 °C	60 °C	60 °C
Estimated total time (hr)	n.a.	3	3
Cycles per 24 hrs	n.a.	8	8
Days per 50 cycles	n.a.	6.25	6.25

- Turn off incubator/load cycles Friday morning. Cool down. Run all characterisation tests at ambient.
- Turn on incubator/load cycles Friday night.
- Leave equipment on during weekend.
- Expected ageing after 7 weeks:
 - approx 20-25% capacity fade for cell 1 [110,234]
 - approx 10-18% or capacity fade for cell 2 [110,235]
 - approx 2-4% capacity fade for cell 3 [235]

CAPACITY MEASUREMENT (SOH) + DTV SPECIFICATION

Temperature	All cells at room temperature
Starting SOC	100%. CC at 10A; 4.2V cut-off; CV at 4.2V; Cut-off at I < 0.25A; Rest for 30 mins
CC discharge	4.2V to 2.7V at 10A (2C) & 7.5A (1.5C) & 5A (1C).

SRCV SPECIFICATION

Temperature	All cells at room temperature
Starting SOC	100%. CC at 10A; 4.2V cut-off; CV at 4.2V; Cut-off at $I < 0.25A$; Rest for 30 mins
Voltage Ramp Rate	150 μ V/s
Upper/ Start Voltage	4.2V
Lower/ End Voltage	2.7V
No. of Crossing	1

EIS SPECIFICATION

Temperature	All cells at room temperature
Static CC Discharge Offset	5A; 4.2V start; 2.8V cut-off; Galvanostatic EIS every 3minutes
Mode	Galvanostatic (GEIS)
Frequency Range	2kHz to 1Hz
No. of points	6 points per decade
N_a	3 average measures per frequency
Amplitude	0.2A rms
Wave	Single sine
Step Increment	Log

A3. 25AH NCM CELL TECHNICAL DETAILS

Table 14. Kokam model SLPB60216216 general information [236].

Item	Value	Remark
-------------	--------------	---------------

Rated Capacity	Typ. 25.0Ah Min. 24.0Ah	Charge@0.2C(5A) Discharge@0.5C(12.5A)
Nominal Voltage	3.7V	
End of Discharge	3.0V	
Max. Charge Voltage	4.15 ±0.03V	
Max. Conti. Charge Current	50A	CC-CV charging is required End Condition: 0.05C(1.25A) or 5Hr Temperature: 23±3°C
Max. Conti. Discharge Current	125A	
Operation Temperature Range	Charge: 10 ~ 45°C Discharge: -10 ~ 55°C	@60±25% R.H.
Storage Temperature Range	1 YEAR 20 ~ 25°C 3 MONTH 25 ~ 40°C 1 WEEK 40 ~ 60°C	@60±25% R.H. SOC 50 ±5%
Weight	Max. 560.0g	
Cell Dimension	Length: Max.222.0mm Width: Max.214.0mm Thickness: Max.6.2mm	Except for tab length Initial full charge

- ❖ Charge : CC-CV, 1.0C, 4.15V, 0.05C cut-off @23°C±2°C
- ❖ Discharge : CC, 1C, 3.0V cut-off @23°C±2°C

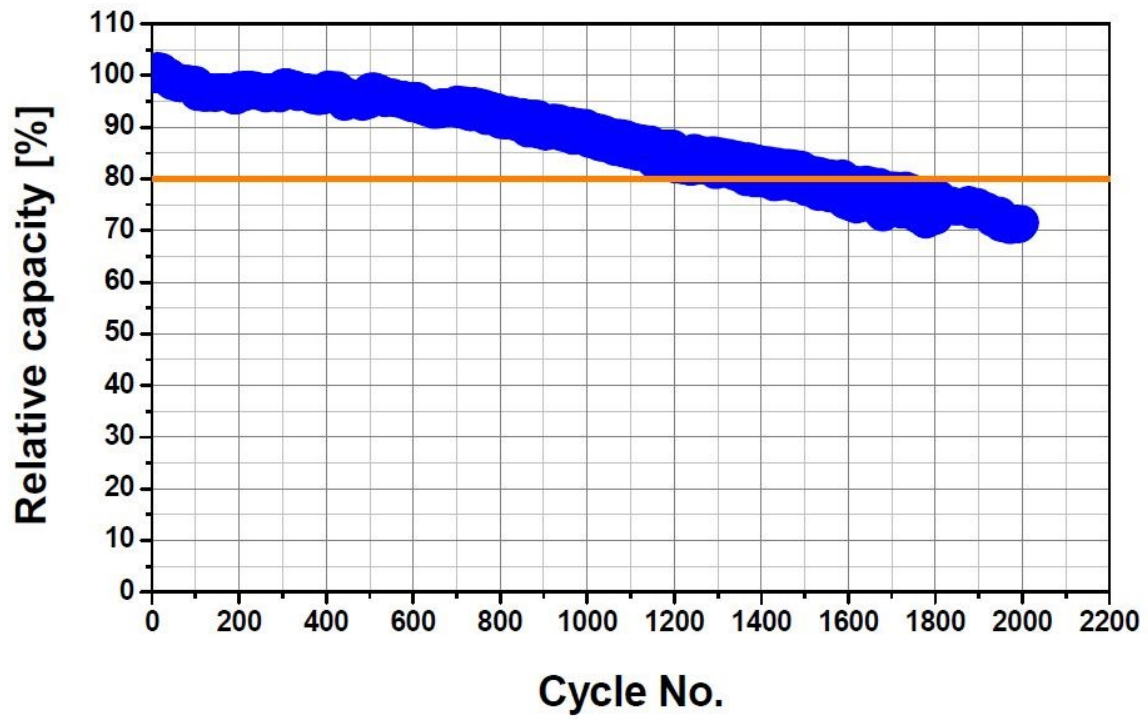


Figure 86. Kokam model SLPB60216216 cycle characteristics [236].

A4. PACK EXPERIMENT RESULTS FOR 0.5C SLOW CHARGE/DISCHARGE OPERATIONS

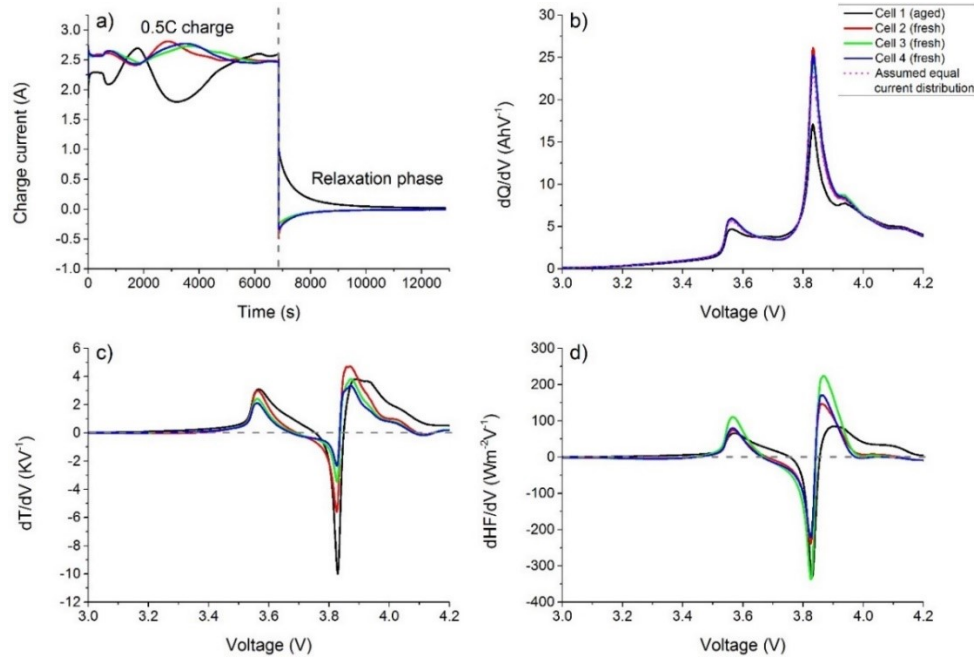


Figure 87. Pack analysis under 0.5C constant current charge. (a) Cell current. (b) Incremental capacity method. (c) Differential thermal voltammetry. (d) Differential heat flux voltammetry. Source: [10].

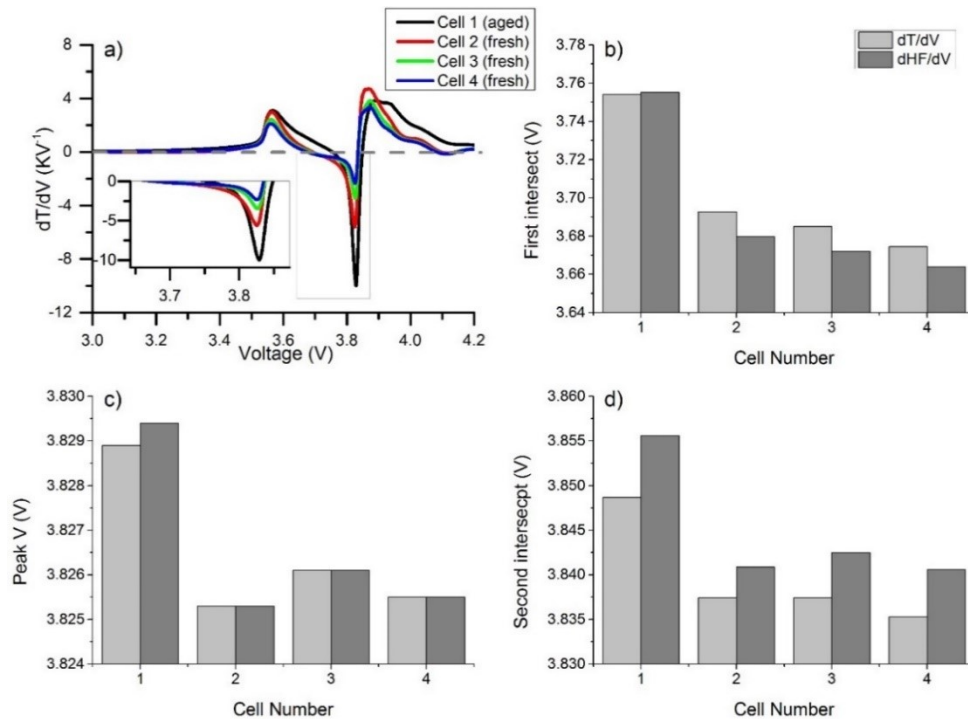


Figure 88. Peak analysis of differential thermal and heat flux voltammetry results for 0.5C constant current charge. (a) Zoomed in differential thermal voltammetry result. Starting potential (b), peak potential (c) and end potential (d) for the positive peak are shown here. Source: [10].

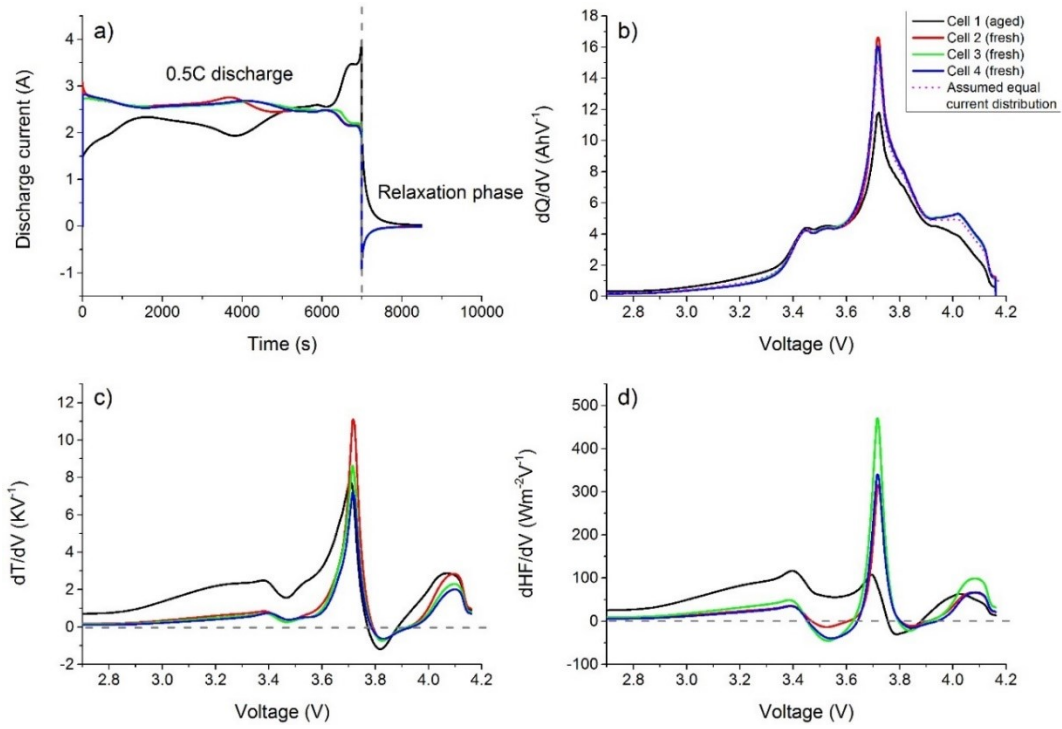


Figure 89. Pack analysis under 0.5C constant current discharge. (a) Cell current. (b) Incremental capacity method. (c) Differential thermal voltammetry. (d) Differential heat flux voltammetry. Source: [10].

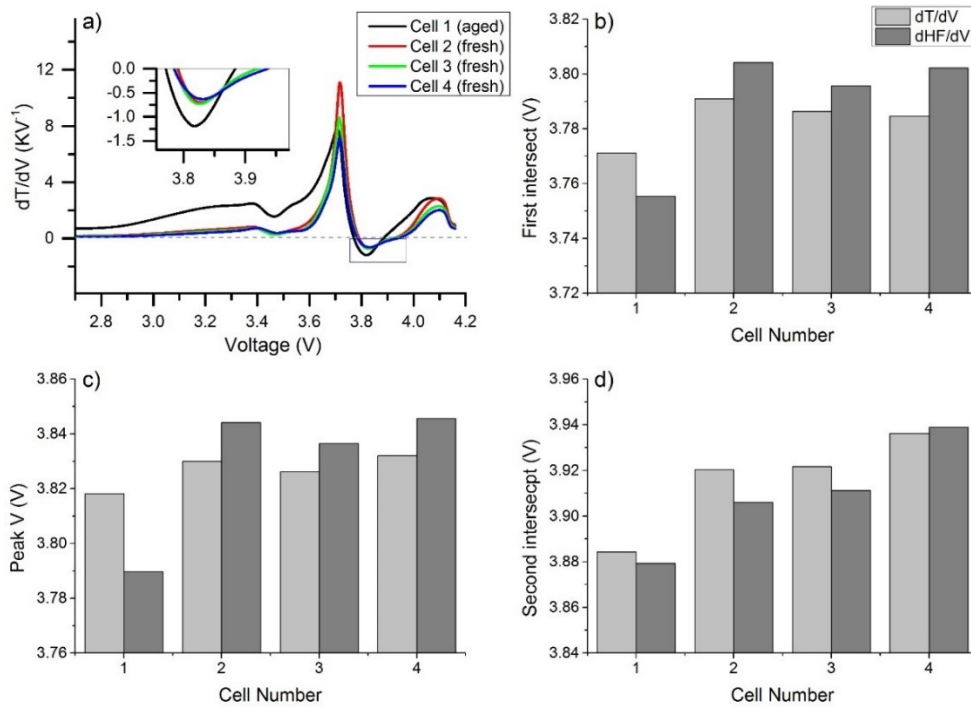


Figure 90. Peak analysis of differential thermal and heat flux voltammetry results for 0.5C constant current discharge. (a) Zoomed in differential thermal voltammetry result. Starting potential (b), peak potential (c) and end potential (d) for the positive peak are shown here. Source: [10].

A5. 20AH LFP CELL TECHNICAL DETAILS

Table 15. AMP20 cell specifications. Source: [232,237].

Cell Dimensions (mm)	7.25 x 160 x 227
Cell Weight (g)	496
Cell Capacity (minimum, Ah)	19.6
Energy Content (nominal, Wh)	65
Discharge Power (nominal, W)	1200
Voltage (nominal, V)	3.3
Specific Power (nominal, W/kg)	2400
Specific Energy (nominal, Wh/kg)	131
Energy Density (nominal, Wh/L)	247
Operating Temperature	-30°C to 55°C
Storage Temperature	-40°C to 60°C
Recommended maximum charge current	60A
Maximum discharge continuous current	200A
Pulse 10s discharge current	600A

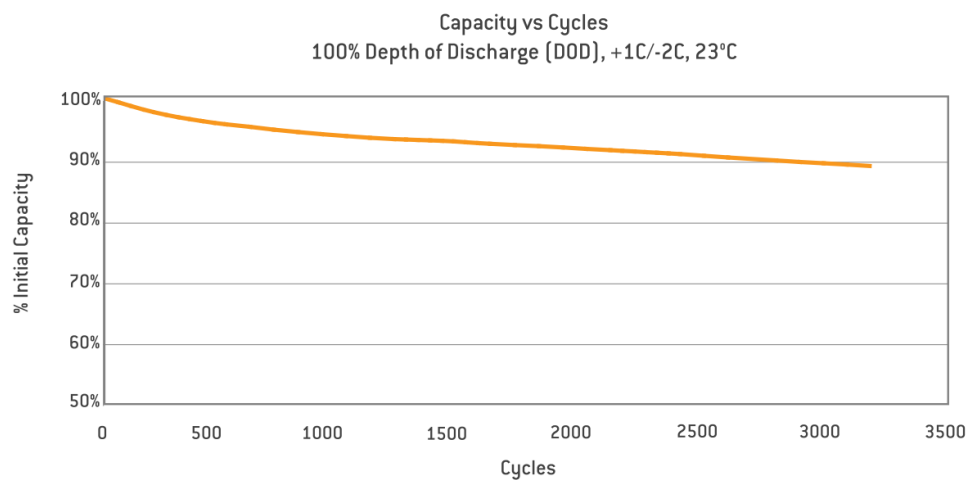


Figure 91. AMP20 cell cycle life specifications. Source: [237].