We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,000
Open access books available

148,000
International authors and editors

185M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

Perspective Chapter: Thermal Runaway in Lithium-Ion Batteries

Iñaki Lalinde, Alberto Berrueta, Juan José Valera, Joseba Arza, Pablo Sanchis and Alfredo Ursúa

Abstract

Lithium-ion batteries (LIBs) are becoming well established as a key component in the integration of renewable energies and in the development of electric vehicles. Nevertheless, they have a narrow safe operating area with regard to the voltage and temperature conditions at which these batteries can work. Outside this area, a series of chemical reactions take place that can lead to component degradation, reduced performance and even self-destruction. The phenomenon consisting of the sudden failure of an LIB, causing an abrupt temperature increase, is known as thermal runaway (TR) and is considered to be the most dangerous event that can occur in LIBs. Therefore, the safety of LIBs is one of the obstacles that this technology must overcome in order to continue to develop and become well established for uses in all types of applications. This chapter presents a detailed study of the general issues surrounding this phenomenon. The origin of the problem is identified, the causes are detailed as well as the phases prior to TR. An analysis is made of the most relevant factors influencing this phenomenon, and details are provided of detection, prevention and mitigation measures that could either prevent the TR or reduce the consequences.

Keywords: thermal runaway, safety, lithium-ion batteries, renewable energies, electric vehicles

1. Introduction

The fight against climate change, primarily due to greenhouse gas emissions, is now a reality. Two key strategies that are directed at tackling this phenomenon are an increase in the generation of electricity from renewable sources and vehicle electrification. Firstly, renewable energies (REs) represent an extremely effective solution, given that they are a clean and unlimited energy source that can substantially reduce the polluting emissions associated with power production. Secondly, electric vehicles (EVs) are the most effective instrument for cutting the emissions associated with transport, particularly in urban environments, and for improving the quality of life of mankind. Energy storage systems (ESSs) play a decisive role in the development of these renewable energy generation and electric mobility technologies. On the one hand, ESSs are essential for REs, permitting energy manageability and enhancing the integration of renewables into the power grid [1]. On the other hand, they play

a key role in EVs, by giving these vehicles the run time required to make this form of transport a viable option.

Of the energy storage systems available on the market, lithium-ion batteries (LIBs) are the most widely used alternative in applications of this type. By the end of 2020, 71.1% of the operational energy storage project capacity in the world, not accounting pumped hydro storage, is based on LIBs [2]. LIBs offer attractive advantages, such as a high energy density (265 Wh/kg), high power density (340 W/kg), long lifetime (more than 5000 cycles), high efficiency (95%) and a low self-discharge rate (0.5–2.5% per month). However, their main drawback is their cost ($137/kWh) [3], which is still too high to be attractive in some applications. Despite the fact that substantial reductions have been achieved in recent years, further reductions are now being held back by the cost of the critical constituent materials such as cobalt, lithium and natural graphite [4]. Furthermore, given that these batteries have a limited safe operating area (SOA) with regard to the voltage and temperature conditions that they can withstand, a battery management system (BMS) is required. If the LIBs operate outside this safe window, certain undesirable chemical reactions may take place, possibly causing degradation, capacity loss or, in the worst case, the self-destruction of the cell.

The most dangerous phenomenon that can occur in a lithium-ion cell, and which may cause its self-destruction, is known as thermal runaway (TR). TR is a sharp increase in the temperature and pressure inside the cell, caused by a series of exothermic chemical chain reactions that feed one other, releasing heat and gases [5]. This phenomenon may be accompanied by the release of flammable and toxic gases and the risk of a fire or explosion. Moreover, one of the main characteristics of this phenomenon is that, despite the fact that it is initiated in one cell, it can then propagate to the rest of the cells making up the module and could even affect the whole battery [6].

To tackle TR, the cells incorporate safety devices. Furthermore, there is a BMS at a module or battery pack level, and on occasions, there is also a battery thermal management system (BTMS). On the one hand, the BMS is responsible for monitoring variables such as the voltage of each cell, the current through the battery and the temperature at some points of the battery. On the other hand, it monitors the battery state to check that it remains within its safe operating limits. By contrast, the BTMS controls the cooling or heating of the cell in order to ensure the right temperature, and it may be controlled by the BMS itself. Despite the safety devices installed at a cell and module level, the possibility of TR cannot be ruled out, in view of the accidents caused by this phenomenon [5, 7]. Furthermore, the number of accidents could increase over the next few years due to the boom in LIBs in applications such as REs or EVs [8]. Therefore, investigations directed at gaining a greater understanding of TR in order to take effective prevention, detection and mitigation measures are essential for the safe development of LIBs.

This chapter aims to make a general analysis of the key factors surrounding the phenomenon of TR in LIBs. It is therefore intended to serve as a guide for all interested parties, including the manufacturers, battery pack designers and even the users of LIBs. The different sections of this chapter explain in detail the TR mechanism, analysing its causes and its phases, during the actual phenomenon and also in the process prior to its initiation. In addition, the factors affecting the characteristics of TR are also indicated and the variables that may permit its early detection. Finally, this chapter looks at the resulting risks and hazards and possible prevention and mitigation strategies.

2. Thermal runaway in lithium-ion batteries

The characteristics of the TR occurring in a lithium cell depend on the type of cell in question. Specifically, the most relevant characteristic of the cell is its chemistry. The chemistry of a cell refers to the materials used in the internal components of the LIBs. The main components are the anode, cathode, electrolyte and separator. These materials provide the electrochemical properties of the cell and, to a larger extent, determine its level of safety as far as TR is concerned. A number of LIB chemistries are currently available on the market, with different characteristics with regard to rated voltage, energy density, lifespan, safety and cost. In general, those chemistries offering higher energy densities are the least safe [5]. However, as a result of the need to use LIBs in ever more demanding applications which require high energy densities, such as EVs, chemistries that are more unstable and unsafe are being used. For this reason, there is a strong emphasis on R&D directed at the development of batteries with the best electrical performance, yet without compromising their level of safety.

TR can be defined as a sharp increase in the cell temperature in a short period of time due to a successive series of exothermic chemical reactions that take place between the internal components of the cell. These unwanted reactions can be caused by abuse conditions such as overtemperatures or overvoltages, which break the stability of the internal components, or even by mechanical abuse, which can pierce the separator and produce an internal short circuit (ISC). The heat generated by these reactions is greater than the amount of heat that the cell is able to dissipate, thereby increasing the cell temperature. As the temperature rises, further chemical reactions occur between the internal components of the cell, causing irreversible damage. Although these reactions, occurring in the initial heating phases, degrade the cell, they still do not trigger TR. However, if the temperature continues to rise, then it finally reaches the TR onset temperature, causing some highly exothermic reactions which produce a tremendous release of energy in a very short space of time, leading to a sharp increase in the cell temperature and to its self-destruction. From that moment onwards, the phenomenon becomes uncontrollable, producing flammable and toxic gases which in turn increase the internal pressure of the cell. This overpressure causes the gases to be released through the pressure relief vents or due to a rupture of the casing, known as venting. When the inflammable gases released come into contact with the outside air, there is a risk of explosion or fire. Once TR has been initiated in a cell, the phenomenon may propagate to the other nearby cells forming part of the module and may even affect the whole battery if suitable containment measures are not taken. Propagation is one of the greatest risks derived from TR, leading it to spread to other healthy cells, exponentially increasing its hazardous potential.

Figure 1 shows the limits of what is known as the Safe Operating Area (SOA) of LIBs. The SOA is the voltage and temperature range in which a lithium cell can operate without causing undesirable reactions leading to accelerated degradation or ultimately to TR. As can be seen in the figure, higher temperatures can trigger a series of chain reactions leading to TR [9]. However, this phenomenon can also occur in other ways, given that charging at low temperatures or overcharging can also cause lithium plating. Lithium plating produces the growth of dendrites within the cell, even inside the safe voltage range if other conditions are satisfied, such as low temperatures and high charge rates [10, 11]. These dendrites could pierce the separator and cause an internal short circuit (ISC) that releases sufficient energy to trigger other exothermic reactions that lead to TR. In **Figure 1** it is also possible to observe how the reactions produce gases that increase the internal pressure, causing venting and the subsequent
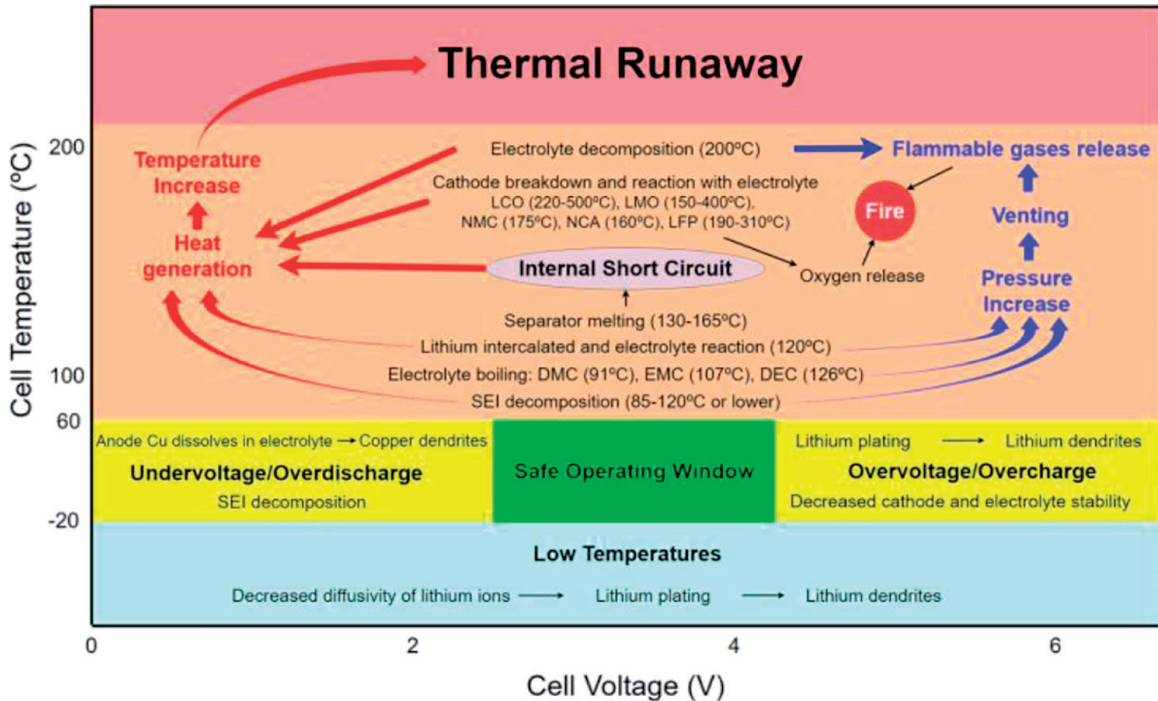
Figure 1.
Safe operating area (SOA) of LIBs and the phenomena that may occur outside of it.

release of these gases into the surroundings. It is therefore essential to maintain LIBs within the SOA to ensure that they remain safe.

In order to improve the safety of LIBs and mitigate the consequences of TR, a number of international commissions and organisations have drawn up and passed certain standards to evaluate their safety [12, 13] . These standards require LIBs to pass certain safety tests in different abuse conditions, including overcharge, over-discharge, over-heating and mechanical impact, among others. The safety test standards are designed to try and ensure that certified LIBs have a sufficiently low risk of accident and, therefore, can be safely used in industrial or household devices. The battery safety test standards
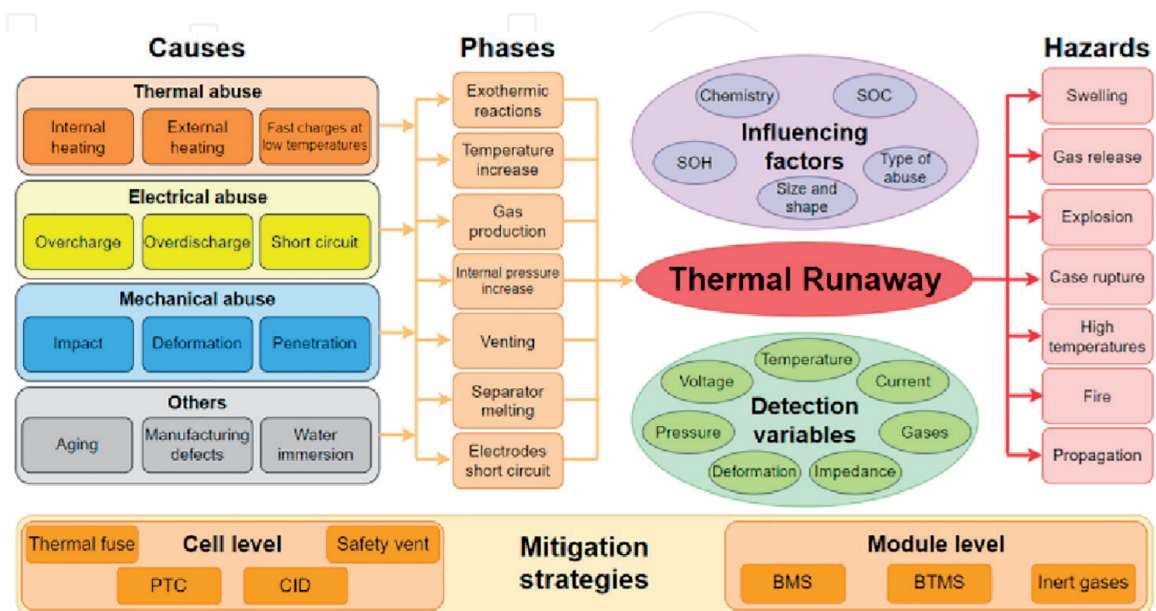

Figure 2.
General TR aspects in LIBs.

are constantly being updated and optimised, given that current tests cannot completely guarantee the safety of LIBs in practical applications. This is a serious problem, due to the fact that battery fires are reported to occur around the world. For this reason, it is essential to gain a complete understanding of the TR phenomenon in LIBs, thereby making it possible to improve the safety-related shortcomings of this technology.

The diagram in **Figure 2** shows the general TR aspects in LIBs. Each of these aspects is analysed in the following sections of this chapter. In the first place, this makes it possible to understand the origin of this phenomenon, based on its causes and the phases occurring. It is also possible to determine which factors influence the initiation of TR and their characteristics. It is also of vital importance to understand the resulting risks and hazards in order to ensure that suitable protective measures are established. Finally, it is crucial to analyse the variables that can help in the early detection of TR and have the prevention and mitigation measures in place, directed at preventing the initiation of TR and to reduce its risks and consequences.

3. Causes of thermal runaway

TR is triggered when the cell is operating outside its SOA. Certain chemical reactions are produced, depending on the voltage and temperature conditions. However, the fact that the cell is operating outside its SOA does not mean that TR is inevitable. This is because the relationship between heat generation and dissipation plays a fundamental role [7]. If the heat generated is greater than the rate at which it is dissipated, then this will lead to a subsequent increase in temperature, which will initiate further exothermic reactions, feeding the process, and which could ultimately trigger a TR. In contrast, if the heat dissipation is greater than the heat generated, then the cell temperature will drop, halting the process before TR is triggered [6].

During the normal operation of the battery, the cells generate heat due to inefficiencies in the charge and discharge processes. If the battery has been designed correctly, then this heat does not put the safety of the battery at risk. Therefore, with regard to the causes that could trigger TR, account is taken of the abuses that could expose the cells to operating conditions that are outside the established limits. It is therefore possible to distinguish three types of abuse: thermal, electrical and mechanical. It should also be pointed out that there are other possible causes that could lead to TR, such as cell degradation, impurities or defects during the manufacturing process or abuses such as immersion in water.

3.1 Thermal abuse

Temperature plays a key role in LIB performance and safety. This variable affects the material properties of the cells and, therefore, the processes and reactions taking place during charge and discharge. For this reason, it is crucial to control this variable, thereby making it possible to maintain the temperature of the cells within the safe operating range. A temperature that is either above or below this range could seriously affect LIB performance, and more seriously still, it may put its safety at risk.

3.1.1 Effect of low temperatures on LIBs

LIB performance is affected by low temperatures (<5°C in most cells). On the one hand, the electrolyte viscosity increases at low temperatures, reducing the mobility of
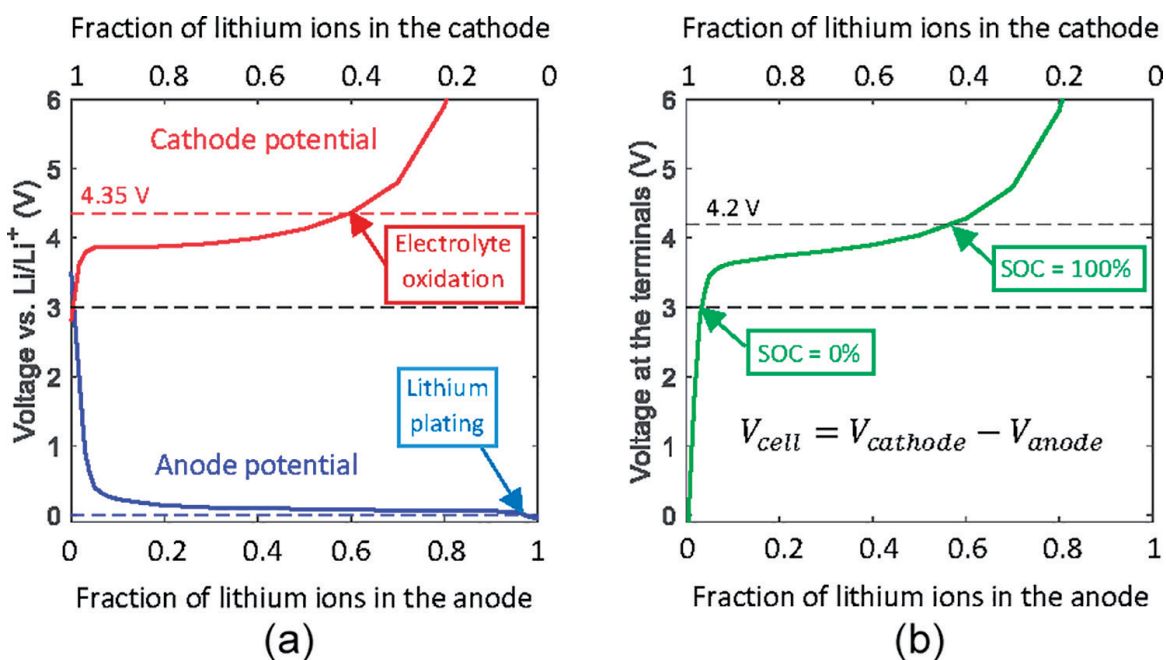
Figure 3.
(a) Voltage of each electrode vs. fraction of lithium ions in the anode; and (b) voltage at the cell terminals vs. fraction of lithium ions in the anode.

the lithium ions, thereby increasing the internal resistance of the cell [14]. On the other hand, the diffusivity of the lithium ions in the electrodes is reduced, restricting their intercalation in the crystalline structure. This causes a lithium concentration gradient in the electrodes, giving rise to a deviation in the intercalation voltage [15]. If the battery charge rate is greater than the anode diffusion rate, then the lithium intercalation voltage decreases even more. If this decrease reaches the voltage of Li/Li⁺ (− 3.05 V vs. SHE, Standard Hydrogen Electrode), then the lithium ions are plated on the anode surface as metallic lithium [16]. **Figure 3a** shows at room temperature the equilibrium voltage in function of the fraction of lithium ions in each electrode [17]. The voltage at the cell terminals is the difference between these two voltages, the cathode voltage minus the anode voltage and is represented in **Figure 3b**. The horizontal axis shows the fraction of lithium ions in each electrode. As the fraction increases from 0 to 1, the voltage of the anode is reduced, whereas the cathode voltage is increased. When the cathode voltage goes over 4.35 V, then the electrolyte begins to oxidise. Furthermore, when the anode is full of lithium ions, which means that its voltage reaches zero, lithium plating occurs. The plated lithium reacts with the electrolyte through irreversible reactions, involving a loss of active material [18]. Therefore, on the one hand, this lithium plating causes the anode surface passivation, thereby reducing the maximum current that the cell can manage. On the other hand, the loss of active material leads to a reduction in the cell capacity [19]. In addition to these degradation phenomena, lithium plating causes the growth of dendrites, which can pierce the separator, giving rise to an ISC, which may trigger a TR. Low temperature charges therefore need to be performed with care, given that they can lead to the formation of metallic lithium dendrites that ultimately pierce the separator membrane.

3.1.2 Effect of high temperatures on LIBs

High temperatures can also put LIB safety at risk. In this case, the problem lies in the poor thermal stability of the materials which, once they reach certain

temperatures, start to decompose or to react exothermically, releasing heat that accelerates the heating process and may trigger TR. Section 4 provides detailed comments on these reactions that take place in the cell as the temperature increases. The cause of this high temperature may be the external or internal overheating of the cell itself, when it exceeds its heat dissipation capacity. External heating can be transferred to the cell by conduction, convection or radiation and can either occur due to an excessive ambient temperature or when the cell is either in contact with or close to hot parts. On the other hand, internal heating refers to the heat generated by the cell during the charge and discharge processes or due to other chemical reactions.

One of the risks associated with overtemperature is that this situation may arise when the battery is not operating, and therefore, the TR detection systems may not be active. If a cell that is not operating is exposed to a high temperature that is above its safe operating limit, then this could ultimately trigger TR. For this reason, precautions need to be taken during the use of LIB and also during their transport and storage.

3.2 Electrical abuse

Just like temperature, voltage and current are crucial variables for the safety of LIBs. Depending on the cell chemistry, LIBs have maximum and minimum voltage values that determine their safe operating range. Outside this range, the materials are unstable, resulting in undesirable chemical reactions that degrade the cell and put its safety at risk. Given that there is a relationship between the cell voltage and its state of charge (SOC), to say that the cell has an overvoltage condition is to refer to the fact that an overcharge has occurred and, in the opposite case, an overdischarge [20].

As well as the voltage, a high current can affect the performance and safety of a LIB. For this purpose, manufacturers provide the maximum charge and discharge ratios that an LIB can withstand. As well as this type of overcurrent, which is sustained over time, the extreme case of an overcurrent is a short circuit that may either be caused outside (external short circuit) or inside the cell (internal short circuit).

3.2.1 Overcharge

Overcharge occurs when the battery is forcibly charged once the cut-off voltage has been reached. Overcharging causes a large amount of lithium ions to leave the cathode structure and to migrate to the anode. From the point of view of the cathode, the loss of a great many lithium ions may make it chemically unstable, and it may react exothermically with the electrolyte [21]. From the perspective of the anode, if the anode structure is unable to house all the lithium ions coming from the cathode, then these start to plate on the anode surface in the form of metallic lithium. The lithium plated may react with the electrolyte, causing an increase in the impedance and heat generated. In the worst-case scenario, it could lead to the formation of dendrites that could pierce the separator and cause an ISC. Finally, the commonly used electrolytes comprising $LiPF_6$ in an organic solvent mixture of EC-DEC-DMC have an electrochemical window that is limited to 4.5 V [22]. It is important to emphasise that a TR caused by an overcharge is more hazardous, due to the fact that the cell stores a greater amount of energy that can be released during the TR process. Moreover, as will be seen in Section 5.4, when the cell is overcharged, the TR trigger temperature drops, and it is therefore easier for the phenomenon to take place.

3.2.2 Overdischarge

Overdischarge means that the cell is discharged to under its lower voltage limit, which depends on the chemistry of the battery. Overdischarge presents less risks than overcharge, given that there is less energy stored in the battery, and therefore, if a TR is triggered, it will be less destructive. However, overdischarging can cause the decomposition of the Solid-Electrolyte Interphase (SEI), the rupture of the electrode materials and the formation of copper dendrites [23]. The SEI decomposition generates gases such as CO_2, methane (CH_4) and carbon monoxide (CO), causing the cell to swell [24]. When the battery is recharged, a new SEI is formed, consuming active lithium ions and electrolyte materials. The new SEI changes the electrochemical properties of the anode, leading to a capacity fade [25]. In the case of a deep overdischarge, once the potential of the anode reaches the copper oxidation potential (3.4–3.5 V vs. Li/Li$^+$), the copper current collector is oxidised [26]. The Cu^{2+} ions are solved in the electrolyte and may migrate through the separator and plate on the surface of the cathode [27]. When the cell is recharged, the solved copper is re-plated on the anode. If this process is repeated, metal dendrites can grow between the electrodes, possibly piercing the separator and creating an ISC [28], which could generate sufficient heat to trigger a TR.

3.2.3 Overcurrent

Based on the cell design, each manufacturer provides the maximum charge and discharge ratios that it is able to withstand without affecting its performance or safety. When there is no proper control of the current passing through the cell and the maximum ratios established are exceeded, then this produces a temperature increase due to greater heat generation [29]. This is due to the fact that the cell has been designed to dissipate a given amount of heat, and when an excessive current flows through the cell, the generation of heat is greater than its dissipation capacity. When the cell temperature increases above its safe range, this can trigger a number of reactions that degrade its materials and affect its performance. If the heat generation is maintained above the dissipation rate, then other reactions may be initiated that may ultimately lead to a TR.

3.2.4 External short circuit (ESC)

The ESC in an LIB takes place when there is a low impedance electrical connection between the cathode and anode current collectors on the battery. An ESC can occur for a number of reasons, such as a connection error, an insulation fault, mechanical abuse permitting the connection of the collectors and even by immersion in water or another substance that creates an electrical path. A high current peak occurs during an ESC, giving rise to great heat generation in a very short space of time and, therefore, a rapid increase in its temperature.

3.2.5 Internal short circuit (ISC)

The ISC is one of the most difficult phenomena to dissipate in LIBs given that, in contrast to the ESC, the electrical connection between two parts at a different potential takes place within the cell, making its prevention and detection more complicated. During the ISC, the heat generated by the Joule effect is inversely proportional to the

ohmic resistance of the whole circuit. This resistance is a simplified way of representing the phenomena involved in heat generation in an equivalent circuit [30]. Its value largely depends on the active parts connecting the ISC. Structurally, the positive side of the cell includes a positive aluminium current collector with a coating of cathodic material, while the negative side consists of a negative copper current collector with its corresponding coating of anodic material. A separator membrane serves to electrically isolate the cathode from the anode. However, if the separator becomes damaged and is no longer able to maintain the isolation between the positive and negative sides, then this may cause an ISC.

Depending on the parts of the cell that come into contact, ISC can be classified into four types: Al-Cu, Ca-Cu, Al-An and Ca-An [31]. As far as the hazard level is concerned, these ISCs take the following order: Al-An > Al-Cu > > Ca-Cu > An-Ca [32]. This classification depends on the value of the equivalent short-circuit resistance which to a large extent determines the current produced and the amount of heat generated.

One of the reasons for which ISCs are exhaustively analysed in the TR study is that an ISC occurs during any TR situation. For example, when a cell is subjected to thermal abuse, the separator collapses when a given temperature is reached, leading to an ISC. Electrical abuse may lead to dendrite growth, piercing the separator and causing an ISC. Finally, mechanical abuse caused by deformation or penetration could rupture the separator and also lead to an ISC. Notwithstanding this, some studies have demonstrated that an ISC alone is not able to release sufficient energy to trigger TR [33]. The said work demonstrates that the ISC only releases a small amount of energy, given that the battery suffers a sharp increase in its internal resistance due to electrolyte consumption, reduction in electrolyte porosity and the separator shutdown. What is clear is that the separator prevents an ISC from occurring in the cell, and it may be damaged by a number of abuse conditions, as shown in **Figure 4**.

3.3 Mechanical abuse

When a lithium-ion cell is subjected to mechanical abuse conditions, such as impact, deformation or nail penetration, then this could pose a serious risk to safety. These factors are particularly relevant in applications such as EVs, which require
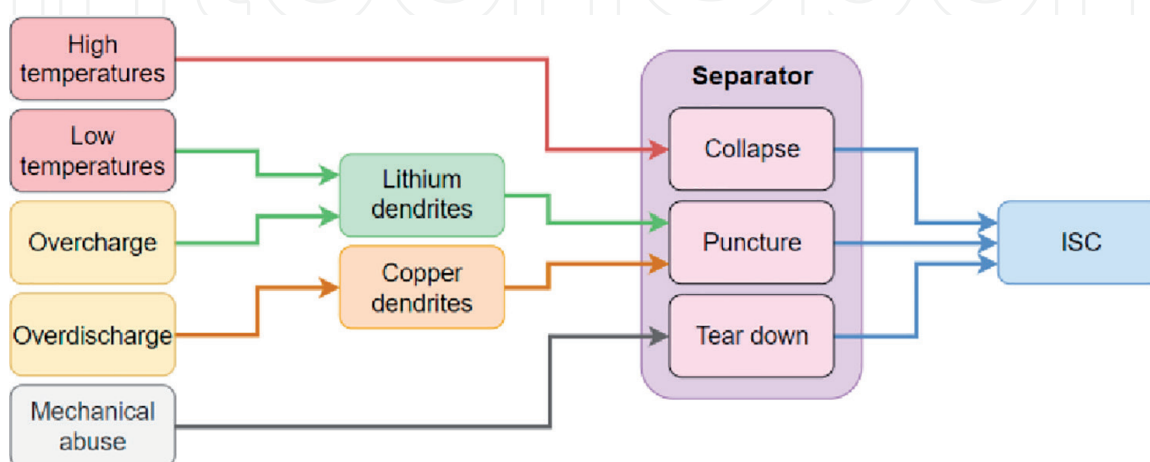

Figure 4.
Damage on the separator due to different causes.

an exhaustive study of the behaviour of LIBs in the event of any type of impact. Mechanical abuse may lead to cell deformation, affecting its internal structure and possibly leading to the rupture of the separator. In the event of a separator failure, a local ISC will occur, releasing heat due to the Joule effect. The heat generated increases the cell temperature and may even trigger exothermic reactions that increase the heat generation and produce gases. The large amount of heat generated in such a short space of time makes dissipation more complicated and may finally lead to the initiation of TR [34]. Therefore, the outer casing of the LIB plays a key role in preventing mechanical abuse and is responsible for withstanding mechanical loads and ensuring that there is no damage to the internal battery structure. In relation to TR, the chemistry of the components, the specific capacity of the battery and its state of charge play a decisive role [35]. A further determining factor is the type of mechanical abuse, given that the cell piercing may lead to the rupture of the casing, permitting the ingress of air which then reacts with the active components and the electrolyte, initiating strong exothermic oxidation reactions [35].

4. Phases of thermal runaway

Any TR phenomenon is associated with prior phases which, although they do not trigger TR, do affect the cell temperature, increasing the probability of the occurrence of those reactions that do cause TR. Each of the reactions between the internal cell components is initiated when the temperature reaches a certain value, while its duration is based on the rate at which the cell temperature increases [36]. Therefore, depending on the cause of the TR, these reactions may occur consecutively or simultaneously. For example, an LIB may be subject to mechanical abuse that causes an ISC, generating a large amount of heat in a very short space of time. In this case, the diverse reactions between the internal components will take place almost simultaneously. However, if the battery is exposed to external heating which slowly increases its temperature, then each reaction will take place when its starting temperature is reached.

In this section, in order to represent the temperature at which the chemical reactions are triggered, an external heating abuse of 2°C/min has been considered. **Figure 5a** shows the evolution of the cell temperature, its voltage and the gases released. These three variables are a good representation of the consequences of each of the TR stages. Furthermore, **Figure 5b** shows the temperature increase rate (dT/dt) in relation to the cell temperature. This is a widely used graph to represent the TR in LIBs, given that it permits the visual analysis of the exothermic behaviour and the moment at which the temperature that initiates the TR is reached. Furthermore, both graphs show the three most significant temperatures that permit the characterisation of a TR incident. These temperatures are identified as T_1, T_2 and T_3, and correspond to the onset temperature of exothermic reactions (T_1), the TR onset temperature (T_2) and the maximum temperature (T3). T_1, T_2 and T_3 provide extremely valuable information on the safety characteristics of a TR [37]. The greater the values of T_1 and T_2, the safer the cell, given that they indicate the safety margin available until the start of the exothermic reactions that degrade the LIB and the temperature of no return. On the other hand, the lower the value of T_3, the safer the cell, given that a lower value for this temperature indicates less energy released during the TR phenomenon which conditions, among other things, its potential propagation to the adjacent cells.
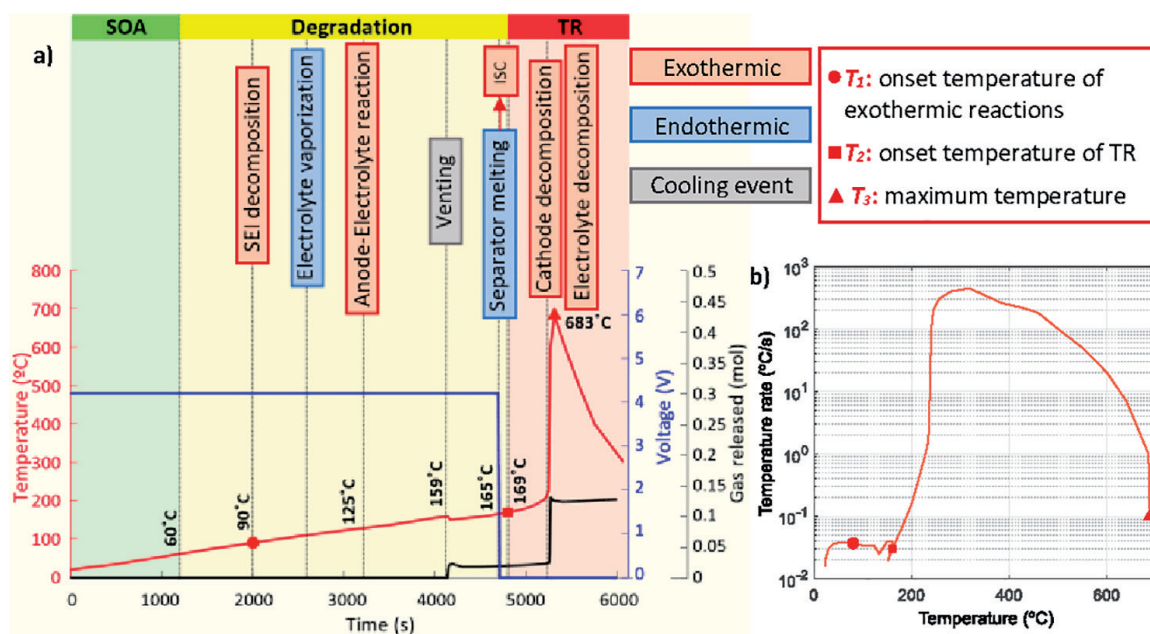
Figure 5.
Phases of TR. (a) Evolution of the temperature, voltage and gases release during an overheating test; and (b) temperature rate vs. temperature.

4.1 SEI layer decomposition

Once the cell temperature is outside the SOA, the decomposition of the SEI is the first exothermic reaction to take place. Therefore, the start of this reaction relates to temperature T_1, as can be seen in **Figure 5a**. Depending on the composition of the SEI layer, T_1 can be between 85 and 120°C [38]. However, it has also been confirmed in some cells that the decomposition of the SEI can start at lower temperatures, ranging from 60 to 80°C [28, 39]. Heat is released during the decomposition of the SEI, which increases the cell temperature. Moreover, flammable gases are produced such as ethylene (C_2H_4) and also some oxygen, due to the fact that the metastable components of the SEI such as (CH_2OCO_2Li)$_2$ are not thermally stable in the presence of lithium ions and may react exothermically [40]. In short, the decomposition of the SEI layer degrades the LIB and generates heat and gases, but does not in itself trigger the onset of TR. However, it does help to accelerate the temperature rise, which could lead to the start of new exothermic reactions. Furthermore, the loss of the protection of the SEI layer exposes the anode and means that it could react with the electrolyte.

4.2 Electrolyte vaporisation

The continued increase in the cell temperature leads to the vaporisation of the organic components of the electrolyte. The organic solvents making up the electrolyte, such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC), have boiling points of 91, 107 and 126°C, respectively [12]. On evaporation, these carbonates are converted into gases, which contribute to increase the cell pressure. Given that the volume remains constant, this causes the temperature to increase. In other words, despite the fact that the change of state from the liquid to vapour phase is endothermic, the energy absorbed is negligible in comparison to the increase in temperature caused by the pressure increase. In this phase, the temperature increases above the flashpoints of the gases produced by the electrolyte.

However, these gases do not combust, given that there is insufficient oxygen inside the cell to cause a fire [41].

Due to the utilisation of highly volatile and flammable organic-solvents-based electrolytes, new electrolyte systems are being developed to achieve safer electrolytes, such as ionic liquids, polymer-based electrolytes and solid-state electrolytes [42]. Ionic liquid electrolytes are characterised by low volatility and/or flame retardants properties. Polymer-based and solid-state electrolytes have the advantage of being free of liquid and organic solvents, avoiding the risk of cell leakage. Thus, this phase can be avoided or delayed with the use of other electrolyte system.

4.3 Lithium intercalated in the anode and electrolyte reaction

The decomposition of the SEI exposes the lithium intercalated in the anode which, at temperatures above 120°C, rapidly reacts with the organic solvent of the electrolyte [38]. This reaction leads to the formation of lithium carbonate and flammable hydrocarbons (ethylene, ethane and propylene). During the temperature rise, a second SEI layer may be formed, which again decomposes as a result of the above-mentioned reactions, with an exothermic peak at a temperature of 230°C [43].

4.4 Cell venting

The formation of gases in the cell interior causes the internal pressure to increase. Normally, the cells are fitted with devices that relieve the pressure when high values are reached, as this would involve a risk of explosion. When the safety vent is activated, the gases produced are released into the surroundings and the internal pressure is reduced. If the cell does not have a built-in safety vent, then the venting may occur through the rupture of the casing at its weakest point, as is the case with the pouch cells. As can be seen in **Figure 5a**, this process lowers the cell temperature due to the Joule-Thomson effect. This drop in temperature is due to the release of the hot gases, which reduces the pressure while maintaining the volume constant and therefore the temperature drops. This event takes place before the TR and, despite the drop in temperature, account should be taken of the fact that it involves a release of inflammable gases which, in contact with the oxygen in the air, could combust, causing an increase in the ambient temperature. This could accelerate the heating of the adjacent cells, favouring the propagation of TR. Finally, it is important to emphasise the fact that the amount of gases released during venting is significantly lower than those released in the TR itself, as can be seen in **Figure 5a**.

4.5 Separator melting and ISC

The separator consists of a porous membrane intended for two principal purposes: to allow ions to pass through and to electrically isolate the electrodes. Therefore, the separator material has high ionic conductivity and low electrical conductivity. At present, polyethylene (PE) and polypropylene (PP) are the most widely used materials for the separator. PE melts at 130°C, while PP does so at 165°C. Once melted, the separator membrane can no longer perform its function, triggering an ISC. As can be seen in **Figure 5a**, at the time when the separator melts, causing the subsequent ISC, the cell voltage abruptly drops to zero. The separator melting process is endothermic and absorbs energy during the change of state. However, the energy absorbed is negligible in comparison with that produced by the ISC.

4.6 Rupture of the cathode material and reaction with electrolyte

At high temperatures (175–250°C), the active material of the cathode (generally an oxide) decomposes exothermically, releasing oxygen. Both the oxygen released and the actual cathode material react with the electrolyte at this temperature. This chemical reaction is highly exothermic, causing the sharpest temperature increase in the TR process [38]. This reaction and the reaction between the intercalated lithium in the anode and electrolyte and the ISC caused by the collapse of the separator are the main triggers of the TR phenomenon in LIBs [6]. Therefore, the value of T_2 will be influenced by the weakest among the cathode, anode and separator.

4.7 Electrolyte decomposition

Both the anode and the cathode materials react with the electrolyte during TR. When the cell temperature exceeds 200°C, the electrolyte decomposes exothermically [38]. However, account should be taken of the fact that certain organic solvents in the electrolyte evaporate at temperatures below 100°C, thus, at 200°C, part of the electrolyte has already evaporated. The electrolyte decomposition produces flammable and toxic gases such as HF from the decomposition of $LiPF_6$ salt [44]. The generation of CO_2, C_2H_4 and HF, among other gases, has been documented in the decomposition of electrolytes comprising $LiPF_6$ and organic carbonates [45].

4.8 Reactions at higher temperatures

Other exothermic reactions that take place at very high temperatures have also been documented. At 220°C, the lithium intercalated in the negative electrode starts to react exothermically with the fluorine-based binder, usually polyvinylidene fluoride (PVDF) [38]. At temperatures above 300°C, metallic lithium can form from the decomposition of the stable components of the SEI layer (LiF and Li_2CO_3), and the graphite portion of the anode can exothermically decompose [43]. However, these take place following initiation of TR, and they have less influence in comparison with the aforementioned reactions [5].

5. Factors influencing thermal runaway

5.1 Chemistry

The chemistry of the batteries determines the characteristics of their TR, given that the reactions involved depend to a large extent on the materials used in the internal components. Depending on the type of chemistry, it is possible to find cells with a higher or lower degree of thermal stability, and therefore, they are more or less prone to TR. As discussed above, there are currently a number of different types of LIB chemistries on the market, which differ with regard to their electrochemical performance, lifespan and safety. In general, the name is determined by the active material used in the cathode. However, even when the same material is used for the cathode, the cells made by different manufacturers may behave differently with regard to the TR phenomenon, depending on the materials used in the rest of the internal components.

The active material of the cathode is either a lithium compound (LCO, LMO, NMC, NCA, LFP...) or a combination of these. The thermal stability of this material is

crucial to determine the safety of the cell. Thermal stability refers to the temperature at which the cathode material decomposes and releases the oxygen contained in its structure. When this oxygen is released, it reacts with the electrolyte, generating heat and even igniting [46]. Cells with an LFP cathode are the safest, given that the strong phosphate bonds prevent the release of oxygen. By contrast, transition-metal oxides have weaker bonds, causing oxygen to be released at lower temperatures.

With regard to the anodic material, graphite is the most widely used due to its good performance and low cost [47]. However, the formation of an SEI layer is required, to prevent it from reacting with the electrolyte. As has been seen, the SEI layer decomposes at temperatures close to 90°C and is the first exothermic reaction to release heat and gases, which also gives rise to the reaction between the electrolyte and the lithium intercalated in the anode. Additionally, the SEI is an element that, to a large extent, suffers the effects derived from ageing. For this reason, other materials are available for the anode, with lithium titanate (LTO) as the most popular commercial alternative. An LTO anode does not need an SEI layer, making it safer. However, the intercalation voltage of lithium in the LTO is higher than that of graphite, leading to cells with a lower voltage and, therefore, with a lower energy density.

Finally, the electrolyte is generally composed of an organic solvent, a lithium salt and other additives. The materials used and their combination determine the stability of the electrolyte. Given that most of the electrolyte components are flammable, manufacturers generally add certain additives such as flame retardants for enhanced safety.

Table 1 provides a summary of the main characteristics of the lithium batteries, based on their chemistry. The last row indicates their safety characteristics. As can be observed, the LTO batteries are the safest, followed by the LFP ones. The LCO batteries are the ones with the lowest safety level. With regard to energy density, an inverse relationship with safety can be seen, whereby the safest batteries are also those with the lowest energy density and vice versa.

Abbreviation	LCO	LMO	NMC	LFP	LTO
Full name	Lithium cobalt oxide	Lithium manganese spinel	Lithium nickel cobalt manganese oxide	Lithium iron phosphate	Lithium titanate-oxide
Cathode	$LiCoO_2$	$LiMn_2O_4$	$Li(Ni_xMn_yCo_z)O_2$	$LiFePO_4$	LMO, NCM, LFP
Anode	Graphite	Graphite	Graphite	Graphite	$Li_4Ti_5O_{12}$
Cell voltage (V)	3.7–3.9	4.0	3.8–4.0	3.3	1.8–2.5
Energy density (Wh/kg)	150–190	100–160	140–200	90–140	70–85
Cycle life (cycles)	500–1000	1000–1500	1000–2000	≥ 2500	6000–27,000
Safety ranking	5	3	4	2	1

Data obtained from [9].

Table 1.
Main characteristics of various types of LIBs.

5.2 Size and shape

The cell size directly affects the energy released during the TR. A study conducted by Son et al. [48] analyses the influence of this factor for three LCO-graphite pouch cells with capacities of 33, 1000 and 3300 mAh. In the heating ramp test conducted in this publication, TR occurred in the 1000 and 3300 mAh cells, while this phenomenon did not occur in the cell with a lower capacity. The authors consider that this is due to the greater proportion of inactive materials in relation to the active materials in the lower capacity cell. Furthermore, they observed that the TR triggered in the 1000 and 3300 mAh cells had different characteristics, given that the cell with the greater capacity released a higher amount of energy, causing TR to be triggered earlier.

In relation to its shape, lithium-ion cells can be divided into three types: cylindrical, prismatic and pouch. Each shape has certain pros and cons with regard to its manufacturing process, assembly in the battery pack and storage capacity, built-in safety devices and safety from TR. With regard to TR, it is important to mention that the cylindrical and prismatic cells have a metal casing that allows them to withstand greater internal pressure before bursting than the pouch cells, whose plastic-aluminium laminate casing easily deforms when gases are generated inside the cell. The studies published report that pouch cells are able to withstand pressure values ranging between 223 and 411 kPa, while cells with a metal casing withstand pressures ranging from 386 to 855 kPa [49]. This causes venting to take place earlier in the pouch cells, allowing the gases to be released into the surroundings.

5.3 Type of abuse

TR is also affected by the type of abuse triggering it. As discussed in Section 3, there are different situations which give rise to TR. Therefore, depending on the type of abuse, the behaviour of the cell is different, and this determines the characteristics of the TR. This means that parameters such as the temperature at which TR is triggered, its maximum temperature, duration, venting and possible fire, may all vary depending on the underlying cause. This fact adds greater complexity to the characterisation of this phenomenon and makes its more unpredictable. For this reason, the correct experimental characterisation of TR involves the performance of different tests, including various possible causes. **Figure 6** shows the main results of an experimental study to analyse the evolution of the temperature and voltage of an NMC pouch cell with regard to three types of abuse: overtemperature (2°C/min), overcharge (1C) and nail penetration [49]. Firstly, looking at the horizontal axis of the figures, it can be observed that each test has a different duration. This shows the length of time during which the cell is able to withstand each abuse condition before the onset of TR. Thus, in the nail penetration test, TR is shown to occur just a few seconds after the cell is pierced. On the other hand, in the overcharge test, TR is triggered at around 1600 seconds and, for overtemperature, at 5000 seconds. Analysing the cell temperature for each test, the maximum temperature reached is observed to vary between 823°C for the overtemperature test and 760°C for the overcharge test. However, even more significant is the difference between the temperature at which TR is triggered in each test, being 206°C for the overtemperature test, around 100°C for the overcharge and just 30°C for the nail penetration. This clearly demonstrates the influence of the type of abuse on the characteristics of the TR phenomenon in LIBs, making its detection and prevention more complex.
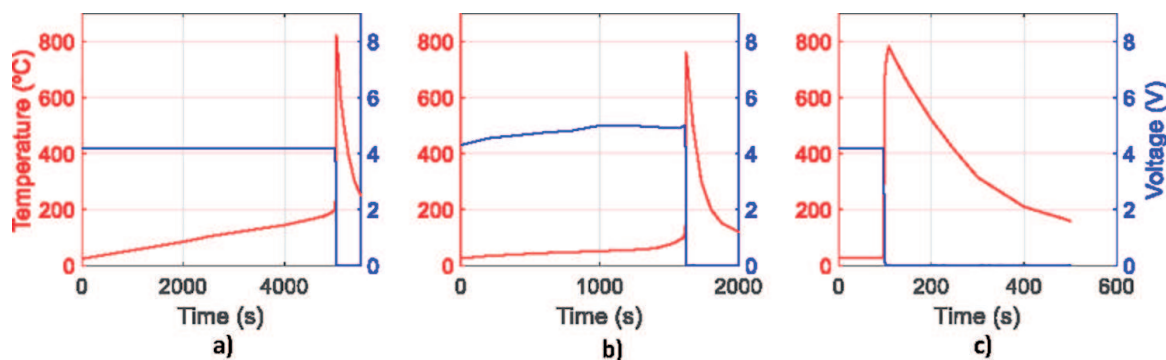
Figure 6.
Temperature and voltage evolution of the cell under different type of abuse. (a) Overheating; (b) overcharge; and (c) nail penetration. Data obtained from [49].

5.4 State of charge (SOC)

The battery state of charge (SOC) is also a determining factor in the analysis of TR. Firstly, the higher the SOC, the higher the amount of energy stored in the cell and, therefore, the greater the severity of TR. This is due to the release of a greater amount of energy during the phenomenon, resulting in a higher temperature T_3. Furthermore, the SOC also affects the value of the three characteristic temperatures that define the TR [50]. A higher SOC means an anode with a higher lithium content—lithiated anode—and a cathode with a lower lithium content—delithiated cathode. On the one hand, the lithiated anode has a reduced stability, which favours the reaction between the intercalated lithium and the electrolyte. This favoured exothermal reaction is triggered at lower temperatures for higher SOC, thereby reducing the onset temperature of exothermic reactions, T_1. On the other hand, the evolution of the TR is mainly related to the reactivity of the cathode with the electrolyte, given that the decomposition of the cathode material releases oxygen that reacts with the electrolyte. Given that the layered transition-metal oxide becomes unstable in the delithiated state—higher SOC, the onset temperature of TR, T_2, is also decreased. In addition, the TR process releases more heat with higher SOC, thereby increasing the maximum temperature during the event, T_3.. In this way, it is important to emphasise that, if the cell is overcharged, it may have lower trigger temperatures [51]. In short, the higher the cell charge, the more prone it will be to TR and the worse the consequences. For this reason, during the transport and storage of LIBs, it is recommended to keep them at low SOC levels in order to reduce the risk of TR. This can be seen, for example, in standard UN 3480 which establishes a maximum SOC of 30% for the air transport of LIBs.

Figure 7 provides a compilation of the overtemperature test results conducted on different types of cells at different SOC, published in the literature [51–54]. **Figure 7a** shows the relationship between temperature at the onset of TR (T_2) and the SOC, observing a decreasing trend as the SOC increases. In contrast, **Figure 7b** shows the relationship between the maximum temperature (T_3) and the SOC, observing an increasing trend, as described in the paragraph above.

5.5 State of health (SOH)

Certain irreversible reactions take place throughout the useful life of an LIB, leading to cell degradation and loss of performance. The degradation primarily affects the
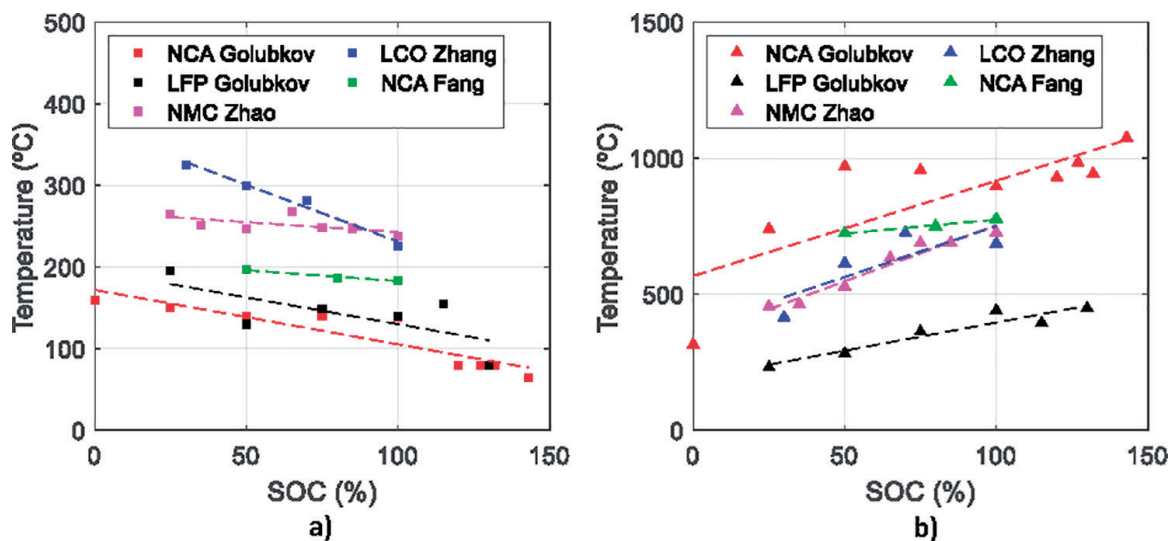
Figure 7.
SOC influence on TR (a) T2 vs. SOC; and (b) T3 vs. SOC. Data obtained from [51–54].

anode and, specifically, the SEI layer. The analysis of SOH as an influencing factor in TR is currently taking on particular importance given the growing interest in second life applications for lithium-ion batteries [55–57]. In this second life, due to the fact that the SOH is below the design value, this could give rise to phenomena for which the cell has not been designed.

It has been confirmed that, when LIBs age due to high temperature cycling, there is an improvement in their thermal stability, with an increase in T_1 and a reduction in heat generation [50]. This is due to the fact that the high temperature permits the formation of a more stable SEI layer. On the other hand, ageing by low-temperature cycling has the reverse effect, with a decrease in T_1 and T_2 and an increase in the self-heating rate.

Lithium plating may also occur in the form of dendrites which, as described in Section 3.2.1, may pierce the separator and cause an ISC that triggers TR. For this reason, an aged cell with a lower SOH is less safe with regard to the initiation of TR. However, as the SOH decreases, so does the amount of active materials available in the cell, thereby reducing the amount of heat released in a possible TR [58].

6. Hazards of thermal runaway

TR is the most dangerous phenomenon that can occur in an LIB, causing its self-destruction. However, the hazards derived from TR are not solely limited to the inoperability of a cell. As a result of a TR, the LIBs are exposed to extremely high temperatures which could cause burn injuries to persons or affect nearby equipment. The formation of gases in the cell interior increases the pressure, which could lead to venting, the rupture of the cell casing or an explosion. In addition to flammable gases, highly toxic gases are also generated such as hydrogen fluoride (HF) and phosphoryl fluoride (POF_3) [59]. The combustion of the released gases is dependent on meeting the three conditions making up what is known as the fire triangle. The fire triangle is the analogy represented in **Figure 8a** and which makes it possible to understand the three components required for combustion to take place: a fuel, an oxidising agent such as oxygen and energy or heat. All three elements are present in LIBs, and
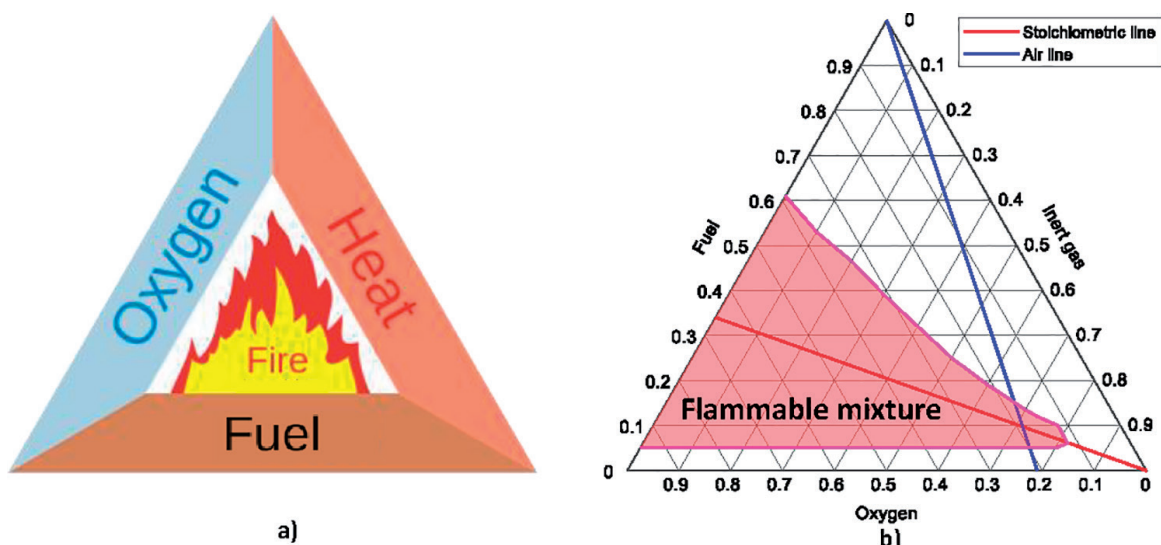
Figure 8.
(a) Fire triangle; (b) flammability diagram.

therefore, there is a probability of fire. The inflammable gases produced are the fuel. Oxygen is present either in the outside air or in the active material of the cathode, which is generally an oxide. Finally, heat is either generated by the actual exothermic reactions taking place, or it could also come from an ignition source such as a spark that may be produced as a result of the friction between the high-speed release of gases and the safety vent. It could also be due to an arc generated by the shorting of the electrodes during the TR [5]. Despite the fact that the three conditions of the triangle are met, combustion is not assured, given that the three elements must be combined in the right proportions for a fire to occur. Whenever any of these conditions are not met, then there can be no combustion. This can be extremely important with a view to extinguishing a fire caused by TR in a LIB [60]. In **Figure 8b** a ternary plot represents the flammability of mixtures of methane (fuel), oxygen and nitrogen (inert gas). Only when the concentrations of all three substances are in the red zone combustion can occur. The blue line is the air line representing all the possible mixtures of the substances under air conditions, from 79% of nitrogen and 21% of oxygen to 100% of methane. The red line is the stoichiometric line, and as the mixture is closer to that line, the combustion is more likely.

Another major thermal runaway hazard is its ability to propagate to other nearby cells, causing faults in "healthy" cells that probably would not have been affected by the abuse causing the TR in the source cell. The propagation of TR significantly increases the risk to the installation and to persons, given that the consequences of TR are multiplied by each cell affected. Propagation occurs through the transmission of heat from the source cell, either through conduction, convection or radiation, raising the temperature of the adjoining cells and initiating the exothermic reactions that lead to TR. The cell itself, as well as the gases released and the materials ejected, is responsible for the said transmission of heat. If the appropriate measures are not taken, once TR has been initiated in a cell, then it may be impossible to prevent propagation. Therefore, it is essential to take the phenomenon of TR into account in the battery design, not only at a cell level but also at a battery pack level, in order to have the necessary measures in place to reduce or prevent propagation.

7. Methods for the early detection of TR

In view of the hazardous nature of TR, it is essential to have devices in place that permit the detection of TR before it can even begin. New regulations such as GB 38031-2020 require the installation of a system in EVs to alert passengers of a battery fault at least 5 minutes in advance. In order to achieve this objective, it is necessary to have an in-depth knowledge of the behaviour of certain measurable variables that could provide information on the potential onset of TR. At present, the key LIB variables measured by the BMS are voltage, current and temperature. The monitoring of these variables permits adequate battery management, maintaining its operating point within the SOA. However, situations may arise in which both the BMS and the sensors may fail and may not be useful in guaranteeing the safety of the LIBs and the early detection of TR. With this in mind, other variables are now being investigated and which are not generally measured by current BMSs, but which are of great interest for the purpose of TR detection. The most important variables are discussed below, indicating their pros and cons.

7.1 Temperature

It has already been mentioned that the LIB temperature is a fundamental variable to be considered. The possibility of triggering TR can to a large extent be reduced by monitoring the temperature to ensure that it remains within the established safety range. Not withstanding this, situations may arise in which temperature is not a reliable variable, such as TR resulting from mechanical abuse or due to dendrite growth. If no account is taken of faults of this type, then temperature can be the most reliable variable for the early detection of the onset of TR. Once the cell temperature has exceeded the recommended limits, an alert can be given regarding the malfunctioning of the battery with sufficient time to prevent the temperature from continuing to rise, thereby avoiding exothermic reactions, cell degradation and the generation of more heat. This would therefore interrupt the path leading to chain reactions that ultimately trigger TR.

Fortunately, BMSs generally incorporate a battery temperature measurement function. Nevertheless, most BMSs do not monitor the temperature of all the battery cells. Instead, the temperature sensors are generally placed in strategical positions in order to reduce their number. In addition, significant thermal gradients may develop inside LIBs during charge and discharge, which are more pronounced with increased cell size and current rate [61]. As a result, it may happen that the temperature of a cell goes outside the safe range yet is not detected by the sensors until it is too late.

Moreover, a further drawback is that the sensors measure the surface temperature of the batteries, while the internal temperature may be greater and the surface-mounted sensor may take some time to detect rapid variations in this variable. **Figure 9** shows the difference between the internal temperature and that measured on the cell surface during rapid charge or discharge [62]. It can be observed that the surface temperature remains in the range between 20 and 40°C, while the internal temperature can exceed 60°C. The internal temperature is the most relevant, given that this is where the chemical reactions between the cell components take place. For this reason, some studies publish methods to measure the internal temperature by means of specific sensors [63]. The problem with these internal sensors is that they may affect the performance of the cell itself. What is more, when there are a
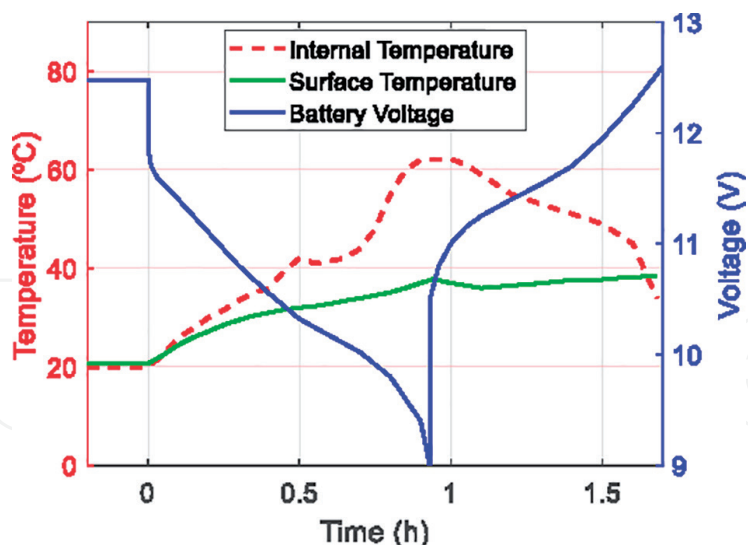
Figure 9.
Internal and superficial temperature during fast charging and discharging. Data obtained from [57].

very large number of cells, it can be expensive to place temperature sensors in each one. Currently, the techniques of internal temperature monitoring can be divided in two main themes of hard sensors and soft sensors [64]. In this reference, the hard sensors include sensors that need to be inserted into the cell, such as thermocouples, thermistors, resistance temperature detectors and optical fibre sensors or contactless methods such as EIS, which will be detailed in Section 7.7. On the other hand, soft sensors are estimators or observers that can estimate the internal temperature from superficial measurements using specific models.

7.2 Voltage

Just like temperature, voltage is another fundamental variable for LIBs, and manufacturers establish a safety range. Therefore, by monitoring the voltage, cells can be maintained at a safe operating point. The possibility of TR caused by overcharge or overdischarge can be avoided by monitoring the voltage (provided that the sensors and BMS are working correctly). However, in view of the results published in the literature for other types of abuse, such as external heating, voltage may not be indicative of the presence of an abuse situation that could trigger a thermal runaway. This is due to the fact that the voltage may not be affected by this type of abuse and a sharp voltage drop may only be detected once the separator melts and the subsequent ISC. However, this event generally occurs at temperatures of between 135 and 165°C, which could be a very late detection of the abuse. **Figure 10** shows the results of three identical tests on the same type of cell, where it can be seen how the voltage behaviour varies in each test [33]. The results of the tests shown in **Figure 10b** and **c** show how the voltage would have provided an early detection of TR with more than 300 seconds to spare. However, in the case of **Figure 10a**, the voltage drop is detected practically at the same time as the start of the TR, and there was therefore no advance warning.

7.3 Current

In the same way as voltage and temperature, this is a variable that is already measured by present-day BMSs, and so there is no need to add new hardware. Given
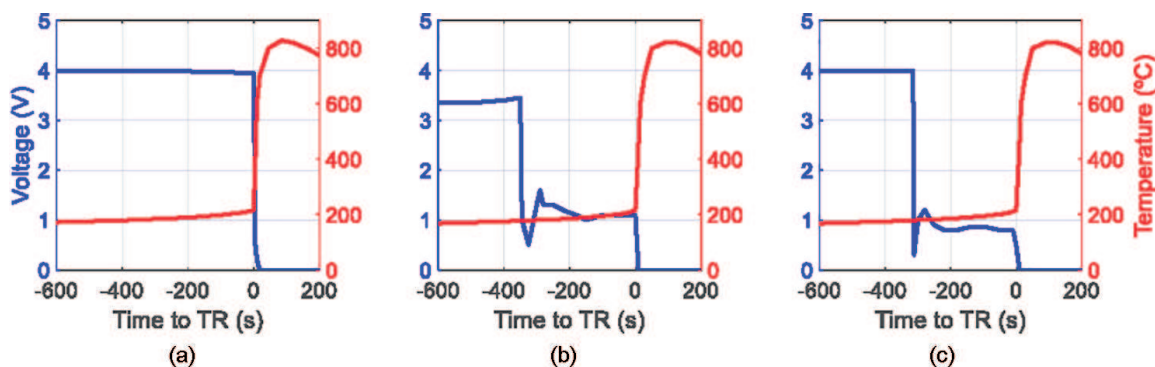
Figure 10.
Temperature and voltage evolution of the cell in three identical overtemperature tests. Data obtained from [28].

that its measurement makes it possible to monitor the battery charge and discharge, it is useful in normal operation in order to avoid excessive currents that may affect the internal processes taking place in the LIB. It also allows for the detection of external short circuits involving large current peaks. However, the main drawback is that the current is generally measured for the entire battery pack. This is because, when the cells are connected in series, the same current passes through all the cells. This may lead to a situation in which, although there is a fault in one cell and an ISC occurs, if the rest of the cells connected in series are operating correctly, then the system will not detect this. It is therefore difficult to detect a fault in large battery systems through current measurement. All the same, there are methods to detect an ISC in a cell in a battery system with cells connected in series and parallel by using $2 \cdot (N_s - 1)$ ammeters, where N_s is the number of cells connected in series [65].

7.4 Pressure

The gases generated in the initial phases of TR, caused by the decomposition of the SEI and the vaporisation of the organic solvents in the electrolyte, create an increase in pressure in the cell interior. This, together with the temperature increase, creates a considerable increase in the internal pressure. This is therefore a variable that provides extremely reliable information on the formation of gases as a result of some type of abuse to the cell, thereby providing very early detection of TR, given that it would be detected at the start of the exothermic reactions that produce gases. Notwithstanding this, it is not easy to measure the internal pressure of the cell without modifying its structure or affecting its performance. On the other hand, it may be more feasible to contain the cells in sealed covers, such as an external casing that permits the mounting of a pressure sensor to detect the release of gases by the cell under abuse. Unfortunately, in this case, gases would be detected when they are released, rather than when they are produced, which would delay the detection of TR.

7.5 Deformation

Although this detection method is related to the internal pressure measurement, in this case the measurement would be taken from the cell exterior. A force or deformation sensor may be able to detect the increase in volume of the cells caused by an increase in internal pressure. This technique offers better results in pouch cells than in cylindrical or prismatic ones, given that they are subject to greater changes in volume during normal operation. The presence of gases produces a larger swelling in pouch

cells, so that the measurement of this deformation provides detection prior to venting, and it may be possible to prevent the release of toxic and flammable gases into the surroundings. However, the drawback is the need for individual sensors for each cell, particularly in those applications in which there are hundreds or thousands of cells, which could make the battery more expensive.

7.6 Gas release

The chemical reactions that take place between the internal components of the cells result in the production of gases, thereby increasing the internal pressure until the gases are finally released into the surroundings. Given that venting is an event that takes place prior to TR, with the installation of gas sensors that are capable of detecting the presence of released gases, then early detection is possible in order to avoid TR [66]. The numerous articles in specialised literature on TR have analysed the composition of the gases released during venting and those released in TR. During TR, a greater amount of gases is released in comparison with venting [67]. In most publications in the literature, the composition of the gases is generally measured once thermal runaway has occurred. As this can vary considerably with the composition of the gases released during venting, with a view to the early detection of this phenomenon, it is essential to analyse the venting process. In general, the gases with the highest concentrations include CO_2, CO, H_2 and hydrocarbons from the vaporisation of the electrolyte organic solvents (DMC, DEC, EC) [49, 68, 69]. In general, the gases produced during venting are dominated by the used electrolyte mixture, whereas while TR, the side reactions are more significant [6, 70].

The main drawback to this detection method is the need for venting to occur sufficiently in advance of the onset of TR. Furthermore, the time between the venting and TR generally varies and depends on a number of factors, such as the abuse conditions, SOC and type of cell [49, 51]. Possibly, at the time when venting is detected, it may be too late to prevent the initiation of TR. Moreover, there is also the possibility that there is no prior venting before TR is triggered in the cell, such as when TR is caused by mechanical abuse, when it can be triggered in just a few seconds [49].

Unfortunately, venting can release flammable gases (which can combust on contact with the air) and toxic gases (which can be harmful to human health). Therefore, account should be taken of the consequences of the detection method failing to detect the venting in time, and that the cell may go into an abuse situation in which it is not possible to prevent TR.

7.7 Impedance

A number of investigators have published articles demonstrating that the cell impedance may provide accurate information on its state. Based on this information, it is possible to estimate the SOC [71], the SOH [72] and even the internal temperature of the cell [73–79]. This makes it possible to improve the performance of the battery, extend its lifespan and guarantee its safety.

An electrochemical impedance spectroscopy is generally used to measure the cell impedance. This is a non-destructive technique that makes it possible to characterise the electrochemical behaviour of the batteries. To do so, the battery is subjected to sinusoidal current or voltage excitation, and the current or voltage response provided by each cell is measured. Based on the voltage and current ratio for each cell, it is possible to determine its complex impedance. Studies have demonstrated that the
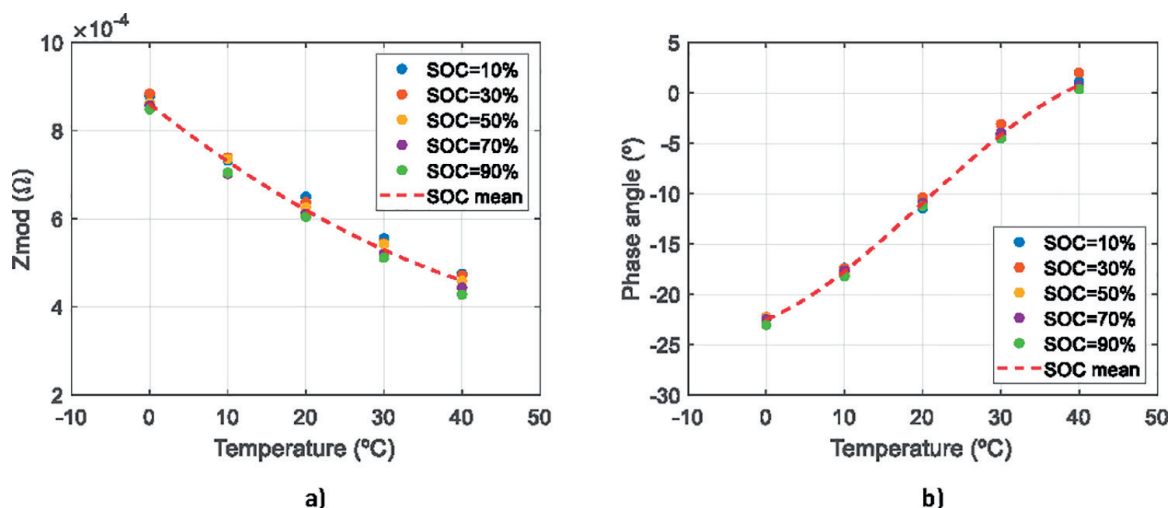
Figure 11.
Relationship between impedance and temperature. (a) Zmod vs. temperature; and (b) phase angle vs. temperature. Data obtained from [69].

impedance module [73], its real part [74], imaginary part [75], phase angle [76, 77] and intercept frequency [78, 79] can provide information on the internal state of the cells. **Figure 11** shows the results obtained from the EIS test data on 46 Ah pouch cells at different SOC and different temperatures [80]. On the one hand, **Figure 11a** shows the relationship between the cell impedance module (*Zmod*) and its temperature. By contrast, **Figure 11b** shows the relationship between the impedance phase and temperature. In both cases, the analysis was made on the impedance data for a frequency of 71.6 Hz, given that this is a frequency at which it has been demonstrated that there is less dependence on the cell SOC level. The study demonstrates that the impedance measurement can provide reliable information on the internal temperature of the cell.

The principal drawbacks of this detection method include the need for an impedance measurement system that does not interfere with battery performance. Moreover, as the excitation signal used for the batteries gives a low response, it is necessary to have extremely accurate sensors if the cell impedance is to be accurately estimated. In turn, given that the cell impedance varies in relation to the SOC and to the SOH, it would be necessary to perform a complete characterisation of the evolution of the impedance in the different scenarios to which LIBs may be exposed in their application.

7.8 Summary of the detection methods and research trends

Table 2 shows the main pros and cons of each detection variable. Despite the fact that no variable guarantees, in all cases, the detection of a TR phenomenon sufficiently in advance, the combination of the measurement of different variables would make the system safer and more reliable, significantly reducing the risk. However, due to the fact that the implementation of the measurement of new variables could increase the cost of the system, the pros and cons of each measurement must be considered in order to obtain a detection system that guarantees greater reliability with regard to safety and the detection of TR.

In this sense, in the roadmap of Battery 2030+ research initiative, R&D efforts are made towards the integration of smart functionalities in LIBs [81]. The integration of smart functionalities aims to enhance the lifetime and safety of batteries by injecting smart embedded sensing technologies and functionalities into the battery

23

Variable	Advantages	Disadvantages
Temperature	• Most indicative variable. • BMSs already measure it.	• It is not measured in all the cells. • Surface temperature is measured, not internal.
Voltage	• BMSs already measure it for all the cells. • Protects from overcharges and overdischarges.	• It does not anticipate TR detection in some abuses such us thermal until ISC occurs.
Current	• BMSs already measure it. • It can measure overcurrents and short circuits.	• In batteries with a large number of cells in series, a fault in one cell may not be detected.
Pressure	• Detects gas formation (internal measure). • Detects gas release (external measure)	• Internal measurement is complex. • Sealed module required.
Deformation	• Detects changes in volume due to gas formation.	• Hard to measure in cylindrical and prismatic. • Complex to integrate into large batteries.
Gas release	• Detects gas release (venting and TR). • Economical and feasible device	• Late detection if no venting is produced prior to TR, or if it is close to TR.
Impedance	• Early detection of TR. • Estimates cell internal temperature.	• New BMS functionality is required. • Complex measurement during operation.

Table 2.
Advantages and disadvantages of each detection variable.

cell, with the ultimate goal of integration into the BMS. SPARTACUS, SENSIBAT and INSTABAT are the three Research and Innovation actions granted under the H2020 topic 'Sensing functionalities for smart battery cell chemistries' with the aim of projects commissioned to develop affordable sensor solution to guarantee the safety of LIBs and to achieve an accurate monitoring of the state and the degradation phenomena. These projects propose alternative variables and measurement devices to ensure the safe operation of Li-ion batteries.

On the one hand, SPARTACUS aims to develop an affordable sensor solution based on acoustic sensors complemented by electrochemical impedance and temperature measurements. By holistic in-operando monitoring of these variables, SPARTACUS is developing a monitoring algorithm for the relevant battery states, with the state of safety (SoS) being one of them. By contrast, SENSIBAT chooses pressure, temperature and electrochemical impedance spectroscopy as indicative variables, developing the required sensing technology to be integrated in the battery cells. The goal of the project is to manufacture a module with the cells incorporating the designed sensors, thereby analysing the scaling-up of the technology, concluding the study with a cost-benefit analysis and a recycling study. Finally, INSTABAT relies on the concept 'Lab-on-a-cell', which is a multi-sensor platform that includes both physical sensors, such as optical fibre, a reference electrode or a photo-acousting sensor, and virtual sensors, with the thermal and electrochemical virtual sensors being the main proposal of the project. INSTABAT aims to enhance battery performance, reduce the required safety margins, improve the cell operation using data from the sensors and enable battery self-healing and second life usage.

The development of multi-variable and affordable sensing techniques able to combine the battery state estimation with the safety supervision is one of the most promising research trends related to the early detection of a TR.

8. Methods for the prevention and mitigation of TR

8.1 Cell safety

Protection at a cell level is primarily achieved through the use of electrical devices and subsystems that prevent excess temperature and pressure in the cell by opening the circuit, increasing the resistance or changing the chemical composition of the cell [41]. These devices include:

8.1.1 Thermal fuse

A thermal fuse is an alloy wire with a resistor and with thermal characteristics that allow it to melt when a given current flows or when exposed to excessive temperature. Once melted, it permanently disconnects the battery and needs to be replaced. Thermal fuses are used to protect against TR and their cut-off temperature is around 30–50°C above the maximum battery temperature in normal operation [21]. At high voltages, the disconnection of the fuse will not interrupt TR [82].

8.1.2 Positive temperature coefficient (PTC)

This is a resistor that increases its resistance as its temperature increases, so that it responds to a temperature increase by reducing the current and, therefore, the heat generated by the cell. At a normal temperature, its resistance is low. The principal purpose of PTC devices is to protect the batteries from external short circuits and also to provide protection in other conditions of electrical abuse [21].

8.1.3 Shutdown separator

The separator consists of a porous membrane intended for the purpose of allowing lithium ions to pass through it and electrically isolating the cell electrodes. As mentioned in Section 4, the most widely used materials for the separator are PE and PP. When used together, the protection achieved is known as a shutdown separator due to the different melting points of each element, 130°C for PE and 165°C for PP. When the PE melting point is reached and it melts, it fills the pores of the PP layer, preventing the lithium ions from flowing through and, therefore, shutting down the cell. This would make it possible to reduce the heat generated by the operation itself and to detect abnormal behaviour of the LIB. However, if the temperature continues to rise and reaches the melting point of the PP, then the separator loses its mechanical integrity and an ISC could occur. This protection must be designed to act at a temperature that is lower than the TR initiation temperature and with a shutdown temperature that is sufficiently below the temperature at which the separator loses its mechanical integrity [83].

8.1.4 Current interrupt device (CID)

Its main function is to protect the cell when the internal pressure increases above a maximum threshold. When the said pressure is reached in the cell interior, the

electrical contact between the cathode and casing opens, interrupting the electric current and stopping the cell from operating. This is useful if the cause of the over-pressure is due to the current flowing through the cell. However, if this is not the cause, then it does not prevent the internal pressure from increasing, and it will be necessary for the safety vent to operate.

8.1.5 Safety vents

The cylindrical and prismatic cells generally incorporate this type of safety device, which opens when the pressure inside the cell reaches dangerous levels that could lead to an explosion or the rupture of the casing. By releasing the gases that were contributing to the internal pressure and temperature increase, cooling occurs due to the Joule-Thomson effect, and this could stop the temperature increase. However, it should be considered that, when the safety vent opens and releases the accumulated gases, atmospheric air (containing oxygen and moisture) also enters the cell and could react with lithium metal and electrolyte, causing ignition or an explosion [84].

8.2 Module safety

Module safety is achieved through the cell external management systems which control the operation of the LIB and monitor variables such as voltage, current and temperature in order to ensure that they remain within the limits of the SOA.

8.2.1 BMS

The BMS is the electronic system that controls the battery status and guarantees safe operation and optimal performance. For this purpose, it monitors variables such as the voltage, current and temperature of the cells and checks that these values stay within the safe operating ranges. It also performs a number of functions such as the balancing of the cell voltages, estimation of SOC and the control of the charge and discharge processes, among others.

Despite the fact that the BMS monitors the variables to ensure that they remain within the safe operating window, it is not able to prevent the onset of TR in all circumstances, in view of the accidents that continue to occur. However, the BMS is capable of detecting a TR and of directing the measures necessary for its mitigation and preventing its propagation. For this reason, there is a need to provide the BMS with new functions that make it possible to better estimate the battery status, as it is actually one of the aims of Battery 2030+ research initiative. Algorithms are currently being developed which, based on voltage, current and temperature, will provide information about the battery status, such as the internal temperature of the cell [85, 86], the triggering of an ISC [31, 87] and SOH [88]. Moreover, in combination with sensors that measure other variables, the detection of TR can be improved.

8.2.2 BTMS

The problems of excessive temperatures or local hot spots (affecting the uniformity of the battery) can be harmful to LIBs, affecting their performance, lifespan and safety. This problem is particularly exacerbated by the fact that, in the battery packs, the cells are placed very close together in order to take full advantage of the high energy and power density of the LIBs. For this reason, TR can propagate and cause the

failure of the entire battery. It is therefore important to design a suitable thermal management system that makes it possible to maintain the temperature within its desired range and to guarantee the uniformity of the temperature in the cell. The BTMS is responsible for performing this function and for monitoring the temperature of the LIBs, ensuring that it remains within the SOA. The BTMS is not only a prevention measure, but can also mitigate the effects of a TR in the battery, by dissipating a large amount of the heat generated and obstructing the propagation of the phenomenon. The BTMS can be active or passive. On the one hand, an active system consumes extra energy to power the fans or pumps responsible for the circulation of a cooling fluid. Furthermore, the components of an active BTMS are integrated as a subsystem of the BMS which, in this case, is given the added function of regulating the cell heating or cooling. On the other hand, a passive system consists of surrounding the cells with layers of materials with the capacity to improve the dissipation of the heat generated, isolate one cell from another and even include certain properties such as flame retardancy, in order to prevent propagation and fire.

Despite the advantages that the BTMS offers, it does have certain disadvantages such as the higher cost and volume of the ESS, reducing its energy density. Moreover, it does not prevent the root causes of TR, given that it is only responsible for providing temperature control, which can get out of control if the generation of heat exceeds the BTMS dissipation capacity. For this reason, it must be accompanied by other devices such as the BMS, which monitors the state of the battery and measures other variables that permit the early detection of TR.

8.2.3 Mitigation and extinguishing systems

Once TR has been initiated in a cell, the mitigation strategy involves taking the measures that make it possible to reduce the dangers of the phenomenon and prevent its propagation. If the battery ignites as a result of the combustion of the flammable gases in contact with the oxygen in the air, the risks increase, given that a greater amount of heat is released, favouring propagation. As detailed in Section 6, for combustion to occur, the elements of the fire triangle must all be present and combined in the right proportions. If one of the three conditions is not met, then combustion will not take place. For this reason, investigations are underway regarding the introduction of inert gas dilutions in order to reduce the concentration of oxygen, as a method to prevent or extinguish the fire, given that these dilutions can reduce the flame temperature and increase the flammability limit [89]. For conventional hydrogen fuels, the limiting oxygen concentration (LOC) of their flame is usually above 12%, so they cannot maintain a flame at a lower oxygen concentration [90]. Nitrogen (N_2) and argon (Ar) are the gases that are most widely used to fight conventional fires. The advantage of inert gases is that they do not react with other gases that may be present, and they have proven to be effective in reducing the concentration of toxic gas emissions. Furthermore, the use of gaseous extinguishing agents makes it possible to occupy all possible spaces without affecting the functioning of the rest of the battery components. However, reducing the oxygen concentration to under 12% is not sufficient to eliminate the battery flame [90]. This may be due to the fact that, during TR, the internal temperature of the battery and the flammable gases released can exceed 800°C, so that these preheated fuel gases can extend the LOC and fuel flammability [89, 90].

Figure 12 collects a scheme of the safety strategies of detection, prevention and mitigation against TR commented in this chapter. The scheme allows to observe the level of implementation of any of the strategies and the data and control communication flows.
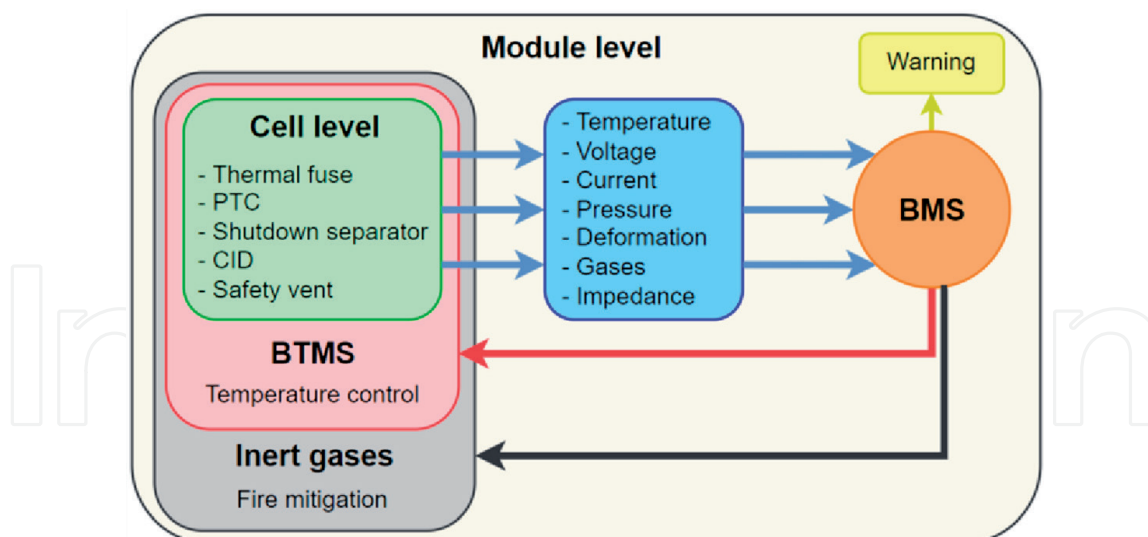
Figure 12.
LIBs safety scheme against TR.

9. Conclusions

The current scenario to combat climate change is providing a strong impetus to ESSs, directed at achieving greater integration of REs and the electrification of the automotive sector. LIBs are the most widely used technology in ESS, leading this transition towards the reduction of CO_2 emissions. While advances are continuing to be made with regard to the materials used in LIBs, in order to overcome the safety-related disadvantages and obtain higher energy densities, there is a need to gain in-depth knowledge of the behaviour of the cells outside their SOA and, in particular, all aspects surrounding the phenomenon of TR.

This chapter has addressed the problems of TR from a general point of view, analysing the main aspects that characterise it. The information provided makes it possible to gain a broad knowledge of this phenomenon and can prove useful as a guide and starting point for anyone interested in LIBs, in order to analyse aspects ranging from cell design and manufacture, battery assembly, right up to the end uses of these batteries.

This review of TR first looks at the causes that can trigger this phenomenon, it then goes on to analyse the phases occurring during the processes prior to the initiation of TR. By understanding the reactions and causes, the root of the problem can be tackled and the correct prevention measures can be taken. On the other hand, one of the particularities of thermal runaway is that it is influenced by a number of factors that may make prevention and detection more complicated. For this reason, a section has also been dedicated to understanding the factors affecting this phenomenon and the extent of the influence of each factor. Particular attention has been given to the variables that permit the early detection of TR and to mitigation strategies, given that, at present, TR in LIBs is a reality that we must learn to live with. Although there is no single variable that permits the early detection of TR, a combination of different variables guarantees greater accuracy in its detection. Once TR has been detected, the appropriate measures can be taken to prevent it from occurring or, should this prove impossible, to reduce its consequences. The BMS plays a crucial role in the safety of LIBs, as it is responsible for monitoring the main variables that determine cell behaviour and can even be adjusted to detect thermal runaway. Other safety measures such

as BTMS for the improvement of the temperature control or inert gas dilutions to prevent battery fires are also helpful to fight TR.

Acknowledgements

Conflict of interest

The authors declare that there is no conflict of interest.

Author details

Iñaki Lalinde[1]*, Alberto Berrueta[1], Juan José Valera[2], Joseba Arza[2], Pablo Sanchis[1] and Alfredo Ursúa[1]

1 Institute of Smart Cities, Department of Electrical, Electronic and Communications Engineering, Public University of Navarre (UPNA), Campus de Arrosadia, Pamplona, Spain

2 Ingeteam R&D Europe, Polígono Parque Tecnológico, Zamudio, Spain

*Address all correspondence to: inaki.lalinde@unavarra.es

IntechOpen

References

[1] Millet L, Berrueta A, Bruch M, Reiners N, Vetter M. Extensive analysis of photovoltaic battery self-consumption: Evaluation through an innovative district case-study. Applied Physics Reviews. 2019;**6**(2). DOI: 10.1063/1.5049665

[2] CNESA. Energy Storage Industry White Paper 2021;**2021**(8610):2021

[3] Statista. Lithium-ion battery pack costs worldwide between 2011 and 2030. 2020. Available from: https://www.statista.com/statistics/883118/global-lithium-ion-battery-pack-costs/

[4] European Commission, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs, Blengini G, El Latunussa C, Eynard U, et al. Study on the EU's list of critical raw materials (2020): critical raw materials factsheets, Publications Office. 2020. DOI: 10.2873/92480. ISBN: 978-92-76-21053-5

[5] Feng X, Ouyang M, Liu X, Lu L, Xia Y, He X. Thermal runaway mechanism of lithium ion battery for electric vehicles: A review. Energy Storage Mater. 2018;**10**(May 2017):246-267. DOI: 10.1016/j.ensm.2017.05.013

[6] Feng X, Ren D, He X, Ouyang M. Mitigating thermal runaway of lithium-ion batteries. Joule. 2020;**4**(4):743-770. DOI: 10.1016/j.joule.2020.02.010

[7] Wang Q, Mao B, Stoliarov SI, Sun J. A review of lithium ion battery failure mechanisms and fire prevention strategies. Progress in Energy and Combustion Science. 2019;**73**:95-131. DOI: 10.1016/j.pecs.2019.03.002

[8] Miao Y, Liu L, Zhang Y, Tan Q, Li J. An overview of global power lithium-ion batteries and associated critical metal recycling. Journal of Hazardous Materials. 2022;**425**(November 2021):127900. DOI: 10.1016/j.jhazmat.2021.127900

[9] Qiu Y, Jiang F. A review on passive and active strategies of enhancing the safety of lithium-ion batteries. International Journal of Heat and Mass Transfer. 2022;**184**(xxxx):122288. DOI: 10.1016/j.ijheatmasstransfer.2021.122288

[10] Petzl M, Kasper M, Danzer MA. Lithium plating in a commercial lithium-ion battery—A low-temperature aging study. Journal of Power Sources. 2015;**275**:799-807. DOI: 10.1016/j.jpowsour.2014.11.065

[11] Vermeer W, Mouli GRC, Bauer P. A comprehensive review on the characteristics and modelling of Lithium-ion battery ageing. IEEE Transactions on Transportation Electrification. 2021;**8**(2):2205-2232. DOI: 10.1109/TTE.2021.3138357

[12] Mikolajczak C, White K, Kahn M, Long RT. Lithium-Ion Batteries Hazard and Use Assessment. SpringerBriefs in Fire. New York: Springer; 2011. XII, 115p. DOI: 10.1007/978-1-4614-3486-3. e-ISBN: 978-1-4614-3486-3

[13] Ruiz V, Pfrang A, Kriston A, Omar N, Van den Bossche P, Boon-Brett L. A review of international abuse testing standards and regulations for lithium ion batteries in electric and hybrid electric vehicles. Renewable and Sustainable Energy Reviews. 2018;**81**(May 2017):1427-1452. DOI: 10.1016/j.rser.2017.05.195

[14] Zhang X, Li Z, Luo L, Fan Y, Du Z. A review on thermal management of lithium-ion batteries for electric vehicles. Energy. 2022;**238**:121652. DOI: 10.1016/j.energy.2021.121652

[15] Berrueta A, Urtasun A, Ursúa A, Sanchis P. A comprehensive model for lithium-ion batteries: From the physical principles to an electrical model. Energy. 2018;**144**:286-300. DOI: 10.1016/j.energy.2017.11.154

[16] Petzl M, Danzer MA. Nondestructive detection, characterization, and quantification of lithium plating in commercial lithium-ion batteries. Journal of Power Sources. 2014;**254**:80-87. DOI: 10.1016/j.jpowsour.2013.12.060

[17] Han-Mei M. Side Reactions in Lithium-Ion Batteries. Berkeley: University of California; 2012

[18] Zhu J, Sun Z, Wei X, Dai H, Gu W. Experimental investigations of an AC pulse heating method for vehicular high power lithium-ion batteries at subzero temperatures. Journal of Power Sources. 2017;**367**:145-157. DOI: 10.1016/j.jpowsour.2017.09.063

[19] Soto A, Berrueta A, Oficialdegui I, Sanchis P, Ursúa A. Noninvasive aging analysis of lithium-ion batteries in extreme cold temperatures. IEEE Transactions on Industry Applications; IEEE. 2021;**58**(2):2400-2410. DOI: 10.1109/TIA.2021.3136808

[20] Soto A, Berrueta A, Sanchis P and Ursúa A. Analysis of the main battery characterization techniques and experimental comparison of commercial 18650 Li-ion cells. In: 2019 IEEE International Conference on Environment and Electrical Engineering and 2019 IEEE Industrial and Commercial Power Systems Europe (EEEIC/I&CPS Europe); 11-14 June 2019: Genova. New York: IEEE. p. 1-6. DOI: 10.1109/EEEIC.2019.8783862

[21] Balakrishnan PG, Ramesh R, Prem Kumar T. Safety mechanisms in lithium-ion batteries. Journal of Power Sources. 2006;**155**(2):401-414. DOI: 10.1016/j.jpowsour.2005.12.002

[22] Aurbach D et al. Design of electrolyte solutions for Li and Li-ion batteries: A review. Electrochimica Acta. 2004;**50**(2-3 SPEC. ISS):247-254. DOI: 10.1016/j.electacta.2004.01.090

[23] Lai X, Zheng Y, Zhou L, Gao W. Electrical behavior of overdischarge-induced internal short circuit in lithium-ion cells. Electrochimica Acta. 2018;**278**:245-254. DOI: 10.1016/j.electacta.2018.05.048

[24] Li HF, Gao JK, Zhang SL. Effect of overdischarge on swelling and recharge performance of lithium ion cells. Chinese Journal of Chemistry. 2008;**26**(9):1585-1588. DOI: 10.1002/cjoc.200890286

[25] Zhang L et al. Capacity fading mechanism during long-term cycling of over-discharged LiCoO2/mesocarbon microbeads battery. Journal of Power Sources. 2015;**293**:1006-1015. DOI: 10.1016/j.jpowsour.2015.06.040

[26] Zhao M, Dewald HD, Lemke FR, Staniewicz RJ. Electrochemical stability of graphite-coated copper in lithium-ion battery electrolytes. Journal of the Electrochemical Society. 2000;**147**(11):3983. DOI: 10.1149/1.1394007

[27] Maleki H, Howard JN. Effects of overdischarge on performance and thermal stability of a Li-ion cell. Journal of Power Sources. 2006;**160**(2 SPEC. ISS):1395-1402. DOI: 10.1016/j.jpowsour.2006.03.043

[28] Arora A, Medora NK, Livernois T, Swart J. Safety of Lithium-Ion Batteries for Hybrid Electric Vehicles. In: Electric and Hybrid Vehicles. Amsterdam: Elsevier B.V; 2010. p. 463-491. DOI: 10.1016/B978-0-444-53565-8.00018-X

[29] Kim KM, Jeong YS, Bang IC. Thermal analysis of lithium ion battery-equipped smartphone explosions. Engineering Science and Technology, an

International Journal. 2019;**22**(2):610-617. DOI: 10.1016/j.jestch.2018.12.008

[30] Berrueta A, Irigaray V, Sanchis P, Ursúa A. Lithium-ion battery model and experimental validation. In: 2015 17th European Conference on Power Electronics and Applications (EPE'15 ECCE-Europe); 08-10 September 2015: Geneva. New York: IEEE. p. 1-8. DOI: 10.1109/EPE.2015.7309337

[31] Lai X et al. Mechanism, modeling, detection, and prevention of the internal short circuit in lithium-ion batteries: Recent advances and perspectives. Energy Storage Materials. 2021;**35**(October 2020):470-499. DOI: 10.1016/j.ensm.2020.11.026

[32] Liu L et al. Internal short circuit evaluation and corresponding failure mode analysis for lithium-ion batteries. Journal of Energy Chemistry. 2021;**61**:269-280. DOI: 10.1016/j.jechem.2021.03.025

[33] Ren D et al. Investigating the relationship between internal short circuit and thermal runaway of lithium-ion batteries under thermal abuse condition. Energy Storage Materials. 2021;**34**(October 2020):563-573. DOI: 10.1016/j.ensm.2020.10.020

[34] Liu B et al. Safety issues and mechanisms of lithium-ion battery cell upon mechanical abusive loading: A review. Energy Storage Materials. 2020;**24**(June 2019):85-112. DOI: 10.1016/j.ensm.2019.06.036

[35] Chen Y et al. A review of lithium-ion battery safety concerns: The issues, strategies, and testing standards. Journal of Energy Chemistry. 2021;**59**:83-99. DOI: 10.1016/j.jechem.2020.10.017

[36] Lalinde I, Berrueta A, Sanchis P, Ursúa A. Applied method to model the thermal runaway of lithium-ion batteries. In: 2021 IEEE International Conference on Environment and Electrical Engineering and 2021 IEEE Industrial and Commercial Power Systems Europe (EEEIC/I&CPS Europe); 07-10 September 2021: Bari. New York: IEEE. p. 1-6. DOI: 10.1109/EEEIC/ICPSEUROPE51590.2021.9584560

[37] Ren D et al. A comparative investigation of aging effects on thermal runaway behavior of lithium-ion batteries. eTransportation. 2019;**2**. Article 100034, p. 1-13. DOI: 10.1016/j.etran.2019.100034

[38] Spotnitz R, Franklin J. Abuse behavior of high-power, lithium-ion cells. Journal of Power Sources. 2003;**113**(1):81-100. DOI: 10.1016/S0378-7753(02)00488-3

[39] Wang Q, Sun J, Yao X, Chen C. Thermal stability of LiPF6/EC + DEC electrolyte with charged electrodes for lithium ion batteries. Thermochimica Acta. 2005;**437**(1-2):12-16. DOI: 10.1016/j.tca.2005.06.010

[40] Richard MN, Dahn JR. Accelerating rate calorimetry studies of the effect of binder type on the thermal stability of a lithiated mesocarbon microbead material in electrolyte. Journal of Power Sources. 1999;**83**(1-2):71-74. DOI: 10.1016/S0378-7753(99)00260-8

[41] Wang Q, Ping P, Zhao X, Chu G, Sun J, Chen C. Thermal runaway caused fire and explosion of lithium ion battery. Journal of Power Sources. 2012;**208**:210-224. DOI: 10.1016/j.jpowsour.2012.02.038

[42] Kalhoff J, Eshetu GG, Bresser D, Passerini S. Safer electrolytes for lithium-ion batteries: State of the art and perspectives. ChemSusChem. 2015;**8**(13):2154-2175. DOI: 10.1002/cssc.201500284

[43] National Highway Traffic Safety Administration (NHTSA). Lithium-ion Battery Safety Issues for Electric and Plug-in Hybrid Vehicles (Report No. DOT HS 812 418). October, 2017

[44] Kawamura T, Kimura A, Egashira M, Okada S, Yamaki JI. Thermal stability of alkyl carbonate mixed-solvent electrolytes for lithium ion cells. Journal of Power Sources. 2002;**104**(2):260-264. DOI: 10.1016/S0378-7753(01)00960-0

[45] Campion CL, Li W, Lucht BL. Thermal decomposition of LiPF[sub 6]-based electrolytes for lithium-ion batteries. Journal of the Electrochemical Society. 2005;**152**(12):A2327. DOI: 10.1149/1.2083267

[46] Duan J et al. Building safe lithium-ion batteries for electric vehicles: A review. Electrochemical Energy Reviews. Springer Science and Business Media B.V. 2020;**3**(1):1-42. DOI: 10.1007/s41918-019-00060-4

[47] Pfrang A, Kriston A, Ruiz V, Lebedeva N, di Persio F. Safety of rechargeable energy storage systems with a focus on Li-ion technology. In: Emerging Nanotechnologies in Rechargeable Energy Storage Systems. Amsterdam: Elsevier Inc.; 2017. p. 253-290

[48] Son K et al. Comparative study of thermal runaway and cell failure of lab-scale Li-ion batteries using accelerating rate calorimetry. Journal of Industrial and Engineering Chemistry. 2020;**83**:247-251. DOI: 10.1016/j.jiec.2019.11.034

[49] Essl C, Golubkov AW, Fuchs A. Comparing different thermal runaway triggers for two automotive lithium-ion battery cell types. Journal of the Electrochemical Society. 2020;**167**(13):130542. DOI: 10.1149/1945-7111/abbe5a

[50] Börner M et al. Correlation of aging and thermal stability of commercial 18650-type lithium ion batteries. Journal of Power Sources. 2017;**342**:382-392. DOI: 10.1016/j.jpowsour.2016.12.041

[51] Golubkov AW et al. Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes— Impact of state of charge and overcharge. RSC Advances. 2015;**5**(70):57171-57186. DOI: 10.1039/c5ra05897j

[52] Zhao C, Sun J, Wang Q. Thermal runaway hazards investigation on 18650 lithium-ion battery using extended volume accelerating rate calorimeter. Journal of Energy Storage. 2020;**28**(January):101232. DOI: 10.1016/j.est.2020.101232

[53] Zhang Q, Liu T, Wang Q. Experimental study on the influence of different heating methods on thermal runaway of lithium-ion battery. Journal of Energy Storage. 2021;**42**(August):103063. DOI: 10.1016/j.est.2021.103063

[54] Fang J, Cai J, He X. Experimental study on the vertical thermal runaway propagation in cylindrical Lithium-ion batteries: Effects of spacing and state of charge. Applied Thermal Engineering. 2021;**197**(May):117399. DOI: 10.1016/j.applthermaleng.2021.117399

[55] Soto A et al. Integration of second-life battery packs for self-consumption applications: Analysis of a real experience. In: IEEE International Conference on Environment and Electrical Engineering and 2021 IEEE Industrial and Commercial Power Systems Europe (EEEIC/I&CPS Europe); 07-10 September 2021: Bari. New York: IEEE. 2021 p. 1-6. DOI: 10.1109/EEEIC/ICPSEUROPE51590.2021.9584809

[56] Braco E, San Martín I, Berrueta A, Sanchis P, Ursúa A. Experimental assessment of cycling ageing of lithium-ion second-life batteries from electric vehicles. Journal of Energy Storage.

2020;**32**(May):101695. DOI: 10.1016/j. est.2020.101695

[57] Braco E, San Martin I, Berrueta A, Sanchis P, Ursua A. Experimental assessment of first- and second-life electric vehicle batteries: Performance, capacity dispersion, and aging. IEEE Transactions on Industry Applications. Jul. 2021;**57**(4):4107-4117. DOI: 10.1109/ TIA.2021.3075180

[58] Wu P et al. A study on thermal runaway of commercial lithium-ion cells: Influence of soc, cell chemistry and ageing status on safety performance. Lecture Notes in Electrical Engineering. 2019;**486**:619-627. DOI: 10.1007/978-981-10-8506-2_42

[59] Larsson F, Andersson P, Blomqvist P, Mellander BE. Toxic fluoride gas emissions from lithium-ion battery fires. Scientific Reports. 2017;**7**(1):1-13. DOI: 10.1038/s41598-017-09784-z

[60] Li W et al. Fire boundaries of lithium-ion cell eruption gases caused by thermal runaway. iScience. 2021;**24**(5):102401. DOI: 10.1016/j.isci.2021.102401

[61] Grandjean T, Barai A, Hosseinzadeh E, Guo Y, McGordon A, Marco J. Large format lithium ion pouch cell full thermal characterisation for improved electric vehicle thermal management. Journal of Power Sources. 2017;**359**:215-225. DOI: 10.1016/j.jpowsour.2017.05.016

[62] Carkhuff BG, Demirev PA, Srinivasan R. Impedance-based battery management system for safety monitoring of lithium-ion batteries. IEEE Transactions on Industrial Electronics. 2018;**65**(8):6497-6504. DOI: 10.1109/ TIE.2017.2786199

[63] Zhu S et al. A novel embedded method for in-situ measuring internal multi-point temperatures of lithium ion batteries. Journal of Power

Sources. 2020;**456**(July 2019):227981. DOI: 10.1016/j.jpowsour.2020.227981

[64] Jinasena A et al. Online internal temperature sensors in lithium-ion batteries: State-of-the-art and future trends. Frontiers in Chemical Engineering. 2022;**4**(February):1-22. DOI: 10.3389/fceng.2022.804704

[65] Pan Y, Feng X, Zhang M, Han X, Lu L, Ouyang M. Internal short circuit detection for lithium-ion battery pack with parallel-series hybrid connections. Journal of Cleaner Production. 2020;**255**:120277. DOI: 10.1016/j. jclepro.2020.120277

[66] Liao Z, Zhang S, Li K, Zhang G, Habetler TG. A survey of methods for monitoring and detecting thermal runaway of lithium-ion batteries. Journal of Power Sources. 2019;**436**(July 2019):226879. DOI: 10.1016/j. jpowsour.2019.226879

[67] Golubkov AW et al. Thermal runaway of large automotive Li-ion batteries. RSC Advances. 2018;**8**(70):40172-40186. DOI: 10.1039/C8RA06458J

[68] Koch S, Fill A, Birke KP. Comprehensive gas analysis on large scale automotive lithium-ion cells in thermal runaway. Journal of Power Sources. 2018;**398**(June):106-112. DOI: 10.1016/j. jpowsour.2018.07.051

[69] Cai T, Valecha P, Tran V, Engle B, Stefanopoulou A, Siegel J. Detection of Li-ion battery failure and venting with carbon dioxide sensors. eTransportation. 2021;**7**:100100. DOI: 10.1016/j. etran.2020.100100

[70] Essl C, Seifert L, Rabe M, Fuchs A. Early detection of failing automotive batteries using gas sensors. Batteries. 2021;**7**(2):1-26. DOI: 10.3390/ batteries7020025

[71] Howey DA, Mitcheson PD, Member S, Yufit V, Offer GJ, Brandon NP. Motor controller excitation. IEEE Transactions on Vehicular Technology. 2014;**63**(6):2557-2566

[72] Kim J, Krüger L, Kowal J. On-line state-of-health estimation of Lithium-ion battery cells using frequency excitation. Journal of Energy Storage. 2020;**32**(September):101841. DOI: 10.1016/j.est.2020.101841

[73] Zhu JG, Sun ZC, Wei XZ, Dai HF. A new lithium-ion battery internal temperature on-line estimate method based on electrochemical impedance spectroscopy measurement. Journal of Power Sources. 2015;**274**:990-1004. DOI: 10.1016/j.jpowsour.2014.10.182

[74] Schmidt JP, Arnold S, Loges A, Werner D, Wetzel T, Ivers-Tiffée E. Measurement of the internal cell temperature via impedance: Evaluation and application of a new method. Journal of Power Sources. 2013;**243**:110-117. DOI: 10.1016/j.jpowsour.2013.06.013

[75] Spinner NS, Love CT, Rose-Pehrsson SL, Tuttle SG. Expanding the operational limits of the single-point impedance diagnostic for internal temperature monitoring of lithium-ion batteries. Electrochimica Acta. 2015;**174**:488-493. DOI: 10.1016/j.electacta.2015.06.003

[76] Srinivasan R, Carkhuff BG, Butler MH, Baisden AC. Instantaneous measurement of the internal temperature in lithium-ion rechargeable cells. Electrochimica Acta. 2011;**56**(17):6198-6204. DOI: 10.1016/j.electacta.2011.03.136

[77] Srinivasan R, Demirev PA, Carkhuff BG. Rapid monitoring of impedance phase shifts in lithium-ion batteries for hazard prevention. Journal of Power Sources. 2018;**405**

(October):30-36. DOI: 10.1016/j.jpowsour.2018.10.014

[78] Raijmakers LHJ, Danilov DL, Van Lammeren JPM, Lammers MJG, Notten PHL. Sensorless battery temperature measurements based on electrochemical impedance spectroscopy. Journal of Power Sources. 2014;**247**:539-544. DOI: 10.1016/j.jpowsour.2013.09.005

[79] Raijmakers LHJ, Danilov DL, Van Lammeren JPM, Lammers TJG, Bergveld HJ, Notten PHL. Non-zero intercept frequency: An accurate method to determine the integral temperature of Li-ion batteries. IEEE Transactions on Industrial Electronics. 2016;**63**(5):3168-3178. DOI: 10.1109/TIE.2016.2516961

[80] Kilnk J, Orazov N, Grabow J, Benger R. Cell characteristics for 46Ah high power Kokam Nano pouch cell. Mendeley Data. 2020. DOI: 10.17632/g443f7cn7p.1

[81] Edström K, Dominko R, Fitchtner M, Otuszewski T, Perraud S, Punckt C, et al. BATTERY 2030+ Roadmap. 2020. Battery 2030+ [Internet]. Available from: https://battery2030.eu/wp-content/uploads/2022/07/BATTERY-2030-Roadmap_Revision_FINAL.pdf [Accessed: 2022-08-23]

[82] Chen YS, Hu CC, Li YY. The importance of heat evolution during the overcharge process and the protection mechanism of electrolyte additives for prismatic lithium ion batteries. Journal of Power Sources. 2008;**181**(1):69-73. DOI: 10.1016/j.jpowsour.2008.03.015

[83] Zhang SS. A review on the separators of liquid electrolyte Li-ion batteries. Journal of Power Sources. 2007;**164**(1):351-364. DOI: 10.1016/j.jpowsour.2006.10.065

[84] Belov D, Yang MH. Failure mechanism of Li-ion battery at

overcharge conditions. Journal of Solid State Electrochemistry. 2008;**12**(7-8):885-894. DOI: 10.1007/s10008-007-0449-3

[85] Anthony D, Wong D, Wetz D, Jain A. Non-invasive measurement of internal temperature of a cylindrical Li-ion cell during high-rate discharge. International Journal of Heat and Mass Transfer. 2017;**111**:223-231. DOI: 10.1016/j.ijheatmasstransfer.2017.03.095

[86] Sun L, Sun W, You F. Core temperature modelling and monitoring of lithium-ion battery in the presence of sensor bias. Applied Energy. 2020;**271**(March):115243. DOI: 10.1016/j.apenergy.2020.115243

[87] Zhang G, Wei X, Tang X, Zhu J, Chen S, Dai H. Internal short circuit mechanisms, experimental approaches and detection methods of lithium-ion batteries for electric vehicles: A review. Renewable and Sustainable Energy Reviews. 2021;**141**(January):110790. DOI: 10.1016/j.rser.2021.110790

[88] Lipu MSH et al. A review of state of health and remaining useful life estimation methods for lithium-ion battery in electric vehicles: Challenges and recommendations. Journal of Cleaner Production. 2018;**205**:115-133. DOI: 10.1016/j.jclepro.2018.09.065

[89] Li S, Zhang Y, Qiu X, Li B, Zhang H. Effects of inert dilution and preheating temperature on lean flammability limit of syngas. Energy and Fuels. 2014;**28**(5):3442-3452. DOI: 10.1021/ef500187s

[90] Weng J et al. Alleviation on battery thermal runaway propagation: Effects of oxygen level and dilution gas. Journal of Power Sources. 2021;**509**(June):230340. DOI: 10.1016/j.jpowsour.2021.230340