Investigation and Application of Safety Parameters for Lithium-ion Battery Systems

For application in battery management systems

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Undersökning och tillämpning av säkerhetsparametrar för litiumjonbatterisystem

För användning i batterihanteringssystem

Axel Relefors
Abstract

Lithium-ion batteries (LIB) have become an essential energy storage technology for our daily lives. As the Swedish military is looking to adopt LIB technology for current and future high-risk applications. Understanding the potential safety risks and evaluating a battery’s instability is crucial for military applications. This report aimed to identify critical safety parameters (temperature, potential, and impedance) in commercial batteries with NMC and LFP electrode chemistries, and to investigate how surrounding cells are affected when a cell in a module developed by FOI suffers from thermal runaway (TR).

Accelerated rate calorimetry (ARC) experiments on Samsung SDI INR21700-40T and INR21700-50E, and A123 Systems ANR26650m1-B batteries were conducted to identify critical onset conditions of thermal runaway. Fully charged Samsung SDI 40T and 50E batteries showed a distinct endothermic reaction from the separator melting between 116 °C and 121 °C, an onset temperature of exothermic self-heating at a temperature of about 120 °C, which progressed to an explosive decomposition at about 170 °C. The TR event resulted in an adiabatic temperature rise of 250 °C to 290 °C and greater than 17 kJ of released heat energy. The temperature rate of the cells increased exponentially from the onset of exothermic reactions to the cell explosively venting. The LFP-based batteries demonstrated exceptional thermal stability during ARC measurements and did not suffer from TR when heated to 300 °C. The onset of exothermic self-heating began at temperatures around 140 °C and intermittent self-heating was detected up until about 220 °C.

ARC experiments of the Samsung 40T batteries were conducted with continuous EIS measurements to correlate their thermal behavior with electrochemical changes in the cell impedance and voltage. A significant increase in the cell’s impedance at about 100 °C indicated that the current interrupt device (CID) triggers due to gas formation and critical pressure build-up within the cell. A sharp drop in the cell voltage occurred during the distinct endothermic reaction suggesting an internal short circuit occurs. The voltage then slowly recovers until at temperatures above 135 °C when it slowly declines, indicating a self-discharge process, up until explosive venting at around 170 °C. The resistance of the 40T battery was observed to increase exponentially from 50 °C to 100 °C, and an 80 mV voltage drop in the open-circuit potential of the S40T cell from around 60 °C until the CID activates at 100 °C.

Cell-to-cell thermal runaway propagation experiments were conducted in a battery module developed by FOI. Overcharging was identified as the best method of initiating TR in the trigger cell. The identified onset temperatures and electrochemical markers were used to evaluate the stability of the module cells. EIS measurements were conducted on each cell to determine changes to their impedance spectra. Cell temperature increase between 16 °C and 48 °C was observed in cells directly adjacent to the trigger cell. Cells further from the trigger cell experienced uniform temperature increases of between 8 °C and 30 °C.

The insulating polymer wrap around each cell was found to be crucial in preventing TR propagation. No propagation was observed when the insulating wrap was present on each cell. TR propagated from cell-to-cell in the module when the insulating wraps were removed, and cells were in direct contact with the thermally conductive heat sink.

Keywords: Lithium-ion batteries, onset temperatures, impedance, thermal runaway
Sammanfattning

Litiumjonbatterier blir en allt viktigare energilagringsteknologi i våra dagliga liv. Forsvaresmakten undersöker tillämpningar där litiumjonbatterier kan ersätta traditionella blysyrabatterier. Att förstå säkerhetsrisker och utvärdera ett batteri s instabilitet är särskilt viktigt för militära tillämpningar. Denna rapport syftar till att identifiera kritiska säkerhetsparametrar (temperatur, spänning och impedans) för kommersiella batterier med NMC- och LFP-elektrodkemier samt undersöka hur omkringliggande celler påverkas när ett batteri i en batterimodul termiskt rusar.


ARC-experiment av Samsung 40T-batteriet utfördes med kontinuerliga EIS-mätningar för att jämföra batteriernas termiska beteende med elektrokemiska förändringar i cellimpedans och spänning. En signifikant ökning av cellens impedans vid cirka 100 °C indikerade att den inre säkerhetsventilen utlösats. Ett kraftigt fall i cellspänningen inträffade under den distinkta endotermiska reaktionen vilket tyder på att en intern kortslutning inträffar. Spänningen återhämtar sig sedan långsamt upp till temperaturer över 135 °C när en självurladdningsprocess sker. Resistansen hos 40T-batteriet ökade exponentiellt från 50 °C till 100 °C, och ett 80 mV spänningsfall observerades från cirka 60 °C tills att den inre säkerhetsventilen utlöses vid 100 °C.

Termiska rusningsförsök genomfördes på en batterimodul utvecklad av FOI. Överladdning identifierades som den bästa metoden för att initiiera termisk rusning i triggcellen. De identifierade starttemperaturerna och elektrokemiska markörerna användes för att utvärdera modulcellernas stabilitet. EIS-mätningar genomfördes på varje cell för att identifiera skador och förändringar i deras impedansspektra. Celltemperaturökningar mellan 16 °C och 48 °C observerades i celler direkt intill triggcellen. Celler längre från triggcellen upplevde likformiga temperaturökningar mellan 8 °C och 30 °C.

Det isolerande polymeromslaget runt varje cell var avgörande för att förhindra propagering av termisk rusning i modulen. Ingen propagering observerades när det isolerande omslagen var närvarande på varje cell. Termisk rusning propagerade från cell till cell i modulen när de isolerande omslagen togs bort och cellerna var i direkt kontakt med den värmefångande kylflänsen.

Nyckelord: Litiumjonbatterier, initieringstemperatur, impedans, termisk rusning.
Acknowledgments

I want to thank my supervisor, Hanna Ellis, for mentoring me and making this project possible. I am very grateful to have had the opportunity to be a part of the battery team at FOI and for all the great help and support I have received.
List of Symbols and Acronyms

Battery cell – The unit of a lithium-ion battery (LIB) that stores and releases electrical energy. It consists of two electrodes of different potentials immersed in an electrolyte solution and electrically separated by a Li+ ion-permeable separator.

Battery module – An assembly of cells electrically connected and mounted in a support structure to protect the cells.

Battery pack – An assembly of modules and supporting control and protection system called the battery management system (BMS).

Symbols

\( T_{\text{endo}} \) Onset temperature of endothermic reactions
\( T_{\text{exo}} \) Onset temperature of self-heating
\( T_{\text{vent}} \) Onset temperature of cell venting
\( R \) Radius of the cylindrical cell
\( h \) Total surface heat transfer coefficient. Including the combined heat dissipation due to conduction, convection, and radiation
\( k \) Combined thermal conductivity of the lithium-ion battery
\( Q_{\text{TR}} \) Total heat released during TR heat addition
\( C_p \) The specific heat capacity
\( \Delta T_{\text{ad}} \) The adiabatic temperature rise
\( |Z| \) Magnitude of the impedance
\( Z_{\text{Re}} \) Real component of the impedance
\( Z_{\text{Im}} \) Imaginary component of the impedance

Acronyms

21700 Commercialized cylindrical cell form factor (21 mm diameter and 70 mm length)
26650 Commercialized cylindrical cell form factor (26 mm diameter and 65 mm length)
A Ampere
Ah Ampere-hour
ARC Accelerating rate calorimetry
BEV Battery electric vehicle
BMS Battery management system
CC Constant Current
CID Current interrupt device
CV Constant Voltage
DEC Diethyl carbonate
DMC Dimethyl carbonate
EC Ethylene carbonate
EIS Electrochemical Impedance Spectroscopy
EV Electrical vehicle
FOI Totalförsvarets forskningsinstitut - Swedish Defence Research Agency
GEIS Galvanostatic Electrochemical Impedance Spectroscopy
HEV Hybrid Electrical vehicle
ISC Internal short circuit
LFP A123 Systems ANR26650m1-B
LIB Lithium-ion battery
LMO Electrode of LiMn$_2$O$_4$
NCA Electrode of LiNi$_x$Co$_y$Al$_z$O$_2$
NMC Electrode of LiNi$_x$Mn$_y$Co$_z$O$_2$
OCV Open-circuit voltage
PC Propylene carbonate
PEIS Potentiostatic Electrochemical Impedance Spectroscopy
PHEV Plug-in hybrid electric vehicle
S40T Samsung SDI INR21700-40T
S50E Samsung SDI INR21700-50E
SEI Solid Electrolyte interphase
SOC State of Charge
TR Thermal Runaway
EU European Union
Wh Watt-hour
1 Introduction

Access to rechargeable and mobile electrical energy storage is crucial for today’s society. The lithium-ion battery (LIB) has filled this need ever since their commercialization in 1991. LIBs are characterized by their high energy density and cycling performance. They offer more than twice the energy density per mass (up to 240 Wh/kg) compared to traditional rechargeable battery chemistries, such as alkaline-based nickel-cadmium (NiCd) and nickel-metal hydride (NiMH), and more than three times that of lead-acid batteries. The LIB is rechargeable, powerful, and lightweight. The superior performance of the LIB stems from a low electrode potential and thus a potent reducing agent (-3.04 V vs. SHE), low atomic weight reducing its gravimetric energy density penalty, and the development of rechargeable intercalation electrodes [1].

LIBs are widely used in a diverse set of electric energy storage applications, spanning from consumer electronics to automotive, aviation, aerospace, and up to large-scale (megawatt) electrical energy storage [2]. Notably in the transportation sector, where environmental concerns and emissions regulations of combustion engines have elevated the priority of zero-emission vehicles and encouraged the development of battery electric vehicles (BEV). The ever increasing demand to drive BEVs further and faster has significantly increased the energy and power capabilities of the LIB while reducing costs [3]. Consequently, LIBs have rapidly gained interest for use in heavy-duty military applications alongside the expanding LIB market [4].

A report by the EU’s Joint Research Centre (JRC), emphasizes the need for defense-related electrical energy storage systems that can deliver improved energy and power performance compared to currently used lead-acid batteries [4]. The Swedish Armed Forces are currently investigating applications were LIBs could replace lead-acid batteries. Since military and defense-related energy storage solutions have stricter requirements and safety standards than most civilian applications. Batteries used in military applications are required to function even during the most demanding operating conditions due to especially high-risk applications. For example, a civilian vehicle can likely be evacuated in the case of a fire; however, a submarine or a combat aircraft cannot be evacuated in the same way and the result of a fire may be more severe considering circumstances such as explosive material onboard.

The steadily improving energy and power capabilities of LIBs come at the expense of thermal stability. Safety concerns over LIBs stem from the combination of highly reactive electrodes and flammable organic electrolytes. Exothermic decomposition reactions of LIB components can rapidly spiral out of control when subjected to elevated temperatures. If the heat generation is greater than the heat lost to the surroundings, the rising internal temperature increases the reaction rate further and rapidly accelerates the cell to higher temperatures. The resulting catastrophic failure is known as a thermal runaway (TR). TR events can cause significant damage to their surroundings and trigger a chain of propagating TR in neighboring cells [2]. LIBs may reach hazardous temperatures due to a variety of abuse conditions which can lead to thermal runaway scenarios. Figure 1 shows the progression of TR for different failure mechanisms. Mechanical damage from energetic collisions damages the electrode and separator layers and creates an internal short circuit (ISC) that develops into TR. Electrochemical abuse from high charge rates, overcharging, or over-discharging can overheat the cell and progress to TR [2] [5]. Thermal abuse via overheating or exposure to fire can lead to TR. Aging destabilizes cells and creates inconsistencies among connected cells which may lead to overheating from unequal charging and discharging.
Safety concerns over LIBs have currently limited their use in heavy-duty military and defense applications [4]. Several recent safety incidents and recalls involving LIBs highlight these safety concerns: BEV fire accidents from vehicle collisions or charging failures [3], the infamous Galaxy Note 7 recall. In particular, the LIB fire incidents of Boeing 787s raises safety concerns for defense applications due to the aviation industry's mature and rigorous safety standards [6].

Although the consequences of the intense heat and potential explosion from TR pose a substantial hazard, the threat to people from asphyxiating smoke and toxic gases in confined spaces like combat aircraft and submarines elevate these safety concerns further. Therefore, defense-related research on battery safety and thermal management of LIBs systems are needed to address specific military requirements [4]. For this reason, the Swedish Defence Research Agency (FOI) is working on characterizing behavior and risk parameters of LIBs, developing, and designing lithium-ion battery module and pack design for defense applications.

Additional mass and volume place a penalty on the energy and power densities of LIB systems and influence design requirements, especially in military aviation and defense applications in general. Excess mass in a battery module is likely needed as a safety margin to dissipate heat and better safeguard against TR [7]. However, at the same time excess mass or volume limits the potential energy and power performance. It is essential to get the right balance and thus, this project aims to better understand the necessary trade-offs in performance capabilities and safety for the design of LIB modules for use in military applications.

Spontaneous internal short-circuit from defects within the cell has resulted in catastrophic failure without an obvious cause [6]. This necessitates a better understanding of TR to design a battery management system (BMS) that detects critical events before TR, such as onset temperatures or electrochemical changes of the cell.

Figure 1. Diagram of a generalized failure progression of lithium-ion cells.
Understanding the level of damage or instability of a battery is critical for safe military applications. This work examines the application of accelerated rate calorimetry (ARC) and electrochemical impedance spectroscopy (EIS) to detect critical markers of unstable conditions and identify the onset of instability. These onset conditions and markers were then used to evaluate the stability and safety risk of a battery. Determining onset conditions and electrochemical symptoms of instability would allow LIBs to be adopted in demanding military applications, which may require exceeding manufacturer-recommended operating temperatures and conditions for short durations. A series of heating experiments coupled with EIS studies were used to identify indicators of battery instability. These indicators were then used to evaluate the TR in a battery module and its effect on the stability of surrounding batteries.

1.1 Project Purpose and Objectives

1.1.1 Purpose

This project seeks to better understand and characterize (1) the degradation processes of LIBs that develop at elevated temperatures and progress to TR, (2) determine the effectiveness of battery design features for achieving safe and high performing battery designs.

The purpose of this project was to investigate characteristic parameters of TR in LIBs for improving their safety. Ultimately, the aim was for these parameters to aid in the design of a BMS that reduces the risk of TR by detecting critical onset conditions. Furthermore, these critical indicators were used in assessing the design requirements of a prototype module to prevent TR propagation.

1.1.2 Objectives

The key questions that this project aims to address, concerning the safety concerns of individual Li-ion cells are:

- Does the cell pose a thermal hazard?
- When does self-heating begin and at what temperature is the cell at risk of suffering from TR?
- Are there electrochemical changes that can indicate cell failure?
- When should cells be considered a safety risk?

The second main objective of this report was to evaluate the TR propagation of the battery module:

- How to best initiate TR in a single cell within the battery module?
- Are surrounding cells within the module at risk of TR propagation?

This work should lead to enhanced perspectives on LIB failure and safety, at the individual cell level and modular level.

1.2 Scope and Limitations

The scope of this master thesis is to study the thermal behavior of LIBs and identify key indicators of TR and evaluate the stability of individual cells in the module. The aim is to gain a deeper understanding of LIB safety and their behavior through correlating EIS and ARC results, possibly leading to improved BMS and higher reliability and safety of LIB for demanding applications. This project is limited to commercially available cylindrical 21700 and 26650 LIBs from battery producers Samsung SDI and A123 systems.
2 Background

This section covers the basic operating principle and cell components of LIBs and is followed by a review of their thermal and safety characteristics. The section ends with a review of prior studies made on characterizing the thermal runaway features of LIBs.

2.1 Lithium-ion Battery Chemistry

A LIB cell consists of two electrodes of different potentials immersed in an electrolyte solution and electrically separated by a Li+ ion-permeable separator (Figure 2b). Cylindrical cells generally contain a cell layer which is spirally wound and housed in an outer cylinder, and commonly called a “jelly roll” (Figure 2a). The working principle of a LIB involves Li+ ion charge transfer between the electrodes and reversible Li+ storage within the electrode materials. The main difference between conventional batteries (galvanic cells) and LIBs is the mass transfer of Li+ ions within the electrode and an accompanied structural and chemical change of the electrode material. While the redox reactions in conventional galvanic cells occur simultaneously on the surfaces of the electrodes. The positive and negative electrodes are intercalation materials which during operation reversibly remove or insert Li+ ions into the electrodes structure. Intercalation electrodes are layered host structures that retain most of their layered structure during Li+ ion insertion and extraction. Copper and aluminum foil are commonly used as current collectors and attached to either the positive electrode (Al) and the negative electrode (Cu) to facilitate electron transport [1]. During the discharge process as shown in Figure 2a-b, the negative electrode material is oxidized through the following reaction:

\[
\begin{align*}
\text{Li}_y\text{C} & \xrightarrow{\text{Discharge}} \text{C} + y\text{Li}^+ + ye^- \\
\end{align*}
\]

Where the carbon negative electrode is represented by C and the Li+ ions are extracted from its structure. The electrolyte provides a conductive medium for the diffusion of Li+ ions, which migrate to the positive electrode where they are intercalated into the positive electrode material through the following reaction:

\[
\begin{align*}
\text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe^- & \xrightarrow{\text{Discharge}} \text{LiMO}_2 \\
\end{align*}
\]

Where, LiMO2, represents a layered positive electrode intercalation material, and M, represents various compositions of different transition metals (M = Ni, Mn, and Co). Electrons from the negative electrode are directed to the Cu current collector and shuttled to an external circuit to do work and recombining at the positive electrode through a reduction reaction.
2.1.1 Electrolytes

The electrolyte solution is a key component of LIB, serving as a bridge for the charge transfer of Li\(^+\) ions to move between the electrodes. The electrolyte is an ionically conductive material, in the form of a liquid solvent or polymer, with a dissolved lithium salt, e.g., LiPF\(_6\). Polymer electrolytes offer improved safety when compared to liquid-based electrolytes, due to polymer electrolytes being less volatile and more stable at elevated temperatures. However, the main disadvantage of polymer electrolytes is generally their lower ionic conductivity relative to liquid electrolytes [1]. This project focuses on liquid electrolyte of commercial Li-ion cells, which is predominately various mixtures of organic solvents, such as carbonate esters, e.g., ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). These solvents dissolve relative high concentrations of lithium salts, of which lithium hexafluorophosphate, LiPF\(_6\), is most commonly used. Electrolyte solvents are often mixtures to obtain favorable properties such as mixing the viscous (solid at room temperatures), high ionic dissociation, and cyclic EC with low viscosity, low relative permittivity, linear EMC to obtain favorable conductivity (aid salt dissociation) and diffusivity (lower viscosity) of Li\(^+\) ions [8].

The electrochemical window of carbonate esters/LiPF\(_6\) electrolyte solutions makes them unstable at positive electrode potentials higher than roughly 4.3 V vs. Li/Li\(^+\) at room temperature [9], [10]. Oxidative decomposition of the electrolyte during overcharging increases the cell’s impedance, reduces capacity, and lowers the onset temperature of self-heating reactions that may lead to TR [3].

The choice of lithium salts is more limited due to the requirement that they need to be resistant to decomposition over time while limiting the corrosion potential of the aluminum collector at the positive electrode. LiPF\(_6\) is widely used due to its high ionic mobility and passivation of the aluminum collector. However, LiPF\(_6\) is hygroscopic, costly, and produces hydrofluoric acid HF\(_{(g)}\) in the presence of water. Furthermore, LiPF\(_6\) thermally decomposes at elevated temperatures about 190-225 °C and reactions with PVDF binder and lithiated graphite to produce HF\(_{(g)}\) among other flammable and toxic gases [11], [12]. HF\(_{(g)}\) is corrosive and toxic and can easily be absorbed via the skin [13].
2.1.2 Positive Electrodes

A majority of commercial positive electrode materials for BEVs are based on lithium cobalt oxide (LCO), LiCoO$_2$ electrode chemistry: layer structured electrodes with Co-based mixtures of varying Ni, Mn, Co, and Al compositions, such as nickel-rich layered lithium nickel manganese cobalt (NMC), LiNi$_x$Mn$_y$Co$_z$O$_2$ (with $x + y + z = 1$) and lithium nickel cobalt aluminum (NCA), LiNi$_{x}$Co$_{y}$Al$_{z}$O$_2$[14]. The capacity is generally dependent on the Ni and Co content, while Mn provides structural and thermal stability[15], [8]. A decrease in thermal stability is seen with increasing Ni and Co content[16]. The NMC and NCA positive electrode materials have gain popularity with the rise of BEVs and the Ni content has gradually increased with growing energy and power demands[17]. However, the increased reactivity of Ni-rich electrodes reduce thermal stability and pose a higher safety risk. Li-rich positive electrodes, such as spinel structured lithium manganese oxide (LMO), LiMn$_2$O$_4$ and olivine structure lithium iron phosphate (LFP), LiFePO$_4$ are other commercialized positive electrode adopted by EV manufacturers, e.g., Nissan Leaf, BMW i3, Chevrolet volt use a blend of LMO and NMC, while the LFP/graphite cells have been implemented in Formula 1 hybrid-engines among other energy storage applications[1]. LFP is characterized by high thermal stability attributed to limited oxygen release during high-temperature decomposition, while typically offering lower capacity than other Ni-rich positive electrodes [18]. Table 1 shows the gravimetric capacity of different positive electrode chemistries and their mean operating potential versus lithium.

### Table 1. Positive electrode chemistries and their energy characteristics [17].

<table>
<thead>
<tr>
<th>Positive electrode chemistry</th>
<th>Gravimetric capacity (mAh/g active material)</th>
<th>Mean operating potential (V vs. Li/Li$^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LCO), LiCoO$_2$</td>
<td>155</td>
<td>3.8</td>
</tr>
<tr>
<td>(NCM111), LiNi$<em>{1/3}$Co$</em>{1/3}$Mn$_{1/3}$O$_2$</td>
<td>150</td>
<td>3.8</td>
</tr>
<tr>
<td>(NCM622), LiNi$<em>{0.6}$Co$</em>{0.2}$Mn$_{0.2}$O$_2$</td>
<td>170</td>
<td>3.8</td>
</tr>
<tr>
<td>(NMC811), LiNi$<em>{0.8}$Co$</em>{0.2}$Mn$_{0.1}$O$_2$</td>
<td>200</td>
<td>3.8</td>
</tr>
<tr>
<td>(NCA), LiNi$<em>{0.8}$Co$</em>{0.15}$Al$_{0.05}$O$_2$</td>
<td>220</td>
<td>3.6</td>
</tr>
<tr>
<td>(LMO), LiMn$_2$O$_4$</td>
<td>147</td>
<td>3.8</td>
</tr>
<tr>
<td>(LFP), LiFePO$_4$</td>
<td>170</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Using differential scanning calorimetry (DSC), Xiang et al., [19] investigate the thermal stability of 1 M LiPF$_6$ dissolved in an EC:DMC (1:1 w/w) solvent with LCO, NCA, NMC111, LMO, and LFP positive electrode materials, and found that all except LFP promotes the exothermic decomposition of the electrolyte by releasing oxygen. The onset temperatures of the decomposition began at 110, 146, 168, 176, 218 °C for LMO, NMC111, LCO, NCA, and LFP electrodes, respectively. Although a relatively early onset temperature was observed for LMO, the exothermic reactivity is more moderate. Comparably, Wang et al., [20] compared the thermal stability of LCO, NCA, and NMC111 in 1 M LiPF$_6$ 1:1 EC:DEC solvent from ARC measurements, and found that NMC111 had better thermal stability compared to both LCO and NCA. Indicating a increasing thermal stability of the different positive electrodes in the order LCO < NCA < NMC811 < NMC622 ≈ NMC111 < LMO < LFP [19], [9], [20].
2.1.3 Negative Electrodes

The most common negative electrodes are various forms of graphite-based intercalation materials due in part to their high conductivity and low intercalation potential around 0 V vs. Li/Li⁺. The low intercalation potential of graphite-based negative electrodes decomposes the organic electrolyte used in LIB during the initial charging cycles of the cell due to its reduction potential of 1.0 V vs. Li/Li⁺. The decomposition products form a surface layer called the solid electrolyte interphase (SEI) on the graphite-based electrode. The SEI provides a passivating layer that reduces the decomposition rate while allowing reversible Li⁺ ion intercalation. The formation reactions of the SEI layer consume lithium, affecting the capacity of the battery [1].

Wang et al. [11], studied the exothermic decomposition of the SEI layer of lithiated graphite and 1 M LiPF₆ EC:DMC at elevated temperatures and found that the exothermic reactions of the SEI layer initiate as early as 61 °C and peaked around 100 °C relatively independent of lithium content. ARC studies by Richard and Dahn [21] measured the thermal stability of lithiated mesocarbon microbeads (MCMB) in LiPF₆ EC:DEC and observed exothermic reactions between the SEI and electrolyte at 70-80 °C. Exothermic reactions between fluorinated binders, PVDF, used with graphite-based negative electrode material and common electrolytes begin around 200 °C [3], [11].

2.1.4 Separators

One of the most crucial safety components of the cell is its separator. The purpose of the microporous separator is to separate the positive and negative electrode materials and current collectors while facilitating the transport of Li⁺ ions to either electrode via the electrolyte. Contact between the electrodes or current collectors from a local or widespread failure of the separator leads to ISC within the cell. Separators can fail from mechanical deformation such as separator rupture or puncture, or losing their structural integrity at elevated temperatures [22]. Most commercially available separators for small cylindrical LIB are single or multilayer microporous sheets of polyethylene (PE) and polypropylene (PP) with a high degree of porosity (≥40%) [23]. ARC studies by [24], found that cylindrical 18650 cells with separators consisting of PE melted between 117-122 °C, while DSC measurements by [23] observed melting temperatures between 130-140 °C for PE separators and around 160-170 °C for PP separators. Multilayer separators of PE and PP are known as thermal shutdown separators due to the lower melting temperature of the PE layer filling the pores of the PP layer at temperatures below the onset of thermal runaway. Thus, shutting down the operation of the cell as the resistance to Li⁺ ion charge transfer is significantly increased.
In summary, the process of TR in LIBs is typically defined by several exothermic reactions that proceed above a critical temperature. The self-heating reactions that lead to TR occur in three main phases determined by the onset of decomposition reactions:

1. The first degradation reaction that causes self-heating of the cell begins with the solid electrolyte interphase (SEI) layer decomposing at around 80 °C and initiates self-heating of the cell [21]. The protective attributes of the SEI layer are reduced and the graphite-based negative electrode material reacts with the electrolyte near 125 °C [19].
2. The polymer separator melts between 120 °C - 165 °C, leading to internal short circuits and critical heat generation [23].
3. At temperatures above 225 °C, the positive electrode materials start to decompose, leading to oxygen gas formation that can react with the electrolyte and generate additional heat [19].

Table 2. summarizes the onset temperatures of the exothermic reactions of common LIB chemistries.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Onset Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive electrode and electrolyte [19]</td>
<td>110–218</td>
</tr>
<tr>
<td>Positive electrode decomposition [19]</td>
<td>&gt;225</td>
</tr>
<tr>
<td>Electrolyte decomposition [19]</td>
<td>202</td>
</tr>
</tbody>
</table>

### 2.2 Safety Features of Lithium-ion Batteries

Due to a greater surface to volume ratio, cylindrical cells have better external heat transfer properties than larger prismatic or pouch cell. In addition to more uniform temperature distribution within the cell and smaller cylindrical batteries typically contains less stored electrochemical energy than larger prismatic or pouch cells. Nevertheless, several safety features are integrated within individual cylindrical cells to prevent unsafe heat generation and reduce the risk of TR, such as current interrupt devices (CID), positive temperature coefficient (PTC) devices, and flame retardants [18]. These safety features are integrated to avoid cell overload from charging or discharging and other abusive conditions. Two identifiable safety features common to LIBs are:

- The current interrupt device (CID) (Figure 3) is a vent-disk that limits the operation when activated due to built-up gas pressure inside the cell. The main function of the CID is to disrupt the electrical connection at one of the cell terminals during overcharge or high current flows that increase the volatility of the electrolyte [1].

- The PTC current limiting device consists of electrically conductive materials that sharply increase their resistance at elevated temperatures. Similar to the CID, it activates from an increase in the temperature. For example, resistive heating from large current rates increases the resistance of the PTC material when the temperature reaches a critical threshold value. Reducing the current flow and limiting further heating. Unlike the CID, once the temperature cools the PTC deactivates as its resistance decreases to normal operating conditions [1].
Figure 3a shows an X-ray image of the positive terminal of a cylindrical Samsung INR18650 25R cell. Illustrating the position of the CID vent disk. Figure 3c illustrates the current path during normal operation, from the positive electrodes via an unactivated CID to the positive terminal button. The connection is disrupted when sufficient internal pressure forces the CID vent disk to disconnect the positive terminal from the cell, as shown in Figure 3d. A non-conducting spacer material between the CID vent disk and positive electrode connection disrupts the connection when the CID activates. An Exploded-view of the integrated safety device within the positive terminal is shown in Figure 3b. The Crimp plate and CID connector have holes to allow an increase in internal gas pressure of the cell to force the CID vent disk to disconnect the terminal.

Figure 3. a) X-ray image of the positive terminal of a Samsung INR18650-25R power cell showing the position of the CID vent disk b) Exploded-view of the integrated CID safety device, modified from [25], c) cross-cut drawing of a positive terminal with an unactivated CID and indicated current path, d) Illustration of the CID vent disk mechanism initiated by built-up internal gas pressure inside the cell, modified from [1].

Safety features at the module level are similar in that the main criteria for reducing the potential of TR are limiting the heat generation rate. Nevertheless, internal LIB safety features and thermal management controls may work properly, but the heat generation rate may be too rapid for the system to alarm or react to the conditions. Therefore, the structural design of the battery module is a safety design feature that prevents mechanical and thermal failure of the cells [12].
### 2.3 Literature Overview

A summary table of ARC experiments conducted on 18650 cells with NCM, NCA, LCO, LMO, and LFP chemistries are presented in Table 3. The table lists the specifics of the test cells used in the experiment and lists characteristic temperatures extracted from ARC experiments.

Table 3. Literature summary of accelerating rate calorimetry and electrochemical impedance measurements of thermal runaway.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Cell type</th>
<th>Electrodes (positive/negative)</th>
<th>Capacity (Ah)</th>
<th>Calorimeter</th>
<th>EIS</th>
<th>SOC (%)</th>
<th>Onset temperature of self-heating (°C)</th>
<th>Separator melting temperature (°C)</th>
<th>Explosive venting temperature (°C)</th>
<th>Max. temperature (°C)</th>
<th>Heat of reaction (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Cylindrical</td>
<td>NMC LFP</td>
<td>4-5</td>
<td>EV-ARC</td>
<td>10kHz-1Hz</td>
<td>100</td>
<td>~120</td>
<td>137-141</td>
<td>~120-140</td>
<td>~170</td>
<td>~590</td>
</tr>
<tr>
<td>Nguyen et al. [24]</td>
<td>Cylindrical</td>
<td>NMC811/graphite-SiOₓ</td>
<td>3.0</td>
<td>ARC</td>
<td>50,</td>
<td>90</td>
<td>117</td>
<td>165</td>
<td>~615</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18650</td>
<td>NCA/graphite-SiOₓ</td>
<td>3.45</td>
<td></td>
<td>100</td>
<td>122</td>
<td>122</td>
<td>171</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhao et al. [26]</td>
<td>Cylindrical</td>
<td>NMC523/graphite</td>
<td>2.0</td>
<td>EV-ARC</td>
<td>25-100</td>
<td></td>
<td></td>
<td>~170</td>
<td>728</td>
<td>~23</td>
<td></td>
</tr>
<tr>
<td>Lei et al. [27]</td>
<td>Cylindrical</td>
<td>NMC LFP LMO</td>
<td>2.2</td>
<td>ARC</td>
<td>100</td>
<td>91</td>
<td>90</td>
<td>−</td>
<td>731</td>
<td>24.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18650</td>
<td></td>
<td>1.1</td>
<td></td>
<td></td>
<td>90</td>
<td>−</td>
<td>−</td>
<td>259</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.65</td>
<td></td>
<td></td>
<td>91</td>
<td>−</td>
<td>−</td>
<td>303</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Jhu et al. [28]</td>
<td>Cylindrical</td>
<td>NMC111 LCO</td>
<td>2.0</td>
<td>ARC</td>
<td>100</td>
<td>175</td>
<td>137</td>
<td>250</td>
<td>666</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18650</td>
<td></td>
<td>2.6</td>
<td></td>
<td></td>
<td>131</td>
<td>−</td>
<td>180</td>
<td>709</td>
<td>18.9</td>
<td></td>
</tr>
<tr>
<td>Feng et al. [29]</td>
<td>Prismatic</td>
<td>NMC</td>
<td>25</td>
<td>EV-ARC</td>
<td>100</td>
<td>85-105</td>
<td>~130</td>
<td>−</td>
<td>−584</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>Ishikawa et al. [30]</td>
<td>Cylindrical</td>
<td>LCO/carbon</td>
<td>2.55</td>
<td>ARC</td>
<td>1 kHz</td>
<td>100</td>
<td>110</td>
<td>118</td>
<td>133</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Mohamedi et al. [31]</td>
<td>Prismatic</td>
<td>LCO</td>
<td>0.5</td>
<td>ARC</td>
<td>25-130°C</td>
<td>0-100</td>
<td>−</td>
<td>133</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Zappen et al. [32]</td>
<td>Pouch</td>
<td>NMC</td>
<td>3.3</td>
<td>ARC</td>
<td>1 kHz-1Hz</td>
<td>95</td>
<td>−</td>
<td>128</td>
<td>&gt;550</td>
<td>−</td>
<td></td>
</tr>
</tbody>
</table>
3 Method and Theory

3.1 Tested Lithium-ion Batteries

Commercially available cylindrical format LIBs from Samsung SDI and A123 Systems were supplied by FOI. Two Samsung SDI LIBs with the 21700 standardized shape format (diameter 21 mm and a length of 70 mm) and NMC positive electrodes (Figure 4a-b). An LFP positive electrode LIB from A123 systems with a shape factor of 26650 (diameter 26 mm and a length of 65 mm) (Figure 4c). The two Samsung SDI INR21700 batteries with NMC positive electrodes are marketed and optimized as energy cells and power cells for the model 50E (Figure 4a) and 40T (Figure 4b), respectively. The Samsung SDI batteries have a charging cut-off voltage of 4.2 V and 3.6 V for the LFP-based A123 cell. Supplier specifications and the abbreviations used for each cell throughout this report are listed in Table 4.

![Figure 4. Shows the selected cell in this project: (a) Samsung SDI INR21700-50E, (b) Samsung SDI INR21700-40T, (c) A123 Systems ANR26650m1-B](image)

Table 4. Battery characteristics of the selected cells

<table>
<thead>
<tr>
<th>Battery Characteristics</th>
<th>INR21700-50E, Samsung SDI [33]</th>
<th>INR21700-40T, Samsung SDI [34]</th>
<th>ANR26650m1-B, A123 Systems [35]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>S50E</td>
<td>S40T</td>
<td>LFP</td>
</tr>
<tr>
<td>Cell mass (g)</td>
<td>69 g (70 g max)(^1)</td>
<td>67 g (69 g max)(^1)</td>
<td>75 g (76 g)(^1)</td>
</tr>
<tr>
<td>Nominal Voltage (V)</td>
<td>3.6</td>
<td>3.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Minimum/Cutoff Voltage (V)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Maximum Voltage (V)</td>
<td>4.2</td>
<td>4.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Nominal Capacity (mAh)</td>
<td>&gt;4,900 @ (0.2 C)</td>
<td>4,000 @ (0.2 C)</td>
<td>2,500 @ (0.5 C)</td>
</tr>
<tr>
<td>Rated Capacity (mAh)</td>
<td>&gt;4,753 @ (1.0 C)</td>
<td>&gt;3,900 @ (2.5 C)</td>
<td>2,400 @ (50 C)</td>
</tr>
<tr>
<td>Max. continuous discharge current (A)</td>
<td>9.8</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>(^2)Internal resistance (mΩ)</td>
<td>≤ 35</td>
<td>≤ 12</td>
<td>≤ 6</td>
</tr>
<tr>
<td>Heat capacity (kJ kg(^{-1}) K(^{-1}))</td>
<td>0.896</td>
<td>0.896</td>
<td>0.896</td>
</tr>
<tr>
<td>Positive Electrode</td>
<td>NMC</td>
<td>NMC</td>
<td>LFP</td>
</tr>
</tbody>
</table>

\(^1\)The manufacturer specified cell mass. \(^2\)The manufacturer specified internal impedance measured at 1 kHz AC after standard charge.
3.2 Calorimetric Studies

3.2.1 Accelerated Rate Calorimetry

Investigations into the critical degradation process at elevated temperatures were conducted using ARC. The ARC was designed to study exothermic reactions by heating a sample in a closed adiabatic environment until self-sustaining thermal runaway conditions. The ARC provided a method of investigating cells during a thermally worst-case scenario, where minimal heat is lost to the environment from the self-heating decomposition reactions of the cell. An ARC approximates an adiabatic environment by matching the temperature between the calorimeter and cell sample and insulating them from the environment. Minimizing the temperature gradient reduces the driving force for heat transfer. Therefore, the heat produced by a LIB confined in the calorimeter causes the cell to increase in temperature until all reacting components are consumed. A pressure-resistant “bomb” container is necessary to gather data on the pressure rise from the cell venting or rupturing due to gas evolution from decomposition reactions, electrolyte vaporization, or combustion [24]. Ultimately, the purpose of an ARC test is to collect time data on the temperature and the pressure change during the thermal runaway process.

The ARC operates in a heat, wait, search (HWS) mode to determine the onset of self-heating, and the flow diagram is shown in (Figure 5). The test cell is initially ramped to a set starting temperature then heated in a series of heating steps where the ARC increases the temperature in incremental steps of 5 °C followed by waiting period [27]. The ARC enters a wait phase where it monitors the temperature difference between the cell thermocouple and the top, bottom, and sidewall thermocouples controlling the heating elements in their respective zones. The waiting phase allows the thermocouples to approach an isothermal equilibrium.

After the waiting phase, an adiabatic environment is maintained by closely matching the test cell and calorimeter temperatures (±0.01°C), called the search or seek phase. If exothermic activity is detected at a set temperature rate, referred to as the detection sensitivity, the adiabatic environment is maintained and the self-heating exothermic phase begins, and the instrument tracks and logs the cell temperature. The temperature difference between the cell and calorimeter is minimized by matching the calorimeter temperature to the cell temperature as it increases. If self-heating is not detected or the self-heating rate falls below the detection value, The HWS operation repeats and enters the heating mode the next temperature plateau. The HWS operation stops at a specified end temperature and the ARC continues to track the exotherm until the end of TR.
Figure 5. Illustration of the heat, wait, and search mode (HWS) for adiabatic testing with a temperature step of 5 °C. Schematic representation modified from [27] and expanded with [24].

The ARC provides tabulated time data such as:

- The cell surface temperature
- The bomb pressure and temperature
- Self-heating rate of the LIB (°C/min)

From this data, it is possible to determine the onset temperatures characteristic of TR.

- The onset temperature of endothermic reactions, $T_{\text{end}}$.
- The onset temperature of self-heating, $T_{\text{exo}}$. At this point, the reaction is self-sustaining in a near-adiabatic environment as the cell is not able to dissipate the heat generated.
- The onset temperature of cell venting, $T_{\text{vent}}$.

In the ARC test, an exothermic reaction will be detected at a specific onset temperature. However, the sensitivity of the test is influenced by the heat step size, heating rate sensitivity, and the heat capacity and mass of the cell and bomb. Due to a heating increment setting of 5 °C during the heating phase, the onset temperature of self-heating during the search phase is within the 5 °C increment. For example, the true onset temperature may be slightly above the previous heat step and only recorded after the next (HWS) 5 °C heating increment. Thus, the true onset temperature would be within the 5 °C increment [36]. The temperature rate sensitivity influences the detection of self-heating. Isothermal aging of the cell can affect the onset temperature [37]. ARC experiments can take several days to reach TR conditions while methodically heating the test cell and monitoring for exotherms.
The ARC experiments have the following assumptions:

1. Negligible heat exchange with the calorimeter's surroundings.
2. Heat losses are entirely absorbed and held within the bomb canister walls and air space.
3. The cell is temperature is uniform and any temperature gradients throughout the inside and surface are negligible.

The first assumption is based on the minimal temperature gradient between the calorimeter and test cell controlled by the ARC heaters and the insulation provided by the calorimeter assembly. The second assumption accounts for the heat loss to the bomb container and the air surrounding the test cell. This is referred to as thermal dilution which limits the adiabatic temperature rise and self-heat rate of a cell test in a nonlinear fashion [36]. Exotherm heating rates are detected at higher temperatures in test cells contained within a bomb of significant thermal mass to absorb some of the reaction heat. The effect of thermal dilution is illustrated in Figure 6. Where no heat is lost to the surroundings, the temperature profile of an ideal-adiabatic environment (A) flattens out at its maximum value. A near adiabatic environment results in some heat loss as shown by line (B). As more heat is lost, the temperature profile decreases as seen by profile (C) to profile (D) were all heat lost to the surrounding. For comparison, Figure 7 shows the near-adiabatic temperature profile of an actual ARC experiment.

![Figure 6. Simplified drawing of the temperature profiles from different systems: a) Ideal-adiabatic, b) Near-adiabatic, c) Non-adiabatic, d) Isothermal.](image)

![Figure 7. Temperature profile produced from the ARC showing the HWS operation.](image)

The third assumption is based on the dimensionless Biot number, which estimates the temperature uniformity within the body of the cell and at its surface. A small Biot number, much less than 0.1, assumes a near-uniform temperature throughout the whole cell and surface. The equation for the Biot number for a cylinder is given as follows:

$$Bi = \frac{R h}{2k}$$  \hspace{1cm} (3)

Where $R$ is the radius of the cylindrical cells, $h$ is the total surface heat transfer coefficient which includes the combined heat dissipation due to conduction, convection, and radiation (7.17 W m$^{-2}$ K$^{-1}$) [38], and $k$ is the combined thermal conductivity (3.4 W m$^{-1}$ K$^{-1}$) of the multiple layers of current collectors, electrodes, separators, and the electrolyte within the cylindrical steel housing. The resulting Biot number for the cells in Table 4 was approximately 0.02 – 0.03, which warrants the assumption that no heat accumulation inside the cell occurs during heating and motivates that the cell surface temperature measurements are a valid representation of the internal cell components temperature.
Due to the assumption of uniform temperature within the cell, the time rate of the temperature of the cell can be expressed as Equation 4.

\[
\frac{dT(t)}{dt} = \frac{Q(t)}{mC_p}
\]  

(4)

The heat energy rate generated by the TR cell is given as \( Q \) (W), where \( m \) (kg) is the mass of the cell, and \( C_p \) is the specific heat capacity of the cell (0.896 kJ kg\(^{-1}\) K\(^{-1}\)) [36]. In an adiabatic system without a bomb container, all the exothermic heat energy goes to the adiabatic temperature rise. Thus, Equation 4 is simplified as follows:

\[
Q_{TR} = mC_p\Delta T_{ad}
\]  

(5)

Where \( Q_{TR} \) (J) is the total heat energy released during TR heat generation, \( C_p \) is the specific heat capacity and assumed to be constant during the test, and \( \Delta T_{ad} \) is the adiabatic temperature rise from the onset of exothermic reactions until the end of heat addition. Equations 4 and 5 were used to estimate the total heat released by the cell during TR and the heat lost to the surrounding air space within the bomb container.
3.2.1.1 Experimental setup

A series of calorimetric measurements were conducted using an extended volume ARC (EV-ARC) manufactured by Thermal Hazard Technology. The EV-ARC consists of the outer blast chamber that holds the calorimeter assembly (Figure 8a). The calorimeter assembly is surrounded by insulation and contained within a safety enclosure, called the blast chamber, which protects against high temperatures, pressures, and offers additional protection when the test cell vents flammable, corrosive, and toxic gases. The sample container is called the bomb, as it is designed to withstand the explosive decomposition of a lithium-ion cell. The bomb (Figure 8d) is constructed out of steel, has a mass of roughly 1.9 kg with a specific heat capacity of 0.46 kJ kg$^{-1}$ K$^{-1}$, and an internal volume of 1.2 dm$^3$. Figure 8c shows the ports designed for inserting thermocouples: the ARC controlling N-type thermocouple to measure the surface temperature of sample cells, and the K-type thermocouple to record the bomb temperature is shown. The thermocouples used in this work are class 1 tolerance K-type and N-type, with accuracies around ±1.1 °C and ±0.004 × T (°C) at temperatures above 275 °C. The port in Figure 8b is used to connect the pressure transducer. The rest of the unused ports were sealed. The calorimeter assembly contains several heaters surrounding the sample container which are regulated by thermocouples in each heating zone: top, bottom, and sidewall heaters. The calorimeter temperature is controlled by the sample thermocouple attached to the surface of the cell. The thermocouple was placed 2 cm below the positive terminal for all tests. The electrically insulating plastic wrap was removed from the cell. The bomb was initially filled with atmospheric air. The large access hole for inserting cells into the bomb was sealed with a Viton O-ring and silicone oil to ensure a good seal without leakage during tests.

![Figure 8. a) calorimeter assembly within the blast chamber, b) simplified drawing of the ARC assembly, depicting the ARC heaters, bomb, and cell sample, c) illustrates the thermocouples and pressure transducer, d) shows an open bomb container with a test cell inside.](image-url)
At least two duplicate ARC measurements were conducted for each cell described in Table 4. The settings used for the ARC trials are given in Table 5. Initially, the ARC was set to heat the cell to a starting temperature of 50 °C. The wait time was set to 40 min for the S40T and S40E cells to improve the precision in detecting onset conditions. The LFP cells were subjected to a lower waiting period of 30 min due to the time required to reach a higher temperature and possibly induce TR in the cells. The exothermic detection rate was set to the manufacturer’s recommended specification for LIB tests. The end temperature was set to 250 °C for the S40T and S50E and 350 °C for the LFP cells. The thermal stability of the LFP cells and the difficulty in inducing TR in prior ARC measurements at FOI warranted a higher end temperature for the LFP cells relative to the other cells.

Table 5. Experimental ARC parameters

<table>
<thead>
<tr>
<th>Settings</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Wait time</td>
<td>40 min (S40T and S50E), 30 min (LFP)</td>
</tr>
<tr>
<td>Detection sensitivity</td>
<td>0.02 °C/min</td>
</tr>
<tr>
<td>End Temperature</td>
<td>250 °C (S40T and S50E), 350 °C LFP</td>
</tr>
</tbody>
</table>

3.2.2 Differential Scanning Calorimetry

A ramp heating test was conducted by DSC to investigate the thermal behavior of the separator and how it influences the thermal runaway characteristics. Separators were extracted from fully discharged S40T cells. The polymer separator samples (1–2 mg) were loaded into an aluminum pan and heated from 20 °C to 170 °C at a heating rate of 10 °C/min and 0.2 °C/min under flowing nitrogen gas. The DSC parameters used are presented in Table 6.

Table 6. Experimental DSC parameters

<table>
<thead>
<tr>
<th>Settings</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate</td>
<td>10 K/min⁻¹ and 0.2 K/min⁻¹</td>
</tr>
<tr>
<td>Temperature range</td>
<td>20-170 °C</td>
</tr>
<tr>
<td>Inert gas</td>
<td>N₂, flow rate: 80 cm³ min⁻¹</td>
</tr>
<tr>
<td>Sample pan</td>
<td>Al 4 ul</td>
</tr>
<tr>
<td>Test sample</td>
<td>1-2 mg sample weight</td>
</tr>
</tbody>
</table>
3.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an analytical technique that quantifies the impedance by capturing the response of an applied sinusoidal wave of sequentially changing frequencies. As previously mentioned, LIBs are composed of current collectors, electrodes, electrolyte, and a separator. Each of the cell components is characterized by various electrochemical, ionic, charge transport and thermodynamic processes, etc. These processes have resistive, capacitive, and inductive properties that impede current flow as electrons and lithium ions interact with components of a cell during operation, and EIS can separate and quantify these different processes [39].

EIS applies a sinusoidal wave of changing frequencies that drives the cell away from its open-circuit value and monitoring the response at the different frequencies. During EIS, the frequency dependence of different electrochemical processes within the cell are probed by changing the frequency of the alternating current (AC). As a result, the frequency response of different components of the cell can be separated from the total response.

EIS can be applied in the following modes:

1) Potentiostatic EIS (PEIS) derives the impedance by monitoring the current response when applying an alternating potential perturbation across a frequency range.
2) Galvanostatic EIS (GEIS) derives the impedance by monitoring the potential response when applying an alternating current across a frequency range.

GEIS is widely used in studies of batteries due to their low internal resistance and the ability to control charge/discharge currents. In PEIS, the potentiostat/voltage controller operates at a fixed potential with a small perturbation added. A small error in measuring the OCV results in an offset. For a low resistance cell, such as for batteries in the order of mΩ, a small error in the OCV may result in large current flow, which could damage or age the cell and whether the resulting current charges or discharges the cell is unknown. PEIS and GEIS experiments usually produce equivalent results. However, if the experimental conditions evolve, e.g., with increasing temperature during an ARC experiment the OCV would change and may take a long time to reach a steady-state value [32]. This drift of the OCV would produce an error during PEIS, while OCV drift is commonly not a concern during GEIS as the current is controlled.

It is convenient to express the sinusoidal amplitude and frequency as a complex number to simplify solving differential equations using algebra. This is performed by converting trigonometric functions to exponential complex numbers using Euler’s Formula.
3.3.1 Impedance Theory

Impedance includes any phenomena of impeding current flow within the cell such as resistance, capacitance, and inductance. The impedance is characterized by the impedance magnitude, $|Z|$, which is the ratio in magnitudes of the applied AC signal and response wave, and the phase angle, which is the shift in phase between the current and potential. Ohm’s Law ($R = V/I$) as it is commonly seen, is defined for an ideal resistor where the resistance is independent of frequency and the current and voltage are in phase. Thus, Ohm’s Law for the impedance of an AC is similar in that it defines the relationship between the potential and current. The impedance, $Z(\omega)$, as a function of radial frequency in polar coordinates and the complex plane, is as follows:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = |Z| (\cos(\phi) + j \sin(\phi)) = Z_{Re} + j Z_{Im}$$  \hspace{1cm} (9)

Where $j$ denotes $\sqrt{-1}$ and the phase angle ($\phi$) at a particular radial frequency is the trigonometric ratio of the imaginary and real impedance components, see Figure 9b.

$$\tan \phi = \frac{Z_{Im}}{Z_{Re}}$$  \hspace{1cm} (10)

The real part of the impedance, $Z_{Re}$, is equal to $|Z| \cos(\phi)$ in polar coordinates, which describes the impedance of a resistor as it is independent of frequency ($\omega$). The current response to a change in the potential of an ideal resistor is immediate with no lag i.e, there is no phase shift ($\phi = 0$). Consequently, the real component of the impedance signifies the resistance of the cell during EIS measurements. The imaginary component of the impedance, $Z_{Im}$ is equivalent to $|Z| j \sin(\phi)$ in polar coordinates and describes the capacitive and inductive contributions of the impedance. Electrochemical cells generally have a capacitive contribution. The current and potential relationship of a capacitor depends on time. In other words, the charging and discharging of a capacitor is not an instant process. The current lags an applied potential with a certain phase shift or angle, $\phi$. Similarly, an inductive contribution is also time-dependent. These are described by the imaginary impedance component.

The EIS instrument performs a Fourier transform on the current and voltage at each frequency to obtain the magnitude of the impedance, $|Z|$, and the phase shift, $\phi$. A table of $|Z|$ and $\phi$ at different frequencies are generated and transformed to the complex variables $Z_{Re}$, and $Z_{Im}$.

Varying the signal frequency probes different electrochemical processes within the cell depending on the frequency. Following Equation 9, the potential response trails or lags the applied current in phase by the phase angle, $\phi$. A simplified diagram is shown in Figure 9a, which illustrates an EIS signal and the relationship between current and voltage. The voltage lags the current by, $\phi$, a negative phase shift, which implies a capacitive circuit. The relationships of the complex impedance in rectangular and polar coordinates, and how they depend on the magnitude and the phase angle is illustrated in Figure 9b.
Figure 9. a) simplified diagram illustrating the current and potential in radial frequency, \( \omega \). The voltage lags the current by, \( \phi \), in phase. b) Diagram showing relationships of the complex impedance in rectangular and polar coordinates, and how they depend on the magnitude and the phase angle. Illustrations modified from [40] and extended from [39].

The impedance spectrum can be represented in different ways, two common diagrams are:

- The Nyquist plot which represents the real and imaginary parts of the impedance using cartesian coordinates (Figure 10, left).
- The Bode plot shows the phase shift and the logarithm of the impedance magnitude and how they depend on frequency. (Figure 10, right)

Figure 10. (left) Nyquist plot representing the real and imaginary components of the impedance (m\( \Omega \)), (right) Bode plot showing the log of the magnitude of the impedance (\( \Omega \)) and phase angle (degrees) against the log of the frequency (Hz).

The advantage of the Bode plot is that it shows both the magnitude of the impedance and the phase as a function of the frequency. The phase shift at different frequencies is observable. The main drawback of the Nyquist plot is that it does not show the frequency dependence of the impedance components. However, it provides meaningful interpretations of the electrochemical phenomena and is often used to characterize LIB.
3.3.2 Equivalent Circuit Model

The impedance of a LIB is commonly modeled as a combination of ideal circuit elements called an equivalent circuit model (ECM). The impedance of the ideal circuit elements is given in Table 13 and described in the Appendix.

The aim is to construct a physically meaningful model, but an ECM is not based on physical parameters. Several ECM with varying arrangements of ideal circuit elements may provide a good fit with the impedance spectrum. Nevertheless, ECMs are widely used to represent the physical properties of electrochemical devices and their impedance spectra [40]. The parallel resistance (R) and capacitor (C) elements are the foundational building block of most ECM. Figure 11 shows an example of a resistor (R) in series with a parallel RC block. The series resistance accounts for the resistance of the lead cables, the contact resistance between the leads and terminals, between the electrodes and current collectors, and the sum of the electrode resistances of the cell [41], [40]. This element shifts the impedance spectra along the real impedance axis (Z_{Re}) in a Nyquist plot. An inductor is added in series with the circuit to account for the inductive impedance of the cables at high frequencies. The parallel RC element represents the impedance of the electrochemical double layer (C_{dl}) in parallel with the charge-transfer resistance (R_{ct}). The parallel RC element generally corresponds with the polarization of an electrochemical reaction and bulk electrolyte resistance [41]. In a Nyquist plot, the parallel RC element is analogous to the shape of the semi-circle shown in Figure 11a. The diameter of the semi-circle along the axis of the real component of the impedance signifies the resistance R_{ct}. The radius of the semi-circle indicates the C_{dl}, which is the point where |Z_{Im}| is at a maximum. A capacitance value C_{dl} can be calculated from the diameter of the semi-circle of the real impedance at the frequency where the imaginary component is at a minimum value (\omega_{(ImZ, min)}) [40], according to the following equation:

\[ \omega_{(ImZ, min)} = \frac{1}{R_{ct}C_{dl}} \]  

(11)

The line protruding from the semi-circle at a constant phase represents the impedance due to the diffusional mass-transfer of Li^{+} ion within the electrode material. This feature is commonly represented by a Warburg element which is based on Fick’s second law of diffusion [42]. Actual electrochemical cells are more complicated than the simple ECM constructed from ideal circuit elements shown in Figure 11b.
The electrochemical double layer between the electrode and electrolyte of actual cells is frequently represented by a constant phase element [43] [40]. This element accounts for the divergence from an ideal capacitor from the non-uniform surface characteristics of real electrodes. This can be seen in Figure 11, the semi-circle pictured is not entirely circular, a perfect semi-circle is represented by the arrow. It is then useful to model the impedance spectra with a constant phase element (CPE) in parallel with a resistor (R). The equivalent capacitance or pseudo-capacitance can be calculated when using a parallel CPE and R circuit instead of a parallel RC circuit. The calculation procedure follows Equation 11 but for a CPE element instead of the \( C_{dl} \) element, then this value is the solution to the following equation:

\[
\omega_{(\text{min})} = \frac{1}{R_{ct}C_{\text{PE}}} = \frac{1}{R_{ct}C_{\text{pseudo}}}
\]  

(12)

Where \( C_{\text{pseudo}} \) is then the pseudo-capacitance. The constant phase element has no physical meaning and calculating an equivalent capacitance provides quantifiable units for comparing different impedance spectra. Figure 12 shows the ECM widely used to analyze the EIS data from LIB [43], [30], [40], [31]. \( R_s \) accounts for the resistance of the lead cables, the contact resistance between the leads and terminals, between the electrodes and current collectors, and the sum of the electrode resistances of the cell [41], [40]. CPE1 and CPE2 are the constant phase elements representing non-uniform surface characteristics of real electrodes. \( R_{ct} \) is the charge transfer resistance, and \( Z_w \) is a constant phase element known as the Warburg element.

Figure 12. The ECM used to analyze the impedance spectra. Reproduced from [43], [30], [40], [31].
3.3.3 EIS Validity – Kramers-Kronig Criteria

The validity of measured impedance spectra requires that the system satisfies conditions of:

1. A linear system, which means that the relationship between the response to a sum of scaled inputs is the scaled and summed response to each input. e.g., the cell’s response to a current input is a scaled potential response. The linearity constraint is the reason why a small-amplitude excitation signal is commonly used in EIS. With a small excitation signal, the system is pseudo-linear and large nonlinear current/voltage responses are avoided.

2. A time-invariant system, the response does not depend on the time the input was applied.

3. A causal system where the response is caused by the input signal.

The Kramers-Kronig (KK) relation can be used to determine if the experimental impedance spectrum satisfies the above conditions or influenced by experimental errors. The KK relation is based on calculating the real or imaginary impedance of the measured spectrum from the opposite part. For example, calculating the real part of the impedance from the measured imaginary part and the other way around. The experimental data and the calculated impedance are then compared and inconsistencies between the results signify that the spectrum fails to satisfy the above requirements and no meaningful interpretation of the spectrum can be done.

The direct application of the KK relation involves integrating the real and imaginary impedance over an infinite frequency range. The experimentally measured frequency range of this work ranges from 10 kHz to 10 mHz for LIB diagnostic and baseline measurements at room temperature (18-20 °C) and 10 kHz to 1 Hz during high-temperature measurements. Thus, the limited frequency range is too narrow for the integration limits of the KK relation. However, the criteria can be checked by fitting an ECM that satisfies the KK criteria. The ECM shown in Figure 13, consists of n-number of series-connected parallel RC elements and reproduces the impedance response of an electrochemical system based on ideal circuit elements. An inductor is added in series with the circuit shown in Figure 13 to account for the inductive effects of the cables and connections at high frequencies. Thus, an accurate fit of the ECM to the experimental impedance spectrum then implies that the experimental spectrum also satisfies the condition of the KK relation [44].

Figure 13. A schematic representation of the equivalent circuit of a series of parallel RC elements.

The Matlab software tool LinKK provides KK test results of the relative deviation between the experimental and back-calculated impedance values.
3.3.4 Experimental Setup

The impedance was measured using a battery testing system (BioLogic BCS-815) with EIS capability. The EIS settings are provided in Table 7. *Experimental EIS parameters*. This project used GEIS to derive the impedance using a peak amplitude of 50 mA. Impedance measurements were performed in the frequency range 10 kHz to 10 mHz with 10 measuring points per decade for a total of 60 frequencies. The mean was taken of two repeat measurements at each frequency.

<table>
<thead>
<tr>
<th>Settings</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current peak</td>
<td>50 mA</td>
</tr>
<tr>
<td>Frequency range</td>
<td>10 kHz to 10 mHz</td>
</tr>
<tr>
<td>Measurement points</td>
<td>60</td>
</tr>
<tr>
<td>Repeated measurements</td>
<td>2 per frequency</td>
</tr>
<tr>
<td>Temperature</td>
<td>19 ± 1 °C</td>
</tr>
</tbody>
</table>

The experimental setup is shown in Figure 14. A two connection setup was used for all EIS measurements, where the current-carrying leads are also used for measurements. Each terminal is connected with two cables (either two red or two blue), and these are the lead and sensing wires. Copper wire was used to connect the terminals of the cells to the leads of the instrument to reduce the length of the cables. A screw clamp used to secure the terminal connections. A K-type thermocouple was used to monitor the temperature of the cell.

Figure 14. *EIS measurement setup with current and sensing leads connected at each terminal.*
3.4 Impedance During Calorimetry

EIS was implemented during ARC studies to correlate electrochemical changes with the thermal behavior of the S40T cell. The bomb container was modified to be able to connect the leads of the EIS instrument to the cell. Two copper rods with a length of 10 cm and a diameter of 4 mm were threaded on either end as shown in the left image of Figure 15. The middle section without thread was wrapped with Kapton tape to electrically isolate the copper rods from the steel bomb. The fastening nuts were isolated from the copper rod by polytetrafluoroethylene (PTFE) spacers. Copper wire was spot welded to the cell terminals and fastened to one end of each copper rod by tightening the nuts. The other end of the rods were connected with copper wire to the EIS Instrument cables. Kapton tape was used to isolate the positive terminal of the cell and the lead wires to avoid short-circuiting the cell.

The EIS settings during ARC test are given in Table 8. The EIS instrument was programmed to continuously perform an impedance scan in three-minute intervals to allow the cell to rest, but frequent enough to catch critical events during heating. The frequency range was set from 10 kHz to 1 Hz to avoid lengthy scanning rates at frequencies lower than 1 Hz so that each scan would take roughly 45 seconds to complete. The maximum heating rate of the ARC during HWS mode was 0.1 °C/min during heating steps. Thus, the cell temperature would fluctuate less than 0.1 °C during impedance measurements to satisfy the KK conditions of a time-invariant system. Two duplicate experiments were conducted on fully charge S40T cells (4.2 V). The cells were charged using a 0.5 C constant current (CC) and constant voltage (CV) charging protocol. A cut-off current of 1 mA was used during CV charging at 4.2 V to ensure the cells were fully charged.

<table>
<thead>
<tr>
<th>Settings</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Current peak</td>
<td>50 mA</td>
</tr>
<tr>
<td>Frequency range</td>
<td>10 kHz to 1 Hz</td>
</tr>
<tr>
<td>Measurement points</td>
<td>41</td>
</tr>
<tr>
<td>Time between measurements</td>
<td>3 min</td>
</tr>
</tbody>
</table>

Figure 15. (left) Shows the computer-aided drafts of the copper rod assembly, (middle) shows he installed copper rods (yellow circles) within the bomb, (right) shows the assembled bomb.
3.5 Module Experiments

A series of five TR propagation tests of the battery module developed at FOI were performed in this project. The module contains 19 batteries of the 21700 size and was designed to prevent TR propagation from cell-to-cell and module-to-module. It is important to note that the design specifications of the battery module are confidential and cannot be shown or disclosed in detail. However, the latest prototype LIB module designs by NASA feature several of the specific TR preventing design strategies implemented in the FOI module. The module by NASA [45] is shown in Figure 16 and is used throughout this report as a visual analogy to the module developed by FOI.

![Module Image](image)

Figure 16. NASA LIB module comprised of an Al heat sink with the batteries arranged in a hexagonal pattern [42].

The module is designed for manned spacecraft application with five main design consideration similar to the module developed at FOI:

1. Hexagonal packing of the batteries to provide the densest packing arrangement possible.
2. Aluminum heat sink which provides structural support and high thermal dissipation during operation.
3. An insulating layer wrapped around individual batteries to provide electrical and thermal insulation.
4. Supporting structures are constructed from lightweight polymers that are fire-retardant and designed to burn slowly and self-extinguish.
5. A modular design that allows several modules to be arranged close together and stacked.

The bulk of the battery module is composed of an effective heat sink material with a cell spacing of approximately 3 mm between adjacent cells. The batteries were new S40T batteries charged to 4.2 V using a CC/CV charging protocol at 0.5 C. The outer shell of the S40T batteries is made of stainless steel and is less than 1 mm thick. The shell is electrically connected with the batteries negative terminal and wrapped with a non-conductive polymer. Three experiments referred to as M1, M2, and M3 were conducted with the outer polymer wrap of the S40T cells intact. Apart from removing a small amount of the plastic wrap to expose the batteries' metal shell and place thermocouples in direct contact with the cell surface. One experiment, labeled M4, removed the insulating polymer wrap from every cell in the module. The insulating outer wrap of each cell in the module was the key parameter that varied during the thermal runaway module test. Table 9 list the parameters of the module experiments and which experiment had EIS diagnostic testing conducted on all the module cells.
Table 9. Module experiments and experimental parameters varied.

<table>
<thead>
<tr>
<th>Test trial</th>
<th>Cell insulation wrap</th>
<th>Post-TR diagnostic with EIS on each cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>Factory wrapped</td>
<td>No</td>
</tr>
<tr>
<td>M2</td>
<td>Factory wrapped</td>
<td>Yes</td>
</tr>
<tr>
<td>M3</td>
<td>Factory wrapped</td>
<td>Yes</td>
</tr>
<tr>
<td>M4</td>
<td>No insulation wrap</td>
<td>No</td>
</tr>
</tbody>
</table>

Three triggering methods for TR were considered and listed in Table 10. Mechanical puncture involves penetrating the cell with a rod or needle. This method aims to damage the electrode and separator layers and create an internal short circuit that develops into TR. The method suffers from difficulties in reaching batteries within an assembled module. Overheating requires an external heating element, which suffers from restricted access to only the end terminals of the batteries within the module. The heating method pre-heats the module and adjacent cells, potentially biasing their temperature measurements. Overcharging is a TR initiating method that adds additional electrical energy without significant pre-heating of the surroundings. The TR outcome is typically more severe with the additional electrical energy and provides a worst-case scenario for the module [46]. For this reason, the overcharge method was chosen to initiate TR for the module experiments.

Table 10. Pros and cons of the triggering methods considered [46].

<table>
<thead>
<tr>
<th>TR trigger method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overcharging</td>
<td>Additional electrical energy typically produces more energetic TR</td>
<td>Passive protection devices like CIDs may prevent excessive charging. Batteries must be electrically isolated from each other.</td>
</tr>
<tr>
<td>Mechanical puncture</td>
<td>An effective method for internally short-circuiting the cell</td>
<td>Difficult to access interior batteries within the module.</td>
</tr>
<tr>
<td>Overheating</td>
<td>Heating elements are efficient in inducing TR in batteries</td>
<td>External heating can interfere with the heat dissipation of the heat sink and bias temperature measurements of surrounding batteries.</td>
</tr>
</tbody>
</table>

A diagram illustrating the experimental setup is shown in Figure 17a-b. The experiments were conducted in a purpose-built steel structure and monitored remotely in a safe location. A DC power supply (Power Supply, EA-PS 9080-100) provided the overcharge current (16-20 A) and potential (10-15 V) used for initiating TR. The charge current for the M1 experiment was set at 16 A (4 C). The charge current for subsequent module experiments (M2-M4) was increased from 16 A (4 C) to 20 A (5 C) due to the CID vent disk activating at the lower charging current. The cells outfitted with thermocouples was changed from the first experiment M1 to the subsequent trials (M2-M4) and is illustrated in Figure 17a. Where M1 indicates the recorded temperature of cells in the M1 experiment, while MS shows which cells were outfitted with thermocouples in the subsequent tests (M2-M4). Nickel tabs were welded to both terminals of the TR designated cell using a spot welder and provided connection points for the leads. The wiring was not in contact with any conductive surfaces within the module, other than the designated cell. Potentially overheating the leads was also addressed by using heavy gauge wire, as the overcharge current has the potential to pre-heat its surroundings or ignite venting gases.
Figure 17a shows the module and the number identifiers of the 19 cells. The module itself consists primarily of a conductive heat sink material with cells spaced about 3 mm apart. The cells were not electrically connected in a series or parallel configuration. A total of 8 K-type thermocouples were used to record the temperature of the batteries and the module. The thermocouples were located 2 cm from the bottom of the batteries. The thermocouples were wired to a TEC-08 (Pico Technology) temperature acquisition device. A multimeter was used to observe the voltage of the TR cell via a digital camera. An infrared camera was used to distinguish vented gases and observe ejected cell material. Figure 17c shows an overcharge test of an S40T cell. Figure 17d shows the location of the pressure relief valve at the positive terminal, and the most likely rupture point and location of gas eruption, material ejection, and intense flaming during TR.

Figure 17. Experimental setup: (a) schematic of the battery module and cell numbering system and which cells were outfitted with thermocouples for first module experiment (M1) and subsequent tests (MS), (b) shows the thermocouple locations (c) single-cell overcharge induced TR experiment showing the test procedure and equipment, (d) S40T pressure relief valve location.
4 Results

4.1 Accelerate Rate Calorimetry

Figure 18. Shows the temperature profile of the measured cell surface temperature of an S40T cell from an ARC experiment. The sealed air temperature surrounding the test cell within the bomb container is superimposed on the cell surface to illustrate the small temperature difference over the course of the experiment. Figure 18 illustrates the initial ramp heating up to 50 °C and subsequent HWS operation until an exotherm is detected above 0.02 °C/min and the ARC tracks to the end of the TR process. The ARC continues to record the cell surface temperature as the test cell cools from the TR event.

Figure 18. The temperature of the Samsung SDI INR21700-40T cell surface (blue) and bomb air temperature (black) against time in hours.

4.1.1 Samsung SDI INR21700-40T

Figure 19 shows the temperature profile and pressure profile of the bomb container from two ARC tests of the S40T cell. The onset temperature of exothermic self-heating was observed at about 117 °C and 121 °C for the two trials, giving rise to a 288 °C and 283 °C adiabatic temperature rise, during which a maximum self-heating rate of 410 and 374 °C/min was recorded (Figure 20). The cell temperature peaked at roughly 590 °C for the duplicate tests. The maximum observed pressures of 9.5 and 2.2 bar were sustained during pressure-leakage of the bomb container and the pressure may have exceeded the recorded values. This is highlighted by the observed pressure drop shortly after the violent venting of the cell. (Figure 19). A well-sealed and pressurized bomb should maintain the pressure increases. The temperature at which the depressurized venting of the cell occurred was roughly 170 °C and 175 °C. However, the sensitivity of the onset temperature of venting or cell rupture suffers from rapid temperature rise during TR. A distinct temperature drop at around 115 °C and 118 °C were observed. About five minutes later, the instrument would detect exothermic self-heating of the cells above the threshold sensitivity of 0.02 °C/min, which lasted until the cells suffered from TR. To better examine the critical temperature drop which occurs prior to the onset of self-heating, a graph of the temperature rate against temperature is shown in Figure 20.
The time derivative of the S40T cell surface temperature against the cell temperature in Figure 20 shows the distinct endothermic reaction that lasted a few minutes and occurred shortly prior to the ARC detecting an exotherm. The distinct temperature drop is commonly attributed to the melting of the polymer separator [24], [29] as the melting point of PE (135 °C) [18] is close to this value. Other ARC studies attributed to an initial pressure-relief venting and accompanying Joule-Thomson expansion cooling [47], [48]. The self-heating rate proceeds exponentially, slow at the onset of detection (117 and 121 °C) but increases sharply after the built-up internal pressure of the reaches critical levels and the cell ruptures.

Figure 19. ARC results plot of temperature (blue) and pressure (red) against time for two trials of the Samsung SDI INR21700-40T battery.

Figure 20. Comparison of the self-heating temperature rates against temperature for two trials the Samsung SDI INR21700-40T battery. (a) The self-heating rate against temperature from the onset of self-heating until the maximum temperature. (b) A magnified figure of the self-heating rate illustrating the onset temperature of the endothermic reaction ($T_{\text{endo}}$) and the venting or rupture temperature ($T_{\text{vent}}$).
Examination of the test cells after the ARC tests showed that the explosive decomposition during TR had expelled the cell contents through the positive terminal of the cell (Figure 21) and bulged the cylindrical cell axially (Figure 22). The cell mass decreased by about 60-70% post-ARC tests. Inspection of the contents within the cell shells revealed that the Al foil had melted, while the Cu foil had not melted. Thus, the internal temperature of the cell from undergoing TR was greater than the melting point of Al (660 °C), but less than the melting point of Cu (1,085 °C).

Figure 21. Post-ARC test of a S40T cell showing where the safety valve ejected cell material during TR.

Figure 22. Post-TR of a S40T cell displaying the axial swelling of the cell at the sealed bottom-end (opposite the positive terminal).
4.1.2 Samsung SDI INR21700-50E

Figure 23 shows the temperature profile of the S50E cells during ARC trials. The first ARC test of an S50E cell noted an initial onset temperature of self-heating at 117 °C where the instrument was detecting close to its calibrated sensitivity limit, and consequently introduced two more heat steps of 5 °C each. An endothermic reaction was recorded during the last heating step at around 119 °C, decreasing the cell temperature by 3 °C. A second and prolonged exotherm was detected after the last heat step at 126 °C, which resulted in the TR of the cell. An adiabatic temperature rise of 255 °C was observed. A maximum self-heating rate of 396 °C/min occurred shortly after cell rupture (Figure 24).

The second S50E test trial gave rise to an endothermic reaction around 120 °C that also decreased the cell surface temperature by 3 °C to 117 °C. Shortly after at a temperature of 119 °C, the initial and final onset of self-heating was detected. The onset of self-heating was slow at first but resulted in a sharp rise in temperature and intense cell venting at roughly 170-175 °C. An adiabatic temperature rise of 248 °C was observed. A maximum self-heating rate of 378 °C/min occurred at a temperature of 283 °C (Figure 24).

Figure 23. ARC plot of the cell surface temperature against time for the Samsung SDI INR21700-50E-2 battery undergoing TR.
Figure 24. Comparison of the self-heating temperature rates against temperature for two trials the Samsung SDI INR21700-50E battery. (a) The self-heating rate against temperature from the onset of self-heating until the maximum temperature. (b) A magnified figure.

The post-TR examination of the S50E cells showed expelled cell contents via the positive terminal vent. Figure 25 shows the remnants of melted Al foil ejected from TR during the ARC test of an S50E cell. This reveals that the internal cell temperature achieved temperatures above the melting point of Al (660 °C).

Figure 25. Post-ARC test of an S50E cell showing where melted Al had ejected from the cell at the positive terminal.
4.1.3 A123 Systems ANR26650m1-B

A very slow exotherm was detected from temperatures as low as 137 °C (Figure 26 and Figure 27). The instrument was detecting close to its calibrated sensitivity limit (dT/dt > 0.02 °C/min) and consequently re-introduced a series of intermittent 5 °C heat steps. The third and final exotherms were detected at 217 °C and 218 °C. The test of the A123 LFP-based cells did not undergo TR.

![Figure 26](image1.png)

Figure 26. *ARC plot of temperature and pressure against time of the A123 Systems ANR26650m1-B*

The A123 LFP-based batteries never suffered from TR and experienced self-heating rates of less than 0.03 °C/min. This can be attributed to the A123 batteries higher thermal stability [48]. Post-ARC examination of the LFP cells indicated that some electrolyte had vaporized and the cell mass had decreased by roughly 18 % from 75.3 g to 61.4 g and 61.7 g.

![Figure 27](image2.png)

Figure 27. *a) comparison of the self-heating temperature rates against temperature for two trials the A123 Systems ANR26659m1-B, b) A magnified figure illustrating the onset temperature of separator melting (T\text{melt}).*
Figure 28 shows the thermal behavior of the S40T, S50E, and A123 cells during ARC measurements. The onset temperatures of the exothermal and endothermic reactions for the NMC-based S40T and S50E were similar at about 120 °C. The maximum cell body temperature of both batteries showed little variation with a mean temperature value of 589 °C and an absolute mean deviation of only ± 1 °C. The onset of the endothermic reactions was also similar among the S40T and S50E batteries tested and given in Table 11.

![Figure 28 ARC provided temperature versus time curves of the three tested cell types.](image)

The onset temperatures for duplicate trials of the S50E and A123 batteries, as well as four separate tests of the S40T cell are summarized in Table 11. The endothermic reaction, $T_{\text{endo}}$, the exothermic reactions of self-heating, $T_{\text{exo}}$, and the onset temperature of cell venting, $T_{\text{vent}}$ are given as mean values and absolute deviation from the mean (°C). Results from all the ARC trials can be found in Table 14 of the Appendix.

### Table 11. Onset temperatures extracted by the ARC.

<table>
<thead>
<tr>
<th>Onset Temperatures</th>
<th>S40T</th>
<th>S50E</th>
<th>A123</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial #</td>
<td>Mean</td>
<td>mean deviation</td>
<td>Mean</td>
</tr>
<tr>
<td>$T_{\text{endo}}$ (°C)</td>
<td>117</td>
<td>± 2</td>
<td>120</td>
</tr>
<tr>
<td>$T_{\text{exo}}$ (°C)</td>
<td>120</td>
<td>± 5</td>
<td>126</td>
</tr>
<tr>
<td>$T_{\text{vent}}$ (°C)</td>
<td>176</td>
<td>± 5</td>
<td>177</td>
</tr>
</tbody>
</table>

1 The sensitivity of the onset temperature of venting or cell rupture suffers from rapid temperature rise during thermal runaway and the onset is within an approximate 28 °C increment.

2 LFP Cells did not suffer from thermal runaway and self-heating occurred intermittently above the detection limit from the onset until the specified temperature.
The semi-log plot of the self-heating rates of the S40T and S50E demonstrate that both cell temperature rate profiles are exponentially proportional to temperature (Figure 29). From the onset temperature of self-heating to the point of maximum temperature rate both S40T and S50E demonstrate similar thermal behavior. At around 135 °C the slope of the exponential temperature rate profile has a slight drop, which might indicate the separator melting point.

Figure 29. Temperature rate versus time curves for the NMC-based S40T and S50E batteries.

A closer view at the exponential heating rate from the onset of self-heating at around 120 °C to the explosive venting that occurs around 170 °C is seen in Figure 30. The deviation from an exponential heating rate profile occurred at onset of about 132 °C. The temperature rate returned to an exponential rate profile at about 144 °C until the explosive venting occurred above 170 °C.

Figure 30. Shows the exponential temperature rate profile against time for the S40T and S50E cells during ARC measurements.
The calculated total energy release from the cell body of all S40T and S50E is shown in Figure 31. The mean total energy released by the S40T cells was 17.3 kJ and 15.8 kJ for the S50E cells. The calculated total thermal energy released per mass was 0.26 kJ/g for the S40T cell and 0.24 kJ/g for the S50E cells. The energy release ratio represents the dimensionless ratio of the total electrical chemical energy stored in the cells over the total heat energy released. The electrochemical energy is the nominal voltage multiplied by the capacity. It indicates the thermal to electrochemical energy released [2].

Figure 31. Shows the total heat energy released during TR and the ratio of stored electrochemical energy to the experimental energy release for trials of the S40T and S50E cells.
4.2 Impedance Spectra

The impedance spectra provide data to the internal behavior of each cell at a specific charge state, temperature, and condition. Baseline impedance spectra, recoded at full state of charge for the S40T (4.2 V), S50E (4.2 V), and A123 (3.6 V) batteries are shown in Figure 32. The measured impedance spectra of each tested cell show little variation in their impedance spectra at the same conditions. The series resistance value ($R_s$) determined from the Nyquist plot (Figure 32) and the intercept of the imaginary part of the impedance is lowest for the “power cells” A123 (7 mΩ) and S40T (9 mΩ), and roughly half that of the “energy cell” S50E (26 mΩ). These values are consistent with the manufacturer’s reported impedance given in Table 4. The NMC-based S40T and S50E exhibited three different and characteristic impedance domains: the first domain below the real impedance (x-axis) represents the inductance of the instrumentation cables in the high-frequency spectrum $10^4$-$10^3$ Hz. The second domain located above the real impedance abscissa is attributed to a capacitive impedance component (semi-circle) between $-10^3$-$1$ Hz, representing the charge transfer and electrolyte resistance within the cell. The third impedance domain is the diffusion-limited impedance at low frequencies between $1$-$10^{-2}$ Hz and demonstrated by the line projecting from the semi-circle. The bode plot illustrates the capacitive and inductive impedances by the phase angle measurement, where large positive phase angle shifts at high frequency are attributed to inductive components and negative phase shifts are contributed by the capacitive impedance of the cell towards lower frequencies.

Figure 32. Impedance spectrum of the S40T, S50E, and A123 batteries at full charge. (left) Nyquist plot showing the real and imaginary components of the impedance. (right) Bode plot illustrating the dependency of the magnitude of the impedance ($\log_{10}|Z|$) and phase shift ($\phi$) on the log of the frequency in hertz.
Figure 33 shows typical calculated KK residuals from measured experiments. The top figure shows a "noisy" measurement of the A123 cell with residuals < 1%. However, little significant bias occurs throughout the frequency scan, except a small bias towards the low frequency from 1-10 mHz. Measuring at lower frequencies takes longer than measuring at higher frequencies. The inverse of the frequency is the period of the signal, for example, a 10 mHz frequency measurement takes at least 100 seconds to record one period of the applied signal. Measurements at lower frequencies are more sensitive to errors due to time and temperature fluctuations. The calculated residuals of the S50E cell illustrates an invalid spectrum with significant biases occurring as the frequency decreases. The temperature decreased by 2 °C during the experiment. The bottom figure of the baseline EIS measurement of the S40T cell shows a valid spectrum, yet noisy measurements, with all residuals below < 1% throughout the frequency domain.

The standard and rated discharge capacities for 5 cycles of the S40T cell are shown in Figure 34. The left figure shows the standard charge/discharge protocol and a capacity of 4.16 Ah after 5 cycles. The right figure shows the rated discharge capacity at 10 A and a discharge capacity of about 3.2 Ah. The standard capacity specified by the manufacturer is a minimum 4 Ah while the rated capacity is a minimum 3.9 Ah. The cell temperatures were not controlled when determining the discharge capacity and it is believed that this may be the reason for the lower-rated capacity relative to the specifications. The temperature increased from an initial 25 °C to a maximum of 40 °C at the end of a 10 A discharge.

Figure 34. Discharge capacity of the S40T cell, (left) standard capacity at 800 mA discharge, (right) rated capacity at 10 A discharge.
4.3 Impedance During Calorimetry

Figure 35 shows a plot of the cell temperature and cell voltage changes as a function of time during the TR experiment in the ARC. The cell voltage gradually decreases by about 80 mV from about 60 °C and roughly 100 °C for both trials of the S40T cell. The initial OCV was 4.20 V at 16 °C before the start of the ARC test, and after ramp heating to 50 °C and a temperature stabilizing wait period of 40 min the OCV remains unchanged (less than 1 mV change of the OCV) before the ARC initiates the HWS protocol and impedance measurements begin. The GEIS applied current from 50 °C to the shutdown at 117 °C resulted in a capacity decrease of 2.3 mAh. This would correspond to SOC drift of only 0.06 % and is not responsible for the OCV drop during the ARC heating test.

Figure 35. Cell temperature and cell terminal voltage over time, b) magnified image showing a characteristic voltage drop during the endothermic reaction.

The voltage as a function of temperature during the ARC test is seen in Figure 36. Abrupt and unstable measurements of the OCV and rapid increase in the cell’s impedance began around 95 and 100 °C for two duplicate trials. The unstable measurements are believed to be caused by the activation of the CID due to built-up internal pressure from gas formation. The impedance increased sharply by several magnitudes from mΩ to kΩ at this point, which suggests that the CID activated and disrupted the connection to the positive terminal [49], [43], [30]. GEIS measurements at these temperatures resulted in large peak voltages to the small current input due to the high impedance. The instrument regulates the potential across the cell to control the current flow, and with such large impedance values, the instrument varied the potential to its maximum range (0 V to 10 V) in an attempt to control the set current. Thus, impedance measurements after this point were not valid. However, the cell potential after this point shows similar behavior to other LIB ARC experiments [30]. The sudden drop in voltage suggesting separator shutdown and then followed by a recovery of the voltage until the cells reach 130-140 °C (melting point of PE separator) and the cell voltage decreases due to ISC during the rapid TR event. A sharp decrease was observed in the noisy OCV at a temperature of 117 °C for both trials. The separator is believed to lose its integrity and melts around 117 °C when the voltage drops rapidly indicating a separator shutdown [24], [30]. The characteristic endothermic reaction occurring around 117 °C for four separate trials corresponds with the sudden OCV drop (Figure 36).
Figure 36. Cell voltage as a function of temperature.

The Nyquist impedance spectra of the S40T cell at temperatures from 50 °C to 100 °C and a baseline spectra at 16 °C are shown in the left plot of Figure 37. The real part of the impedance ($Z_{\text{Re}}$) increases significantly with increasing temperature, shifting the spectrum to the right. The impedance spectra indicate that from 16 °C to about 50 °C the real resistance first decreases, and then above 50 °C the resistance increases. The semicircular shape observed in EIS spectra close to room temperature is not visible in the S40T spectra above 50 °C. This indicates that at temperatures above 50 °C the value of the bulk electrolyte and charge transfer impedance, linked to the kinetics of the electrochemical reaction significantly decreases with temperature. The dominating capacitance contribution of the imaginary impedance above the real impedance component is a straight line at 45° (constant phase) which was attributed to the Li+ diffusion process within the electrode host material, seen in Figure 37. The length of the 45° line corresponds with the diffusion resistance of Li+, which is much shorter relative to EIS at room temperature and decreases in temperature from 50 °C to 100 °C. The right figure in Figure 37 shows the calculated KK residuals (%) of the impedance spectra at different temperatures. The calculate residuals from the EIS spectra at different temperatures are very small (> 0.5 %) demonstrating the linearity of the EIS measurements and that they do not change with time. Thus, the conditions of valid spectra are satisfied. Due to the inherent temperature-control of the ARC experiment, the EIS measurements are less noisy than the ambient EIS measurements. Although the temperature is slowly increased during the ARC experiment during HWS operation at an average of 0.02 °C/min during heating steps, the impedance spectra are taken after the 40 min temperature stabilizing wait period.
Figure 37. (left) Nyquist plot of the complex impedance in the range from $10^4$ kHz to 1 Hz of the cell during an ARC test. (right) Calculated KK residuals (%) of the impedance spectra at different temperatures, demonstrating that conditions of valid spectra are satisfied.

Examining the impedance spectra at individually selected temperatures provides insufficient information on the onset of thermal decomposition. Therefore, analyzing the impedance throughout the ARC experiment was considered.

This is shown in Figure 38 for the intersect of the imaginary part with the real axis. The ohmic resistance of the cell increases by several magnitudes above 100 °C.

Figure 38. The real part of the impedance at the intersection of the imaginary impedance ($\text{Im}(Z) = 0$) during heating.
Next, the evolution of the real and imaginary part for selected frequencies from $11 - 0.1 \, \text{Hz}$ is shown in Figure 39. The impedance scans in the lower frequencies exhibited greater variability and noise between individual measurements due to the inherently long measurement time. The imaginary component of the impedance demonstrated greater variations between measurements than the real component. This behavior was observed by [32], and corrected for by using a median filter. For this reason, the imaginary part of the impedance spectra in Figure 39 was filtered using a 3-point moving median to reduce outliers but preserve the sharp transitions between measurements.

Figure 39. The real and imaginary part of impedance over temperature for different frequencies.

The real part of the impedance increases with increasing temperature for the frequencies in which the charge transfer process is visible in the impedance spectrum, shown in the left figure of Figure 39. The dashed lines correspond with measurements during the wait-phase of the ARC where the temperature is stabilized. The real part of the impedance for frequencies between $11 - 0.1 \, \text{Hz}$ is increased by about 4 % from 50 °C to 95 °C and experiences an approximate 16 % increase from 95 °C to 100 °C. At around a temperature of 100 °C, the cell’s CID activates, and the impedance rises to several kΩ. For 1 Hz, the real part increases more rapidly at approximately 69 °C. From about 89 °C this increase accelerates strongly so that at 95 °C the real part for all frequencies has already increased significantly. This corresponds to the reported temperature range, at which strong SEI dissolution starts [21].

The charge transfer process is observable in the $10 - 0.1 \, \text{Hz}$ frequency range and is likely attributed to an increase in the charge transfer resistance of the electrodes. This is more prominent to the lower the frequency where the rising temperature significantly reduces the imaginary part of the impedance spectrum. From 50 °C to about 95 °C, for example, the imaginary part at the lowest frequency is reduced by more than 50 %. The real and imaginary components are connected via the KK relationship. However, the relationship is frequency-dependent as the real part at higher frequencies increase more over the temperature range than the lower frequencies, while the opposite is observable in the imaginary part. Over the temperature range, the imaginary part at lower frequencies decreases more than the higher frequencies. It is believed that this process is the result of reactions between the electrolyte and the SEI at elevated temperatures affecting the double layer capacitance of the electrodes.
4.4 Separator Melting Point

Figure 40 shows the melting point measurements on two separator samples extracted from the S40T cell using DSC at a heating rate of 10 °C/min−1. An endothermic peak was observed for both samples, with an inflection point at 137 °C indicating the melting point of the separator. The onset temperature occurs around 130 °C during rapid heating (10 °C/min−1). The results indicate that the separator consists of PE which has a melting point of around 130-140 °C [23]. An exothermic peak was observed at around 146 °C, which may be attributed to the exothermic decomposition of impurities, such as the electrolyte.

Figure 40. DSC measurement of the S40T cell at a 10 °C/min−1 heating rate.

Figure 41 shows a DSC measurement of the S40T separator at a slower heating rate, which was similar to the mean heating rate during the ARC studies. The separator appears to consist of PE (137 °C). A distinct endotherm at about 150 °C was observed. The melting point of PP is around 160-170 °C [23]. Thus, the separator was not likely to consist of a mixture of both PE and PP, as the melting temperature is significantly lower than the melting point of PP.

Figure 41. DSC thermograph of the S40T separator at a heating rate of 0.2 °C/min−1 similar to the mean heating rate of the ARC tests.
4.5 Thermal Runaway Initiation Method
Abuse experiments were conducted on single-cells to determine the best method for inducing TR. Externally short-circuiting the cell was difficult to achieve and overcharging was selected due to the additional electrical energy and more energetic TR. Figure 42 shows the experimental setup for overcharge-induced TR in an S40T cell (left) and the resulting flame and hot material ejected during TR (right). Initiating TR by way of overcharging did not produce a catastrophic TR event each time. The CID vent disk activated in several trials due to the built-up internal pressure of the cell, which disconnected the positive terminal of the cell and prevented further charging. Gas venting was commonly observed by the infrared camera prior to TR. This was believed to mitigate the protective function of the CID as the internal pressure could not reach the critical pressure required to force the CID vent disk to activate.

Figure 42. Shows the resulting TR from an overcharge test of an S40T cell.

4.6 Thermal Runaway Propagation Test of the Battery Module
4.6.1 The Effect of the Factory Polymer Wrap
Figure 43 shows the intense flaming and ejected sparks from a single-cell initiated TR event within the module. Due to the confidential design of the module, the image intentionally obscures the features of the module. Nevertheless, it illustrates the intensity of the combustion process and high-temperature material ejection from a single S40T cell suffering from TR. The TR triggered cell explosively ruptured and ejected its cell components, such as electrodes and current collectors through the positive terminal during the test. This was not observed for the S40T cells during the ARC heat abuse experiments, where the vent-disk had ruptured and the positive terminal assembly was largely intact. This indicates that overcharge-induced TR results in an uncontrolled venting due to gas formation and a rapid increase in the internal pressure. The temperature of the flame arrestor plate (visible in Figure 43) reached temperatures higher than 1,100 °C. The flame arrestor plate stops the ejected high-temperature cell material and combustion process from propagating upwards.
The temperature profile of selected cells within the module for the M1 experiment is shown in Figure 44. Thermal runaway was initiated after about 385 seconds of overcharging a fully charged cell (4.2 V) at 16 A. Approximately 1.7 Ah of additional charge (SOC ~143%) was introduced to the cell before catastrophic TR. The initial temperature of the cells within the module was around 19 °C and increased less than 12 °C during the approx. six minutes the triggered cell was overcharged before the cell suffered from explosive TR. The temperature profile of the trigger cell was not recorded as its thermocouple malfunctioned. No TR propagation occurred to neighboring cells. The moment the triggered cell ruptured and subsequent TR-induced flaming was indicated by the temperature recorded from the flame arrestor plate. The #10 cell directly adjacent from the triggered cell was subjected to a temperature rise of 48 °C and reaching a maximum temperature of 79 °C approx. 70 seconds after the triggered cell undergoes TR and ruptures. Cell #15 experienced a temperature rise of about 27 °C and a maximum temperature of 57 °C approx. 105 seconds after the TR venting event. Cell #15 is an equal distance from the triggered cell as cell #10. However, cell #15 experienced a significantly lower temperature rise compared to cell #10. The maximum temperatures of cells #10 and #15 varied by 22 °C. Analysis of the cell after the experiment showed that combustion products from the triggered cell had deposited on the surface of the #10 cell. This was not observed on cell #15, which indicates the significance of the high-temperature TR material depositing on surrounding cells.
Figure 44. Temperature profiles of selected cells from the M1 module experiment.

The position of the cells within the module relative to the triggered cell is shown in Figure 45. Three concentric circles labeled A, B, and C indicate the relative positions of the cells to the triggered cells. The maximum temperature reached by the cells is highlighted in each cell. The neighboring cells not adjacent to the triggered cell recorded a slow increase of approximately 13 °C from the onset of the TR event to their maximum temperature. Indicating that conductive heat transfer of the heat sink was the dominant source of heating.

Figure 45. Showing the position of the cells relative to TR triggered cell and their maximum recorded temperatures for the M1 module experiment.

The charge current for subsequent module experiments (M2-M4) was increased from 16 A (4 C) to 20 A (5 C) due to the CID vent disk activating at the lower charging current. A higher charge current increased the resistive heating within the cell. The higher current and subsequent heat generation increased the probability of initiating TR before the CID could disrupt the overcharge process.

The second module test, M2, was overcharged for about 200 seconds when gas eruption and an intense flame appeared from the TR triggered cell. About 1.1 Ah of additional charge (SOC ~125%) was introduced to the cell before catastrophic TR. Figure 46 shows the triggered cell temperature gradually increasing to about 90 °C, where the cell temperature rapidly spikes
beyond the limit of the K-type thermocouple (~1,370 °C). The temperature is high enough to melt the copper collector of the cell (1,085 °C). The maximum temperature was sustained for less than 20 seconds, at the end of which the temperature rapidly declines as the stored energy of the cell has been spent. The intense flaming and sparking from the TR event were observed on camera and lasted roughly 3-4 seconds. No TR propagation occurred to surrounding cells in the module. Before the explosive TR event, volatile gas was released from the trigger cell and observed in the IR camera. The gas ignited and combusted when the triggered cell exploded, and intense flaming was observed. The brief and fluctuating temperatures immediately after the explosion are likely a consequence of the flame. Since temperature measurements were taken from the surface of the cells, the fluctuating temperatures indicate that the flame rapidly affected the thermocouples.

Figure 46. M2 cell temperature against time data and the maximum cell temperature reached within the module.

All battery cells noted an increase in their surface temperatures. Among them, cell #13 directly adjacent to the triggered cell, recorded the highest temperature of roughly 60 °C.
The module experiment, M3, was the last repeated module experiment with the cells wrapped in the factory polymer. Figure 47 shows the cell surface temperature during the course of the experiment. The cells did not show any visible damage or melting of the polymer wrapping. The maximum adjacent cell temperatures were about 60 °C (cells #18 and #10). The maximum temperatures of the cells further away ranged from 52-55 °C. Cell #16 experienced a brief maximum temperature of 136 °C, which rapidly decreased to about 80 °C less than 5 seconds after reaching its maximum temperature. The thermocouple of cell #16 was located close to its positive terminal facing upwards in the module where the TR flame is redirected by the flame arrestor plate. Indicating that the TR flame rapidly heated the thermocouple of cell #16. However, the flame self-extinguished before sustained heating of the cell and the cell temperature rapidly declined to the temperature of the heat sink. The heat sink reached a maximum temperature of about 60 °C. The temperature fluctuations of the trigger cell thermocouple were attributed to the coating of the power supply cables overheating.

![Figure 47. The M3 module test showing the temperature profile of the cells against time.](image)

Table 12 provides a summary of the M1, M2, and M3 experiments and includes the following:

- The temperature readings before the triggering cell underwent explosive TR.
- The maximum cell temperature reached.
- The time until the maximum temperature was recorded.
- The increase in temperature due to the TR event.

The recorded cell temperatures for the M1, M2, and M3 were less than the critical separator melting point (117 °C) identified in the ARC studies. Except for the thermocouple located on cell #16 in the M3 experiment, which recorded an instantaneous maximum temperature of 136 °C. However, the temperature dropped to about 80 °C less than 5 seconds later.
Table 12. Summary of the maximum cell temperatures reached during the M1, M2, M3 experiments.

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<tr>
<th>Identifier</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
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<th>ΔT rise after TR (°C) M1</th>
<th>ΔT rise after TR (°C) M2</th>
<th>ΔT rise after TR (°C) M3</th>
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</table>

† Indicates that the thermocouple was located near the positive terminal of the cell and towards the top of the module, the location where the explosive decomposition and flaming from the triggered cell occurs.

Figure 48 compares the TR heat effects on neighboring cells based on their relative distance from the triggered cell. The temperature increase of the cells at the onset of the TR explosion to the maximum temperature was considered. The cell directly adjacent to the triggered cell experienced the largest temperature rise ranging from 27 °C to 48 °C and recorded the highest cell temperatures from about 60 °C to 80 °C. In experiment M3, the maximum temperature increase of cells furthest and directly surrounding the triggered cell showed a similar temperature increases from 27 °C to 33 °C. While cells not directly next to the triggered cell in experiment M1 and M2 demonstrated a uniform temperature increase. Suggesting the main source of heat absorbed by these cells was conductive heat transfer via the heat sink.

![Figure 48](image)

Figure 48. Shows the maximum cell temperature increase and their relative distance from the trigger cell. The temperature rise was determined by the cell temperatures recorded immediately before the TR explosion until the maximum temperature of the cells. Dashed lines indicate the maximum temperature reached for each relative distance and module experiment.
4.6.2 The Effect of No Insulation Wrap

The factory polymer wrap was removed from each cell in the module to determine its effect on protecting cells. The cylindrical outer steel shell of the cells was in direct contact with the heat sink.

A TR-induced explosion was observed after about 190 seconds of overcharging a fully charged cell (4.2 V) at 25 A. Figure 49 shows the cell temperatures against time during the experiment. The triggered cell increased exponentially in temperature until explosive decomposition occurred at a temperature of about 122 °C. Five seconds later, the triggered cell reached a maximum temperature of 533 °C. The observed maximum temperature of the trigger cell was much less than the > 1,000 °C recorded in the previous module experiments. At first, this suggested a more moderate TR event. However, eight and ten seconds later cell #18 and cell #10, which were both directly adjacent to the trigger cell, suffered rapid TR-induced explosive decomposition. The time at which the trigger cell exploded, cells #18 and #10 recorded a cell temperature of 26-27 °C. The initial cell temperatures at the start of the experiment were about 25 °C. Less than 15 seconds after the trigger cell exploded, both cells suffered TR-induced explosions and reached maximum temperatures of 350 °C and 500 °C. Approximately 10 seconds after the trigger cell explodes, the thermocouple attached to the outer surface of the module heat sink recorded a temperature of over 250 °C. This indicated that the moderate temperature increase of the trigger cell relative to previous experiments was attributed to significant conductive heat transfer to the heat sink. Furthermore, the significant thermal mass of the heat sink and temperatures well beyond the critical melting point of the S40T separator (117 °C) resulted in rapid TR propagation within the module. The temperature of the sink stayed above 200 °C for the remainder of the TR propagation experiment.

The thermocouple located at the top of cell #16 recorded a maximum temperature of roughly 600 °C, while the thermocouple located near the bottom of the same cell recorded a temperature of 68 °C. Indicating that the conductive heat transfer from the heat sink was the dominant heat source compared to the convective heat transfer from the flame. Cells 16, 5, and 3 exhibited a mean temperature rate increase of 0.5-0.6 °C per second after the trigger cell exploded until they suffered from explosive TR. The TR propagation time was strongly dependent on the distance of the cell relative to the trigger cell, as shown in Figure 49.

![Figure 49. Module TR propagation experiment (M4) showing the cell temperature against time. The varied experimental parameter was the removal of the manufacturer’s polymer wrapping on each cell.](image-url)
4.7 Post-Thermal Runaway Diagnostic on Module Cells

This section examines each cell from the M2 and M3 module experiments to assess any potential damage from the TR propagation test. The cells from both M2 and M3 showed no charring or visible damage. Cell #2 from the M2 experiment was briefly short-circuited when connecting the EIS instrumentation cables. The OCV of cell #2 after the external short-circuit was 3.45 V. The mean OCV of the other M2 cells was 4.135 V with an absolute mean deviation of 5.5 mV. The mean OCV of the M3 cells was 4.156 V with an absolute mean deviation of 5.6 mV. Cells from both the M2 and M3 experiments exhibited close OCV values and the slight deviation was attributed to self-discharge during the extended time between the module propagation experiments and EIS diagnostics. All cells were able to hold a charge.

In this section, the real impedance at the intersection of the Nyquist plot with the real axis (R_s) and the charge transfer resistance (R_{ct}) corresponding to the diameter of the depressed semi-circle on the real impedance axis were determined from fitting the ECM described in section 3.3.2.

Figure 50 shows the Nyquist diagram of all the cells in the M2 (left) and M3 (right) propagation experiment for comparison. Temperature fluctuations during the EIS measurements contributed to large deviations in the variance of low-frequency measurements during the measurements of the M2 cells. Nevertheless, the Nyquist representations of the impedance are visibly similar between the M2 and M3 cells. However, to investigate the frequency dependence of the impedance it is not helpful to look at a Nyquist plot. Rather, the spectrum is fitted to the ECM model described in section 3.3.2 used by several authors [43], [30], [31].

![Figure 50. Nyquist plot of the real and imaginary component of the impedance for (left) the M2 cells and (right) the M3 cells.](image)
The series resistance ($R_s$) and charge transfer resistance ($R_{ct}$) components of the ECM model are shown in Figure 51. The larger variations observed in the values of the M2 cells are attributed to the temperature fluctuations during the measurements. The temperature was controlled to a higher degree for the EIS measurements of the subsequent M3 cells. The modeled resistance values in cells directly adjacent to the trigger cell (relative distance indicated by 1) to the cells furthest away (relative distance indicated by 3) showed no significant trends which can be observed in either the cells from the M2 and M3 experiments. Cell #2 from the M2 propagation experiment, which was briefly discharged when connected with instrument cables, showed a 2 mΩ larger charge transfer resistance compared to mean resistance of the other cells and is indicated in Figure 51.

Figure 51. Series and charge transfer resistance components of the (left) M2 cells and (right) M3 cells defined by their relative distance to the trigger cell.

The equivalent capacitance components of the ECM exhibit no significant outliers suggesting the cells are unsafe or unstable.

Figure 52. Fitted pseudo-capacitance components of the (left) M2 cells and (right) M3 cells defined by their relative distance to the trigger cell.
It was evident from the impedance spectra of the cells from both propagation experiments that significant damage had not occurred to the cells. Therefore, charge and discharge cycles were performed on selected cells from the M2 and M3 module propagation experiments. Figure 53 shows two charge cycles of the #18 cells from the M2 and M3 propagation experiments. Cell #18 was located directly adjacent to the trigger cell and experienced the highest temperature increasing. The maximum temperature recorded for cell #18 from the M2 and M3 experiments was 42 °C and 60 °C, respectively. The charge cycle was a standardized 0.5 C (2 A) charge and 0.2 C (0.8 A) discharge cycle to a cut-off voltage of 2.5 V. The discharge capacities recorded were ranged from about 4.0 – 4.1 Ah, while all cells exhibited discharge capacities above the manufacturer’s rated capacity of 4 Ah. Suggesting that the maximum observed temperature of around 60 °C was not detrimental to the cells. The maximum operating temperature of the S40T, specified by the manufacturer, was 80 °C on the cell surface during discharge.

Figure 53. 0.5C/0.2C charge and discharge cycle of the cell #18 from the M2 and M3 experiments.
5 Discussion

5.1 The Endothermic Reaction and the Onset of Self-heating

During the ARC measurements, an apparent endothermic reaction occurred between 116 °C and 121 °C for the NMC-based S40T and S50E cells. The cell temperature decreased by about 4-5 °C and consistently occurred within a few degrees of the onset of self-heating at around 120 °C. ARC studies by [24] and [30], on NMC and NCA 18650 cell chemistries also noted the distinct endotherm at temperatures ranging from 117 to 122 °C and attributed it to the melting of the PE separator. However, DSC results from this study, [23], and [18] on PE separators indicate a melting point closer to 135 °C. The structural failure of the separator is a critical safety concern due to the internal short-circuit that develops [18].

However, Lammer et al. [47] conducted ARC experiments on 18650 NCA-based cells and investigated the gas evolution during TR and determined that Joule-Thomson cooling between 120-130 °C initiated the distinct drop in cell temperature. A critical pressure increase and subsequent venting from the gaseous decomposition products of the electrolyte and separator at temperatures above 120 °C resulted in a throttle expansion cooling the cell. Golubkov et al. [48] also attributed the decrease in temperature around 130 °C of NMC-based 18650 cells to the Joule-Thomson effect. While [30] suggested that the heat of vaporization of the electrolyte, whose boiling points may be exceeded at 118 °C, was responsible for the temperature drop. The pressure leaking of the bomb container made it impossible to observe any initial venting events that may correspond with the distinct temperature drop. However, previous ARC measurements at FOI with a well-pressurized bomb container had observed a step increase in the pressure corresponding with the temperature drop.

As previously mentioned, the failure of the separator is a crucial marker for unsafe battery cell conditions. Therefore, the discrepancy over the characteristic temperature drop and whether it may be the melting point of the separator motivated this project to examine the electrochemical changes of the cell during the ARC experiments. It was found that a sharp drop in the OCV of the S40T cell, during combined EIS and ARC experiments, correlates with the distinctive temperature drop around 119 °C. The cell voltage at this point experienced a sharp decline and subsequent slow recovery to around 3.9-4.0 V at about 125 °C. At around 135-140 °C the cell voltage steeply declines, which is closer to the measured melting point of the PE separator (137 °C) determined via DSC. The Semi-log plot in Figure 30 show the exponential heating rate at the onset of self-heating for the S40T and S50E cell, and indicates a temperature rate decrease below 140 °C. A slight deviation to the exponential temperature rate can be observed at this temperature, which could possibly be attributed to the separator melting. Research by [50] on the internal short-circuit behavior of 1 Ah pouch cells with NCM electrodes at elevated temperatures, reported a similar trend in the OCV. The cells experienced an initial ISC and a sharp decrease and subsequent recovery of the voltage. This behavior was described as a fusing phenomenon, where the initial ISC current path is burnt-out and disrupted due to the resultant Joule heating and the cell voltage recovers.

The voltage drop from around 60 °C to 100 °C until fluctuating voltage measurements are the regions of interest for early detection of cell instability [32]. The events occurring prior to the onset of self-heating (~120 °C). The elevated temperature regions where damage or capacity fade may be occurring within the cell, but not at the point of critical instability are of interest in evaluating the adoption of LIB in mission-critical military applications. Critical applications that may require the operating temperature limits of the batteries to be exceeded for a brief period of time. Implementing on-line EIS measurements of the cells may offer such flexibility. The critical parameter identified by EIS measurements during heating in this
project was the activation of the CID vent disk and characterizing the ohmic resistance with increasing temperature.

5.2 The Heat Release During Thermal Runaway

The total heat released during the TR by the S40T and S50E cells were extracted from the ARC experiments. The mean total heat released of 0.26 kJ/g for the cells were in good agreement with ARC studies on 18650 NMC cells by [28], which reported around 0.29 kJ/g of heat released when accounting for the different heat capacities used. However, studies by [2], [5] using a specially constructed calorimeter to measure the heat generated from the cell body and ejected material during TR found that the cell body of 18650 cells accounted for less than 20 % of the total heat energy released. While the ejected high-temperature cell material accounted for 80 %. The ARC studies conducted in this work could not account for heat from the released ejecta. The cell orientation changed during TR and the thermocouple placed within the air-space of the bomb did not record the ejecta from the cell. These findings have a significant impact on future design considerations of the battery module.

5.3 Module Propagation Experiments

The results of the module propagation experiments indicated the significance of insulating the cells from the heat sink. The manufacturer’s non-conductive polymer wrapping of the cells provided sufficient thermal insulation to protect the cells directly adjacent to the TR suffering cell. This insulation between the cell and the heat sink reduced the temperature of adjacent cells during TR. At the same time, the heat sink dissipates the heat reducing the temperature further. Thus, the combination of both an insulating wrapper around the cell and a conductive heat sink was beneficial for protective surrounding cells. However, without the insulating layer, the heat sink was too effective at dissipating heat, which was shown to result in catastrophic TR propagation. The question arises if the cell spacing can be reduced to decrease the total weight of the module. Coman et al., [7] performed a numerical analysis of the heat propagation in a similar battery module which was developed by NASA. The authors concluded that varying the thickness of the insulating layer in steps of ± 10 % had a stronger influence on the maximum temperature of adjacent compared to varying the cell spacing by an equal percentage. Suggesting that a corresponding increase in the insulation layer should accompany further experiments with decreased cell spacing.

6 Conclusion

This work performed thermal characterization experiments on LIBs with NMC and LFP electrode chemistries at 100 % state of charge using an EV-ARC and a BSC-815 battery testing instrument with EIS capabilities.

Key findings from the ARC experiments are summarized below:

- Battery cells consisting of LFP electrodes demonstrated exceptional thermal stability during heat abuse testing using ARC and did not suffer from TR reactions. Initial self-heating reactions in the LFP cells were extinguished and did not progress to TR.
- The S40T and S50E cells exhibited similar thermal onset characteristics and temperature rates. A distinct endothermic reaction between 116 °C and 121 °C and self-heating onset within the same temperature range.
- ARC test of the S40T and S50E resulted in cell temperatures of 590 °C and more than 17 kJ of released heat energy.
- Impedance and cell voltage measurements of the S40T indicated that the cell voltage decreased sharply at the onset of the temperature drop between 117 °C and 122 °C.
and slowly recovered during the self-heating. Until temperatures above 135 °C where the cell voltage decreased slowly to 0 V as the cell progressed to explosive decomposition. Further work is needed in clarifying this critical temperature region and determining the cause of the temperature drop.

- DSC analysis of the separator extracted from the S40T cell revealed a melting point of approx. 137 °C.
- The internal resistance of the S40T cell was observed to decreased from room temperature to 50 °C and as the temperature increased from 50 °C to 100 °C, the resistance began to increase. The CID vent disk activated at temperatures above 100 °C during, significantly increasing the impedance of the cell from a few mΩ to several kΩ.

Key findings from the module propagation experiments are summarized below:

- Preventing cell to cell propagation is possible with the current design features.
- No TR propagation occurred to neighboring cells when each cell had an outer polymer wrap.
- The largest temperature increase was observed in cells directly adjacent to the trigger cell. Cells not directly adjacent experienced similar temperature increases and maximum temperature. This suggested that the conductive heat transfer from the heat sink is the main heat source for cells further away from the trigger cell. While convective and radiation heat transfer from the combustion process and ejected cell material has a greater impact on cell directly surrounding the trigger cells.
- Impedance spectra of surrounding cells post-TR in the module experiments did not show significant impedance changes to suggest cell damage.
- All module cells were able to hold a charge post-TR module experiments and cycling of select cells directly adjacent to the trigger cells demonstrated that the cells are operational.
- Minimum cell material from the trigger cell reached surrounding cells.
- It was evident that the insulating layer is crucial for further design consideration. The insulation wrap should have high thermal resistance and fire-retardant capabilities to reduce the possibility of extended burning.

Future design changes to reduce the weight penalty of the module by decreasing the cell spacing should consider the insulation material and thickness surrounding individual cells.
7 Appendix

Table 13. The current and voltage relationship, and impedance of ideal circuit elements

<table>
<thead>
<tr>
<th>Component</th>
<th>Current and Voltage</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>V = iR</td>
<td>Z = R</td>
</tr>
<tr>
<td>Inductor</td>
<td>V = L di/dt</td>
<td>Z = jωL</td>
</tr>
<tr>
<td>Capacitor</td>
<td>i = C dV/dt</td>
<td>Z = 1/jωC</td>
</tr>
</tbody>
</table>

Table 14. Onset temperatures extracted by the ARC.

<table>
<thead>
<tr>
<th>Onset Temperatures</th>
<th>Samsung SDI INR21700-40T</th>
<th>Samsung SDI INR21700-50E</th>
<th>A123 Systems ANR26650m1-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trial #</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>T_{endo} (°C)</td>
<td>115</td>
<td>118</td>
<td>120</td>
</tr>
<tr>
<td>T_{exo} (°C)</td>
<td>121</td>
<td>117</td>
<td>119</td>
</tr>
<tr>
<td>T_{vent} (°C)</td>
<td>170</td>
<td>176</td>
<td>180</td>
</tr>
</tbody>
</table>

^1 The sensitivity of the onset temperature of venting or cell rupture suffers from rapid temperature rise during thermal runaway and the onset is within an approximate 28 °C increment.

^2 LFP Cells did not suffer from thermal runaway and self-heating occurred intermittently above the detection limit from the onset until the specified temperature.
8 References


[15] H.-J. Noh, S. Youn, C. S. Yoon and Y.-K. Sun, "Comparison of the structural and electrochemical properties of layered Li[NixCoyMnz]O2 (x = 1/3, 0.5, 0.6, 0.7, 0.8 and 0.85) cathode material for lithium-ion batteries," Journal of Power Sources, vol. 223, pp. 121-130, 2013.


[20] Y. Wang, J. Jiang and J. Dahn, "The reactivity of delithiated Li(Ni1/3Co1/3Mn1/3)O2, Li(Ni0.8Co0.15Al0.05)O2 or LiCoO2 with non-aqueous electrolyte," Electrochemistry Communications, vol. 9, no. 10, pp. 2534-2540, 2007.


[36] Thermal Hazard Technology, "THT Technical Information Note 006".


