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Abstract

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Contents

Abstract	i
Abstract in lingua italiana	iii
Contents	v
Introduction	1
1 Lithium-ion batteries	3
1.1 Overview	4
1.2 Positive Electrode	5
1.3 Negative Electrode	6
1.4 Electrolyte	7
1.4.1 Solvents	8
1.4.2 Conducting Salts	10
1.4.3 Additives	11
1.5 Separator	12
1.6 Current Collectors	13
1.7 Cell Geometries and Designs	14
2 Battery Failure	17
2.1 Thermal Runaway	18
2.1.1 Causes for Thermal Runaway	18
2.1.2 Semenov Model	20
2.1.3 Energy Balance	21
2.1.4 Basic Reactions	23
2.2 Safety Standards	23
2.2.1 Safety Tests	25
2.2.2 Hazard level	28

2.3	Safety Features in Commercial Batteries	28
2.4	CT for Degradation Studies	28
3	Synchrotron X-Ray Imaging	31
3.1	X-ray Sources	31
3.1.1	European Synchrotron Radiation Facility (ESRF)	31
3.2	Light-Matter Interaction	31
3.3	X-ray Computed Tomography	31
3.3.1	CT-Scan Segmentation	31
4	CT-scans segmentation	33
5	Conclusions and future developments	35
 Bibliography		 37
A	Appendix A	43
List of Figures		45
List of Tables		47
Acknowledgements		49

Introduction

1 | Lithium-ion batteries

The Earth stands at a critical juncture in its history, where the consequences of human activity on the environment have reached a crossroads of global significance. Climate change, driven primarily by the relentless emission of greenhouse gases, has manifested itself in increasingly severe weather patterns, rising sea levels, and ecological disruptions. The urgency of the situation cannot be overstated, as nations grapple with the complex challenge of reducing carbon dioxide (CO_2) emissions to mitigate the impending climate crisis [1–3].

The dire need for sustainable energy solutions has never been more evident. Various sectors of the economy are challenged to reduce their carbon footprint in order to restrict their impact on climate change. The transport sector was responsible for 23% of global emissions from fuel combustion in 2021 and emerges as a critical contributor to the climate change predicament [4].

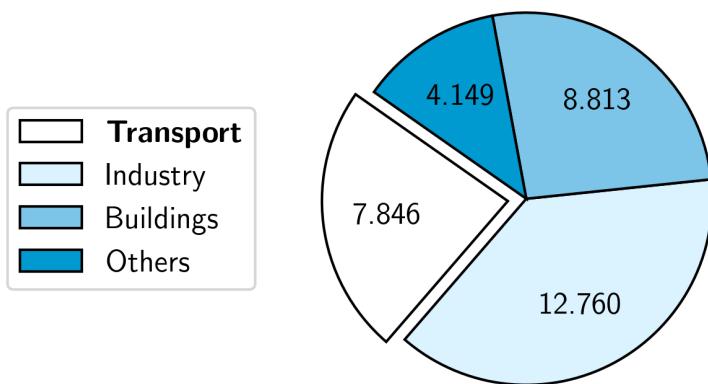


Figure 1.1: 2021 Global CO_2 emissions from fuel combustion by sector [Gt CO_2]. Source: IEA (2023) [4].

As societies evolve and the global population continues to grow, the demand for transportation, particularly in the form of automobiles and other fossil-fuel-reliant means, has risen dramatically. Innovative solutions are crucial to decouple the connection between

personal mobility and CO₂ emissions. Electric vehicles (EVs) have emerged as a promising alternative to traditional internal combustion engine vehicles. They offer the potential to revolutionize the way we commute, significantly diminishing the transportation sector's contribution to carbon emissions.

At the heart of the electric vehicle industry's transformation lie lithium-ion batteries (LIBs). These energy storage devices have rapidly gained prominence as the primary means of powering EVs [5, 6]. The suitability of LIBs for this role is driven by their impressive energy density, rechargeability, and relatively low environmental impact compared to conventional fossil fuels [7]. As we explore the potential of lithium-ion batteries, it becomes evident that their development and adoption may hold the key to mitigating the environmental impact of the transportation sector.

The shortcomings of LIBs are their narrow operational temperature range and charge-discharge rates. The capacity of the battery degrades faster if working at a high temperature, and the lifetime is shortened, too [8, 9]. When LIBs are subjected to conditions outside of their design window, they may fail through a rapid self-heating or thermal runaway, which may ignite the surrounding materials [10]. Hence, LIBs require meticulous safety testing in order to guarantee safe use in all usage frameworks. Safety tests must produce reliable parameters to enable satisfactory evaluation and classification of safe battery specifications. The consumer and industrial market demands safe, low-cost, high-power batteries produced with low environmental impact, using sustainable components that enable easy recycling [11].

In the following sections the functioning of lithium-ion batteries is described, followed by a discussion of the safety and degradation issues that arise in LIBs.

1.1. Overview

A lithium-ion battery consists of two electrodes, an electrolyte, a separator, two current collectors and a metal casing. The positive and negative electrode materials are powders that are applied as coatings on current collector foils, resulting in composite electrodes. The ion-conducting electrolyte (containing a dissociated lithium conducting salt) is situated between two electrodes. The separator, an electrolyte-permeable membrane to electrically isolate the two electrodes, is also in that position [12].

The electrolyte conducts the ionic component of the chemical reaction between the anode and the cathode, but it forces the electronic component to traverse an external circuit where it does work. Metallic current collectors deliver electronic current from/to the redox

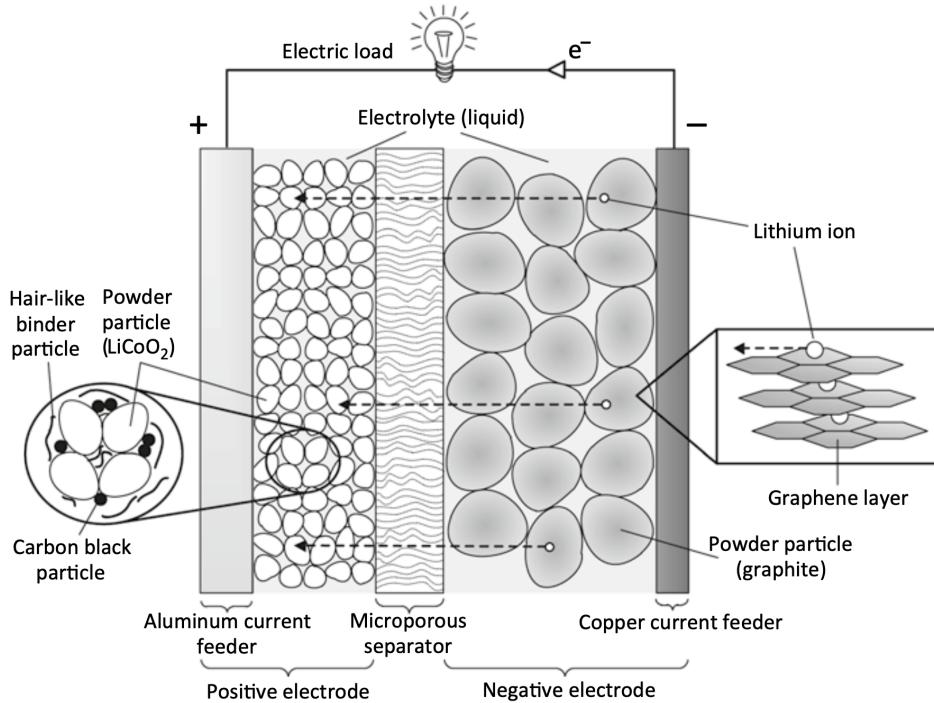


Figure 1.2: Components of a traditional lithium-ion battery during discharging. Source: Korthauer (2018) [7].

centers of the electrodes to/from the external circuit. These elements are used to produce cylindrical, prismatic and pouch cells. Depending on the application, a single battery cell is used or several cells are connected in series in a module. Also, a parallel connection is possible, dependent on the required capacity. Several connected modules form a battery system for auto-motive applications [7, 12].

1.2. Positive Electrode

Lithium transition metal compounds are employed as positive electrode materials. These composites can develop mixed crystals over an ample composition range and can deintercalate lithium ions from the structure during the charging process. The traditional positive electrode material is lithiated cobalt oxide, LiCoO_2 . It has a layered structure with alternating cobalt, oxygen, and lithium ion layers. During charging, lithium leaves the crystal (deintercalation); during discharging, it returns (intercalation). However, only 50% of the lithium may be utilized. If more than half of the lithium leaves the crystal, the structure may collapse and liberate oxygen. This can cause thermal runaway, as oxygen is able to burn the electrolyte [7, 13].

For complete discharging, the reaction at the positive electrode is:



Thus for one mole (7 g) of active lithium, two moles (189 g) of $\text{Li}_{0.5}\text{CoO}_2$ are needed as host for lithium during discharge.

The use of cobalt oxide as positive electrode material is not safe. If it is kept “fully” charged as $\text{Li}_{0.5}\text{CoO}_2$, it reacts slowly with the electrolyte, thus losing performance. If it is slightly overcharged, there is a clear loss in capacity and service life. In case of severe overcharging, the cobalt oxide crystal collapses which can cause thermal runaway and fire. Overcharging easily happens, as there is no obvious voltage difference between normal charging and overcharging. Cobalt oxide is expensive, as cobalt ore is scarce. This problem is getting worse as the demand grows. Economics of scale do not apply here. Last but not least, cobalt is toxic.

The main commercial alternatives for cobalt oxide are listed in Table 1.1. Each of the alternative materials solves some of the problems but they all are compromises. LMO is safer and very cheap but has a limited service life. NCM is safer and cheaper, but has a sloping discharge voltage. NCA is cheaper and lighter (more specific capacity, mAh/g) but it is hardly safer. LFP is very safe and slightly cheaper, but it gives 0.5 V lower voltage than cobalt oxide. At the moment, NCM and LFP seem to be the most promising candidates for large-scale batteries [13, 14].

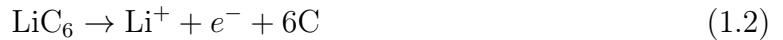
Compound	Abbreviation	Chemical structure
Manganese oxide	LMO	LiMn_2O_4
Nickel manganese cobalt oxide	NCM	$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$
Nickel cobalt aluminum oxide	NCA	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.15}\text{O}_2$
Iron phosphate	LFP	LiFePO_4

Table 1.1: Commercial alternatives for cobalt oxide. Source: Korthauer (2018) [7].

1.3. Negative Electrode

By far the most common negative electrode material is graphitic carbon. It has carbon atoms in parallel graphene layers. During charging, the lithium ions are intercalated into the graphite, between its layers. During discharging, lithium leaves the graphite. Unlike

cobalt oxide, graphite is stable even without lithium, so it can be almost completely discharged. For complete discharging, the reaction at the negative electrode is:



Thus for one mole (7 g) of active lithium, there are six moles (72 g) of carbon that act as host for the lithium during charging [7].

Graphite as negative electrode is not safe either. For graphite, the lithium intercalation potential is only about 80 mV more positive than the lithium metal plating potential. Even a small design failure or charging error causes deposition of metallic lithium on the electrode surface. Small amounts of metallic lithium increase the reactivity of the graphite surface, thus consuming electrolyte in secondary reactions. Large amounts of deposited lithium metal can grow as metallic peaks, “dendrites”, that short-circuit the negative and positive electrodes. This might cause excess heating and ignite the electrolyte resulting in a fire.

The potential of lithiated graphite is far beyond the stability window of the common electrolytes. During the first charging of the battery, graphite reacts with the electrolyte, building a protective layer on the graphite surface. This solid electrolyte interface (SEI) layer should prevent further secondary reactions. However, some secondary reactions take place throughout the lifetime of the battery, reducing its cyclic and calendar life. Some commercial alternatives for graphite exist. Soft and hard carbons are used due to their slightly more positive intercalation potentials. This means less risk of lithium metal deposition and a possibility of faster charging. However, the energy density is considerably lower when these materials are used. Lithium titanate is a very safe negative electrode material with an amazingly long service life, but the 1.4 V lower cell voltage limits the use of lithium titanate to very few applications. The newest commercial alternative, silicon, gives a formidable energy density, but low stability limits its service life [14, 15].

Graphite is cheap and lightweight, especially when compared to cobalt oxide. Therefore, it can be expected that graphite retains its position as standard negative electrode material in the near future [7].

1.4. Electrolyte

Electrolytes are an essential component of a lithium-ion battery. The requirement profile of the perfect electrolyte is manifold and encompasses, among other things:

- high conductivity across a wide temperature range (-40°C to 80°C);
- cycling stability over several thousands of cycles;
- chemical/electrochemical compatibility with the electrode and inactive materials;
- risk minimization of thermal runaway and other hazardous reactions during battery operation;
- ecological sustainability;
- balance between cost and performance.

The tool box for each electrolyte for lithium-ion batteries consists of three classes of materials: conducting salt, organic aprotic solvents, and additives. It is the combination of these components which largely determines the physico-chemical and electrochemical characteristics of the electrolyte and contributes to fulfilling the above-mentioned objectives.

At the same time, the electrolyte is not an independent component of the cell. It needs to be chosen in dependence on the materials for the anode and the cathode side. That, in turn, calls for close collaboration between the electrolyte manufacturer and the cell and battery developers [7].

1.4.1. Solvents

In lithium-ion batteries highly reductive materials are used for the negative electrode and highly oxidizing components for the positive electrode. This is the reason why solvents with an active acidic proton are unsuitable. This would immediately lead to a development of hydrogen. The same reason excludes water as a solvent. Other mandatory requirements for the solvent are:

- high permittivity ϵ : the solvent must be able to dissolve lithium salts in a sufficiently high concentration;
- low viscosity η : unimpeded ion transport in the electrolyte is needed, especially at low temperatures and for high-voltage applications;
- inertia towards all other cell components in all operating conditions;
- low melting point T_m and high boiling point T_b : the electrolyte must be liquid over the entire operating temperature range of the battery;
- low toxicity and low cost.

Two classes of organic solvents that are simultaneously aprotic and highly polar have gained recognition as suitable materials for lithium-ion batteries: ethers and esters, including organic carbonates.

Ether-containing electrolytes for the most part exhibit a low viscosity and therefore a very high conductivity. But their electrochemical stability is restricted and they are already oxidized at potentials around 4 V vs. Li/Li⁺. With the introduction of 4-V transition metal oxides as positive electrode materials, ethers have therefore disappeared as solvents for high-energy lithium-ion batteries.

Esters, especially organic diesters of carboxylic acid (so-called carbonates), are current state of the art. In general, the following are employed: blends of cyclic carbonates (e.g., ethylene carbonate [EC] and, to some extent, propylene carbonate [PC]) that exhibit a high dipole moment at moderate viscosity. Also, open-chain carbonates (dimethyl carbonate [DMC], diethyl carbonate [DEC], and ethyl methyl carbonate [EMC]) are used, which exhibit a moderate dipole moment at low viscosity [16–18].

Solvency	Structure	Melting point [°C]	Boiling point [°C]	Viscosity (25 °C) [cP]	Permittivity (25 °C)
EC		36	247-249	1.9 (40 °C)	90 (40 °C)
PC		-48	242	2.53	65
DMC		2–4	90	0.59	3.1
DEC		-43	125-129	0.75	2.8
EMC		-55	108	0.65	3.0

Table 1.2: Psycho-chemical characteristics of selected battery solvents. Source: Korthauer (2018) [7].

1.4.2. Conducting Salts

The electrolyte provides for the lithium ion transport between the electrodes. Therefore, a suitable lithium salt must provide maximum solubility and complete dissociation in aprotic solvents to ensure a high lithium-ion mobility. Very high electrochemical anion stability is also needed, in addition to high chemical stability in respect to the solvent. This requirement profile leads to mostly complex anions in which the negative charge is distributed to a high extent across the anions. This reduced charge density in turn causes a low attraction between the anion and the lithium cation, which determines the free movement of the cation and is therefore necessary for a high mobility.

In terms of the compounds possible in principle, lithium hexafluorophosphate (LiPF_6) plays a special role. Nowadays, commercial lithium-ion batteries are almost exclusively equipped with LiPF_6 . This is on the one hand not by reason of a single outstanding characteristic, but of an unparalleled unique combination of characteristics. And on the other hand it is based on the willingness to accept individual disadvantages.

Having a conductivity of 8 to 12 mS/cm (room temperature, 1 mol/l), LiPF_6 forms highly conductive electrolytes in blends of organic carbonates. These electrolytes are, in addition, electrochemically stable up to almost 5 V vs. Li/Li^+ . LiPF_6 is one of the few conducting salts that very effectively prevent the corrosion of the aluminum current collector of the positive electrode at potentials above 3 V vs. Li/Li^+ . Production process, quality, and purity, crucial for a battery's performance, have been improved over the course of the years: high-purity LiPF_6 has been available on an industrial scale for more than 30 years. Today's lithium-ion technology has been developed based on this conductive salt.

The limited chemical and thermal stability of LiPF_6 are its main disadvantages. In its pure form it very slowly disintegrates into traces of lithium fluoride (LiF) and phosphorous pentafluoride (PF_5), creating an equilibrium. High temperatures promote this process.



Lithium-bis(trifluoro- methylsulfonyl)imide (LiTFSI) and lithium-bis(fluorosulfonyl)imide (LiFSI) have increasingly been introduced into the market as alternatives to LiPF_6 . They are characterized by a high thermal stability, however they are not as electrochemically stable as LiPF_6 and are not as effective in preventing corrosion of the aluminum current collector. In addition, they are more expensive and less soluble in organic solvents. LiTFSI and LiFSI are therefore used in combination with LiPF_6 [16].

1.4.3. Additives

Additives mainly are employed to optimize the so-called solid electrolyte interface (SEI), the boundary surface between the negative electrode and the electrolyte. The SEI significantly influences service life and performance of the lithium-ion cell. Lithium ions do not exist in the form of “naked” cations in organic polar solvents, but rather as complex cation solvent adducts. This so-called solvate complex is many times larger than the naked lithium ion. Solvated lithium ions penetrate into the outer structures of the graphite anode during charging of the lithium-ion cell. The solvents (and in part also the anion of the lithium salt) degrade owing to the extremely reductive conditions and form hardly soluble precipitates. They accumulate on the electrode and in the outer structures of the graphite and form the layer that is called SEI. This layer is permeable for lithium ions. At the same time it is electrically isolating and prevents the direct contact of electrode and solvent, a characteristic that prevents further degradation of the solvent. All carbonates employed in lithium-ion batteries nowadays form an SEI. The quality and composition of the layer, however, strongly depend on the chosen solvent combination [7].

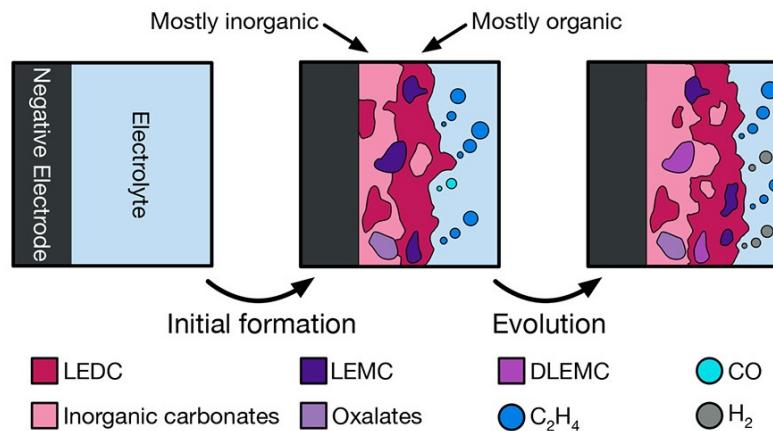


Figure 1.3: Mechanistic model of the SEI. Source: Spotte-Smith (2022) [19].

The SEI's structure and characteristics might be influenced significantly by the additives. The SEI additives must be more reactive electrochemically than all other components of the electrolyte in order for the SEI to be reduced during the first charging cycle of the lithium-ion cell before the solvents react. This way, an SEI is formed before the solvents react. The best-known example of this class of additives is vinylene carbonate. It is used in almost every commercial lithium-ion cell and leads to a significant improvement of the cycling stability. It becomes effective during the first charging and discharging cycles of the lithium-ion cell [16].

1.5. Separator

Battery separators are flat materials situated between the positive and negative electrodes of a battery cell. Their function is to prevent physical contact and, therefore, short circuits. At the same time, they must enable ions to be transported as freely as possible within the electrolyte between the electrodes. This is essential for charge equalization and the electrochemical cell to work. To achieve this, separators are usually porous flat designs filled with an electrolyte [7].

Property	Description
Thickness	The separators of consumer application lithium-ion cells are relatively thin. They have a thickness of less than μm . However, thicker separators (up to $40 \mu\text{m}$) are used for the production of large-size lithium-ion cells. These have considerably higher mechanical stability and puncture resistance.
Porosity	Standard separators for lithium-ion cells have a porosity of around 40%. Controlling the porosity is of great importance in separator manufacturing and immensely influences the porosity of the end product. In addition, high porosity enables a larger electrolyte reservoir. Non-uniform porosity, on the other hand, leads to non-uniform current densities which result in the electrodes aging more rapidly.
Pore size	The pores must be small enough to prevent an electrical connection caused by loose electrode particles. Also, they need to prevent dendrite growth in the lithium-ion cell. Separators with a thickness of $< 25 \mu\text{m}$ are assumed to have an average pore size in the submicron range. The pore size distribution in battery separators must be as homogeneous as possible, as is the case for requirements related to porosity. This enables a uniform current density and thus uniform aging of the cell.
Chemical stability	The separators must be chemically and electrochemically stable in both the battery and its electrolyte. In particular, the development of high-voltage materials has given rise to new requirements for separators.

Table 1.3: Separators essential properties. Source: Korthauer (2018) [7].

In lithium-ion cells, battery separators are mostly based on polyolefins into which submicron-sized holes are introduced by means of a physical process. These battery separators can be divided into two classes based on their production process: microporous polyolefin membranes and wet membranes. Resulting from their chemical and physical compositions, these two separator classes exhibit in part extremely different characteristics.

Microporous polyolefin membranes exhibit a thickness up to 12 to $40 \mu\text{m}$, a maximum pore size of $< 0.5 \mu\text{m}$, and a high tensile strength. The low thickness positively influences the energy density of the battery. The pore distribution protects them against dendrite for-

mation quite well. The disadvantages of these membranes are their low porosity (around 40%), low melting point (around 160 °C for PE), and very high shrinkage (20% at 120 °C/10 min) at higher temperatures. This is increasingly true for larger cells because they dissipate heat poorly. If the separator loses its structure, there will be contact between the electrodes and thus a reaction of the electrode materials. This can cause the battery to explode [7].

Wet membranes have a thickness of up to 25 μm , uniform pore distribution with short distances ($< 1 \mu\text{m}$), and high tensile strength. The low thickness positively influences the energy density of the battery. The short pore distances effectively prevent dendrites from forming. As with the microporous polyolefin membranes, the tensile strength is beneficial for producing cylindrical cells. The disadvantages of these membranes are their low melting point (around 135 °C) and very high shrinkage (7 to 30% at 120 °C/10 min) [20, 21].

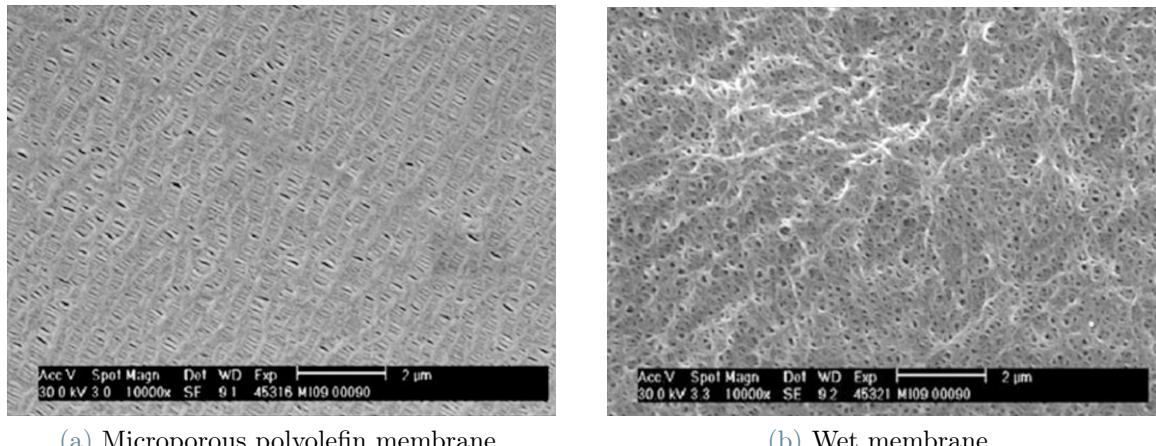


Figure 1.4: Scanning electron microscopic pictures of a microporous polyolefin membrane and a wet membrane. The samples were metallized with gold to achieve a higher resolution. Source: Korthauer (2018) [7].

1.6. Current Collectors

By enabling conduction of electrons between the electrodes and the battery terminals, the current collectors greatly impact the performance of the battery. The current collectors are viewed as un-active components of the cell but can however make up 15% of the cell weight. Properties such as electrochemical stability, electrical conductivity, mechanical strength, density, sustainability and cost has to be thoroughly evaluated. In conventional lithium-ion batteries the most commonly used materials are copper and aluminum foil

for the negative and the positive electrode respectively. A high electrical conductivity is required for efficient transportation of electrons through the external circuit of the battery.

As for any other component of the battery, the ability of the current collectors to sustain in an electrochemical environment and not to undergo undesired reactions is vital. Furthermore, it is crucial to maintain a satisfying adhesion between the current collectors and the electrodes; to achieve this, polymeric binders such as PVDF are commonly used. Both aluminum and copper show high electrical conductivity and valuable mechanical properties. The low density of aluminum ($2.70 \text{ g}\cdot\text{cm}^{-3}$) contributes to an increase in gravimetric energy density, while copper on the contrary has a high density of $8.96 \text{ g}\cdot\text{cm}^{-3}$. Consequently, for the case of the copper foil there is a trade-off between high electrical conductivity and thickness. In terms of heat generation, the current collectors act as efficient heat dissipators due to their high thermal conductivity and play an important role in the events leading up to a thermal runaway [22].

1.7. Cell Geometries and Designs

Battery cells come in various shapes and sizes, featuring diverse component assemblies and chemistries based on the manufacturer. The effectiveness of cell design is pivotal for ensuring safety and suitability in different applications. The selection of materials and dimensions significantly influences a battery's ability to prevent or minimize catastrophic events. To ensure optimal and secure functioning, meticulous consideration is given to the design of all aforementioned components and their collaborative functions to fit within the specified cell dimensions. Additionally, the choice of casting material and its thickness should be carefully designed to facilitate the handling of critical events by enhancing heat dissipation and pressure management.

All of today's lithium-ion cells exhibit metal-based housing and packaging material. One reason is that it prevents the entry of moisture into the cell, which would initiate a hydrolysis of the conducting salt LiPF_6 into hydrogen fluoride (HF). Another is the prevention of loss of solvent by means of diffusion from the cell. Only metal is able to fulfill these tasks. A housing made of pure plastics is not suitable because no plastic (not even polypropylene) is completely moisture leaktight. The solid metallic housings (hardcase) are typically made of aluminum or stainless steel [7].

The most common cell geometries are cylindrical, prismatic, and pouch cells. The main difference between the cell formats lies in the design of the cell casing and the arrangement of the cathode, anode, and separators.

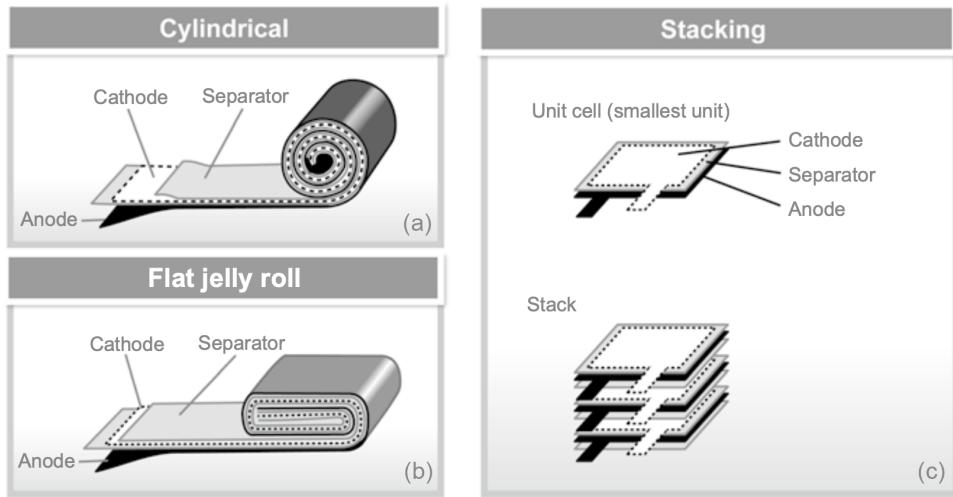


Figure 1.5: Inner structure of lithium-ion cells. Source: Korthauer (2018) [7].

The **cylindrical cells** (Figure 1.5a) are the oldest and most common cell type. The introduction on the market of a cylindrical round cell in a stainless steel housing for consumer applications by Sony ensued in 1991. The batteries measure 18 mm in diameter by 65 mm in length, giving them the name 18650 [7].

18650 battery is widely regarded as the most produced lithium-ion cell size. This cell type is used in many laptop computer batteries, cordless power tools, many electric cars, electric scooters, most e-bikes, older portable powerbanks, electronic cigarettes, portable fans and LED flashlights [23].

Cylindrical cells consist of a tubular cylindrical can and are crafted using a "jelly roll" technique. This involves creating a singular elongated "sandwich" by rolling together the positive electrode, separator, negative electrode, and separator into a single spool. An inherent advantage of cylindrical cells, in contrast to those featuring stacked electrodes, lies in their faster production speed. However, a notable drawback of cylindrical cells may manifest as a substantial radial temperature gradient within the cells under high discharge currents [24].

Cells possessing a cylindrical morphology incorporate safety mechanisms that will interrupt current flow and/or enable venting of gas to avoid overpressure of the can. Cylindrical cells have better thermal management efficiency because of small size, but low packaging efficiency because of their round cross-section [25].

Aluminium or steel cans are typically used for the housing of solid container-encased prismatic lithium-ion cells, more commonly called **prismatic cells** (Figure 1.5b). The metal can ensure structural stability, mechanical robustness, and humidity protection. In

addition, it allows for the use of safety features such as pressure relief vents, which are not possible in pouch cells. In some cases, prismatic cells may allow packaging to be more efficient than cylindrical cells because of their form factor [25].

The **pouch cells** (Figure 1.5c) employ a streamlined fold-stacking approach for individual sheets of both the positive and negative electrodes, enclosed in a lightweight foil casing. This configuration yields a cell characterized by high packing efficiency, flexibility, and low weight. The resulting compact and lightweight design contributes to an elevated volumetric energy density, cooling advantages, and adaptability for diverse applications due to its flexible nature. Nevertheless, the drawback of pouch cells lies in their limited physical strength, necessitating mechanical support in the form of a module or pack. Commonly addressed challenges include cell swelling during gas formation, which can alter the internal structure and pose risks to adjacent cells, thereby increasing the likelihood of failure and catastrophic events [26].

2 | Battery Failure

The increasing interest in lithium-ion batteries stems from their potential to offer efficient energy storage and contribute to environmental sustainability. Not only are LIBs widely employed in portable electronics like computers and cell phones, but they have also become integral to the power systems of electric and hybrid vehicles. The increasing popularity of LIBs in these applications can be attributed to their outstanding performance and high energy density [27]. Moreover, LIBs dominate the battery market for portable electronics, owing to inherent advantages such as high specific capacity and voltage, absence of memory effect, excellent cycling performance, minimal self-discharge, and a wide temperature range of operation [5].

No.	Date	Accidents Replay
1	Mar 2010	Two iPod Nano music players overheated and caught fire, Japan
2	Apr 2010	Acer recalled 2700 laptop batteries, as Dell, Apple, Toshiba, Lenovo and Sony did in 2006
3	Apr 2011	EV taxi caught fire, Hangzhou, China
4	Jan-Dec 2013	Three fire accidents of Boeing 747, happened in Boston America, Taka-matsu, Tokyo Japan, respectively
5	Oct-Nov 2013	6 Tesla Model S EV cars caught fire
6	Apr 2015	EV bus caught fire during charge, Shenzhen, China
7	May 2016	The storage room of the LIB caught explosion, Jiangsu, China
8	Aug 2016	Samsung Note 7 smart phone explosion
9	May 2017	Panasonic announced to recall over 270 thousand LIBs
10	Oct 2017	EV car caught fire, Austria
11	Jan 2018	Tesla Model S EV car self-ignited, China
12	Jul 2018	4 MW/12 MWh energy storage system (ESS) caught fire and explosion, Korea
13	Jul 2018	Electric scooter caught fire and explosion during charging, China

Table 2.1: Lithium-ion battery fire and explosion accidents in the past few years. Source: Wang (2019) [28].

Despite these merits, the broader expansion of the LIB market, especially in electric vehicles, faces significant challenges due to safety concerns [29–31]. Recent years have witnessed numerous recalls of LIBs, prompted by incidents of explosions and fires (Table 2.1), leading to substantial economic repercussions in related market sectors and tarnishing the reputation of LIBs [32, 33]. As a result, there is a growing emphasis on addressing LIB safety issues, with the development of numerous safety strategies aimed at mitigating the risks associated with these batteries.

2.1. Thermal Runaway

Even under normal operating conditions, battery-generated heat cannot be entirely removed. Rising battery temperature would trigger undesirable parasitic reactions, causing thermal runaway, where battery heat generation cannot be controlled [34].

Generally, thermal runaway occurs when the heat generated by exothermic reactions is not offset by the heat losses to the environment. This accumulated heat drives the temperature increase which, in turn, produces an exponential increase in the reaction rates. If the rate of heat generation exceeds the rate of heat dissipation into the environment, the temperature will continue rising. When reaching some critical temperatures, especially the collapse temperature of separator, the cell will breakdown.

2.1.1. Causes for Thermal Runaway

In the normal voltage and temperature range, only Li^+ shuttle occurs in the electrolyte during the insertion/extraction cycles at the cathode and anode. At high-temperature and high-voltage conditions, the electrochemical reactions become more complex, including decomposition of the solid electrolyte interface (SEI) film, oxygen release at the cathode side, and additional electrolyte/electrode parasitic side reactions [35]. SEI film decomposition and interfacial reactions initially accelerate the temperature increase, thereby increasing risks of oxygen release from the active cathode materials. These reactions eventually lead to LIB thermal runaway, which causes battery rupture and explosion due to the reaction of hot flammable gases from the battery with the ambient oxygen [36].

During mechanical (damage to shell casing, compression, punching, and twisting of cells), electrical (overcharge/discharge and short circuit), and thermal abuse (thermal shock and local heating) situations, which could occur during accidents, thermal runaway will occur even quicker [37–39].

Figure 2.1 shows the origins of thermal runaway in LIBs, including side reactions of electrolyte, cathode, anode, and interfacial reactions at the surface of electrodes and Li plating. These side reactions are triggered by mechanical, thermal, and electrical abuse. Breakage of the separator and the oxygen evolution from the cathode side are the root causes to batteries' thermal runaway (as shown in the solid lines of Figure 2.1d).



Figure 2.1: Schematic of the causes of LIBs thermal runaway. Source: Chen (2020) [32].

The five types of causes for thermal runaway are listed below.

1. **Uncontrollable internal heat generation** causes oxygen release from the cathode material, leading to numerous side reactions [40];
2. **Separator defects** (due to thermally-induced shrinkage or mechanical damage) create short circuits in the battery and rapid discharge of the energy stored in it, accompanied by undesirable chemical chain reactions and release of massive amounts of heat [41];
3. **Electrical abuse**, especially in a high state of charge, causes electrolyte decomposition at the cathode interface. This leads to heat accumulation and consequently release of oxygen from the cathode and damage to the separator [42];
4. **Thermal abuse** gives rise to electrochemical side reactions and heat generation. If the heat cannot be dissipated quickly enough, the separator will shrink or rupture [43, 44];

5. **Mechanical abuse** causes short circuits and/or air to penetrate the battery, originating a failure [45].

2.1.2. Semenov Model

The Semenov plots [46] shown in Figure 2.2 can be used to further illustrate the dynamics of the thermal runaway. The curved line (line 4) represents the heat generation due to the exothermic reaction (exponential function, following the Arrhenius law), while the straight lines 1, 2 and 3 represent the heat loss under different ambient temperatures (ambient temperature A , B and C , respectively) which is a linear function following the Newton's law of cooling.

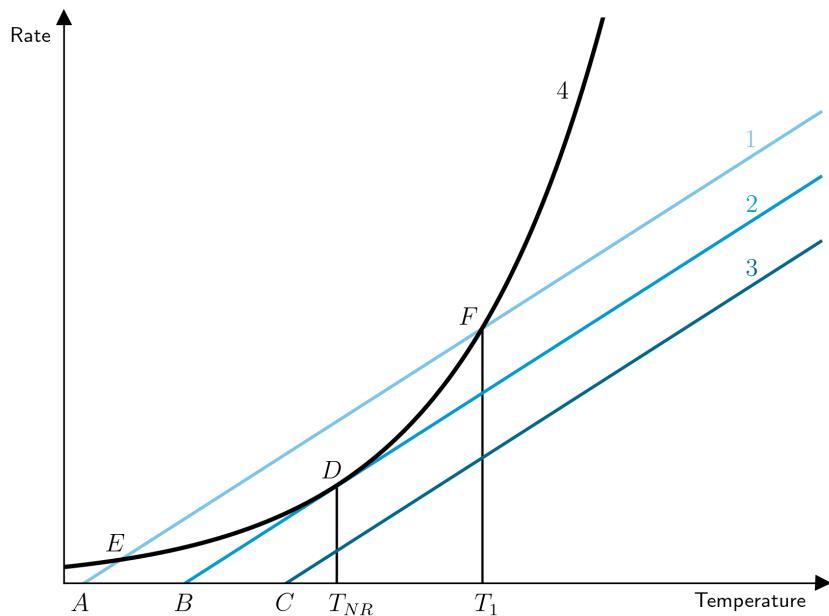


Figure 2.2: Temperature dependence of reaction rate and heat loss from a system at three ambient temperature: A , B and C . Source: Semenov (2013) [46].

When the ambient temperature is A , there are two intersection points (E , F) between line 4 and 1, where the heat generation rate is equal to the heat loss rate. The lower point E is a stable thermal balance point. If temperature deviates upwards, the cooling rate is higher than the heat generation rate, so the system will return to point E . If temperature drops, the heat generation rate is higher than the cooling rate, so the system will return to point E again. Point F is an unstable and also an unreachable point, because the heat loss rate is higher than the heat generation rate before T_1 , so the system will cool to point E rather than heat to point F . When the ambient temperature increases to B , line 2 has one tangent point D with line 4. At this point, the heat loss rate is equal to

the heat generation rate, and once the system temperature increases a little, the system's temperature will continue to rise at a progressively higher rate. This critical equilibrium temperature is called the "Temperature of No Return, T_{NR} ", and the ambient temperature B is the self-accelerating decomposition temperature (SADT). LIB can be regarded as a reaction system, in which the heat comes from the electrochemical reactions between its components.

Semenov plots illustrate only a special case for LIB thermal runaway rather than a universal model. In the realistic reaction process, the system is hard to reach uniform temperature distribution, but Semenov model can simplify the problem. In fact, many realistic situations could be solved based on the assumption of uniform temperature distribution. Many investigators still assumed that the temperature inside the battery was spatially uniform before thermal runaway in external heating and self-heating test [47, 48].

2.1.3. Energy Balance

Semenov model allows a simple and clear interpretation of the thermal runaway process, in which the heat generated by the reactions is the key issue. The heat generation is due to chemical and electrochemical reactions and Joule heating inside the battery. The heat dissipation to the ambient is controlled by radiation and convection. In general, the energy balance between the heat generation and dissipation can be described as follows [34, 49]:

$$\frac{\partial(\rho C_p T)}{\partial t} = -\nabla(k \nabla T) + Q_{ab-chem} + Q_{joul} + Q_S + Q_p + Q_{ex} \quad (2.1)$$

where ρ [g cm^{-3}] is the density, C_p [$\text{J g}^{-1} \text{K}^{-1}$] is the heat capacity, T [K] is the temperature, t [s] is the time and k [$\text{W cm}^{-1} \text{K}^{-1}$] is the thermal conductivity. $Q_{ab-chem}$ is the abuse chemical reaction heat in the battery (reactions will be discussed in detail in Section 2.1.4), Q_{joul} is the Joule heating in the battery, Q_S is the entropy change heat, Q_p is the overpotential heat and Q_{ex} is the heat exchange between the system and the ambient.

The reaction heat generation is the total result of all possible reactions when the battery is undergoing a thermal runaway, mainly including SEI decomposition, electrodes reaction with electrolyte, electrodes decomposition. For the individual reaction, the heat generation can be expressed as $Q_{ab-chem}$ [50]:

$$Q_{\text{ab-chem}} = \frac{dH}{dt} = \Delta H M^n A \exp\left(-\frac{E_a}{RT}\right) \quad (2.2)$$

where ΔH is the heat of reaction, M is the mass of the reacting material, n is the reaction order, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature. The total heat generation is the summarized value of all the reactions in the battery.

When a current flows through a device it induces Joule heating. In a lithium-ion battery, the electrical resistance consists of the resistance of the positive and negative electrodes, electrolyte and separator. In each region, the current passes through different phases, hence Joule heating should be considered in all the phases. Therefore, Joule heating can be written as [49]:

$$Q_{\text{joul}} = \sum_j |\phi_j \cdot i_j| \quad (2.3)$$

where ϕ_j and i_j represent the electric potential [V] and current density [A cm^{-2}] in phase j , respectively. In this equation, the absolute value signs should be present since Joule heating is always positive and contributes to a rise in temperature.

The heat Q_S by entropy change is described by the following equation [51]:

$$Q_S = IT \frac{\partial E_{\text{emf}}}{\partial T} \quad (2.4)$$

where T is the battery temperature, I is the charge/discharge current (defined as positive during charge cycle) and E_{emf} is the cell potential for open-circuit. The reaction directions for charge and discharge cycles are opposite to each other, thus Q_S is endothermic for charge cycle and exothermic during discharge cycle.

When electric current flows through the cell, cell voltage V deviates from open-circuit potential V_0 due to electrochemical polarization. The energy loss by this polarization dissipates as heat. This overpotential heat Q_P is described as following equation [51]:

$$Q_P = I(V - V_0) = I^2 R\eta \quad (2.5)$$

where Q_P is exothermic during both charge and discharge cycles. When the difference between V and V_0 is expressed as $IR\eta$, Q_P can be determined from the overpotential resistance $R\eta$.

The radiation and the convection heat transfer are the main thermal exchanges between the cell surface and environments. When the battery temperature exceeds the ambient temperature, the convection starts to dissipate the thermal energy. When the battery is working at low temperatures, the effect of radiation can be neglected. But in high temperature batteries, radiation plays an important role and should be considered. Convective and radiative heat flux out to ambient are evaluated in the following equations [49]:

$$Q_{\text{conv}} = hA(T_{\text{surf}} - T_{\text{amb}}) \quad (2.6)$$

$$Q_{\text{rad}} = \sigma\varepsilon A(T_{\text{surf}}^4 - T_{\text{amb}}^4) \quad (2.7)$$

where h is the convective heat transfer coefficient, A is the surface area of the battery case, T_{surf} is the surface temperature of the battery, T_{amb} is the ambient temperature, σ is the Stefan-Boltzmann constant and ε is the emissivity of the battery surface.

2.1.4. Basic Reactions

The term $Q_{\text{ab-chem}}$ involves several stages contributing to the buildup of the thermal runaway, and each one causes progressively more permanent damage to the cell.

Reactions	Temperature range [°C]
SEI decomposition: $(\text{CH}_2\text{OCO}_2\text{Li})_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + \frac{1}{2}\text{O}_2$	100-130
Li_xCoO_2 decomposition	178-250
Li_xCoO_2 /electrolyte	167-300
Electrolyte decomposition	225-300

Table 2.2: Temperature ranges and enthalpies of various exothermic reactions occurring in LIBs. Source: Chen (2021) [32].

2.2. Safety Standards

Safety standards and corresponding assessments have been established to analyze battery performance and key factors, aligning with the necessary safety requisites. The stringent and rigorous battery safety tests are designed to minimize the likelihood of safety issues in routine working conditions and ensure that batteries available on the market are of sufficient quality for intended purposes. Thanks to these measures, contemporary LIBs exhibit a significantly enhanced safety profile compared to their predecessors. Nonetheless,

ongoing advancements are imperative to further improve battery safety standards [32].

Hence, various international organizations regulate battery safety, and governments of different countries have formulated standards in accordance with national requirements and conditions and have gradually improved the safety standards of lithium-ion batteries. Academics and industrial groups have also carried out extensive research on battery safety.

Most countries and international organizations have developed LIB safety oriented standards, which include:

1. Chinese standard GB/T 31485 [52];
2. Society of Automotive Engineers (SAE) standard 2464 [53];
3. International Electrotechnical Commission (IEC) standard IEC62133 [54];
4. United Nations (UN) standard UN38.3 [55];
5. Japanese Industrial Standard (JIS) C8714 [56];
6. Underwriters Laboratories (UL) standard UL2580 [57];
7. International Standardization Organization (ISO) standard ISO 16750-2 [58].

Since the various safety test standars apply different methodologies, a summary of some test requirements and comparisons of five test items are presented in Table 2.3.

	GB/T31485	IEC62133	UL2580	SAE J2464
Heating	Heating at $5\text{ }^{\circ}\text{C}/\text{min}$ from $25\text{ }^{\circ}\text{C}$ to $130\text{ }^{\circ}\text{C}$, hold for 30 mins	$130\text{ }^{\circ}\text{C}$, 10 mins	$150 \pm 2\text{ }^{\circ}\text{C}$, 60 mins	Max. stable temperature
Short-circuit	Short circuit for 10 mins, $R \leq 5\text{m}\Omega$	$80 \pm 20\text{m}\Omega$	Short with $R \leq 5\text{m}\Omega$ until explosion, fire or no temp change	$R \leq 5\text{m}\Omega$ for hard short; $R \geq 5\text{m}\Omega$ for soft short
Overcharge	100% SOC Overcharge to 1.5 V_{max} or charge for 1 hour at 1C	Overcharge to 250% SOC at 1C	Overcharge to 200% SOC at 1C	Overcharge to 200% SOC at 1C
Over-discharge	Over-discharge the 100% SOC cell at 1C for 1.5 hours	Over-discharge the 0% SOC cell at 1C for 90 mins	Over-discharge the 0% SOC cell at 1C for 90 mins	Over-discharge the cell to -100% SOC
Nail penetration	Penetration rate 25 mm/s, φ 5~8mm, 100% depth	/	80 mm/s, φ 3mm, 100% depth	80 mm/s, φ 3mm, 100% depth

Table 2.3: Testing standards comparison of selected items. φ represents the nail diameter.
Source: Chen (2021) [32].

2.2.1. Safety Tests

Analysis of the presence of various LIB defects and shortcomings can help to define specific LIB safety issues or hazards. Extensive testing uncovers these issues to assist efforts to ensure that future generations of batteries are safer and more reliable. In a safety test possible trigger modes are simplified so batteries thermal runaway characteristics are measurable in the laboratory. Laboratory environment test conditions must generally be more stringent than "real-world" conditions to ensure safety during actual use. For example, batteries being tested have to be maintained at a 100% state of charge (SOC). The three principles of operability, repeatability and reproducibility should be met in the process of formulating a safety standard.

Here follows a brief description of the main safety tests used to examine key LIB properties.

Electrical Abuse Tests

When a battery is in an overcharge or over-discharge state, or is undergoing a short circuit, it experiences electrical abuse, and a series of undesirable electrochemical reactions occurs in it.

There are many reasons for battery overcharging. One of the main reasons is the inconsistency of battery cells. If the voltage of any battery cell cannot be effectively monitored by the management system, there will be risks of its overcharging. Since excess energy is stored into the battery, overcharging is very dangerous.

Overcharge first causes electrolyte decomposition at the cathode interface [59]. This reaction slowly increases the battery temperature. Subsequently, excessive Li⁺ deintercalation from the cathode occurs. The cathode material becomes unstable and start to release oxygen, while excess Li⁺ deposits on the anode to form Li dendrite [60]. Heat and gas generation during the side reactions would lead to safety accidents, such as cell overheating and rupture [61].

The principle of over-discharge is similar that of overcharge. Some cells reach the set state of discharge (SOD) in advance. Thus, an over-discharge occurs if a cell is forced to continue to discharge [62]. Forced over-discharge continuously releases Li⁺ from the anode, which change the graphite structure and destroy the SEI. At very deep SOD, a copper current collector is oxidized, with the released copper ions potentially being deposited on the cathode surface [63]. Too much copper deposition results in the short-circuit of cell.

- **Overcharge/over-discharge tests** are intended to assess processes that occur in a cell when the charge or discharge processes are out of control. According to the IEC

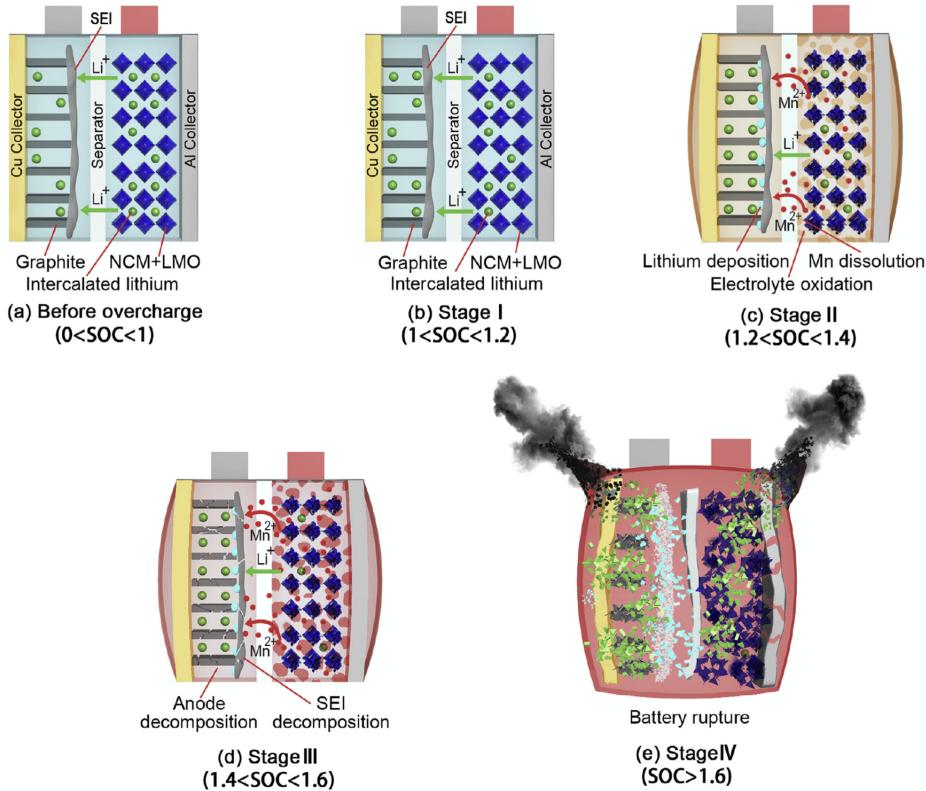


Figure 2.3: Overview of the overcharge side reactions at each stage for lithium ion batteries with NCM + LMO cathode. Source: Ren (2017) [42].

standard test, the cell is first discharged to 3.0 V, and then is charged under 10 V. If the battery does not combust or explode during or after the test it is considered safe, its materials (electrolyte, active electrode materials, separators etc.) are regarded as having adequate properties, and the structural design is deemed satisfactory. The safety performance under overcharge is closely related to the charge rate, so overcharging is performed at different rates to establish at which extreme rate and voltage failure occurs [32].

- **Internal short circuit (ISC) tests** assess the short circuiting that is caused by internal electrical connections of battery poles under abnormal conditions. Several methods are used to initiate an internal short circuit, including nail penetration, heavy impact, crush and forced ISC [32].
- **External short circuit tests** assess the short circuiting that is caused by external electrical connections of battery poles under abnormal conditions. According to the GB31485-2015 procedure, the battery is kept at 25 ± 2 °C in a fully charged state for 30 minutes, then the cathode and anode terminals are connected with a wire, and the external resistance is kept at 5 mΩ. During this test, the temperature

and voltage are monitored simultaneously, throughout the entire test. The test is considered successful if the cell does not explode or combust [32].

Mechanical Abuse Tests

Due to the high energy density of LIBs, local damage caused by external influences, for example in case of collisions, will release a significant amount of heat, which can easily cause thermal runaway. As a result their safety risk is high. As the number of EVs (containing LIBs) on the roads continues to increase, safety concerns over battery behavior during potential vehicle collisions are becoming more prominent [32].

Mechanical abuse tests are conducted in order to assess LIB safety under mechanical abuse conditions (e.g. crushing, penetration, and vibration) that may occur during battery production, transportation, and use.

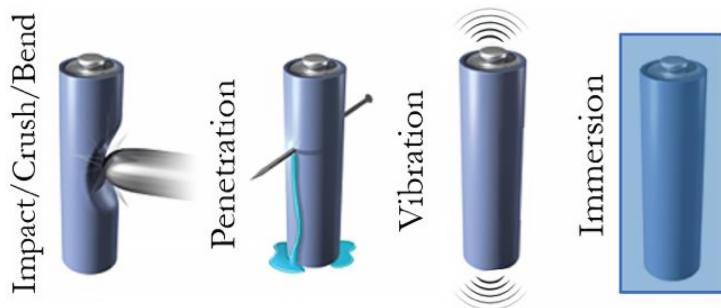


Figure 2.4: Illustration of various mechanical abuse mechanisms. Source: Fransson [64].

Nail penetration tests are the most common type of mechanical tests, and they are designed to simulate internal battery short circuits arising when a battery's internal membrane is penetrated by impurities. According to GB/T 31485, a fully-charged battery should be penetrated with a high temperature-resistant steel spike of $\varphi 5\sim8$ mm in a direction perpendicular to the polar plate at a speed of 25 ± 5 mm/s. The penetration position should also be close to the geometric center of the penetrated surface, with the steel spike retained inside the battery. The test is considered successful if the cell does not explode or combust [32].

Thermal Abuse Tests

In thermal abuse situations, a battery experiences thermal shock, or its local temperature is too high [65]. In theory, battery cycling cannot cause safety accidents because the heat generated during normal anodic and cathodic reactions is insufficient to cause a sharp temperature increase. In reality, however, the electrode heat release rate is often higher

than its cooling rate. Heat dissipation of a LIB depends on its external surface area and geometry. Heat dissipation by radiation helps to alleviate some of the generated heat. As a result, some of the heat remains stored inside the battery. At some point, if this heat continues to accumulate instead of being dissipated, exothermic side reactions start to occur, further concentrating thermal stress [66].

Heating tests assess the thermal runaway caused by a battery being heated due to local overheating, and the subsequent thermal runaway expansion. Heating is used to analyze LIBs' thermal stability and heat distribution to ensure they have sufficiently efficient heat management and capability to forecast potential hazards. The results are then used to assess how thermal abuse consequences can be alleviated. Specifically, data obtained from hot box experiments are used to simulate their thermal characteristics, and distributions of internal and external temperatures, then assess possible improvements in their design, materials and cooling systems [32].

2.2.2. Hazard level

In evaluations of batteries' safety condition based on results of the above abuse tests, the EUCAR Hazard Levels [67] and the associated criteria that are widely applied. Typically, hazard levels of Electrical Energy Storage System (EESS) devices according to their responses to abuse conditions are assigned by EUCAR and presented in Table 2.4. Manufacturers and integrators may find it helpful and useful to take these levels into consideration when evaluating a given EESS design's abuse response.

2.3. Safety Features in Commercial Batteries

Can be found in "Safety Issues - 770", "Failure description - 43"

2.4. CT for Degradation Studies

Hazard Level	Description	Classification Criteria & Effect
0	No effect	No effect. No loss of functionality.
1	Passive protection activated	No defect; no leakage; no venting, fire or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell reversibly damaged. Repair of protection device needed.
2	Defect/Damage	No leakage; no venting, fire or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell irreversibly damaged. Repair needed.
3	Leakage (Δ mass < 50%)	No venting, fire or flame; no rupture; no explosion. Weight loss < 50% of electrolyte weight (electrolyte = solvent + salt).
4	Venting (Δ mass \geq 50%)	No fire or flame; no rupture; no explosion. Weight loss \geq 50% of electrolyte weight (electrolyte = solvent + salt).
5	Fire or Flame	No rupture; no explosion (i.e. no flying parts).
6	Rupture	No explosion, but flying parts of the active mass.
7	Explosion	Explosion (i.e. disintegration of the cell).

Table 2.4: EUCAR hazard levels and associated criteria. Source: EUCAR (2019) [67].

3 | Synchrotron X-Ray Imaging

3.1. X-ray Sources

3.1.1. European Synchrotron Radiation Facility (ESRF)

Beamline ID19

3.2. Light-Matter Interaction

3.3. X-ray Computed Tomography

3.3.1. CT-Scan Segmentation

4 | CT-scans segmentation

Algorithm 4.1 Segmentation algorithm

```

1: SET hypervolume, hypervolume_mask
2: previous_volume = hypervolume[0]
3: threshold = find_threshold(previous_volume)
4: previous_mask = segment3D(previous_volume, threshold)
5: filtering3D(previous_mask)
6: rename_labels(previous_mask)
7: hypervolume_mask[0] = previous_masks
8: for t = 1 to end do
9:   current_volume = hypervolume[t]
10:  current_mask = segment3D(current_volume, threshold)
11:  filtering3D(previous_mask)
12:  current_mask = propagate_labels(previous_mask, current_mask)
13:  rename_labels(current_mask)
14:  hypervolume_mask[t] = current_mask
15:  previous_mask = current_mask
16: end for

```

Algorithm 4.2 Segmentation algorithm

- 1: get the hypervolume memmap and initialize the hypervolume mask memmap
- 2: set previous volume to the first volume in the hypervolume
- 3: find the threshold using previous volume
- 4: segment the previous volume with the threshold and get previous mask
- 5: filter previous mask
- 6: rename the labels in previous mask
- 7: set the first mask in the hypervolume mask to previous mask
- 8: **for** $t = 1$ to *end* **do**
- 9: set current volume to the volume at time t in the hypervolume
- 10: segment current volume with the threshold and get current mask
- 11: filter current mask
- 12: propagate the labels from previous mask to current mask
- 13: rename the labels in current mask
- 14: set the mask at time t in the hypervolume mask to current mask
- 15: set previous mask to current mask
- 16: **end for**

5 | Conclusions and future developments

A final chapter containing the main conclusions of your research/study and possible future developments of your work have to be inserted in this chapter.

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A | Appendix A

List of Figures

1.1	2021 Global CO ₂ emissions from fuel combustion by sector	3
1.2	Components of a traditional lithium-ion battery during discharging	5
1.3	Mechanistic model of the SEI	11
1.4	Scanning electron microscopic pictures of separators	13
1.5	Inner structure of lithium-ion cells	15
2.1	Schematic of the causes of lithium-ion battery thermal runaway	19
2.2	Temperature dependence of reaction rate and heat loss	20
2.3	Overview of the overcharge side reactions	26
2.4	Illustration of various mechanical abuse mechanisms	27

List of Tables

1.1	Commercial alternatives for cobalt oxide	6
1.2	Psycho-chemical characteristics of selected battery solvents	9
1.3	Separators essential properties	12
2.1	Lithium-ion battery accidents	17
2.2	Exothermic reactions occurring in LIBs	23
2.3	Testing standards comparison	24
2.4	EUCAR hazard levels	29

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Here you might want to acknowledge someone.

