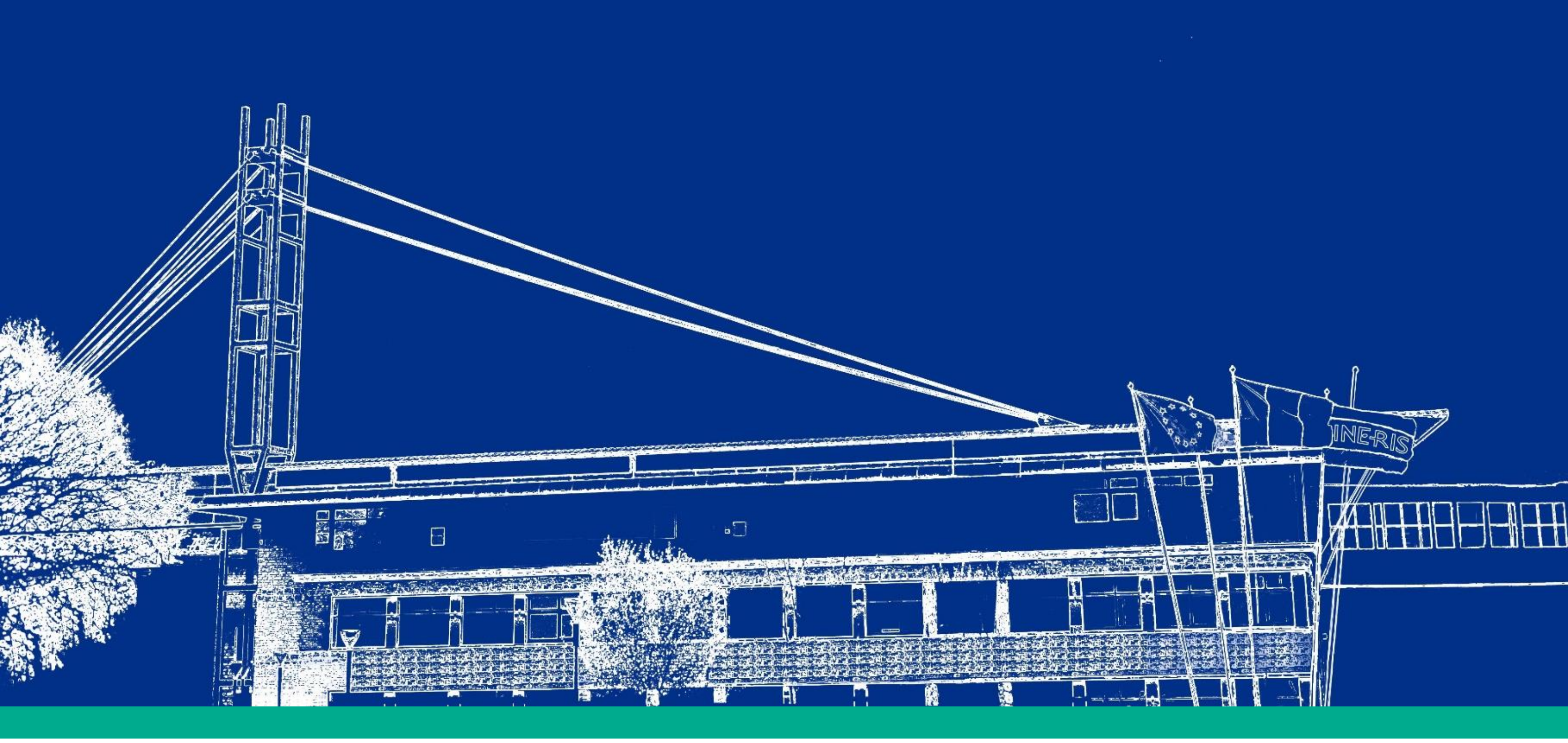

(Model ID = 454913)

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18/12/2024

Risk profile for Li-ion LFP batteries

controlling risks
for sustainable development

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Abbreviations

FEC:	Fractional Effective Concentration
HRR:	Heat Release Rate
LEL:	Lower Explosive Limit
UEL:	Upper Explosive Limit
LFP:	Lithium Iron Phosphate oxide
NCA:	Nickel Cobalt Aluminum Oxide
NMC:	Nickel Manganese Cobalt Oxide
PNEC:	Predicted Non Effect Concentration - calculated threshold value at which an effect on the environment is observed
SOC:	State of Charge
THR:	Total Heat Release
TR:	Thermal Runaway
VCE:	Vapour Cloud Explosion

1 Introduction and context

Li-ion technology is currently undergoing rapid development and is at the focal point for most players in the electrochemical energy storage sector.

To meet the specific needs of various applications in terms of cost and performances, and depending on the know-how of the manufacturers, several variants of Li-ion batteries have been developed and are now available on the market.

These variants differ in the composition of their electrolyte, the chemistry of the electrodes (anode or cathode), the type of separator used, and the format of the cells produced (pouch, cylindrical, prismatic). Each of these variations will have a greater or lesser impact on the behaviour of cells in abusive situations, and therefore ultimately on the safety of the system integrating those cells.

Among existing cathode chemistries, three families stand out and account for a very large share of the market: NMC (Nickel, Manganese, Cobalt) and its sub-variants (depending on the proportions of lithiated metal oxides involved), LFP (Lithium, Iron, Phosphate) and NCA (Nickel, Cobalt, Aluminium). LFP chemistry has a lower energy density than NMC and NCA, but a lower production cost, and many manufacturers point out the supposedly gains in safety.

This note therefore focuses on LFP cathodes and the consequences of using this cathode chemistry on the risk profile of Li-ion battery cells and systems. After presenting accidentology data, the reactivity and risks associated with Li-ion LFP batteries will be detailed and compared with other cathode chemistries. Finally, the parameters that can affect the reaction of these batteries will be presented.

2 Accidentology

Numerous accidents involving Li-ion LFP batteries that led to fire or explosion have been reported for mobile and stationary applications. The aim here is not to provide an exhaustive list of accidents, but to summarize the main lessons learned from this technology.

2.1 Accidentology in the field of electromobility

Several fires involving Li-ion LFP batteries in light electric vehicles and electric buses were reported in China between 2008 and 2022. It should be noted that LFP chemistry is widely deployed for this type of application in China.

These fires have many causes:

- Fires resulting fromcCollision fires (Taxi fire in Shenzhen, China in 2012),(1),
- Fires initiated by overheating of the Li-ion LFP battery (at least 4 cases reported in China on electric cars),(2),
- Fires caused by initial failure of the BMS which did not stop charging, resulting in overcharging of the Li-ion LFP battery pack, leading to thermal runaway and fire (Wuzhou Dragon electric bus - Shenzhen 2015). (3) / suspected cause of the Olectra electric bus fire in Hyderabad, India in 2022),
- Fires triggered by battery short-circuit (Wuzhou Dragon electric bus - 2016 / suspected but unconfirmed cause of Beijing bus depot fire - Crab Island in 2017).

Eleven fires involving electric vehicles manufactured by the Chinese automotive leader using LFP technology were recorded between 2020 and 2022. The cause of these fires remains unknown.

At least one case of *Vapour Cloud Explosion (*VCE) (which corresponds to the ignition of the gas cloud emitted by the battery) was recorded in China (Tongling) on an electric bus in a tunnel on August 26, 2018.

2.2 Accidentology in the field of stationnary application

At least ten accidents involving LFP chemistry batteries have been recorded for stationary applications. These accidents are listed in the Appendix. Some led to fires (Port Angeles, 2013, Standish 2021, LaSalle County 2021, Neuhardenberg 2021, ...), others to explosions (like ATEX ignition) followed by fires (Brisbane 2020, Perles et Castelet, 2020, Beijing 2021). Some of these incidents are detailed in the note “Ineris-204512-2707374-v1.0.”(4).

The causes of the accident in Beijing 2021 were recently revealed. As a reminder, on April 16, 2021, a fire started in a shopping mall integrating a 25 MWh Li-ion system was associated with 1.4 MW rooftop solar panels to supply 94 electric vehicle charging points. While firefighters were responding to a fire on the southern part of a shopping mall, an explosion occurred on the northern part of the installation. This explosion resulted in the death of 2 firefighters, one injured person and one missing (an employee of the facility).

According to the available investigation report, the fire in the south building was caused by an internal short-circuit of the LFP battery, which led to its thermal runaway. The cause of the explosion in the north building is attributed to the emission of combustible and flammable components generated by the fire in the south building, which entered the energy storage room in the north building through the underground cable trench. The emissions generated mixed with air to form an explosive gas mixture (ATEX), which exploded in the presence of sparks (5).

To sum up, accident analysis shows that hazardous phenomena (fire, explosion, toxic gas emissions, etc.) with potentially significant effects can occur on LFP chemistry battery systems, whatever the application considered (electromobility, stationary, etc.).

3 Reactivity of Li-ion LFP batteries

Li-ion LFP batteries ($LiFePO_4$) are often presented as safer than other Li-ion cathode chemistries (*e.g.* NCA, NMC, LMO, etc.), given their lower energy density. With less on-board energy, lower reactivity during thermal runaway is assumed. Although this chemistry presents some difference in terms of reactivity and effects in abusive situations, the risk of thermal runaway is still very real.

3.1 Thermal stability

An important parameter for assessing the risk of thermal runaway and propagation associated with a technology is the temperature at which the first notable exothermic reaction occurs (noted T_{onset}). According to this parameter, Li-ion batteries with LFP cathodes start reacting at a higher temperature (T_{onset}) than other Li-ion chemistries.

In ascending order of thermal stability, Li-ion cathodes are classified as following: $LiCoO_2$ (LCO) < $LiNi_xCo_yAl_zO_2$ (NCA) < $LiNi_xCo_yMn_zO_2$ (NMC) < $LiFePO_4$ (LFP) (6). This stability is directly attributed in the scientific literature to the chemical nature of the LFP material (7) and in particular to the stability of the phosphate group, in which the dissociation energies of the oxygen bonds are greater than in the case of the transition oxide mixtures used in the active materials of NMC cathodes, for example.

However, this apparent window of stability needs to be nuanced, since the temperature at which thermal runaway is triggered (T_{onset}) can drop sharply with the state of the battery and various environmental data. For example, Golubkov *et al.* reported a T_{onset} of 80°C for batteries in an overcharged state (8) compared with 200°C in new condition observed by Yuan *et al.*(9). Thus, the mere gain in thermal stability of cathode active materials in LFP batteries does not constitute an effective safety barrier against the risk of thermal runaway in Li-ion batteries featuring this cathode chemistry.

In addition, once thermal runaway is triggered, the reactivity of LFP batteries can be violent and/or spread out over time (10), leading to numerous risks: heat and toxic release, explosion (VCE).

3.2 Thermal hazard

3.2.1 Heat generated during thermal runaway

When a Li-ion battery goes into thermal runaway, heat generation is induced. In the case of Li-ion LFP batteries, this heat generation is characterized, as described in this document, by:

- Hot gaseous phase release,
- An increase in cell temperature,
- A high thermal energy release compared to the electrical energy stored in these batteries.

These three parameters, common to all Li-ion chemistries, are not systematically lower in the case of LFP chemistries, and in some cases may even be higher.

3.2.2 Thermal hazards associated with the gas phase

During thermal runaway, gases are emitted. Gas emission is also accompanied with release of heat due to gas temperature.

In the absence of combustion, the gases emitted during thermal runaway of Li-ion LFP batteries have a temperature of the same order of magnitude (250-300°C), or even higher than some chemistries considered as highly reactive to thermal runaway. For example, Yuan *et al.* measured gas temperatures for LFP of 275°C, higher than those for LTO (245°C) or some NMCs (NMC 1 - 244°C and NMC 2 - 313°C*).* (9).

In the event of gas combustion, which can be observed during thermal runaway at cell, module and pack level, the gas temperature values previously described are largely exceeded. The flame temperature of the gas phase can exceed 850°C, as reported by Peng *et al.* during overheating tests on LFP 68 Ah cells.) (11).

The combustion of gases is responsible for a significant proportion of the thermal energy released in the event of thermal runaway. As discussed in section 3.3.2, the ignition of gases from a Li-ion LFP battery is far from systematic at cell level, but it is still possible and is often observed more significantly on a larger scale (pack, system).

3.2.3 Thermal hazards associated with the solid phase

An important parameter for the propagation of thermal runaway is the cell body temperature. During thermal runaway, the maximum cell body temperature of Li-ion LFP batteries is generally lower than for other battery chemistries but remains significant (400-600°C). As an example, the maximum cell body temperature observed by Yuan *et al.* remains lower for LFP than for NMC, but is nonetheless significant in terms of thermal risk (LFP: 399°C vs. NMC1 and NMC2: 835°C and 998°C). (9).

In other studies, the maximum temperatures recorded are closer to those of other Li-ion chemistries:

- 386°C for overheating tests on LFP 7 Ah pouch cell in nitrogen atmosphere (12),
- 457°C for ARC tests on LFP 26650 cell (7),
- 496°C for ARC tests on LFP 26650 cell (13),
- 733°C for ARC tests on LFP 18650 cells (14),
- 775°C for external heating tests on LFP 18650 cell (15).

As for the heat released by gases, combustion plays a critical role here too. Temperatures above 600°C recorded for Li-ion LFP cells are in fact the result of combustion.

In scenarios where combustion occurs, cathode chemistry is no longer the predominant parameter for thermal emissions. Thus, Rappsilber *et al.* attributed most of the energy produced to electrolyte combustion and not to the nature of the cathode, which explains in a way the common temperatures of all Li-ion battery chemistries (as the same types of electrolytes are used).

3.2.4 Thermal risk associated with the release of large amounts of energy

The release of thermal energy is often measured by two parameters:

- HRR (Heat Release Rate) which corresponds to the instantaneous heat power,
- THR (Total Heat Release) which equals to the overall energy release.

In the event of a combustion reaction, the HRR values in kW/Wh and THR in kJ/Wh of Li-ion LFP batteries can be higher than those of other conventional Li-ion battery chemistries. Ghiji *et al.* concluded that Li-ion LFP and LCO batteries have higher HRRs than Li-ion NMC batteries (respectively 1245 W/Wh for LFP, 375 W/Wh for LCO and 446 and 650 W/Wh for two types of NMC). (16).

In parallel, the total energy released (THR) during thermal runaway of LFP batteries in a combustion scenario is remarkable compared to the electrical energy stored in the battery as highlighted by the cross-analysis of THR values found in the literature by Rappsilber *et al*. (17). The THR of LFP appears even more significant when compared with that of other Li-ion chemistries, whatever the cell format considered.

The maximum THR reported for LFP is over 60 kJ/Wh in cylindrical format, around 70 kJ/Wh in pouch format and over 110kJ/Wh in prismatic format (compared with 30 kJ/Wh, 50kJ/Wh and 25-30 kJ/Wh respectively for all other chemistries reported in the study). (17). Nevertheless, it is worth noting the wide disparity in values observed in the literature, particularly for LFP chemistry.

Ineris results on HRR and THR tend to nuance the trends observed by Rappsilber *et al. (*with LFP cells that are slightly less reactive). Considering all the thermal energies that can be released, average THR values respectively of 39.2 kJ/Wh for NMC and 38.9 kJ/Wh for LFP were observed at Ineris.

In short, the thermal stability of fresh Li-ion LFP batteries at SOC 100% is higher than that of other Li-ion chemistries.

However, when thermal runaway is triggered, LFP chemistry generates gases whose ignition is far from systematic at cell level but is nevertheless possible.

At pack and system levels, the ignition of these gases is widely reported in the literature and leads to a violent reaction with high heat production, comparable to any other Li-ion battery. The thermal risk associated with LFP batteries should therefore not be overlooked.

3.3 Risk of producing hazardous smoke (toxicity, corrosiveness, environmental impact)

Thermal runaway of Li-ion LFP batteries is usually accompanied by the release of gaseous and aerosol emissions which may include the following:

- solvents (emitted in vapour form) from the electrolyte,
- mixture of gases resulting from the decomposition or combustion of Li-ion cells during thermal runaway,
- carbonaceous and non-carbonaceous particles resulting from the ejection of active materials from cells and the combustion of Li-ion cells during thermal runaway. Given the current state of knowledge, it should be noted that these particulate emissions are very different from the "soot" (essentially made of elemental carbon) found in cellulosic fuel fires.

The risks associated with these smokes are described below.

3.3.1 Description of smoke generated by LFP thermal runaway

3.3.1.1.1 Gaseous phase

Numerous studies have been (and still are) devoted to the study of the gas phase emitted during the thermal runaway of Li-ion LFP batteries. It appears that the quantity of gas formed can vary greatly depending on the case studied and the analysis method considered, whatever the chemistry. This is all the more true for LFP, as illustrated in the study by Rappsilber *et al.* who reported literature values ranging from around 9 to 45 mmol/Wh of gas emitted for cylindrical LFP cells at SOC 100%) (17).

However, Li-ion LFP cells tend to emit less gas than NMC cells, when gas production is related to mass, as illustrated by the study by Sturk *et al.* (12). At Ineris, results obtained on a limited number of samples tend to confirm this trend (LFP: 0.3 NL/Wh and NMC: 0.5 NL/Wh in confined environments). This may be explained by the lower energy density of Li-ion LFP cells. Also, in some cases, the temperature reached by Li-ion LFP cells is low enough to result only in electrolyte vaporization (18) and therefore little outgassing.

It should also be noted that Li-ion LFP cells tend to outgas over a longer time range than NMC. As an example, Golubkov et al. recorded an outgassing time of 0.2 s for Li-ion NMC (18650 1.5 Ah) versus 30 s for Li-ion LFP cells (18650 1.1 Ah) (19). Amano *et al*. have shown that the gas phase release time for NMC is one-tenth that of LFP (20). More specifically, Yang *et al.* studied the time between cell opening and the end of emission for several Li-ion NMC cells vs. one Li-ion LFP cell, and recorded a duration of this phase between 62 s and 84 s for Li-ion NMC cells vs. 408 s for LFP (18). This confirms the trend for Li-ion LFP cells to degas over a long period of time.

Although from one study to another, the composition of gases emitted by Li-ion LFP cells (and other chemistries) can vary greatly as reported by Golubkov et al.(8), the gas mixture is essentially composed of : CO_2 , CO, H_2 , light hydrocarbons (8, 12, 17, 19), fluorinated compounds like HF (12, 17, 19) and POF_3 (12) and organic carbonates from vaporized electrolyte (*e.g.* EC, PC, DMC). More specifically, NO, HCl (17), SO_2 (11, 17), HCN and NH_3 (20) are also detected.

3.3.1.1.2 Particulate aerosol emissions

The smoke emitted by Li-ion LFP batteries are also characterized by particulate emissions. Premnath *et al.* studied particulate emissions from Li-ion LFP modules, comparing abuse situations triggered by nail testing and overcharging. Overcharging resulted in significant emission of partlcles due to the propagation observed at module level (21). A particle mass production of 380 g/h associated with a total particle number of 1.3 e7 particles/cm^3 was estimated for this 115 Wh Li-ion LFP module (compared with 581 g/h and 1.9 e^7 particles/cm^3 for the 2.5 kWh Li-ion NMC module propagated during the nail test).

Barone *et al.* also analysed the size and composition of particles forming aerosols from Li-ion LFP batteries. The particles obtained in this study were carbonaceous cenospheres of homogeneous size. It should be noted that they can be inhaled, given their breathable size ranging between 0.6 and 5 µm. A further statement is that they are mainly composed of carbon, fluorine and silicon, i.e. the components of the LFP cell anode. (22)

In terms of particle nature, considering only cathode components, in the smoke from Li-ion LFP batteries, it is expected to find Fe, Li, P and Al, unlike Li-ion NMC batteries, for which the expected cathode species include the metallic elements Ni, Mn and Co.

3.3.2 Risk of gas combustion

Given the composition of the gaseous phase of the smoke emitted by LFP batteries, the risk of combustion should not be overlooked.

Although the risk of combustion does exist, LFP cells lead less systematically to combustion. This is partly due to the lower temperatures reached, but also to the greater crystallographic stability of the LFP cathode. When decomposed at high temperatures, LFP cathodes release less oxygen (23) yet this compound is necessary for combustion, as long as the cell casing retains its integrity and therefore its airtightness. The thermal runaway reactivity of LFP cells is therefore more affected by ambient oxygen supply than that of other chemistries.

Garcia *et al*. demonstrated that an inert atmosphere (nitrogen), which prevents the supply of oxygen from the ambient air, leads to a lower maximum temperature, as well as to an extended smoke emission (17.5 to approximately 19 min). However, once under air, the temperature rises significantly, reflecting improved combustion (increase from just under 500°C to over 650°C). (23)

Despite less systematic ignition, the gas mixture released remains composed of highly flammable gases (*e.g.* CO (17) hydrocarbons such as CH_4 and C_2H_4 (18)). The flammability window for gases released by Li-ion LFP cells remains comparable to those of other Li-ion battery chemistries (24) (LEL and UEL between 5 and 52% for LFP and NMC 811 and 5 and 62% for NMC 622, the LEL of LFP remaining lower than for other chemistries) (18).

Significant combustion of these elements can be induced, as observed in the literature (11, 25) at any level of integration. It is important to emphasize that the impact of integration is critical on the risk of combustion (26). Indeed, at module and pack level, the increase in temperature induced by the level of integration can facilitate the combustion of gases emitted by Li-ion LFP cells, despite the reduced availability of oxygen. In addition, the integration environment has a strong influence on combustion, as observed by Zhai *et al* (study of the impact of the slope of the ceiling overhanging the battery) (25).

3.3.3 Risk of explosive atmosphere formation

The gaseous phase emitted during thermal runaway induces an explosion risk (18, 22, 27) given the high CO, H_2 and ethylene content of the gas phase, which can form an explosive atmosphere, as reported by Quin et al. (27) but also because of the strong flammability of the electrolytes constituents (*e.g.* DMC with an LEL of around 4%) (28).

Counter-intuitively, the lower energy density of Li-ion LFP batteries is associated with a higher risk of explosion (compared with NMC batteries). This increased risk is partly explained by the lower LEL values around 5-6%. (18, 29). Wang *et al.* pointed out to this explosion risk which is according to them more critical for LFP than for NMC at the light of the explosion pressures obtained for different chemistries (651 kPa for LFP vs. 496-512 kPa for different types of NMC) and the explosion index (>4 MPa.m.s^{-1} for LFP vs. <3.5 MPa.m.s^{-1} for different types of NMC). (29).

The larger the scale is, the greater the risk of explosion increases. On the cell scale, long-term smoke production can occur, rapidly mixing with the ambient air. On a module or pack scale, the stagnation of these smoke within the element, combined with a rise in temperature as thermal runaway spreads, accentuates the risk of explosion of the gaseous phase generated.

For 32-cell Li-ion LFP modules, Qin *et al.* demonstrated the impact of battery integration on the risk of explosion. In the case of insufficient gas evacuation, the LEL (Lower Explosive Limit) was exceeded for H_2 and C_2H_4 , whereas in the case of more favourable gas evacuation, the very rapid exceeding of the LEL for H_2 did not lead to an explosion (27). The authors also noted that extrapolation of cell-scale results to estimate the safety of modules or stationary LFP-type batteries is unreliable, given the relatively complex scale effects involved. According to this study, such extrapolations should be avoided.

3.3.4 Toxic risk

3.3.4.1 Gas toxicity

As with other Li-ion battery chemistries, the composition of the gaseous phase in the smoke emitted during thermal runaway of Li-ion LFP batteries presents a toxic risk.

Even though toxicity values for hydrocarbons are not readily available, it appears that, at a minimum, EC presents a risk of acute toxicity (30).

DMC has a PNEC (Predicted Non Effect Concentration) of 500 mg/L, demonstrating ecotoxic effects. (31). Yang *et al.* also mentioned the toxicity of the hydrocarbons emitted, and the contribution of CO_2 to a greater absorption of other asphyxiating species, which can pose serious problems for people exposed in a confined space over a fairly long period of time (18).

Ineris has already highlighted the risks associated with contamination by POF_3 and HF (26) which are also found in the gaseous mixture of LFP batteries. Peng *et al.* identified the following toxic gases emission by LFP batteries: CO, HF, SO_2 , NO_2 , NO and HCl, and highlighted the greater toxicity of HF and SO_2 when quantifying the gas mixture. (11). Compared with other Li-ion chemistries, Premnath *et al.* pointed out that the production of HF, a particularly toxic gas, is higher for LFP (21).

Peng *et al*. also identified that the effects of irritant gases (HF, SO_2 , NO_2 , NO and HCl) have a greater impact on human evacuation compared to the one of asphyxiating gases as they lead to a maximum value of 0.8 for the "FEC" parameter. FEC stands for "Fractional Effective Concentration". This parameter was developed by the fire smoke toxicity experts of the ISOTC 2 SC3 committee (whose work is followed by Ineris). The critical value of "1" means simplistically that half of a normal population (healthy adults) exposed will lose its ability to evacuate the danger zone on its own.

Finally, it should be remembered that toxic risk analysis remains a complex topic, since it depends in particular on the routes of exposition (inhalation, ingestion, percutaneous toxicity), and may be systemic in nature (cf. the various toxicity hazards for humans recognized by CLP).

3.3.4.2 Particle toxicity

Aerosols emitted by Li-ion batteries in general, including thermal runaway LFP chemistries are at least for most of them in the respirable aerosol range. This poses a problem, as the particles emitted can enter the respiratory system and impact the health of those exposed. Following thermal runaway of LFP cells, Barone *et al.* detected carbon, fluorine and silicon cenospheres in particular, which represent a health risk due to their size (32).

It should be noted that the chemical nature of soot resulting from Li-ion cell thermal runaway is different from that of soot emitted by conventional fires. The effects induced by their inhalation are therefore still poorly understood, and studies need to be carried out to better quantify their effects.

For example, LFP-type cathodes are composed of iron and phosphorus (22) which can theoretically be found in soot. It has already been shown that inhalation of iron can lead to the formation of oxygen species that damage DNA (33). It is true that iron is not necessarily observed in all tests (cf. study by Barone *et al*. (22)) but depends on the case and given the initial concentrations, an emission of iron compounds (oxides, salts, etc.) in the aerosols produced by thermal runaway can be expected.

Compared with NMC cathodes, the absence of cobalt and manganese in LFP cathodes seems favourable in terms of human toxicity and environmental impact.

In short, Li-ion LFP batteries emit smoke composed of toxic particles and gases whose impact on human and environment must not be overlooked.

As with other Li-ion battery chemistries, the gaseous mixture creates the risk of an explosive atmosphere. According to some studies, this risk is even favoured by several factors, notably the lower oxygen release rate, which limits combustion and favours the formation of an explosive mixture.

These risks increase with the scale considered, and extrapolation of experimental results obtained at cell scale to higher scales is not relevant.

4 Factors influencing the response of LFP batteries

4.1 Origin of failure (means thermal runaway triggering)

Thermal runaway of Li-ion batteries, including LFP batteries, can be caused by a variety of faults (*e.g.* overheating, overcharging, short-circuiting, mechanical deformation, etc.). It is important to emphasize that the reactivity of Li-ion batteries in thermal runaway will strongly depend on the nature of the failure encountered (15, 34, 35). It is therefore vital to assess the risks presented above for the different types of failure that may be encountered.

For example, in the study by Larson *et al.,* overcharge and overheating tests were carried out on identical Li-ion LFP cells, leading to very different behaviours depending on the initiation, as shown by the difference between the maximum temperatures observed (more critical in the case of overcharge, with over 800°C compared with 350°C obtained with overheating). (15). Brand *et al.* also reported greater sensitivity of LFP to initiation by overcharge than by overheating (notably compared with other NMC or NCA chemistries) (36). For their part, Premnath *et al.* pointed out to the more significant particle emission noted when overcharging an LFP module compared with the case of module deformation during nail testing (21).

In addition, the intensity of a given initiation also plays a role. For example, in the case of overheating, Ghiji *et al.* reported an increase in the energy released (HRR) from 710 to 1056 kW/m² when the intensity of thermal aggression rises from 50 to 75 W/m². (16).

It should be noted that for the same initiation (nature and intensity) and under identical test conditions, variable results were observed by Larsson *et al.* Thus, a violent runaway was triggered once out of the four identical attempts (with high temperatures and significant combustion observed)(15). A battery remains a heterogeneous and complex object, which for the same "manufacturer" specifications can present variations that are not insignificant in terms of response to an abusive situation. Similarly, numerous environmental parameters can influence test results. It is therefore important to duplicate the tests before concluding on the quantification of real effects due to an initiation method, given the variability inherent to the thermal runaway phenomenon (37-39).

4.2 Cell format

Cell format (shape and size) also impacts the thermal runaway behaviour of Li-ion cells, including LFP. For example, Rappsilber *et al*. compiled data from several studies, highlighting the impact of cell format (in the sense of shape) on the thermal runaway reactivity of Li-ion LFP cells. The total energy released during thermal runaway by LFP cells spreads over a wider range for prismatic cells than for cylindrical cells (highest value achieved with prismatic) (17). It should be noted that cell dimensions are not considered in their study (only shape is), yet cell dimensions also have an impact on thermal runaway reactivity.

For example, with regard to cell size, Duh *et al.* recorded a higher reactivity for larger cylindrical cells, as illustrated by the heating rate below:

- 12 °C/min for a 14500 cell,
- 34.4 °C/min for an 18650 cell,
- 194 and 1392 °C/min for 26650-A123 and 26650-Sony cells.(7)

Also, as the on-board energy increases (which is made possible by the increased diameter), a rise in the energy released in thermal runaway is also noted in their study. Duh *et al.* attributed this discrepancy to the structural instability of large cells, which explains in particular the significant fires observed on bus batteries using large LFP cells (7).

4.3 State of charge

State of charge impact on Li-ion cells thermal runaway is surely the most well-documented parameter. For example, it has been shown that the state of charge can have a strong impact on the thermal runaway of Li-ion LFP cells. For example, Golubkov *et al.* highlighted the variation in thermal runaway initiation temperature versus state of charge.

A state of charge of over 50% is sufficient to trigger high reactivity. This reactivity increases as the charge state rise (the maximum temperature climbing from 283 to 448 °C in their study). (8). Ghiji *et al.* also confirmed the maximum temperature increase (349 to 455 °C for a state of charge rising from 0 to 100%) as well as the drop in initiation temperature (by 15°C from 115°C to 100°C) for LFP 26650 cells.

In addition, Ghiji *et al.* reported the effect of state of charge on the power released during thermal runaway, with HRR increasing from 2 to 8.3 kW for LFP cells at 0 and 100% SOC respectively (16). It is important to note that the dependence on state of charge is not linear.

The impact of the state of charge on the gas components is more mixed. Amano *et al.* have pointed out that, unlike Li-ion NCA whose gas production decreases with decreasing state of charge, the amount of gas produced by Li-ion LFP cells is only slightly influenced by this parameter (20).

However, the composition of the gaseous phase varies, which affects the toxicity of the gas mixture. The evolution of the FEC of irritant gases (SO_2, HCl, NO_2 and HF) as well as the evolution of the FED of asphyxiating gases (CO and CO_2) are strongly impacted by the state of charge:

- FEC and FED at SOC 100%: around 0.8 and 0.012;
- FEC and FED at SOC 75%: around 0.6 and 0.010,
- FEC and FED at SOC 50%: around 0.3 and 0.004;
- FEC and FED at SOC 0%: less than 0.1 and around 0.0015 (20).

Here again, the impact of the state of charge is not linear.

Rappsiler et *al.* and Lecocq et *al.* have reported, in the case of LFP cells or modules, lower HF production with increasing SOC, and explain this by the higher temperatures reached, which break down the HF into by-products (17, 40).

The impact on the gas phase does not end with the toxicity of the gas mixture. For example, Peng *et al.* highlighted the impact of charge state on combustion. Increasing the state of charge greatly affect the risk of combustion, as illustrated by the increase in combustion-induced heat flux (from 2.5 to around 25% for a change in SOC from 0 to 100%). (11).

4.4 Ageing

The ageing of Li-ion cells in general, including LFP, also has an impact on thermal runaway behaviour. Abada *et al.* have shown that the first exothermic reaction peak occurs at a higher temperature in calendar-aged cells. However, this does not prevent the thermal runaway onset (sudden, abrupt heating) to occur at a lower temperature (41). This reflects greater instability with ageing.

The time lag of the first self-heating phase is also highlighted by Preger *et al.,* who reported an increase from +10°C to +52°C in aged LFP samples. Here too, the apparent time lag in the onset of reactivity does not prevent a thermal runaway start at -20 °C compared with fresh cells. (42).

Yang *et al.* have shown that ageing by cycling with a slight overcharge weakens the thermal stability of batteries (due to lithium plating on the anode, which facilitates internal short-circuits) (43).

Taking ageing into account is therefore crucial in determining the battery's safe temperature range and the protection required.

4.5 Integration level

The integration of Li-ion LFP cells in batteries has a strong impact on their thermal runaway. As a key example, Quin *et al.* studied two different pack configurations with varying vent diameter and free volume. Depending on the configuration chosen, an explosion may or may not occur, drastically altering pack safety. Qin *et al.* pointed out the importance of considering the risk of thermal runaway on a large scale, highlighting the difference between the weak behaviour observed on single cells compared with stationary systems (27).

Dubaniewicz et al. have also highlighted the impact of free volume on thermal runaway (13). While Zhai *et al.* study focused more on the impact of building integration (25).

Battery integration does not stop at the battery itself, but also depends on the environment and the protective systems used. For example, Larsson *et al.* reported higher HF production when certain extinguishing agents are used. (44)

So, as demonstrated in this paragraph, it is of paramount importance to consider the battery as a whole and test it on a large scale to understand the real risk of thermal runaway associated with it.

In summary, there are many parameters impacting thermal runaway of Li-ion cells in general, including Li-ion LFP (origin of failure, cell format, state of charge, ageing and level of integration). All these parameters can have a significant impact on thermal runaway behaviour and the risk of explosion.

To understand the risk of thermal runaway, it is crucial to take into account all the parameters that can affect thermal runaway, to ensure that the protective measures put in place are capable of detecting and correctly protecting the battery and its environment.

5 Conclusion

Li-ion LFP batteries, like all current Li-ion battery chemistries, are subject to the risk of thermal runaway. Although not intrinsically safe, they are sometimes presented as safer than other battery chemistries because of certain particularities:

- their low energy density,
- better stability against thermal abuse,
- stabilization of oxygen in the cathode structure, making them less prone to combustion.

These particularities tend to create a smoky phase during thermal runaway (with no visible flame) that can last for an extended period. As long as this combustion-free reaction phase takes place, thermal emissions are lower and the propagation of the event from one cell to another can be more easily controlled, depending on the integration choices made. On the other hand, this combustion-free reaction produces a large number of flammable gases, which can form an explosive atmosphere if they accumulate. Accidentology shows that this risk is particularly sensible to confined environments (e.g. contained stationary systems).

The occurrence of a combustion regime remains possible, even if it seems less systematic at cell level, and is difficult to predict. At cell level, it depends on numerous parameters (state of charge, type of abuse, etc.). At system level, the risk of ignition is more pronounced, influenced both by integration choices and by elements other than batteries (electronics, converters, etc.). Thus, experience feedback and the literature show that a sustained combustion regime, even if it may be delayed, is observed and must be considered.

Once a combustion regime is established, the thermal effects are equivalent to those observed on other Li-ion battery chemistries under the same conditions.

Finally, regarding toxic effects, emissions prove to be hazardous to human and the environment as any other Li-ion chemistry. Indeed, the LFP emission are roughly equivalent to the ones of other chemistries with yet a possible higher HF proportion in the smoke and the notable absence of cobalt and nickel in particulate emissions.

LFP-derived cathode chemistries such as LMFP (LFP also containing a proportion of manganese), SLFP (trade name for an assembly containing a proportion of NCA) or spend LFP (LFP from recycling also known as SLFP) have, at first glance, the same risk profile.

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Date and place	Technology	Brief description of accidents
03/07/2013 **Port Angeles[1] (United States)**	Li-ion LiFePO chemistry$_4$ (LFP)	▪ A fire broke out in the battery room of a shopping center. The 50 kWh battery was connected to a wind turbine. **An electrical fault in the battery system is believed to be the cause of the fire.** ▪ The fire was extinguished by powder spraying. ▪ No injuries, evacuation of the mall due to smoke, temporary closure of the mall and surrounding streets - destruction of the battery room (no spread to adjacent buildings). ▪ **The battery caught fire again 1 week after the fire on 03/07/2013**. The renewed fire is thought to have originated from a single battery in the system, which survived the 1er fire. The fire was extinguished with a powder extinguisher.
2017-2022 **South Korea**	Li-ion (various chemistries - NMC and LFP - **at least 2 cases of LFP),** various applications - wide range of capacities/installed power (MW/MWh)	▪ **At least 36 fires** involving Li-ion batteries for stationary applications **(at least 2 involving LFP chemistry).** ▪ No injuries. ▪ **4 main causes identified**: 1/ Insufficient battery protection against short-circuits, 2/ Insufficient management of environmental conditions (condensation, dust), 3/ Negligence during installation (human error during installation), 4/ Insufficient integrated protection and management system. ▪ **Various measures were taken following these incidents:** installation of electrical protection and emergency shutdown, management of load and temperature, humidity and dust, firewalls and separation distances from other installations for indoor facilities, government financial support for the implementation of some of these safety measures, and so on.
15/03/2020 **Griffith University, Brisbane (Australia)**	Li-ion (LFP)	▪ A fire broke out in a battery room on the 5ème floor of a building. The room was closed **and the sprinkler system was active.** ▪ **3 explosions occurred** ▪ **A firefighter was slightly injured as a result of an apparent "flashover" phenomenon.** ▪ Cause attributed to an internal short-circuit on a cell. ▪ Destruction of the battery room (no propagation to adjacent buildings).

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[1] https://www.peninsuladailynews.com/news/fire-erupts-again-in-landing-battery-room/

Date and place	Technology	Brief description of accidents
01/12/2020 **Perles et Castelet Ariege[2] ,[3]** **(France)**	Li-ion (LFP) / supercapacitor	▪ Fire in a container of Li-ion batteries/supercapacitors at an electrical transformer station (supplying a quarry and a factory). The batteries were 96% charged and the supercapacitors 45% charged at the time of the incident. When the batteries were connected to the power converter, an initial under-voltage/over-voltage alarm was triggered, followed by an audible alarm on the energy storage container (superimposed above the power electronics container). Operators on site noticed the emission of white smoke. Fire alarm triggered. Around 40 minutes after the first detection, the overpressure caused the container doors to open **(an "explosion" was heard**), and the container caught fire. When the fire department arrived, flames were coming out of the container door. The extinguishing system (potassium salt-based powder) installed in the container proved ineffective. ▪ Traffic disrupted on RD719, no water points nearby ▪ No injuries. ▪ Risk of pollution of the Ariège river (located nearby) controlled. ▪ The procedure was declared complete the following morning. The first failures were measured in the Li-ion battery racks. Within these racks, an abnormally high current (in the kiloampere range) was said to have flowed from one battery rack to another. The Li-ion cells through which this current flowed exceeded their safe operating conditions, which may have led to thermal runaway.
16/04/2021 **Beijing[4]** **(China)**	Li-ion LFP	▪ **An explosion** occurred while firefighters were responding to a fire on a 25 MWh Li-ion system combined with 1.4 MW rooftop solar panels, powering 94 electric vehicle charging points, in a Beijing shopping mall. ▪ The fire mobilized 235 firefighters, 47 trucks and over 10 hours of intervention. ▪ **2 firefighters dead, 1 injured + 1 employee missing.** ▪ The cause of the fire in the south building was an internal short-circuit in the LFP battery, which led to its thermal runaway. The cause of the explosion in the north building was that combustible and explosive components generated in the south building entered the north building's energy storage room through the underground cable trench and mixed with air to form an explosive gas, which exploded in the presence of sparks.

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[2] https://france3-regions.francetvinfo.fr/occitanie/ariege/foix/batteries-au-lithium-prennent-feux-container-ariege-1900866.html

[3] Investigation report BEA-RI- 07/27/2021 - http://www.cgedd.developpement-durable.gouv.fr/IMG/pdf/rapportperlesvdif_cle286783.pdf

[4] https://www.pv-magazine.com/2021/04/21/two-firefighters-killed-and-one-missing-after-beijing-battery-blaze/

Date and place	Technology	Brief description of accidents
30/01/2023 **US, PA, Millvale (United States)[5]**	Li-ion LFP	- **The basement of a commercial building contained a battery system that powered the building's kitchen from solar panels on the roof. As a result of the incident, the battery system was destroyed and the basement severely damaged.**

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[5] Failure Event - US, PA, Millvale - 30 Jan 2023 - EPRI Storage Wiki

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