LEARNING FROM 10 YEARS OF LI-ION BATTERY FIRE TESTS

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ABSTRACT

During the last decade numerous thermal runaway tests were carried out with Li-Ion batteries. Those experimental data now enable having a quite good knowledge on the relative influence and the interaction between the various physical phenomena, mainly, individual cell reaction to heat increase, combustion process for the different components and thermal conduction influence. It is then possible, based on this experimental database to draw generic principle regarding Li-Ion battery fire safety management but the currently available database also raises some new questions about LIB fires. These questions concern the different topics of fire including HRR curves but also toxic gas emissions. Based on the analysis of available experimental data, it is more and more obvious that being able to predict LIB fire from cell fire test is crucial for safety design.

Keywords: Li-Ion batteries, smoke toxicity, LIB fire modelling

1. INTRODUCTION

According to the global warming process, new energy carriers (NEC) are currently more and more used in the field of transport. Among the various existing NEC, electric energy stored in rechargeable batteries for use in power train of Electric vehicles (EV) is the most advanced NEC. Consequently the number of EVs in the traffic has constantly increased in number all along the last decade and should continue to increase strongly [1], Figure 1.

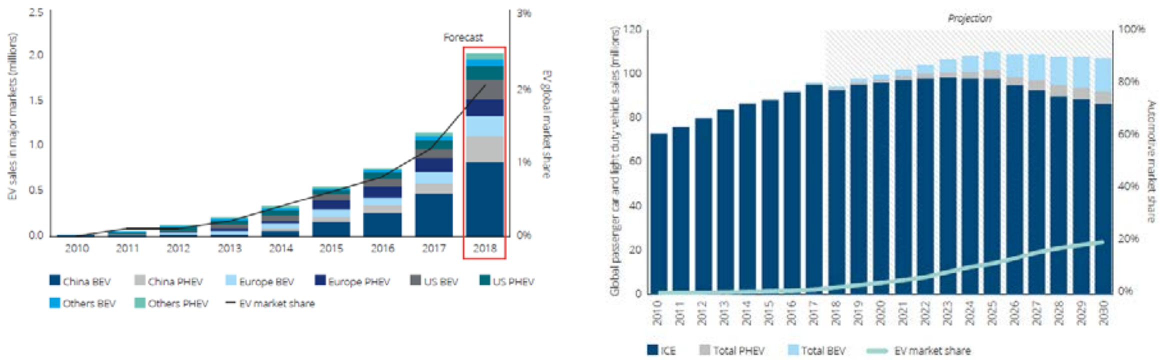

Figure 1: Evolution of EV vehicles along the last decade, from [1].

Such a situation makes obvious the need to consider such EVs in updating risk evaluation in traffic tunnels. It is then important to identify the fire characteristics to be modified when Li-Ion batteries (LIB) are present. Two aspect should then be addressed, fire consequences, considering both thermal and toxic threats, and fire probability.

2. THE BEGINNING OF LIBS FIRE TESTS

When EV became a reality, at the end of years 2K, the fire risks for such vehicles had to be investigated since their use increase in numerous situations. As usual, the underground use of this technology appears to be critical, then car parks and tunnels were first considered.

Since, very few information were available at that time, preliminary studies were launched trying to understand LIBs fire phenomena and related potentially hazardous scenarios on the whole value [2][3].

2.1. Brief description of LIBs

Appropriate risk characterization of batteries preliminary requires basic data describing such electrochemical energy storage technology. A good description of LIBs is given is [4][5]. To describe a LIB in a nutshell, it may just be considered that it is composed of positive and negative electrodes, a separator allowing galvanic isolation but porous to lithium ions, electrolyte solution and electric current collectors. The liquid electrolyte is most of the time composed of a mixture of flammable organic carbonates (DMC, EC, DEC…) [6][7], enriched with a Lithium salt, typically $LiPF_6$. For a basic understanding of LIBs aiming at illustrating i) operating principle (from electrochemistry viewpoint) and ii) manufacturing technology (cell layer stacking or rolling), figure 2 is provided, clearing both aspects: the basic principle of LIB in terms of electrochemistry and various cell configurations with their modular assembly principle in a battery pack.

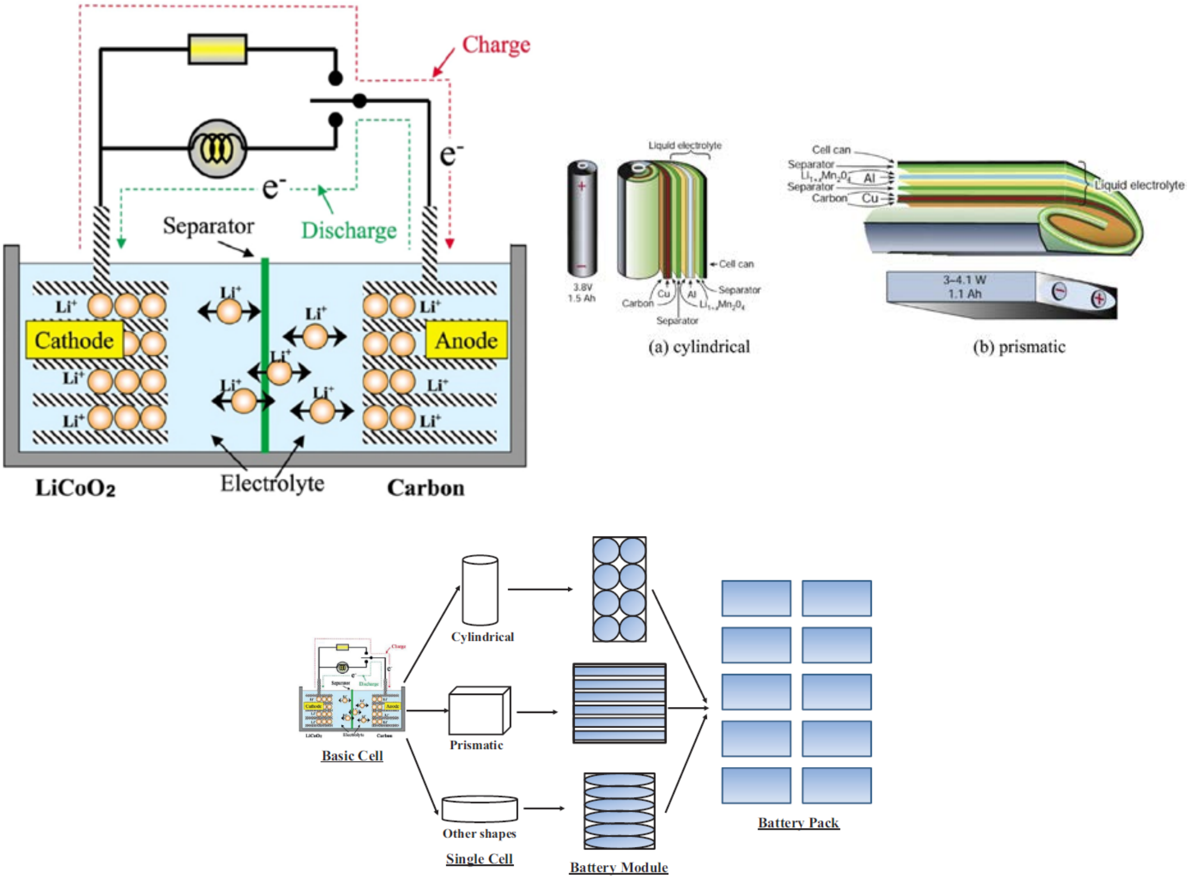

Figure 2: Basic principle of LIBs electrochemistry (left), geometrical view of a cell (right) and organisation in pack (bottom) reproduced from [8].

As illustrated in figure 2, configurations of LIB cells may adopt various geometries (cylindrical, prismatic, pouch…) according to best fit-for-purpose and selected integration strategy followed by battery pack manufacturers and downstream OEMs.

A simple risk analysis leads to quick identification of the flammability hazard pertaining to the electrolyte solution and the potential release of fluoride compounds due to the presence of potentially 4 F-containing components (mostly the lithium salt, but also the binder in electrodes (often PVDF), and potentially also fluorinated flame retardants or fluorinated solvent components. Fluorinated emissions are typically hydrogen fluoride (HF) but also POF_3 [9], carbonyl fluoride (COF_2) [10]. The toxic thresholds of those chemicals, respectively 34 ppm and 0,35 ppm for the 30 minutes exposure AEGL2 (Acute Exposure Guideline Levels), are highly lower than those commonly considered for fire, as carbon monoxide or hydrogen chloride for instance, respectively 150 and 43 ppm for the same AEGL2. In addition, fire-fighting or rescuing activities have to take account of specific concern of HF, which in addition to inhalation toxicity threat also present toxicity threats to other types of exposure. Similar concern may arise for COF_2 and possibly other F-containing species, see Figure 3.

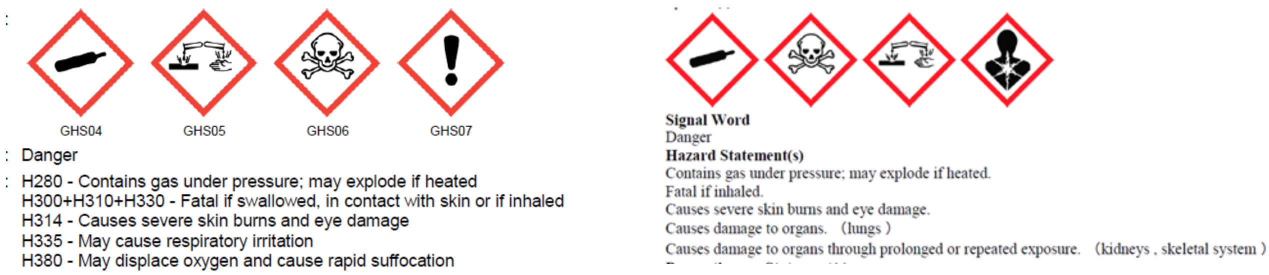

Figure 3: Hazard pictograms and statements for labeling of HF (left-hand side) and COF_2 (right hand side) according to GHS (purple book) and relating CLP European Regulation

2.2. First fire tests

In the beginning of years 2010's, several tests were performed to evaluate the influence of batteries on electric vehicle fire development and related impacts [11][12][13]. The first interest of those campaigns was to evaluate the influence of the battery on the global heat release rate (HRR) for the vehicle. Based on existing batteries when those tests were carried out, those campaigns showed that batteries did not significantly influence the global HRR.

During those tests, very few gas analyses were done. In the early 2010's, only the work performed by Lecocq et al [11] introduced such gas analysis in the context of EV fires. The main interest of such a study consist in the comparison of fire-induced toxic emissions from ICE and EV cars when involved in a fire scenario. It was demonstrated that, in the test conditions, the toxic emissions were fairly identical between ICE car and EV.

This analysis also pointed out the concern raised with regard to pertinent and efficient gas analysis for qualifying such a fire. When dealing with passenger vehicle fire in confined spaces, one commonly considers carbon monoxide and carbon dioxide and rarely some other gases. Dealing with batteries (but this is also true to some extent with other halogen containing materials burning in fire conditions) lets appear a new problem in terms of gas analysis since some toxic compounds, and among them hydrogen fluoride, are very difficult to analyze because of their fierce hygroscopicity and ability to be trapped by any material in the surrounding. Specific gas analysis should be adapted for such an experiment.

It should also be kept in mind that those tests were aiming to qualify the fully developed fire, whilst the gas composition could be strongly different during the gas venting phase, with potentially only partial combustion. Furthermore, during those campaigns, only acute toxicity was considered, while other potentially emitted substances like metals of PAH (Polycyclic-Aromatic-Hydrocarbons) which are more prone to trigger chronic toxic risks were not considered.

This series of tests, in the beginning of 2010's, had the significant benefit to initiate the provision of valuable information about EV fire profiles and could provide some first answer to the scientific community and to EV value chain stakeholders. This also influenced early regulations set up notably in France for underground car parks welcoming EVs and dedicated charging devices.

2.3. Intermediate state of the art

At the end of this period, fire scientist knowledge about LIB fire was significantly increased but characteristics of LIBs in the meantime were continuously moving, due to sharp innovation in many aspects of EV battery pack development and relating electric power train of EVs, essentially motivated by increased performance and reduction of production costs. Then, while a first evaluation was made possible according to this large series of fire tests, it was still very difficult to provide a consolidated global risk overview as far as LIBs were concerned.

According to the large number of varying parameters characterizing a LIB from one EV battery pack to the other (selected cathodic and anodic chemistries, electrolyte and separator, cell geometry and arrangement scheme in terms of modules, electrical binding arrangement (series, parallel or series & parallel connections), mode of integration and location in the EV a specific analysis may appear recommended as far as a new technology emerges on the road. Fire safety engineers have concluded at that time that LIB evolution had to be considered as a new hot topic. Subsequently, the LIB behavior in case of fire was more and more studied in the following years.

3. KNOWLEDGE IMPROVEMENT: MULTIPLICATION OF CELL TESTS

As described above, based on the first large scale EV fire tests, some data were made available for fire safety engineers. But significant lack of information concerning the influencing parameters of LIB and EV fire behaviors was very rapidly identified. Typically, since it was commonly admitted that the worst case, in terms of HRR was a fully charged battery configuration in case of a fire, most of the tests were done in such a situation. While this provides design fire curves with the highest fire impact as far as HRR is concerned, the gas composition as a function of SOC started to be considered. This analysis was crucial for many aspects of LIB fire safety.

3.1. Influence of the chemistry

LIBs are commonly considered as a unique family of devices while it consists in many different systems and situations. As described previously, in the brief description chapter, a LIB is composed mainly of an electrolyte, a positive and a negative electrode and a separator. For each part of the battery, several materials can be used. Then, LIBs are commonly named using the cathode material, LCO (Lithium cobalt Oxide), LFP (Lithium iron phosphate), NMC (Nickel Metal Cadmium) and some others, including variation inside a given family. Typically, nickel enriched NMC receives more and more attention according to more energetic NMC based battery systems [14].

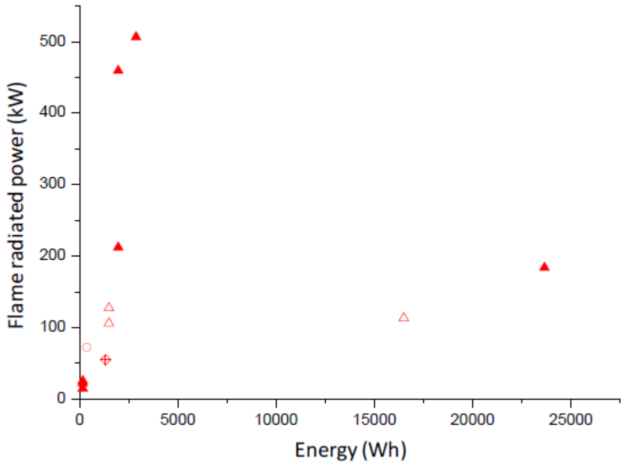

Figure 4: Released energy (radiation) as a function of available electric energy for several chemistries, tests performed at cell size.

Having in mind this distribution of possibilities, consequently a key question might be to have a cartography of the typical HRR for a given chemistry. This objective is however impossible, the HRR distribution for a given chemistry, cathode composition speaking, may varied from 1 to 10 for the same available electric energy, Figure 4.

Such a curve highlights the influence of internal parameter that govern the thermal runaway mechanism. Considering that those tests were managed using cells, the scale factor should be considered. Since the cell characteristics have a so strong influence on the cell HRR, it is fundamental to take into account the influence of the geometry and internal safety system as thermal insulation, heat sinks, and even cell ageing aspects [15] on the global HRR when dealing with full battery.

3.2. Influence of the SOC (State Of Charge)

The other very important parameter to kept in mind is the SOC, even if we are able to define the worst case in terms of HRR. Several tests were managed in that sense in the field of aerial transportation [16] in order to define the SOC limitation to authorize batteries for air transportation. Some tests were also managed at INERIS in order to evaluate the influence of the SOC on both HRR and gas emissions. Those tests were achieved using the FPA (Fire Propagation Apparatus) calorimeter, an enriched version of ISO12136 FPA, for two different compositions of the electrolyte, LiFSI and $LiPF_6$ [17]. Those tests clearly confirm the influence of the SOC on the HRR, the peak HRR value is divided by a factor 5 between a 100% SOC cell and a 0% SOC one. However, the gas analysis made during this test pointed out the unclear influence of the SOC on gas emissions. While CO is strongly reduced when SOC diminishes, whatever the chemistry is, this is not necessarily the case for HF. Indeed, the total amount of HF released by a discharged cell was found higher than the one release by a fully charged LIB. Based on this analysis, [17] proposes a toxicity evaluation by use of the FED (Fractional Effective Dose) and FEC (Fractional Effective Concentration) approaches [19]. Without going into details of FED and FEC calculations, it should be reminded that FED is based on asphyxiant gas dose response, hydrogen cyanide and carbon monoxide essentially, while FEC is based on irritant gas concentrations, including hydrogen fluoride. When FED or FEC reached 1 (for ordinary grown-up and healthy people) , this means that half of the exposed people losses their capability to evacuate by themselves.

The comparison of the FEDs and FECs in a ventilated compartment in case of LIB fire, for two specified scenarios a and b, shows that discharge battery could produce more severe toxic effect on people, [18]. In both cases and for both chemical compositions of the electrolyte, the FEC for 0% SOC case becomes higher than the 100% SOC one, after two to four minutes.

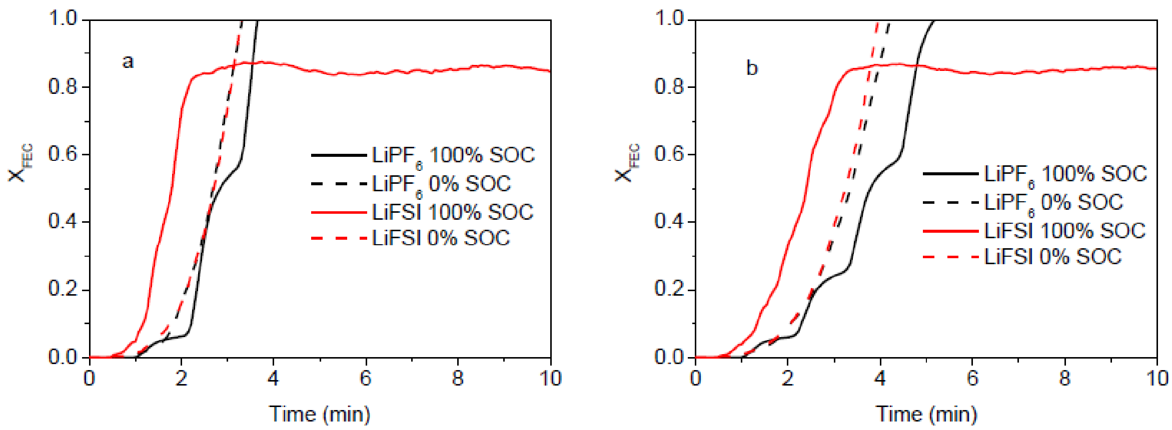

Figure 5: FED and FEC evolution for a semi-confined LIB fire, reproduced from [18].

Such a result is a key factor when dealing with risk analysis in tunnels since it is impossible to predict the EV LIB SOC when they are crossing the tunnel.

The relation between HRR evolution, cell sensitivity and intrinsic toxicity should be considered all together since for a reduced SOC, cell reactivity is reduced, HRR is diminished, that lead to a reduction of the potential for thermal runaway propagation between cells, but toxicity could be increased. It shall also be noted that thermal runaway cascading propagation from cell to cell not only depend on cell reactivity and SOC, but also on technical passive (heat sinks) and active (thermal battery management system) barriers provided by design while assembling the cells in the modules and battery pack.

3.3. Synthesis and future works

The two aspects of fire consequences should be distinguished here.

Regarding thermal consequences, it appears that both chemistry and SOC are key influencing factors, but some simple assumptions can be considered to define a reasonably operational design situation for fire safety engineering purposes. Having in mind that battery fire tests are commonly performed using a 100% SOC status, measured HRR with relevance to modern EVs can be considered as the maximum possible value. Then, the full scale EV fire tests briefly described can be considered as quite representative of the current situation, assuming that the electro-chemical energy density, as well as the speed at which energy can be released in a fully developed EV fire are not too much increased.

Regarding smoke toxicity, the problem is much complex since a reduction of the SOC leads to an increase of the potential toxic consequences of the fire. Since tests were made at cell scale, it is difficult to estimate the crosslinked relation between the reduction of battery reactivity and HRR release and the toxic emissions.

Then, considering the influence of uncontrolled parameters, mainly the detailed information about the chemistry, getting a design fire for such a vehicle is not realistic since too strong and unreliable assumptions should be considered for EVs. The current objective in such a way is to be able building a realistic model to predict the whole battery HRR based on cell-scale fire test. To build such a model, one should consider the different aspects of thermal runaway phenomena that occur in LIBs [8].

Some quite simple fire models were developed in the past, for evaluating the HRR for a truck transporting LIBs [20]. Such a model, highly useful for large scale fire prediction, was based on experimental data and does not consider the thermal mechanisms that occur inside a battery during the thermal runaway.

More recently, some approaches were developed to model the thermal runaway mechanism and its propagation taking into account more details and especially thermal transfer between the cells [21]. Another approach under development consists in coupling CFD (Computational Fluid Dynamic) model with thermal conduction model to take into account both the cell heating due to the surrounding combustion inside the battery and the thermal conduction that occur between the battery cells [22].

4. SUMMARY AND CONCLUSIONS

The analysis of existing data about LIBs provides a contrasting overview. While such a technology is quite new, a lot of experimental tests were managed in order to provide information regarding fire safety. Fire curves for batteries or for EV were then made available in the literature but LIB technology is moving very fast and fire safety engineers should be aware of that more-than-ever fast-moving situation to evaluate whether the fire curve is relevant for their application or not.

Two main aspects were illustrated in this paper. The first is the importance of nature of the chemistry and associated uncertainties. Under the largely used LIB name, there is numerous different chemical arrangements inducing various fire behaviors, in terms of both HRR and toxic emissions. The second aspect mentioned is the influence of the SOC. While decreasing the SOC leads systematically to an HRR decrease, some experiment highlights that, in some situation, the emission of toxic products can be significantly increased. Then, since most of the fire tests are managed with 100% SOC to maximize the LIB reactivity, the question of toxic emission for low SOC LIB pack is still open. Developing a model able to predict fire propagation inside a battery appears as a requirement nowadays. Such a model should be able to consider the various LIB characteristic and to predict both HRR and toxic gas emissions.

It should finally be pointed out that not only acute toxicity should be consider but long term as well as environmental impacts should also be studied. The large fires that currently appear for LIB stationary application development let people in the neighborhood more and more concerned about this environmental impact of LIB fires. The development of battery storages will increase this aspect that appear crucial for our decarbonated future.

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