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A NUMERICAL AND EXPERIMENTAL ANALYSIS OF
BATTERY THERMAL RUNAWAY PHENOMENA TO
ENHANCE THE DEVELOPMENT OF HYBRID AND
ELECTRIC VEHICLES

Doctoral Thesis

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Valencia, May 2025

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Abstract

The effects of global warming are evident nowadays due to the increasing intensity of environmental catastrophes occurring worldwide. Clean and renewable energy sources are crucial for mitigating this phenomenon in order to reduce CO₂ emissions. In this context, lithium-ion batteries are essential as they can enhance energy storage systems by minimising intermittent energy production problems and spreading clean propulsion systems such as hybrid and electric powertrains.

However, batteries still face some drawbacks, such as limited energy density and the need for fast charging to ensure widespread applicability. Moreover, as advancements in energy density and fast charging are achieved, safety concerns regarding thermal issues that can lead to thermal runaway (TR) have been raised. For this reason, the present thesis focuses on understanding cell-to-cell variability by analysing heat release from both the main chain reactions and the entire cell using electrochemical modelling and optical techniques. A TR model is proposed to predict abuse thermal behaviour under different battery conditions. Batteries were electrically characterised and modelled using a P2D approach in both pristine and aged conditions, and their impact on vehicle range was studied. Using data from the model, the influence of different battery components was evaluated through stepwise reactions to predict thermal runaway behaviour.

The batteries were tested using an ARC system coupled with optical techniques under thermal and mechanical triggers to assess cell-to-cell variability through statistical analysis. Finally, a model was proposed based on battery behaviour, considering different inputs such as state of charge (SOC), state of health (SOH), and energy density. The results show that the final battery mass plays a significant role in determining the maximum surface temperature of the battery. A higher mass can store more energy and transfer heat through the battery casing. This effect explains why batteries with different SOC and SOH levels can reach similar temperatures. In the case of nail penetration as a trigger, lateral ruptures and local combustion

led to misleading temperature measurements, as demonstrated by the applied optical techniques and statistical analysis.

A model was developed based on the findings of this thesis, correctly predicting thermal runaway behaviour while accounting for different battery conditions and the mass trapped during the event. Additionally, the temperature rise rate at the onset temperature of the exothermic process needs to be considered as a model input. The reason is that it varies from the original settings, depending on the experimental setup constraints. The main effect of this parameter is to influence the duration of the thermal runaway process under adiabatic conditions.

Resumen

Los efectos del calentamiento global son evidentes hoy en día debido al aumento de la intensidad de las catástrofes ambientales que ocurren en todo el mundo. Las fuentes de energía limpias y renovables son fundamentales para mitigar este fenómeno y reducir las emisiones de CO_2 . En este contexto, las baterías de iones de litio son esenciales, ya que pueden mejorar los sistemas de almacenamiento de energía al minimizar los problemas de producción intermitente y promover sistemas de propulsión limpia, como los trenes motrices híbridos y eléctricos.

Sin embargo, las baterías aún presentan algunas limitaciones, como la densidad de energía limitada y la necesidad de carga rápida para garantizar su aplicación a gran escala. Además, a medida que se logran avances en densidad de energía y carga rápida, han surgido preocupaciones sobre la seguridad en relación con problemas térmicos que pueden derivar en fuga térmica (TR). Por esta razón, la presente tesis se centra en comprender la variabilidad entre celdas mediante el análisis de la liberación de calor tanto de las principales reacciones en cadena como de la celda en su conjunto, utilizando modelado electroquímico y técnicas ópticas. Se propone un modelo de TR para predecir el comportamiento térmico en condiciones de abuso bajo diferentes estados de la batería. Las baterías fueron caracterizadas eléctricamente y modeladas utilizando un enfoque P2D en condiciones tanto prístinas como envejecidas, y se estudió su impacto en la autonomía del vehículo. Con los datos del modelo, se evaluó la influencia de los diferentes componentes de la batería a través de reacciones escalonadas para predecir el comportamiento de la fuga térmica.

Las baterías fueron ensayadas en un sistema ARC acoplado con técnicas ópticas bajo activaciones térmicas y mecánicas para evaluar la variabilidad entre celdas mediante análisis estadístico. Finalmente, se propuso un modelo basado en el comportamiento de la batería, considerando diferentes parámetros de entrada, como el estado de carga (SOC), el estado de salud (SOH) y la densidad de energía. Los resultados muestran que la

masa final de la batería desempeña un papel significativo en la determinación de la temperatura máxima en la superficie de la batería. Una mayor masa puede almacenar más energía y transferir calor a través de la carcasa de la batería. Este efecto explica por qué baterías con diferentes niveles de SOC y SOH pueden alcanzar temperaturas similares. En el caso de la penetración por clavo como activación, las rupturas laterales y la combustión localizada llevaron a mediciones de temperatura engañosas, como se demostró mediante las técnicas ópticas y el análisis estadístico aplicados.

Se desarrolló un modelo basado en los resultados de esta tesis, que predice el comportamiento de la fuga térmica al considerar diferentes condiciones de la batería y la masa atrapada durante el evento. Además, se debe considerar como parámetro de entrada la velocidad de aumento de temperatura en la temperatura de inicio del proceso exotérmico, ya que varía respecto a los valores originales dependiendo de las limitaciones del sistema experimental. El principal efecto de este parámetro es influir en la duración del proceso de fuga térmica en condiciones adiabáticas.

Resum

Els efectes de l'escalfament global són evidents hui en dia a causa de la creixent intensitat de les catàstrofes ambientals que ocorren arreu del món. Les fonts d'energia netes i renovables són fonamentals per a mitigar aquest fenomen i reduir les emissions de CO₂. En aquest context, les bateries d'ions de liti són essencials, ja que poden millorar els sistemes d'emmagatzematge d'energia en minimitzar els problemes de producció intermitent i impulsar sistemes de propulsió neta, com els trens de potència híbrids i elèctrics.

Tanmateix, les bateries encara presenten algunes limitacions, com la densitat energètica limitada i la necessitat de càrrega ràpida per a garantir la seua aplicació a gran escala. A més, a mesura que s'aconsegueixen avanços en densitat energètica i càrrega ràpida, han sorgit preocupacions sobre la seguretat en relació amb problemes tèrmics que poden derivar en fuga tèrmica (TR). Per aquesta raó, la present tesi se centra a comprendre la variabilitat entre cel·les mitjançant l'anàlisi de l'alliberament de calor tant de les principals reaccions en cadena com de la cel·la en el seu conjunt, utilitzant modelatge electroquímic i tècniques òptiques. Es proposa un model de TR per a predir el comportament tèrmic en condicions d'abús sota diferents estats de la bateria. Les bateries van ser caracteritzades elèctricament i modelades utilitzant un enfocament P2D en condicions tant prístines com envellides, i es va estudiar el seu impacte en l'autonomia del vehicle. Amb les dades del model, es va avaluar la influència dels diferents components de la bateria a través de reaccions escalonades per a predir el comportament de la fuga tèrmica.

Les bateries van ser assajades en un sistema ARC acoblat amb tècniques òptiques sota activacions tèrmiques i mecàniques per a avaluar la variabilitat entre cel·les mitjançant anàlisi estadística. Finalment, es va proposar un model basat en el comportament de la bateria, considerant diferents paràmetres d'entrada, com l'estat de càrrega (SOC), l'estat de salut (SOH) i la densitat energètica. Els resultats mostren que la massa final de la bateria té un paper significatiu en la determinació de la temperatura màxima

en la superfície de la bateria. Una massa major pot emmagatzemar més energia i transferir calor a través de la carcassa de la bateria. Aquest efecte explica per què bateries amb diferents nivells de SOC i SOH poden assolir temperatures similars. En el cas de la penetració per clau com a activació, les ruptures laterals i la combustió localitzada van donar lloc a mesures de temperatura enganyoses, com es va demostrar mitjançant les tècniques òptiques i l'anàlisi estadística aplicades.

Es va desenvolupar un model basat en les troballes d'aquesta tesi, que prediu correctament el comportament de la fuga tèrmica en considerar diferents condicions de la bateria i la massa atrapada durant l'esdeveniment. A més, cal considerar com a paràmetre d'entrada la velocitat d'augment de temperatura en la temperatura d'inici del procés exotèrmic, ja que varia respecte als valors originals depenent de les limitacions del sistema experimental. L'efecte principal d'aquest paràmetre és influir en la duració del procés de fuga tèrmica en condicions adiabàtiques.

*A mi madre y a mi hermana
En memoria de mi padre y de mi hermano*

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Nomenclature

Latin

A	Transport property
a	Reaction surface area
ARC	Accelerating Rate Calorimeter
BEV	Battery Electric Vehicle
BTR	Battery Thermal Runaway
C	Capacitance
c	Molar concentration of lithium ions
CCCV	Constant-Current Constant-Voltage
CIV	Combustion Image Velocity
CO ₂	Carbon Dioxide
D	Diffusion coefficient
DFN	Doyle-Fuller-Newman Model
DoD	Depth of Discharge
DSC	Differential Scanning Calorimetry
E _a	Activation Energy
ECM	Equivalent Circuit Model
EV	Electric Vehicle
EVs	Electric Vehicles
f	Normalisation terms of error
F	Faraday's Constant
GA	Genetic Algorithm
GITT	Galvanostatic Intermittent Titration Technique
HEV	Hybrid Electric Vehicle
HWS	Heat-Wait-Seek

i	Exchange current
INR	Lithium-Ion Nickel Rechargeable
IR	Infrared
j	Reaction current
K	Conductivity of the electrolyte through the porous SEI layer
k	Ionic conductivity
LAM	Loss of Active Material
LBT	Arbin Laboratory Battery Testing
LCO	Lithium Cobalt Oxide
Li	Lithium
Li ⁺	Lithium-ion
LIB	Lithium-Ion Battery
LIBs	Lithium-Ion Batteries
LLI	Loss of Lithium Inventory
LMO	Lithium Manganese Oxide
LFP	Lithium Iron Phosphate
M	Molar mass
NCA	Nickel Cobalt Aluminium Oxide
NMC	Nickel Manganese Cobalt
n	Bruggeman exponent
OCV	Open Circuit Voltage
ODE	Ordinary Differential Equation
ODEs	Ordinary Differential Equations
P2D	Pseudo-Two-Dimensional Model
p	Bruggeman tortuosity exponent
PIV	Particle Image Velocimetry
q	Specific capacity
$\dot{q}$	Heat flow
R	Gas constant / Resistive film layer / Resistance
r	Radius of the particle
SEI	Solid Electrolyte Interface

SNR	Signal-to-Noise Ratio
SOC	State of Charge
T	Temperature
TR	Thermal Runaway
TR10	Temperature Rate Equal to 10 °C/min
TR100	Temperature Rate Equal to 100 °C/min
U	Open-Circuit Potential of the Solid / Equilibrium Potential
VE	Vehicle Electrification
w	Weight factor
WLTC	Worldwide Harmonised Light Vehicles Test Procedure
XRD	X-ray Diffraction Analysis

Greek

ε	Porosity
σ	Conductivity
ϕ	Potential
α	Charge transfer coefficient
η	Overpotential
	Ratio of first discharge and first charge capacity
γ	
δ	Thickness
ρ	Density

Subscripts

e	Electrolyte
	Solid phase/ abbreviation in the plural/ specific/
s	surface
D	Diffusional

u	Universal
SEI	Solid electrolyte interface
	Cathode/ Contact resistance at the current
c	collectors
a	Anode
max	Maximum
fcc	First charge capacity
fdc	First discharge capacity
th	Theoretical
amb	Ambient
rxn	Redox reactions
rev	Reversible
ohm	Ohmic
V	Voltage
T	Temperature
EC	Electrolyte components
ref	Reference

Superscript

eff	Effective
Li	Lithium
cat	Cathode

Chapter 1

Introduction

Content

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1.1 Introduction

The present chapter describes the obstacles and directions that justify the development of this work. Firstly, an overview of the current environmental issues and the energy transition will be presented. Then, the role of batteries in the decarbonisation path will be discussed, addressing the main advances and difficulties related to their application. Finally, the thesis structure is presented, providing a general overview of the different topics developed in this work.

1.2 Global challenges and the energy transition scenario

Catastrophic events such as flooding, heat waves, and hurricanes have been occurring more frequently over the years due to the intensified effects of global warming [1]. The major contributor is greenhouse gas (GHG) emissions, which correlate directly with the average global temperature. According to Figure 1.1, the increase in CO₂-equivalent (GHG) emissions has caused an increase in the average global temperature in a similar way. CO₂-equivalent is the emissions of CO₂, CH₄ (methane) and N₂O (nitrous oxide). However, the impact of CH₄ and N₂O is calculated based on the impact of CO₂, as CH₄ and N₂O are equivalent to 28 and 265, respectively, in terms of the amount of warming as CO₂ [2]. This occurs because GHGs trap the heat in the atmosphere, reducing the amount of thermal radiation in space. Therefore, the continuous accumulation of GHGs leads to a gradual increase in global temperatures. In 2024, the temperature anomaly reached approximately 1.2°C, nearing the maximum target of 1.5°C set by the Paris Agreement [3].

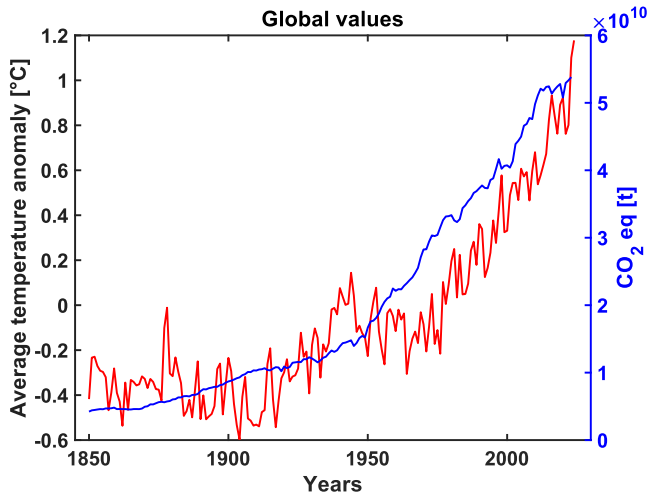


Figure 1.1. Global average temperature and CO₂ equivalent emissions trend. Data modified from [4].

The electricity, heat, and transport sectors are the two main contributors to GHG emissions. Figure 1.2 (a) and (b) present the absolute values and the percentage of total emissions from each sector. The results show that the electricity and heat sector accounts for approximately 33% of emissions, while the transport sector contributes around 16%. In addition, it is possible to observe that both sectors, especially electricity and heat, have shown an increasing trend in emissions over the years.

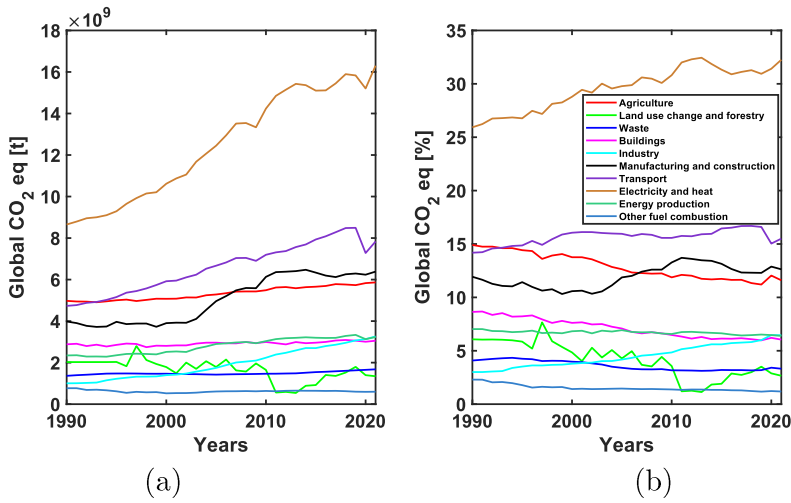


Figure 1.2. Global CO₂ equivalent absolute (a) and percentage (b) values as a function of the past years [4].

The main concern regarding the largest contributors to GHG emissions is the energy source used for electricity, heat, and the transport sector. Figure 1.3 shows the raw sources of energy production. The conclusion is that a large portion of energy comes from fossil fuels such as oil, coal, and natural gas. About 84% of energy is produced from highly polluting sources, while only 16% comes from environmentally friendly sources. Therefore, these non-renewable sources emit significant GHGs, as the primary mechanism for converting chemical energy into electricity relies on a combustion process first. Furthermore, in the transport sector, part of the energy used comes from power plants fueled mainly by coal and natural gas. This reduces the potential environmental benefits of electric vehicles, even though they are more efficient than internal combustion engine vehicles [5].

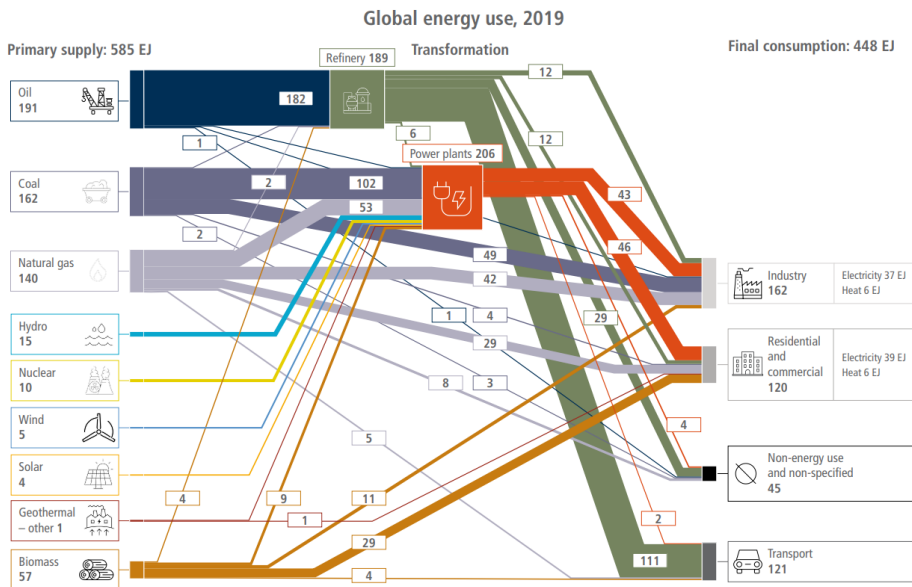


Figure 1.3. Source of energy production used in the Electricity, heat, and transport sector [6].

To achieve the target of reducing CO₂-equivalent emissions and decreasing the impact of global warming, it is necessary to accelerate the development of energy sources that can be produced without harming the environment. Figure 1.4 depicts the options for mitigating global warming effects, considering enablers and barriers related to geophysical, environmental-ecological, technological, economic, socio-cultural, and institutional potential. In the energy sector, solar and wind energy emerge as strong candidates for the energy transition. Solar energy has significant enablers, including physical potential, abundant geophysical resources, minimal environmental impact, technological feasibility for large-scale implementation, financial and economic viability, public engagement and support, as well as social and political acceptance. In the wind energy sector, despite its advantages, barriers mainly related to socio-cultural and institutional aspects decrease the potential of this sector in the energy transition. Other potential solutions, such as carbon capture and bioenergy, are constrained by technological maturity and scalability. Meanwhile,

geothermal and hydroelectric power face major barriers related to environmental-ecological and institutional factors.

Electric and hydrogen fuel cell vehicles can be potential solutions for mitigating global warming in the transport sector, but both have significant technological, socio-cultural, and institutional barriers. In addition, other possible solutions also have limitations, decreasing their potential for widespread adoption. Their implementation depends on regional factors that may favour one technology over another and the applicability of each vehicle type to specific transport needs [7].

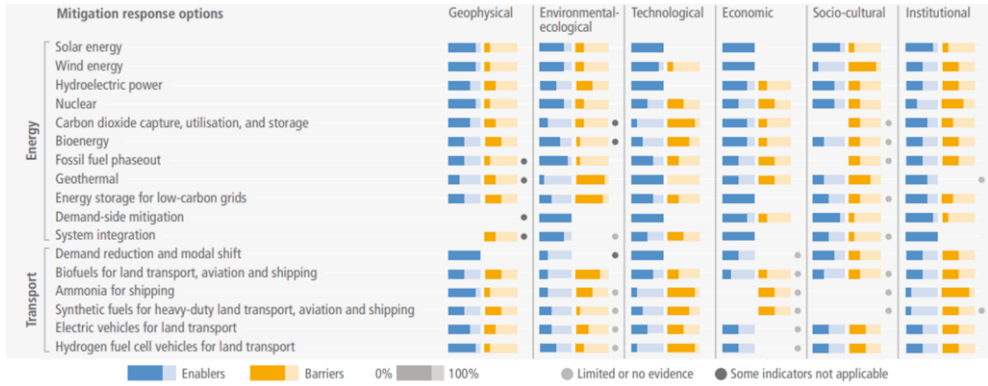


Figure 1.4. Mitigation response options to global warming [6].

Due to the feasibility of energy production from solar power, projections indicate that 2050 solar energy will be the dominant source, followed by wind and biomass, according to Figure 1.5. Oil will still be used, as it remains difficult to fully replace in specific transport sector applications where electricity is not a viable alternative. However, energy sources like wind and sun have problems since they do not provide energy continuously. Thus, their production is dependent on the environment. Poor environmental conditions lead to poor energy output, which impacts grid use [8]. Therefore, one way to reduce the issue of intermittent energy generation is to adopt energy storage devices. This can be achieved by using lithium-ion batteries, which can store the energy produced in excess and release it when required, providing a more stable energy supply [9]. Furthermore, lithium-ion batteries

are widely applied to electric vehicles, which present a powertrain that is more efficient and less polluting, considering that the energy used in the electric vehicle is from the sources shown in Figure 1.5. In addition, considering well-to-wheel analysis, this is concluded by considering that an electric vehicle can achieve an efficiency of approximately 70% at the wheels. In contrast, an internal combustion engine has an efficiency of about 15% [10].

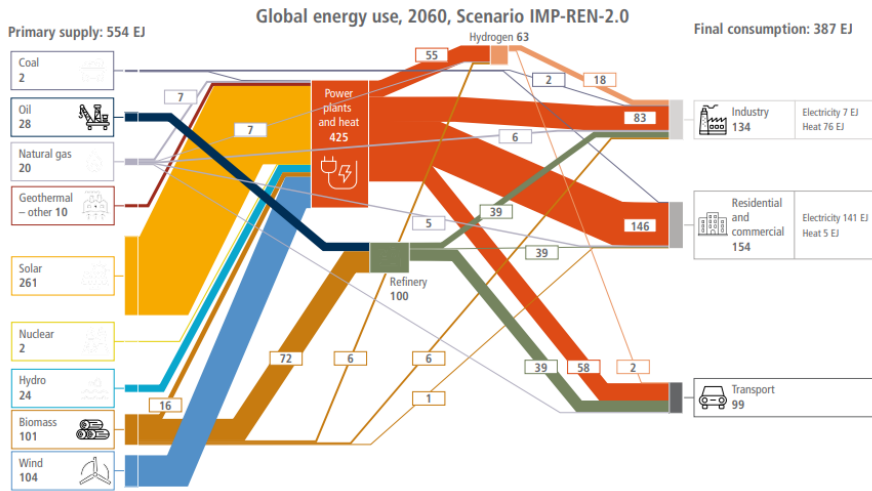


Figure 1.5. Future energy use to mitigate global warming by different sources [6].

1.2 The battery role in the decarbonisation path

Lithium-ion batteries are widely adopted for their high energy density, efficiency, and relatively long lifespan. Furthermore, lithium-ion batteries are improving storage capacity, charging speed, and cost-effectiveness, making large-scale energy storage more accessible [11]. However, although the emissions generated by a battery during its working cycle can be considered negligible (due to its closed volume and safe operating conditions), the GHG emissions from its manufacturing process can be significant. This occurs because battery production involves energy consumption processes such as

mining, refining, transportation, electrode production and cell assembly, all contributing to GHG emissions. For example, Figure 1.6 shows that the GHG emissions generated during the production of an electric vehicle battery are higher than those of other powertrains, such as internal combustion engines or hybrids. The main reason for this is the GHG emissions associated with battery manufacturing (5702 kg CO₂eq), which account for up to 50% of the total emissions in the study conducted [12]. However, in other studies, the values can vary from 726.1 to 4,100 kg CO₂-eq emitted, depending on the battery pack size and other variables considered in the methodology, such as the energy mix, recycling process, etc. [13–17]. In general, a greener energy mix will produce cleaner batteries, further enhancing the sustainability of battery applications, particularly in the transport sector.

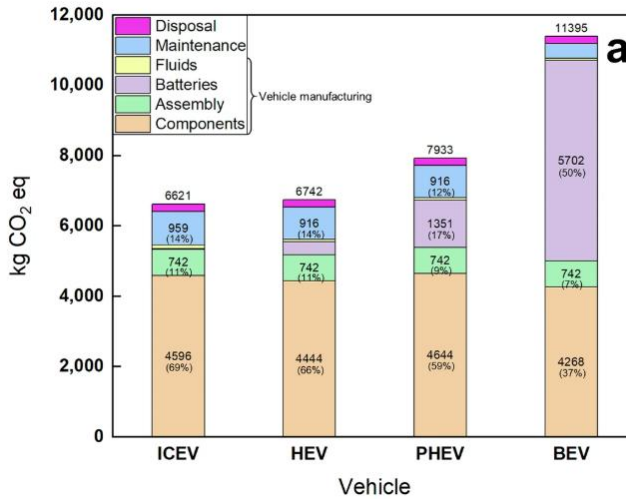


Figure 1.6. kg CO₂ equivalent emitted during the production of different vehicle types [12].

Although battery production currently can generate a higher amount of GHG emissions, using batteries in vehicles can be advantageous during the fuel cycle. A vehicle powered by a battery to supply energy to the powertrain does not emit GHGs during operation. Figure 1.7 shows different light-duty vehicle (LDV) powertrains, including a LDV powered by an internal

combustion engine (ICEV), two LDVs that use an internal combustion engine with a battery system (HEV and PHEV), and a LDV powered exclusively by a battery system (BEV). The key difference between HEVs and PHEVs is their charging process and battery size. In an HEV, the internal combustion engine charges the battery, which is considered small and assists the powertrain at low loads. In contrast, a PHEV typically has a larger battery, which is mainly charged through an external power supply, allowing for extended electric driving. Based on that, the results of Figure 1.7 explore which powertrain is more efficient over the driving distance for different energy matrices. A battery system can offset the emissions produced during manufacturing, depending on the energy matrix. In a clean energy matrix like Norway, the advantages of a BEV become apparent sooner. However, in carbon-intensive energy matrices, the transition from HEV to BEV is more gradual but still evident. ICEV shows the poorest performance on GHG.

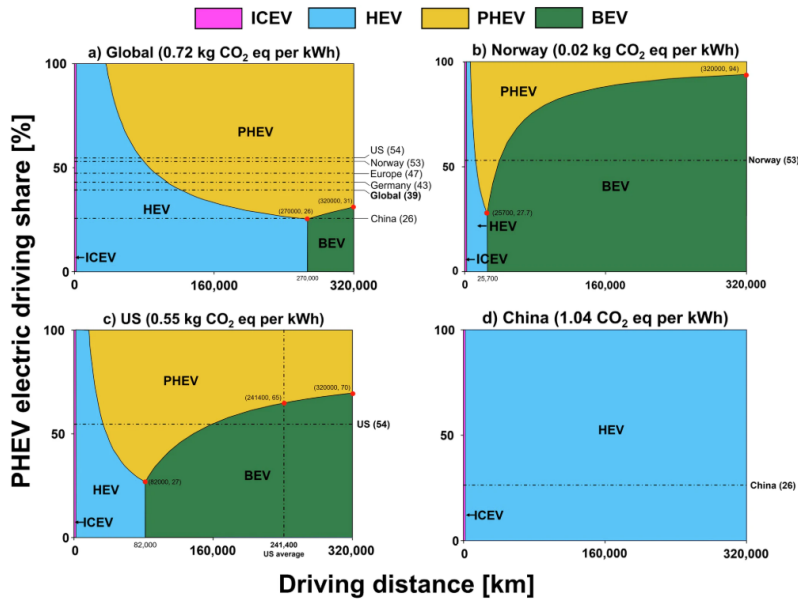
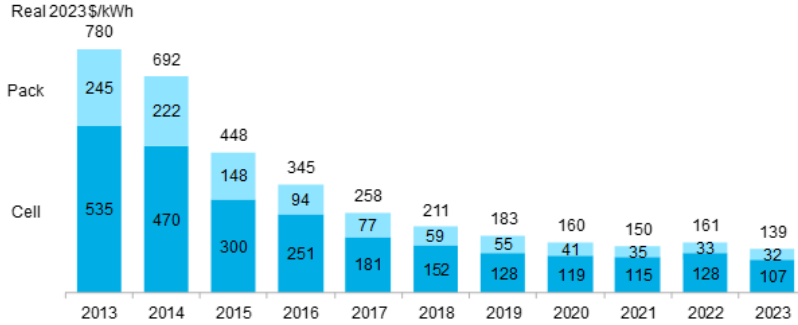


Figure 1.7. Vehicle and fuel cycles combined to explore the potential of the different powertrains on GHG emissions [12].

The batteries show potential on the decarbonisation path of the energy, being a fundamental element. In addition, the price of the batteries at cell and pack levels has decreased over the years, according to Figure 1.8. The technology has become reliable, with the price at cell levels decreasing 80% from 2013 to 2023, and 87% for pack level in the same period.



Source: BloombergNEF. Historical prices have been updated to reflect real 2023 dollars. Weighted average survey value includes 303 data points from passenger cars, buses, commercial vehicles, and stationary storage.

Figure 1.8. Battery prices at cell and pack levels [18].

The low price boosts battery production in Europe and other regions, increasing the participation in the market share for transportation and energy store systems, according to Figure 1.9. China dominates the battery production market, holding 83% of the global share in 2023. Europe and the United States account for 13% of global battery manufacturing capacity. In the future, battery production is expected to quadruple by 2030, with China share decreasing to 67% due to expansion in other regions [19].

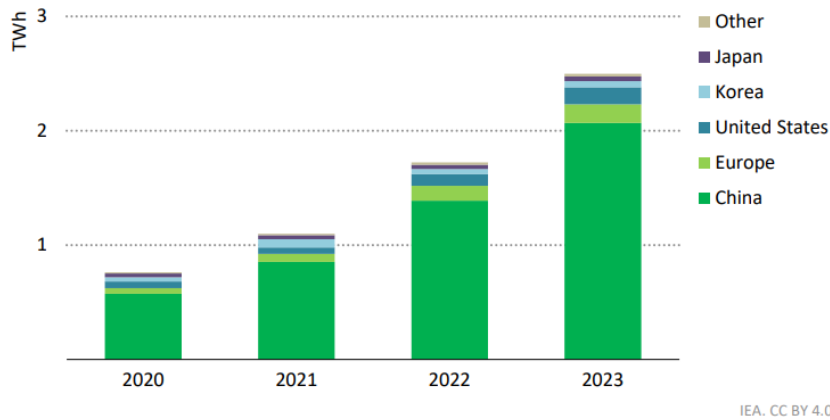


Figure 1.9. Battery production capacity worldwide [19].

The global expansion of battery production raises concerns due to accidents reported in recent years. The thermal runaway process risks human safety and environmental well-being, especially under unsafe operating conditions in lithium-ion batteries that can occur due to a mechanical, thermal or electrical failure. Some works report a sequence of examples showing fire incidents with lithium-ion batteries (LIB) [20,21], which can be from a portable device, a battery electric vehicle (BEV) or an energy storage system (ESS). In the work carried out by Baisheng Nie et al. [22], a summary table with some main accidents involving mainly energy storage devices was reported and depicted in Table 1.1.

Table 1.1. Fire incidents with lithium-ion batteries were reported by [22].

Year	Device	Location
2010.1	LIB	UPS plane
2011.1	LIB	Korean Air cargo plane
2016.1	LIB	Company in the Shenzhen industrial park
	Button battery	
2016.1	LIB	Plane of Southwest Airlines
	Portable device	
2021	LIB	Korea Hongcheng ESS
	ESS	
2021	LIB	Fengtai ESS in Beijing
	ESS	
2021.1	LIB	Victoria Battery Project in Australia,
2022	ESS	Chandler ESS in the US
2022.1	ESS	LIB system at Banqiao Data Center in
		Korea
2023.1	ESS	Guangdong at China
2023.1	ESS	Valley Center Energy Storage Facility in
		northern San Diego County, California.
2024	LIB	Recycling group SNAM.

A work carried out by Haoran Zhang et al. brings the number of incidents related to battery thermal runaway reported and occurred in China from 1984 to 2019, correlating the data with the type of injuries suffered by the people, according to Figure 1.10 [23].

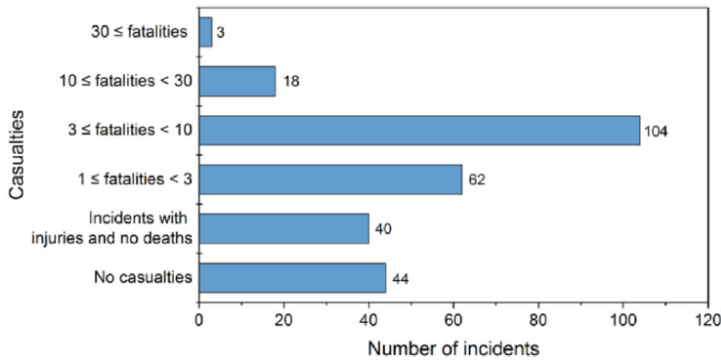


Figure 1.10: Number of incidents and the consequences that occurred in China between 1984 and 2019 related to battery thermal runaway, according to [23].

The number of tragedies involving lithium-ion batteries has raised safety concerns, and a series of studies have been developed to understand thermal runaway in lithium batteries. Additionally, governments have begun setting safety standards to ensure the widespread applicability of lithium-ion batteries [24,25].

1.3 Document content and structure

This thesis is organised into 7 chapters, from the introduction to the conclusion. The following summarises the key points of each succeeding chapter:

Chapter 2 presents a literature review addressing the working principles of batteries, their main components, and future trends, which are crucial to understanding due to their direct impact on thermal runaway chain reactions. Subsequently, thermal runaway is described, covering the main thermal, mechanical, and electrical triggering mechanisms. The effects of key battery conditions, including state of charge, state of health, and other factors, are discussed. Chapter 2 also details the gaps in the current research findings in

this field, which will be the focus of this thesis, as outlined in the objectives presented in the final section of the chapter.

Chapter 3 details the experimental facilities used in the tests, including the main characteristics of the bidirectional source, climate chamber, and calorimeter. The protocols for electrical characterisation and thermal abuse conditions are also presented. Additionally, the optical techniques and their underlying principles are described. The computational tools are introduced, covering electrochemical, thermal, and ageing models.

Chapter 4 aims to evaluate the impact of the ageing process on vehicle range. Energy density is important in battery pack design, but ageing can lead to significant capacity fading and safety problems. For this reason, electrical characterisation is conducted, and the electrical and thermal behaviour of different batteries is analysed. The data is used to calibrate and validate a P2D model, which is the foundation for the vehicle battery pack model. Additionally, it provides valuable insights into battery materials that influence the thermal runaway chain reaction, information that is otherwise difficult to measure. Finally, the battery vehicle model simulates the degradation process with different driving cycles.

Chapter 5 analyses unsafe battery conditions under different scenarios. First, a theoretical study is conducted using data from the P2D model developed in Chapter 4 to predict the thermal runaway potential of each battery chemistry based on the material composition used in their manufacturing. Additionally, the degradation process and state of charge are included in the theoretical analysis to assess their impact on the thermal runaway chain reaction. Next, experimental test results obtained using an accelerating rate calorimeter coupled with optical techniques are discussed, addressing mechanical and thermal abuse. Finally, statistical analysis and insights gained from applying optical techniques under controlled conditions are presented to understand better the scattering behaviour observed in the literature.

Chapter 6 proposes a model capable of replicating the thermal runaway process with statistical analysis. The proposed model is a result of the experimental findings of this thesis and can accept different input parameters, making it more dynamic than currently available models. The calibration and validation of the thermal runaway model are presented and discussed.

Chapter 7 highlights the investigation contributions and the work most important findings. Furthermore, improvements and more research on this subject are suggested as future projects.

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Chapter 2

Lithium-ion battery fundamentals and thermal runaway mechanisms

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2.1 Introduction

In the transition to zero emissions in the transportation sector, lithium-ion batteries play an important role as an energy storage solution for hybrid and electric powertrains [1,2]. Clean and renewable energy can be stored as chemical energy and released as electrical energy, significantly reducing carbon footprint[3]. This contrasts with liquid hydrocarbon fuels, which depend on combustion to convert chemical energy into mechanical energy [4], through a process of combustion that produces pollutants [5]. Some concerns about material mining and battery manufacturing make this technology not totally carbon emissions-free. However, recycling processes are being developed and enhanced, which should help reduce emissions associated with mining and manufacturing [6]. In addition, lithium-ion batteries are widely used in different portable devices, becoming common in daily life [7]. Characteristics such as life duration, high energy density, and low self-discharge make lithium-ion batteries the preferred technology for energy storage systems compared to other types [8]. Energy density, in particular, is crucial because it enables wide applicability in small portable devices by providing sufficient autonomy. Additionally, it ensures an acceptable driving range for electric vehicles. Figure 2.1 shows the energy density of different battery types and demonstrates that lithium-ion batteries offer superior specific energy in terms of both volume and mass, making them the preferred battery type for a wide range of applications.

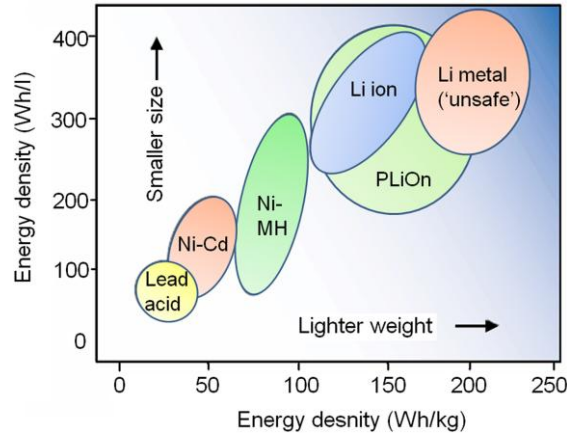


Figure 2.1. Battery energy density for different battery types [9].

Over the years, the composition of lithium-ion batteries has evolved to improve performance and durability. The main changes have occurred in the cathode components, which serve as the lithium metal carrier and represent the primary bottleneck for energy density [10]. In addition, other improvements in battery materials have contributed to enhanced performance, such as modifications in the electrolyte composition, which is trending towards solid electrolytes, and changes in the anode materials, including mixtures of graphite and silicon. Figure 2.2 shows these advancements and highlights that, over the years, the composition of the cathode, electrolyte, and anode has evolved to increase energy density and deliver higher performance.

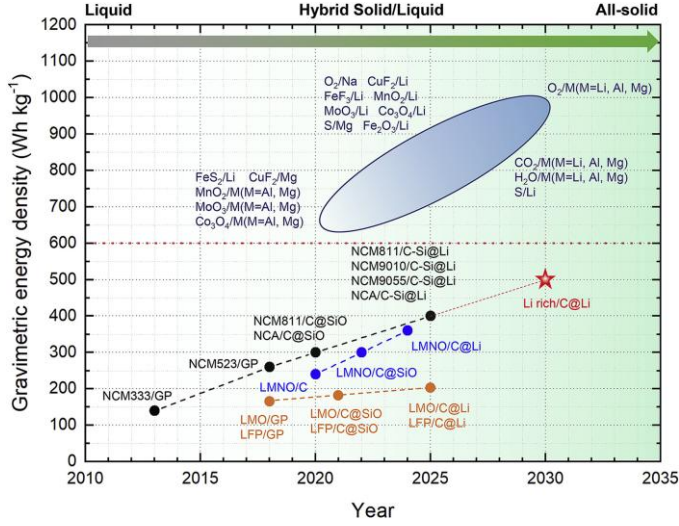


Figure 2.2. Evolution of Lithium-Ion Battery Materials for Higher Energy Density: Past Developments and Future Perspectives [11].

However, lithium-ion batteries operate effectively within a temperature range of approximately 15°C to 40°C [12]. Outside this range, the degradation effect can be boosted, decreasing drastically the battery capacity and performance [13,14]. For example, SEI growth is boosted at high temperatures, while lithium plating is boosted at lower temperatures. Other degradation mechanisms are linked to the battery temperature, reducing battery useful life, as seen in [15]. In addition, higher specific energy increases the risk of thermal runaway. Figure 2.3 presents the relationship between battery energy density and the potential for thermal runaway, expressed in terms of the maximum temperature reached during unsafe conditions.

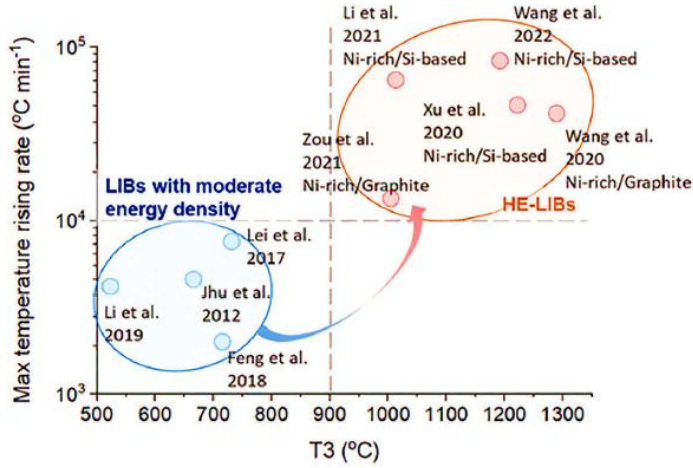


Figure 2.3. Battery specific energy and thermal runaway potential [16].

Battery thermal runaway occurs due to a sequence of events that lead to uncontrollable reactions, resulting in a significant risk to human safety. A single cell in thermal runaway can trigger neighbouring cells, potentially resulting in a vehicle explosion. Different factors, such as external heating, mechanical abuse, or electrical abuse, can initiate thermal runaway, each causing a different chain of reactions [17]. However, a primary cause of thermal runaway is the separator rupture, which can occur through various mechanisms depending on the specific trigger [18].

This thesis focuses on studying the thermal runaway in lithium-ion batteries. To support this, this chapter will detail the components, functionality, and materials of the battery to provide an understanding of its operation. Additionally, it will explore how battery construction and future trends in battery development for vehicle applications impact thermal runaway. The chapter will then discuss thermal runaway, detailing the main reaction based on different triggers to understand the phenomenon better. The three primary thermal runaway triggers will be examined, along with the effects of battery conditions such as state of charge (SOC), state of health (SOH) and specific energy. Finally, thermal runaway models will also be discussed.

2.2 Cell technology and working principles

This subsection discusses the main components of a lithium-ion battery, the principles of battery operation, the main chemistries used in lithium-ion batteries, and battery manufacturing considerations. It will also discuss the impact of these factors on battery performance and safety.

2.2.1 Cell components and functions

The components of a lithium-ion battery play an important role in the battery capacity, performance, safety, and lifespan. Fundamentally, the battery comprises positive (cathode) and negative (anode) electrodes. These electrodes are typically immersed in an electrolyte (liquid), a salt solution dissolved in an organic solvent that facilitates the transport of ions. Additionally, a separator is essential to avoid direct electron flow between the electrodes, ensuring the proper functioning and safety of the battery.

The negative electrode is denominated as anode, and the lithium elements are stored in this battery component during charge. The main component for the anode of a lithium-ion battery is graphite. The main advantages of graphite material are its good intercalation capacity, long cycle life, good electrical conductivity, cost-effectiveness, and stability [19]. Typically, copper is used as the current collector, as its properties are suitable to the graphite anode material, including good stability when operating in the low voltage range and excellent thermal and electrical conductivity [20]. The positive electrode is called the cathode, and lithium ions are intercalated into the cathode during the discharge process. One of the main constraints on battery energy density is related to the cathode material [21]. The primary composition of the cathode consists of lithium metal oxides, which offer high energy density and high voltage, providing suitable power and energy performance for electric vehicles. Thermal and electrochemical stability is also important for cathode materials, aiming for a longer useful life and enhanced safety. The main materials used for cathode chemistry are Lithium

Cobalt Oxide (LiCoO_2 , LCO), Lithium Iron Phosphate (LiFePO_4 , LFP), Lithium Nickel Manganese Cobalt Oxide (LiNiMnCoO_2 , NMC), and Lithium Nickel Cobalt Aluminum Oxide (LiNiCoAlO_2 or NCA) [22]. The composition of each lithium metal oxide can be tuned to achieve higher performance according to the application. The current collector for the cathode electrode is primarily aluminium. This material exhibits good stability with high-voltage materials, preventing corrosion and increasing the useful life of the battery, as well as providing good electrical performance [23]. In recent years of battery development, the cathode material has undergone the most significant changes, as shown in Figure 2.4, improving battery performance and addressing its role as the primary bottleneck.

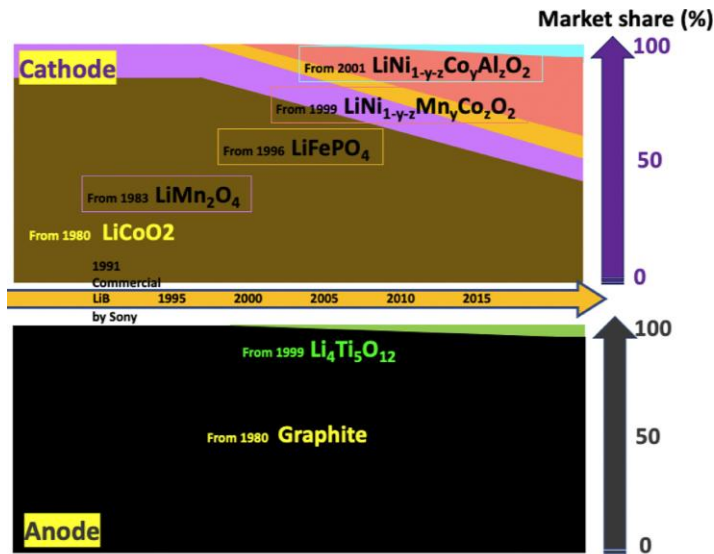


Figure 2.4. Cathode and anode material evolution over the years [19].

For the battery to function correctly, an electrolyte solution is required to facilitate the transport of lithium ions between the electrodes. The electrolyte is mainly composed of salt dissolved in an organic solvent solution. Nowadays, the typical composition of the electrolyte in lithium-ion batteries is LiPF_6 salt dissolved in organic solvents such as EC (ethylene carbonate), DMC (dimethyl carbonate), and EMC (ethyl methyl carbonate) [24]. The

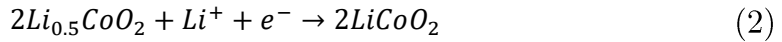
proportion of each component can vary to optimise battery performance. The main characteristics of the electrolyte in a lithium-ion battery are high ionic conductivity, as its function is to enable lithium-ion transport between electrodes, and chemical, electrochemical, and thermal stability to withstand the battery operating voltage range and working temperature, while avoiding side reactions with other battery components [25]. Another important component is the separator. The primary function of this component is to prevent direct contact between the electrodes while allowing only lithium ions to pass through. The standard materials for separators are polypropylene (PP) and polyethylene (PE), often coated with ceramic to improve thermal stability [26].

2.2.2 Electrochemical reactions and energy storage mechanism

A lithium-ion battery operates through the process of intercalation and de-intercalation of lithium ions in the anode and cathode, depending on whether the battery is charging or discharging. Figure 2.5 shows a simplified schematic of the battery with its main components. The anode is a negative electrode in a lithium-ion battery during discharge. The anode is called the negative electrode because the negative charge is present in the component [27]. It consists of a porous material saturated with electrolytes. This porous structure is composed of an active material, typically graphite, along with a binder and additives. The binder enhances mechanical stability and adhesion to the current collector, and the additives, such as conductive carbon, enhance electrical conductivity (contact with the current collector). The active material of the anode, primarily graphite, can be approximated as spherical particles for modelling purposes. Thus, when a load is attached to the circuit, the electromotive force pulls out the ions in the direction of the cathode through the electrolyte, and the free electrons travel through the electric circuit. The anode suffers a reaction called oxidation (loss of electrons), as can be seen in Reaction (1) [28]. This process is also called de-intercalation or de-lithiation.



The positive electrode is called the cathode during the discharge process, and it receives lithium ions from the electrolyte and negative charge (electrons) through the electric circuit. As this electrode receives electrons, it undergoes a reaction called reduction, as shown in Reaction (2) for an example of LCO battery cathode chemistry. This process can also be referred to as lithiation or intercalation, which means the insertion of lithium ions into the host material [28]. In addition, binder and additive materials are also present in the cathode to improve battery performance.



The reverse reaction occurs during the charging process. However, an external energy supply, such as a charger, is required to reverse the reaction, causing an oxidation reaction at the ‘positive electrode’ and a reduction reaction at the ‘negative electrode’ [29]. These names are fixed to clarify the roles and locations of the electrodes in Figure 2.5.

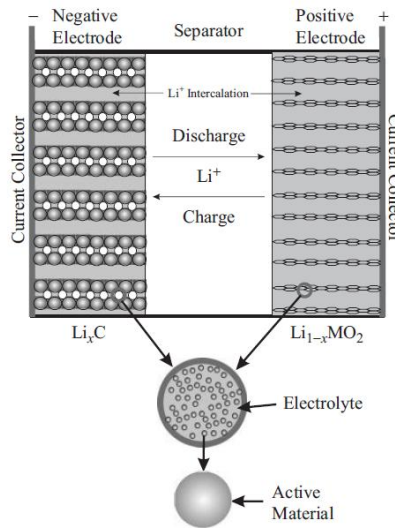


Figure 2.5. Lithium-ion battery scheme [30].

2.2.3 Advances in cell chemistry

Over the years, lithium-ion batteries have changed their active material and electrolyte composition to achieve desired characteristics, mainly safer and higher energy density. High nickel-content materials, such as NMC and NCA, currently dominate the market for cathode chemistry. However, due to safety concerns, LFP batteries are gaining a significant share of the market [31]. LFP batteries have a lower energy density than NMC, approximately 160 mAh/g. However, their superior thermal stability makes them attractive for applications where safety is a primary concern [32]. NMC811 is a promising cathode chemistry for electric vehicle applications due to its higher energy density than LCO, around 200 mAh/g [33]. Nevertheless, challenges related to capacity fading persist, especially when compared to other battery chemistries with lower nickel content in the NMC cathode composition [34].

NCA offers a similar capacity to NMC cathode chemistry, with the advantage of lower capacity fading. However, it is more expensive and less thermally stable [35,36]. LCO batteries have a lower energy density than

modern cathode chemistries, approximately 140 mAh/g. The voltage cut-off of this chemistry is limited to 4.2 V, as higher values, while aimed at increasing energy density, result in structural instability between the cathode and the electrolyte [37]. LNMO batteries provide the advantage of a higher voltage cut-off at 4.7 V but have a lower capacity than NMC811, around 140 mAh/g. Additional limitations for electric vehicle applications include capacity fading [38]. Table 2.1 compares the main cathode chemistry and related challenges.

Table 2.1. Summary of cathode chemistry and its energy density and challenges.

Cathode	Energy density (mAh/g)	Challenges
LCO	140	Structure unstable [37]
NMC811	200	Capacity fading [33]
LFP	160	Energy density [32]
LNMO	140	Moderate energy density, capacity fade [38]
NCA	200	Expensive and thermal unstable [35]

For the anode composition, the main material still is graphite. However, recently, development with the addition of silicon (3579 mAh/g) increases the anode capacity, but addresses problems such as volumetric expansion (>300%) between intercalation and de-intercalation of the anode material [39,40]. For the electrolyte, developing solid-state electrolytes (SSE) is considered a key factor for the continued and widespread adoption of lithium-ion batteries. Replacing flammable liquid electrolytes with SSE enhances safety and enables the development of high-energy-density batteries. Promising types of SSE include solid polymer electrolytes (SPEs), inorganic solid electrolytes (ISEs), and composite polymer electrolytes (CPEs) [41]. Figure 2.6 depicts an overview of the advances in cell chemistry.

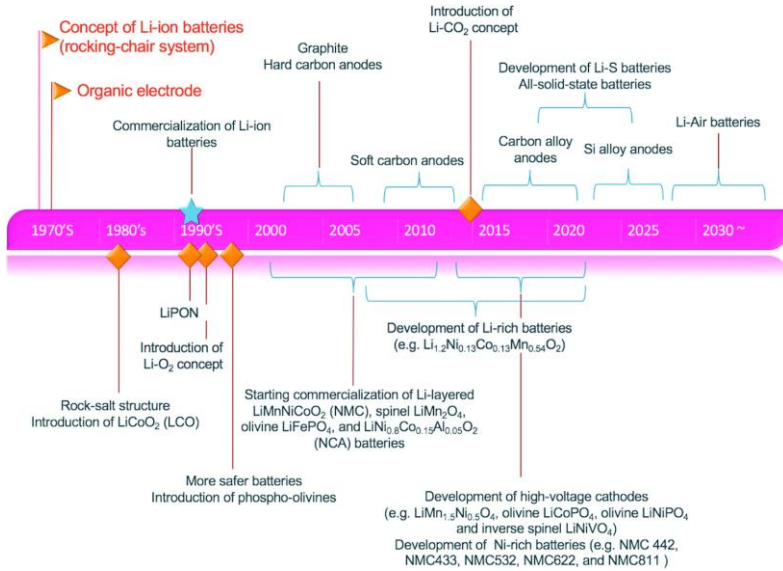


Figure 2.6. Overview of the advances in cell chemistry [42].

2.2.4 Manufacturing and design considerations

Figure 2.7 shows how a cylindrical cell is assembled and the main components. Rechargeable lithium-ion batteries have safety features to maintain consistent functioning and prevent failure under abuse conditions. One device is called venting cap (pressure release valve), which releases the internal pressure when it reaches critical levels due to the generation of internal gases. In addition, two other safety features, PTC (Positive Temperature Coefficient) components and CIDs (Current Interrupt Devices), can be included to improve safety. The PTC element protects the battery by raising resistance as temperature rises, decreasing current flow during overheating [43]. The CID works as a pressure-sensitive device, permanently disconnecting the circuit if the internal pressure reaches a certain threshold, preventing thermal runaway due to electrical abuse, for instance [44].

These batteries are made of 4 layers, commonly of materials wrapped in cylindrical form. The conventional arrangement consists of a positive electrode (cathode with current collector), a separator, a negative electrode

(anode plus current collector), and an extra separator layer to avoid contact between electrodes. The positive electrode is connected to the top terminal, while the negative electrode is attached to the bottom terminal. Lithium-ion batteries typically have a nominal voltage between 3 V and 3.7 V. Individual cells are connected in series to achieve higher voltages and in parallel to increase overall capacity or, alternatively, by increasing the battery size [45]. The number of tabs connected to the current collectors affects the battery performance. Single-tab designs, for example, are simpler and more cost-effective, but they produce higher electrical resistance and heat, limiting their capacity to work with high current. Multi-tab designs minimise resistance, improve thermal management, and increase power output, making them perfect for applications that need fast charge and discharge cycles [46–48]. The performance and longevity of a battery are directly impacted by cell design. Higher energy density can be achieved by increasing electrode thickness or using advanced materials. In addition, improving tab configuration and electrode arrangement enhances power delivery. Another important effect related to battery design is thermal management. According to the application, overheating can boost degradation, which can be avoided by improving battery design. Proper assembly prolongs battery life and preserves performance by ensuring improved heat dissipation.

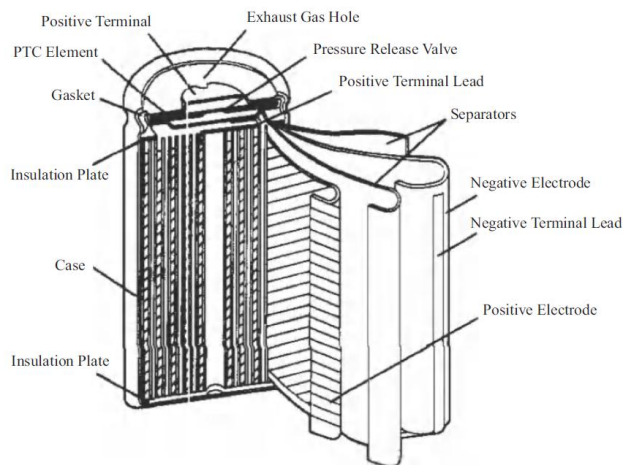


Figure 2.7. Cylindrical battery design [30].

2.3 Thermal runaway principles

This section will discuss the principles of thermal runaway (TR), the main topic studied in this thesis. First, an overview of the three main triggers for TR will be provided: external heating, mechanical abuse, and electrical triggers, addressing the main mechanisms and reactions that occur inside lithium-ion batteries. In addition, the potential for TR associated with different cathode compositions will be explored. Furthermore, the effects of cell conditions on TR will be discussed, including energy density, state of charge (SOC), and the impact of battery degradation processes. Finally, strategies for mitigation will also be presented.

2.3.1 General overview: Key mechanism and definitions

Thermal runaway can be understood as a rapid increase in battery temperature within a short time due to uncontrollable reactions. The cause of the TR can be associated with thermal, electrical and mechanical abuse [49]. Thermal abuse can occur due to heat generation, which can be internal or external, and when the heat dissipated by the battery is lower than the internal heat generated and/or external supplied to the battery. As a result, the battery temperature increases, triggering other exothermic reactions that further increase the temperature rise rate due to the higher heat generation. When thermal runaway (TR) is activated, uncontrollable reactions occur, leading to a sharp increase in battery temperature [17]. Although TR can be stopped before reaching the critical point (when exothermic reactions become unstoppable), excessive temperatures cause battery degradation, reducing performance [50]. In addition, before reaching the critical point of thermal runaway (TR), gases are generated inside the battery, causing the internal pressure to increase and reach dangerous levels that can compromise the structural integrity of the battery. A venting valve with a mechanical fuse bursts when the internal pressure exceeds a critical value. Subsequently, during the TR process, flammable gases are produced and released into the atmosphere through this venting valve. These gases and hot particles can

form a mixture with ambient air at a fuel-to-air ratio sufficient to initiate combustion[51].

Mechanical abuse occurs when an impact, deformation, or penetration causes significant damage to the battery, potentially triggering thermal runaway. TR caused by mechanical abuse can occur instantaneously if it results in separator rupture, leading to a rapid heat release due to an internal short circuit. Alternatively, it can occur gradually, as mechanical abuse causes minor damage that generates heat in a similar way as explained above. Finally, electrical abuse, such as overcharging, can enhance the lithium plating formation. This can be defined as dendrites that grow inside the battery and can rupture the separator by penetrating through, generating an internal short circuit [52]. Figure 2.8 summarises the main unsafe conditions that can lead to TR. This process will be detailed later.

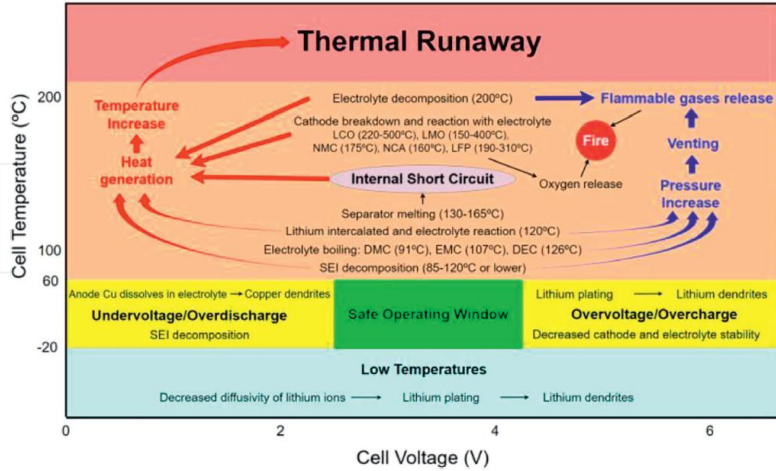


Figure 2.8. Summary of unsafe conditions that can lead to TR [52].

Different battery conditions may affect the mechanism described depending on its usage. For example, battery degradation depends on the conditions under which the battery was cycled, which can accelerate SEI growth or lithium plating. Additionally, cathode chemistry plays an important role in the mechanism because, according to Figure 2.8, during the

cathode decomposition reaction, the cathode can release oxygen depending on the lithium metal oxide material used. Other important factors include the battery state of charge (SOC) during thermal runaway (TR). A higher SOC means more energy can be released during an internal short circuit or cathode decomposition, as the lithium metal oxide state is more stable than the de-lithiated state. A similar analysis can be applied to the specific energy of the battery, where higher values result in a greater propensity for TR. Figure 2.9 presents a scheme of the TR causes, phases, influencing factors and the hazards associated with the unsafe condition.

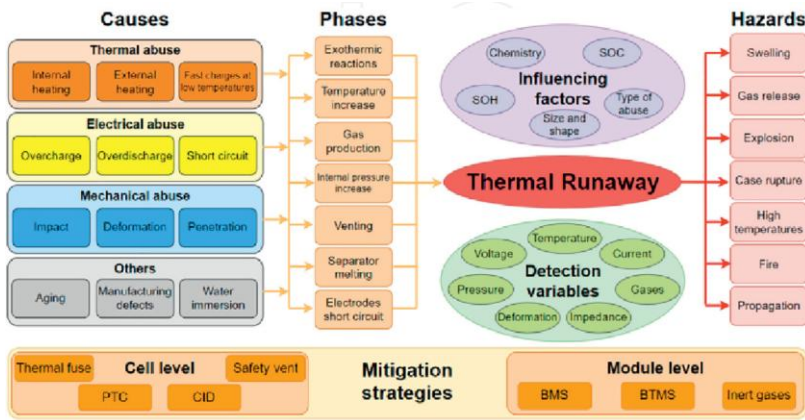


Figure 2.9. Cause, phases, influencing factors and hazards of the TR process [52].

2.3.1.1 Thermal trigger

Thermal triggers for TR can occur due to an external or internal heat source. Possible causes include damage to the resistor connector from impact, vibration, poor manufacturing quality, or other factors. The heat generated must exceed the heat that the battery can dissipate. Thus, the battery temperature will continue to rise, potentially leading to TR. As the temperature increases due to exothermic reactions, additional exothermic reactions may be triggered, further contributing to heat generation and accelerating the temperature rise rate. Figure 2.10 presents step-by-step the

exothermic reaction due to the thermal trigger up to the TR. The process begins with the decomposition of the solid electrolyte interphase (SEI), a protective layer formed by reactions between the electrolyte and the lithium intercalated in the anode. This layer reduces direct contact between the electrolyte and the lithium in the anode. However, when the battery reaches $\sim 90\text{ }^{\circ}\text{C}$ to $\sim 100\text{ }^{\circ}\text{C}$, the SEI layer decomposes, initiating an exothermic reaction between the lithium in the anode and the electrolyte [53]. At this temperature, gases are formed due to electrolyte vaporisation and reactions between lithium and the electrolyte, producing gases [54]. In sequence, at a higher temperature, the protective layer on the cathode side, known as the cathode electrolyte interface (CEI), begins to decompose, further contributing to self-heating and accelerating the progression toward thermal runaway [55]. This decomposition is similar to the SEI decomposition [56]. Cathode decomposition starts at approximately $\sim 170\text{ }^{\circ}\text{C}$, releasing oxygen that reacts with the electrolyte. This mechanism plays a crucial role in thermal runaway, as more thermally stable cathode chemistries require more energy for decomposition and typically release a lower amount of oxygen, reducing the TR impact [57]. Depending on the properties of the separator material, the rupture of this barrier between the cathode and anode can initiate thermal runaway due to the resulting short circuit, leading to a sharp temperature increase. The melting temperature of the separator can range from 110 to 220 $^{\circ}\text{C}$ [58]. At high temperatures, the electrolyte can decompose [54,59], producing molecules that, under conditions such as high temperature and oxygen, can initiate a combustion process [16]. By this point, the venting cap is already open due to the initial gas generation at the beginning of the process, and the thermal runaway becomes unstoppable, potentially propagating to adjacent cells due to heat transfer [59]. Other reactions with binder material can further intensify the TR process [60].

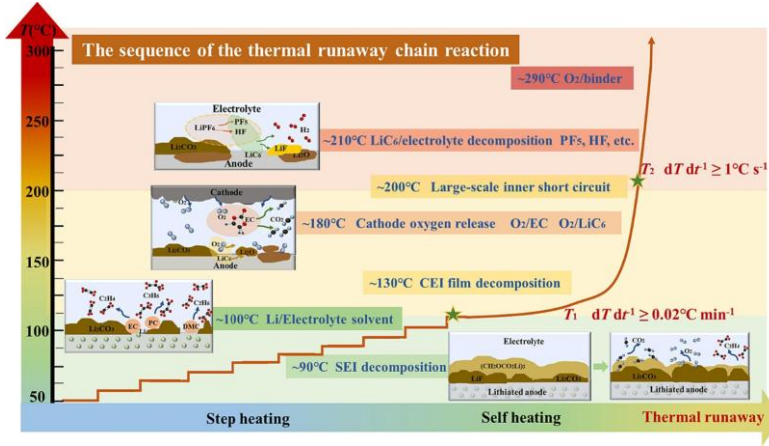


Figure 2.10. TR main reactions for thermal trigger [61].

Different components in the battery can affect the general sequence of events described [62]. For instance, Li et al. [63] used an accelerating rate calorimeter (ARC) to conduct experimental thermal abuse testing on batteries with different cathode chemistries. The results show a comparable onset temperature of around 90 °C. This can be explained by the fact that the first reaction is driven by SEI decomposition and the reaction between lithium and the electrolyte. Since these batteries share similar components in terms of anode and electrolyte, they exhibit a similar onset temperature. Nevertheless, the heat release, maximum temperature, and maximum temperature rise rate of the batteries were different. The NCM has shown the greatest values, followed by LFP and LMO. This means that the cathode decomposition plays an important role in the TR process.

Another problem related to the thermal runaway process with external heating as a trigger is scatter behaviour. Zhang et al. [64] have used the heat-wait-see (HWS) methodology in an ARC to investigate the impact of cell-to-cell variability in nine pristine LCO cathode chemistry cells. The battery TR parameters were compared in terms of maximum and onset temperatures. The results present a scatter behaviour cell-to-cell. However, the root cause is not understood. The authors highlighted problems from the existing models

that cannot accurately predict the cell-to-cell dispersion, which leaves potential for future improvements in modelling.

2.3.1.2 Mechanical trigger

A mechanical trigger can occur in different ways: impact, deformation or penetration. Additionally, depending on the mechanical damage the battery suffers, it may not go into thermal runaway instantaneously. However, a small hotspot, caused by increased resistance or a minor short circuit, can heat the battery, leading to a chain reaction similar to a thermal runaway triggered by external heating. In this case, however, the heat generation is internal.

In most cases, the thermal runaway is instantaneous when using a mechanical trigger as nail penetration. This is frequently used to understand the internal short circuit [65]. Compared to a battery TR triggered by external heating, the heat release from a battery TR triggered by nail penetration is higher [66]. Walker examined the thermal runaway of different battery chemistry using distinct triggers such as nail penetration, external heating and an internal short circuit coupled with external heating. The total heat release of each test condition shows that the TR triggered by nail penetration exhibits the highest value [67]. TR triggered by external heating is mainly driven by the electrolyte and anode reaction until the separator melts, causing an internal short circuit [64]. Otherwise, nail penetration directly causes a short circuit, which theoretically leads to higher heat release [68]. Figure 2.11 shows the difference in the battery temperature evolution as a function of the TR trigger used, where T_{in} , T_f and T_b are the internal battery temperature, and front and side surface temperature of the battery, respectively. The nail penetration trigger, Figure 2.11 (a), presents the most dangerous scenario compared to electrical and thermal triggers. The main difference is in the time available to detect the unsafe situation. In the case of a mechanical trigger such as nail penetration, the sharp increase in temperature occurs almost instantaneously, transitioning from a safe

condition to an unsafe one with no time for any mitigation strategy to prevent thermal runaway. In contrast, other types of triggers exhibit a delay before the sharp increase in battery temperature, as seen in Figure 2.11(b), with thermal trigger and Figure 2.11 (c) with electrical trigger.

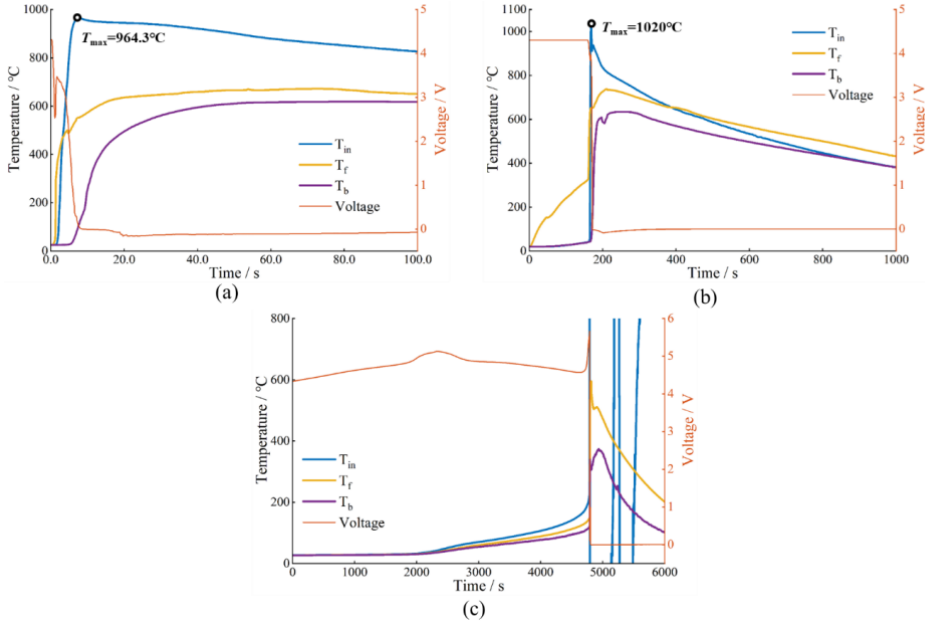


Figure 2.11: Battery temperature behaviour during a TR test with different triggers (a) mechanical/nail penetration, (b) thermal/external heating and (c) electrical/overcharge.

Mao et al. examined the impact of nail penetration location, depth, speed, and state of charge (SOC) [69]. The nail penetration device was manufactured by Beier Experiment Apparatus, and the battery is an NMC cell with a 2 Ah capacity in an 18650 format. The results show that the depth of nail penetration has little effect on the temperature distribution on the battery surface. However, a higher penetration velocity resulted in a more uniform temperature distribution. A notable effect was observed with different states of charge (SOC), as lower SOC led to a weaker short circuit due to less lithium being intercalated in the anode. Regarding nail position,

penetration at the middle of the battery resulted in the highest surface temperature. The author attributed this to faster heat propagation when the nail is in the centre. However, these results may vary, as other factors can influence this behaviour, such as lithium concentration, which is higher near the connector tab, and the effect of gravity, which may cause the electrolyte to accumulate in the middle and bottom of the battery [66,70]. This becomes evident when analysing the work conducted by Huang et al. [71], who investigated battery TR triggered by nail penetration in an ARC. The test conditions covered different nail positions and SOC. Higher SOC produced a higher maximum temperature. However, nail penetration at the centre of the battery led to lower temperatures than the nail position located at the top and bottom.

The lack of repeatability makes it challenging to establish safety criteria. Furthermore, the limited number of experimental tests documented in the literature, typically conducted on single cells, restricts future advancements in this field [17,72]. Thermocouples are typically the sole method to measure the battery surface temperature [73].

2.3.1.3 Electrical trigger

An electrical trigger can be applied in different ways, such as external short circuit, overcharge, or over-discharge. An external short circuit occurs when the electrodes come into contact with an external conductor. In real-world scenarios, this could happen in a car accident that deforms the battery pack, leading to a short circuit. Another example is the battery pack being submerged in water due to a manufacturing defect or an electric shock during maintenance [17]. An external short circuit can also be called an overcurrent due to the low resistance when both electrodes are connected, causing an overcurrent. The issue with an external short circuit is that the battery is designed to deliver a maximum current, dissipating the heat generated by the battery and maintaining safe conditions. When overcurrent occurs, the heat generated exceeds the battery heat dissipate capacity, increasing the

battery temperature and triggering exothermic reactions that further increase the temperature, potentially leading to thermal runaway.

Overcharge occurs when a battery is charged beyond its voltage limits. Thus, a large amount of lithium is intercalated into the anode. Consequently, the minimum value of lithium in the cathode makes it unstable, leading to reactions with the electrolyte in an exothermic process. Excessive lithium intercalation on the anode side promotes lithium plating and dendrite formation. These lithium deposits can react with the electrolyte, generating heat through exothermic reactions [74]. Additionally, lithium plating may penetrate the separator, causing an internal short circuit. Moreover, liquid organic electrolytes become unstable at voltages above 4.5 V [75], increasing the risk of thermal runaway. This scenario is particularly hazardous because the cell contains a high amount of stored energy, unlike in cases of overdischarge. Overdischarge, on the other hand, can lead to the decomposition of the solid electrolyte interphase (SEI) and the formation of copper dendrites, which may cause internal short circuits [76]. During the recharge process after overdischarge, the SEI reforms; however, this results in capacity fade.

2.3.2 Cell condition considerations for thermal runaway

The main concepts of thermal runaway (TR) are described in the 2.3.1 General overview: Key mechanism and definitions, focusing on three main triggers: thermal, mechanical, and electrical abuse. For each type of abuse, the key reactions have been introduced, along with comments on the potential impact of each event and possible combinations of multiple triggers. However, specific battery characteristics significantly influence the TR process regardless of the TR trigger, as discussed in this subchapter.

2.3.2.1 Energy density

Energy density plays a crucial role in the severity of TR. A higher energy density results in higher temperatures, as a greater amount of reactive material is available for the exothermic chain reactions. For example, a larger amount of lithium in the anode can react with the electrolyte when the self-heating phase starts. Similarly, more lithium is present in the anode to contribute to an internal short circuit when the separator ruptures. Son et al. [77] manufactured pouch cells with different capacities, ranging from 33 mAh to 3300 mAh. TR tests were conducted using an ARC with the HWS protocol. The results showed that higher-capacity batteries reached higher maximum temperatures during TR. Additionally, the 33 mAh cell did not exhibit all the distinct stages of the thermal abuse chain reaction, which were visible in the 1000 mAh and 3300 mAh cells. This suggests that the amount of active material available for exothermic reactions, relative to the amount of inactive material with high heat capacity, significantly influences the TR behaviour.

2.3.2.2 state of charge

State of charge (SOC) has an effect comparable to the energy density. A higher state of charge means a higher temperature. Chen et al. [78] used an ARC to investigate the TR behaviour of a NMC 611 at different SOC. Using four stages, a model was developed to determine kinetic parameters based on the battery temperature rise rate profile. The study showed higher SOC levels resulted in higher maximum temperatures during thermal runaway. The largest deviation between the model predictions and experimental data was 7%. To account for the effect of SOC, a heat of reaction was assigned for the last stage based on its capacity for each SOC, excluding the heat released during the initial stages. Consequently, within the calibrated region, the model can assess the thermal runaway effect as a function of SOC. However, the TR model was based on a single experimental

test. Further investigation of TR variability is necessary to evaluate its impact on predictive accuracy and validate the proposed model.

Understanding the effect of SOC requires an understanding of how the cell operates. When the battery is charged, lithium is intercalated into the anode. Therefore, SOC influences the initial stage of TR, which is characterised by the reaction between lithium in the anode and the electrolyte. The second effect of SOC is that a higher lithium content increases the amount available of reactant for a short circuit in the event of separator rupture. A third effect is that at higher SOC levels, more oxygen is released during cathode decomposition. This occurs because lithium metal oxide is highly thermally stable in the presence of lithium, making it difficult to decompose at high temperatures. However, when lithium is absent in the cathode active material, it becomes more susceptible to decomposition, releasing oxygen and further fuelling the TR process [79]. Figure 2.12 shows a comparison of the SOC effect on the thermal runaway. Figure 2.12 (a) depicts the heat generation of the thermal runaway of a NCA battery chemistry, showing that a higher SOC leads to greater heat generation. Figure 2.12 (b) presents the mass loss due to TR, which was higher for higher SOC. Finally, Figure 2.12 (c) shows a safety operation map as a function of SOC. Thus, lower SOC has resulted in lower heat generation and maximum temperature, increasing the safety region.

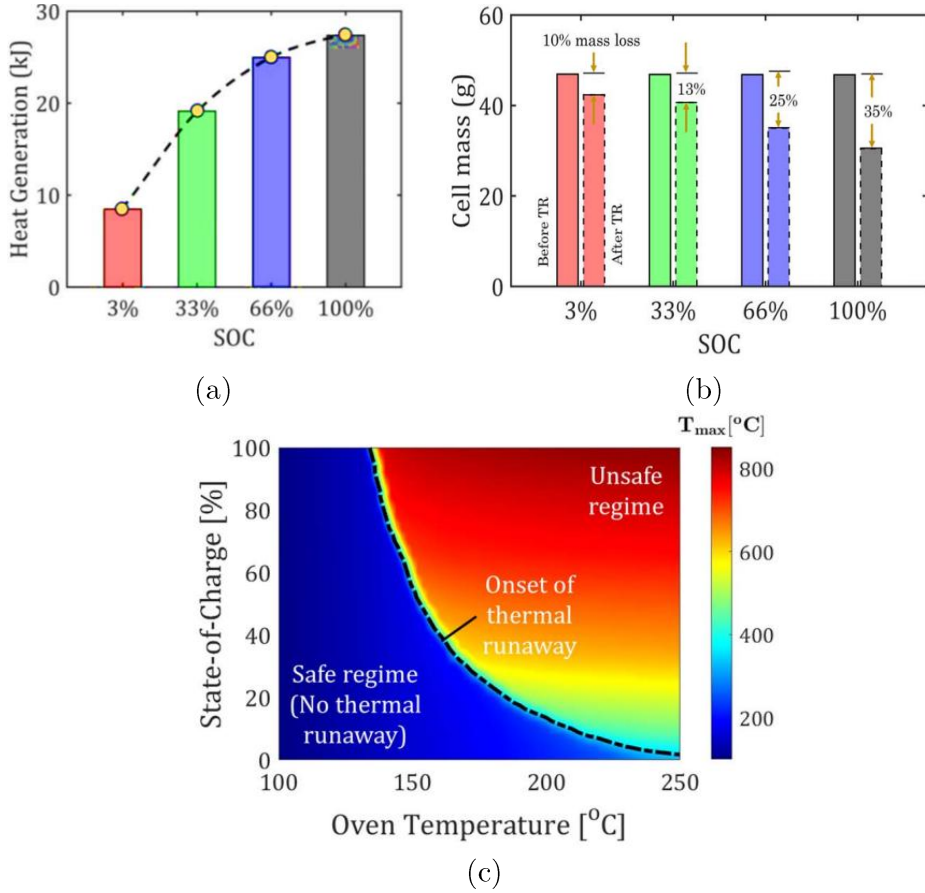


Figure 2.12. SOC of charge effect for a NCA lithium-ion battery in an ARC test with HWS protocol. (a) heat generation as a function of SOC, (b) Cell mass loss as a function of SOC and (c) safety operation condition map [80].

However, contradictions exist in the literature regarding the relationship between SOC and TR. While the theory suggests that higher SOC leads to higher temperatures during TR, experimental tests using an ARC with the HWS protocol have shown that batteries with different SOC levels can exhibit similar maximum temperatures. For instance, Kvasha et al. [81] tested 3 different cells at 3 different SOC. The results showed that for cell B (LFP), the maximum temperatures were similar for different SOC, while for cell A (NCA), the maximum temperature at SOC 50% was higher

than at SOC 100%. The causes of these variations in maximum temperature require further investigation.

Few studies have explored optical techniques to characterise the TR process, particularly battery surface temperature, jet formation, and ejected particles as a function of state of charge. Kong et al. [82] proposed a model to understand jet formation and flame characteristics during TR. The comparison between experimental and simulation shows uncertainties of about 30%, with higher SOC leading to a more violent flame process. Similar results can be seen [83]. The results presented by Kong were obtained using natural luminance and thermocouples. However, the work does not present data related to particle ejection despite particles contributing significantly to the total mass ejected. Furthermore, flow characteristics were not discussed, leaving room for further research. Understanding hot particles and flaming behaviour is important for safety concerns, as seen in [84].

2.3.2.3 Ageing effect

Another battery condition that may impact thermal runaway is the degradation process of the battery, known as the ageing effect. This effect is less documented in safety studies but cannot be ignored. Thermal runaway can be dangerous depending on the battery degradation process. Using an ARC, Waldmann and Mehrens [85] have examined the ageing impact at 0 to boost lithium plating phenomena and evaluate the safety concerns. The findings demonstrated that battery ageing resulted in more mass ejected, injecting the jelly roll from the cell container, and an earlier thermal runaway event. The impact of ageing on thermal runaway is complex. A review conducted by Ren et al. [86] highlights the difficulty in understanding the thermal runaway behaviour of aged cells. Factors such as cathode particle cracking, CEI film formation, and transition metal dissolution do not show apparent effects on TR. However, electrolyte consumption due to side reactions reduces the maximum temperature reached during TR, while lithium plating appears to decrease thermal stability. The first effect related

to electrolyte consumption can be understood as SEI growth, where an effective protective layer increases thermal stability and reduces the amount of thermally reactive material, leading to a lower maximum temperature during thermal runaway. However, depending on the cycling protocol, the presence of metal in the SEI layer can negatively impact [87]. The second effect of lithium plating is that it accelerates SEI decomposition. Consequently, thermal runaway occurs earlier, reducing battery safety [88]. A similar degradation mechanism can be induced through calendar ageing, where a battery is stored at a specific SOC for an extended period. This process can also impact the parameters of the thermal runaway process, as depicted in Figure 2.13.

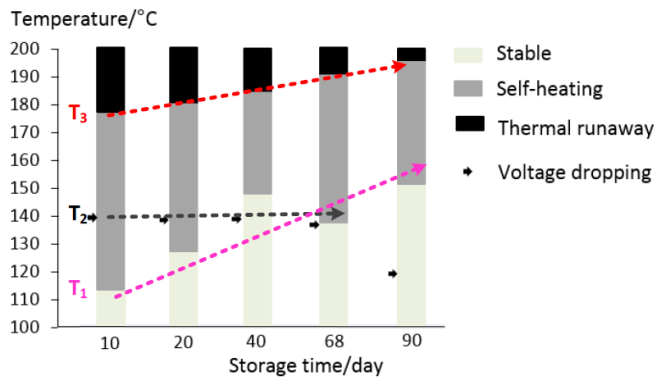


Figure 2.13. Calendar ageing effect in TR [89].

Some contradictions are found in the literature [90,91], which make it difficult to understand the effect of ageing on the maximum temperature during thermal runaway. In some cases, the maximum temperature is similar between aged and pristine cells, while significant differences are observed in others. For second-life applications, it is essential to understand the impact of ageing on safety concerns, considering cell-to-cell variability that is rarely discussed, guaranteeing economic benefits [92]. Figure 2.14 presents the dispersion of lithium-ion batteries when comparing degraded and pristine cells in TR tests with ARC using HWS. There is no clear trend in battery temperature across different cases, highlighting the need for further investigation to understand the experimental results better.

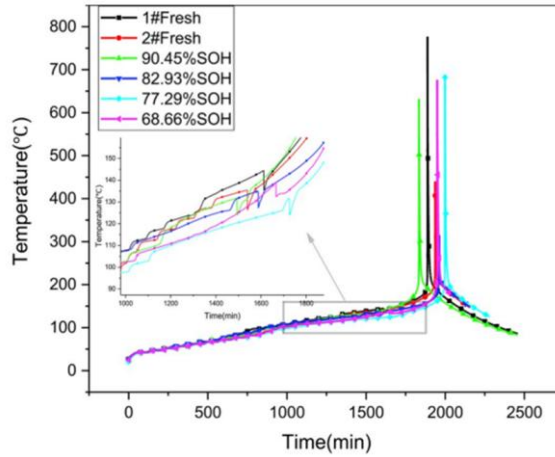


Figure 2.14. Thermal runaway of pristine and aged batteries performed in an ARC with HWS protocol [93].

2.3.3 Thermal runaway modelling

The models to predict thermal runaway are typically validated using a single experimental test [94]. Differential Scanning Calorimetry (DSC) is used to evaluate different reactions between different battery components, and the results are used to feed the Arrhenius equation that will be calibrated to replicate the thermal runaway behaviour [95]. The problem arises because the results correspond to the composition of materials used in the anode, electrolyte, cathode, binder, and other components. The electrolyte varies from cell to cell, depending on the manufacturer and battery performance. The same applies to the cathode and anode chemistry. For example, in NMC batteries, the concentration of nickel, manganese, and cobalt can vary. In addition, additives used to enhance electrical conductivity or improve safety can also lead to differences in results from cell to cell [96–98]. Therefore, the models developed with this methodology are specific to the battery used, as different battery materials would result in different behaviour.

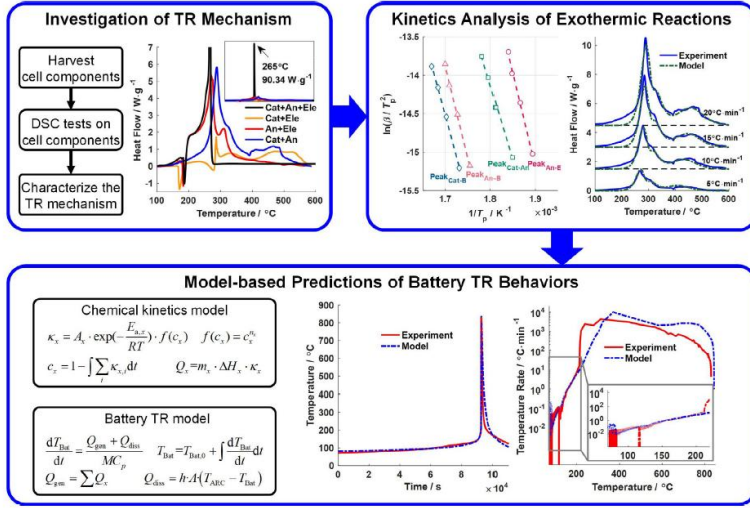


Figure 2.15. Thermal runaway model scheme obtained with DSC tests [95].

In addition, the Arrhenius equations derived from the different reactions tested are treated as if they occur independently and are not affected by other reactions. For example, some fundamental works have shown that the cathode and anode reaction can suffer a short circuit after the separator rupture, occurring internal short circuit [99]. However, depending on the material, the separator melts at high temperatures, around 160 - 200 °C [100]. Before this, the exothermic reaction was mainly driven by the anode-electrolyte interaction, which consumes reagents such as the electrolyte and lithium in the anode, reducing their concentrations [79,101]. Therefore, while DSC tests capture the full reaction of each component in real applications before separator rupture, the non-simultaneous reactions should reduce the intensity of subsequent reactions. In addition, the interactions of overlapping reactions after separator rupture make it challenging to predict or calculate the heat generation for each reaction when this event occurs. For this reason, an adjustment is required to balance the heat release of each reaction, which can be done by modifying the reaction order. This parameter is not measured in experiments in the current models available. This helps to fit the temperature curve generated by the DSC model with the experimental results obtained from ARC tests using the HWS

protocol. Furthermore, the data obtained from thermal runaway (TR) models represent a pristine battery at SOC 100%, while other battery conditions have been few explored, limiting the accuracy of TR behaviour prediction. Another difficulty is that these models require knowledge of the mass quantity of battery materials involved in the chain reaction, which may be difficult to determine.

Another approach used is to model the thermal runaway directly from the data obtained from the ARC using HWS protocols. The process to obtain this model can be seen [102]. Therefore, activation energy and the pre-exponential factor can be directly calculated from ARC data, saving time and reducing the need for extensive experimental testing. Most models using this approach are calibrated from single experimental tests, similar to DSC models. However, some models can adjust the SOC conditions for specific battery chemistry [78].

2.4 Approach of the study

2.4.1 Motivation of the study

This chapter described the working principle of batteries, their main materials, and components, focusing mainly on cylindrical cells, which are the focus of this study. As discussed, batteries can be constructed from different materials, significantly impacting the thermal runaway process and making them more or less safe for vehicle applications. In addition, different energy densities, states of charge, and degradation mechanisms can affect the severity of thermal runaways based on the thermal abuse applied to the battery, such as thermal, mechanical, or electrical abuse. Therefore, understanding the battery thermal runaway from the reaction between single-cell components to the failure of an entire cell is essential for designing safety systems. However, the randomness reported in studies and the lack of statistical analysis in some works make it difficult to draw concrete

conclusions about specific effects, such as battery chemistry and ageing under specific conditions.

The present difficulties in experimentally characterising the process are reflected in the current models, which are based on a specific battery condition and cannot be easily extended beyond the calibration conditions, typically derived from single-cell tests. This limitation increases the constraints when simulating and predicting battery thermal runaway under different operating conditions, loads, or stress factors. To understand this issue, this thesis could develop TR characterisation using optical techniques to analyse the random behaviour and assess cell-to-cell variations, concerning battery surface temperature distribution, as well as visualising and characterising the venting process during TR. Different optical techniques could be applied under controlled conditions to measure the sequences of the TR event, providing insights into the cell-to-cell variability. Finally, a model could be proposed, incorporating the insights obtained from experimental tests and decreasing simulation constraints. Therefore, based on the literature review presented in the current chapter, the following topics could be explored:

- Understanding the heat release during battery thermal runaway based on the materials (reactants) involved in chemical reactions under different abuse conditions and linking it to morphological changes due to degradation mechanisms can help establish a solid foundation for comprehending the scattering behaviour of thermal runaway.
- Optical techniques such as thermographic cameras, the Schlieren technique, and natural luminance remain underexplored and are rarely applied under controlled conditions, such as in an accelerating rate calorimeter. Implementing these techniques in controlled environments would help standardise metrics for comparing thermal runaway events by accounting for ambient conditions. This would make key thermal runaway parameters more comparable while also

providing insights into the behaviour of the entire cell during thermal runaway.

- Existing models are typically developed based on single-cell tests calibrated for specific conditions, limiting their applicability to different battery states, such as degradation, varying energy densities, and state of charge (SOC), with only a few models considering SOC effects. Additionally, the random behaviour of thermal runaway introduces difficulties in ensuring the reliability of model predictions.

2.4.2 Objective of the study

Considering the gaps identified in the literature review, the general objective of this thesis is to *understand cell-to-cell variability by analysing the heat release from both the main chain reactions and the entire cell using electrochemical modelling and optical techniques, proposing a thermal runaway model capable of predicting thermal runaway behaviour under different battery states.*

The specific objectives to achieve the goal of the main objective can be listed as:

- To assess material quantity and morphology changes, calibrate and validate an electrochemical model for pristine and aged conditions.
- Develop a calculator capable of predicting heat release based on stepwise reactions to evaluate the effect of battery materials on the heat release of a pristine cell and the impact of material degradation due to cycling.
- Investigate the thermal runaway behaviour of both pristine and aged cells using a thermal and mechanical trigger to understand scattering behaviour under controlled conditions (ARC) coupled with optical

techniques for diagnostic purposes to improve the understanding of the thermal runaway event.

- Propose a calibrated and validated TR model which accepts different inputs related to the battery state to enhance TR prediction.

2.4.3 General methodology and research development

The thesis is planned to include experimental and numerical approaches, which interact according to Figure 2.16. The research first characterises the electrical and thermal behaviour of NMC and LFP batteries to calibrate and validate a pristine model in GT-AutoLion. Ageing is performed using a climate chamber and a bidirectional source, which will be used to calibrate and validate the ageing model from the pristine model in GT-AutoLion. In addition, an optimisation methodology is used to define parameters that are difficult to measure in the batteries, reducing experimental complexity through P2D modelling. This part is presented in Chapter 4, which addresses normal operating conditions. The results can be used to feed a table containing stepwise reactions to understand the impact of cell materials such as the cathode, electrolyte, and anode on the thermal runaway. This is achieved by assessing the active material content, electrolyte quantity, lithium content, SEI thickness, electrode porosity, and other parameters resulting from the modelling performed in the first part. Insights based on the material composition of the battery, including SOC, energy density, and ageing mechanisms in thermal runaway, can serve as a basis for the proposed TR model. This comprises the first part of Chapter 5, which is related to abusive operating conditions. The study of thermal runaway in the entire cell will be conducted using an ARC coupled with a fast and high-speed thermographic camera. Techniques such as infrared imaging, Schlieren photography, and natural luminance analysis will describe the TR event and understand the process, identifying the root causes of cell-to-cell variability highlighted in the literature for different battery conditions. Post-processing will be performed using MATLAB and Python code to compare conditions related to temperature distribution, particle velocity, jet

formation and phase, and other parameters. The thermal runaway investigation of the entire cell will conclude in Chapter 5. Finally, a proposed model will be presented, based primarily on the results obtained in Chapters 4 and 5. This model may be able to predict thermal runaway by considering the root causes of cell variability and using different battery conditions as input, reducing the constraints of current thermal runaway models.

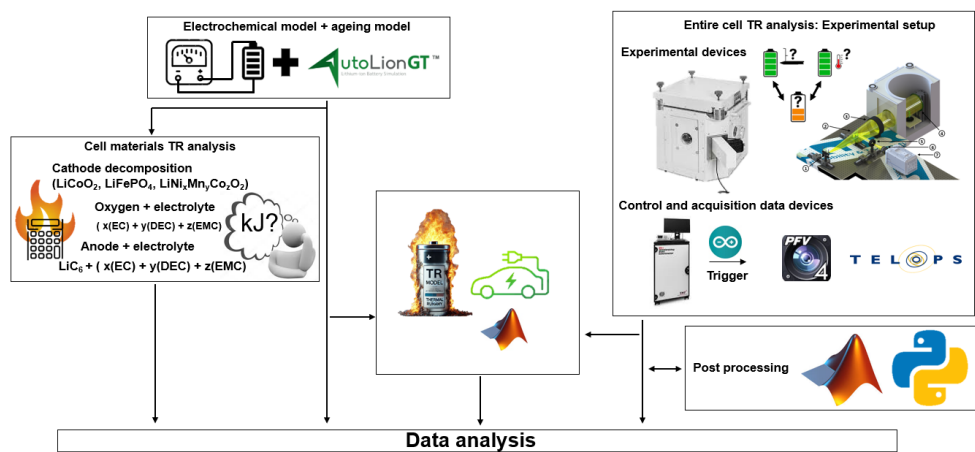


Figure 2.16. General overview of the thesis structure.

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Chapter 3

Tools and methodology

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3.1 Introduction

This study investigates the impact of different battery chemistries and conditions on vehicle range, as well as the impact of cells under a thermal runaway process caused by distinct triggers. Thus, the present work combines experimental testing and modelling to characterise the batteries and predict their state of health. Battery abuse conditions were carried out using different techniques, employing external heating and a mechanical trigger to assess the thermal runaway potential coupled with optical techniques. For better understanding, this section will be broken into different sections. The experimental facilities for electrical and thermal characterisation are described first, as well as the methods used. In sequence, battery electrochemical modelling based on the pseudo-two-dimensional model is described.

3.2 Experimental facilities

This section addresses the battery specifications, the equipment used for electrical and thermal characterisation (abuse tests), and the operating principle and methodology applied during each experimental test.

3.2.1 Electrical characterisation of batteries

The battery was characterised using an Arbin Instruments bidirectional power source, model LBT-10V-100A [1]. This instrument offers high precision, providing current outputs ranging from 500 mA to 100 A with an accuracy of 0.04% across the entire range. Additionally, it can supply voltage outputs from 0 to 10 V, with an accuracy of 4 mV. This equipment provides a 4-wire or Kelvin connection to prevent data bias. It can happen because the wire used to provide or demand current from the battery can be thicker due to high current demands. This might result in a high voltage drop, indicating that the voltage behaviour is due to the bidirectional source system

rather than the battery, leading to measurement mistakes. Connecting two wires on the battery to monitor voltage ensures practically negligible voltage drop because this test requires a near-zero current draw. Furthermore, a climate chamber MZTC, manufactured by Arbin Instruments, was coupled with the bidirectional source to guarantee a constant ambient temperature. Figure 3.1 shows the equipment used for battery electrical characterisation and the 4-wire connection scheme.

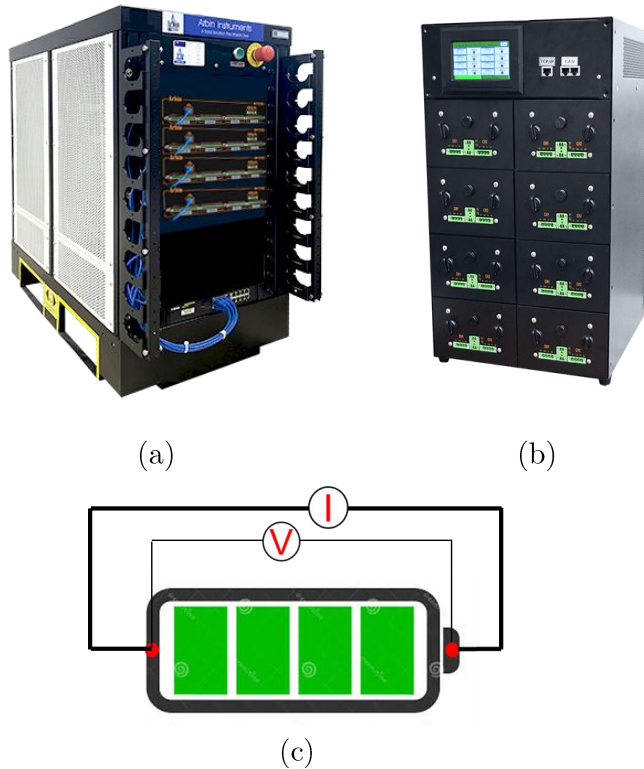


Figure 3.1. (a) Bidirectional source Arbin LBT-10V-100A, (b) Climate chamber Arbin MZTC and (c) 4-wire or Kelvin connection scheme for the battery.

3.2.1.1 C-rate characterisation

The batteries were characterised by applying different C-rates of discharge at constant ambient temperatures. The charge process was maintained constant, according to the standard defined by the manufacturer for each cell. In addition, a thermocouple T-type was used to measure the battery surface temperature for thermal model calibration. The accuracy related to the measured temperature range (-40 up to 133 °C) is ± 1 °C and the precision is ± 0.1 °C. The ambient temperature was maintained consistently using a climate chamber MZTC manufactured by Arbin Instruments.

3.2.1.2 Open circuit voltage (OCV)

OCV was characterised by using a low C-rate during the charge and the discharging process. An average process between both curves is carried out to approach the open circuit voltage of the battery. A similar result can also be achieved using HPPC or GITT measuring the voltage during the relaxation time, considering a maximum acceptable variation between values, representing OCV for a given SOC [2].

3.2.1.3 Aging process characteristics

Battery capacity fading is related to the degrading processes that occur during cycling. Several factors can impact these degradation pathways, affecting the battery lifespan. In this present work, the target mechanism is to boost SEI growth. SEI is a protective layer that isolates the electrons and lithium in the anode from the lithium-ion and electrolyte components, respectively [3,4]. SEI formation mechanism is defined as a new product formed from a reduction reaction of organic materials present in the electrolyte, and it is deposited on the anode surface to form SEI [5]. This process causes capacity fading as this reaction consumes lithium [6]. However, SEI growth can stabilise with battery usage. Basically, there are three

different stages: early, stable, and decline, according to Figure 3.2. The SEI growth mechanism dominates the first stage, followed by a stable stage where battery capacity decreases. At the end of life, lithium plating is the main mechanism responsible for the decline stage[7,8].

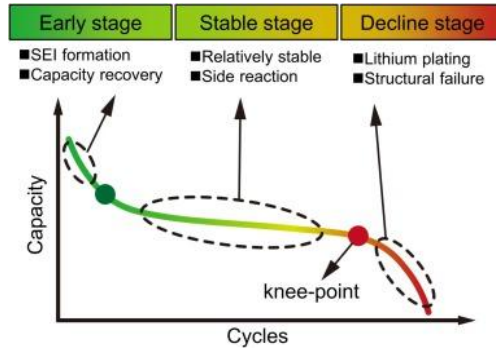


Figure 3.2. Characteristic of decreasing lithium-ion battery capacity during its useful life [7].

The ageing mechanisms are complex and can occur simultaneously during battery cycling. However, there are external factors that can boost different mechanisms. For example, higher temperature tends to increase SEI growth, while lower temperature and higher current increase lithium plating [9]. Figure 3.3 summarises the main mechanisms, the location of the degradation process within the battery, the external factors that contribute to accelerating the deterioration, and the main consequences for the battery. Besides boosting SEI growth, higher temperatures can also cause binder decomposition in the anode and cathode and a solid permeable interface in the cathode. However, it is widely agreed that SEI growth is the main degradation mechanism at temperatures above ambient. Furthermore, other degradation processes within the battery are triggered by long-term SEI growth. For instance, the SEI can penetrate through the pores of the active material, causing what is known as "pore clogging." As a result, porosity decreases and tortuosity increases, hindering the accessibility of lithium ions to intercalate into the anode and increasing impedance. These factors are directly linked to the battery power fade. Additionally, pore-clogging can lead

to the accumulation of lithium metal, forming dendrites on the negative electrode [10].

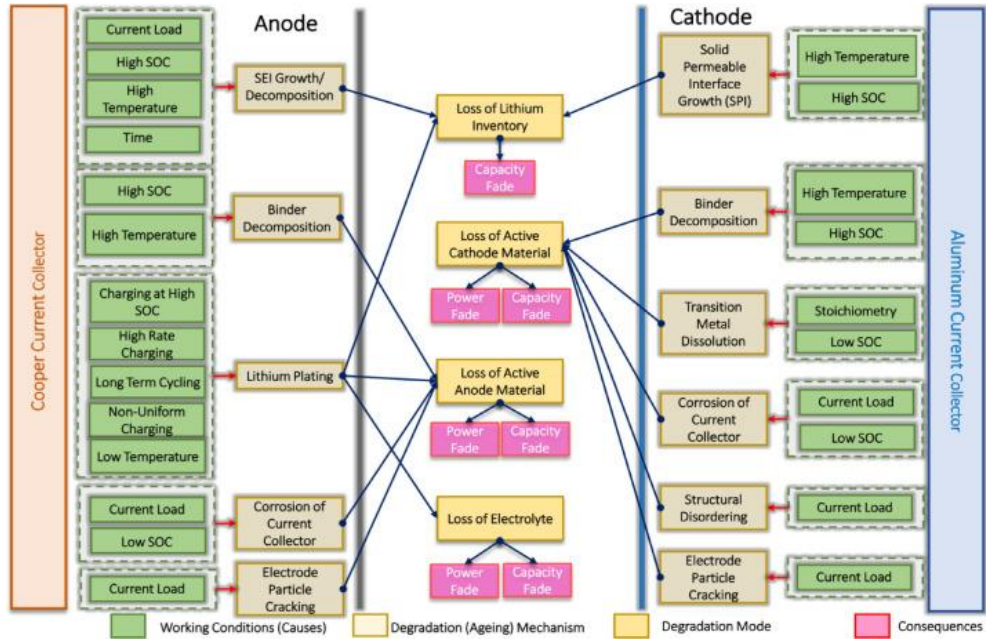


Figure 3.3. Ageing mechanism summary [6].

In this way, the ambient temperature was maintained at 25 °C and 50 °C, as the negative temperature would result in the lithium plating degradation mechanism. In addition, the charging process used was 1 C-rate as higher charge C-rates can also result in a lithium plate degradation mechanism. To decrease the time during the cycling process, the battery was only charged up to the maximum voltage using constant current. Therefore, the constant voltage step from the CCCV protocol was not applied during the cycling. The battery remained for 30 minutes for voltage and temperature stabilisation, and, in sequence, the battery was discharged using a 2 C-rate up to the minimum voltage. Before starting the charging process of the next cycle, the battery also rested for 30 min for voltage and temperature stabilisation. Figure 3.4 illustrates the process described above.

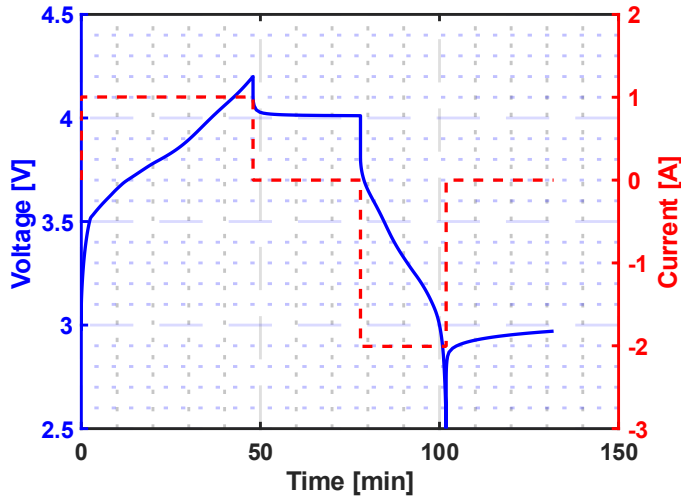


Figure 3.4. Battery cycling (charging, rest and discharging) for the ageing process. The voltage values are from a NMC cathode battery chemistry.

3.2.2 Accelerating rate calorimeter

An accelerating rate calorimeter (ARC) was used to develop the current work, evaluating the thermal runaway (TR) potential using different triggers, thermal and mechanical, to induce the abuse condition [11]. The ARC is the ARC THT EV+ model, manufactured by Thermal Hazards Technologies. The calorimeter has a size of $\varnothing 40 \times 44$ cm, and it is constructed with a thick aluminium jacket equipped with resistances, which can work independently, located on the bottom, side and top walls that can provide a maximum heat rise rate of $15\text{ }^{\circ}\text{C}/\text{min}$ and reach a maximum temperature of $300\text{ }^{\circ}\text{C}$. Figure 3.5 (a) depicts an overview of the calorimeter with the nail penetration device attached to the calorimeter and, Figure 3.5 (b), a schematic of the location of the resistances used to maintain the desired ambient temperature for the experimental test.

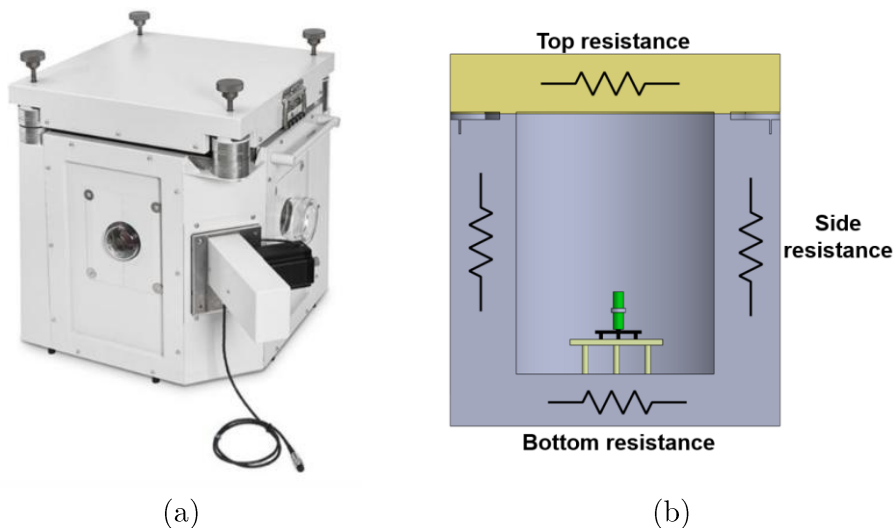


Figure 3.5. (a) overview of the ARC with coupled nail penetration motor, (b) resistance location scheme of the ARC.

Ambient temperature control can be achieved by providing isothermal temperature control or by performing a heat wait seek (HWS) protocol. Isothermal control was used for battery characterisation and to establish an initial condition for nail penetration tests (mechanical trigger for TR). The HWS protocol performs different steps to detect exothermic reactions and thus, in sequence, only track the battery temperature to guarantee a quasi-adiabatic environment. Furthermore, the ARC also has the function of a safety chamber due to the robustness of the walls and the cooling system after the TR process. In addition, the magnetic system of the lid releases the internal gases when the pressure is greater than 1 bar, avoiding the risk of explosion of the system.

A modification was made to allow the application of the infrared technique in the study of the TR in a controlled ambient. The original glass available for optical access was replaced with a sapphire window, as the original does not permit infrared rays to pass through. Then, mechanical parts were machined in steel to accommodate the sapphire window holder. A graphite gasket was used between the contacts to avoid leakage, maintaining

the original ARC design to guarantee the quasi-adiabatic ambient. Figure 3.6 presents the sapphire window and the holder manufactured in steel to accommodate the modifications in the ARC.

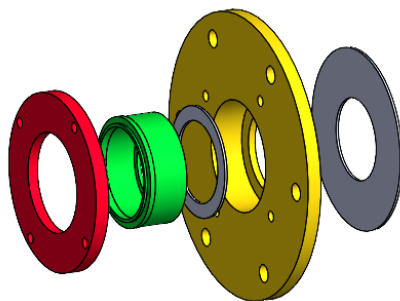


Figure 3.6. Window modification was carried out to measure battery temperature through the infrared technique.

3.2.2.1 Heat-Wait-Seek

The HWS protocol starts with the heat process, where the battery temperature increases to the first target temperature. The wait period starts when the battery achieves the target temperature. Due to thermal inertia, the calorimeter begins stabilising the ambient temperature to ensure that the ARC is not supplying any heat that could increase the battery temperature. In sequence, the ARC looks for exothermic reaction in the seek period. The condition to detect exothermic reaction is when the battery temperature rise rate is higher than the sensitivity calibrated. Otherwise, if the battery temperature rise rate is lower than the sensitivity, the ARC will heat again up to the next target temperature. Once an exothermic reaction is detected, the calorimeter will only track the battery temperature, maintaining the wall temperature equal to the battery temperature, preventing the battery from losing or receiving heat, and creating a quasi-adiabatic ambient. Figure 3.7

describes the battery temperature as a function of time during the heat-wait-see protocol performed by the ARC.

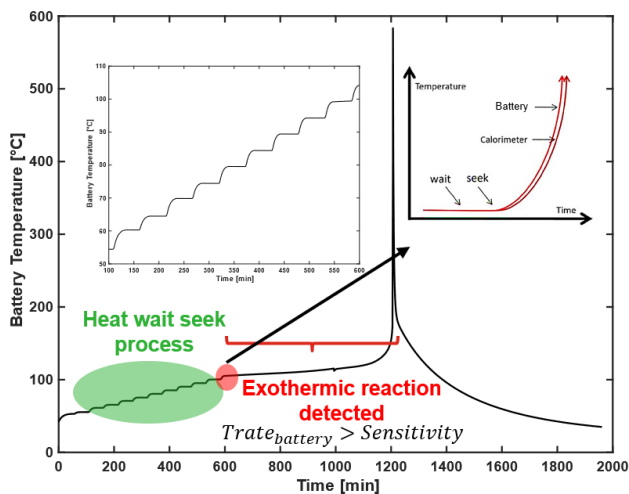


Figure 3.7. The heat wait seek protocol performed by the ARC.

Before each experimental test batch, a calibration procedure is required to detect accurately the exothermic reaction and avoid drift problems. This can be explained by the fact that two thermocouples will measure different temperatures for a body at temperature X. If the ARC control adjusts both temperatures to the same value, the battery temperature will decrease or increase. Thus, an offset must be determined between the thermocouple of the battery and the thermocouples from the calorimeter walls. Therefore, using a dummy, a calibration protocol is carried out every 100 °C, starting at 50 °C. The protocol starts by heating the dummy to the target temperature, followed by a wait time to allow for isothermal equilibration. A calibration mode is activated in sequence. This mode tests different offsets until the temperature rise rate of the dummy is lower than half the sensitivity chosen for the experimental test of TR. This ensures that during a battery TR test, any temperature rise rate higher than the sensitivity during the seek period is a result of an exothermic reaction, as the ARC temperature offset is previously known. In summary, the ARC knows which temperature to set in the wall to maintain the battery temperature with a temperature rise rate

lower than configured, as it was calibrated beforehand with a dummy (without an exothermic reaction). The parameters used for the heat wait seek protocol can be seen in Table 3.1. In addition, according to the manufacturer, the ARC is equipped with N-type thermocouples with 0.001°C resolution and an accuracy of 0.7%.

Table 3.1. ARC standard settings.

Parameters	Value
Start Temperature ($^{\circ}\text{C}$)	50
End Temperature ($^{\circ}\text{C}$)	300
Temperature Step ($^{\circ}\text{C}$)	5
Temperature rate sensitivity ($^{\circ}\text{C}/\text{min}$)	0.02
Wait time (30 min)	30

In addition to the ARC original system, a parallel acquisition system provided additional information from the battery thermal runaway when external heating was used as a trigger. The acquisition system integrated with the ARC system is shown in Figure 3.8. The thermocouple for the ARC control temperature (or bomb temperature) is connected to the middle part of the battery. This thermocouple can also be known as the reference temperature, which means that the ARC uses this temperature to analyse any exothermic reaction or track the battery temperature when the battery is in an exothermic reaction. The acquisition rate of the ARC system can reach a maximum sampling rate of 1.6 Hz. On the other hand, the parallel acquisition system can reach 10 Hz, given a better temporal resolution than the original. In addition, two more thermocouples were connected to the battery, one in the upper position (10 mm from the vent cap) and another in the lower position (10 mm from the opposite side of the vent cap). Voltage measurement was also performed, as well as ambient temperature measurement throughout the process. Data acquisition was carried out by using a DL850 ScoperCorder.

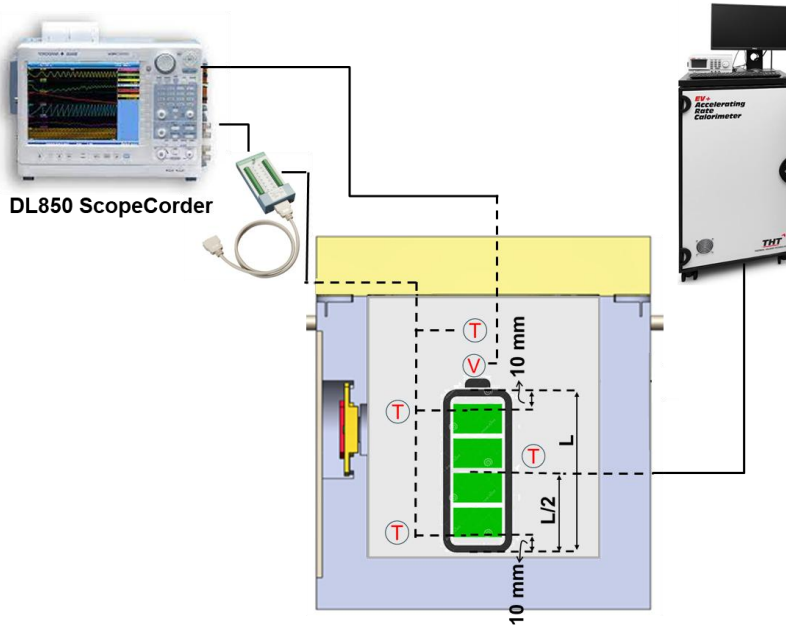


Figure 3.8. Acquisition system for the battery thermal runaway with external heating as the trigger.

3.2.2.2 Nail penetration

Nail penetration consists of a system composed of a motor coupled in the outside part of the ARC. An arm is attached to the motor through a hole that enables testing the mechanical trigger for thermal runaway on batteries inside the calorimeter. The nail and its holder are mounted on the end of this arm. A special frame is installed inside the ARC to brace the cell against the force of the motor. Figure 3.9 shows a scheme of the system used.

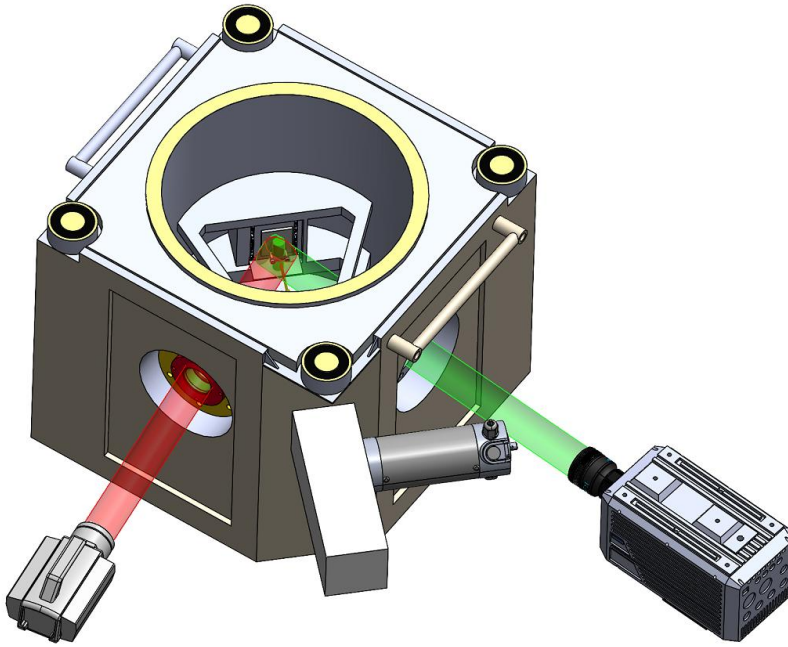


Figure 3.9. Nail penetration device fixed to the ARC.

In addition, the nail penetration device has a tray, which is part of the battery holder, and can be moved up or down, adjusting the position of the nail on the battery surface. Then, once the battery is positioned, the tray is fixed by tightening a screw on the side of the battery holder. Figure 3.10 depicts the battery holder and the system to adjust the nail position.

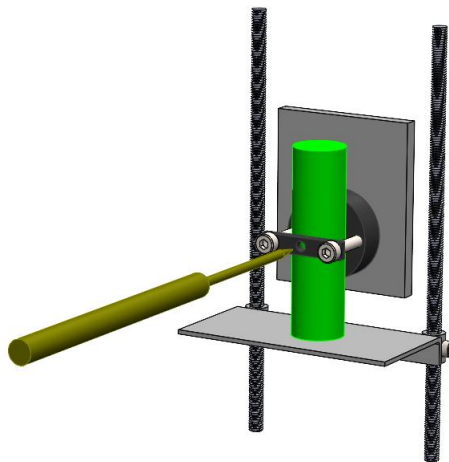


Figure 3.10. Battery holder and the tray, which is used to adjust the nail position on the battery surface.

The system from the calorimeter can control the speed, penetration, initial temperature and retraction time (the duration that the battery remains with the nail inside). The nail diameter used in the experimental tests performed is 3 mm. Table 3.2 shows the nail penetration system parameters.

Table 3.2. Nail penetration system parameters.

Parameter	Description
Abuse test temperature (°C)	Ambient - 300
Abuse test speed (mm/s)	0 - 300
Abuse test distance (mm/s)	0 - 100
Abuse test period (min)	0.1 - 5

3.2.3 Optical techniques

Different optical techniques were applied to understand and measure parameters related to the jet format, temperature and velocity field. Schlieren technique was applied in the first venting process, where it was possible to identify the different compositions and behaviours. For the second venting, the thermal runaway itself, thermographic images and combustion image velocity were applied to characterise the process in terms of particle temperature and velocity field. Therefore, different approaches were used to mount the equipment inside the ARC system, where the battery was submitted to TR. Constraints are described in sequence for each optical technique and working principles.

3.2.3.1 Schlieren technique

Doble pass Schlieren technique was applied to the first venting process, which happens during the self-heating phase of a thermal runaway caused by external heating. This process implies that the battery is not operating in a safe condition. For this reason, the first venting process is critical since it can serve as an early warning to TR. Different strategies can be adopted in the case of detecting the first venting due to the time available up to the unstoppable reactions of the TR. However, the time available depends on a series of factors that need to be understood.

The technique requires a point light source to create a beam of light, which is then collimated using a converging lens. As the light passes through the test section, the density gradient refracts the collimated beam of light. A mirror reflects the light beam back through the test section, refracting it again due to the density gradient, maximising the refraction by making the light travel twice through the test area. A beam splitter reflects a portion of the received light towards the camera detector. At the cut-off plane, positioned at the lens focus point, an iris diaphragm blocks the refracted light, allowing only the parallel light rays to pass through [12,13].

Double-pass Schlieren is used because it requires only one optical access, while the other optical access is used for the thermographic camera. According to Figure 3.11, using the mirror inside the calorimeter and the beam split outside the calorimeter, all the other equipment can be mounted in the peripheral area of the calorimeter.

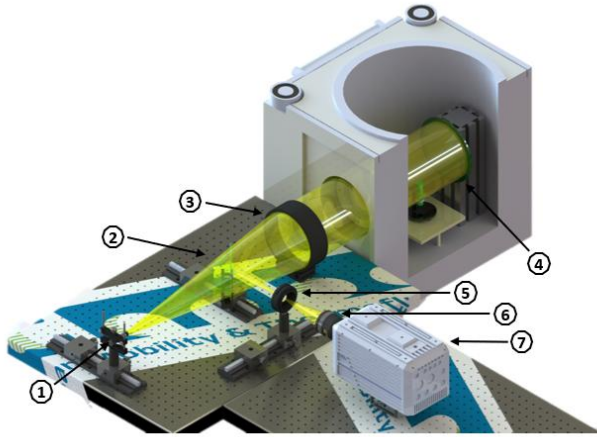


Figure 3.11. Double-pass Schlieren coupled with the ARC.

Table 3.3 contains a list of the equipment displayed and identified by callouts with numbers in Figure 3.11.

Table 3.3. Specification of the components used in the optical experimental setup.

Item number	Component	Specification
1	Light Source Karl Storz Nova 300	Xenon lamp 300 W
2	Beam splitter [mm]	178x127 - 50 %T/50 %R - range 450 to 750 nm
3	Spherical lens [mm]	Focal length = 450/ $\varnothing$ 150
4	Flat mirror [mm]	$\varnothing$ 300
5	Iris diaphragm [mm]	Max. $\varnothing$ 13 . Open $\varnothing$ for experiment 5
6	Lens Carl Zeiss Makro- Planar [mm]	Focal length 100 mm, f/2 lens
7	Photron Fastcam NOVA	12-bit, up to 16000 fps in max. resolution

3.2.3.2 Infrared images

The ARC has a common glass to prevent heat transfer and gases from exiting the ARC through the optical accesses. However, this type of glass does not allow infrared to be transmitted, necessitating some modification and the use of specific materials to be possible to measure battery particles and/or surface temperature.

A sapphire window was mounted in one of the two optical accesses in the ARC to permit the transmissivity of the infrared (IR) light emitted by the battery surface or particles ejected during the TR. The thermographic camera was installed in front of the sapphire window, ensuring a safe ambient and temperature for the camera operation, as shown in Figure 3.12. The sapphire window specifications are 50mm in diameter and 15mm in thickness. The model of the IR camera is Telops FAST-IR M1K, with a maximum frame rate (fps) of 1012 at a frame of 640x512 pixels. The settings used during this work were at 2000 fps with a resolution of 320x256 pixels. The camera is connected with an IR 50 mm f/2 lens measuring from 1.5 μ m to 5.5 μ m

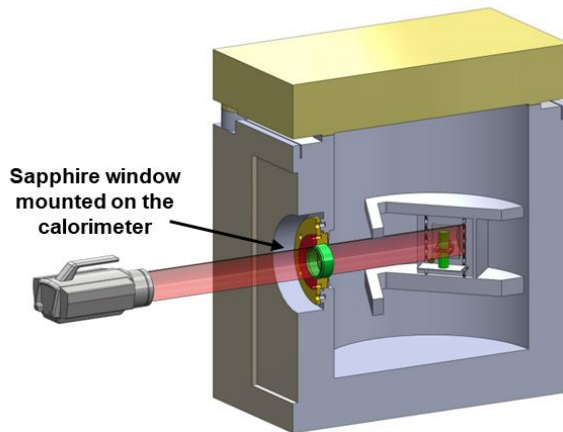


Figure 3.12. Optical setup for the thermographic camera and nail penetration mechanism.

The proposed setup has some constraints that need to be considered to ensure a reliable temperature measurement. The camera calibration is performed with the object in the camera focus. Thus, the radiation intensity received by the camera is attributed to the object temperature. In addition, the ambient conditions are strictly controlled for the standard one. Therefore, the addition of an apparatus and the heating process of the test procedure decrease the intensity of the radiation as the transmissivity is not 100%, according to Figure 3.13. Furthermore, during thermal runaway and HWS protocol, the gases and particles ejected during thermal runaway change the ambient condition to a different from the standard condition.

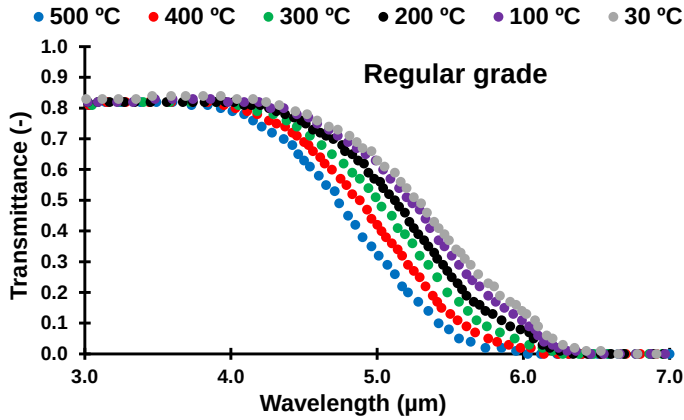


Figure 3.13. Effect of temperature and wavelength on the Sapphire window transmittance. Modified from [14].

For these reasons, the methodology consists of adjusting the distance between the thermal imaging camera and the battery to the focal point. With the sapphire glass removed from the ARC and the dummy painted black with known emissivity, the thermographic camera temperature is similar to the temperature measured by the thermocouple. Nevertheless, the presence of the sapphire window is crucial to maintaining a quasi-adiabatic ambient during the HWS process, avoiding excessive heat transfer to the environment. In this way, in sequence, the sapphire window is mounted in the ARC, and the transmissivity of the window is characterised at room temperature and during the HWS protocol.

3.2.3.3 Natural luminosity

This approach is commonly used in internal combustion engines to investigate the combustion process regarding soot generation and the chemiluminescence of molecules during chemical reactions [15]. Based on this, particles from the thermal runaway injected through the venting cap can be characterised using a fast-speed camera to take advantage of the natural luminosity emitted by the hot particles. Therefore, by adjusting the exposure time and recording the event at a high frame rate, the particle path can be identified, and the velocity can be calculated using different techniques to enhance particle contrast and, thus, cross-correlation to estimate the particle path. This post-processing method is known as combustion image velocity (CIV), which uses raw natural luminosity images.

3.3 Computational tools

GT-Autolion software was used to characterise lithium-ion batteries in terms of chemical composition, electrical responsiveness, and thermal behaviour. Thus, battery components that are difficult to measure can be accessed and used to provide a deeper analysis of the experimental results.

The battery can be modelled using different approaches, such as an equivalent circuit model (ECM) or a pseudo-2D (P2D) model. GT AutoLion pseudo-2D model is a physicochemical model that can predict cell behaviour of different material compositions and designs from electrodes, tabs, electrolytes, and other cell components. The proposed study calibrates the model using experimental data from a specific operation condition. The model is validated sequentially with additional experimental data under different operating circumstances. As a result, the model may be used to predict battery performance based on load demand and the degradation process (ageing) faster than in real-time. Additionally, the calibrated and validated battery model can be easily scaled to a battery module or pack, allowing it to be integrated with other vehicle subsystems and run through driving cycles

or any dynamic test designed to predict emissions or performance of the entire vehicle.

3.3.1 Electrochemical model

The mathematical description was first proposed by Newman et al. [16], and it is also referred to as the Doyle-Fuller-Newman (DFN) model. The battery performance is estimated based on the transport rate of electrons and lithium ions from the anode to the cathode. In addition, the modelling considers the effects of temperature changes due to increased resistance due to the charging and discharging process and increased resistance due to degradation processes throughout battery use. The main mechanisms that can be considered during modelling are solid electrolyte interface (SEI) growth, anode SEI crack model, cathode film growth, lithium plate and others. The mechanical-electrochemical model for active material swelling caused by intercalation and delithiation may also be simulated to assess the impact on battery performance.

In summary, this model takes into account limits imposed by the casing and foam packaging, as well as a battery pressure limit. However, detailed cell analysis incurs a higher processing cost and is only appropriate to specific studies, depending on the topic. Therefore, the present work focuses on the fundamental electrochemical concept in non-extreme working circumstances. The first stage ignores the effects of ageing to understand better how this calibration technique should be performed in a pristine cell. In sequence, the ageing parameters are incorporated and calibrated using experimental data.

The model relies on the porous electrode theory, which assumes that the electrode material acts as a solid porous medium composed of particles. Lithium-ion intercalation happens on these particle surfaces and is transported from one electrode to another via the electrolyte solution. A first longitudinal route is designated from anode to cathode, with the separator in between to allow for species movement at the macroscopic level. The difference in ion concentration causes a potential differential in the cell. A

second dimension is introduced via a pseudo-dimension that accounts for the radial direction inside the particles of both electrodes, in which lithium-ion radial diffusion regulates the lithium intercalation process. Figure 3.14 depicts the schematic for the P2D model utilised in GT AutoLion.

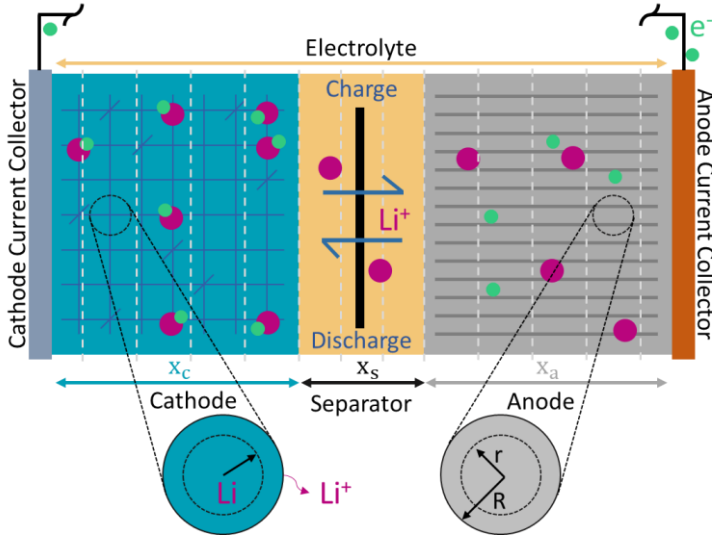


Figure 3.14. Scheme of the P2D model from GT AutoLion.

Lithium ions are thought to occur exclusively in electrolyte solutions for electrolyte conservation species because lithium is stored in active material. When a load is attached to the battery external circuit, the lithium contained in the active material emits electrons that go via the external circuit, while the lithium-ion passes through the electrolyte and crosses the separator [17,18]. The movement of lithium ions is regulated by the porous media and the potential difference [19], as described in Equation (1).

$$\frac{\partial}{\partial x} [\varepsilon c_e] = \frac{\partial}{\partial x} \left(D_e^{eff} \frac{\partial c_e}{\partial x} \right) + \frac{1 - t_+^0}{F} j^{Li} \quad (1)$$

where c_e is the molar concentration of lithium ions in the electrolyte, ε means the porosity, D_e^{eff} denotes the electrolyte effective diffusion coefficient,

F is the Faraday's constant, t_+^0 is the transference number, and j^{Li} is the reaction current of lithium.

The superscript *eff* denoted as effective is related to the porous effect on those parameters, which is governed by the Bruggeman relation [20]. The Equation (2) depicts that the effective transport property (A^{eff}) is a function of the transport property (A) times porosity (ε) raised to the Bruggeman tortuosity exponent (p). The value for $p = 1.5$ is widely accepted for mass, thermal, electric, and ionic conductivities, according to different studies [21,22].

$$A^{eff} = A\varepsilon^p \quad (2)$$

The intercalation process is described at the microscale, representing the formation of lithium when the lithium-ion and electron strike the solid particle at the electrode. Mass diffusion and the electric potential dictate the lithium concentration in the radial direction of the active material particle. Equation (3) describes the behaviour of the lithium concentration based on Fick and Ohm's law [23].

$$\frac{\partial c_s}{\partial x} = \frac{1}{r^2} \frac{\partial}{\partial x} \left(D_s r^2 \frac{\partial c_s}{\partial r} \right) \quad (3)$$

where D_s means the diffusion coefficient of lithium in the solid phase and r means the particle radius.

Furthermore, charge conservation in the solid and electrolyte phases is needed due to the potential difference in the current generation and transport of species. For the DFN model, the electroneutrality hypothesis is used as a base. This considers that each unit of volume inside the porous electrode is neutral. A high quantity of force is required to split the charge over a considerable distance. The main drive of the charge is the electrical

conductivity of solid-phase materials. Thus, Equation (4) shows the equation defining the current behaviour.

$$0 = \frac{\partial}{\partial x} \left(\sigma_s^{eff} \frac{\partial \phi_s}{\partial x} \right) - j^{Li} - a_{dl} C \frac{\partial (\phi_s - \phi_e)}{\partial x} \quad (4)$$

Being j^{Li} the lithium reaction current, σ_s^{eff} means effective solid-phase conductivity, ϕ_e is the liquid phase potential, ϕ_s means the solid phase potential, C means the capacitance and a_{dl} means the specific interfacial area.

For the electrolyte material, charge conservation is dictated by ionic and diffusion conductivity. For simplicity, the degradation mechanism, such as lithium plating may occur in the presence of lithium ions and electrons in the electrolyte, is not considered. Therefore, charge conservation in the electrolyte is given in Equation (5).

$$0 = \frac{\partial}{\partial x} \left(k^{eff} \frac{\partial \phi_e}{\partial x} \right) + \frac{\partial}{\partial x} \left(k_D^{eff} \frac{\partial \ln c_e}{\partial x} \right) + j^{Li} + a_{dl} C \frac{\partial (\phi_s - \phi_e)}{\partial x} \quad (5)$$

the electrolyte effective ionic conductivity is represented by k^{eff} , and c_e is the lithium-ion concentration in the electrolyte. The ion diffusional conductivity, k_D^{eff} , is obtained by Equation 6.

$$k_D^{eff} = \frac{2RTk^{eff}}{F} (t_+^0 - 1) \left(1 + \frac{d \ln f_{\pm}}{d \ln c_e} \right) \quad (6)$$

being t_+^0 means the transference number, R the gas constant, T means the temperature, F means the Faraday's constant and $f_{\pm}$ means the molar activity coefficient in the electrolyte.

Butler-Volmer equation is used to connect the species and charge conservation described in Equation (1), Equation (3), Equation (4) and Equation (5). This equation describes how the current depends on the voltage potential and electrolyte mass. Using the principle of the charge neutrality of an electrode-electrolyte interface, the charge production rate is the net result of the forward and backward current output [24]. Thus, the current density can be defined as Equation (7).

$$j^{IC} = a_s i_0 \left[e^{\frac{\alpha_a F}{R_u T} (\eta - \frac{R_{SEI}}{a_s} j^{Li})} - e^{\frac{\alpha_c F}{R_u T} (\eta - \frac{R_{SEI}}{a_s} j^{Li})} \right] \quad (7)$$

Where, in Equation (7), a_s means the volume-specific reaction surface area, i_0 means the exchange current density, α is the charge transfer coefficient, R_u is the universal gas constant, and R_{SEI} the resistive film layer. In addition, battery operating conditions at a normal temperature are one of the hypotheses taken into consideration throughout this investigation. Then, even though it appears that the charge transfer coefficients for the cathode (α_c) and the anode (α_a) only vary under severe circumstances. In this study, the value is considered 0.5 based on earlier research done by [25,26].

The term, η , is the overpotential, which is the difference of overpotential between the solid (ϕ_s) and liquid phase (ϕ_e), subtracting the open circuit potential of the solid phase (U), according to Equation (8).

$$\eta = \phi_s - \phi_e - U \quad (8)$$

Theoretical battery capacity ($C_{s,max}$) and the actual battery capacity available is different as not all lithium in the battery can be used. The quantity of lithium available to cycle is defined as the capacity from the discharge process. Based on this, stoichiometry can be defined as the relation of lithium available in relation to the theoretical battery capacity, as seen in Equation (9).

$$\text{Stoichiometry} = \frac{C_s}{C_{s,max}} \quad (9)$$

The specific first capacity of charge (q_{fcc}^{cat}) and specific first capacity of discharge (q_{fdc}^{cat}) divided by the theoretical value (q_{th}^{cat}) can be used as a reference to compare how the capacity deviates from the maximum value. The Equation (10) and Equation (11) summarise the above mentioned.

$$\gamma_{fcc}^{cat} = \frac{q_{fcc}^{cat}}{q_{th}^{cat}} \quad (9)$$

$$\gamma_{fdc}^{cat} = \frac{q_{fdc}^{cat}}{q_{th}^{cat}} \quad (11)$$

3.3.2 Thermal model

The thermal model is an energy balance equation considering internal heat generation and convective heat transfer [27]. Equation (12) depicts the zero-dimension thermal model for the battery. The battery temperature is crucial because it influences the qualities of the battery material. In this equation, ρ is the battery density, c_p is the battery-specific heat, T is the battery temperature, $\dot{q}_{gen}$ is the internal heat generation, h is the specific heat transfer coefficient, A_s is the total surface area of the battery, and T_{amb} is the ambient temperature.

$$\rho c_p \frac{dT}{dt} = \dot{q}_{gen} + hA_s(T - T_{amb}) \quad (12)$$

The internal heat generation of the battery can be divided into 4 different heat sources. The first can be defined as the heat resulted of kinetic heat ($\dot{q}_{kinetic}$), the reversible heat due to the intercalation and de-intercalation ($\dot{q}_{rev}$), and the ohmic heat ($\dot{q}_{ohm}$) due to the electrons and ion movement within the cell (electronic resistance, ionic resistance, and concentration overpotential). Equations 13 through 16 define these concepts using Bernardi's approach [28–31]. The term A_e means electrode area and is the sum of the anode, separator, and cathode thicknesses.

$$\dot{q}_{gen} = A_e(\dot{q}_{kinetic} + \dot{q}_{rev} + \dot{q}_{ohm}) \quad (13)$$

$$\dot{q}_{kinetic} = \int_0^L j^{Li}(\phi_s - \phi_e - U) dx \quad (14)$$

$$\dot{q}_{rev} = \int_0^L j^{Li} \left(T \frac{\partial U}{\partial T} \right) dx \quad (15)$$

$$\begin{aligned} \dot{q}_{ohm} = \int_0^L \left[\sigma^{eff} \left(\frac{\partial \phi_s}{\partial x} \right)^2 + \kappa^{eff} \left(\frac{\partial \phi_e}{\partial x} \right)^2 \right. \\ \left. + \kappa_D^{eff} \left(\frac{\partial \ln c_e}{\partial x} \right) \left(\frac{\partial \phi_e}{\partial x} \right) \right] dx \end{aligned} \quad (16)$$

3.3.3 Ageing model

In addition to the described electrochemical model, the software also includes a series of degradation mechanisms such as solid electrolyte interface (SEI) growth, lithium plating, anode SEI crack model, cathode film growth, cathode/anode active material isolation as well as mechano-electrochemical interaction through an active material swelling model. Since only high-temperature conditions (20 °C and 50 °C) are considered for the ageing

process, the dominant mechanisms were simplified to only SEI growth. Other mechanisms like lithium plating are more relevant in conditions with problems for lithium allocation, like low-temperature operation or very high current demands. Additional equations are considered to model this effect. These equations will add a lithium loss term affecting the total capacity and an increase in the internal resistance.

The SEI growth is a reaction between the electrolyte and the lithium-ion and electrons in the anode. Experimental studies have demonstrated that the main molecule of SEI formation is lithium alkyl carbonate because of ethylene carbonate (EC) (electrolyte component) and lithium-ion. The kinetic equations for this reaction can be written as in Equation (17) and Equation (18).

$$i_{SEI} = -i_{0,SEI} \exp \left(-\frac{a_{c,SEI} F}{RT} \left(\phi_s - \phi_e - U_{SEI} - \frac{j^{Li}}{a_s} R_{SEI} \right) \right) \quad (17)$$

being j_{SEI} the side reaction current density, U_{SEI} is the equilibrium potential, j^{Li} is the total current density (lithium intercalated and side reactions), and R_{SEI} is the resistance of the SEI.

The exchange current density depends on the EC concentration at the reaction surface ($c_{EC}^{surface}$), being defined in Equation (18). F in Equation (18) denotes de Faraday's constant.

$$i_{0,SEI} = k_{0,SEI} c_{EC}^s F \quad (18)$$

Because this process consumes EC and happens at the interface of the active material and the SEI layer, the electrolyte must diffuse through the porous SEI layer to reach the reaction site. Equation (19) describe the diffuse rate for the EC electrolyte component.

$$\frac{\partial c_{EC}}{\partial t} = D_{EC}^{eff} \frac{\partial^2 c_{EC}}{\partial r^2} \quad (19)$$

Being the effective EC diffusivity (D_{EC}^{eff}) defined in Equation (20).

$$D_{EC}^{eff} = D_{EC}(\varepsilon_{SEI})^n \quad (19)$$

where ε_{SEI} is the solid electrolyte interface porosity, n is the Bruggeman exponent, D_{EC} is the electrolyte diffusion coefficient. Thus, following the Bruggeman relationship, the EC diffusivity considers the torturous path up to the SEI and active material interface by relating the porous media and the diffusivity.

The growth of the SEI layer is dictated by Equation (20). The SEI thickness variation is a function directly related to the current (i_{SEI}) and molecular weight of the solid electrolyte interface (M_{SEI}), and inversely proportional to the SEI density (ρ_{SEI}) and Faraday constant (F).

$$\frac{d\delta_{SEI}}{dt} = -\frac{i_{SEI} M_{SEI}}{2F \rho_{SEI}} \quad (20)$$

Finally, the total resistance of the SEI is computed, taking into account its thickness and effective conductivity (K_{SEI}^{eff}) as presented in Equation (21) and Equation (22) [11,12].

$$R_{SEI} = \frac{\delta_{SEI}}{K_{SEI}^{eff}} \quad (21)$$

$$K_{SEI}^{eff} = K_{SEI}(\varepsilon_{SEI})^n \quad (22)$$

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Chapter 4

Impact of Battery Chemistry Under Normal Operating Conditions

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4.1 Introduction

From the literature review, it can be concluded that lithium-ion batteries have different characteristics, owing mainly to the cathode chemistry. Nickel Manganese Cobalt Oxide (NMC) and Lithium Iron Phosphate (LFP) are the most common batteries used. NMC batteries have a higher energy density than the LFP. The energy density range can vary from 150 to 220 Wh/kg for the NMC and 90 to 160 Wh/kg for the LFP. On average, the NMC has a 45% higher energy density than the LFP. However, despite the differences in energy density, evaluating the ageing effect on vehicle range and safety concerns is essential for packaging design. Different battery components in terms of geometry and composition can lead to different ageing behaviour. A battery can age faster than others, resulting in a lower useful life for a vehicle. In addition, understanding the effect of ageing on thermal runaway and comparing it with pristine condition is critical for developing a safety mechanism to mitigate this problem. Safer batteries require less hardware for the safety system and less sophisticated materials, resulting in better vehicle energy density and lower costs for end users.

For these reasons, this chapter focuses on the electrical characterisation of the battery, first with experiments and then using computational models. The experimental tests were conducted with NMC and LFP batteries. Different discharge C-rates were performed at different temperatures to evaluate each battery cell performance. In addition, driving cycles were carried out for modelling calibration purposes. In sequence, the batteries were aged at different temperatures using a protocol that targeted accelerating the SEI growth degradation mechanism. The battery characteristics were modelled in sequence, and parameters difficult to measure were calibrated to match the experimental results with acceptable error. The modelling approach used is a pseudo-two-dimensional (P2D) from GT-AutoLion. With the model for the pristine battery calibrated and validated for 2 different temperatures, the ageing model for SEI growth was also calibrated and validated. A vehicle was created in GT-Suite and equipped with a validated battery pack. The vehicle performed different driving cycles, and the ageing

effect on vehicle range was evaluated. In the next chapter, the safety concerns will be evaluated.

4.2 Electrical characterisation

This section will discuss the methods and experimental results for the battery characterisation, including battery performance and ageing behaviour for two different temperatures. This subsection aims to understand battery performance for two different cathode chemistries and how their capacity decreases. These data will be used to calibrate and validate a battery model that will be used to predict vehicle range and, in the next part, to determine the root causes and main source of heat release during thermal runaway.

4.2.1 Battery characteristics

From the literature review, NMC and LFP are two widely used lithium-ion battery cathode chemistries in the automotive section. For this reason, two commercial batteries were chosen to study the ageing effect on vehicle range and the effect on the thermal runaway in the next section. The battery model Samsung INR18650-20R has a NMC cathode chemistry, with the cathode composition as 1:1:1, resulting in a battery capacity of 2 Ah and an energy density of 169 Wh/kg. The other battery is a NX 9073, with cathode chemistry of LFP. The LFP battery has 1.8 Ah and an energy density of 139 Wh/kg. The battery specifications used for this study are presented in Table 4.1.

NMC and LFP voltages at full charge are 4.2V and 3.65V, respectively, with a cut-off voltage (minimum safety voltage) of 2.5 V. Both anodes are graphite. The conventional charge time for these batteries is 180 minutes (with a cut-off of 100 mA), while the quick charge time is 50 minutes at 25 °C.

Table 4.1. Battery description.

Parameter	NMC	LFP
Cathode Chemistry	LiNiMnCoO ₂	LiFePO ₄
Anode Chemistry	Graphite	
Electrolyte Chemistry	Lithium hexafluorophosphate, organic carbonates	
Dimensions [mm]	18.3 x 65.0	18.2 x 65.2
Weight [g]	42.4	41.5
Nominal Voltage [V]	3.6	3.2
Nominal Capacity [Ah]	2.0	1.8
Current Charge Continuous/Peak [A]	2.0/4.0	1.8/-
Current Discharge Continuous/Peak [A]	22.0/30.0A	5.4/10
Total Energy [Wh]	7.2	5.8
Vent Cap holes	3	3
Voltage at 100% SOC [V]	4.2	3.65
Cut-off voltage [V]	2.5	2.5
Temperature use Range [°C]	-20 to 60	-20 to 50

4.2.2 Test procedure

The cells were charged using the manufacturer recommended protocol. The constant current constant voltage (CCCV) was applied using 0.5 C-rate up to maximum voltage, and the current cut-off was 0.5% of 1-C-rate. This guarantees that before each performance test, the charge capacity is similar. In sequence, after a rest period of 30 minutes at room temperature, the batteries were discharged using the C-rates of 1/6, 1/2, 1 and 3 C-rate. Therefore, CCCV was used to charge the cell and, after, a rest period of 30 min was applied to battery relaxation. Thus, the discharge process at a determined C-rate was carried out. After a rest period of 30 min for battery relaxation, the process was repeated (CCCV-rest-discharge).

Furthermore, the batteries were submitted to dynamic loading tests. The bidirectional source can simulate current demands according to the current profile as a function of time. The current profile was obtained by

simulating an electric vehicle with a battery package of around 70 kWh, which provides an acceptable vehicle range.

The cells were cycled after the pristine characterisation. The charging protocol differs from the CCCV due to the time spent on the last part (constant voltage). Thus, the cells were charged up to maximum voltage with 1 C-rate. In sequence, a rest period of 30 min was performed for voltage relaxation. The discharge process was carried out at a 2 C-rate to have more severe conditions and save testing time. Before starting the next cycle, a rest period of 30 min was carried out. The cycling was done with the battery allocated inside the ARC, which can also work as a climate chamber, maintaining the temperature constant with a variation of less than 0.2%. The target was to achieve 250 cycles (charge-rest-discharge-rest). This protocol implies 30 days of testing without stopping. The temperature, voltage and current were recorded with a time step of 10 seconds.

4.2.3 Pristine battery performance

Figure 4.1 (a) and Figure 4.1 (b) depict the battery behaviour voltage output as a function of the discharge capacity for different current demands and ambient temperatures (20 °C and 50 °C). A higher ambient temperature resulted in a higher discharge capacity for both cathode chemistries. According to the material safety data sheet provided by the battery manufacturers, the electrolyte is formed mainly by lithium hexafluorophosphate and organic carbonates [2]. 3 main effects on the battery performance can be related to the temperature due to the electrolyte physical-chemical properties. Higher temperatures can cause salt material dissociation, which increases ion current, resulting in a higher discharge capacity. In contrast, higher temperatures decrease the solvent dielectric constant, increasing ionic interaction probability. However, increasing the battery temperature can reduce the electrolyte viscosity, lowering resistance to ion movement during the migration process. [3,4]. For these reasons, increasing

ambient temperature would increase the capacity provided owing to better electrolyte conductivity.

Lower C-rates resulted in increased discharge capacity, considering the analysis of the same ambient temperature. Lower C-rate indicates that internal battery processes occur slowly, which improves lithium-ion transport efficiency and intercalation/de-intercalation processes owing to the longer time available, resulting in increased discharge capacity. Furthermore, when comparing the NMC and LFP, the latter has a higher voltage plateau curve, resulting in a more consistent power output (measured as voltage times current). On the other hand, the NMC power output decreases with a constant current demand.

Figure 4.1 (c) and Figure 4.1 (d) demonstrate the battery potential to accomplish a driving cycle at 20 °C of ambient temperature. The cycling with the NMC battery gradually moved down the voltage curve. Nonetheless, the voltage behaviour appears to be consistent during the driving cycle. This may be connected to the NMC battery continuously dropping voltage during the discharge process, as shown in Figure 4.1 (a). Conversely, the LFP battery maintains a consistent voltage throughout the discharge process, which leads to comparable performance during driving cycles, as depicted in Figure 4.1 (b). Figure 4.1 (e) and Figure 4.1 (f) present the effect of ambient temperature at 50 °C on voltage during the driving cycles carried out. No significant difference can be pointed out compared with the battery performance at 20°C.

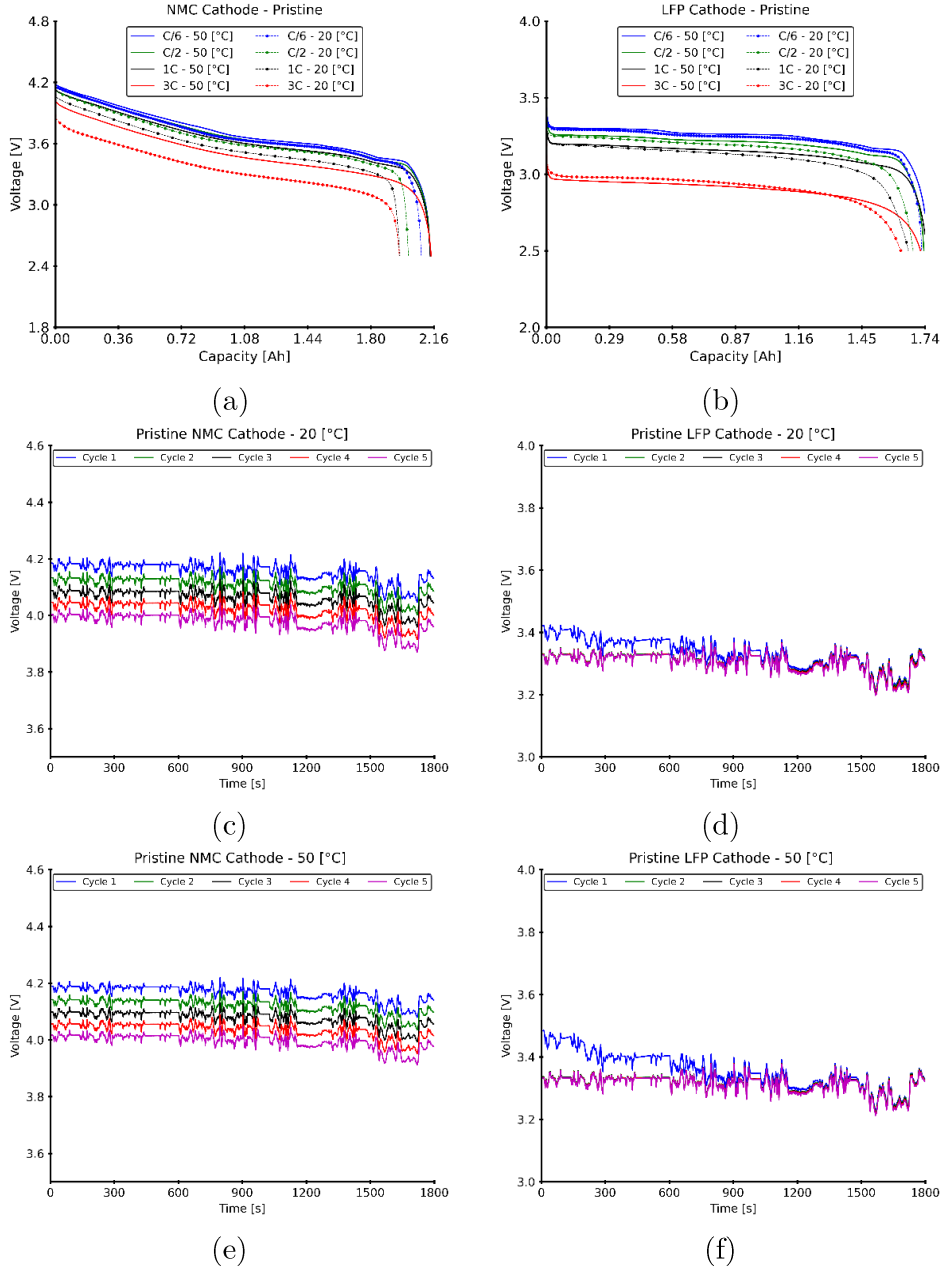


Figure 4.1. (a) NMC - discharge capacity for different C-rates and ambient temperatures. (b) LFP - discharge capacity for different C-rates and ambient temperatures. (c) NMC - driving cycle performance at 20 °C. (d)

LFP - driving cycle performance at 20 °C. (e) NMC - driving cycle performance at 50 °C. (f) LFP - driving cycle performance at 50 °C.

Figure 4.2 (a) and Figure 4.2 (b) depict the battery temperature as a function of capacity delivered for two different ambient temperatures and different C-rates. Higher C-rates resulted in a higher battery temperature during the discharge process. The higher C-rates increase the battery temperature as an effect of higher local current density and overpotential, increasing the heat generation [5]. However, the higher temperature decreases the battery internal resistance, which may increase the capacity delivered. This would explain the better performance of batteries working at a higher ambient temperature. However, a trade-off effect is related to the greater C-rate and the same ambient temperature. Despite higher C-rates resulting in higher battery temperature, the discharge capacity is lower when compared with lower C-rates. One reason can be the more prominent drop in dynamic voltage rate, reaching the cut-off voltage before the lithium-ions leave the anion, resulting in less discharge capacity [6,7].

In addition, Figure 4.2 (c), Figure 4.2 (d), Figure 4.2 (e) and Figure 4.2 (f) show battery temperature during the driving cycle test at 20 °C and at 50 °C ambient temperature. Both cathode chemistries had similar temperature profiles along the driving cycles, with differences not exceeding 2 °C.

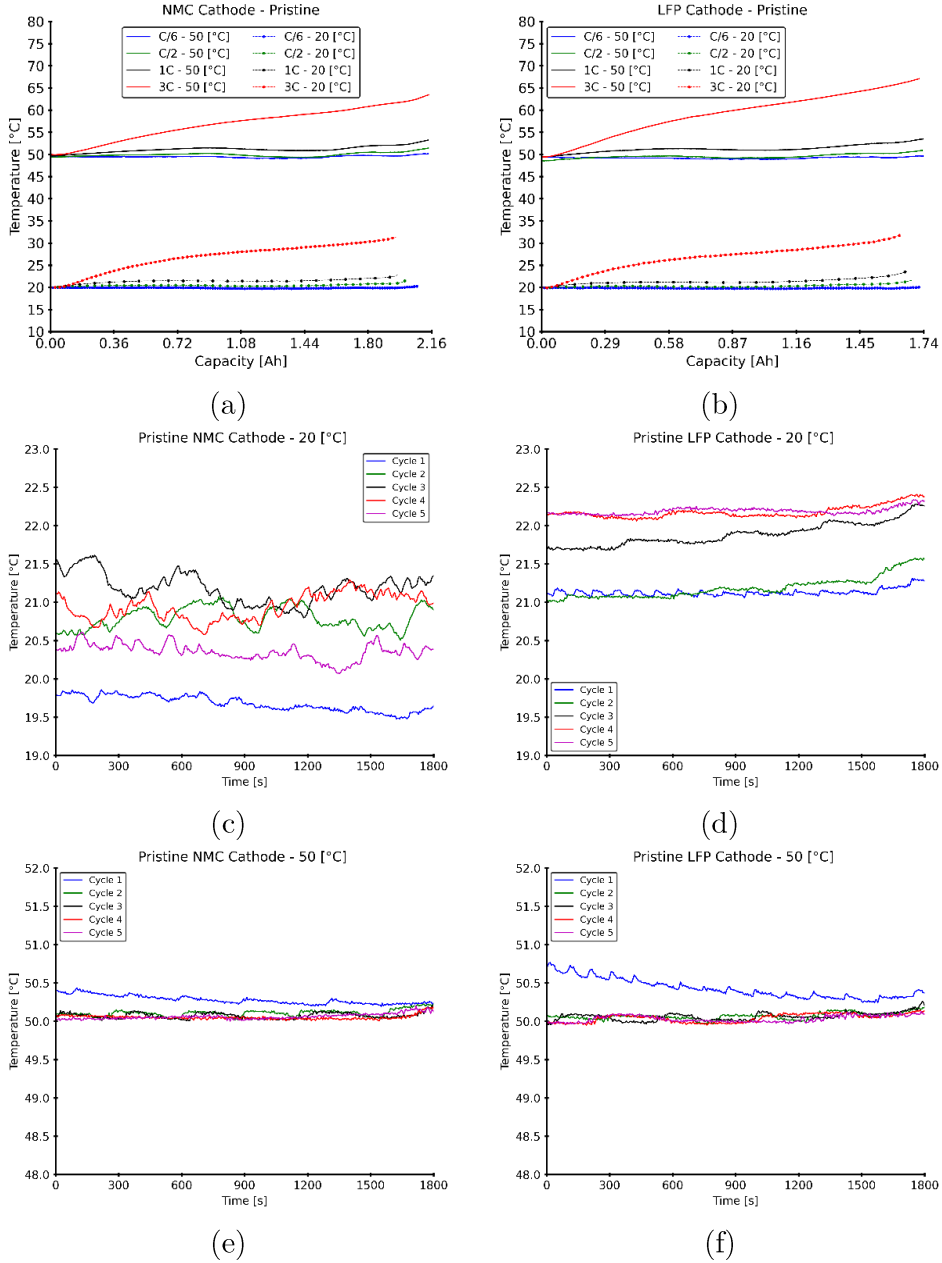


Figure 4.2. (a) NMC – battery surface temperature for different C-rates and ambient temperatures. (b) LFP – battery surface temperature for different C-rates and ambient temperatures. (c) NMC – Battery surface temperature

during a driving cycle with ambient temperature at 20 °C. (d) LFP – Battery surface temperature during a driving cycle with ambient temperature at 20 °C. (e) NMC – Battery surface temperature during a driving cycle with ambient temperature at 50 °C. (f) LFP – Battery surface temperature during a driving cycle with ambient temperature at 50 °C.

4.2.4 Battery ageing behaviour

Experimental ageing tests were performed in the NMC and LFP cathode chemistry cells. Figure 4.3 shows the experimental results regarding voltage for the ageing process of up to 250 cycles submitted in two ambient temperatures. The charge\discharge protocol used was different from that used in the performance tests. In this case, the battery was charged with 1 C-rate up to maximum voltage, resting for 30 min and, in sequence, discharged with 2 C-rate. For the NMC battery at 20 °C, Figure 4.3 (a), the maximum voltage showed a drop in relation to the NMC battery at 50 °C, Figure 4.3 (c). One reason may be that the charging protocol does not maintain constant battery voltage while the current progressively decreases to a minimum value (protocol CCCV). Then, during the rest period, the voltage dropped, resulting in poor performance during the ageing tests.

According to Figure 4.3 (a), Figure 4.3 (b), Figure 4.3 (c) and Figure 4.3 (d), the capacity fade was higher at higher ambient temperature for both cathode chemistries. Different mechanisms can cause performance deterioration during battery cycling. At 20 °C ambient temperature, the capacity fade is mainly attributed to the solid electrolyte interface growth [8]. However, when the battery is cycled at a higher temperature, such as 50°C, different mechanisms result in a complex system of capacity fade. The loss of lithium inventory is attributed mainly to SEI growth, SEI decomposition and electrolyte decomposition [9]. In addition, other mechanisms, for instance, related to the cathode electrolyte interface, can have a significant effect on the capacity fade, as reported by Wang et al. [10].

For these reasons, higher ambient temperatures result in a higher loss of capacity.

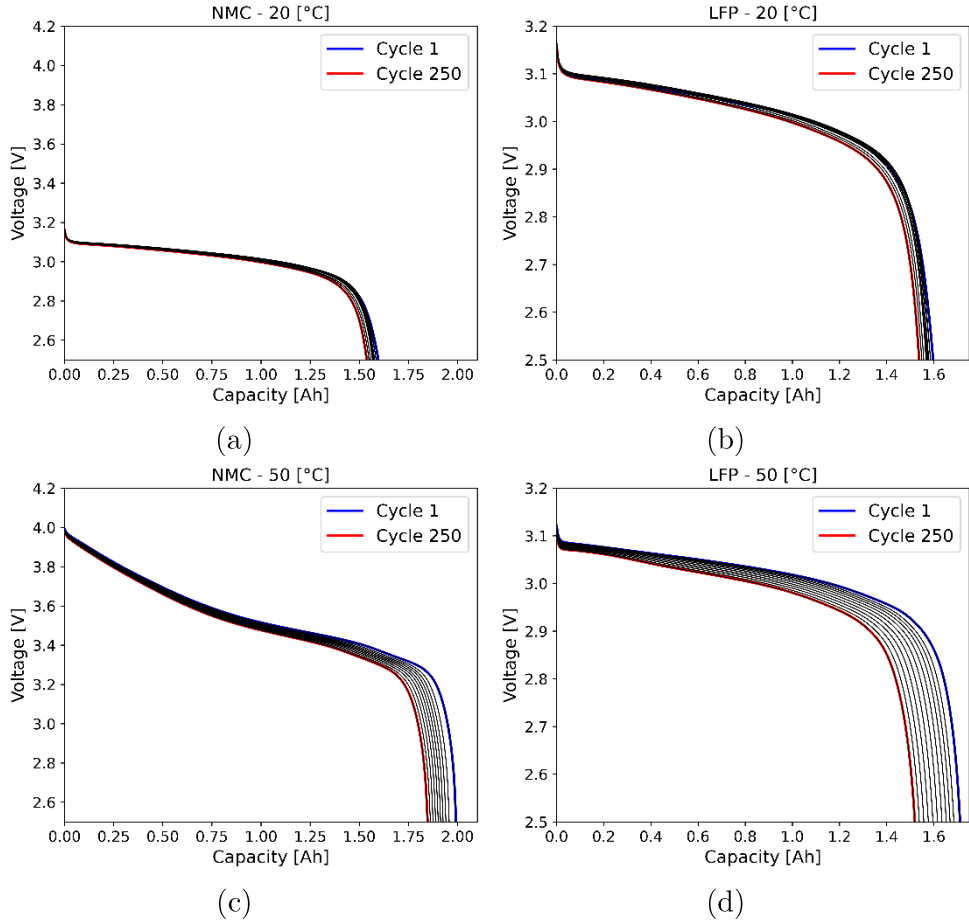


Figure 4.3. Voltage behaviour as a function of discharge capacity during cycling. (a) NMC at 20 °C – ambient temperature, (b) LFP at 20 °C – ambient temperature, (c) NMC at 50 °C – ambient temperature and (d) LFP at 50 °C – ambient temperature.

Figure 4.4 depicts the battery temperature over three discharge cycles of the ageing process for NMC and LFP cathode chemistry at two different ambient temperatures. For the ambient temperature at 20 °C, Figure 4.4 (a) and Figure 4.4 (b), the battery temperature difference between the first and

last cycle was small, depicting that the ageing process did not affect the battery temperature in this case. Nevertheless, at 50 °C of ambient temperature, the battery temperature difference, green line in Figure 4.4 (c) and Figure 4.4 (d), was higher. The main difference is observed in both batteries during the last part of the discharge curve (after 50% of discharge capacity). The degradation due to the ageing process would increase the Joule effect, increasing the battery temperature. In addition, the higher ambient temperature decreases the convection heat transfer between the battery and the ambient, resulting in a higher temperature reached by the battery compared to the ambient temperature at 20 °C.

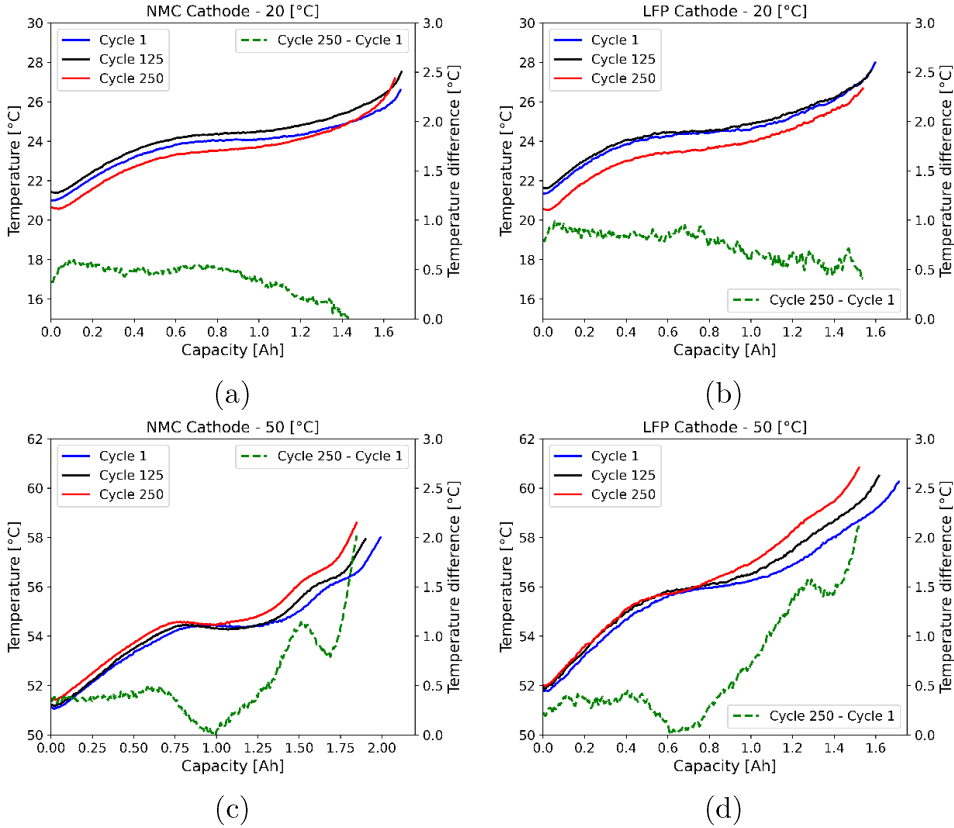


Figure 4.4. Battery surface temperature during the cycling process. (a) NMC at 20 °C – ambient temperature, (b) LFP at 20 °C – ambient

temperature, (c) NMC at 50 °C – ambient temperature and (d) LFP at 50 °C – ambient temperature

Figure 4.5 (a) summarises the capacity fade as a function of the number of cycles for NMC and LFP at 20 °C and 50 °C ambient temperatures. The higher degradation of batteries is clearly due to a higher ambient temperature. The LFP battery showed a higher reduction in capacity than the NMC. The normalised capacity, Figure 4.5 (b), shows that the LFP battery reached 90% of the pristine capacity with 250 cycles. Meanwhile, the NMC battery achieved about 92.5% of the pristine value at the end of the ageing process. Decreasing the ambient temperature to 20 °C, the decrease in battery capacity is reduced. However, the degradation process was still higher for the LFP battery.

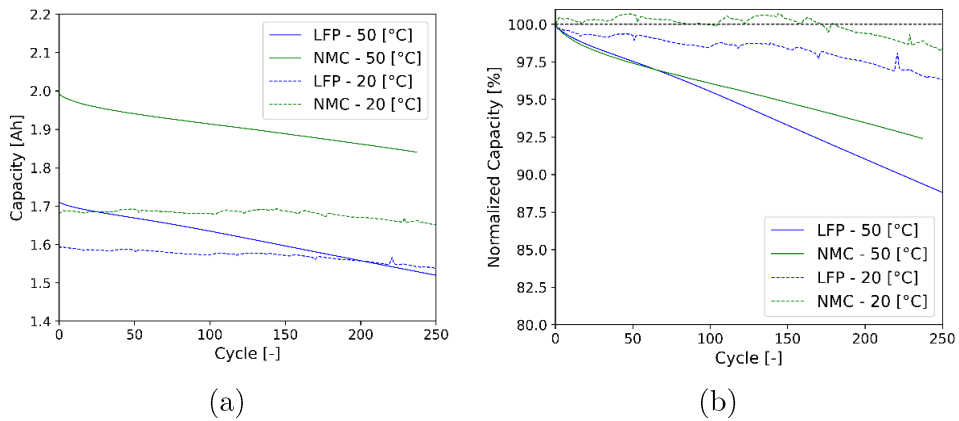


Figure 4.5. Capacity fading during cycling. (a) Actual values and (b) Normalised values.

Figure 4.6 presents the output capacity of the pristine (Figure 4.6 (a) and aged Figure 4.6 (b) batteries (NMC and LFP) as a function of C-rates for two ambient temperatures (20 °C and 50 °C). NMC and LFP pristine batteries reached the maximum output capacity at a higher ambient temperature. In addition, lower C-rates resulted in a higher discharge capacity in general. However, aged batteries showed greater capacity fade when subjected to 50 °C of ambient temperature, with the NMC battery

capacity being similar to at 20°C and the LFP battery capacity being lower than at 20°C.

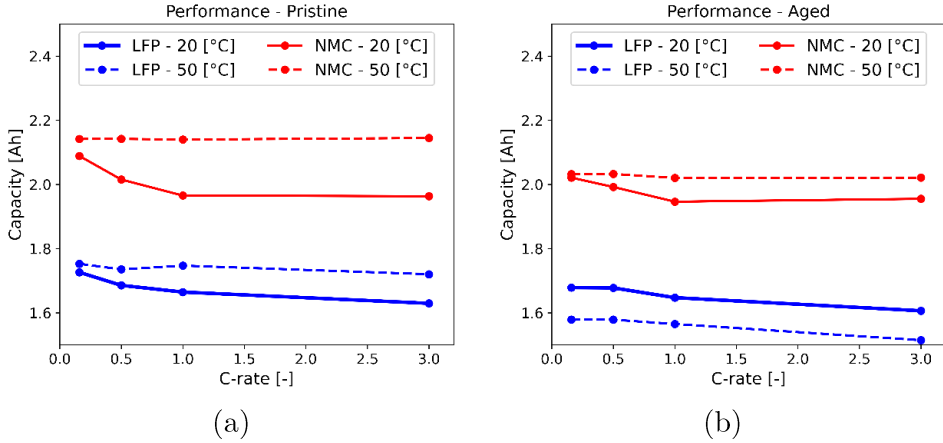


Figure 4.6. Battery discharge capacity as a function of the discharge current. (a) Pristine batteries at 20 °C and 50 °C. (b) Aged batteries at 20 °C and 50 °C.

4.3 Electrochemical modelling

P2D modelling was used to virtually replicate the battery behaviour under a current demand and access battery parameters that are difficult to measure experimentally. In section 4.2 Electrical characterisation, the batteries were characterised in terms of performance at different C-rates and ambient temperatures. Thus, in sequence, the batteries were cycled and characterised. This data will feed models developed to replicate the battery response and thus be used in a vehicle for autonomy capacity studies. First, the battery in its pristine state will be characterised, calibrated using experimental data (in a determined condition), and validated using experimental data from another battery-tested condition. With this achievement, the ageing models will be enabled to characterise the degradation process in battery components. The SEI growth model will be activated, and calibrated using experimental data from a predetermined

condition and validated with data from another ageing condition. The vehicle equipment with a package formed with the battery model validated will go through different driving cycles. The results will be used to understand better the effect of ageing on vehicle range and its implications for the end user. Furthermore, the model will be useful for the next chapter, in which a fundamental study will be performed to understand the role of battery components and the effect of ageing on thermal runaway.

4.3.1 Model calibration method

The battery model using the P2D modelling requires information about the cell geometry, jelly roll dimensions, thickness and height of battery layers and tab configurations. However, some parameters are required to be optimised in order to replicate the battery behaviour. These parameters are listed below:

- Cathode, anode, and separator thicknesses [μm].
- First charge capacity of anode and cathode [mAh/g].
- First discharge capacity of anode and cathode [mAh/g].
- Particle size of the anode and cathode active material [μm].
- Specific heat capacity of the cell [$\text{J}/(\text{kgK})$].
- Convective heat transfer coefficient [$\text{W}/(\text{m}^2\text{K})$].
- Contact Resistance [Ωm^2].
- Anode and Cathode capacity [Ah].

The calibration procedure, which involves optimising 14 parameters, is performed through a genetic algorithm (GA), which minimises the difference between experimental and simulation results. The thermal model is adjusted

to consider convective heat transfer, heat capacity, and other related parameters, such as contact resistance. The cell output depends on the battery parameters described here that interact with each other, resulting in the final battery behaviour.

The GA for optimising the battery parameters has an objective function that minimises the voltage output and the battery temperature when a current demand is applied to the battery. In the optimisation process, the thermal part has a lower weight in the objective function [11]. Therefore, the relative discrepancy in the temperature profile is less important than the voltage output profile. It is there to ensure that the algorithm chosen thermal parameters make sense. The objective function is expressed mathematically in Equation (1), Equation (2), Equation (3).

$$E_{ov} = \frac{1}{n} \cdot \sum_{k=1}^n \left(w_V \cdot \frac{E_V^k}{f_V} + w_T \cdot \frac{E_T^k}{f_T} \right) \quad (1)$$

$$E_V^k = \sqrt{\frac{\int_{t_{start}^k}^{t_{end}^k} (V_{sim}^k(t) - V_{exp}^k(t))^2 dt}{(t_{end}^k - t_{start}^k)}} \quad (2)$$

$$E_T^k = \sqrt{\frac{\int_{t_{start}^k}^{t_{end}^k} (T_{sim}^k(t) - T_{exp}^k(t))^2 dt}{(t_{end}^k - t_{start}^k)}} \quad (3)$$

being f_V and f_T the voltage and temperature error normalised, respectively, n is the number of experimental tests used to calibrate the model, and w_V and w_T are the factors used to weigh the importance of the parameters on the voltage and temperature, respectively. The index k is each voltage and temperature curve used in the calibration method.

The experimental tests were conducted with LFP and a NMC cathode chemistry. 3 different discharged current profiles were imposed on the battery. The constant current demand of 1/6 C-rate (0.33 A) and 3 C-rate (6 A) were used, and a dynamic load representing a WLTC European homologation cycle of an electric vehicle with 70 kWh. Figure 4.7 shows the current profiles used during the electrochemical model calibration for the NMC battery. In this case, positive value means a discharging process, while negative values mean a charging process. During the driving cycle, the current demand was between $(-2\text{A} < I < 2\text{A})$ due to the capacity of the battery package equipped in the vehicle.

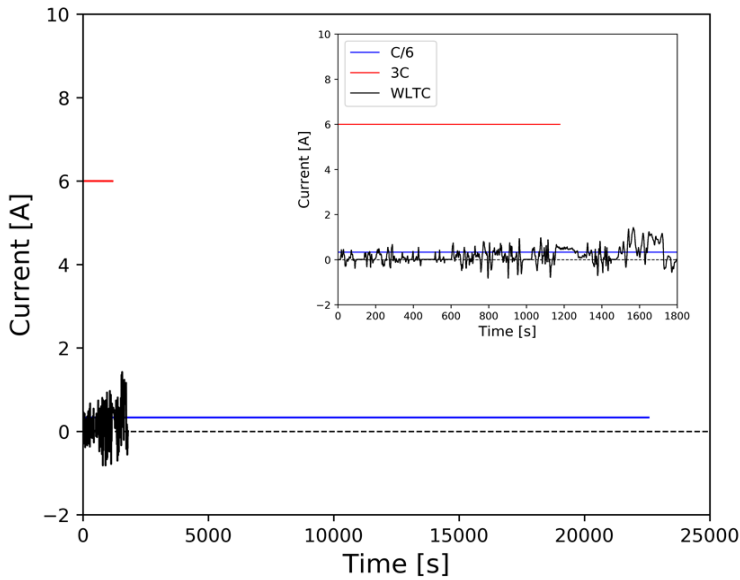


Figure 4.7. Current profiles used for the NMC electrochemical calibration model.

4.3.2 Calibration results

The calibration procedure achieved the desired result after 1500 simulated cases, considering the experimental results for the current demand of 1/6 and 3 C-rate, as well as the voltage response when the vehicle is performing a driving cycle (WLTC). All experimental results used in the calibration were obtained at 20 °C of ambient temperature. Figure 4.8 shows the experimental and simulated curves from the calibrated model for the voltage behaviour with different current demands: 1/6 C-rate NMC (Figure 4.8 (a)), 1/6 C-rate LFP (Figure 4.8 (b)), 3 C-rate NMC (Figure 4.8 (c)), 3 C-rate LFP (Figure 4.8 (d)), WLTC NMC (Figure 4.8 (e)), WLTC LFP (Figure 4.8 (f)). Despite the LFP battery showing a higher discrepancy between simulated and experimental results, the average error was about 2%, considering the 3 tested conditions.

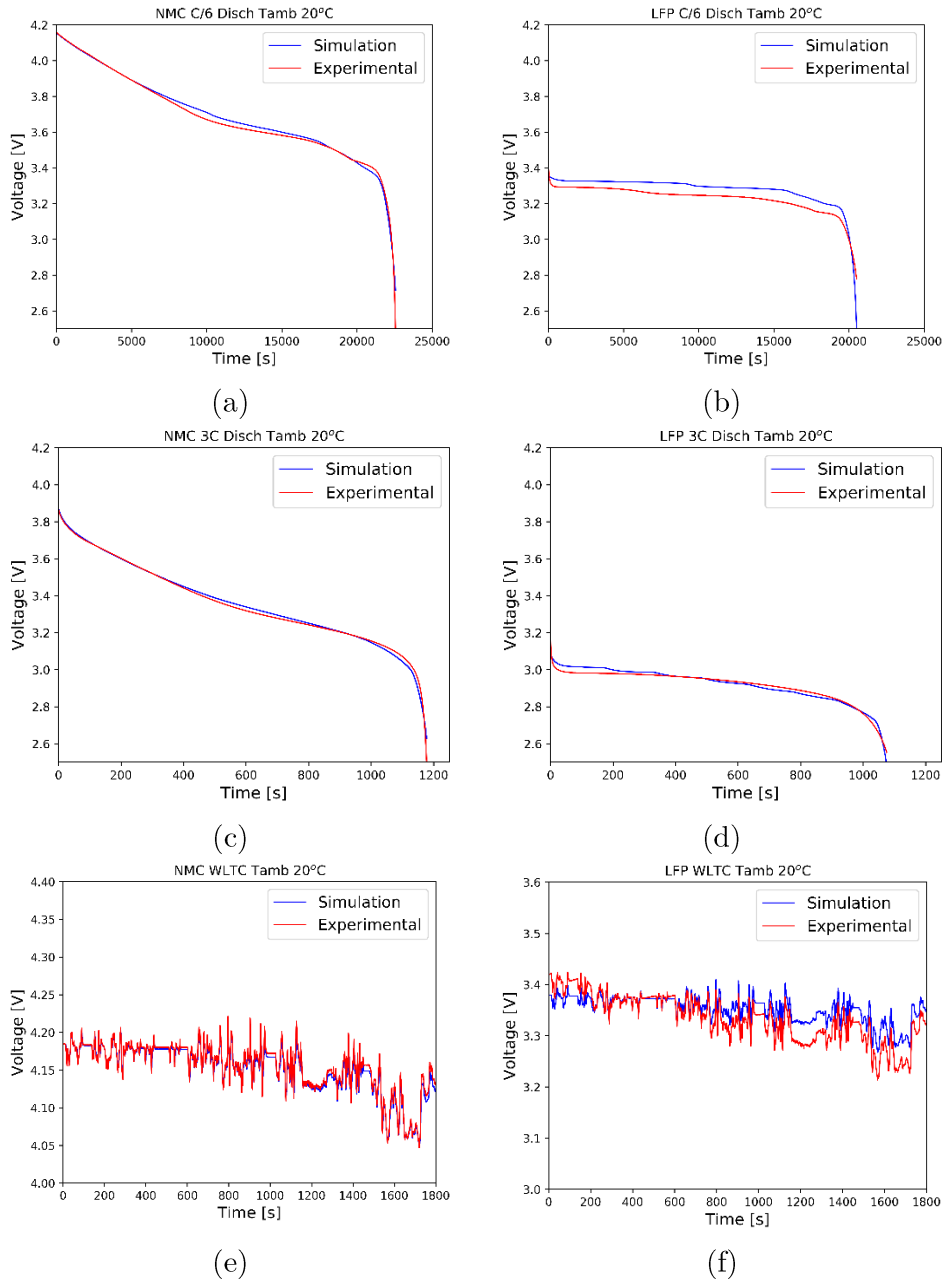


Figure 4.8. Voltage curves comparison between simulated and experimental tests for different current demands at 20 °C of ambient temperature. (a) –

1/6 C-rate NMC, (b) – 1/6 C-rate LFP, (c) – 3 C-rate NMC, (d) – 3 C-rate LFP, (e) – WLTC NMC, (f) – WLTC LFP.

Figure 4.9 depicts the battery temperature difference between the simulated and the experimental tests. Different current demands were applied on the battery as 1/6 C-rate (Figure 4.9 (a) – NMC, and Figure 4.9 (b) – LFP), 3 C-rate (Figure 4.9 (c) – NMC, and Figure 4.9 (d) – LFP), and WLTC profile (Figure 4.9 (e) – NMC, and Figure 4.9 (f) – LFP). The difference compared to the voltage results is higher, on average of 4%. The calibration process used, which optimises the settings to reduce the relative error of the voltage output rather than the temperature relative error, explains the larger discrepancy.

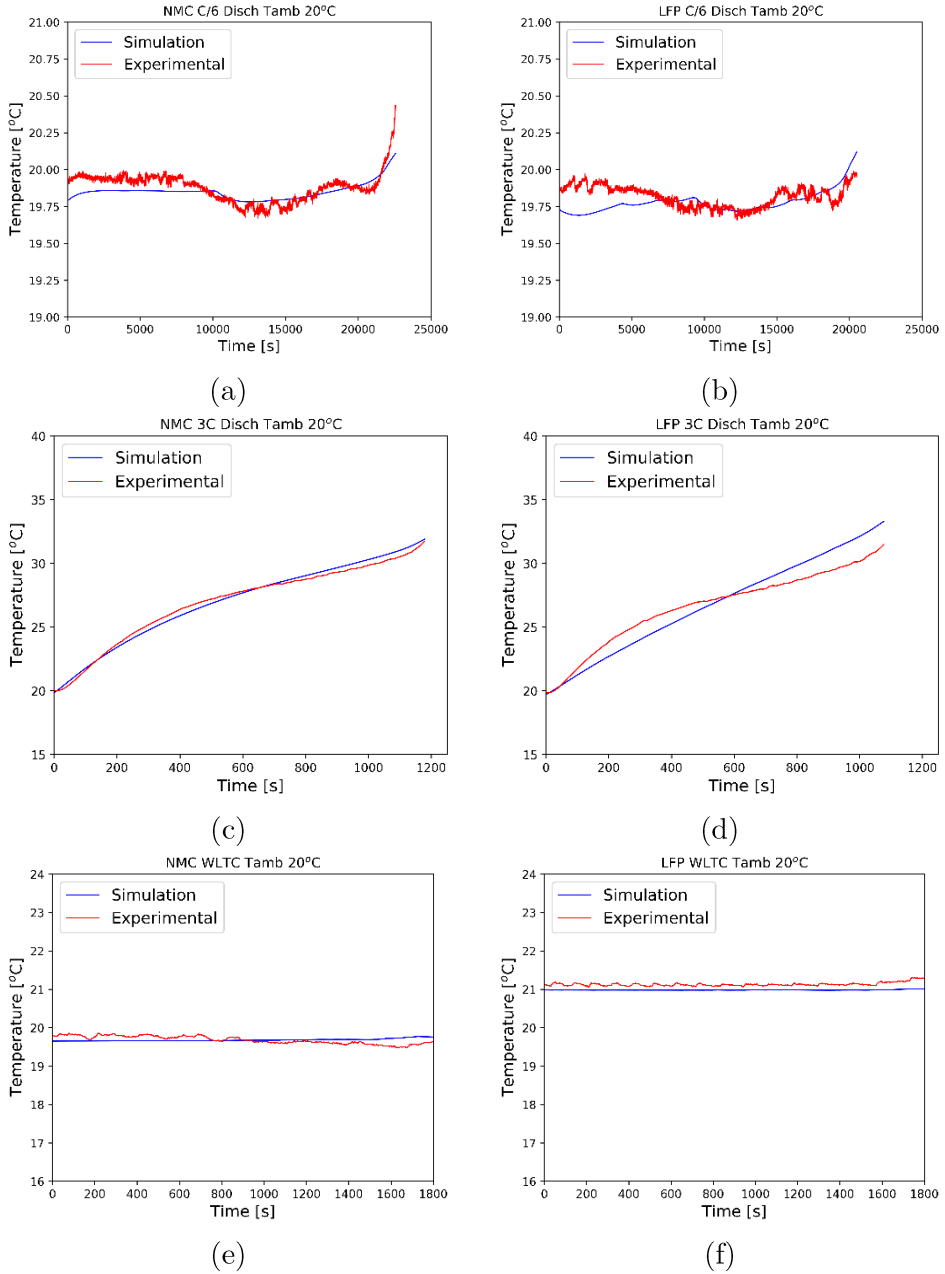


Figure 4.9. Voltage curves comparison between simulated and experimental tests for different current demands at 20 °C of ambient temperature. (a) –

1/6 C-rate NMC, (b) – 1/6 C-rate LFP, (c) – 3 C-rate NMC, (d) – 3 C-rate LFP, (e) – WLTC NMC, (f) – WLTC LFP.

The results of the optimised battery parameters are presented in Table 4.2 for the NMC and LFP cathode chemistry. The values were obtained using data from the experimental condition at 20 °C. NMC has larger particles than LFP on the cathode side, NMC has larger particles than LFP on the cathode side, which is the main difference between the cells according to the calibration results. On the other hand, the LFP battery has a separator thickness almost twice that of the NMC battery.

Table 4.2. NMC and LFP battery parameters results for the calibration methodology applied.

Parameter	Unit	Range Optimizer	Optimum value NMC	Optimum value LFP
Particle Size Anode	Micron	5 - 30	12.53	10.53
Particle Size Cathode	Micron	0.05 - 30	5.43	0.007
Thickness Anode	Micron	25 - 150	89.12	65.81
Thickness Cathode	Micron	25 - 150	92.14	99.48
Thickness Separator	Micron	5 - 40	26.69	43.14
Cathode Capacity	Ah	2.0 - 6.0	2.47	2.05
Anode Capacity	Ah	2.0 - 6.0	2.76	2.07
Contact Resistance	mOhm.m ²	0.1 – 1.0	0.86	1.0
FCC Cathode	mAh/g	150 - 220	193.34	171.76
FDC Cathode	mAh/g	140-210	174.19	166.10
FCC Anode	mAh/g	320-430	403.91	379.37
FDC Anode	mAh/g	300-400	362.86	334.09
HTC	W/m ² K	3 - 40	37.40	26.05
CP	J/kgK	800-1500	1266.61	1255.00

4.3.3 Model Validation

The model was calibrated using the data obtained at 20 °C. For the validation procedure, the ambient temperature was changed to 50 °C. Thus, the battery model was simulated, and the results were compared with the experimental test at the same ambient temperature, 50 °C. Figure 4.10 presents the validation results for voltage output with different current demands: 1/6 C-rate (Figure 4.10 (a) – NMC, and Figure 4.10 (b) - LFP), 3 C-rate (Figure 4.10 (c) – NMC, and Figure 4.10 (d) - LFP), and WLTC profile (Figure 4.10 (e) – NMC, and Figure 4.10 (f) - LFP). The difference between experimental and simulation results is small for both cases, NMC and LFP. The error observed in Figure 4.10 is about 2%. A higher difference can be seen in the final part of the voltage drop. Consequently, the SOC variation will be kept between 100% and 20% for numerical purposes.

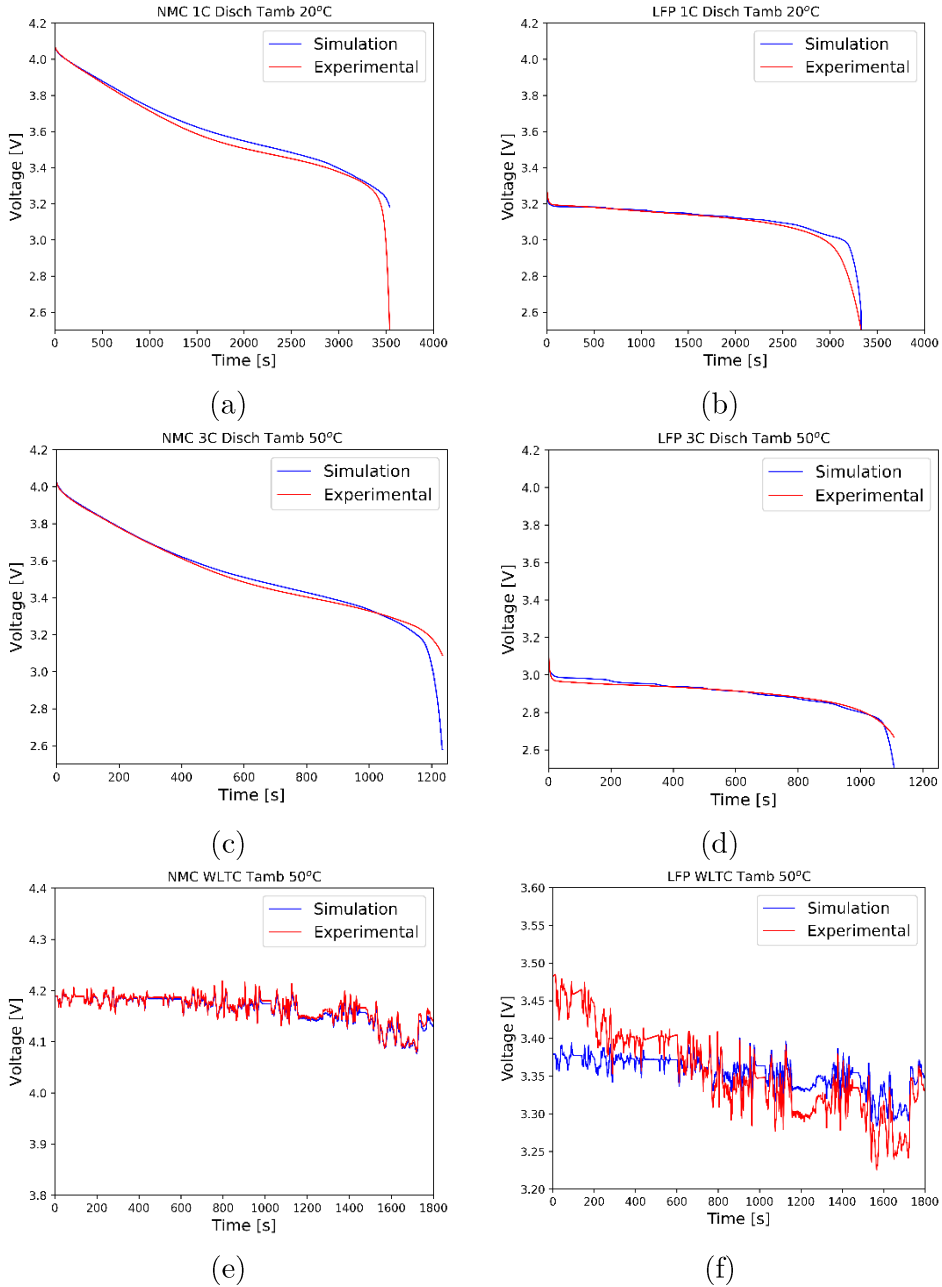


Figure 4.10. Validation results comparing simulated voltage curves and experimental test for different current demand at 50 °C of ambient

temperature. (a) – 1/6 C-rate NMC, (b) – 1/6 C-rate LFP, (c) – 3 C-rate NMC, (d) – 3 C-rate LFP, (e) – WLTC NMC, (f) – WLTC LFP.

4.4 Ageing model

4.4.1 Ageing calibration

A cell cycler was implemented in GT-AutoLion to cycle the battery for ageing model calibration purposes. The model overview can be seen in Figure 4.11. Output voltage and capacity fading information can be obtained and compared with experimental tests. Only the SEI growth degradation mechanism at the anode was activated to decrease the computational cost and avoid useless mechanisms, with a lower impact on capacity fading due to the cyclic procedure used. The computational cost is reduced without affecting the battery degradation behaviour. The main terms to be optimised related to the ageing mechanism model are the SEI density (ρ) and porosity, as well as the activation energy (EASEI) linked to the SEI formation reaction rate.

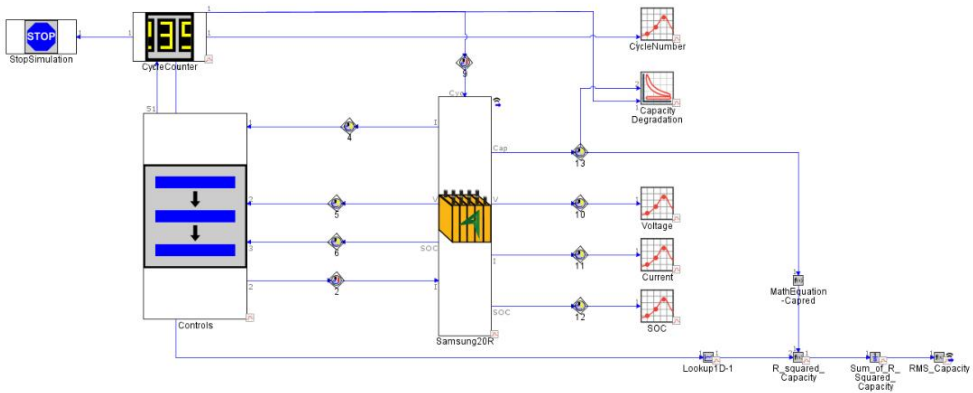


Figure 4.11. Scheme showing the numerical model used to calibrate the aged cell.

The degradation process of SEI growth is accelerated at a higher. For this reason, the data used for calibration purposes were at 50 °C. The GA target is to adjust the capacity fade through the optimisation of the SEI density, SEI porosity and the activated energy of the SEI reaction rate. The cycling procedure during the simulation was the same as during the experimental test. The battery was charged up to maximum voltage with 1 C-rate, followed by a rest period of 30 minutes. In sequence, the battery was discharged with 2 C-rate, and the battery was left to rest for 30 minutes before starting the cycle again. The objective function of the GA decreases the root mean square of the difference between the capacity fade from the simulation and experimental results. Figure 4.12 shows the objective function behaviour as a function of the case number (up to 140 cycles) for the NMC battery (a) and LFP battery (b). For each case number, the optimiser adjusts the parameters for 250 cycles. This means the simulation performs 250 times the charging, rest, discharging, and rest again. The high computational cost is compensated with the calibrated model as it can be used to predict vehicle range during a driving cycle without expensive experiments. In summary, the optimiser has achieved the best solution after 80 interactions. Furthermore, the NMC battery cathode chemistry showed to be faster than LFP cathode chemistry in the optimising process, with lower error between simulation and experimental results.

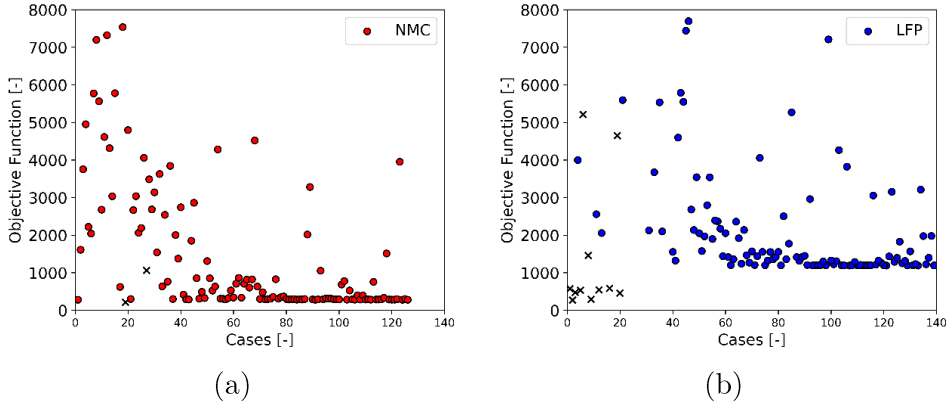


Figure 4.12. Objective function values for 140 cases simulated targeting to decrease the discrepancy in capacity fade between simulated and experimental test. (a) NMC battery and (b) LFP battery.

Figure 4.13 presents the sensitivity resulted during the optimisation process for the ageing model parameters for both cells, NMC (Figure 4.13 (a)) and (Figure 4.13(b)). The parameter that most affects the ageing model is the SEI porosity, which has a 70% impact on both cathode chemistry. The activation energy sensitivity from the LFP is higher than that of the NMC battery, which is in accordance with the experimental results due to the higher degradation process. However, in general, the sensitivity value is similar for both cases.

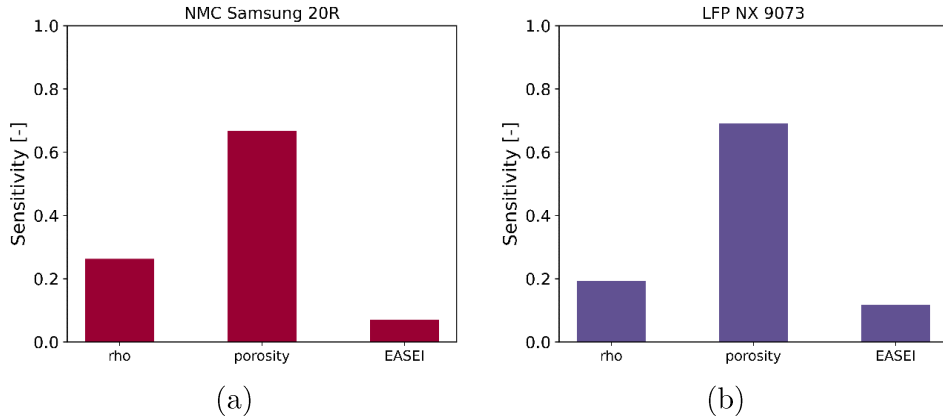


Figure 4.13. Sensitivity of the ageing model parameters for the NMC (a) and the LFP (b).

Table 4.3 shows the results (optimum value) of the optimisation procedure for the ageing model and the range used to find the minimum error between simulation and experimental results. A higher difference was found for the activation energy, meanwhile, porosity and density have similar values. However, it is noticeable that this higher difference can be less notable as the sensitivity of this parameter is lower when compared to the other parameters, Figure 4.13.

Table 4.3. Optimised ageing parameters for NMC Samsung 20R and LFP NX9073 in GT-AutoLion.

Parameter	Unit	Range Optimizer	Optimum value NMC	Optimum value LFP
Rho (ρ_{SEI})	g/cm ³	0.2 – 5.0	3.57	2.08
Porosity (ϵ)	-	0.001 – 0.99	0.111	0.077
Activation Energy ($E_{a,SEI}$)	J/mol	10 - 10000	35.7	5439.8

Figure 4.14 compares the calibrated model and the experimental results for the capacity fade of both batteries, NMC and LFP, at 50 °C of ambient temperature. The maximum difference between the curves is 1% for both

cells along the 250 cycles carried out. The NMC battery has lower capacity fading at this condition, about 8% for the experimental results and 7.6% for the calibrated model, as seen in Figure 4.14 (a) and (c). For the LFP battery, the experimental test resulted in a capacity decrease of 11.2% against the 11.1% calibrated model, according to Figure 4.14 (b) and (d). The trend on the capacity decay is similar for both cases, resulting in a lower difference between experimental and simulated values, as depicted in Figure 4.14 (e) and (f).

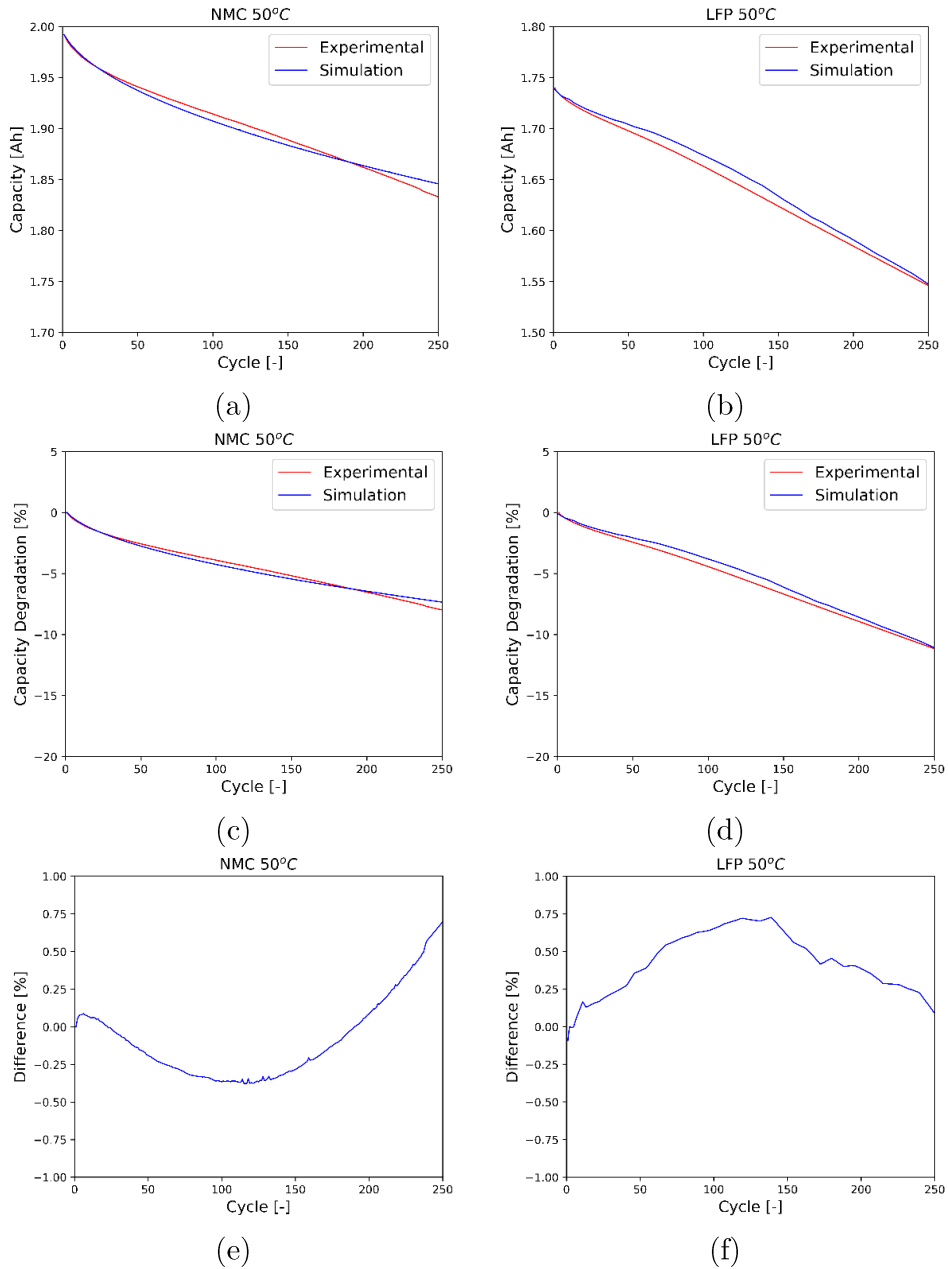


Figure 4.14. Comparison of the capacity fading from the calibration model and experimental result: Absolute, normalised and difference values for the

NMC battery in (a),(c), (d), and for the LFP battery in (b),(e) and (f), respectively.

4.4.2 Ageing model validation

Model validation was carried out with the experimental results obtained at 20 °C of ambient temperature. Figure 4.15 compares the ageing model and the experimental result for the capacity fading at 20 °C of ambient temperature. The maximum capacity decrease at this temperature is about 2% for the NMC battery, Figure 4.15 (a), and about 4% for the LFP battery, Figure 4.15 (b). The model has accurately predicted this trend, with a maximum difference of 2% for the NMC battery during the 250 cycles. This difference can be understood by the work of Guo et al. [12]. Starting to cycle a NMC pristine cell, the anode graphite structure may grow, boosting the diffusion of lithium ions. The ageing model can not predict this behaviour as it is not considered due to the high computational cost of mechanical deformation models. However, this effect has resulted in a maximum difference of less than 2%, with the final values between the simulated ageing model and experimental results similar.

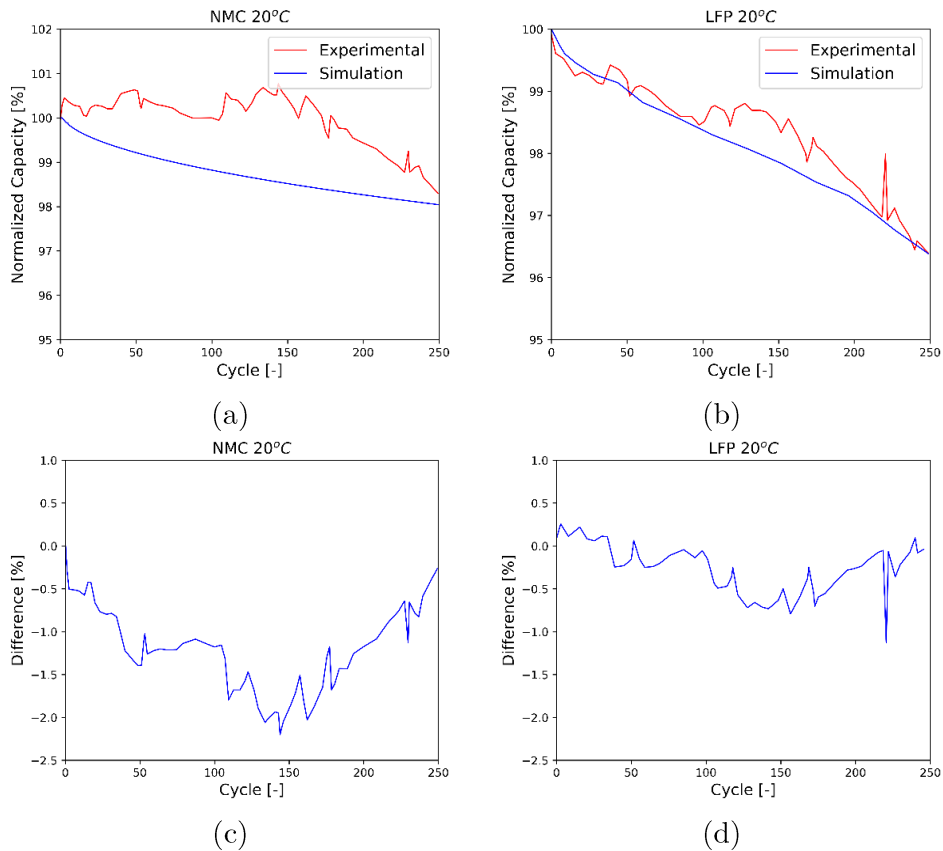


Figure 4.15. Comparison between model validation and experimental results of the capacity fading at 20 °C of ambient temperature: Normalised and difference for the NMC battery in (a) and (c), and for the LFP battery in (b) and (d), respectively.

4.5 Real application: driving cycles

Driving cycles will be conducted with the battery model calibrated and validated. In this way, the model with the optimised parameters resulted from the calibration procedure will be used in the battery model. The capacity decrease will be predicted up to the state of health (SOH) of 80% through cycling. Figure 4.16 presents the results of the capacity fade for the

NMC and LFP at 50 °C of ambient temperature. For the NMC battery, SOH of 80% was achieved with 200 cycles, Figure 4.16 (a) and (c). The LFP battery reached this value with approximately 750 cycles, showing a higher capacity decay than the NMC battery, according to Figure 4.16 (b) and (c).

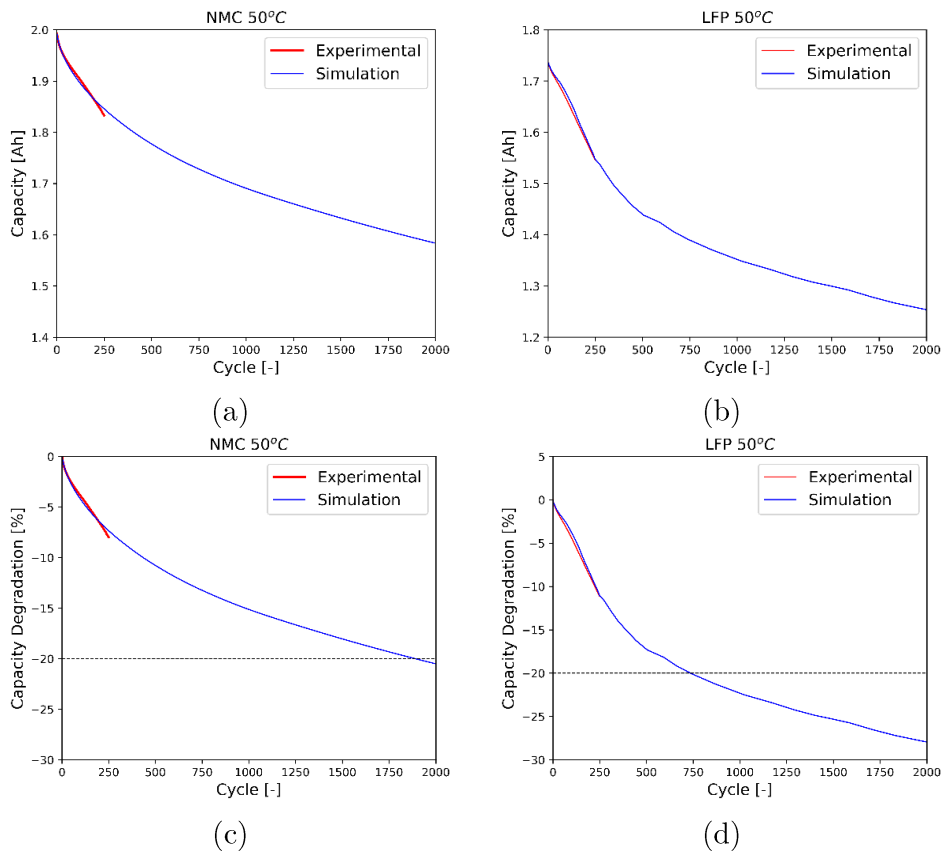


Figure 4.16. Battery capacity fading prediction and in comparison of the experimental results up to 250 cycles at 50 °C of ambient temperature: Absolute and SOH for the NMC in (a) and (c), and for the LFP in (b) and (d).

4.5.1 Vehicle model description

An electric vehicle (EV) model was implemented in GT-Suite to perform different driving cycles representative of homologation conditions as Worldwide Harmonized Light Vehicles Test Cycle Class 3b and real driving situations. For this last driving condition, information about the traffic was collected from a GPS in Madrid, Spain. The vehicle is equipped with a tyre size 215/65/R16, supporting a total weight of 1075 kg without the battery package. The vehicle front area is 2.7 m², resulting in a drag coefficient of 0.29. More information can be found in the Table 4.4. In addition, the sub-models attached, representative of the vehicle, can be seen in Figure 4.17.

Table 4.4. Vehicle model characteristics.

Vehicle characteristics	Value
Max power (kW)	150
Weight (kg) – Without battery package	1075
Drag coefficient (-)	0.29
Vehicle frontal area (m ²)	2.7
Vehicle wheelbase (m)	2.6
Horizontal distance from last rear axle to centre of mass (m)	1.2
Vertical distance from axles to centre of mass (m)	0
Rolling friction (-)	0.011
Tyres	215/65/R16

The electrical motor used in the vehicle utilises a base map that results in a maximum power of 150 kW. The map-based approach has the efficiency depicted on the z-axis, the torque in the y-axis and the motor speed in the x-axis. The driver model is responsible for calculating the torque demand from the electric motor to achieve the desired vehicle speed based on the current vehicle speed. Different driver conditions can be adjusted to the aggressiveness desired. In the present work, the driver-forward approach was used because it can preserve the physical causality of the system. The automatic transmission was assigned to the driver, as the electric motor is directly coupled to the differential, which has a final drive ratio of 7.

Furthermore, the vehicle brake strategy applies torque directly to the wheel. If the vehicle speed is lower than 0.1 kph and the torque demand is lower than 0.1 N.m, the EV will stop. If the torque demand is lower than 0 and the motor minimum torque is higher than the torque demand, thus the requested torque demand minus the motor minimum torque will be divided by 4 and applied directly to each wheel. A DCDC converter is used to transform the high-voltage circuit to the low-voltage circuit (12 V battery), maintaining the battery charge to supply energy for the auxiliary devices. In addition, the energy consumption was set to 300 W for both EV, with NMC or LFP batteries.

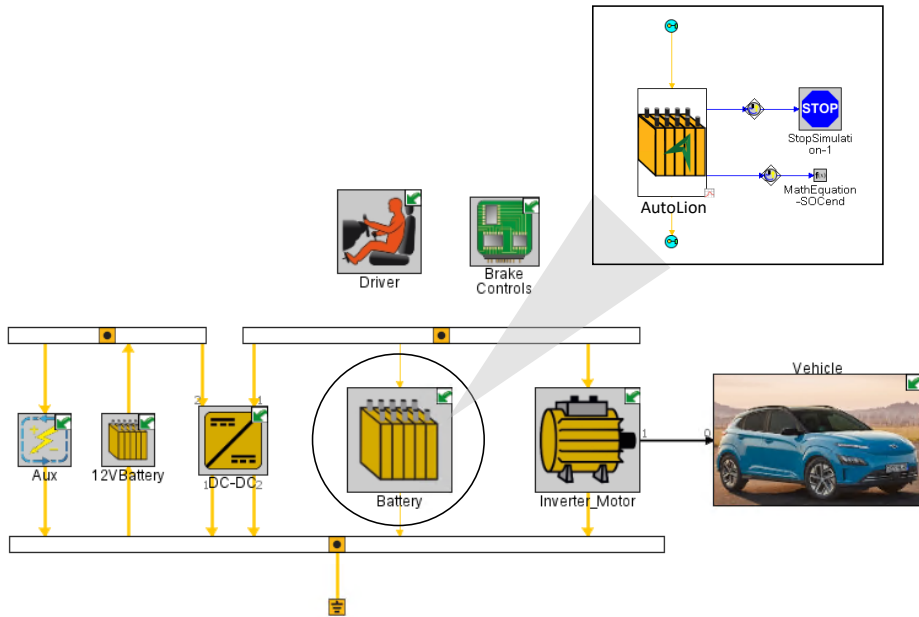


Figure 4.17. Vehicle submodels are attached, including the battery electrochemical model.

The energy balance solved by the vehicle model to calculate the vehicle power required to surpass resistance and maintain the vehicle velocity or to accelerate takes into account the longitudinal forces as the vehicle acceleration (F_a), the vehicle aerodynamic drag (F_D), the tyre rolling

resistance (F_R), the gravity forces ($F_{gravity}$) and any braking forces (F_b), according to Equation (4) and Equation (5).

$$P_v = F_a + F_D + F_g + F_R + F_b \quad (4)$$

$$P_v = m_v a_v + \frac{1}{2} C_D \rho_{air} A_v S_v^2 + m_v g \sin \alpha + C_R m_v g \cos \alpha + F_b \quad (5)$$

Being a_v the vehicle acceleration, m_v is the vehicle weight, C_D is the aerodynamic drag coefficient, ρ_{air} is the air-specific mass, A_v is the vehicle front area, S_v is the vehicle speed, g is the gravity, and C_R is the coefficient of rolling resistance. The distribution and the angles depicted in Equation (5) can be seen in Figure 4.18, where all the forces related to the energy balance equation for a moving vehicle are shown.

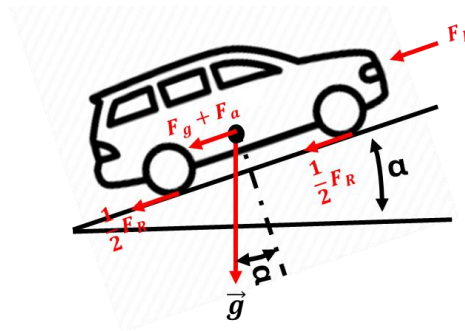


Figure 4.18. Vehicle model scheme for energy balance equation.

The SUV vehicle used in the simulation has a system developed to work with a nominal voltage of 600 V. Thus, using the cells proposed in the current work, the number of batteries in series is 167 for the NMC and 187 for the LFP. Some assumptions need to be considered to have a fairer comparison between NMC and LFP batteries, considering the effect of ageing. For instance, considering the energy equal in both packages, the number of cells is higher for the LFP than NMC (2469 cells higher). Thus, the package total mass and volume will be 22.3% and 25% higher, respectively, compared to

the NMC, resulting in a penalty. In this case, the ageing effect of LFP could be intensified due to the higher load on the available cells (higher vehicle mass). Otherwise, If the available volume remains constant, the LFP batteries would have lower energy and capacity than the NMC batteries. Given the fixed volume of 180 litres, the energy and capacity would be 25% lower for the LFP than the NMC package. Consequently, the LFP batteries would require higher current demands, leading to an accelerated ageing process due to fewer batteries being in parallel. To address this issue, the package used in the vehicle simulation was designed with the same number of batteries in parallel, minimising differences in total mass and available output energy. Ensuring the same number of cells in parallel in the package guarantees that each cell demand (current) ideally remains the same, preventing the ageing effect from being boosted by package architecture. As a result, the total energy of the package is 72 kWh for the NMC and 65 kWh for the LFP. Therefore, the same current profile is imposed for both cathode chemistries for the experimental campaign. The weight of the cells in the proposed NMC battery package is 424 kg (10020 cells x 0.424 kg), while for the LFP, it is 465 kg (11220 cells x 0.415 kg). The analysis is summarised in Table 4.5.

Additionally, the final vehicle weight includes the battery enclosure, cooling system, controller, and cabling. According to the research by Löbberding et al. [1], the specific energy density decreases by 40% when considering the entire battery package, not just the battery cells. Consequently, the NMC battery pack is expected to weigh 593 kg, while the LFP pack is estimated to weigh 651 kg. These values are utilised to calculate the vehicle weight.

Table 4.5. Summary of different package designs and their impact on energy and total mass.

Fixed variable →	Energy			N° cells - Parallel			Total volume (l)		
Package Parameters	NM C	LFP	diff (%)	NM C	LFP	diff (%)	NM C	LFP	diff (%)
N° cells - Parallel	58	65	11.1	60.0	60.0	0.0	65.0	58.0	12.5
N° cells - Serie	167	187	12.5	167	187	12.5	167	187	12.5
Voltage (V)	600.0	600. 0	0.0	600.0	600. 0	0.0	600.0	600. 0	0.0
Energy (kWh)	70.0	70.0	0.0	72.0	64.8	11.1	78.4	62.7	25.0
Capacity (Ah)	116.7	116. 7	0.0	120.0	108. 0	11.1	130.6	104. 5	25.0
Total weight (kg)	412.2	504. 3	22.3	424.0	466. 9	10.1	461.4	451. 6	2.2
Total volume (l)	160.8	201. 0	25.0	165.4	186. 1	12.5	180.0	180. 0	0.0

4.5.2 Vehicle range in driving cycles

Figure 4.19 shows the results for the driving cycle simulation (WLTC, Urban and Highway) carried out with the SUV equipped with a battery package of NMC and LFP batteries. The driving cycles were carried out up to the batteries, which achieved a SOC of 20%. The battery-age characteristics of each cycle condition were updated in the model to represent the electric vehicle. Therefore, driving cycles were performed with the batteries at 1, 500, 1000, 1500, and 2000 cycles. The battery temperature was maintained at 50 °C, and the initial SOC was 100%. The advantage of the simulation is that it can use distinct battery ageing cycles under many drive cycles without costly experimental tests. The results show that the NMC battery achieves 390 km in pristine condition, but the ageing effect can reduce up to 80 km with 80% of SOH. In the case of the LFP, the vehicle range is lower (311 km) than the vehicle with the NMC battery. The main reason is the approach used to define the vehicle package, according to Table 4.5. The decrease in the vehicle range due to ageing was 85 km, similar to the NMC battery vehicle case. Considering the urban cycle, the EV with NMC achieved

a high driving range above 400 km during the first 250 cycles, and the LFP battery resulted in 330 km. The EV is in higher demand in highway conditions, resulting in the worst cycle due to high energy consumption (higher velocity). The EV reached only 245 km using the NMC package and 195 km using the LFP battery package under pristine conditions. Using the ageing condition with 2000 cycles, the autonomy decreased to 195 km for the NMC and 140 km for the LFP.

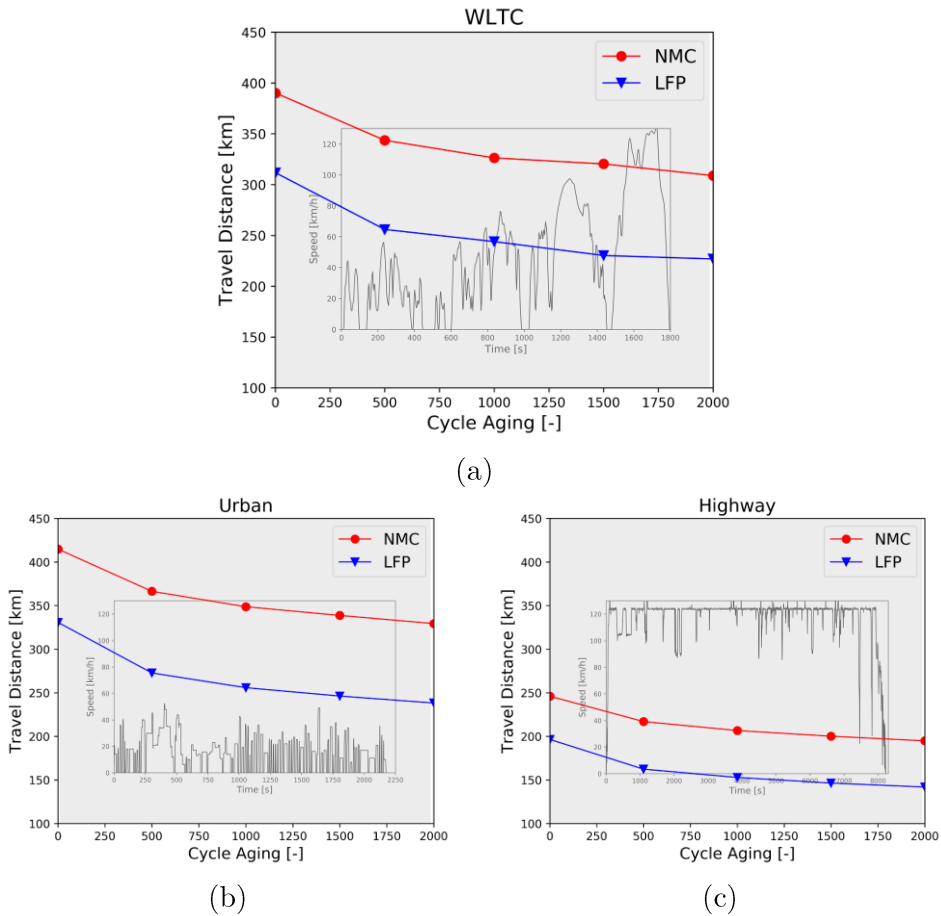


Figure 4.19. Simulation results performing driving cycles in different scenarios such as WLTC (a), urban (b) and highway (c) with an SUV and LFP and NMC battery pack.

4.6 Summary and conclusions

This chapter describes the experimental tests performed to calibrate and validate two P2D models (NMC and LFP) to be replicated at the battery pack level and used in the vehicle range study. The P2D model was created using GT-AutoLion, and the vehicle was created using GT-Suite. Different experimental tests were performed using an Arbin bidirectional source and a climatic chamber to control the ambient conditions. Two ambient temperatures of 25 °C and 50 °C were imposed for both test, performance and cycling test. Different discharge C-rates and a driving cycle were carried out to calibrate and validate the P2D model with static and dynamic load demand. Ageing tests were performed using the following protocol: charge at 1 C-rate, rest for 30 minutes, discharge at 2 C-rates, and a rest period of 30 minutes for voltage relaxation. The aged batteries were characterised to evaluate battery behaviour under degraded conditions. Consequently, the model allows access to different geometric characteristics of battery components, which can provide information on problems related to temperature and capacity loss. Additionally, simulations at the vehicle level were conducted. The vehicle model and the validated and calibrated P2D battery model can predict capacity fade over the vehicle lifetime. Therefore, vehicle simulation was performed using different driving cycles, including WLTC, urban and highway cycles for different battery conditions, covering from pristine up to 80% SOH.

Based on the results, the following conclusions can be drawn:

- NMC and LFP cathode chemistry cells were calibrated using a P2D electrochemical model. The ageing behaviour was also described and modelled. With a discrepancy of less than 2%, the findings showed good agreement with the experimental data.
- The LFP battery deteriorated more than the NMC battery at both ambient temperatures, reducing driving range.

- High ambient temperature accelerated the degradation process during cycling. The validated model has an estimated 30% less capacity for the LFP than the NMC battery.
- When employed in urban cycles, the vehicle simulation demonstrated better autonomy due to the velocity profile.
- In comparison to an LFP battery, an NMC battery offers an extra 84 km of driving range in cities and 50 km on highways.
- At the end of its useful life (20% capacity loss), an NMC battery provides 91 km more driving range in urban areas and 53 km more on highways.

The current chapter has shown that the NMC cathode chemistry can provide a longer vehicle range and reduced capacity fade than the LFP battery through modelling and experimental testing. This would mean a longer vehicle life, allowing the battery pack to travel farther than the LFP battery. With the calibrated and validated P2D model, it is possible to understand the ageing process and its impact on the battery cell components. Safety concerns related to thermal runaway need to be investigated, and the chain mechanism needs to be understood. For this reason, in the next chapter, the study will focus on abuse or thermal runaway. The model developed here will serve as a baseline of information about the composition of each battery part and will feed step-wise reactions, which results can demonstrate what battery components play a more important role and possible implications on thermal runaway. Only the NMC battery will be considered due to the results obtained in the current chapter and the propensity to TR. In addition, the ageing effect on battery TR will be investigated similarly.

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Li Batteries Behaviour Under Different Abuse Tests

Content

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5.1 Introduction

In Chapter 4, battery characterisation was conducted using static and dynamic loads to characterise two P2D models of a pristine battery with NMC and LFP cathode chemistries, respectively. The batteries were then cycled following a protocol of charging at a 1 C-rate up to maximum voltage, resting for 30 minutes, discharging at a 2 C-rate up to minimum voltage, and resting again for 30 minutes. This cycling was repeated up to 250 cycles, equivalent to approximately 30 days of testing. An ageing model was activated in the P2D model, which was calibrated and validated. These battery models were used to construct battery packs for vehicle-level simulations. The results showed that the NMC battery offers a higher vehicle range due to its greater energy density and exhibits lower capacity fade, thus extending vehicle life. However, battery chemistry is closely linked to thermal runaway risk. Additionally, the ageing process increases the complexity of the thermal runaway chain reaction, necessitating a better understanding of designing effective mitigation mechanisms.

This chapter analyses the primary reactions responsible for heat release during the thermal runaway process, allowing for a comparison of the thermal runaway potential of various battery components with different cathode chemistries. The effect of ageing is also addressed, focusing on the main reactions associated with the proposed ageing mechanisms. The simplified approach presented here is a helpful guide for evaluating battery component materials, their impact on thermal runaway, and the effects of degradation processes. However, battery thermal runaway is a complex phenomenon that requires deeper investigation due to its random nature, as reported in the literature. For this reason, the venting process during thermal runaway and statistical analysis of key related parameters were conducted to understand further the variables resulting from the combustion process that impact the cell safety parameters. Optical techniques such as Schlieren imaging, infrared, and natural luminance were employed to capture the venting process behaviour under controlled conditions provided by an ARC. Key thermal

runaway parameters were studied using statistical analysis to identify correlated results.

5.2 In-cell thermal runaway characterisation with thermal trigger

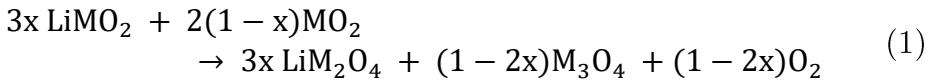
Battery thermal runaway triggered by external heating occurs due to a sequence of reactions. To understand the impact of each reaction on the heat release of the thermal runaway, step-wise reactions were proposed by [1]. This methodology does not require a kinetic mechanism to calculate material concentrations, as it only considers a few steps. In addition, the computational cost is reduced due to this simplification, making it useful for quickly obtaining insight into the effects of battery component materials on thermal runaway. However, this simplification does not account for reactions such as binder decomposition and other side reactions.

The material quantity in each battery part was calculated using the P2D model developed in chapter 4. The pristine battery was first calibrated with an experimental condition and validated with experimental data in another test condition. The ageing effect shows how capacity fading affects battery material composition. Nevertheless, only the SEI growth mechanism was activated due to the characteristics of the cycling process.

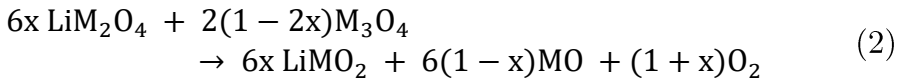
5.2.1 Description of Step-Wise reactions

Sandia has proposed a heat release calculator that uses step-wise reactions to calculate the heat energy release from a thermal runaway triggered by external heating. For the NMC cathode chemistry, the path recommended for the thermal runaway chain reaction considers the release of oxygen of the lithium metal transition in the cathode. Thus, the delithiated form of the layered lithium transition metal oxide, MO_2 , where **M** stands for Ni, Co and Mn composition, can decompose in two main reactions. This

occurs because the delithiated form of the lithium transition metal is less stable than the lithiated form of the transition metal. This would be one of the reasons for the higher thermal runaway intensity of charged cells. Therefore, the recommended path describes that oxygen release can occur from the lithium transition metal, leading to the formation of an intermediate non-lithiated spinel, M_3O_4 . The other possible path occurs without oxygen release, resulting in the lithiated spinel component LiM_2O_4 . These two reactions combined represent the first part of the cathode decomposition and can be written as in Reaction (1).



The products from Reaction (1) result in a stable molecule. The non-lithiated spinel M_3O_4 transform into rock salt and can release oxygen. The other molecule, the lithiated spinel (LiM_2O_4) also can produce rock salt and layered lithium transition metal oxide, releasing oxygen. Both reactions can be summarised as



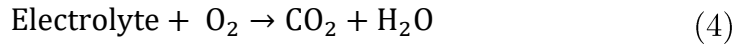
Considering the battery as charge (SOC 100%), the global reaction for cathode decomposition can be written as



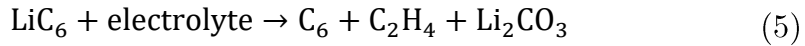
A Gibbs free energy analysis shows that Reaction (1) is more likely to occur than the global reaction [2]. In addition, rock salt is not observed during a cathode decomposition using the X-ray diffraction (XRD) technique to visualise the process [3]. However, electrolytes enhance rock salt production via Reaction (2) and Reaction (3). Therefore, compared with calorimeter data, the path described by Reaction (1) and Reaction (2) seems

to be more adequate for the cathode decomposition model as there is evidence that, during the thermal runaway with a venting process, the electrolyte substance drives the reaction rate towards products of Reaction (1) [4].

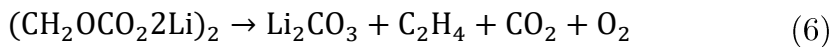
Another important reaction is the oxidation of the electrolyte with the oxygen released from the cathode decomposition. Complete oxidation is boosted by the increase in the ambient pressure (considering a closed volume, without a venting cap bust). In contrast, partial oxidation is favoured if the venting cap is open. As a simplification and considering that most of the gases released during the thermal runaway are carbon dioxide (CO₂), the current analysis considers the complete oxidation process to predict the heat release. Therefore, the reaction can be shown as [5]



The internal temperature of the battery increases until the solid electrolyte interface (SEI) dissolves. At this temperature, the electrolyte can react with the lithium intercalated in the anode, resulting in the Reaction (5) [6,7]. This reaction is similar to the global reaction of SEI formation.



The main degradation mechanism is SEI growth. The SEI, or solid electrolyte interphase, is a protective layer between the active material and the electrolyte, preventing reactions between lithium in the anode and the electrolyte. Additionally, this layer controls lithium-ion diffusion into the anode, defining the battery's performance behaviour. Over time, the SEI can thicken, potentially accelerated by specific usage conditions. This results in reduced lithium content and electrolyte volume, leading to decreased capacity and performance and increased internal resistance. The SEI decomposition reaction is given by [8]



The heat of reactions was calculated based on the composition of each component participating in the respective reaction. The values were obtained considering the following works [2,7,9], as depicted in Figure 5.1.

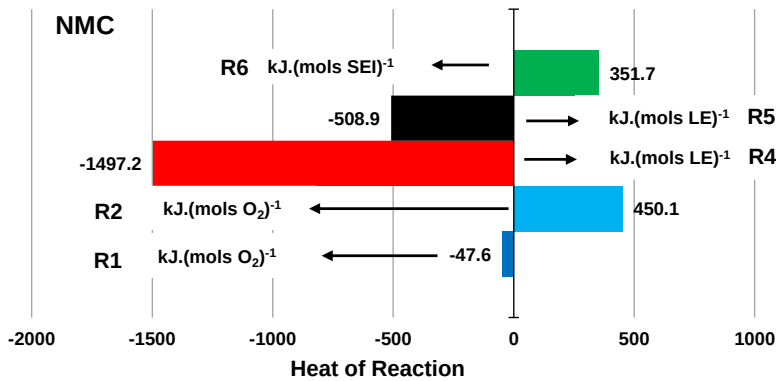


Figure 5.1. The heat of reaction from the step-wise reactions is used to predict the heat release energy.

Furthermore, the step-wise reactions require information on the in-cell components, such as electrolytes, lithium, and cathode active material quantity, as well as the quantity of SEI growth, to calculate the lithium loss. This information can be accessed by optimising the battery components to fit experimental data. For this reason, this methodology avoids complicated experimental tests, the teardown of the cell, and analysis using equipment such as X-ray or magnetic resonance imaging (MRI). Table 5.1 shows the battery parameters used for feeding the step-wise reactions.

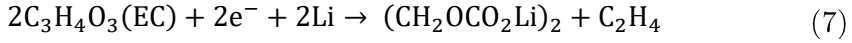
Table 5.1. P2D results from the calibrated and validated NMC battery.

		Anode	Cathode	Separator	Electrolyte
Thickness	μm	89.12	92.14	34.31	-
Active Material Mass	g	6.82	12.80	-	-
Binder Mass	g	0.22	0.41	-	-
Conductive Agen Mass	g	0.22	0.41	-	-
Active Material Volume	mL	3.05	2.66	-	-
Binder Volume	mL	0.12	0.23	-	-
Conductive Agen Volume	mL	0.11	0.21	-	-
Total Mass	g	7.26	13.62	1.09	8.72
Total Volume	mL	3.28	3.11	1.51	7.27
Coated Volume	mL	4.91	4.80	1.51	
Density	g/cm^3	2.21	4.38	1.20	1.2
Porosity	(-)	0.33	0.35	0.40	-
Electrolyte volume	mL	3.00	3.10	1.16	
Electrolyte Coated moles	mol	0.04	0.037	0.014	
SEI Lithium	mol	1.45 E-04			
Electrode Capacity	mAh/g	371.93	275.51	-	-
Stoichiometry at 100% SoC	-	0.88	0.32	-	-
Stoichiometry at 0% SoC	-	0.006	0.92	-	-
Active Material moles	mol	0.095	0.131		0.087
Lithium moles at 100% SoC	mol	0.088	0.045	-	-

The quantity of coated electrolyte in each part is calculated considering the Equation (1)

$$\begin{aligned}
 &\text{Electrolyte coated moles} \\
 &= \left(\frac{\text{Electrolyte volume} * \text{density electrolyte}}{\text{Molar weight electrolyte}} \right) \quad (1) \\
 &- \text{Lithium loss}
 \end{aligned}$$

The lithium loss is the ageing process that increases the SEI thickness layer. Therefore, part of the electrolyte of the pristine condition, calculated on the first part of Equation (7), is used to react with the lithium to produce SEI, being a relation 1:1, according to the Reaction (7).



The lithium loss quantity is calculated considering the battery pristine capacity minus the battery ageing capacity, divided by the lithium charge. The lithium charge is a theoretical value considering the electrochemical reaction of lithium as in Reaction (8).



As the reaction of the oxidation of lithium occurs as monovalent, the equivalent molar weight is equal to 6.94 g/mol. The Faraday constant means how much charge can be carried in one mole of electrons, which is 96485 C/mol. In addition, 1 Ampere is equal to 1 C/s. Based on that, to obtain the maximum amount of charge in 1 gram of lithium, the mathematical procedure in Equation (2) can be done.

$$\begin{aligned} \text{Lithium charge} &= \frac{\text{Faraday's constant}}{\text{Lithium equivalent molar weight}} = \frac{96485 \text{ As/mol}}{6.94 \text{ g/mol}} \\ &= \frac{96485 \text{ Ah/mol}}{6.94 \text{ g/mol} * 3600} \cong 3.87 \text{ Ah/g} \end{aligned} \quad (2)$$

The SEI quantity in mols is calculated considering the lithium charge available in its thickness in the pristine condition, and the lithium loss due to the ageing process, which is the main degradation mechanism considered in the current work, is the SEI growth. Therefore, Reaction (7) indicates that for every 2 moles of lithium, 1 mole of SEI is produced [10]. Thus, the quantity of SEI can be calculated according to Equation (3).

$$SEI = \frac{SEI \text{ lithium charge}}{Lithium charge * Molar Weight * 2} + \frac{lithium loss}{2} \quad (3)$$

The quantity of cathode active material in mols is calculated using Equation (4).

$$Active \text{ Material (moles)} = \frac{Active \text{ Material Mass}}{molar \text{ weight}} \quad (4)$$

The total lithium quantity at SOC 100% is calculated using Equation (5).

$$\begin{aligned} &Lithium \text{ moles (at SOC 100\%)} \\ &= \frac{Elec. Capacity * total mass * stoichiometry (at SOC 100\%)}{lithium charge * lithium molar weight} \end{aligned} \quad (5)$$

5.2.2 Thermal runaway experimental tests

5.2.2.1 Methodology and test matrix

Heat-wait-seek protocol was used to perform an abuse test of the NMC battery with different state of health. The result obtained will be compared with the results of the step-wise reactions. 3 experimental tests of each battery condition were performed to understand cell-to-cell variability. The parameters used to perform the heat wait seek protocol in the accelerating rate calorimeter are summarised in Table 5.2.

Table 5.2. ARC parameters used for the HWS protocol.

Parameters	Value
Start temperature (°C)	50
Step temperature (°C)	5
Wait period (min)	30
Exothermic sensitivity (°C/ <i>min</i>)	0.02
Exothermic step calculation (°C)	0.2

The battery characteristics are described in Table 5.3. The battery has a cathode of Nickel-Manganese-Cobalt chemistry, resulting in 169 Wh/kg of specific energy. The battery was instrumented with N-type thermocouple with an uncertainty of 0.7%, with the thermocouple located in the middle of the cell. This thermocouple was used as the reference temperature for the ARC exothermic calculation and tracking temperature and for the exothermic parameters such as heat release, maximum temperature, onset temperature and other temperatures. All batteries were charged up to SOC 100% according to the CCCV protocol, with a maximum voltage of 4.2 and a current cut-off of 100 mA, using the Arbin bidirectional source. Further details of the process and equipment can be found in Chapter 3 of this document.

Table 5.3. NMC Samsung 20R battery description.

Parameter	NMC
Cell format	18650
Cathode Chemistry	LiNiMnCoO ₂
Weight [g]	42.4
Nominal Voltage [V]	3.6
Nominal Capacity [Ah]	2.0
Current Charge Continuous/Peak [A]	2.0/4.0
Current Discharge Continuous/Peak [A]	22.0/30.0A
Total Energy [Wh]	7.2
Vent Cap holes	3
Cut-off voltage [V]	2.5
Temperature use Range [°C]	-20 to 60

5.2.2.2 Tests results

Figure 5.2 shows the battery surface temperature rise rate and heat released as a function of the battery surface temperature for three NMC battery conditions: pristine, and aged at 20 and 50 °C of ambient temperature. The battery aged at 50 °C has presented a lower maximum temperature, but a higher temperature rise rate for the same battery surface temperature. The battery capacity of the aged battery at 50 °C is lower than that of the pristine and aged batteries at 20 °C ambient temperature. Compared with the pristine condition, the difference is about 7.5% lower capacity for the aged battery at 50 °C, while the aged battery at 20 °C is only 1.5%. One possible explanation for the different degradation mechanisms and their impact on the thermal runaway process is that they alter the battery internal composition and materials. However, the general pattern of the temperature rise rate as a function of battery temperature is similar among the batteries, reaching comparable maximum temperature rise rates. The accumulated heat release can be calculated as the difference between the temperature at the start of the exothermic reaction and the maximum temperature, using $mc_p\Delta T$. The onset temperature of the exothermic reaction

was similar between the batteries. However, the TR has resulted in a higher maximum temperature for higher battery capacity, releasing more heat.

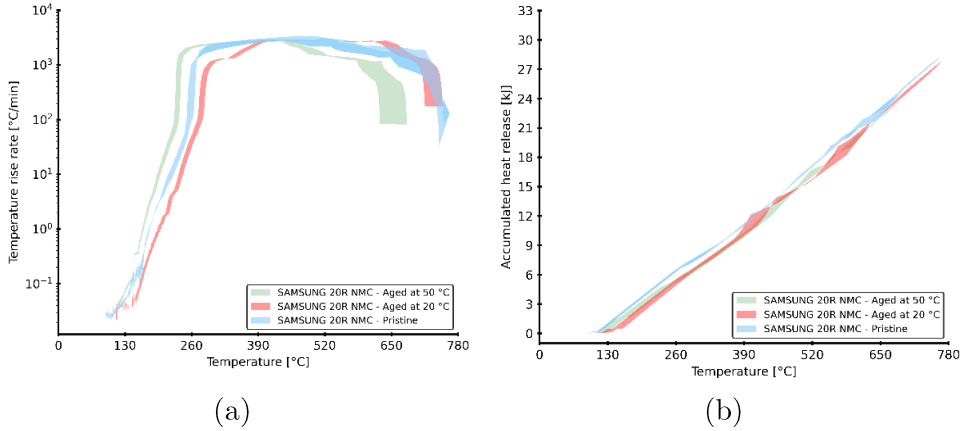


Figure 5.2. Temperature rise rate (a) and heat released (b) as a function of the battery temperature for the self-heating phase.

Table 5.4 shows the mean value and variability of the battery temperatures during the thermal runaway and the initial and final mass for the pristine condition. The average maximum temperature was 753 $^{\circ}\text{C}$, with a variability of 0.9%. The onset temperature when the battery temperature rise rate was equal to 10 $^{\circ}\text{C}/\text{min}$ was of 216 $^{\circ}\text{C}$, and the crucial temperature, which is defined when the battery temperature rise rate is equal to 100 $^{\circ}\text{C}/\text{min}$, was of 247 $^{\circ}\text{C}$. Comparing both parameters, the onset temperature has obtained a lower variability (2.7%) compared to the crucial temperature (7.6%), indicating that it would be a more consistent parameter for a first alarm for thermal runaway in addition to the higher time available for any strategy to mitigate TR. Furthermore, the heat released by the self-heating phase and thermal runaway was 28 kJ, with a maximum temperature rise rate of 3100 $^{\circ}\text{C}/\text{min}$. The mass injected during the process was 10.8 g with a variability of 2.5 % among cells.

Table 5.4. Battery thermal runaway parameters for the pristine NMC Samsung 20R.

	Mean value	Variability (%)
Maximum temperature [°C]	753	0.9
Onset temperature [°C] (at 10 °C/min)	216	2.7
Crucial temperature [°C] (at 100 °C/min)	247.3	7.6
Maximum accumulated heat release [kJ]	28	1.0
Maximum temperature rise rate [°C/min]	3100	7.3
Initial mass (g)	42.8	0.3
End mass (g)	32.0	1.0
Mass difference (g)	10.8	2.5

Table 5.5 shows the battery TR parameters for the aged batteries at 20 °C and 50 °C of ambient temperature. The maximum temperature was higher for the less degraded cells (80 °C higher). The lower battery capacity plays an important role in the maximum temperature. The difference of 7.5% in capacity in relation to pristine batteries should impact the maximum battery temperature, decreasing its value due to the lower energy available. In addition, the mass loss difference was 2.3 g between the pristine and aged battery at 50 °C, considering the mean values of each case. A lower mass quantity inside the battery casing at the end of the venting process of the TR means lower energy can be transferred to the battery surface, resulting in a lower battery temperature. The heat released is linked with the temperature difference between the start of the self-heating phase and the maximum temperature achieved. For this reason, the battery with higher capacity fade presented lower heat released than the battery degraded at 20 °C.

Table 5.5. Battery thermal runaway parameters for the NMC aged batteries at 50 °C and 20 °C.

	Mean Value Aged at 20 °C	Variability (%)	Mean Value Aged at 50 °C	Variability (%)
Maximum temperature [°C]	740	1.5	660.2	2
Onset temperature [°C] (at 10 °C/min)	230.2	3	195.5	3.5
Crucial temperature [°C] (at 100 °C/min)	263.2	8	226.1	7.5
Maximum accumulated heat release [kJ]	25.5	1.1	24.2	1.0
Maximum temperature rise rate [°C/min]	2806.5	7.2	2806.5	7.4
Initial mass (g)	42.5	0.5	42.4	0.3
End mass (g)	32.6	1.1	30.2	1.0
Mass loss (g)	9.9	3.0	12.2	2.5

5.2.3 Theoretical analysis of heat release using step-wise reactions

Table 5.5 and Figure 5.3 depict the total heat released for the pristine NMC battery and the contributions of each step-wise reaction, such as the anode-electrolyte reaction, cathode decomposition, electrolyte oxidation and SEI decomposition. The results are similar to the step-wise reaction and the experimental test. Reactions 4 and Reaction 5 have a higher impact on the total theoretical heat release, resulting in a similar value. Lithium comes into direct contact with the electrolyte during Reaction 5, which is associated with

SEI breakdown. Furthermore, the energy generated in Reaction 4 occurs due to cathode decomposition, which releases oxygen that can react (oxidise) with the hydrocarbons that compose the electrolyte. The heat release was calculated using a step-wise reaction, considering the battery material and composition from the P2D model calibrated and validated, which resulted in 33 kJ. In comparison, the experimental result was 28 kJ. Mass loss due to the process of TR, heat transfer, battery surface temperature distribution, and using a simplified quantity of reactions (a simple chemical mechanism) to represent the thermal runaway can result in some difference between experimental and theoretical heat release. However, considering this discrepancy, the results can be considered similar, and the objective is to compare the ageing effect on heat release using the same methodology, identifying the materials that can play a more important role in TR.

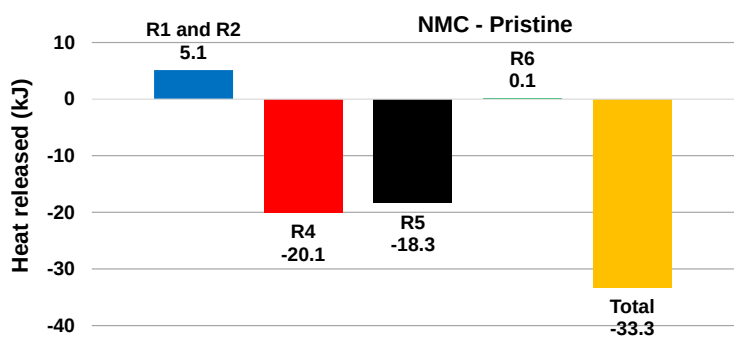


Figure 5.3. Theoretical heat release calculated using step-wise reaction for the NMC pristine battery.

Figure 5.4 shows the heat release results for the aged NMC battery at 50°C. The model used in GT-AutoLion considers SEI growth as the main mechanism of capacity fading during cycling based on the characteristics of this process. The SEI growth is characterised by a reduced cycled lithium, which reacts with the electrolyte to form a protective layer known as the SEI. Consequently, the heat release resulting from the Reaction (5) is reduced due to the lower lithium and electrolyte available. In addition, due to the higher SEI thickness, the Reaction (7) plays a more important role in the net heat

release than the battery in a pristine condition. It is important to note that all the assumptions consider the battery state of charge to be 100%. Compared to the pristine case shown in Figure 5.3, the heat release for the aged NMC battery is 12.3% lower, reflecting the impact of SEI growth on the available reactive materials.

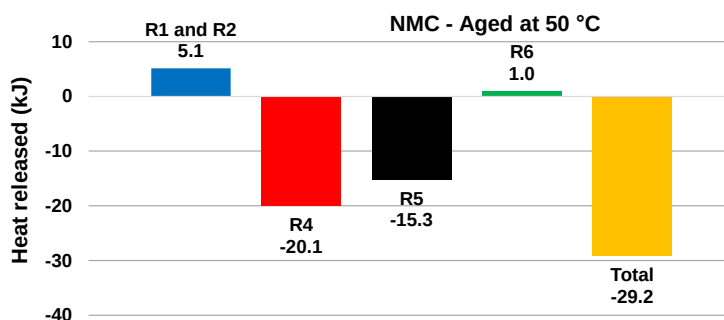


Figure 5.4. Theoretical heat release calculated using step-wise reaction for the NMC aged battery at 50 °C of ambient temperature.

Figure 5.5 presents the heat released, calculated through a step-wise reaction, for the aged battery at 20 °C ambient temperature. The lower temperature ambient decreased the mechanism velocity to produce SEI. For this reason, the capacity fading was lower than at 50°C, leading to reduced SEI growth. This preservation of more lithium and electrolyte in the anode resulted in a higher heat release for Reaction 5. Furthermore, Reaction 6 has a lower impact on heat release, resulting in net heat release similar to that of a battery in pristine conditions. These findings are in accordance with the experimental results depicted in section 5.2.2 Thermal runaway experimental tests, confirming that the heat release for the NMC battery aged at 20°C was higher than at 50°C and comparable to the pristine battery. Therefore, the ageing effect uses SEI growth as the main mechanism to decrease the electrolyte and lithium quantity, reducing the heat released by the battery. In addition, the reduced electrolytes and lithium directly increase the SEI thickness. The higher SEI quantity means the higher energy required to decompose this layer, further decreasing the net heat release of the battery during the thermal runaway.

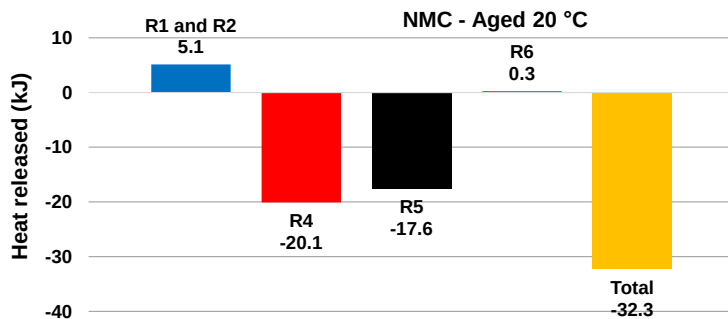


Figure 5.5. Theoretical heat release calculated using step-wise reaction for the NMC aged battery at 20 °C of ambient temperature.

5.3 Out-cell thermal runaway characterisation with external heating

This section will discuss the outside thermal runaway characterisation with external heating as a trigger for pristine and aged battery conditions. Different from section 5.2 In-cell thermal runaway characterisation with thermal trigger, where the focus was comprehending the impact on the thermal runaway with the main internal battery components, the current section focuses on the understanding and consequence of the thermal runaway in an out-cell perspective. Mass ejected, temperature distribution and energy released are key factors that need to be considered when designing safety mechanisms. For this reason, the quasi-adiabatic ambient provided by the heat wait seek protocol was used to guarantee a controlled condition for each experimental test in the ARC. The main TR parameters are discussed by considering mean values and the standard deviation to understand cell-to-cell variability. Furthermore, the tests were performed with optical techniques coupled in the ARC during the heat wait seek tests. Therefore, the venting process was characterised by jet format and penetration, particle temperature and velocity. Furthermore, the batteries were characterised using mechanical trigger for TR, using different nail positions and SOC. A thermographic camera was used to capture the battery surface temperature distribution.

5.3.1 Methodology and Test matrix

A NMC battery was used to study the cell-to-cell variability, understand the impact of different parameters in the thermal runaway and characterise the venting process, including gases and particle phases. This battery was used for thermal and nail penetration abuse testing. The battery is an LG MH1 model, and the main battery specifications are in Table 5.6. The batteries were charged up to SOC 100% using a bidirectional source manufactured by Arbin Instruments, LBT-10V-100A. The CCCV protocol was used during the charging process, applying a constant current according to the recommended by the manufacturer up to the maximum voltage of 4.2 V. The current cut-off during the constant voltage phase was of 50 mA. A SOC different than 100% was set up by first charging the battery up to SOC 100% and, in sequence, discharging the battery with the standard constant current for the discharge process up to the SOC desired.

Table 5.6. NMC battery specifications.

Parameter	Description
Battery model	INR18650 - LG MH1
Cell format (diameter * height) [mm]	18*65
Cathode Chemistry	LiNiMnCoO ₂ (NMC 811)
Anode Chemistry	Graphite
Electrolyte Chemistry	Lithium hexafluorophosphate, organic carbonates
Weight [g]	49
Nominal Voltage [V]	3.67
Nominal Capacity [Ah]	3.2
Current Charge Continuous/Peak [A]	1.55/3.2
Current Discharge Continuous/Peak [A]	0.62/10.0
Total Energy [Wh]	11.7
Vent Cap holes	3
Voltage at SOC 100% [V]	4.2
Cut-off voltage [V]	2.5
Temperature use Range [°C]	-20 to 60

Table 5.7 presents the test matrix used in the current section. Each test condition was repeated 5 times, resulting in 15 tests. The number of tests is considered sufficient to statistically analyse the thermal runaway. The battery conditions comprehend SOC at 100% and SOC at 50% for the pristine state of health and SOC at 100% for an aged condition with 250 cycles.

Table 5.7. Test matrix and quantity of batteries used in each test condition.

	SOC 100% - Pristine	SOC 100% - Aged	SOC 50% - Pristine
Quantity (-)	5 cells	5 cells	5 cells

5.3.2 Optical techniques

Different optical techniques were applied to study the venting process before and during the battery thermal runaway. Schlieren technique was used to visualise the first venting process that can be used as a first alert for thermal runaway. A counter detector method was used to capture different phases described as only gas or/and not only gas. In addition, jet penetration and jet format can be detailed. Infrared images were used to measure the particles temperature, using an approach that most of the particles ejected are carbon. It was also used to measure the battery surface temperature distribution. Furthermore, combustion image velocity (CIV) was applied to identify particles ejected by the battery and calculate their velocity based on a method of cross-correlation. Further post-processing details for each optical technique are described in the current section.

5.3.2.1 Contour detector post-processing for Schlieren technique

Figure 5.6 (a), (b), (c) and (d) depicts the application of the contour method to a raw Schlieren image to define the jet contours. The first step involves removing the background from the images to enhance the visibility of the jet contours. This is achieved by subtracting an image without the jet from the images containing the jet (raw Schlieren images), Figure 5.6 (b). A Gaussian filter is applied to reduce noise and smooth the image. Subsequently, the images are binarised for segmentation. This process converts the grayscale image into a binary scale (black and white), enabling clear identification of the jet contour and preparing the image for morphological operations. Closure and filling are the morphological

operations applied to the images, resulting in Figure 5.6 (c). In order to provide more consistent contour detection, closing morphological techniques are utilised to smooth out abnormalities and close gaps in the jet contour (boundary). Filling procedures, on the other hand, fill in the gaps in the jet boundaries. When combined, these procedures enhance contour identification based on defined thresholds, making it possible to repeat the process for different jet circumstances and produce a more reliable analysis and accurate jet format extraction, as shown in Figure 5.6 (d).

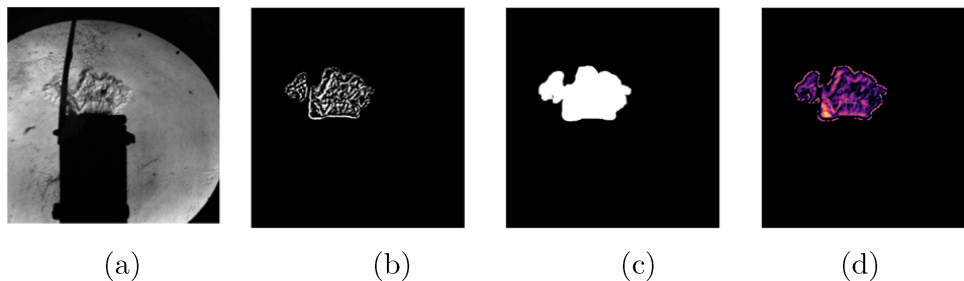


Figure 5.6. Schlieren contour detection method. (a) schlieren image, (b) background removal and Gaussian filter, (c) binarisation and morphological operations, (d) contour definition.

5.3.2.2 Thermographic camera images

Infrared images were used to measure the battery temperature surface distribution and the particle temperature. The spatial and temporal temperature distribution were obtained by creating a map. For this reason, the image containing the battery surface temperature was divided into 10 distinct zones, as presented in Figure 5.7. In sequence, the average temperature was calculated for each zone. The map is divided into multiple zones since it enhances spatial resolution and does not reduce spatial temperature variability. Bringing all of the frames in sequence from this method will result in the temporal resolution for the map. Furthermore, for the line plot, the number of zones was reduced in order to avoid polluting the graph with a lot of similar data. Zone 1 ranged from 0 (venting cap) to 5mm, zone 2 from 5 to 15mm, and zone 3 from 15 to 30mm. Due to the 45

mm (diameter) sapphire window provided, only half of the cell can be visible, with the remaining length employed to monitor the particle venting process temperature (15mm).

A post-processing technique similar to that employed in 5.3.2.1 Contour detector post-processing for Schlieren technique was utilised to detect the jet area with the vented particles. Nevertheless, the method has considered the intensity-based gradient between pixels. Basically, the gradient is calculated in the direction x and y, and the magnitude is calculated. Based on a threshold, the counter is detected. The average value and standard deviation were calculated for each jet area. In addition, an average standard deviation and mean value were computed considering the five cells in each test condition to account for cell-to-cell variability.

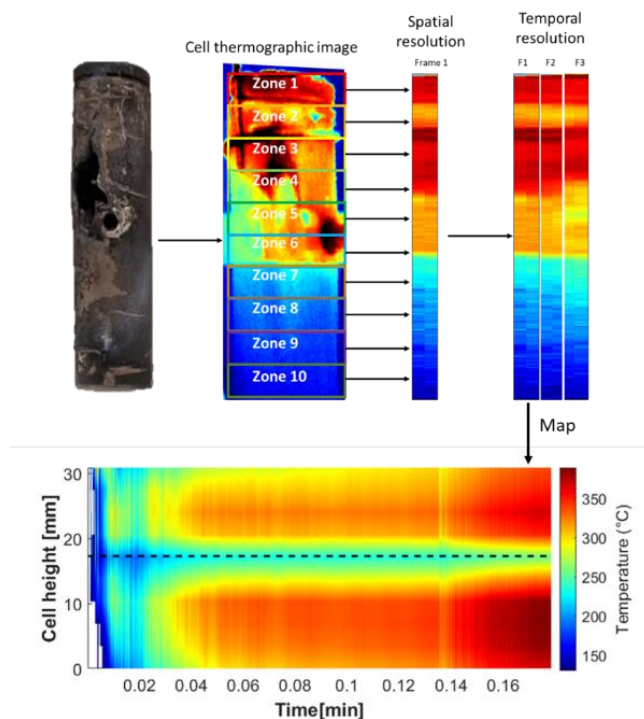


Figure 5.7. Map plotting method for the battery spatial and temporal temperature distribution.

5.3.2.1 Combustion image velocity (CIV)

The velocity field during venting and thermal runaway (TR) events was measured using CIV technology. This technique tracks particles ejected by the battery cell. Unlike the conventional PIV technique, which requires intentionally introducing particles into the flow with controlled size and distribution, the venting and TR processes generate the particles used for this measurement [11,12].

Two techniques were used in the current study to identify the particles: the natural luminosity of incandescent particles for the TR, while the background illumination was used for non-incandescent particles produced during the first venting process. A summary of the full procedure is shown in Figure 5.8. The post-processing is done first by improving particle contrast and lowering picture noise. This step uses a particle-free image to subtract the background from the images with particles. After that, the CIV post-processing is used, employing an interrogation window of 120x120 pixels.

The cross-correlation method determines particle movement by examining changes in pixel intensity between the interrogation window and the overlapping search area, which is a second interrogation window. It estimates particle displacement by maximising the similarity between these regions. The reliability of the cross-correlation is evaluated using the signal-to-noise ratio (SNR), which measures the ratio of the highest correlation value (primary peak) to the second-highest value (secondary peak). A higher SNR reflects greater confidence in the results.

The method requires a short particle displacement for proper application of the cross-correlation function. For this reason, the frame rate of 20,000 frames per second (50 μ s between frames) was used. Three-dimensional particle clouds are produced since the measurement does not isolate a particular plane due to the lack of a laser sheet. A short focal length is employed to counteract this distortion, enabling an approximation of a particular plane.

Therefore, Figure 5.8 depicts the start of the post-processing by improving the battery particle and, in sequence, using the cross-correlation function to track the particle motion. The sequence begins with defining an interrogation window in frame A (marked by a blue square), containing a group of particles. The same group is located in frame B (marked by a red square), and their displacement along the x and y axes is calculated. Knowing the time interval between frames ($50\text{ }\mu\text{s}$), the particle velocity is determined. This process is applied across the entire image to analyse all identifiable particles.

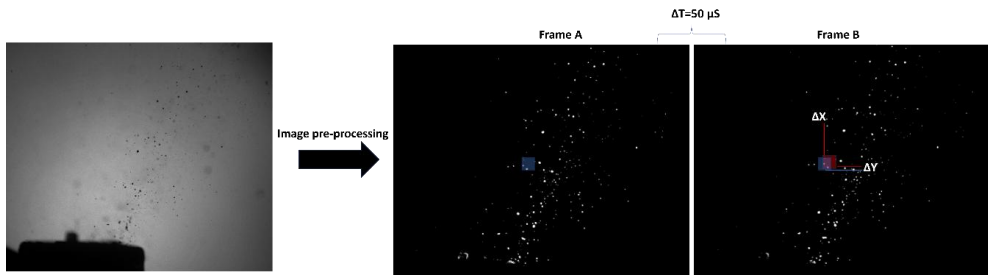


Figure 5.8. Tracking particle motion and estimating its velocity using the CIV approach.

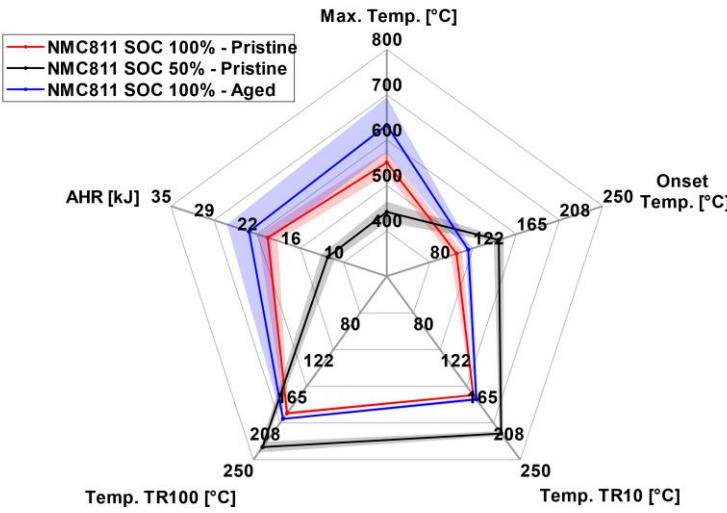
5.3.3 Main thermal runaway parameters

Figure 5.9 presents the thermal runaway parameters for three battery conditions: pristine at SOC 100%, pristine at SOC 50%, and aged (after 250 cycles) at SOC 100%. The maximum temperature was higher for the pristine condition at a higher SOC, consistent with findings from other triggering methods [13]. However, the aged battery at SOC 100% exhibited a higher maximum temperature than the pristine condition at the same SOC, even when accounting for cell-to-cell variability. This observation is unexpected because the growth of the solid electrolyte interphase (SEI) reduces the battery available lithium in the anode, which should decrease the energy released during the exothermic reactions of TR [14]. This result can be explained by the end mass of the battery, as presented in Figure 5.9 (b). The aged battery loses less mass, resulting in a higher weight than the pristine

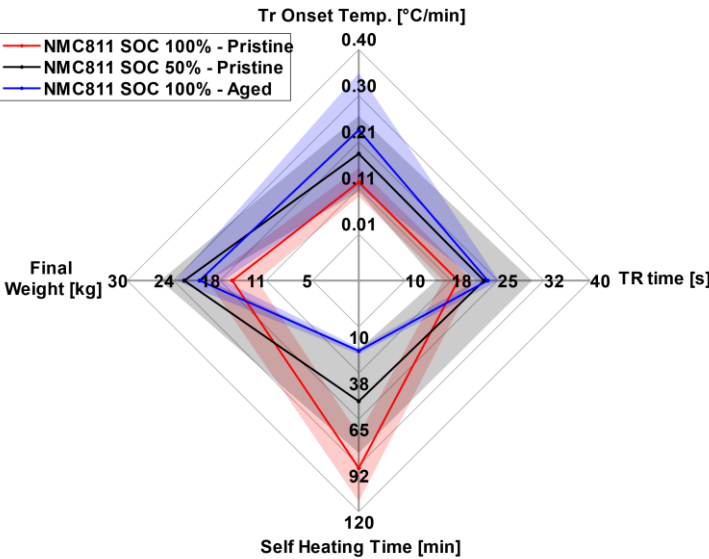
condition at SOC 100%. This can be interpreted as a lower amount of energy being released to the ambient, while the pristine battery ejects a higher quantity of energy. As a result, more energy is transferred to the external surface of the battery, leading to a higher temperature. Only exothermic periods are considered when calculating the battery heat release using $mcp \frac{dT}{dt}$. Quasi-adiabatic condition is achieved using the HWS protocol to detect the exothermic reaction and during the ARC exothermic mode. While the calorimeter tracks the battery temperature during the exothermic phase, the temperature increases due to heat released from internal reactions, not external sources. Therefore, during the first venting process, when the battery cools down and the ARC switches to heating mode, not ensuring a quasi-adiabatic environment, the heat released is not considered in the calculation.

The onset temperature for the exothermic reaction detection was earlier for the pristine battery at SOC 100%. The initial reaction that triggers the thermal runaway mechanism with external heating is the interaction between the anode and lithium, resulting from the decomposition of the SEI. A higher quantity of reactants makes the reaction more intense, allowing it to be detected at lower temperatures. The temperatures when the battery achieves 10 and 100 °C/min of temperature rise rate are also affected by the same reason. The greater concentration of energy compensates for the lower temperature, achieving a higher reaction rate. The self-heating phase duration was for the pristine battery at SOC 100% compared to the other battery conditions, according to Figure 5.9 (b). The temperature rise rate when the exothermic reaction is detected plays an important role in the duration of the self-heating phase. The reason is that the calorimeter will only track the battery temperature, as the heating rate only depends on the exothermic reaction of the battery. Thus, if the exothermic reaction is detected with a lower temperature rise rate, the battery takes more time to increase its temperature. Figure 5.9 (b) shows that a lower temperature rise rate at onset temperature leads to a higher self-heating timing duration. In addition, Figure 5.9 (b) shows that the thermal runaway time (TR time) appears to be influenced by both the battery capacity and its final weight. A shorter TR time may result from lower energy released to the battery casing

due to a reduced final mass. However, as demonstrated with the pristine battery at SOC 50% and the aged battery at SOC 100%, a higher battery capacity (higher SOC) can yield a similar TR time, even with a lower final weight.



(a)



(b)

Figure 5.9. Comparison of thermal runaway parameters under three different conditions: pristine at SOC 100%, pristine at SOC 50%, and aged (after 250 cycles) at SOC 100%. (a) shows the maximum temperature

(Max. Temp.), onset temperature (Onset Temp.), the temperature at which the rate of temperature rise reaches $10\text{ }^{\circ}\text{C}/\text{min}$ (Temp. TR10), the temperature at which the rate of temperature rise reaches $100\text{ }^{\circ}\text{C}/\text{min}$ (Temp. TR100), and accumulated heat release (AHR). (b) presents the temperature rise rate at the onset temperature (Tr Onset Temp.), the duration of the thermal runaway process (TR time), the duration of the self-heating phase (Self-heating time), and the final weight.

5.3.4 Venting process characterisation

5.3.4.1 Battery surface temperature distribution and particle temperature

Figure 5.10 shows the venting temperature (particles) and the battery surface temperature for 3 distinct cell conditions: Pristine at SOC 100% (a) and (b), Pristine at SOC 50% (c) and (d), Aged at SOC 100% (e) and (f). The right side of the figure represents the battery surface temperature of 3 different zones and the particles temperature. Zone 1 shows the area between 0 (venting cap) and 5 mm, Zone 2 shows the area between 5 and 15 mm, and Zone 3 shows the area between 15 and 30 mm. Because of the 45 mm (diameter) sapphire glass, only half of the cell is visible; the remaining length is utilised to record the temperature of the particle venting process (15 mm). For all the cases, the line means the average temperature of each zone for 5 different cells at the same battery condition. Furthermore, the standard deviation is included for each line, which represents the average standard deviation of the five cells under the same battery conditions. The standard deviation indicates the temperature variability within the evaluated area of the zone.

The higher surface temperatures were measured for the battery at the aged and pristine conditions at SOC 100%. The temperatures were $\sim 630\text{ }^{\circ}\text{C}$ and $\sim 560\text{ }^{\circ}\text{C}$, respectively, while the battery with SOC 50% achieved the maximum temperature of $\sim 450\text{ }^{\circ}\text{C}$, resulting in a difference of $110\text{ }^{\circ}\text{C}$ between the batteries at pristine condition. The energy released during the thermal runaway increases with a greater SOC. Because of the interaction between

the anode and electrolyte as well as the short circuit that occurs when the separator ruptures, the lithium intercalated in the anode increases the amount of heat released [15]. Nevertheless, the aged battery has had a higher surface temperature than the pristine condition at the same SOC. Aged batteries have lower capacity due to the SEI growth mechanism being boosted during cycling. The higher-end mass of the aged batteries can result in a higher thermal energy released through the battery casing [16]. Otherwise, lower-end mass means more energy is released as enthalpy to the ambient as more mass is ejected. According to Figure 5.10, the temperature resulting from the venting process increases and decreases before the surface temperature increases. This means that the venting process occurs before the heat generated inside the battery can be transferred to the external surface, where the temperature is measured. For this reason, the end mass of the battery plays an important role in the surface temperature. The standard deviation obtained for each battery condition was about 30 °C.

The particle temperature from the venting process showed similar values, comparing aged and pristine battery conditions at SOC 100%, with a maximum temperature of around 750 °C. Lower SOC means lower energy to be released, and consequently, the maximum particle temperature was around 600 °C. The difference between the cases was 150 °C, and comparable results can be seen in [17]. Furthermore, as already discussed, the venting process occurs before the battery temperature increases. For example, for a pristine battery at SOC 100%, the temperature recorded on the battery surface is only about 250 °C, whereas the venting temperature is around 750 °C. Unstoppable reactions inside the battery cause materials to be expelled to the outside through the opening venting cap. This may roughly indicate that the internal temperature of the battery may be similar to the venting temperature. However, due to heat transfer from the inner parts of the battery to its exterior, the surface temperature rises after the venting process. This may be associated with the amount of mass remaining inside the battery.

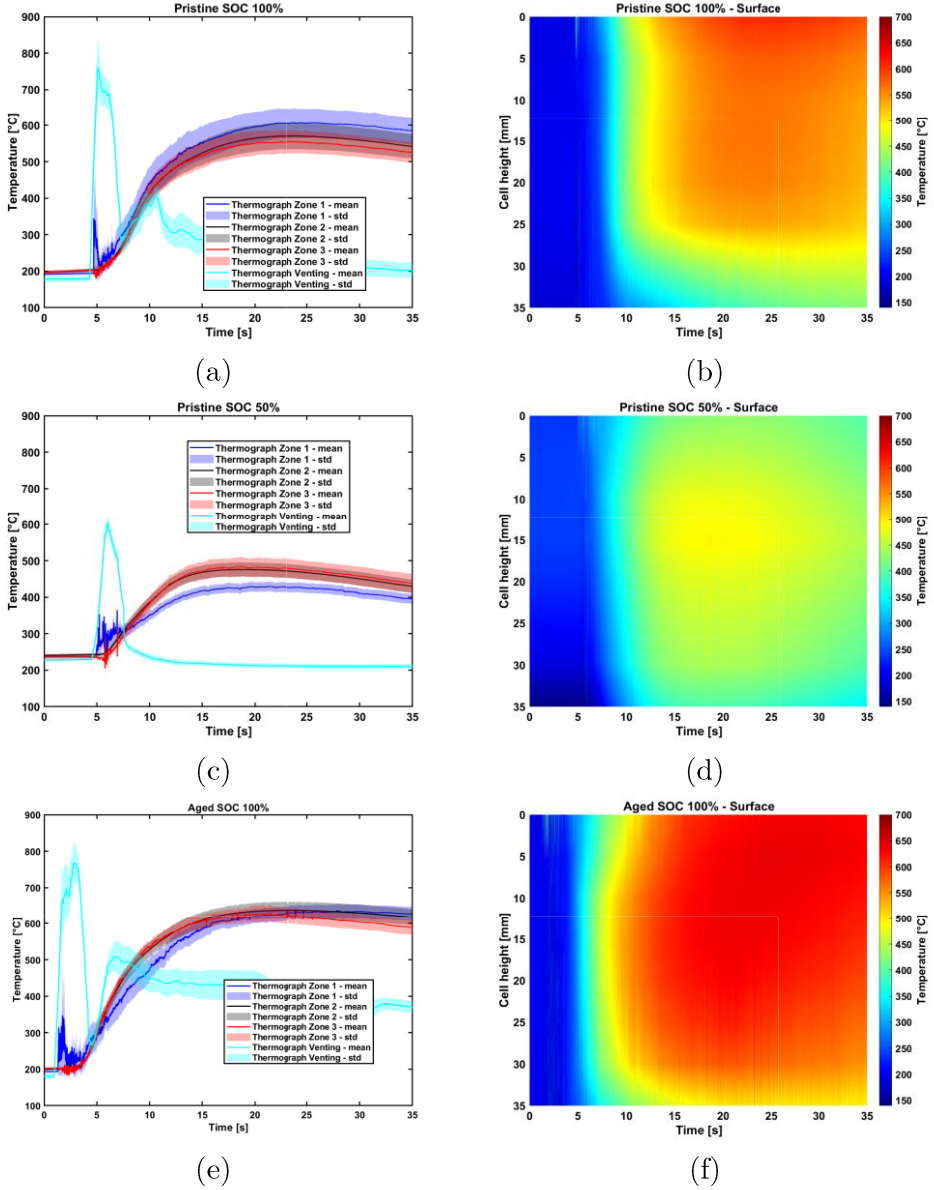


Figure 5.10. Venting and battery surface temperature for 3 different cell conditions: Pristine at SOC 100% (a) and (b), Pristine at SOC 50% (c) and (d), Aged at SOC 100% (e) and (f).

5.3.4.2 Jet Characteristics of the venting process

Figure 5.11 depicts the battery temperature when the first venting process occurs for 3 different battery conditions: Pristine at SOC 100%, pristine at SOC 50% and an aged condition at SOC 100%. The main goal of the first venting process is to release the gases inside of the cell, reducing the internal pressure and preventing cell explosion. This procedure can also be used as a thermal runaway early warning, giving time to apply mitigation strategies. Depending on the heating rate, there is a window of available time between the first venting process and thermal runaway, where further strategies can be done to decrease the risk of this event.

The venting process occurs in different battery temperatures, Figure 5.11, depending on the battery condition as SOC and SOH. Despite the venting cap being calibrated to rupture at the same pressure, additional factors, such as reactant concentrations affecting the reaction rate, can produce different amounts of gas. The main variables that influence the reaction rate are the temperature, concentration of reactants and the pressure. In addition, a longer duration can increase gas generation and internal pressure. A trade-off can be present in the results depicted in Figure 5.11. Lower onset temperatures occur in batteries with higher SOC, resulting in a longer time to produce gas due to the lower temperature rate (more time is required to heat the battery). For this reason, the venting process occurs earlier than the pristine battery at SOC 50%. Additionally, although the exothermic reaction is noticeable at a higher temperature for lower SOC levels, considering that higher temperatures result in a higher reaction rate, the time available between the onset of the exothermic reaction in a battery at SOC 100% and the temperature equal to the onset temperature of the battery at SOC 50% is sufficient to generate enough gas to rupture the venting cap. Pristine and aged batteries at SOC 100% showed similar results because the exothermic process for both batteries was similar.

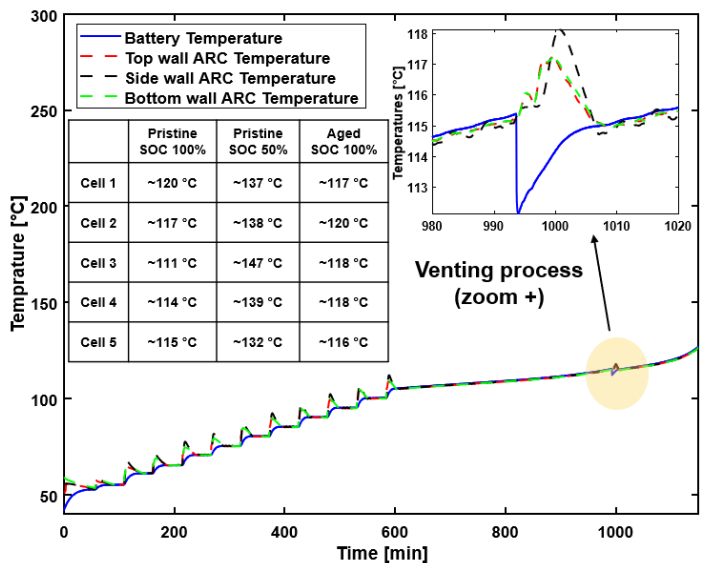


Figure 5.11. The temperature at the first venting process for different battery conditions.

Figure 5.12 shows the different phases of the first venting process for 3 different battery conditions: Pristine at SOC 100%, pristine at SOC 50% and an aged battery at SOC 100%. Comparing the pristine cases, for the SOC 100%, a dark area appears sooner and covers a larger jet area. Comparing the same SOC, but with different SOH, the results show that the black area appears at a similar time. However, the jet format is different from the pristine battery. Some reasons can be attributed to the process, which may differ depending on how the vent cap rupture occurs. Additional research is necessary to validate a conclusion on the mass of gas, liquid, or solid particles. The current finding sheds light on the impact of the battery conditions during the venting process, which must be considered when the thermal runaway alert depends on this parameter.

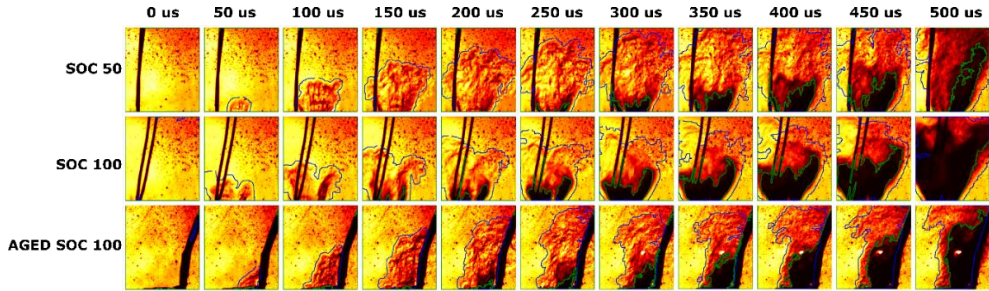


Figure 5.12. Distinct phases of the venting process for three different battery conditions: pristine battery at SOC 100%, pristine battery at SOC 50%, and aged battery at SOC 100%.

The venting penetration velocity is presented in Figure 5.13 and represents the jet displacement over time from Figure 5.12. The pristine at SOC 100% has higher penetration than the aged battery at SOC 100% and the pristine battery at 50%. Figure 5.11 shows that the venting process occurs at a lower temperature for the pristine battery at SOC 100% and the aged than the pristine battery at SOC 50%. Considering the gas composition and the burst pressure are similar, the lower temperature would result in a higher gas density. For this reason, the gases of the pristine battery at SOC 100% have more momentum, resulting in a higher penetration as a function of time.

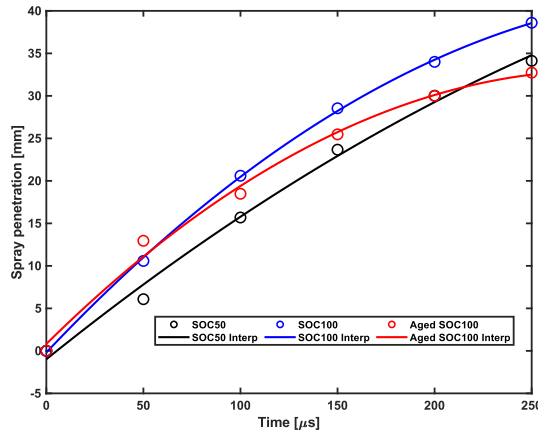


Figure 5.13. Jet penetration calculated from Schlieren images for 3 different battery conditions: Pristine at SOC 100%, pristine at SOC 50% and an aged condition at SOC 100%.

5.3.4.2 Particle velocity during the venting process

Figure 5.14 presents the particle velocity of a pristine battery at SOC 100% as a function of time. The process starts with a particle velocity of up to 50 m/s and gradually drops to zero. The venting cap bursts when the maximum safety pressure is reached, preventing cell explosion or lateral rupture, and releasing the battery internal gases into the environment. For this reason, this is the expected behaviour of the velocity profile. Because of the greater pressure differential, particles inside the gas initially had the maximum velocity and decreased as the mass was expelled.

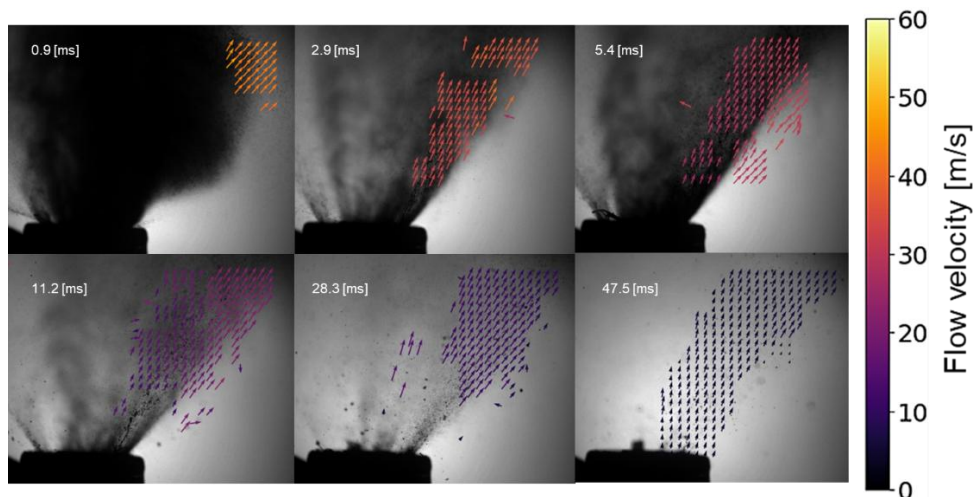


Figure 5.14. Particle velocity as a function of time for the first venting process of a pristine battery at SOC 100%.

Figure 5.15 shows the particle velocity for the pristine battery at SOC 100% during the thermal runaway. The particle velocity of the thermal runaway is lower than the velocity recorded during the first venting process. The primary cause is that the venting operation left the venting cap open. As a result, the particles released due to the unavoidable exothermic reaction move more slowly than those released during the venting process. This result is important for studies of flammability limits and arc ignition. The particle velocity achieved 30 m/s at 4.1 ms and dropped to 10 m/s at 6.7 ms. In relation to the first venting process, the velocity reached is 40% lower.

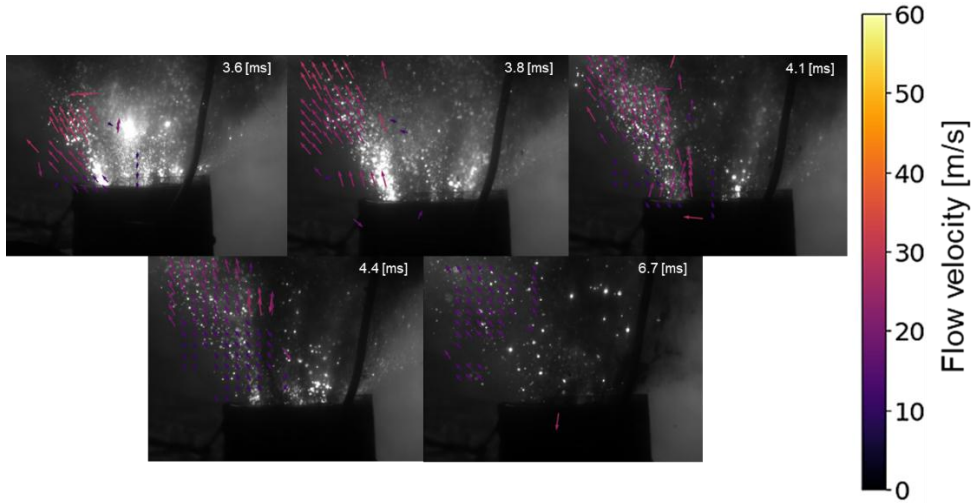


Figure 5.15. Particle velocity of the thermal runaway process as a function of time for a pristine battery at SOC 100%.

5.4 Mechanical abuse

This section will discuss the impact of the mechanical trigger for thermal runaway using different configurations of nail penetration, such as the nail position on the cell surface, the initial ambient temperature, and the battery state of charge (SOC). The same battery described in the previous section was used in this part. A thermographic camera was coupled with the ARC, enabling the measurement of the battery surface temperature distribution and the visualisation of sparks that may occur near the nail region due to lateral surface rupture of the battery. A correction procedure was proposed to address constraints in the experimental setup, such as using a sapphire window for optical access to maintain quasi-adiabatic conditions. The cell-to-cell variability was studied with statical analysis, and the root causes of high dispersion were discussed using nail penetration tests.

5.4.1 Test procedure

An accelerating rate calorimeter (ARC), model EV+, manufactured by THT technology, was used to perform experimental thermal runaway tests using nail penetration as a trigger. The equipment can track the battery temperature when the exothermic reaction is detected up to a temperature rate of $15\text{ }^{\circ}\text{C}/\text{min}$. The heat released can be estimated by measuring the temperature, indicating the maximum heat a battery in thermal runaway can generate. The ambient temperature is monitored with N-type thermocouples with a precision of 0.001°C and an accuracy of 0.7%. This ARC has two optical accesses where different optical techniques can be employed. The test was carried out under constant pressure, as the pressure generated during the TR is released to the surroundings through the ARC lid with a magnetic closing system [18].

The main components of the nail penetration system are a nail, a rod, and a motor. The motor is located outside the calorimeter and is connected to a rod that holds the nail at its tip. The rod passes through the walls of the ARC into its interior, where the battery is located. Figure 5.16 illustrates how the rod has a nail fixed to its tip and how the battery is held inside the calorimeter. Different penetration positions on the cell surface can be achieved by adjusting the plate, which changes the longitudinal axis relative to the nail. This is accomplished using an up-and-down tray held in place with a screw.

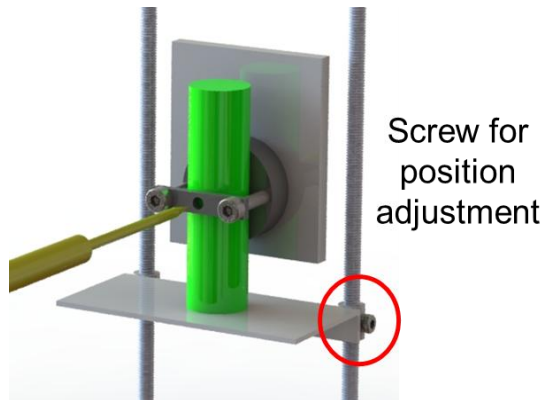


Figure 5.16. Nail penetration scheme inside the ARC.

An infrared technique was coupled with the ARC to measure the battery surface temperature distribution and visualise the mechanical abuse process, which can result in lateral rupture. The ARC is equipped with two optical access points, where the original glass was replaced with sapphire to allow the transmissivity of infrared rays.

The camera focuses on the centre of the ARC, where the battery is located. The sapphire glass has a diameter of 50 mm and a thickness of 15 mm. The camera model is a FAST-IR M1K, manufactured by Telops, with a maximum frame rate of 2000 frames per second, using a resolution of 320x256 pixels. The camera is coupled with a 50 mm f/2 IR lens, which measures wavelength from 1.5 μm to 5.5 μm .

The effects of different SOC, nail positions, and ambient temperatures were studied to evaluate the mechanical trigger for thermal runaway (TR). The nail position was varied across three locations: bottom, middle, and top. The battery SOC's were set at 100% and 50%, while the initial ambient temperatures were 20°C and 50°C. To compare the various effects, the reference case was the nail positioned in the middle, with a SOC of 100% and an initial ambient temperature of 20°C. For instance, the test matrix to study the SOC effect considers the nail position in the middle and the initial temperature at 20°C. The other cases follow the same logic, according to Figure 5.17.

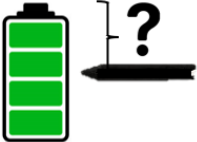
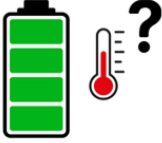
Analysis Parameter	Fixed condition	Variable condition
Nail Position 	20 °C Initial temperature SOC 100%	• Top 15 mm from venting cap • Middle 32.5 mm from venting cap • Bottom 50 mm from venting cap
SOC 	20 °C Initial temperature Middle nail position	• SOC 100% • SOC 50%
Initial temperature 	SOC 100% Middle nail position	• 20 °C Initial temperature • 50 °C Initial temperature

Figure 5.17. Test matrix summary for nail penetration as a trigger for TR.

Each battery was prepared before the test using the same protocol. First, the battery was charged up to the SOC 100%, following the CCCV protocol. For SOC at 50%, first, the battery was completely charged and, in sequence, discharged up to the target capacity. The plastic wrapping was removed, and the initial weight was measured. To improve the emissivity of the battery surface and the accuracy of the temperature measured by the infrared camera, the battery was painted matte black. The battery surface temperature was measured using 2 N-type thermocouples tied with a metallic wrap, thus preventing the thermocouple from loosening during the test. A narrow tie wrap was chosen because it securely attaches the thermocouple while occupying minimal space, ensuring it does not significantly reduce the useful area recorded by the thermographic camera. The nail penetration test is then conducted using the boundary conditions specified in the test matrix

once the battery has been positioned as desired. The nail moves at a steady 50 mm/s under all tested circumstances, using the maximum displacement. This guarantees that the nail will penetrate through the battery. The camera is triggered when the nail starts to move. The battery has its weight measured after the end of the test to know the mass loss during the test. A total of 25 tests were performed, with 5 tests conducted for each condition to enable statistical analysis.

5.4.2 Infrared image post-processing

The sapphire window used in the ARC allows the transmissivity of infrared rays while ensuring robustness with its 15 mm thickness, which makes it capable of withstanding the high temperatures generated during thermal runaway tests. However, this type of glass does not provide 100% infrared transmissivity, and its transmissivity decreases with increasing thickness. Therefore, it is essential to characterise this window. A model was proposed to correct the temperature measurements based on additional constraints of the thermal runaway test. Further details can be found in [19].

Using the Stefan-Boltzman law, the thermal radiation (I) is calculated according to Equation (6) [20].

$$I = \sigma \cdot \varepsilon \cdot A \cdot T^4 \quad (6)$$

σ is the Stefan-Boltzman constant, ε is the surface emissivity, A is the battery surface area, and T is the battery surface temperature. The camera receives only a portion of the radiation emitted by the battery surface, which can be calculated by considering a solid angle that represents the surface of the lens concerning the radiation source [20]. The Equation (7) shows the radiation intensity received by the camera (I_D).

$$I_D = I \cdot \frac{A_{Op}}{4 \cdot \pi \cdot r^2} \quad (7)$$

A_{Op} is the area of the camera lens, and r is the distance between the camera and the battery. Figure 5.18 depicts a scheme of the optical model described here.

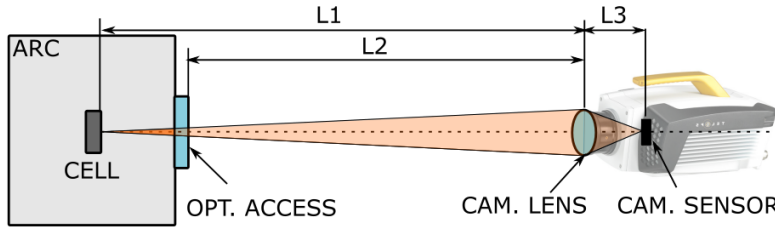


Figure 5.18. Scheme of the optical model.

The camera generates a thermal image with a resolution of 3.22 pixels per millimetre. The size of each pixel in the camera sensor is $25\text{ }\mu\text{m}$, meaning that the thermal image generated by the optical system over the camera sensor has a magnification ratio (M) of 0.081, computed as the ratio of the image cell to the size of the battery. Accordingly, each pixel corresponds to a 0.0963 mm^2 cell area (A_{cell}). Equation (6) uses this number to determine the radiation that the cell surface emits.

The camera lens can be assumed to behave as a thin lens. For this reason, the magnification can also be written as the ratio between the distance from the cell image to the camera lens (L_3), and the distance from the camera lens to the cell (L_1). Thus, the equivalent focal length (f) is obtained, according to Equation (8).

$$\frac{1}{f} = \frac{1}{L_3} - \frac{1}{L_1} \quad (8)$$

The same procedure was used to calculate the area of the optical access (sapphire window) represented by each pixel. The object is close to the camera lens, which causes the focus to be out of position relative to the camera sensor. Figure 5.19 show how is the image resulted of the optical access in relation to the camera sensor because of the object being out of the

camera focus. Therefore, the area of the optical access generated by the optical system over the camera sensor can be calculated using the similarities between triangles and the magnification ratio. This area will calculate the radiation intensity that reaches the camera sensor from optical access.

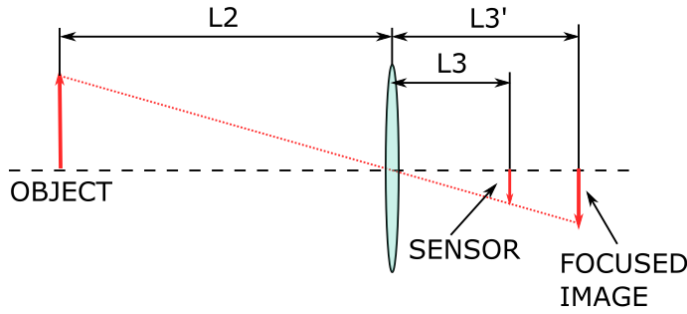


Figure 5.19. Focused image from the optical access with respect to the camera sensor.

Using Equation (6) and Equation (7), the radiation emitted by the cell can be detected by the sensor and the temperature estimated as in Equation (9).

$$T_{cell,th} = \left(\frac{I_D}{\sigma \cdot \varepsilon \cdot A \cdot \frac{Aop}{4 \cdot \pi \cdot r^2}} \right)^{\frac{1}{4}} = \left(\frac{I_D}{\sigma \cdot \varepsilon \cdot K} \right)^{\frac{1}{4}} \quad (9)$$

Being $T_{cell,th}$ battery surface temperature is measured by the thermographic camera. Constant K represents uncertainties of geometrical aspects that are important for camera calibration. For instance, the radiation source area and its distance. The camera interprets the radiation source as a black body with $\varepsilon = 1$ if no emissivity is specified.

The battery surface temperature can be calculated using a similar equation, considering Equation (6) and Equation (7). Equation (10)

exemplifies how to calculate the battery surface temperature based on the radiation intensity emitted by the battery when heated up.

$$T_{cell,r}^4 = \frac{I}{\sigma \cdot \varepsilon_r \cdot A_{cell}} \quad (10)$$

The K value can be calculated by replacing Equation (10) and Equation (9) into Equation (7), which connects the radiation that the camera receives to the intensity that the battery surface emits. Based on this, Equation (11) shows how the K value is calculated.

$$K = \frac{\varepsilon_r \cdot A_{cell} \cdot T_{cell,r}^4 \cdot \left(\frac{A_{op}}{4 \cdot \pi \cdot L_1^2} \right)}{T_{cell,th}^4} \quad (11)$$

Using the thermographic camera to define the values of $T_{cell,th}$ and the thermocouple attached to the battery is used as the value for $T_{cell,r}$. In this way, the value of K can be estimated, allowing the overcome uncertainties correlated with the optical system calculations.

In the normal operation of the ARC, the optical access also heats up, emitting radiation that the camera will receive. The first source of radiation emission from the optical system is attributed to the radiation emitted by the battery. According to Kirchhoff's law, with the transmissivity (τ_{OA}) of the material is 100%, the emissivity will be 0% [20]. In this case, the radiation emitted by the cell will not be absorbed, resulting in the camera sensor only receiving radiation from the cell. However, if the transmissivity of the sapphire window is less than 100%, part of the radiation will be absorbed by the glass, emitting radiation that will reach the camera detector. The second source that will be discussed later is linked to the heating suffered by the optical access due to the HWS process. Therefore, Equation (12) can be written, correlating the total radiation with the radiation emitted by the cell and the optical access.

$$I_D = I_{Dcell} + I_{Doa} \quad (12)$$

Being I_{Doa} is the radiation intensity from the optical access that reaches the detector, and I_{Dcell} is the radiation intensity from the cell that reaches the detector. The radiation intensity received by the camera detector relative to the cell can be calculated according to Equation (13), which takes in account the transmissivity of the optical access.

$$I_{Dcell} = \sigma \cdot \varepsilon_r \cdot A_{cell} \cdot T_{cell,r}^4 \cdot \frac{A_{op}}{4 \cdot \pi \cdot L_1} \cdot \tau_{oa} \quad (13)$$

being τ_{oa} calculated as $(1 - \varepsilon_{oa})$, considering no reflection on the optical access. Furthermore, I_{Doa} is calculated in a similar way as described in Equation (14).

$$I_{Doa} = \sigma \cdot \varepsilon_{oa} \cdot A_{oa} \cdot T_{oa}^4 \cdot \frac{A_{op}}{4 \cdot \pi \cdot L_2} \quad (14)$$

Combining Equation (9), Equation (12), Equation (13) and Equation (14), the value for ε_{oa} is calculated according to Equation (15).

$$\varepsilon_{oa} = \frac{K \cdot T_{cell,th}^4 - A_{cell} \cdot \varepsilon_r \cdot T_{cell,r}^4 \cdot \frac{A_{op}}{4 \cdot \pi \cdot L_1^2}}{\frac{A_{op}}{4 \cdot \pi} \cdot \left(\frac{A_{oa} \cdot T_{oa}^4}{L_2^2} - \frac{\varepsilon_r \cdot A_{cell} \cdot T_{cell,r}^4}{L_1^2} \right)} \quad (15)$$

Equation (15) can be manipulated to calculate the real temperature of the cell surface, knowing ε_{oa} . Equation (16) shows the final equation for the battery surface temperature.

$$T_{cell,r} = \left[\frac{K \cdot T_{cell,th}^4 - \varepsilon_{oa} \cdot A_{oa} \cdot T_{oa}^4 \cdot \frac{A_{op}}{4 \cdot \pi \cdot L_2^2}}{\varepsilon_r \cdot A_{cell} \cdot \frac{A_{op}}{4 \cdot \pi \cdot L_1^2} \cdot (1 - \varepsilon_{oa})} \right]^{\frac{1}{4}} \quad (16)$$

The terms $T_{cell,r}$ in Equation (11) and Equation (15) mean the temperature measured with the thermocouple, while Equation (13) means the real battery surface temperature. It is possible to note that the emissivity and the temperature of the optical access are important to calculate the battery surface temperature. The current work used an approach to calculate the optical access temperature through heat transfer using electrical resistance. Figure 5.20 shows a scheme of heat transfer calculation using electrical resistance applied to the ARC system in optical access. The diagram represents a unidimensional heat transfer with a convective mechanism in the ARC outside and inside and a conductive mechanism through the glass. Radiation is not considered in the current work. In Figure 5.20, T_{ARC} and T_{EXT} mean the ARC air temperature inside and outside, respectively. $T_{oa,int}$ is the internal surface temperature of the apparatus and $T_{oa,ext}$ is the external surface temperature of the apparatus.

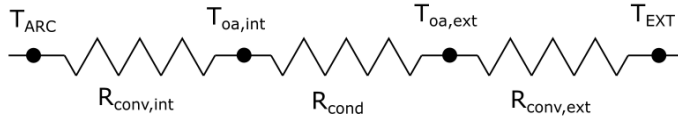


Figure 5.20. Heat transfer calculation through electrical resistance.

The equivalent thermal resistance is calculated as the sum of the resistance shown in Figure 5.20. Equation (17) and Equation (18) demonstrate how convection and conduction resistance are calculated.

$$R_{conv} = \frac{1}{h \cdot A} \quad (17)$$

$$R_{cond} = \frac{E}{k \cdot A} \quad (18)$$

h means the heat convection coefficient, which was assumed to be between 5.1 to 8.8 W/m²K for the natural convection, as is the case of the ARC system [21]. Churchill & Chu's correlation was used to estimate this value [22]. The area of the optical access (A) is equal to 19.63 cm² with a thickness of 15 mm. In addition, the thermal conductivity of the glass is equal to 27 W/m · K [23].

$T_{oc,int}$ and $T_{oc,ext}$ are first approximated in an iterative procedure when T_{ARC} and T_{EXT} are known. The heat transfer through optical access is computed using Equation 19 applied between T_{ARC} and T_{EXT} . To compute $T_{oc,int}$ and $T_{oc,ext}$, Equation 19 is then used, taking into account each convection term independently.

$$Q = \frac{T_1 - T_0}{\sum_0^1 R_i} = \frac{T_{ARC} - T_{EXT}}{R_{conv,int} + R_{cond} + R_{conv,ext}} \quad (19)$$

The K characterisation was performed by removing the sapphire glass to prevent radiation loss due to transmissivity. A dummy was used during this procedure and painted matte black. A thermocouple was attached to the dummy to measure the temperature. The K value was then calculated at 100, 150, 200, 250, and 300 °C temperatures. The emissivity, ϵ_r , was assumed to be 0.95.

The sapphire window transmissivity was characterised subsequently using the same protocol described but with the window assembled in the optical path. The window was positioned so no heat from the ARC reached it, keeping it at ambient temperature. This approach was used because the nail penetration method starts close to ambient temperature, leaving no time for the window to heat up during the thermal runaway test. Therefore, the calibration aimed to mimic this situation by placing the window in front of the camera (rather than the ARC), as shown in Figure 5.21.

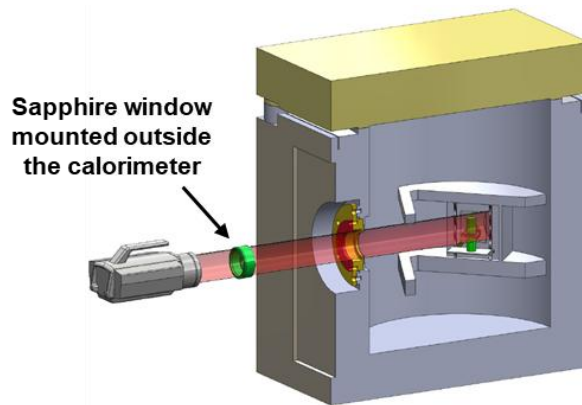


Figure 5.21. Position of the sapphire window for transmissivity characterisation.

Furthermore, during the TR test, many particles and fouling are ejected by the battery, further decreasing the window transmissivity due to the layer of dust on the surface. The battery was heated to 300 °C, calibrating the proposed model at five different temperatures starting at 100 °C. The emissivity of the optical access is depicted in Figure 5.22 (a). In addition, Figure 5.22 (b) shows the validation of the proposed correction, where the difference between the original temperature measurement by the thermographic camera and the corrected temperature can be seen.

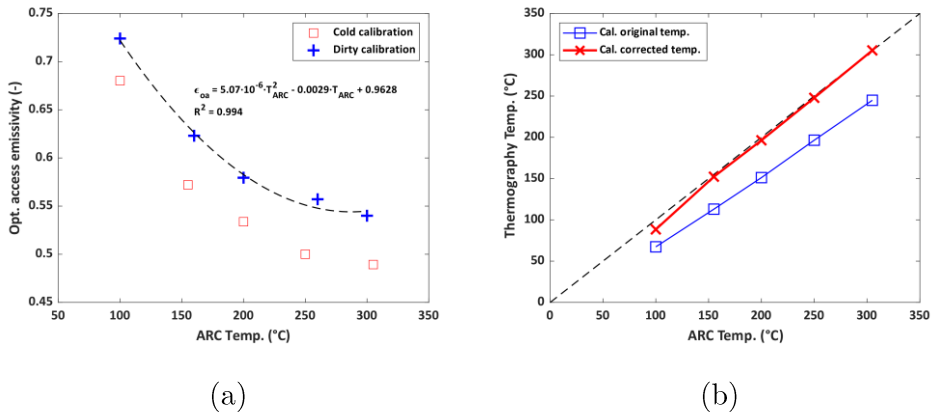


Figure 5.22. (a) Optical apparatus emissivity calculated using dirty and clean conditions. (b) Validation of the proposed correction procedure.

5.4.3 Statistical analysis

standard deviation to understand the temperature variability between cells. Test anomalies can be identified using this methodology, as issues such as a detached thermocouple or local combustion, which can affect the measurement, are easily detected as curves deviating from the trend. The methodology first comprises a curve fitting called Gompertz function, Equation (20), which describes the curve format of a nail penetration test.

$$f(t) = ae^{-be^{-ct}} \quad (20)$$

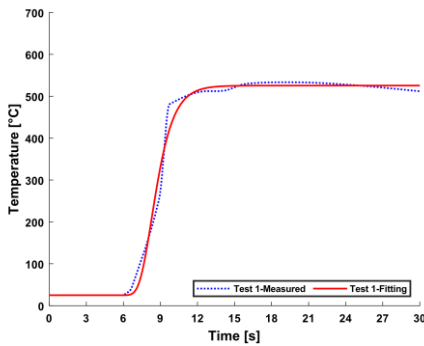
where the last-square approach was used to modify the coefficients a , b , and c as the original temperature curve.

The curve representing the average temperature for a battery test condition was obtained by calculating the mean value of each coefficient from the five tests conducted. For instance, the a value in Equation (20) was determined by averaging the a values from the 5 tests performed under the same test conditions. The standard deviation was calculated by first

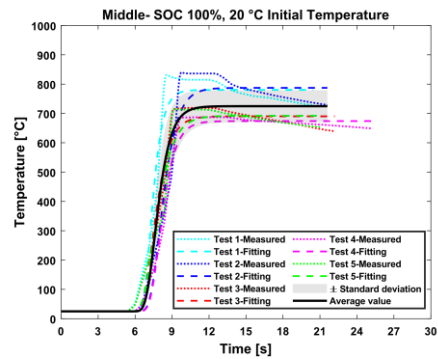
calculating the standard deviation in relation to the 5 experimental tests for each coefficient. The lower and upper limit was defined by adding or decreasing the standard deviation on each coefficient from the average value. Curves that are beyond the upper and lower limits were removed from the analysis.

5.4.4 Battery TR parameters measured with a thermocouple

Curve fitting is used to quantitatively assess the variability and find potential out-of-trend curves in the nail penetration tests, as seen in Figure 5.23. The fitting applied to a single temperature curve is displayed in Figure 5.23 (a). A coefficient of determination (R^2) of 0.98 indicates that the adjustment agrees with the experimental data. Every fitting produced an R^2 value between 0.98 and 0.99. The experimental and fitting curves for the 5 tests that represent an experimental test condition are displayed in Figure 5.23 (b). Tests 1 and 2 temperatures are much higher than the maximum limit, indicating that these curves deviate from the expected trend. Consequently, the curves were eliminated and not considered for additional analysis. The same methodology was applied to the other test conditions.



(a)



(b)

Figure 5.23. Temperature measurement of a nail penetration test (a) and the curve fitting procedure for statistical analysis applied (b).

The thermographic images can explain the higher temperature reached in Test 1 and Test 2 from Figure 5.23, according to Figure 5.24. The TR trigger by nail penetration starts with the venting process. During this phase, particles and combustion gases are injected into the ambient. In sequence, sparks begin to emerge. It is possible to observe that in 3 of the 5 tests conducted under this condition, lateral ruptures occurred near the thermocouple location. This can result in higher temperature measurements because the interior of the battery is at a higher temperature, and the heat and sparks escaping through the rupture can cause measurement errors.

On the other hand, Figure 5.24 shows, at the bottom part, the thermal runaway event sequence for test number 3, conducted under the following conditions: SOC 100%, nail penetration at the middle of the battery and initial ambient temperature at 20 °C. No combustion occurred near the thermocouple location. Images 1 and 2 show the first event, the high-temperature combustion gas and particle venting process, while the battery surface remains at a lower temperature. Sparks also emerge after 0.2 seconds, and a little hole is made in the battery bottom, indicating a high internal temperature that is still invisible on the battery surface (image 3). On the surface, the battery temperature tends to become homogeneous, with measurements similar to the temperature achieved at the hole. Nevertheless, the hole temperature is still higher. Furthermore, the rise in surface temperature is delayed in relation to the venting process.

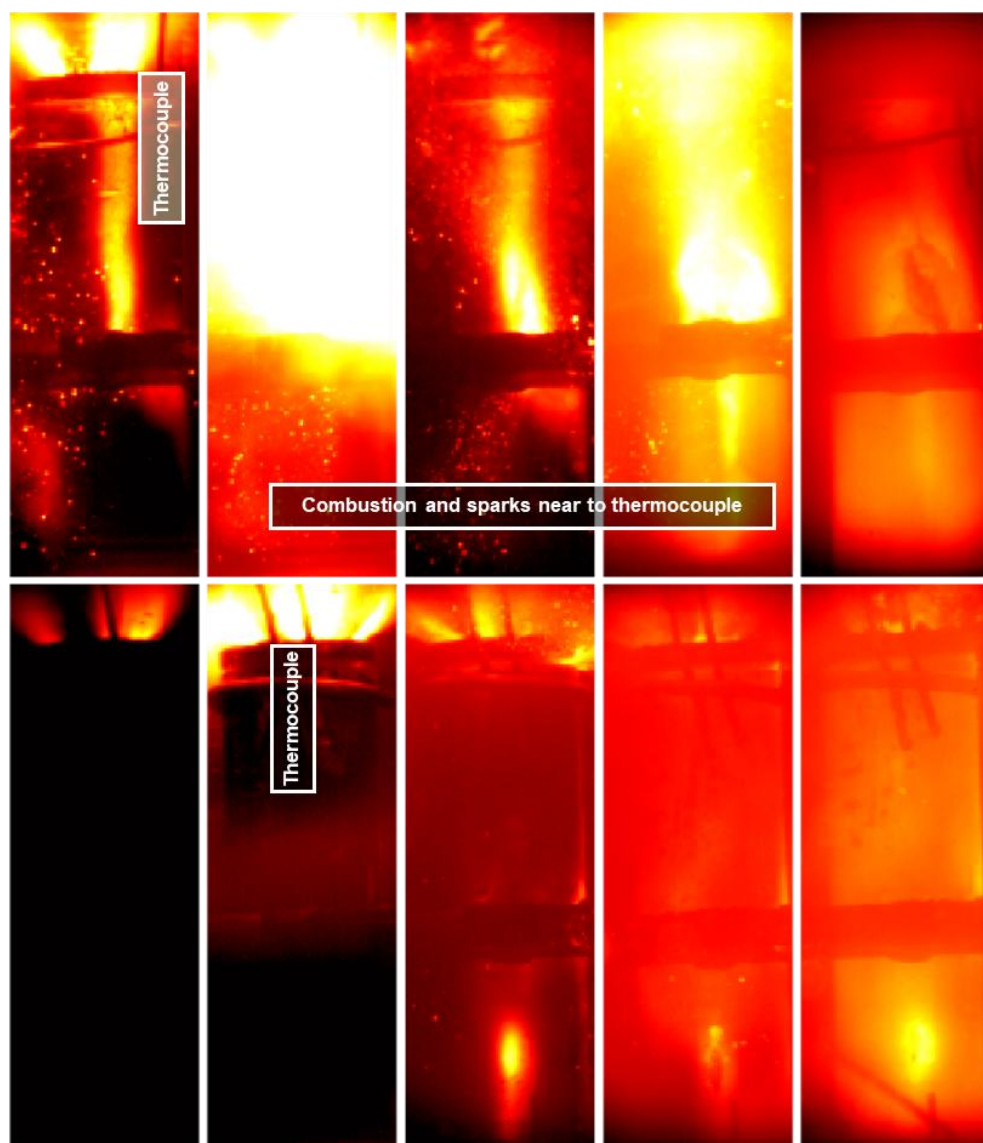


Figure 5.24. Nail penetration thermal runaway event sequence: At the top, test number 2 with the combustion process near the thermocouple location. At the bottom is test number 3, with no combustion near the thermocouple location. Test conditions are as follows: SOC 100%, nail penetration at the middle, and initial temperature at 20 °C.

Figure 5.25 demonstrates the effect of different test conditions on the thermal runaway using nail penetration as a trigger as follows: (a) nail penetration position, (b) state of charge and (c) different initial ambient temperatures. The results represented consider only the output of the statistical analysis. The results show that the nail position at the bottom and middle can lead to a higher temperature. The distribution of battery component materials can explain the results obtained. Depending on the arrangement of the electrode connections, the lithium concentration can vary throughout the anode. The study by [24] showed that a higher degree of lithium inhomogeneity (both radial and axial) is expected when the tab connections are located in the middle of the cathode/anode collector. This is justified by the larger gradient of current density within the cell associated with this arrangement. During the charging process, the lithium-ion travels from the cathode to the anode, which undergoes a reduction reaction upon receiving an electron. Lithium is not uniformly distributed across the battery height. Instead, it accumulates in the negative tab region due to a diffusion process. Also, the authors considered that it also affects the electrode material format, electrolyte, and wetting for the non-homogeneity of lithium distribution. Moreover, gravity can be an additional effect, which can cause electrolytes to accumulate at the bottom of the battery, thus enhancing lithium ion transport. Another factor that may affect the battery surface temperature distribution may be related to the internal mass distribution of the battery. This is evident from the observation that the venting process occurs before the surface temperature increases. Further investigations need to be performed to conclude the possible effects concretely.

Figure 5.25 (b) presents the effect of SOC when nail penetration is used as a trigger for thermal runaway. Lower SOC levels generate less heat due to reduced lithium intercalated in the anode. This occurs because the primary mechanism of nail penetration is a short circuit, where the cathode and anode are in direct contact, releasing energy [7]. The initial ambient temperature has shown no apparent effect on the thermal runaway, according to Figure 5.23 (c).

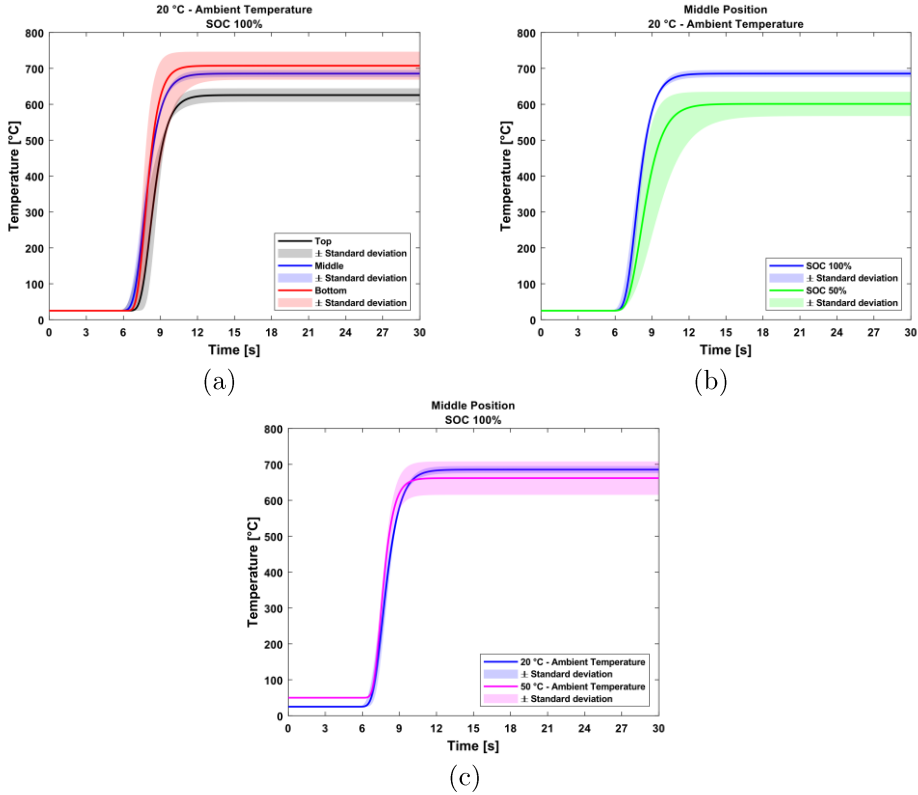


Figure 5.25. Effect of penetration position (a), state of charge (SOC) (b) and initial temperature (c).

Table 5.8 presents the main parameters for the experimental tests in each condition. For the condition with different nail positions and fixed SOC and initial temperature, the middle and bottom positions had higher maximum temperatures than the top nail position. For the temperature rise rate, the cell-to-cell variability was higher, making it difficult to conclude when considering the nail position. However, some noticeable effects can be seen for the temperature rise rate when comparing the initial ambient temperature. The SOC effect was higher for the higher SOC, and the initial ambient temperature presented no noticeable effect. The higher initial temperature can speed up the TR reactions, increasing the temperature rise rate.

The heat release was calculated considering the $m * cp * \Delta T$ [25]. Among the experimental tests under the same conditions, the values were similar, as they mainly depended on the temperature delta (the difference between the maximum temperature and the starting temperature). The main differences were observed in different states of charge, with SOC 100% releasing 20% more energy than SOC 50%. Additionally, energy from internal reactions during thermal runaways is released into the environment through the venting process as combustible gases, which can further increase heat generation [26]. Because of the combustion of the gases (local combustion) and lateral rupture near the thermocouple, the heat released in the out-of-trend tests frequently displayed a higher value. On the other hand, thermocouple detachment was the primary cause of the other out-of-trend experiments, resulting in a lower temperature and heat release.

Table 5.8. Main TR parameters as: Maximum battery surface temperature, temperature rise rate, and heat released for each test condition.

Cell		Temperature (max)		dT/dt (max)		AHR	
		[°C]	Avg. diff. (%)	[°C/s]	Avg. diff. (%)	(KJ)	Avg. diff. (%)
Top SOC 100%	Test 1	533.5	21.4	353.6	25.9	25.3	22.0
	Test 2	630.7	7.1	495.1	3.7	30.1	7.2
	Test 3	655.1	3.4	372.2	22.0	31.4	3.3
	Test 4	646.7	4.7	461.3	3.3	30.9	4.8
	Test 5	926.7	36.6	703.8	47.5	44.6	37.4
Middle SOC 100%	Test 1	834.0	9.9	641.2	25.5	40.1	10.1
	Test 2	840.4	10.7	572.9	12.1	40.5	11.2
	Test 3	719.0	5.3	395.3	22.6	34.4	5.4
	Test 4	687.4	9.5	365.1	28.6	32.8	9.9
	Test 5	714.8	5.8	580.5	13.6	34.2	6.0
Bottom SOC 100%	Test 1	705.6	15.1	534.6	37.8	33.8	15.6
	Test 2	610.2	0.5	431.7	11.3	29.0	0.7
	Test 3	275.4	55.1	174.8	55.0	12.6	56.8
	Test 4	705.0	15.0	392.7	1.2	33.8	15.7
	Test 5	768.6	25.4	405.9	4.6	36.9	26.2
Middle 50 °C	Test 1	570.7	18.8	455.6	28.7	25.6	20.2
	Test 2	798.9	13.5	735.5	15.0	36.7	14.3
	Test 3	648.6	7.7	574.4	10.1	29.5	8.1
	Test 4	715.8	1.7	685.6	7.2	32.7	2.0
	Test 5	782.3	11.2	746.6	16.7	35.9	12.0
Middle SOC 50%	Test 1	656.3	9.9	641.2	25.5	31.2	14.9
	Test 2	596.6	10.7	572.9	12.1	28.3	4.1
	Test 3	593.9	5.3	395.3	22.6	28.3	4.1
	Test 4	588.1	9.5	365.1	28.6	28.0	3.0
	Test 5	428.5	5.8	580.5	13.6	20.1	26.1

Table 5.9 shows other battery thermal runaway parameters, such as delay time, which is defined as the time between the nail penetrating the cell, the battery temperature rise rate reaching 100 °C/min, and the battery mass

loss. The delay time showed no significant differences among the experimental tests, indicating no apparent effect. The battery thermal runaway time depicted that the nail penetration at the top position resulted in a longer TR time, possibly due to the lower quantity of reactants in this position, which led to a lower temperature. For the middle and bottom positions, the TR time duration was similar. Regarding battery mass, the lower mass observed when using the top position may also contribute to this outcome. In addition, lower energy has resulted in a higher duration of the thermal runaway, for example, for the batteries with SOC 50%. A lower reactant concentration may play an important role in the reaction rate. The lower SOC also ejects lower mass to the ambient.

Table 5.9. Main TR parameters such as delay time, TR duration, and battery initial and final weight for each test condition.

Cell		Delay time		TR time		Mass		
		(s)	Avg. diff. (%)	(s)	Avg. diff. (%)	Bef. (g)	After (g)	Avg. diff. (%)
Top SOC 100%	Test 1	6.6	0.2	12.6	59.1	44.8	0.0	24.1
	Test 2	6.7	0.7	9.0	13.6	44.8	0.0	23.3
	Test 3	6.0	9.3	8.4	6.1	44.9	0.2	22.1
	Test 4	7.2	8.9	7.2	9.1	44.8	0.0	21.8
	Test 5	6.6	0.2	2.4	69.7	44.7	0.2	22.3
Middle SOC 100%	Test 1	6.0	3.8	2.4	37.7	44.8	0.0	21.2
	Test 2	6.6	5.8	3.0	22.1	44.9	0.2	20.9
	Test 3	6.0	3.8	4.2	9.0	44.8	0.0	23.4
	Test 4	6.6	5.8	6.7	72.9	44.7	0.2	24.4
	Test 5	6.0	3.8	3.0	22.1	44.8	0.0	22.9
Bottom SOC 100%	Test 1	6.6	0.0	7.9	0.6	44.8	0.0	25.1
	Test 2	6.6	0.0	14.4	84.3	44.7	0.3	24.8
	Test 3	6.6	0.0	9.6	22.9	44.9	0.2	22.3
	Test 4	6.6	0.0	4.2	46.2	44.9	0.2	24.4
	Test 5	6.6	0.0	3.0	61.6	44.8	0.0	26.0
Middle 50 °C	Test 1	6.1	0.2	12.7	144.2	44.7	0.1	22.7
	Test 2	6.1	0.2	2.4	53.7	44.5	0.4	22.3
	Test 3	6.0	0.8	4.3	17.8	44.8	0.3	20.1
	Test 4	6.1	0.2	4.2	19.0	44.7	0.1	20.0
	Test 5	6.1	0.2	2.4	53.7	44.6	0.1	20.8
Middle SOC 50%	Test 1	7.2	8.5	12.7	19.8	44.6	0.2	33.4
	Test 2	6.1	8.7	10.2	35.4	44.6	0.2	33.7
	Test 3	6.1	8.7	17.5	10.6	44.8	0.2	33.2
	Test 4	7.3	9.4	18.1	14.4	44.8	0.2	28.8
	Test 5	6.6	0.5	20.5	30.0	44.7	0.0	31.0

Figure 5.26 shows the heat release rate as a function of time for the nail penetration tests in different conditions as follows: (a) SOC effect, (b) different initial temperatures and (c) different nail position. The heat release rate showed a similar trend among the tests. It is possible to identify two distinct zones, indicating that two distinct reactions occur. The whole process is characterised by a gradual release of heat followed by a rapid release of heat. Similar behaviour is seen in the heat release for SOC 50%, but a slower

and smaller amount is released following the abrupt peak. This can result from a longer heat transfer caused by the larger battery mass.

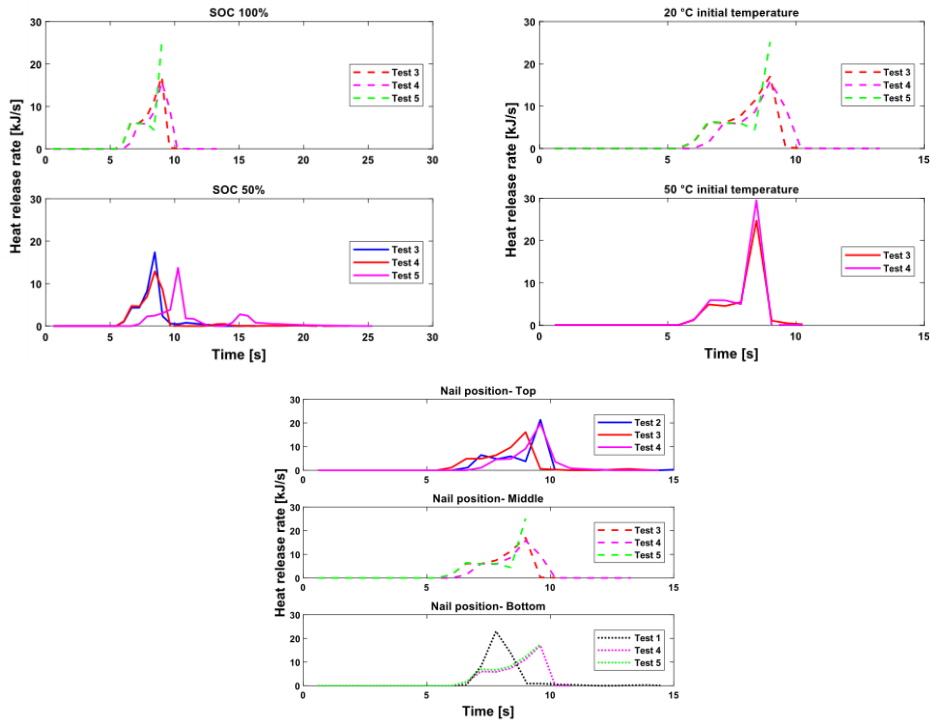


Figure 5.26. Heat release during nail penetration test for different nail position, SOC and initial temperature.

5.4.5 Battery surface temperature distribution

Figure 5.27 depicts the temperature measurement by the thermographic camera and the thermocouple for the test condition with SOC 100%, initial ambient temperature at 20 °C and nail position in the middle of the battery, specifically test number 3. The difference between the infrared image measurements and the thermocouple in the region labelled as number 1 in Figure 5.27 is due to the calibration range selected for the camera. Lower temperatures are outside the camera range, as the calibration was chosen to prioritise higher temperatures associated with thermal runaway. In number

2, the temperature peak captured by the camera is mainly due to a combustion process that occurs in the battery surroundings. Therefore, the thermocouple location and the short duration of this process prevent it from being recorded by the thermocouple. The gases produced during the combustion process also interfere with the thermographic camera measurements. As the gases dissipate from the optical field, the thermocouple and thermographic measurements show similar values. This can be observed in regions 3 and 4 of Figure 5.27.

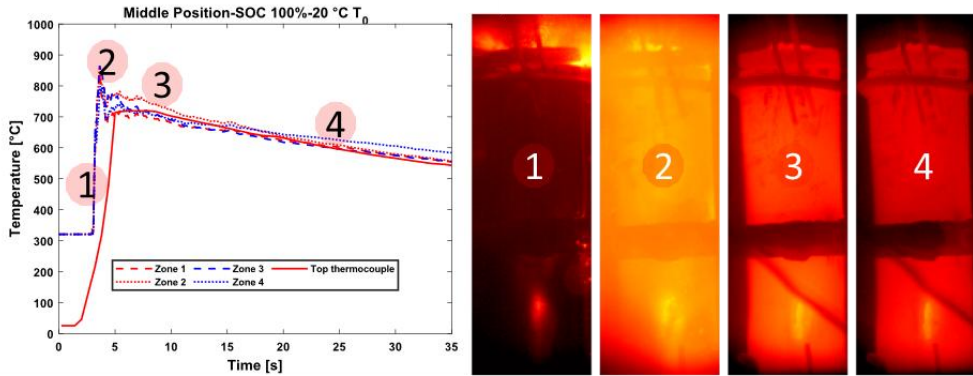


Figure 5.27. Comparison between thermographic and thermocouple temperature measurement.

Figure 5.28 presents the surface temperature distribution as a function of time for the following condition: SOC 100%, initial temperature at 20 °C and nail at the middle position (a), at the top position (b) and at bottom position (c). The temperature distribution on the cell surface is different depending on the nail position. The surface temperature distribution for the nail at the middle position looks quite regular between the top and bottom. The bottom part has a higher temperature for the nail at the top position than the top side. Similarly, the nail at the bottom position has the top side with a higher temperature. According to Figure 5.32, The region where the nail penetrates is prone to rupture, increasing the area for heat transfer. This leads to decreased temperature, as the larger area facilitates heat exchange due to the enhanced convective effect inside the battery. In addition, the strip where the nail penetrates the battery presents a lower temperature

because of the support holding the battery. Thus, the temperature registered is not from the battery surface.

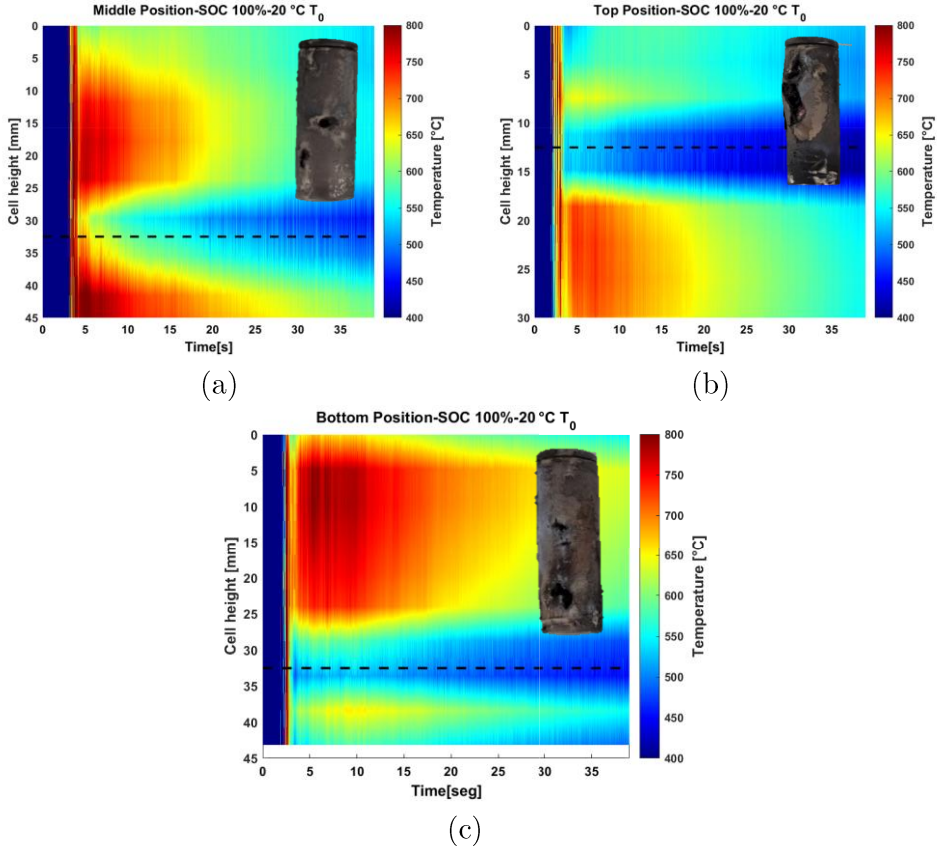


Figure 5.28. Battery surface temperature distribution as a function of time for the following conditions: SOC 100%, initial temperature at 20 °C, nail at middle position (a), at top position (b) and bottom position (c).

Figure 5.29 battery surface temperature variability, considering cell-to-cell, for the same experimental test condition as follows: SOC 100%, initial temperature at 20 °C and nail position at the middle (a), at the top (b) and at the bottom (c). For each test condition, graphs were made considering the variation between tests within the standard deviation determined by

statistical analysis. Therefore, the difference between tests was computed according to Equation (21).

Composite diff

$$= \frac{|Test_1 - Test_2| + |Test_1 - Test_3| + |Test_2 - Test_3|}{3} \quad (21)$$

For all experimental tests, it is important to understand that the first vertical band on the map, the area with the most variability, cannot be regarded as true. The emissivity of the window employed for temperature correction is inappropriate for this initial condition (clean window), which is related to the beginning combustion process. The nail penetration positions in the middle showed the greatest variability on the upper side. The reason for this is attributed to the rupture of the battery casing. According to Figure 5.32, some tests showed a casing rupture in the upper part of the battery, while others did not when the nail penetration occurred in the middle. Consequently, the variability increases due to lower temperatures in the ruptured region, resulting from enhanced heat transfer. For the top nail position, all the tests used to plot presented lateral rupture, decreasing cell-to-cell variability as the heat transfer conditions were similar. Except for the area near the venting cap, the variability remained consistent across the map for the bottom position. Although the temperature variability in this region increased from 40 to 70 °C, it still represents ~10% of the maximum battery temperature.

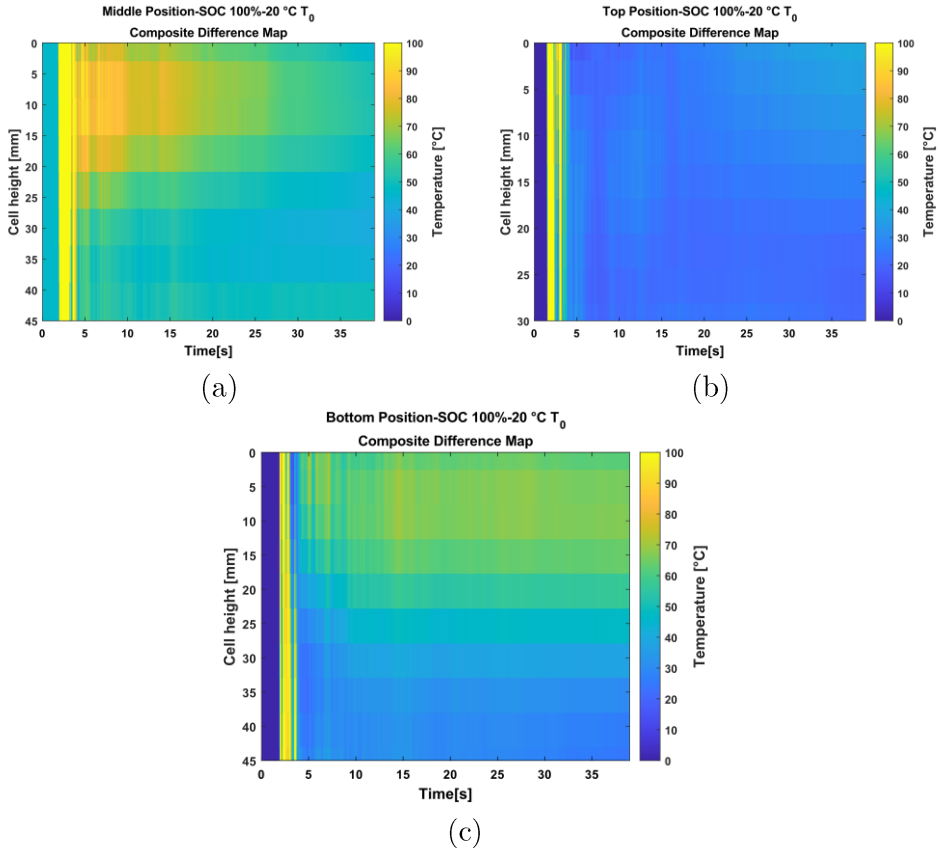


Figure 5.29. Difference between the battery surface temperature of different tests at same experimental conditions: SOC 100%, initial temperature at 20 °C and nail position at the middle (a), at the top (b) and at the bottom (c).

Figure 5.30 (a) shows temperature variability for the case with SOC 50%, initial ambient temperature at 20 °C and nail position in the middle of the battery. In addition, Figure 5.30 (b) depicts the cell-to-cell variability of the experimental tests carried out in this condition. Compared to SOC 100%, the battery surface temperature was lower due to the reduced reaction intensity, resulting from the smaller quantity of available reactants. The temperature gradient between the battery surface and the ambient temperature is lower, decreasing the heat transfer. Moreover, the battery with a SOC of 50% did not exhibit lateral rupture (within the standard deviation

range), which explains the low variability in cell-to-cell temperature distribution.

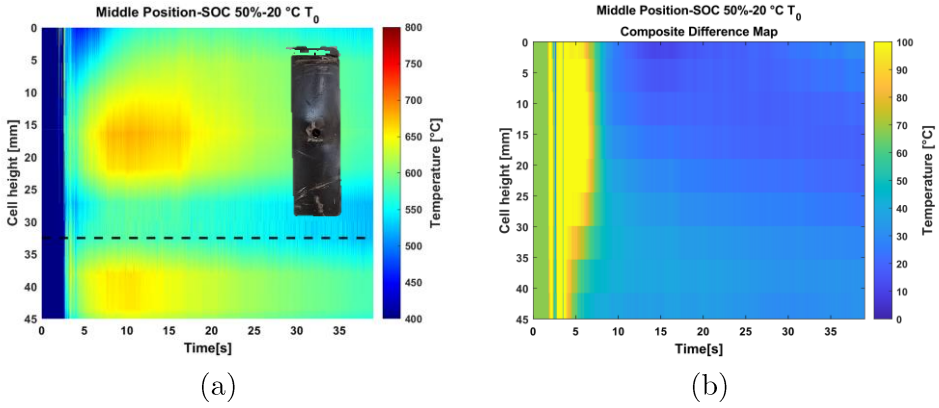


Figure 5.30. Difference between the battery surface temperature of different tests at the same experimental conditions: SOC 50%, initial temperature at 20 °C and nail position at the middle (a). Cell-to-cell surface temperature variability (b).

The effect of a higher initial temperature (50 °C) for nail penetration at the middle and SOC 100% on the battery surface temperature is depicted in Figure 5.31 (a), and in Figure 5.31(b) is presented the variability between the testes cell at this condition. Compared to Figure 5.28 (a) and Figure 5.29 (b), which represent the case for the initial temperature of 20 °C, the battery surface temperature distribution was similar. However, when comparing the cell-to-cell variability in both cases, the higher initial temperature resulted in lower variability. This reduced variability is explained by the fact that, for the case with an initial temperature of 50 °C, only two cells were included in the study, as the others did not meet the criteria for the statistical analysis performed.

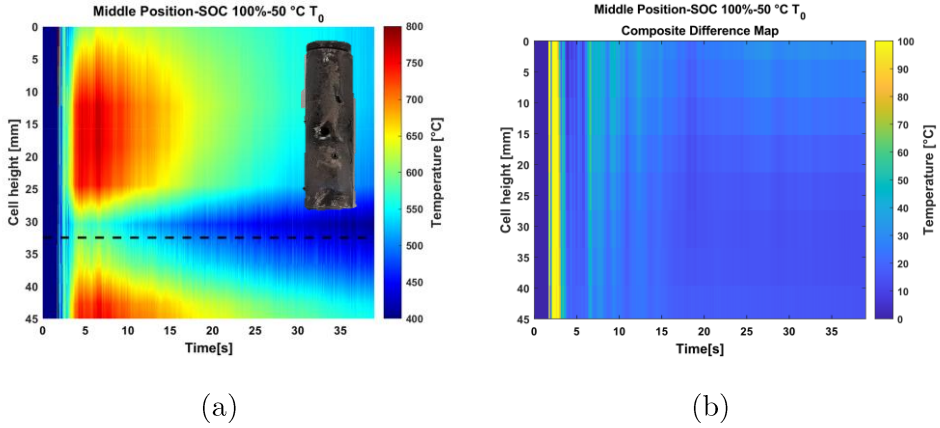


Figure 5.31. Difference between the battery surface temperature of different tests at the same experimental conditions: SOC 100%, initial temperature at 50 °C and nail position at the middle (a). Cell-to-cell surface temperature variability (b).

Figure 5.32 shows images from the experimental tests conducted with nail penetration at different positions: top (near the venting cap), middle, and bottom. Additionally, two different ambient temperatures (20 °C and 50 °C) and two different state of charge (SOC 100% and SOC 50%) were tested. Regarding the nail position, all batteries exhibited casing rupture at the top, while the other positions did not. This can be identified as a key factor in reducing local temperature due to enhanced heat transfer. Furthermore, casing rupture can also occur at lower SOC levels, such as SOC 50%, despite the reduced energy available to be released as heat.

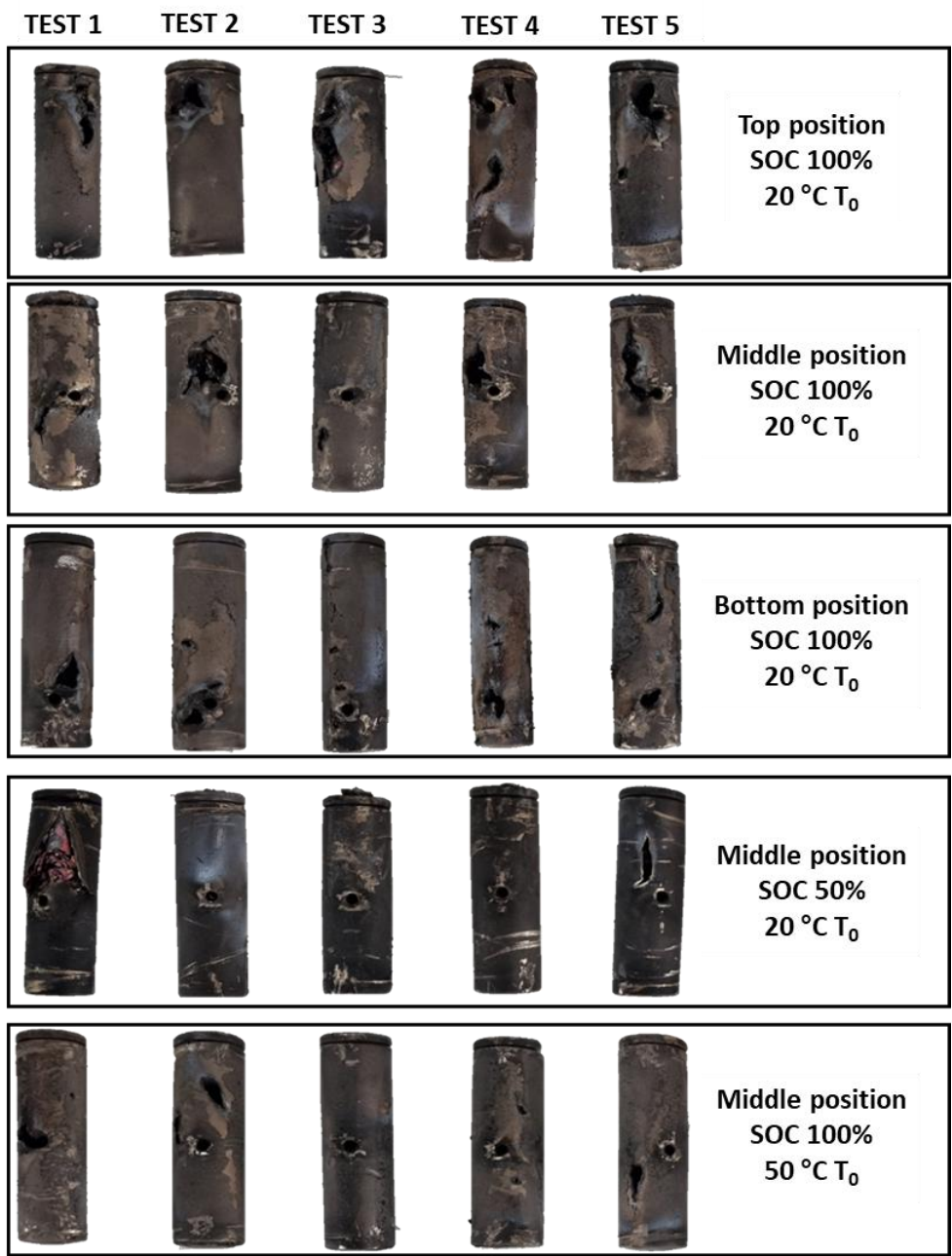


Figure 5.32. Battery images after nail penetration test for different experimental conditions.

5.5 Summary and conclusions

This chapter was divided into 3 main subchapters: 5.2 In-cell thermal runaway characterisation with thermal trigger, 5.3 Out-cell thermal runaway characterisation with external heating and 5.4 Mechanical abuse. The first part is related to the in-cell components and the impact of each component on the thermal runaway. This study used step-wise reactions to describe the thermal runaway process when external heating was employed as a trigger. This reaction mechanism requires knowledge of the battery's internal materials to determine the molar quantities for each reaction and calculate the theoretical heat release. For this reason, electrical and thermal characterisation was performed using a bidirectional source and a climate chamber. The results were used to calibrate and validate a P2D model representative of the battery and, consequently, to use the material quantity results to feed the step-wise reaction mechanism.

Furthermore, ageing was carried out following a specific protocol to promote solid electrolyte interface growth. The aged cells were also characterised thermally and electrically, and the results were used to calibrate and validate an ageing model within the pristine battery model initially proposed. Therefore, the impact of thermal runaway on the ageing process was also studied and analysed using the step-wise reaction mechanism. Thermal runaway tests were conducted using an accelerating rate calorimeter under a heat-wait-seek protocol to compare the theoretical results. From this first study, the main conclusions that can be drawn are:

- The experimental tests showed a higher thermal runaway propensity for the pristine NMC battery, which can release approximately 28 kJ, compared to the aged battery, which releases about 14% less energy.
- The step-wise reactions show that the electrolyte plays a crucial role in the thermal runaway chain reaction, primarily due to its reaction with the lithium intercalated in the anode and its oxidation process with the oxygen released during cathode decomposition.

- Mitigation strategies would be valuable, such as employing cathode materials with a more difficult decomposition process and electrolyte materials that are less combustible.
- Based on the step-wise reaction mechanism, the oxidation reaction between the electrolyte and oxygen accounts for about 52% of the chemical energy released, while the reaction between the anode and electrolyte accounts for about 47%.
- Due to the ageing protocol used, the SEI growth is the main mechanism for capacity fade. This protective layer grows by using the electrolyte and lithium. For this reason, the reaction between the anode and electrolyte is the most impacted, as the reactant in this reaction is consumed during the SEI growth process.

The second study focused on the effects of external cells during thermal runaway. 5 cells for each SOC condition (100% and 50%) and five aged cells at SOC 100% were tested in an ARC under the HWS protocol. The original optical access of the ARC was modified to attach different optical setups to characterise the thermal runaway event using different optical techniques, such as the Schlieren technique, infrared imaging, and natural luminance. The study aimed to understand the impact of different thermal runaway parameters on the energy released, considering the standard deviation and mean values. The first venting process and venting during thermal runaway were characterised to understand the behaviour better and inform future safety mechanism development. Jet formation, angle, penetration, and particle temperature were measured during thermal runaway. Battery surface temperature distribution was measured with the thermographic camera and compared across the tested conditions. Furthermore, the particle venting velocity was measured using combustion imaging velocity based on the cross-correlation method. The following conclusions can be drawn:

- The exothermic detection was earlier for batteries with a higher state of charge. The higher concentration of lithium intercalated in the anode increases the reaction rate, being detectable at a lower

temperature. Safety mechanisms can be activated earlier, resulting in more time to mitigate the thermal runaway.

- Considering the sensitivity of $0.02\text{ }^{\circ}\text{C}/\text{min}$ for the heat-wait-see protocol, the time up to the thermal runaway in a quasi-adiabatic condition is reduced by about $\sim 40\%$ for SOC 50%.
- The energy the safety mechanism would need to manage, considering only the heat released from the battery through its surface, is 42% lower than the SOC of 50%.
- Considering the results for the aged and pristine batteries at SOC 100%, the end mass plays an important role in the heat released. Higher end mass
- Despite the reduced safety response time, the energy to be managed during such incidents is approximately 42% lower (for SOC 50%). However, this parameter has shown dependency on the final mass inside the battery, mainly when comparing aged and pristine cells at SOC 100%. The maximum temperature rises as mass increases. This emphasises how crucial the design of the venting cap is.
- According to infrared imaging results, particle temperatures can reach up to $900\text{ }^{\circ}\text{C}$. A higher state of charge led to higher particle temperatures, with a difference of approximately $150\text{ }^{\circ}\text{C}$ between SOC 100% and 50%.
- Particle velocity for pristine at SOC 100% was 30 m/s , indicating the severity of thermal events in batteries with higher SOC.

The last part of this chapter focused on studying the mechanical trigger for thermal runaway. Optical techniques were also employed, primarily to analyse the combustion process due to the higher cell-to-cell variability reported in the literature for this trigger type. A setup with a thermographic camera was mounted on the ARC to study the battery surface temperature distribution across cells. 5 batteries were used for each test condition, which included different nail positions (top, which is near the venting cap, middle,

and bottom), different SOC levels (100% and 50%), and two initial temperatures (50 °C and 20 °C). The conclusions can be illustrated as:

- Side ruptures occurred in many tests, regardless of the nail penetration position or cell condition. Gases escaped through the rupture and could cause local combustion, which may affect the thermocouple measurement. This work recommends attaching the thermocouple on the side opposite the nail penetration, as ruptures most frequently occur in the region of nail penetration.
- Related to the nail position, the nail position at the top part of the battery showed a lower temperature, which can be attributed to ruptures in the nail region that increased the heat transfer. The heat released by the battery when the nail penetrates in the top position was 30.8 ± 0.6 kJ, while the middle and bottom position was 34.3 ± 1.37 kJ.
- Batteries with SOC at 100% presented an energy released higher than SOC at 50%. The increase was about 20% (33.8 ± 0.88 kJ vs 28.2 ± 0.16 kJ).
- Except for the tests with casing rupture, which significantly increases the variation of the temperature distribution, the temperature distribution over the battery surface was very consistent.
- The average temperature variability across the cell surface for the same experimental test condition was 40 °C. However, greater values are caused mainly by casing rupture.

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Chapter 6

Thermal runaway prediction

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6.1 Introduction

This chapter discusses the development of a thermal runaway model designed to predict key parameters using an approach based on the Arrhenius equation. For calibration and validation, experimental tests were conducted using batteries with different chemistries, sizes, and states of charge (SOC). Additionally, the effect of ageing was considered in the developed model. The ageing protocol was designed to accelerate solid electrolyte interphase (SEI) growth, which is the main mechanism responsible for capacity fade.

Insights from previous studies on the main characteristics of thermal runaway were incorporated into the modelling and simulations. The final weight of the battery was included in the analysis due to its impact on the maximum battery temperature, as discussed in Chapter 5. Furthermore, the SOC is directly linked to the initiation of exothermic reactions and the maximum heat released. Also, the SEI growth mechanism plays a critical role in reducing the lithium inventory in the battery, decreasing its capacity and the maximum heat released, as shown in Chapters 4 and 5.

For these reasons, the model was tested under a virtual ARC (Accelerating Rate Calorimeter) environment, where different experimental conditions were simulated to calibrate and validate the model with inputs that influence thermal runaway outcomes. The model equations and the fitting procedures used to determine the Arrhenius parameters are presented. The model comprises five steps based on the evolution of the temperature rise rate, with defined intervals. The algorithm used for the model simulations is detailed, replicating the heat wait seek (HWS) process conducted in the ARC from the experimental test conditions.

6.2 Cell-to-cell variability from ARC

The present subsection will discuss the experimental test campaign to calibrate and validate the proposed model to predict thermal behaviour. Different battery sizes, chemistry and SOC were tested under ARC using heat wait seek protocol. Main TR parameters are discussed, considering cell-to-cell variability main value and standard deviation.

6.2.1 Testing Framework

Different battery sizes were tested, 18650 and 21700, for two different cathode chemistries: NMC, which is $\text{LiNi}_8\text{Mn}_1\text{Co}_1\text{O}_2$, and NCA, which is LiNiCoAl . The anode of the batteries has graphite as the main component, and the electrolyte is composed of hexafluorophosphate and organic carbonates. The batteries have comparable weight and similar nominal voltage, with the cathode chemistry being the main difference between the battery types. Table 6.1 shows the battery characteristics used for the experimental tests.

Table 6.1. Battery specifications.

Battery model	INR18650/INR21700	NCR18650/INR21700
Cathode Chemistry	LiNiMnCoO ₂ (NMC 811)	LiNiCoAl
Anode Chemistry	Graphite	Graphite/and silicon
Electrolyte Chemistry	Lithium hexafluorophosphate, organic carbonates	Lithium hexafluorophosphate, organic carbonates
Weight [g]	49.0/69	49.5/69
Nominal Voltage [V]	3.67/3.6	3.60
Nominal Capacity [Ah]	3.20/4.5	3.45/4.9
Current Charge Continuous [A]	1.55/2.25	1.475 /2.45
Current Discharge maximum [A]	10.0	10.0
Total Energy [Wh]	11.7/16.2	12.4/17.6
Cut-off voltage [V]	2.5	2.5
Temperature use Range [°C]	-20 to 60	-20 to 60

For each battery test condition, 5 cells were used for statistical analysis. The total of experimental tests performed was 40 batteries, the test matrix depicted in Table 6.2.

Table 6.2. Experimental test matrix used to supply data for the calibration and validation of the model.

Cathode	NCA				NMC			
Size	21700		18650		18650		21700	
SOC	100%	80%	100%	50%	100%	100%	50%	80%
Health	Pristine	Pristine	Pristine	Pristine	Aged	Pristine	Pristine	Pristine
N° cells	5	5	5	5	5	5	5	5

The batteries were charging following manufacturer instructions and CCCV protocol. The equipment used was an Arbin Instruments, model 10V-100A[1]. For states of charge (SOC) other than 100%, the battery was fully

charged using the CCCV protocol and then discharged to the desired SOC. This was done with a constant current and discharged during the time required to remove the capacity target based on the nominal capacity specified by the manufacturer. The cycling performed is presented in Table 6.3, repeated up to 250 cycles, corresponding to 30 days of testing. This process is characteristic of boosting SEI growth mechanism for degradation, according to [2]. Using a climate chamber, the ambient temperature during charging and cycling was maintained at 25 °C and 50 °C, respectively.

Table 6.3. Cycling protocol performed to capacity fading.

Operation	Current/time
Charge	1 C-rate up to max. Voltage
Rest	30min
Discharge	2 C-rate up to min. Voltage
Rest	30min

The batteries were electrically characterised, primarily to measure the capacity of both the pristine and aged batteries. The capacity of the aged battery is important because it serves as an input for the model, as heat release is linked with this parameter. Additionally, the open-circuit voltage (OCV) is crucial to measure, as it can be directly correlated with the battery capacity, according to the state of charge (SOC) for the batteries presented in this study. Therefore, the battery was charged using the CCCV protocol up to 100% SOC and discharged at 0.25, 0.5, 1, and 2 C-rate. The OCV measurement was performed using the Galvanostatic Intermittent Titration Technique (GITT), measuring the relaxation voltage for every 5% SOC. The relaxation time was defined as when the voltage variation was less than 0.1%. One advantage of this technique is that it avoids kinetic contributions [3].

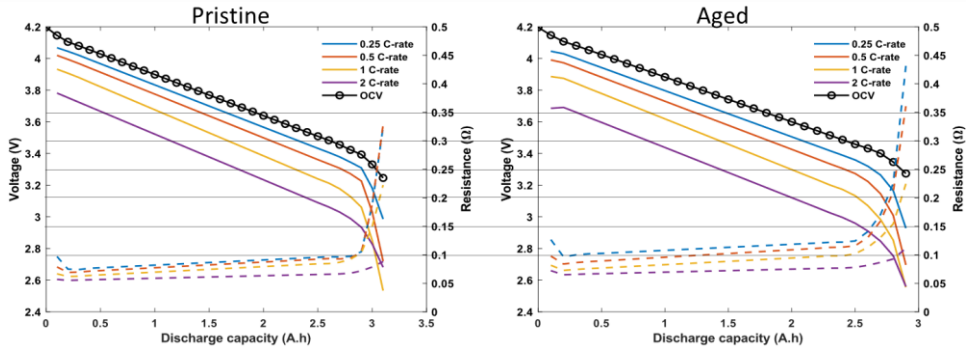


Figure 6.1. Battery capacity for the pristine and aged battery NMC 811 18650. Approach for internal resistance: $\frac{(OCV - V_{out})}{current}$.

Table 6.4 brings the results of capacity measure with different C-rate of discharge for pristine and aged battery 18650. The capacity fade was about 6%, reaching 7.6% when measured with a higher C-rate.

Table 6.4. Ageing vs pristine battery capacity for different C-rate of discharge.

	Pristine	Aged	Diff. (%)
0.25 C-rate	3.16 Ah	2.96 Ah	6.3
0.5 C-rate	3.12 Ah	2.93 Ah	6.0
1 C-rate	3.10 Ah	2.91 Ah	6.1
2 C-rate	3.14 Ah	2.90 Ah	7.6

A thermal runaway test was performed using the ARC under the HWS protocol [4]. The start temperature of the heat wait seek protocol is 50 °C, performing steps of 5 °C up to detecting the exothermic reaction. Exothermic mode is activated whether, during the seek period, the battery temperature rise rate is higher than 0.02 °C/min. Before the seek period, a wait period of 30 min is used for temperature stabilisation between the battery and ARC walls. In addition, before each experimental test condition, a calibration procedure was performed to guarantee the quasi-adiabatic condition from the

exothermic detection up to the thermal runaway. The calibration process calibrates the offset between the measurement of the dummy temperature and the ARC walls to maintain the dummy temperature rise rate lower than 0.01 °C/min. More information about the calibration procedure, heat wait seek protocol, and ARC instrumentation uncertainties can be found in Chapter 3.

The battery was fixed in a metal base to prevent movement during the thermal runaway. Furthermore, two N-type thermocouples were attached to the battery surface using metallic tape rather than glass cloth electrical tape, which prevented detachment from the surface. The tests are conducted at ambient pressure due to a magnetic mechanism that opens the lid when the pressure exceeds this value.

6.2.2 Experimental results

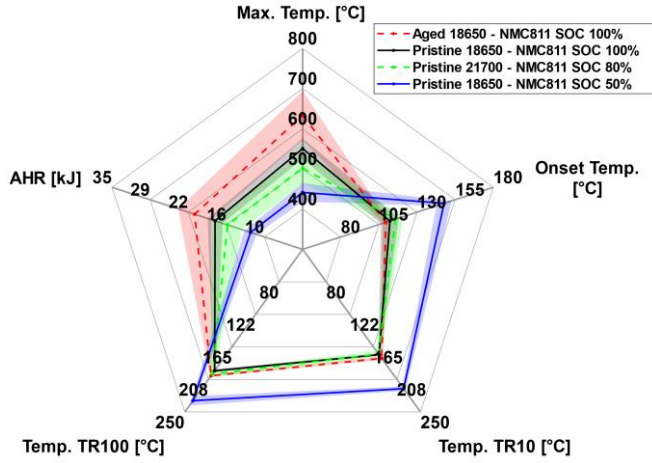
Figure 6.2 depicts the main thermal runaway parameters for 2 different cathode chemistry: Figure 6.2 (a) – NMC and Figure 6.2 (b) – NCA. Cell-to-cell variability is discussed in terms of the average value (the line) and standard deviation (the shadow) for 5 cells in each condition, which comprehend different battery sizes, SOC and state of health (SOH).

Comparing NMC and NCA mean values for maximum temperature, NMC thermal runaway resulted in a lower temperature considering the size of 18650 and SOC at 100%. The difference was 150 °C. One reason can be linked to the lower energy density of the NMC battery, which is 860 J/g compared to 902 J/g for the NCA battery. These results can be found in [5]. Comparatively, this principle also applies to the battery SOC, even with different battery sizes, a lower SOC in the NMC battery results in a lower temperature. This is because less lithium is intercalated into the anode, reducing the amount of lithium available to react with the electrolyte and participating in an internal short circuit after a separator failure. This behaviour can be explained by a step-by-step reaction analysis [6].

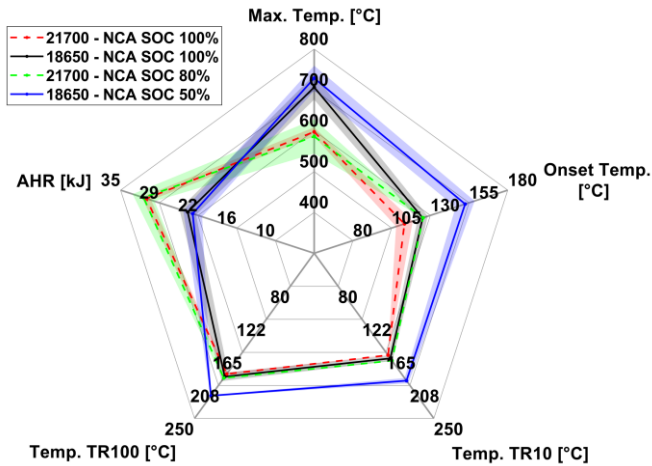
Nevertheless, this is not the case with the NCA battery. The highest temperatures for SOC, 100% and 50%, are comparable. Additionally, the findings imply that if only the mean values were considered, the battery with a lower SOC would produce a greater temperature. However, because of cell-to-cell variability, it is hard to conclude that, regardless of battery size, the maximum temperature for the NCA cathode chemistry is equal for both SOC conditions since both standard deviation zones overlap. In addition, similar results were found in [7], where the maximum temperature during TR for the NCA cathode chemistry was comparable for different SOC.

The onset temperature of the exothermic process, depicted in Figure 6.2, reveals that the SOC impacts this parameter more than the cathode chemistry. Since the region associated with standard deviation overlaps with each cathode chemistry in a given SOC, similar onset temperatures resulted. However, when comparing SOC at 100% and 50%, the lower SOC had a greater onset temperature. The lower lithium concentration in the anode can slow down the reaction rate, requiring a higher temperature for the reaction rate to be noticeable. It can be concluded that the main driver of the exothermic reaction when starting is the anode + electrolyte reaction and the solid electrolyte interface (SEI) decomposition.

Results for NMC and NCA at SOC 100% and SOC 80% are comparable in terms of temperature at temperature rise rate of 10 °C/min and 100 °C/min (TR10 and TR100, respectively). However, the results for TR10 and TR100 are different at SOC 50%, with NMC displaying greater values. $mc_p\Delta T_{AB}$ was used to compute the heat released, and the results showed a behaviour comparable to the battery maximum temperature.



(a)



(b)

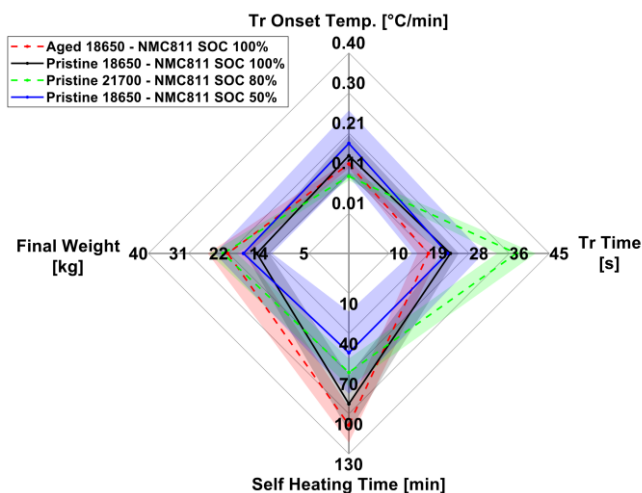
Figure 6.2. Comparison of the main thermal runaway parameters for different batteries SOC and size: (a) NMC and (b) NCA.

Figure 6.3 depicts the thermal runaway parameters related to the battery final weight, temperature rise rate at the onset of the exothermic reaction and event durations for different SOC (100%, 80% and 50%), SOH and size (18650 and 21700): (a) NMC and (b) NCA. Comparing the

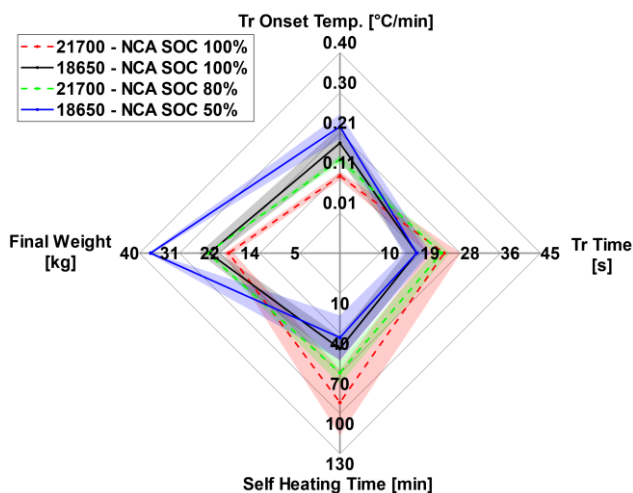
temperature rate at which the ARC detects the exothermic reaction (Tr onset Temp.) is crucial for comprehending cell-to-cell dispersion. Although the ARC system is calibrated to detect exothermic reactions at 0.02 °C/min, the results of Tr Onset Temp. values are greater than this value, which does not imply that the reaction is detected precisely at this value and instead contributes to scattering results. Thermal inertia during the heat is one of the causes, which can lead to temperatures that are not exactly the same during the wait-and-see phases when comparing different tests. This can differ the onset temperature and the temperature rise rate when the exothermic reaction is detected. Higher temperatures imply higher temperatures rise on average, which can result in a short self-heating phase when detected. For example, the time required is equal to 100 minutes if the average temperature rise rate is equal to 0.05 °C/min over a 5 °C interval, which is not true because this value fluctuates from lower to higher values as the battery temperature increases. However, if the exothermic reaction is detected at another temperature and thus at a different temperature rise rate, the duration of the self-heating phase will be different. This may occur because the steps performed for each cell are not the same when comparing cells to cells, and the 5 °C step may cause a greater variation in this parameter. This is why it must be taken into account when comparing the results.

The battery end mass seems to be linked to the battery surface temperature. Higher mass ejected during the battery thermal runaway would mean more energy is ejected to the ambient and less energy is transferred to the battery casing. In addition, the results for 18650 NCA batteries at different SOC, 100% and 50%, suggest a trade-off effect between the ejected mass and the SOC. The lower mass ejected for the battery with SOC at 50% compensated for the lower energy available, generating a surface temperature similar to the battery with SOC at 100%, which had greater ejected mass. Furthermore, the final weight of the battery affects the duration of the thermal runaway itself. However, this parameter shall consider the difference between the initial and final battery masses when comparing different battery sizes. The period for BTR was shorter for the smaller mass that was ejected.

However, the residual mass of the battery (reactants) throughout this process can also impact the speed of the process.



(a)



(b)

Figure 6.3. Comparison of the main thermal runaway parameters related to the battery final weight, temperature rise rate for the onset of exothermic

reaction and durations for different batteries SOC, SOH and size: (a) NMC and (b) NCA.

6.3 0D model for predicting thermal runaway behaviour

In this subsection, the model used to predict the thermal runaway will be described, and the virtual ARC will be used to compare the simulation with the experimental results obtained. The calibration and validation of the model will be presented.

6.3.1 Arrhenius equation for thermal runaway model

The heat released via the battery surface during the thermal runaway event can be computed using a simplified energy balance, as shown in Equation (1).

$$Q_{gen} + Q_{diss} = MC_p \frac{\partial T_{Bat}}{\partial t} \quad (1)$$

where M is the battery weight, C_p is the battery-specific heat value, T_{Bat} is the battery surface temperature, and Q_{gen} and Q_{diss} are the total heat release generated and the heat released via the battery surface by convection, respectively. The current work assumes that the battery is homogeneous, with an average specific heat value. The convective term can be calculated according to the Equation (2).

$$Q_{diss} = h \cdot A \cdot (T_{ARC} - T_{Bat}) \quad (2)$$

being T_{ARC} the ARC inner temperature, A is the battery surface area, and h is the convection coefficient. Since the ARC only tracks the battery temperature during the self-heating phase and maintains a quasi-adiabatic

ambient, T_{ARC} should be equal to the battery temperature. This will be assumed to be zero for simplicity purposes. For an adiabatic ambient, the exothermic reaction releases heat that will increase the temperature rise rate due to reaction consumption (c). For an exothermic reaction at adiabatic ambient, any heat release results from the consumption of reagents (c) and causes a temperature rise. Consequently, the reaction rate can be correlated with a single reactant, as in Equation (3).

$$\frac{dc}{dt} = k * [c] \quad (3)$$

being k the constant rate. The Arrhenius equation widely represents the thermal runaway. The rate constant (k) can be related to the temperature using Equation (4).

$$k = A * e^{-\frac{Ea}{k_b T}} \quad (4)$$

Being A the pre-exponential factor, k_b is the Boltzmann constant, and Ea is the activation energy. It is feasible to obtain the consumption rate as a function of temperature as in Equation (5) by substituting Equation (3) in Equation (4).

$$\frac{dc}{dt} = A * [c] * e^{-\frac{Ea}{k_b T}} \quad (5)$$

According to Equation (6), the heat released can be connected to the reagent consumption.

$$\frac{dq}{dt} = \text{LHV} * \frac{dc}{dt} \quad (6)$$

being LHV is the maximum energy released in adiabatic conditions. Replacing Equation (6) in Equation (5), the heat release can be calculated directly from temperature measurement, as represented in Equation (7).

$$\frac{dq}{dt} = A * LHV * [c] * e^{-\frac{Ea}{k_b T}} \quad (7)$$

By substituting $\frac{dq}{dt} = c_p \frac{dT}{dt}$ for the heat release rate, the temperature rise rate may finally be connected to the battery temperature. According to Equation (8), the Arrhenius equation can be expressed as a function of quantifiable factors like battery temperature.

$$\frac{dT}{dt} = A * \frac{LHV}{c_p} * [c] * e^{-\frac{Ea}{k_b T}} \quad (8)$$

$A * \frac{LHV}{c_p} = A * \Delta T_{AB}$ is called as A_{global} for mathematical simplification. The Equation (9) show the result.

$$\frac{dT}{dt} = A_{global} [c] * e^{-\frac{Ea}{k_b T}} \quad (9)$$

To obtain Equation (10), logarithms are applied on both sides of Equation (9) and mathematical procedures are performed.

$$\ln\left(\frac{dT}{dt}\right) = \ln(A_{global}) - \frac{Ea}{k_b T} \quad (10)$$

From Equation (10), the activation energy and the pre-exponential factor are unknown. However, this can be known by plotting the graph representing Equation (10), and the parameters can be obtained by calculating the slope and y-intercept. Therefore, linear regression is applied to the data plotted in the logarithm format of the temperature rise rate versus the inverse of the temperature, as depicted in Figure 6.4.

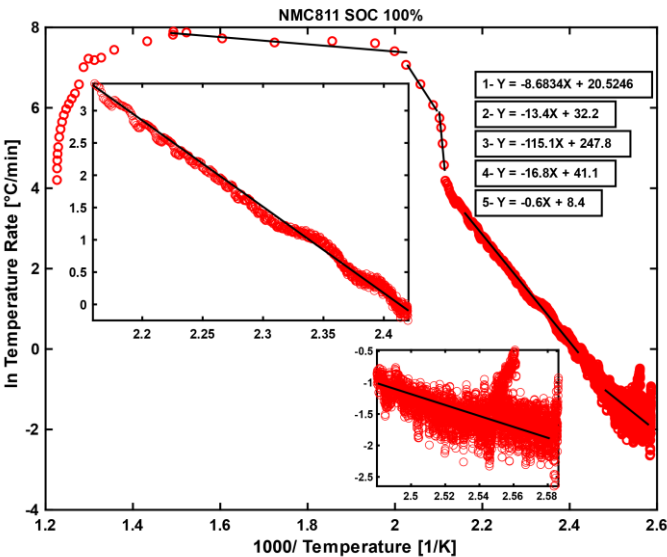


Figure 6.4. Fitting data for calculate the pre-exponential factor and activation energy.

The temperature interval where the linear regression was applied is shown in Table 6.5, where the equations represent the points and were generated using ordinary least squares. The model was calibrated for both the pristine NMC at SOC 100% cells and the pristine NCA at SOC 100% cells in 18650. The pre-exponential factor and activation energy may be computed using the obtained equation.

Table 6.5. Interval of each step to apply linear fitting using ordinary least squares technique.

	Pristine – NMC SOC 100%	Pristine - NCA SOC 100%
Step 1	115 – 130 °C	120 – 130 °C
Step 2	140 – 180 °C	140 – 180 °C
Step 3	~196 - ~198	~196 - ~198
Step 4	206 – 220 °C	206 – 220 °C
Step 5	220 – 400 °C	230 – 350 °C

Each interval, denominated as Steps 1, 2, 3, 4 and 5, is based on events that succeed in the thermal runaway, according to Figure 6.5. In general terms, the entire process may be divided into three main phases, each producing three main temperatures. Due to the interaction of the disintegration of the SEI and the reaction between lithium and the electrolyte at the anode, the initial phase is characterised by a gradual self-heating process. The onset temperature of the self-heating process under a quasi-adiabatic ambient provided by an ARC is often detected using the heat-wait-seek protocol, with a temperature rise rate greater than $0.02\text{ }^{\circ}\text{C}/\text{min}$. The melting process of the separator is responsible for the characteristics of the second phase. In the self-heating phase, the energy released heats the batteries, preventing heat loss to the environment due to the heat-wait-seek process. Gases inside the battery are generated throughout the self-heating phase. When the maximum pressure inside the battery is reached, a vent cap bursts, releasing the gases to prevent the cell from exploding. However, this does not prevent reactions in a quasi-adiabatic ambient. The continuous increase in battery temperature causes an internal short circuit due to the melting of the separator. The BTR start temperature is set when the temperature rise rate reaches $100\text{ }^{\circ}\text{C}/\text{min}$. Compared to the self-heating phase, the thermal runaway phase can increase the temperature to its maximum in less than 20 seconds.

In order to improve the modelling capability of predicting the experimental behaviour, the above description was divided into 5 stages based on the temperature rate profile observed during the thermal runaway process under the HWS protocol. Before the temperature rise rate increase, the first phase is characterised by ups and downs. This might be considered a stage between the creation and disintegration of SEI. The temperature rise rate is gradually increased by the second phase as the battery temperature increases under adiabatic conditions [8]. The third step was characterised by the start of the TR. This was defined as the temperature when the temperature rise rate equals $100\text{ }^{\circ}\text{C}/\text{min}$. The inflexion point of the second derivative of the battery temperature rise rate was used to define the end of the third step, indicating that the temperature rise rate decreases. The

endpoint of the third step to a constant temperature rise rate characterises the fourth step. In sequence, the fifth step is defined up to the maximum temperature.

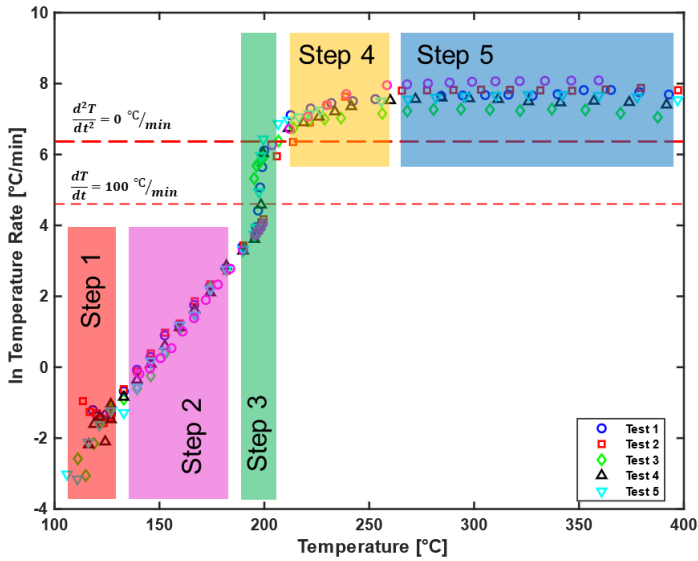


Figure 6.5. Definition of battery events that followed thermal runaway based on the rate of battery temperature rise.

6.3.2 Simulation and Model description

In order to compare the results of the simulations with the experiments, a virtual ARC approach was used to generate a virtual ambient temperature in accordance with the HWS protocol. The starting temperature is set to 50 °C. As a result, the battery is maintained under adiabatic ambient conditions for 30 minutes during the wait period. The TR modelling is deactivated while the heat-and-wait mode is on. If no exothermic reaction has been previously detected, these modes are used solely to adjust the battery temperature and stabilise it with the ambient temperature following the new target temperature. The TR model is sequentially activated during the 10-minute

seek time. The exothermic phase occurs when the battery temperature rise rate is higher than the selected sensitivity threshold. Otherwise, the heat mode is activated, the ambient temperature increases according to the temperature step, and the wait-and-seek phase is repeated. During the exothermic phase, an adiabatic ambient temperature is established by tracking the battery temperature. As a result, the virtual calorimeter does not provide extra heat for the battery. When the battery reaches its maximum temperature (the conclusion of the exothermic process), the cool phase is triggered. Figure 6.6 explains the process described schematically.

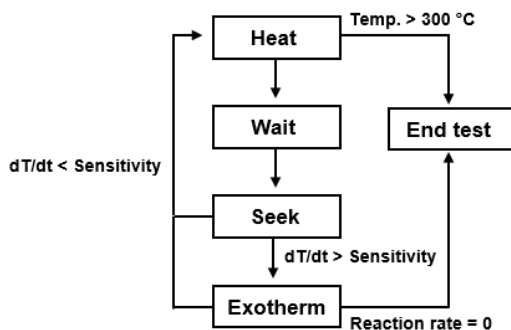


Figure 6.6. HWS scheme for simulation.

Figure 6.7 shows the mathematical model description when the seek block is activated after the wait period. The ambient temperature dictates the battery temperature. At the same time, the reaction rate from steps 1 and 2 are calculated. Due to different activation energy, the reactions start at different moments. The heat release is determined each time step after calculating the reaction consumption. In the sequence, the temperature rise rate due to the heat released is calculated using the battery heat capacity equation, considering a global specific heat for the battery. The exothermic mode is activated if the resulting temperature rise rate is higher than the sensitivity in the virtual ARC.

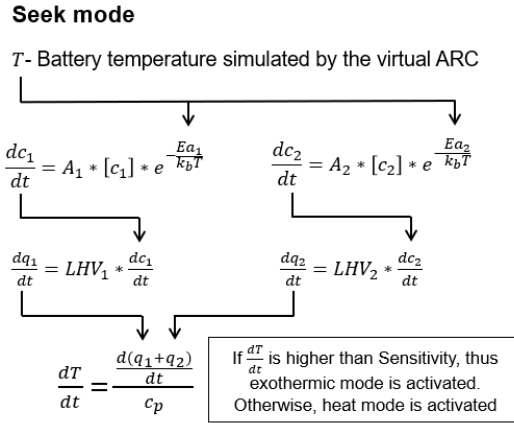


Figure 6.7. Depiction of mathematical modelling while seek block is on.

Figure 6.8 shows the description of the exothermic block's mathematical process. For every time step, the consumption rate for steps 1 and 2 is computed. However, the activation energy determines the reaction rate magnitude for each reaction. High activation energy value results in a noticeable reaction rate at high battery temperatures. The heat released is calculated, and the resulting increase in battery temperature is added to the current battery temperature. The battery assumes this updated temperature for the next step. ARC ambient temperature is adjusted to the battery temperature to avoid heat transfer, guaranteeing an adiabatic condition.

During the exothermic mode, the temperature of the battery and the temperature rise rate gradually increase. The primary cause of battery thermal runaway is the rupture of the separator, which leads to high-temperature rise rates. Low activation energy is produced by the linear regression fitting in stages 3, 4, and 5. Thus, in addition to other superimposed exothermic processes, these reactions are brought on by the separator breaking down, starting a short circuit. A trigger is required to initiate these reactions at the appropriate time. Otherwise, they would occur at a lower temperature. In this study, the temperature rise rate achieved by the battery was used as a criterion, and it appears to be less variable than the battery temperature. The values used were 40 °C/min and 60 °C/min for

the NMC and NCA, respectively. These values were obtained from the calibration performed for the size of 18650 and at SOC 100%.

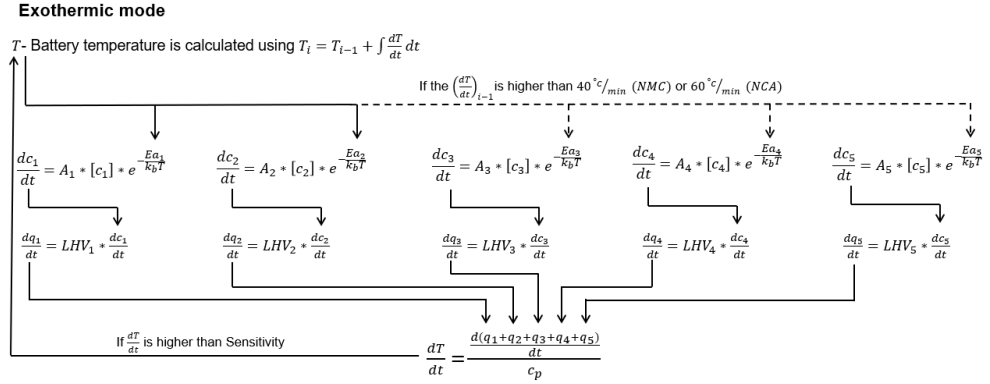


Figure 6.8: Depiction of mathematical modelling while exothermic block is on.

Since some factors cause higher cell-to-cell dispersion in the experimental tests, they must be considered for simulation purposes to compare the results of the experiments and simulations. The thermal runaway process leads to battery mass loss, and due to factors such as vent cap design, particle size, degradation, and other variables, the final battery mass (M_{end}) varies from cell to cell. Based on the discussion of the experimental tests, the final battery mass affects the battery surface temperature. This effect was accounted for by incorporating the final battery mass into the LHV calculations in step 5. Another important effect on the thermal runaway is the specific energy. Batteries with higher specific energy release higher heat during thermal runaway [5,9]. For this reason, incorporating a variable that accounts for the specific energy is important when simulating batteries that differ from the calibrated ones. In addition, the calibration process considers pristine batteries with SOC at 100%. In the current work, SEI growth was the mechanism for ageing the battery. The charge, rest and discharge protocol boots its mechanism and the ambient temperature used. Furthermore, the primary reaction driving SEI growth is the interaction between lithium intercalated in the anode and the electrolyte

[10–12]. Consequently, one ageing effect on the battery is capacity fade, which reduces the heat released, as discussed in [6].

SOC of the battery during TR impacts its behaviour [13]. A short circuit is potentially impacted with lower lithium intercalated in the anode, decreasing heat released [14,15]. When calculating the LHV for step 5, where a significant portion of the energy is discharged, the suggested model considers these inputs. Furthermore, a paper indicates that during the self-heating phase, lower SOC has a higher activation energy [16]. It makes sense that a lower SOC would result in a lower anode lithium concentration, a slower reaction rate, and a higher activation energy is needed. Given the proportional relationship between SOC and cell open circuit voltage for the cell types studied, the activation energy (for step 2) will be determined as proportional to $\left[(Ea_2)_{SOCx} = (Ea_2)_{calibrated} * \frac{V_{SOCx}}{V_{calibrated}} \right]_{OCV}$. The LHV values for each step of the modelling are presented in Table 6.6.

Table 6.6. Calculation of the LHV value for each step and battery chemistry.

	NMC	NCA
	LHV	
Step 1	$1.1 \text{ kJ/kg} * M$	$1.1 \text{ kJ/kg} * M$
Step 2	$190 \text{ kJ/kg} * M$	$228 \text{ kJ/kg} * M$
Step 3	$0.5 \text{ kJ/kg} * M$	$0.5 \text{ kJ/kg} * M$
Step 4	$1.1 \text{ kJ/kg} * M$	$1.1 \text{ kJ/kg} * M$
Step 5	$650 \text{ kJ/kg}_{M_{end}} * M_{end} * Aged$ $* SOC * \emptyset$	$730 \text{ kJ/kg}_{M_{end}} * M_{end} * Aged$ $* SOC * \emptyset$

The normalised specific energy ($\emptyset$) is required as the model was calibrated using pristine batteries with a specific energy. The energy density

of the NCA is 0.075 Ah/g, while the NMC is 0.071 Ah/g. Thus, Equation (11) is used to derive the $\emptyset$.

$$\emptyset = \frac{\text{Specific energy (Ah/g)}}{(\text{Specific energy})_{ref}(\text{Ah/g})} \quad (11)$$

The capacity fading was considered as a parameter called *Aged*, which considered the actual battery capacity related to the capacity in pristine condition. It would only be applicable in situations where the SEI growth is the ageing process. Further research is needed if the battery has other mechanisms of deterioration. The current work considers the battery original capacity as 3.20 Ah and 3.45 Ah for the NMC and NCA chemistries, respectively. Equation (12) illustrates how capacity fade is accounted for in the TR model prediction.

$$Aged = \frac{\text{Actual capacity (Ah)}}{\text{Original capacity (Ah)}} \quad (12)$$

The SOC variable is linearly scaled, with 100% denoting a value of 1.0 and 50% denoting a value of 0.5. Consequently, a variable value of 0.8 equals a SOC of 80%.

6.3.3 Fitting Model Parameters to Experimental Data

The 18650 NMC and NCA batteries at 100% SOC were considered during calibration. Each experimental data set was used for linear regression fitting (5 cells for each chemistry), and the average value was applied to the model coefficients at each step (activation energy and pre-exponential factor). The proposed model was calibrated with other parameters (battery size, SOC, and state of health) using the same coefficients. The coefficients derived

from the linear regression fit of the model are summarised in Table 6.7. Since each battery chemistry has a unique curve shape, it has its coefficient.

Table 6.7. Activation energy and pre-exponential factor used during the model calibration.

Variable		Phases	Mean
18650 Pristine NMC811 SOC 100%	Activation Energy [eV]	1	0.98
		2	1.15
		3	12.93
		4	0.79
		5	0.08
18650 Pristine NCA SOC 100%	Pre-exponential factor [1/min]	1	2.0E+10
		2	7.7E+11
		3	1.7E+140
		4	2.2E+09
		5	3.1E+01
18650 Pristine NCA SOC 100%	Activation Energy [eV]	1	1.33
		2	1.33
		3	14.25
		4	0.79
		5	0.06
18650 Pristine NCA SOC 100%	Pre-exponential factor [1/min]	1	3.8E+14
		2	7.3E+13
		3	5.6E+153
		4	4.4E+09
		5	34.14

The calibration results for the 18650 NMC at SOC 100% are shown in Figure 6.9 (a, b, and c), and the 186500 NCA at SOC 100% are presented in Figure 6.9 (d, e, and f). During the calibration, three scenarios were employed. In the mean scenario, the model inputs are the average final mass, and the sensitivity is the average temperature rise rate at the onset temperature from the experimental tests. The maximum and minimum Tr

Onset Temp. and battery end mass, respectively, provide the maximum and minimal scenarios.

Using this approach, it is possible to note that the model can capture different onset temperatures for the exothermic period. The data in Figure 6.9 represent only the exothermic part of the HWS process. For the battery temperature, Figure 6.9 (a) and (d), for the NMC and NCA, respectively, lower temperature rise rate at onset temperature resulted in a lower onset temperature, being in accordance with the experimental results. The same conclusion can be taken for the other scenarios. This impact is significant for the model and explains this variation across cells for both battery chemistries.

Additionally, considering the constraints employed, the time from the thermal runaway and self-heating is comparable between simulation prediction and experimental tests. A discrepancy results from the challenge of accurately predicting the cell behaviour about the experimental temperature rise rate profile, which fluctuates as the model steadily rises. Another important impact is the venting process, which experimentally decreases the battery surface temperature due to the process itself. During this process, the ARC control switches from exothermic to heat mode, causing the battery temperature to rise to levels close to the temperature before venting. This effect is not considered in the simulation, which may explain some differences between the simulated and experimental values.

Despite the aforementioned constraints, the model can accurately replicate the temperature rise rate profile versus the battery surface temperature, as shown in Figure 6.9 (b) and (e), and can identify the abrupt temperature changes that occur during thermal runaway. The trend of the heat release rate is also comparable, and the effect of lower battery final mass, which translates into lower battery heat release, is replicated by varying the final battery mass used as input. The heat release rate can be seen in Figure 6.9 (c) and (f).

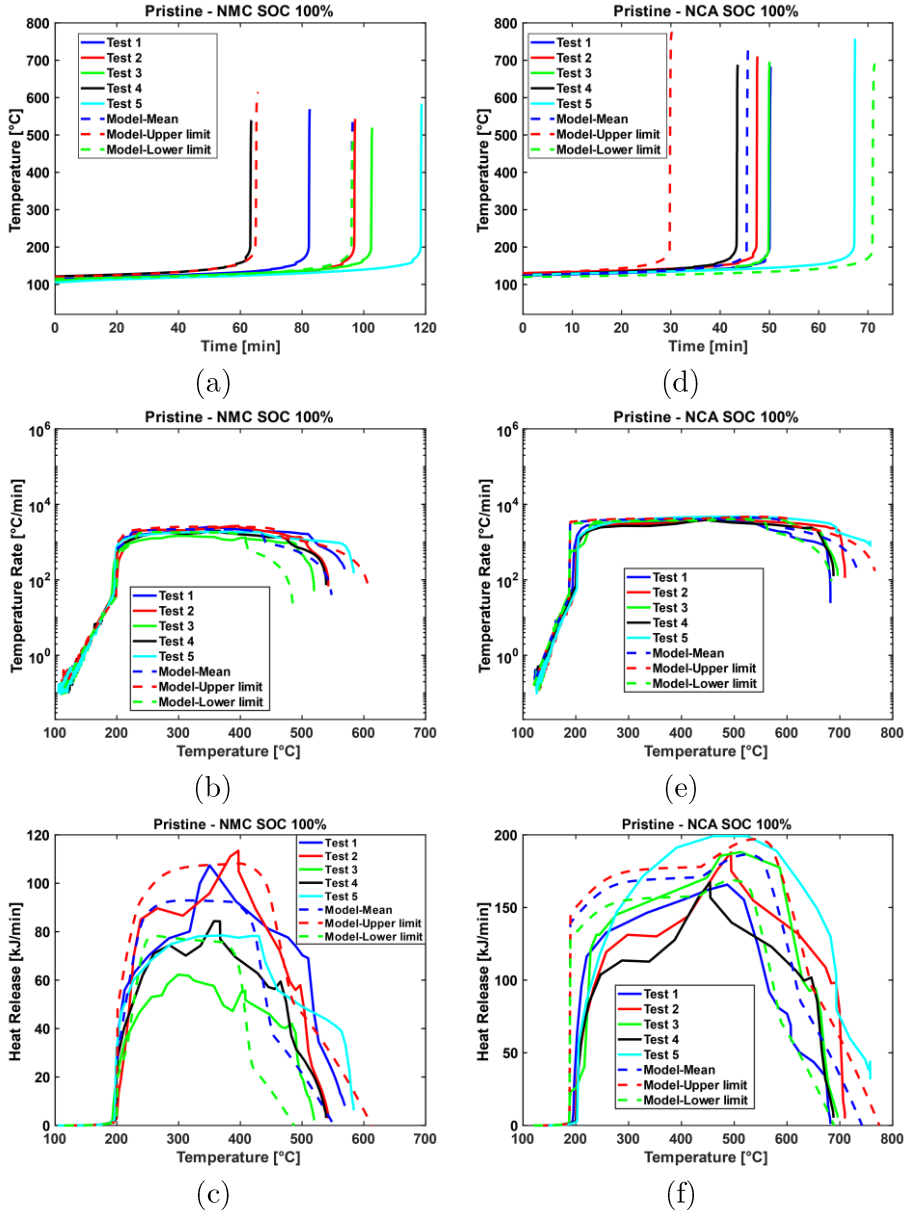


Figure 6.9. Modelling and experimental results for two cathode chemistries at the same SOC (100%). In (a) and (d) is presented the battery surface temperature as a function of time for only the exothermic part of the HWS protocol, in (b) and (e) show the battery temperature rise rate versus

battery surface temperature, and in the (c) and (f) is presented the heat release rate as a function of battery temperature.

6.3.4 Model Validation Against Experiments

The battery thermal runaway parameters from the experimental and model results are comparable in Figure 6.10, where the data are in a function of 2 battery chemistry (NMC and NCA), 2 battery sizes (18650 and 21700), 2 battery state of health (pristine and aged), and 3 SOC (100%, 80% and 50%). The upper and lower limits and the average value are depicted in the figure as a shaded area. Given the constraints of the experimental tests, any value within the shaded region is possible from the simulation.

Using the constraints from the experimental tests to limit the analysis, the experimental tests and simulations for the maximum temperature in Figure 6.10 (a) were under the same range. Based on Table 6.6 (step 5), the maximum temperature mainly depends on the SOC, energy density, ageing (capacity fading), and the battery final weight. Thus, the model has reacted well to the change in the cell state, forecasting the outcomes per the experimental testing, demonstrating that the parameters used to determine the LHV in step 5 directly affect the maximum battery temperature during thermal runaway. Taking into account each measured outside the limits for the maximum temperature, the average difference was less than 1%.

Figure 6.10 (b) shows the onset temperature that the model predicted. The onset temperature has shown a higher variability between experimental and model results when compared to the maximum temperature values. One explanation is that the model ignores some effects demonstrated in experiments, such as thermal inertia. The temperature step (target) that deviates from the intended goal results from thermal inertia. This, in addition to the temperature step used along the heat-wait-see, makes the process different from cell to cell. Although this is a small discrepancy, due to the step temperature selected, it can cause a 5 °C variation between tests. Thus, the detected onset temperature and the temperature rise rate vary from cell

to cell if the battery temperature is not precisely at the onset temperature (for 0.02 °C/min) during the seek mode. The model decreased variability because it flawlessly executes the heat-wait-seek procedure without experiencing thermal inertial issues.

Furthermore, the temperature rise rate of the battery is more variable while the exothermic process is beginning. As the battery temperature and temperature rate rise, its variability decreases. However, since the ARC control relies on the temperature rate at the end of the calculation window during the seek period, it may introduce dispersion at the initial temperature (which can result in false exothermic detection). Meanwhile, this initial variability is not predicted by the model. Compared to the tests, the temperature rise rate from the models is more consistent. Small variations in manufacturing quality, such as battery chemistry, can also impact. Nevertheless, there was an average difference of 2.2% across the conditions examined.

Figure 6.10 (c) and (d) show, respectively, the temperature at which the temperature rise rate is equal to 10 °C/min and 100 °C/min. The results have shown an even lower scatter behaviour than the onset temperature for the simulations and experimental tests. Since the ARC control relies on detecting the battery temperature and maintaining the quasi-adiabatic ambient, a slight variation can be ascribed to it. Therefore, slight convection losses can explain a few variations in the experimental data and their discrepancy from the model values. The studied circumstances had an average difference of 2.1%.

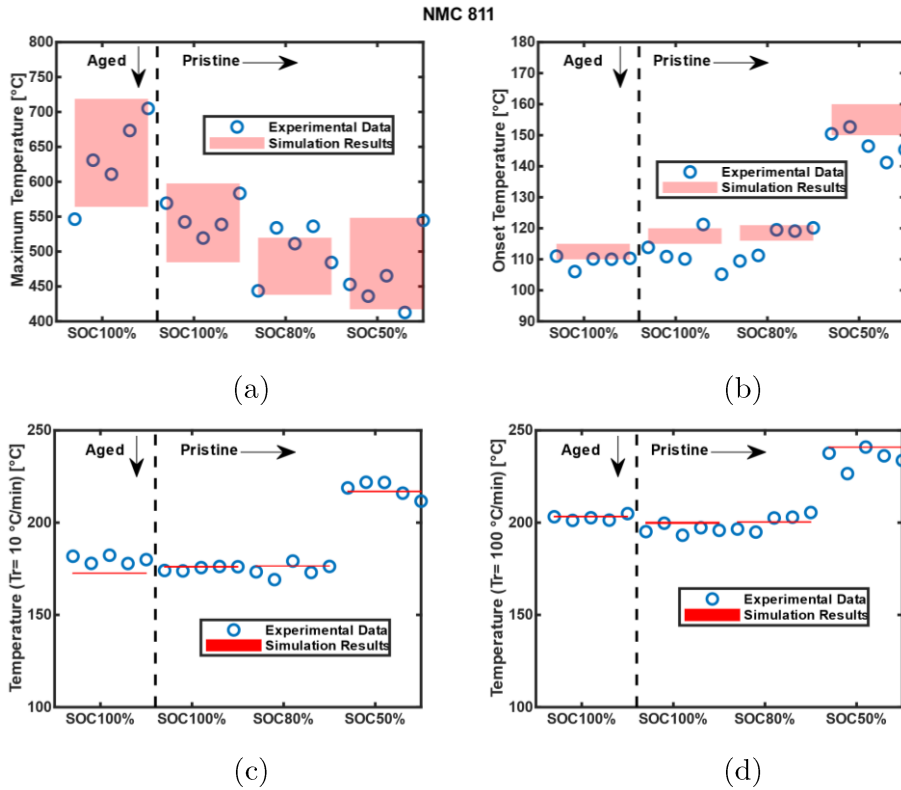


Figure 6.10. Parameters from experimental tests versus simulation results for different battery conditions (SOC, size and SOH) for the NMC battery. (a) – Maximum temperature, (b) – Onset temperature, (c) – Temperature at TR10, (d) – Temperature at TR100.

The maximum temperature from the model prediction for the NCA battery chemistry is displayed in Figure 6.11 (a) for two distinct battery sizes and SOC: 100%, 80%, and 50%. The maximum temperature predicted matches the results of the experiments. The modelling and experimental test results showed a maximum discrepancy of 0.4%, less than the NMC battery value. Consequently, the suggested model correctly predicted the maximum temperature in line with the experimental test by interacting with the variable that affects the battery maximum temperature.

Figure 6.11 (b) shows the onset temperature of the exothermic reaction predicted by the model compared to the experimental results. For

this parameter, the deviation from the tests was lower than the difference found for the NMC, 0.8% of the value found. In addition, the values outside the shadow are within the 5 °C limit, which is explained by the temperature step used during experiments and simulations, as commented for the NMC battery results. Figure 6.11 (c) and (d) depict the temperature results where the temperature rise rate achieved by the battery was 10 and 100 °C/min, respectively. The average difference found was 1.3 and 1.4%, respectively. The same remarks that were mentioned regarding the NMC also can be applied. The calorimeter capability to track battery temperature, avoiding battery heat transfer to the ambient, can account for the difference in these parameters.

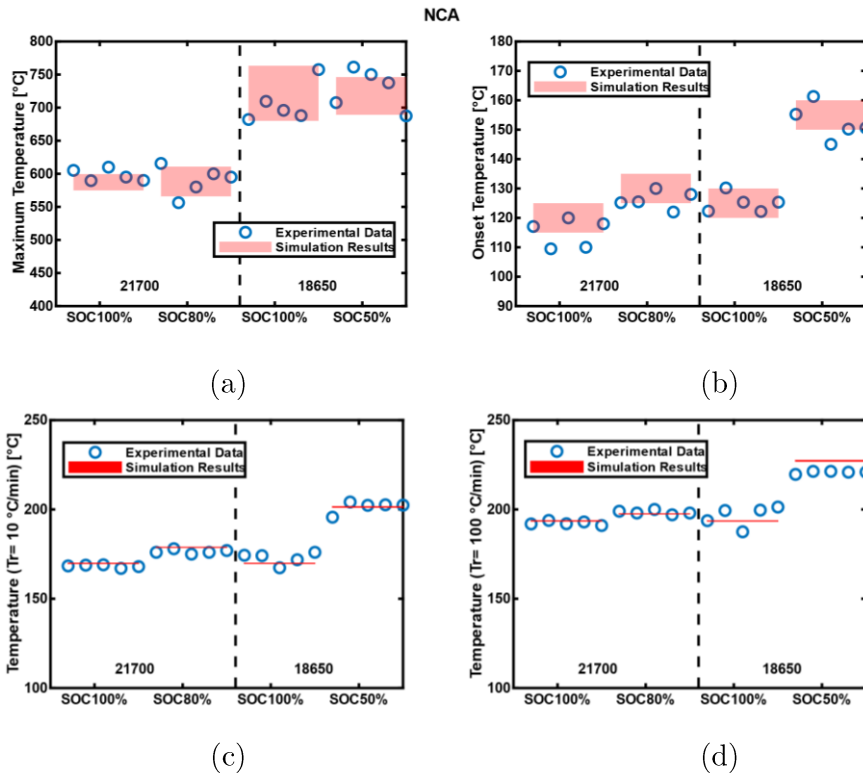


Figure 6.11. Parameters from experimental tests versus simulation results for different battery conditions (SOC and size) for the NCA battery. (a) –

Maximum temperature, (b) – Onset temperature, (c) – Temperature at TR10, (d) – Temperature at TR100.

6.4 Summary and conclusions

The current work modelled and experimentally evaluated the thermal runaway effect for two cathode chemistry (NMC and NCA), for different battery sizes (18650 and 21700), for different SOH (pristine and aged), and for different SOC (100%, 80%, and 50%). External heat abuse using an accelerating rate calorimeter was used to cause the battery thermal runaway. In order to prevent heat transfer from the calorimeter to the battery during the exothermic reaction, the experimental test employs the heat-wait-see protocol. 5 samples of each test condition were tested, and a statistical analysis was performed. A thermal runaway model was developed to predict the experimental results and evaluate the cell-to-cell variability. Based on the studied battery temperature rise rate behaviour, the model comprises 5 steps. Additionally, the model considers the impact of factors such as battery ageing, energy density, and state of charge. The following conclusion can be made:

- In the case of the NMC, the maximum temperature increases with a higher SOC. During the thermal runaway phase, the higher lithium content is crucial. However, the maximum temperature was comparable when analysing NCA battery at SOC of 100% and 50%. The greater final mass at SOC of 50% compensates for the lower quantity of lithium intercalated in the anode.
- The ARC control strategy for the venting process and thermal inertia affects the self-heating phase in terms of onset temperature and duration. The temperature rise rate at which the exotherm is identified (sensitivity) is typically higher than the setting and must be considered input for the model.

- The model predicted the battery thermal runaway process using the constraints of the experimental test conditions, mainly when analysed as a function of battery temperature. The average difference between the experimental results and the validated model predictions was less than 3%. Constraints associated with the experimental testing and variations in battery composition can increase the variability.
- The model has appropriately responded to variations in SOH, SOC, and energy density for two different battery chemistries, NMC and NCA, in alignment with the experimental results. However, only the SEI growth mechanism was considered in the model for different SOH conditions, as it was the primary mechanism boosted during the cycling procedure performed. Other types of degradation mechanisms associated with different SOH conditions require further analysis.

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Chapter 7

Conclusions and suggestions for future work

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7.1 Introduction

This last chapter aims to expose an overview of the key findings from this study. Lastly, recommendations for other works are considered and listed based on the many observations made throughout the work.

7.2 Summary and conclusions

This thesis aimed to understand the scattering behaviour of the thermal runaway process observed in the literature by conducting experimental tests on different battery chemistries and thermal runaway conditions. These tests were performed under controlled conditions and coupled with optical techniques to understand the abuse event better. Furthermore, a numerical model (P2D) was used to understand the degradation process and assess the impact of each battery component on the potential for thermal runaway under different conditions, including ageing. Lastly, with the knowledge acquired during the development of this thesis, a thermal runaway model is proposed to address the weaknesses of existing models.

In the literature review, it was possible to conclude that the thermal runaway abuse process presented by different batteries exhibits a scattering behaviour. Batteries with similar sizes and cathode chemistry resulted in different main thermal runaway maximum temperatures, temperature rates, and onset temperatures of the exothermic process. In general, the studies conducted and addressed in the literature review are carried out with single cells, lacking data related to statistical analysis. Current thermal runaway (TR) models calibrated to specific conditions reflect the lack of data, resulting in inconsistent results. Furthermore, the ageing effect due to cycling affects battery performance by changing the material composition of the battery, such as solid electrolyte interface growth. For this reason, the thermal runaway process differs from that of a battery in pristine condition. Published works have also shown a random behaviour in the main TR parameters,

increasing the complexity of understanding the abuse conditions and incorporating them into a model that can replicate this scenario. There is no evidence of a TR model capable of reproducing the thermal behaviour of batteries while considering the degradation process.

Normal operating conditions were investigated to understand the degradation mechanisms of two different cathode chemistries: Nickel Manganese Cobalt (NMC) and Lithium Iron Phosphate (LFP). The batteries were first electrically characterised, and subsequently, cycling was carried out to accelerate SEI growth. A P2D model was created to replicate the battery thermal and electrical response, and the aged model was calibrated and validated. The model was extrapolated until the battery reached 80% of its original capacity. Driving cycles were performed with a vehicle equipped with two different batteries, and the decrease in vehicle range was analysed. Through this study, the analysis of changes in battery material composition due to the degradation process was made possible and quantified, which is experimentally challenging and beyond the scope of the current thesis.

Considering abuse operation conditions, the results obtained in the first part were used to theoretically understand the effect of the battery materials on the thermal runaway, analysing the ageing effect using step-wise reactions. This study helped to know the expected behaviour of a determined battery chemistry and condition, comprehending: Pristine or aged, fully charged or not, as well as the energy density of the battery. In sequence, experimental tests were carried out using an accelerating rate calorimeter (ARC) to study thermal runaway using thermal and mechanical triggers coupled with optical techniques. From the literature review, it was concluded that the nail penetration test results in a higher degree of randomness compared to other types of triggers. For this reason, five cells were tested at 100% and 50% state of charge (SOC), measuring the battery surface temperature distribution with a thermographic camera and thermocouples attached to the battery surface. A methodology was developed to correct the thermographic temperature measurements, accounting for the uncertainty related to the loss of infrared transmissivity along the optical path. Statistical analysis was

performed, and the camera results helped understand the root cause of the scattering observed.

A thermal trigger was also applied using the HWS protocol to calculate heat release and characterise the thermal runaway parameters of different battery chemistry, state of charge, energy density, and state of health. Optical techniques, including infrared image, Schlieren, and natural luminance, were applied to the experimental tests. The venting process was characterised in terms of jet formation and penetration. Particle temperature and velocity, as well as battery surface temperature distribution, were also analysed. Statistical analysis was performed to evaluate cell-to-cell variability and provide insights into the process.

Finally, a model was proposed to replicate thermal runaway for different battery chemistries, states of charge, energy densities, and state of health, considering solid electrolyte interface (SEI) growth as the main mechanism of capacity fade. According to the literature review, this model accommodates more battery conditions than currently available, being more dynamic in predicting different thermal abuse behaviours across different types of simulations. Based on this summary, the main conclusions for each study can be drawn as follows:

7.2.1 Normal operation condition

Electrical characterisations in pristine and aged conditions were performed on cylindrical batteries with LFP and NMC chemistries. In the pristine condition, the LFP battery presents a flat discharge curve compared to the NMC battery. This impacts the driving cycle behaviour of lithium-ion batteries, as LFP cells maintain a steady voltage throughout the driving cycle. In contrast, the NMC battery experiences a decrease in voltage output as a function of discharge capacity, meaning less power is available while maintaining the same current demand. Higher temperatures during ageing cause increased capacity fade, primarily by accelerating SEI growth. At ambient temperature, the battery degraded by about 1.5%, while at 45 °C,

the NMC battery degraded by approximately 7.5% and the LFP battery by about 12%, indicating that, under this protocol, the LFP battery undergoes accelerated degradation compared to the NMC battery.

A P2D model was created, calibrated, and validated using experimental data from the electrical characterisation. An optimisation process was carried out following a specific methodology. Due to the lack of information and the complexity of determining specific data related to the internal components of the battery, optimising the model to fit the experimental data proved to be a more cost-effective and efficient method. Several parameters, including component thickness, particle size, electrode capacity, contact resistance, first charge and discharge capacity, thermal conductivity, and specific heat capacity, were optimised by considering voltage output and battery surface temperature, with weights of 60% and 40%, respectively. The model for the pristine battery showed good agreement with the experimental tests, with an average deviation of 2% in voltage and 4% in temperature. The most significant difference was observed at lower voltages due to the voltage drop at low SOC. For this reason, the simulation only considers cycling from 100% to 20% SOC.

The ageing model was calibrated and validated by optimising the SEI density, porosity and activation energy. The results showed good agreement in the capacity fade prediction compared with the experimental tests. Throughout all cycles during calibration, the variation remains below 1%. For the NMC battery, the final capacity degradation after 250 cycles is 8.0% in the experimental data and 7.3% in the numerical model. In the case of the LFP battery, the experimental degradation is 11.2%, while the simulated degradation is 11.1%. Although the final degradation value for the LFP battery closely matches the experimental results, the NMC battery exhibited a better agreement with the experimental data along the cycles. Similar results were found in the validation process. The model was extrapolated to eliminate the need for costly and time-intensive testing to determine the battery end-of-life. The results suggest that the NMC battery experiences a 20% degradation at 2000 cycles, which is considered the maximum acceptable

limit for vehicle applications. In contrast, the LFP battery shows more severe deterioration, with a capacity loss exceeding 30% at 2000 cycles.

A battery pack was modelled using the calibrated and validated battery, incorporating the ageing model. The battery pack was designed to operate at 600V and to have the same current demand for each battery, ensuring that no individual battery would degrade faster due to the higher current demand required for the driving cycle. The results showed that the vehicle simulation demonstrated better autonomy when employed in urban cycles. The NMC battery provides an additional 84 km of city driving range and 50 km more on the highway than the LFP battery. Finally, The NMC battery provides 91 km longer driving range in cities and 53 km more on the interstate at the end of its useful life (20% capacity loss).

7.2.2 Abuse operation condition

Step-wise reactions were used to evaluate the impact of components on the potential of the thermal runaway using the data from the calibrated and validated electrochemical model, which has activated the aged model for SEI growth. The analysis of the experimental data related to the thermal runaway shows that the pristine NMC battery has a significantly high propensity for thermal runaway, releasing approximately 28 kJ of energy. NMC batteries exhibited pronounced heat release due to the higher oxygen released during the cathode decomposition process, which reacted with the electrolyte. The analysis also revealed that the electrolyte plays an important role in the thermal runaway process, primarily through its reaction with the lithium intercalated in the anode and the oxidation process involving the oxygen released during cathode decomposition. This step-wise reaction mechanism showed that the oxidation reaction between the electrolyte and oxygen accounted for about 52% of the chemical energy released during thermal runaway. In comparison, the reaction between the anode and electrolyte contributed around 47%. Furthermore, the ageing process of the batteries can significantly impact the thermal runaway behaviour. The SEI layer growth, which is accelerated during battery cycling at high temperatures, was

identified as the main mechanism for capacity fading. As the SEI layer grows, the SEI formation reaction consumes lithium and electrolyte on the anode side, reducing the heat released during thermal runaway from the reaction between the anode and electrolyte. This suggests that aged batteries exhibit less severe thermal runaway events than pristine batteries.

After understanding, in theory, the thermal runaway effect of different battery conditions, experimental tests were performed with different battery conditions in ARC coupled with optical techniques, characterising the venting process and main TR parameters. The experimental test results showed that the onset of the exothermic reactions occurs earlier in batteries with a higher state of charge. This behaviour is attributed to the increased concentration of lithium intercalated in the anode, which increases the reaction rate between lithium and electrolyte, being detectable at a lower temperature. Thus, safety mechanisms can be triggered earlier for batteries with higher SOC, providing a longer response time to mitigate thermal runaway. However, the drawback is the higher energy these mechanisms need to manage. At SOC 50%, the heat released through the battery surface is 42% lower than SOC 100%. The sensitivity of the heat-wait-see protocol, set initially at 0.02 °C/min, revealed that the time from onset temperature up to thermal runaway in quasi-adiabatic conditions is reduced by approximately 40% for batteries at SOC 50%. This indicates that lower SOC levels decrease the total energy released and shorten the time available for mitigation.

Furthermore, the end mass of the battery played an important role in heat release during TR, mainly comparing aged and pristine batteries at SOC 100%. A higher-end mass increases maximum temperatures, as the higher mass held in the battery can transfer more heat to the battery surface. From the optical technique results, infrared imaging showed that particle temperatures can reach 900 °C. Batteries with a higher SOC exhibited significantly higher particle temperatures, with a difference of approximately 150 °C between SOC 100% and SOC 50%. In addition, particle velocity in pristine batteries at SOC 100% was recorded at 30 m/s. These findings highlight the strong dependency of thermal runaway behaviour on SOC,

ageing conditions and battery mass, showing that design to optimise safety features can reduce the dangers related to thermal abuse incidents.

Mechanical abuse was also tested using nail penetration as a trigger. The tests were conducted in the ARC coupled with optical techniques, mainly infrared. A raw cause for cell-to-cell variability with nail penetration was the side ruptures. These ruptures allowed gases to escape, potentially leading to local combustion, which could affect thermocouple measurements. Based on these findings, it is recommended that thermocouples be attached to the side opposite to the nail penetration, because ruptures occurred in the region where the nail penetrated. The position of the nail penetration also influenced the thermal abuse characteristic of the battery. The recorded temperatures were lower when the nail was positioned at the top of the battery. In this case, the total heat released by the battery was 30.8 ± 0.6 kJ, while the middle and bottom nail penetration resulted in higher heat release values of 34.3 ± 1.37 kJ. Additionally, the SOC significantly affected the energy released, with batteries at SOC 100% exhibiting approximately 20% more energy release than those at SOC 50% (33.8 ± 0.88 kJ vs. 28.2 ± 0.16 kJ). Despite these variations, the temperature distribution across the battery surface remained consistent, except in cases where casing rupture occurred, significantly increasing temperature variations. The average temperature variability across the cell surface was measured at 40 °C. These results show the need to comprehend rupture patterns when planning safety measures and how structural integrity affects thermal behaviour under mechanical abuse.

7.2.3 Model to predict thermal runaway behaviour

A thermal runaway model was developed to predict experimental results and assess cell-to-cell variability. The model consists of five steps, based on the observed battery temperature rise rate behaviour, and incorporates the effects of battery ageing, energy density, and state of charge. The results indicate that for NMC batteries, the maximum temperature increases with a higher SOC, as the higher lithium content in the anode plays a crucial role during the thermal runaway phase. However, in the case of

NCA batteries, the maximum temperature at SOC 100% and SOC 50% was comparable, explained by the higher end mass at SOC 50% (measured after TR), which compensated for the lower lithium intercalation in the anode.

The ARC control influenced the self-heating phase, affecting both the onset temperature and duration. The temperature rise rate at which the exotherm is identified, known as sensitivity, is typically higher than the set value. It shall be considered an input parameter in the model as it leads to discrepancies between experimental and predicted results. The model successfully predicted the thermal runaway process under the specific constraints of the experimental test conditions, mainly when analysed as a function of battery temperature. The average difference between the experimental results and the model predictions was less than 3%. Therefore, the model effectively predicted the influence of ageing, SOC, and energy density for different battery chemistries. Nonetheless, the model only accounted for SEI growth as the main degradation mechanism.

7.3 Suggestions for future work

Some aspects of this work could not be further developed due to time constraints and the scope of the current thesis. The following section outlines key ideas for improving the study presented in this thesis and proposes suggestions for future research.

7.3.1 Mechanism to predict gas generation from TR

Future work should focus on integrating gas evolution mechanisms into the step-wise reactions (transposing to the Arrhenius equations), considering electrolyte decomposition, cathode breakdown, and anode-electrolyte interactions. Predicting gaseous by-products such as CO, CO₂, H₂, and hydrocarbons is essential for understanding the venting process, combustion risks and propagation. Quantifying the relationship between heat release and gas production under different battery ageing conditions, SOC, and energy

densities will be possible by incorporating gas-phase reactions into a thermochemical model. Additionally, experimental validation using advanced diagnostic tools, such as mass spectrometry and gas chromatography, should be used. These techniques will provide insight into the kinetics reaction of gas formation and improve the predictive capabilities of thermal runaway models. For this, experimental tests with statistical analysis with reactive and non-reactive ambient conditions would benefit the development of gas prediction models. In addition, coupling experimental data with computational fluid dynamics (CFD) models can also help simulate gas propagation patterns in confined spaces, targeting battery pack safety design.

7.3.2 Study of venting caps to comprehend mass effect after TR

The present study identified that the end mass is a critical factor in determining the severity of thermal runaway. However, the mechanisms behind this relationship remain unclear. A more detailed analysis of venting dynamics and structural deformation during thermal runaway is necessary to establish a relationship between venting behaviour and the mass trapped after the event. Future research should investigate how different venting designs influence the end mass retention and thermal behaviour. This can be achieved by designing controlled experiments where vent sizes, formats, and casing materials are systematically swept. In addition, high-speed imaging combined with pressure and temperature sensors could provide important information, revealing how the gas ejection is affected. Finally, X-ray imaging should be employed to evaluate different venting designs to understand internal structural changes after thermal runaway. This technique would identify bottlenecks in gas release pathways and regions where material deformation restricts the venting process.

7.3.2 TR model for module-level abuse condition

Experimental tests with battery modules should be conducted to evaluate the robustness of the proposed thermal runaway model, considering the thermal runaway propagation. These tests would directly compare simulated and experimental tests with module propagation. High-speed imaging, thermocouples, and gas analysis should be employed to capture TR events. In addition, the model could be used to test different cooling systems, cell spacing, and materials applied to TR mitigation. Cycling could be performed with different driving cycles, different ambient temperatures, and fast charge techniques to evaluate safety concerns at a package level. Aged cells exhibit different thermal and electrochemical behaviours than pristine cells, potentially affecting propagation dynamics.

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