STATIONARY ENERGY STORAGE: RISKS AND POSSIBLE SOLUTIONS

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PREFACE FROM CEA

In compliance with recommendations from the IPCC and following the Paris Agreement, France has committed, as part of its National Low-Carbon Strategy set out in 2015 and the energy-climate law enacted in 2019, to reaching carbon neutrality by 2050. To this end, the CEA is carrying out research on low carbon energy sources. Through its research activity, it is contributing to providing industry with the innovations necessary to implement this sustainable energy strategy, and meeting the need to reduce dependence on fossil fuels and critical materials, all while conforming to the highest demands regarding safety and protection of the environment.

The CEA-Liten institute located on the Grenoble and Chambéry (Ines campus) sites, focuses its operations on renewable energy and is developing technologies at a world-leading level in key domains such as solar panels, energy supply networks and how to manage them, and energy storage such as hydrogen and battery packs.

With over 30 years' experience in battery Research & Development, the CEA has gained well-renowned expertise in this domain across the value chain of materials and components all the way to their integration into vehicles or stationary storage applications. Beyond the question of innovation on performance and longevity, one of the main branches of development concerns improving battery reliability and safety. To do this, the CEA has technological platforms and advanced digital design, modelling and simulation software to measure, understand and predict physico-chemical phenomena in order to offer solutions that are more effective, sustainable and safe.

In order to help with mass roll-out of these technologies, CEA-Liten contributes to the development of standards and regulation with recommendations based on its expertise, test results in the lab, using normal, poor and extreme working conditions. In addition, the CEA-Grenoble management department provide support regarding prevention, control, monitoring, information and maintenance on systems used on various sites.

As a major R&D player in this domain, both in technological and risk management and prevention, we are glad at the instigation of the Savoie Fire and Emergency Department to contribute to the working group whose objective is to analyse risks in anticipation of the development of the domain. As such, this document is the result of work to produce a summary which is both pedagogical and operational so that all parties involved can better anticipate battery technology, its usage, for various industrial, residential and vehicular usages.

François LEGALLAND, *Director of CEA-Liten*
Bruno FEIGNIER, *Director of CEA Grenoble*

PREFACE FROM DGSCGC

In recent years, the fight against climate change has encourages politicians, through law and regulation, to implement ambitious objectives to reduce greenhouse gas emissions and the implementation of more and more widespread use of renewable energy sources. The intermittent nature of energy production inherent to these technologies is not without its problems for users and network operators to ensure stability. To limit this constraint, the sector has put in place electrochemical energy storage systems using Lithium-Ion batteries. These systems are as such connected to renewable energy sources in various types of building.

In this context, new risks can appear and circumvent the existing emergency and fire plans as well as the security of the building concerned. Because of the chemical specificity and energy densities of Li-ion battery technology, the reactions in these systems can lead to dangerous behaviours for operators and for buildings.

In the face of this problem, I have appointed my services so a cross-discipline working group could be set up and a document could be created, intended for emergency services in all their missions (operations, prevention, training) but also for sector professionals, insurers, standard creators. This large work was carried out in order to identify the reactions at risk, the equipment to deal with them through operations but also regarding prevention with the goal of better understanding accidents that could occur on electrochemical energy systems in an enclosed space.

Today I am particularly proud to see this work completed and would like to highlight the commitment and professionalism of the contributors to this project.

This report, without having the pretention of dealing with the problem exhaustively, will I'm certain enable progression throughout the sector and especially in fire and emergency services in terms of considering safety restrictions, and therefore freeing up the potential to implement this key sector to meet France's commitment in the fight against climate change. Finally, I would like to thank the fire and emergency services that have participated in this work, for equipment implemented, the expertise share and the openness of mind and curiosity in which this work has been carried out. I would likely finally to thank the financial contributors who have enable such a document to be graciously given in service of the profession.

Alain THIRION,

Regional prefect, Head of the French General Directorate for civil protection and crisis management

1 - ELECTROCHEMICAL STORAGE SYSTEMS: STATE OF THE KNOWLEDGE AND TECHNOLOGY 15

2 - CHARACTERISATION OF RISKS AND ACCIDENTS IN ELECTROCHEMICAL ENERGY STORAGE SYSTEMS 55

3 - TESTS: CONDITIONS AND LIMITS 79

4 - SYSTEMIC ANALYSIS AND POSSIBLE SITUATIONS 103

5 - OPERATIONAL RECOMMENDATIONS 131

FOREWORD

For several years now, the emergence of renewable energies and the search for alternatives to centralised distribution of electrical energy has encouraged the introduction of electrochemical batteries. These systems enable intermittent energy made by renewable sources to be stored for other uses.

Operations on these systems, in case of fault or accident, present risks that need to be taken into account to better manage interventions undertaken by emergency services.

The following pages are the practical summary of questions relating to observed risks presented by electrochemical storage components and associated electrical systems.
They are the fruit of numerous exchanges between emergency services, researchers and industry partners concerned with providing clear answers to the questions posed by the fire service.

The goal of this document is to represent the knowledge of the authors at the time of writing. It is in no way exhaustive and cannot be considered as an absolute reference document concerning the safety of electrochemical energy storage systems in buildings.
The recommendations in this report are not regulations. They are the result of shared experience between the experts in this working group. They enable key decision-making, interpretation and prevention information to be provided to standard/regulation makers, insurers, fire and emergency services, industry members, researchers and other parties in the field. They enable solutions to be provided for the problems raised both theoretically and practically.
This work is bound to change according to understanding, emergence of new technologies and feedback.

GLOSSARY

A

AC: **A**lternating **C**urrent: Alternating Current

B

Battery: assembly of electrochemical components: uninterruptible source (24/7)

BMS: **B**attery **M**anagement **S**ystem: System for managing batteries with the role of controlling battery charging and discharging as well as the security and balancing the cells that make it up

C

COS: **C**ommandant des **O**pérations de **S**ecours (Emergency Operations Commander)

CTA: **C**entre de **T**raitement de l'**A**lerte (Alert Processing Centre)

Customer: entity connected to the public energy distribution network

D

DC: **D**irect **C**urrent

E

ENR: Renewable Energy

ERP: **É**tablissements **R**ecevant du **P**ublic (Public-receiving facility) from French Home Office Regulation

ERT: **É**tablissements **R**ecevant des **T**ravailleurs (Worker-receiving facility) from French Labour Office Regulation

H

Habitat: Systems installed in a domestic context taken from the French Ministry for Ecological Transition.

I

ICPE: **I**nstallations **C**lassées pour la **P**rotection de l'**E**nvironnement (Installation Classified for the Protection of the Environment) from French Ecological Transition Office.

IRD: **I**nsulating **R**espiratory **D**evice

P

PPE: **P**ersonal **P**rotection **E**quipment

PV: (Photovoltaic source) energy source based on converting solar energy into electricity: uninterruptible source (in the presence of light)

S

Self-supply: act of consuming the energy produced by the customer in their own system

SOC: **S**tate **O**f **C**harge - battery's charge level

SOH: **S**tate **O**f **H**ealth - battery's health level

T

TNT: **T**ri **N**itro **T**oluene

U

UPS: **U**ninterruptible **P**ower **S**upply

V

VFN: **V**ariable **F**low **N**ozzle

W

Wh: **W**att **h**our: Unit of measurement for the energy stored in a battery.

OVERVIEW

The Working Group “SYSTEMES DE STOCKAGE ELECTROCHIMIQUE DE L’ENERGIE” (ELECTROCHEMICAL ENERGY STORAGE SYSTEMS) has been created in order to:

- Study electrical, physical and chemical risks of energy storage systems in buildings and infrastructures, not including vehicles (except in the specific circumstance of electrical vehicles parked in a confined space, see Introduction).
- To offer operational methods and potential standards provisions for implementation in order to limit these risks.

The studies carried out have allowed us to see that the literature has not fully covered the possible risks in extreme conditions.

The remaining risks have as such been identified and been subject to testing in order to study their behaviour and quantify the various danger areas for operators.
Tests were carried out over 3 different series spread over 3 years. This enabled testing of application domains from single cell systems measuring only a couple of watt hours (Wh) to battery systems up to 40kWh. Roughly 6 tonnes of batteries were used at various charge states and in various configurations.

These tests were carried out notably on:

- Fire-resistance behaviour in open and closed environments (external attack).
- Identification and quantification of toxic chemicals produced
- Behaviour when overcharged and risk of subsequent propagation (fault linked to the battery itself or its management system)
- Behaviour when crushed
- Scale effects linked with the volume of the battery and criticality of risks

Processing and risk reduction methods were implemented and analysed during dedicated trials.

These methods are:

- First Response Measures such as extinguishers
- Powders
- Foam
- Water spray
- Immersion

The results show clearly that the best extinction method remains water. It must be used in large quantities, generally more than normally used for regular fires of a comparable size, in order to stop thermal chain reactions. The quantities need to be adapted to the situation and notably in relation to battery capacity (kWh), any possible confined space and its charge level. Immersion remains the best solution for treating a thermal runaway of a battery.

According to the tests performance and summaries produced, the toxicity of fumes is not greater than that of a normal fire in an open environment. Nevertheless, it is important to be particularly careful concerning the effects of toxic concentration in an enclosed space.
A particular reaction that should bear careful attention was discovered during tests carried out by the working group. It is characterised by the emission of cold white fumes on inerting (via an inert gas or method of extinction) of a battery in thermal runaway. These fumes are unique due to the fact they are cold and spread across the floor and also because of their high flammability. In a confined space, and notably when opening the door of this confined space, if the fumes are ignited this could lead to an explosive pressure wave endangering emergency personnel. Unfortunately, this reaction was observed from feedback in the United States during a fire on a 2MWh storage container that caused serious injury to 4 fire-fighters.
As a result, an operational methodology solution has been written with the goal of dealing with various extreme situations analysed throughout this work.

This study has required considerable means to be implemented both in terms of number of tests (over 50 tests were performed) and analysis methods (mobile lab fitted with mass spectrometer: Detection, Identification and Sampling Vehicle (VDIP)). Although not exhaustive, it can certainly certainly be considered a remarkable work on the subject and makes a great effort to provide the clearest and most complete answers possible to the problems of implementation: and safety concerning Li-ion batteries in a stationary storage context.

INTRODUCTION

The emergence on the market of electrical energy distribution and electrochemical storage systems of varying sizes (several kWh to several MWh), mainly in building applications, has highlighted the risks that this type of system represents for its environment but also for emergency service personnel. The study is restricted to building applications. Embedded systems are excluded with the exception of electric or hybrid vehicles parked in a confined space (garage, small underground garage) and in the exclusive context where due to operational complexity, access difficulties or inability to implement the operational measures set out in the Operational Briefing Note regarding operations on electrical vehicles (Operational Briefing Note on electric and hybrid vehicles, June 2012).

The work of this group consists of:

- Surveying system typologies installed (industrial buildings; ERP, etc.) to facilitate identification,
- Survey existing battery technologies,
- Survey international work led on fire risks resulting from batteries,
- Survey feedback on battery fires,
- Categorise battery behaviour in case of accidents,
- Define, carry out and interpret tests to alleviate risks,
- Offer different operational methodologies depending on the context and the technologies present,
- Try these methodologies,
- Propose, if necessary, standards-based implementation provisions in order to limit these risks (domain of prevention).

The working group is comprised of the following fire and emergency services:

- SDIS 73 (Savoie): manager and creator of the operation
- SDMIS (Rhone and Greater Lyon area)
- SDIS 38 (Isère)
- DGSCGC: French General Directorate for Civil Protection and Crisis Management: project owner of this study

The CEA participates in the working group via its LITEN institute by bringing expertise in the electrochemical domain and in extreme battery testing. The CEA is also represented by the FLS (Local Security Force of Grenoble) which provides expertise through feedback from experience and risk management as firefighters for the CEA.

Alain Menir (Elektek), and Raymond Alazard contribute to standards expertise and electrical engineering.

Companies Accuwatt and SNAM participate in the working group by bringing their expertise, equipment and batteries needed for the tests.

The members of the working group:

David BRUN-BUISSON:
David BRUN-BUISSON is a materials engineer with a degree from the conservatoire National des Arts et Métiers, Paris. He has worked for the CEA for 15 years in research and development of batteries. His work has allowed him to develop expertise in batteries, more specifically Li-ion batteries, on work to understand the mechanisms of degradation by aging and in extreme conditions, by using post-mortem techniques and electrical / physico-chemical specifications. Today, he is in charge of the technical management of a CEA test platform for extreme Li-ion battery testing, from single cells to full packs. The goal of his work is to understand behaviour of Li-ion in extreme conditions, in order to develop workaround solutions to improve safety in Li-ion technology.

Expert Nicolas CHAINTREUIL:
Expert researcher-engineer on electrical safety issues of photovoltaic systems at the CEA. Nicolas is a voluntary firefighter and senior expert firefighter in charge of emerging risks resulting from new energy technologies in the Savoie Regional Fire and Emergency Department. With 15 years' experience in the domain of new energy sources, he has notably contributed to raising awareness among firefighters about these issues and is also a contributor to the French national guide for risks linked to photovoltaic systems as well as operational good practice guides with the DGSCGC. He has contributed to this document as Senior Firefighter Advisor.

Serge CORONNEL:
Serge was a Paris firefighter for 19 years, from 1983 to 2002. He directs firefighting operations, human rescue and technology-related accidents. In recent years, he has carried out prevention-prevision operations for the François Mitterand National Library of France as a détaché for the Culture Ministry. In 2002 Serge joined the CEA in Grenoble. His role is head of the fire department and safety engineer for the FLS (the company's operation safety department). Since 2017 he has been in charge of physical protection (safety/theft) on site. He is certified by the CNPP for fire risk (INSSI) and safety/theft (CERIC).

Julien DEVILLE:
Chemical engineer, specialised in environment and industrial risks, Julian has occupied several safety engineer roles over the past 14 years within the CEA. His varied experience has allowed him to gain a high level of experience in managing major risks in the lab for development and industrialisation. He is currently safety engineer at the National Institute for Solar Energy, notably in charge of managing risks in the Stationary Storage Laboratory for application in the domain of Renewable Energies.

Sébastien DUMENIL:

Holder of a diploma in chemistry from the Université de Mans, he joined RENO in 2003 analysing fertilisers. In 2004, he joined start-up APIBIO/Biomérieux to develop DNA chips. In 2005, he worked for Vernis Soudé creating new vehicles tints for PSA. Since 2006, he has been a research technician for CEA. Initially at INAC in fundamental research on biotechnologies and SPR (Surface Plasmon Resonance). Then in 2012 in the electrochemical storage lab based in INES on specifying lithium batteries and various extreme tests. He develops experiments looking at gas generation in lithium batteries and collaborates with industry partners such as Thalès, Airbus, Samsung, etc. He participates in several European projects such as STALLION or ESA (European Spacial Agency).

In 2021 he joined the laboratory for management and electrical network integration.

Lieutenant Colonel Christophe GAY:

Director of the group having led to the publication of this report.

Head of the technical resources department within the Savoie regional fire and emergency service after spending 10 years as head of the operations department in charge of operational good practices. It was as part of this role that he managed the working group that led to the publication of this report.

Regional technical advisor for chemical risks at the Interministerial Department in the Southeast defence zone.

Advisor for ENSOSP in the domain of Chemical Risks.

Dr. Nicolas GUILLET:

Dr. Nicolat Guillet is a specialist in materials and design of electrochemical systems. Following a doctorate and the Ecole des Mines in St Etienne, and two years' post-doctorate specialisation at the INRS Energy and Materials in Varennes (Qc, Canada), he joined the hydrogen and fuel cell team at CEA Liten in 2005. Based on the INES Bourget du Lac campus since 2013, he takes advantage of his knowledge and expertise on the study and design of electrochemical storage systems (batteries, fuel cells, electrolysis systems, etc.) for electrical energy storage in stationary applications.

Loïc LONARDONI:

Researcher-engineer at the CEA, Loïc has worked for over ten years on the topic of design and safety of systems incorporating Li-ion batteries. He started his career as an engineer in the domain of aerospace on satellite power distribution (solar panels and batteries to various communication equipment). Then he worked on the design of battery packs in the transport domain (functional validation of BMS and overall system). Finally, he moved towards the domain of safety in Li-ion cells by joining the extreme test platform of the CEA.

Captain Christophe MARRA:

Head of the industrial and technological risks office of the provision department of the SDIS in Isère, he is the representative for operators and services of the state for subjects relating to industrial prevention and emerging risks.

He participates in emergency operations and feedback as the brigade leader and technical advisor for chemical risks.

Alain MENIER:
Director of ELEKTEK C&L and director of the global ELEKTEK department (86 domains and offers, 300 people), A. Menier has previously been Technical and Marketing Director for various groups and leading industrial MSBs in the electrical and energy sector and is still a standards creator at AFNOR in various commissions. He has also been involved in PV standards and firefighting issues for operations on PV sites. He currently works on structuring the RE industry abroad commissioned by the CE and DUE (Diplomatic Missions of the European Union).

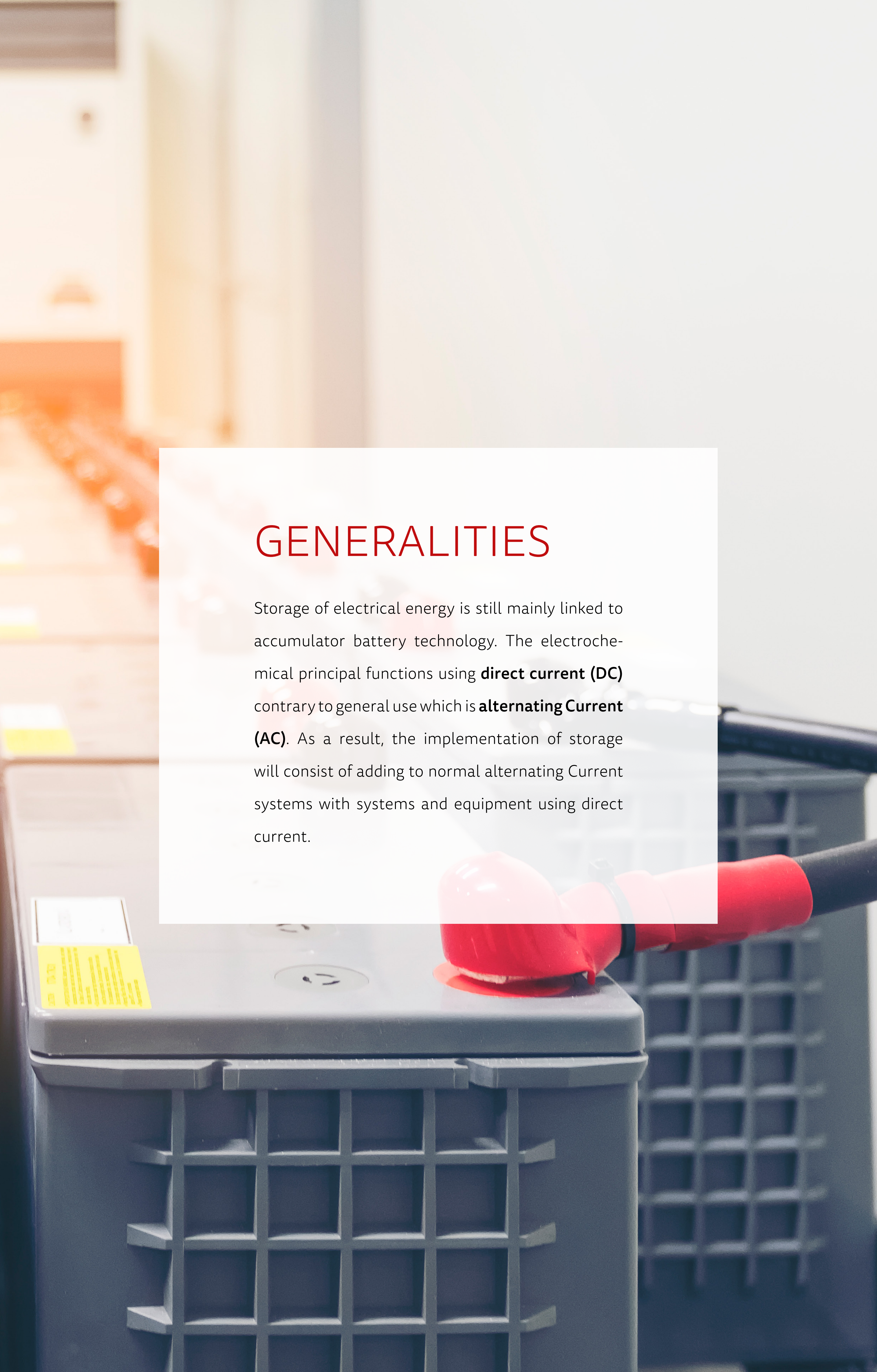
Captain Cédric PASQUIER:
Firefighting captain and formation chemistry engineer, Cédric works in the major crisis response department and for the Rhone Regional Fire and Emergency Service. He is also a regional technical advisor for chemical risks and in charge of implementation the VDIP in the southeast zone. In this role, he has participated in several projects testing the toxicity of fire fumes, on balancing national NRBC capacity, and improving soil biological responses.

Commander Mathieu RIEDINGER:
Holder of an advanced engineers degree in industrial risk management, Mathieu is a professional firefighter commander within the Savoie Regional Fire and Emergency Service. There he has the role of deputy director of the department for operations, strategy and operational good practices and more specifically he is in charge of analysis and conception of operational response. He is also regional technical advisor for chemical risks and is in charge of the specialised team that numbers 150 firefighters. Mathieu also regularly contributes to writing the operational good practices for Savoie firefighters, and is involved in several projects in the NRBC domains.

Eric ZIMMERMANN:
Holder of a DESS higher degree in radioprotection, Eric has worked for 10 years in various roles in the radioprotection domain within the CEA. In 2009, he converted over to nanoparticle risk prevention, notably carrying out numerous analyses on all types of work stations in France and abroad. He also participated in writing the methodological guide published jointly by the CEA, INERIS and INRS which sets out recommendations regarding specifications of potential emissions and exposure to aerosols during operations by implementing nanomaterials. Since 2017, Eric has been in charge of training and feedback within the FLS at CEA Grenoble.

1

ELECTROCHEMICAL STORAGE SYSTEMS: STATE OF THE KNOWLEDGE AND TECHNOLOGY



GENERALITIES

Storage of electrical energy is still mainly linked to accumulator battery technology. The electrochemical principal functions using **direct current (DC)** contrary to general use which is **alternating Current (AC)**. As a result, the implementation of storage will consist of adding to normal alternating Current systems with systems and equipment using direct current.

APPLICATION

The joint development of RE technologies such as solar, storage such as Lithium and digital information has meant that centralised production of energy from fossil fuels will be able to partially substituted by energy that is more based on decentralised sources and storage elements.

This decentralisation approach, aside from the considerable reduction in online losses due to energy transportation, will enable energy to be stored in case of overproduction, in order to use it in peak consumption times.

The removal of peaks will enable great optimisation of centralised sources and the distribution network.

The international installation standard IEC 60 364-8-2 is implemented on this subject; its goal is to define the general principles of decentralisation of production and the measures to put in place in order to ensure safety of people, pets and properties that are faced with it.

Electrochemical storage can be found in various contexts and applications:

- UPS - Parked car
- Solar storage (SSol) - Storage connected to Power Utility network (SCPU) - Storage connected to residential network (SCRR)
- Cos phi correction - Super capacity (Nice airport bus)

ELECTRICAL DIAGRAMS

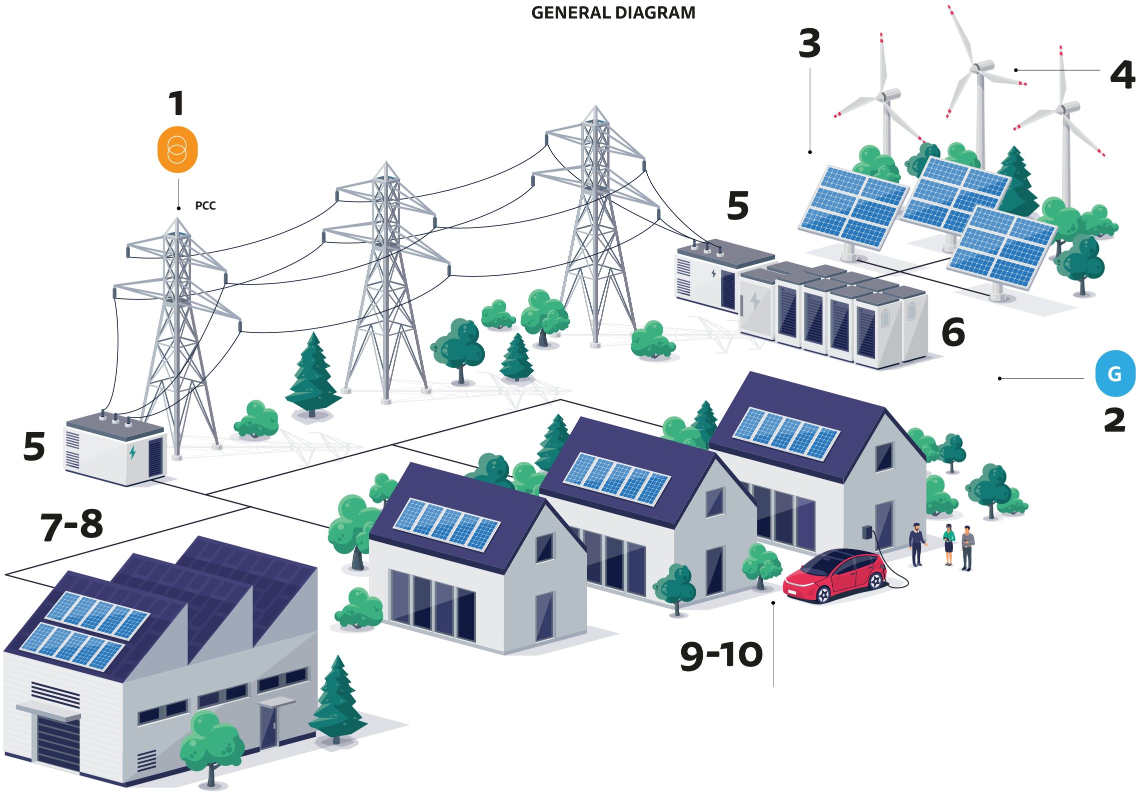
CHAPTER GOALS

This chapter describes the location possibilities for storage with the secondary goal of better anticipating electrical risks. Similar to the PV problem, which, for firefighters, created a major risk related to the fact that at one point of the electrical installation the dangerous sources could supply said point by two places (DC PV field, AC distribution network), adding storage means that now the danger at one point could be linked to the arrival of electrical danger at three sources, which would preferably be localised and separated.

This chapter is to understand the diversity of diagrams and therefore the impossible task of an exhaustive analysis.

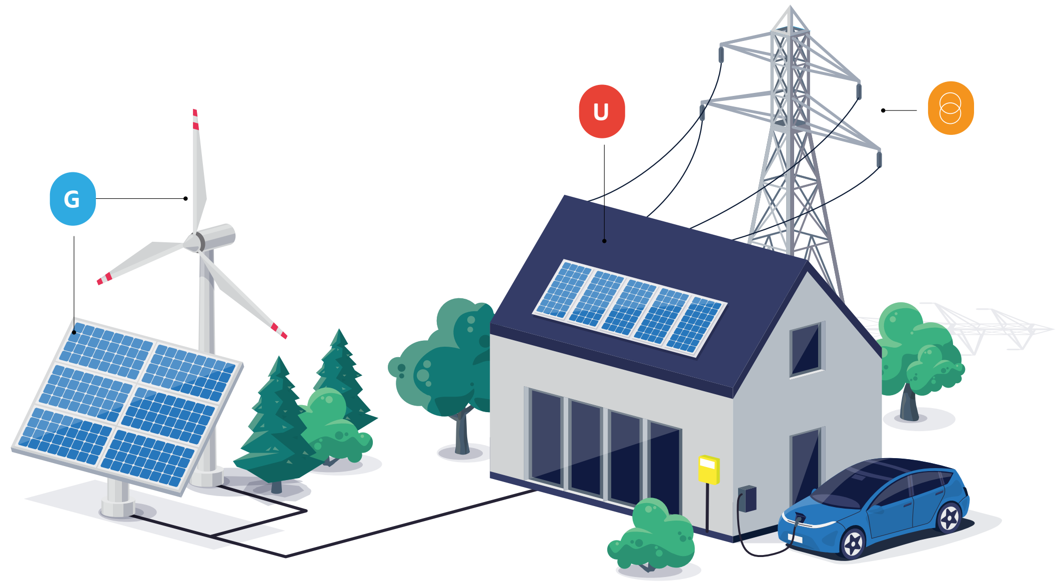
Regarding dangerous voltages (risk of electrocution), notably the idea of direct contact (>60Vdc) and indirect contact, the problem of storage adds no other technical complexity to that of PV.

General diagram



__1 -__ Distribution network transformers __2 -__ Generator units __3 -__ PV generator __4 -__ Turbines __5 -__ Transformers
__6 -__ Electrochemical storage __7 -__ Converters __8 -__ Motors __9 -__ Distribution panels __10__ - Domestic equipment

Diagram of an individual self-supplying system (no storage)



G **Independent generator (PV, generator unit, turbine, etc.)**
U **Usage**
kwh **Counter**

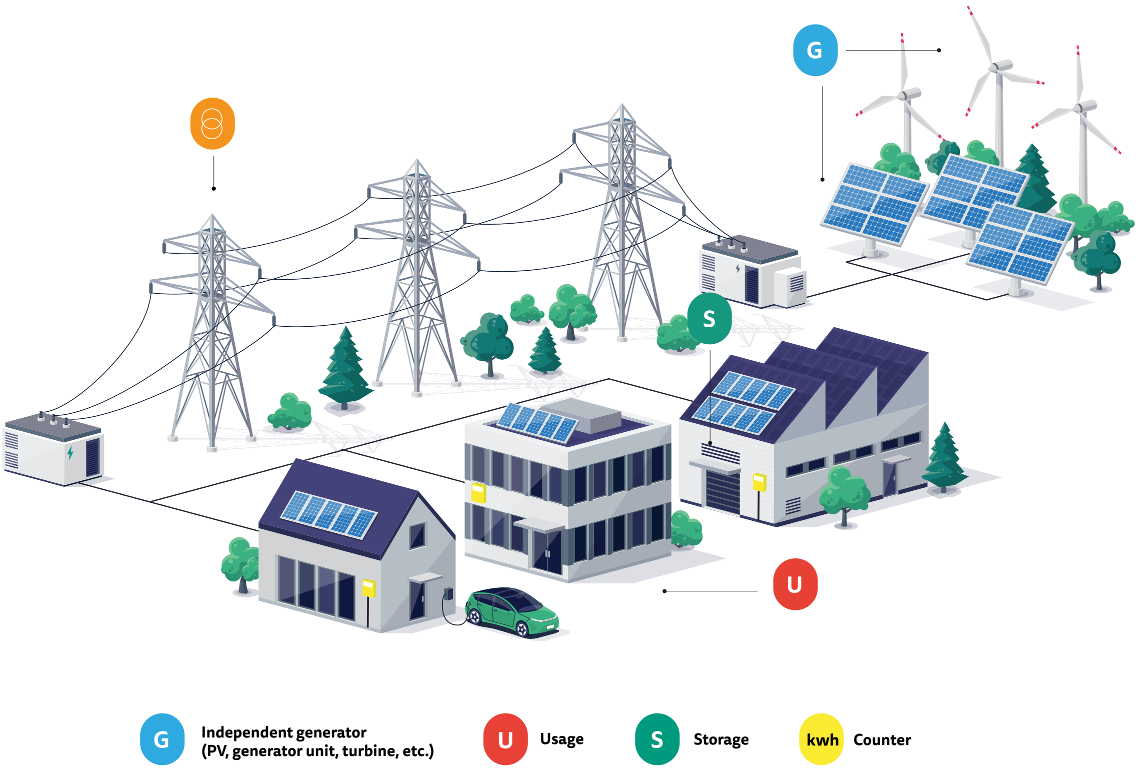
In this system, connected to a distribution network, at the connection point, the energy can be counted as well when it leaves the distribution network as when it is inserted into the network in case of overproduction compared to local consumption.

Diagram of an individual self-supplying system (with storage)

G **Independent generator (PV, generator unit, turbine, etc.)**
U **Usage**
S **Storage**
kwh **Counter**

In this system, connected to the distribution network, as above, a storage unit allows you to improve the independence of the customer. This independence allows energy needs to be responded to better either during spikes in consumption when the independent source, often intermittent, in insufficient, or in case the distribution network fails.

Diagram of a collective self-supplying system with shared production and individual production



In the self-supply diagrams (or decentralised production), the storage units are represented after the respective counters of each "party". These storage units can then be found either in the shared spaces or in each apartment/lot of each co-owner.

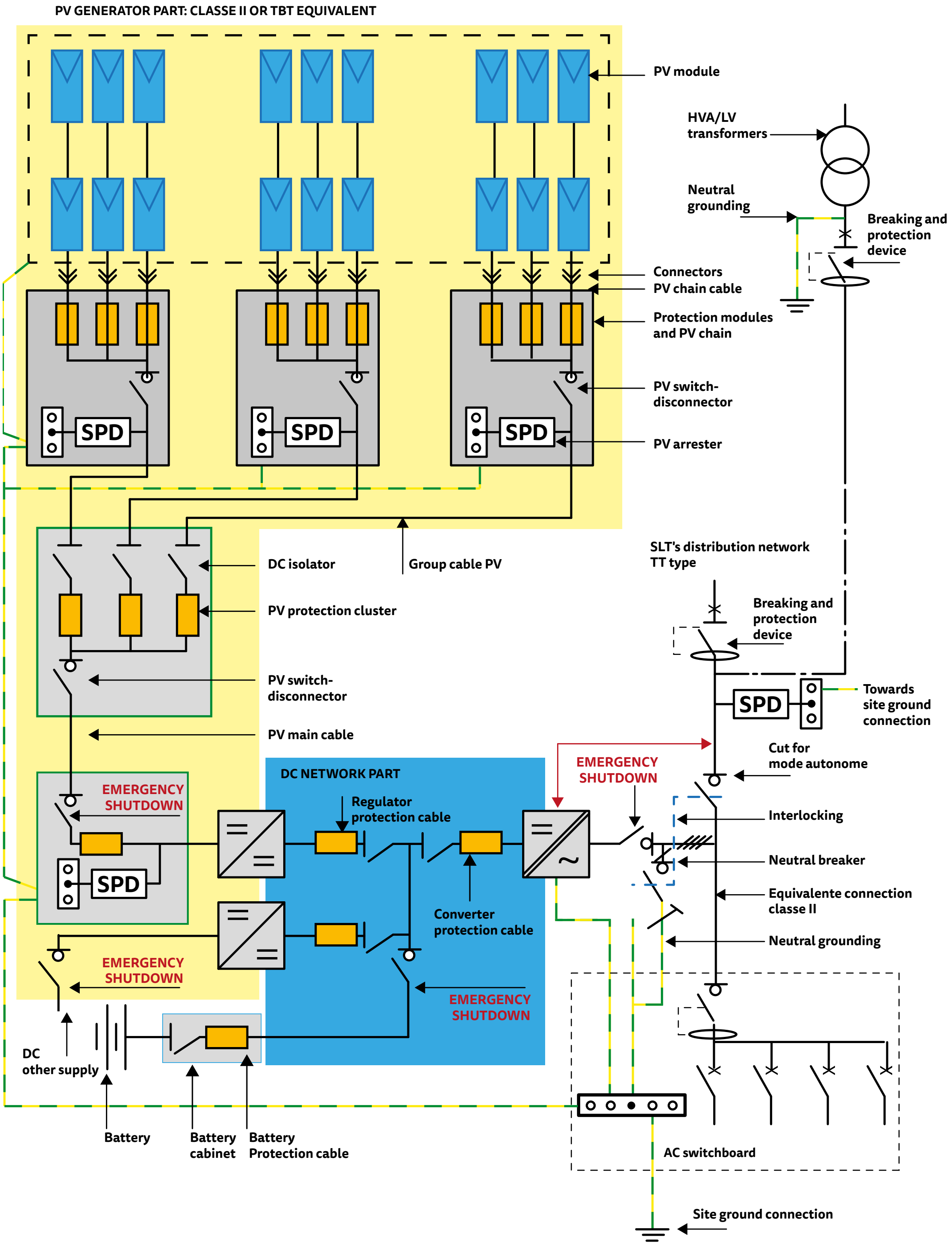
Each party/user (U) can also be supplied through:

- Either the collective production/storage system
- Or the collective production/storage system and its own production/storage system
- Or just its own production/storage system

PV system with storage

Aside from the international standards from the IEC 60 364 series, the installation standards in France (NF C 15 100 and UTE C 15 712) set out more specifically the electrical distribution principles where storage units are taken into account.

This example diagram below, from the standard XP C 15 712-3, sets out the mandatory cut-off system to isolate the battery from the rest of the system. It must be noted that this represents only a guideline for PV solutions + storage being implemented. Certain solutions will be characterised by integrated systems where the storage will be incorporated with converters in a unique housing.

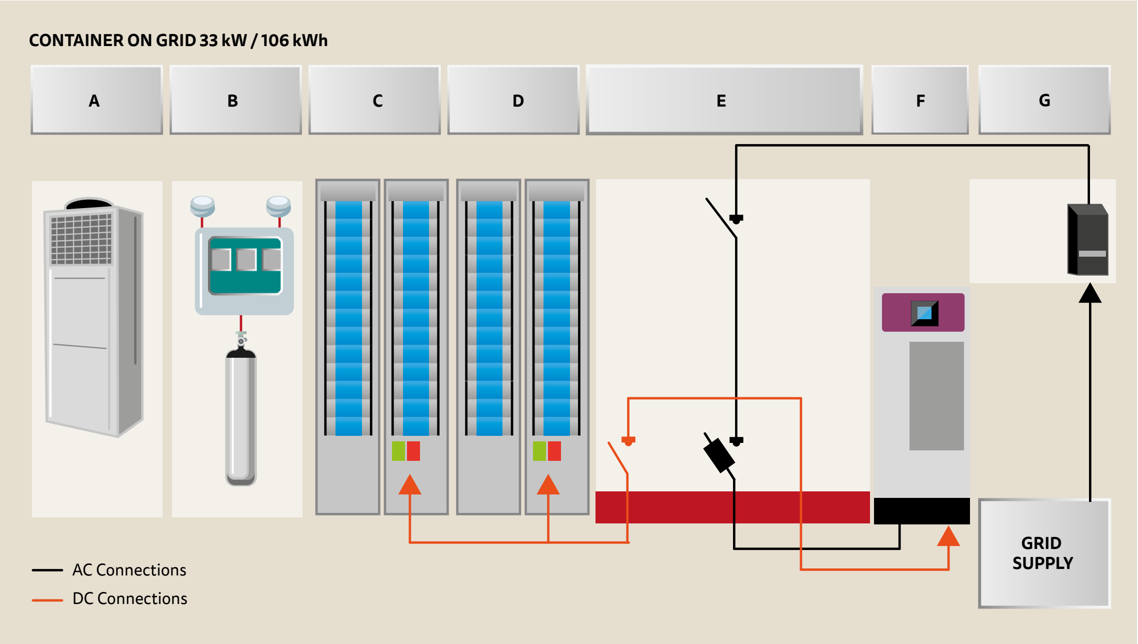


Independent industrialised storage installation

Certain other installations will be reduced to a battery directly supplying the network with alternating current through an AC/DC converter without integrating the PV part. This type of installation has the goal of bringing "system services" to the network controller (ENEDIS), which means helping management of the network, maintaining frequencies and voltages through balancing production and consumption.

In the example below of a 33kWh industrialising independent storage module, the batteries constitute a large part of the assembly and are attached to the module conversion and control systems.

Aside from enclosure in a metal container type cell, the assembly is often further secured by an automatic fire safety system using inert gas.



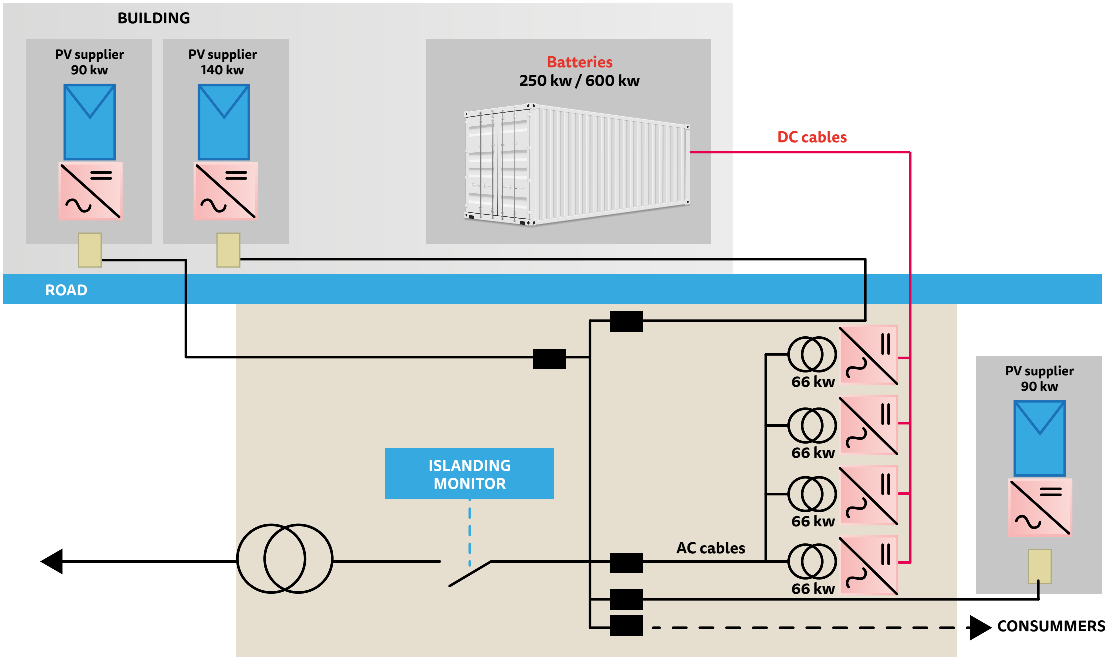
Source : Raymond Alazard

A - *Air conditioning system* **B -** *Fire protection* **C / D -** *Storage modules* **E -** *Electrical control and protection cabinet* **F -** *PCS^2 Sunsys UPS* **G -** *Main circuit breaker*

Storage installation integrated into the distribution network

In the example below, the storage will be connected via UPS directly at the distribution network Low Voltage panel. In this case, the size of the battery units necessitate delocalised implementation and the battery container must be located on the other side of the public highway.

In this installation, the energy also comes from generators located ahead of the transformation unit; it must also be noted that in case the network fails, a unit may be controlled remotely, and the installation of the local network can be operated on.



Source : Raymond Alazard

CONCLUSION

In conclusion, storage systems can be found on site in any location on properties that are domestic (garage, cupboard, cellar, etc.), industrial (battery rooms, maintenance rooms, decentralised or on-site electrical cabinets, etc.), or infrastructure-based (specialised buildings, external shelters, transformer/distribution units, etc.).

An emergency cut-off to electrically separate the storage unit and the electrical system is normally installed and easily accessible.

It must be noted that this cut-off does not exclude the fact that the battery and electrical conduit between the battery and the cut-off will continue to have current flowing through them that could be dangerous while battery units are not switched off (voluntarily or by destruction).

In case of intervention for an accident where storage units are implemented, the electrical risks for operators are of two types: risk of electric shock and burn risk, which could occur during an electrical arc fault with flying incandescent materials or even explosion.

STANDARDISATION

CHAPTER OBJECTIVES

One of the goals of this chapter is to answer the following question: when current standards are followed, do they increase safety for firefighters, and if so, how and to what extent.

Standards in the electrical world

Geographical range of a standard:

- Worldwide level by zone of influence: CEI, UL (USA, ...), JIS (Japan), ISO etc. (E.g.: Installation standard IEC 60 364
- European EN level but in association with the CEI and controlled by CENELEC
- National level (Example: France, managed by AFNOR, after including links with Cenelec and CEI commissions, meaning that if these standards can be more complete than the EN or CEI standards, they cannot contradict CEI 60364. Example NFC C15100)

Level of integration that the imply:

We can, for example, group them from the highest level of integration to the lowest:

- Installation standards (example: NF C 15100 or IEC 60 364)
- Equipment standards (example: CEI 61439)
- Product standards (example: CEI 60947)

The cross-discipline standards enable these to cover more general points, such as:

- The environment (Temperature, Humidity, Salt Spray, Impact, Vibration, etc.)
- Fire- Explosion (Atex)
- Isolation coordination, physiological effects of current,
- Etc.

Applications that they cover, for example

- Buildings and infrastructure.
- Transport (rail - road - sea, etc.)
- Others (PC, electronic cigarettes)
- Etc.

As such it is possible to position a standard at the crossroads of all these segments:

- The site will be in France (NFC coherent with EN and CEI
- It will be in Equipment and Product installation
- It will in Building

The electrical standards to take into consideration are therefore **NF C 15100** and **UTE C15712-2 and -3** and secondarily CEI 61 439 for assemblies and CEI 60 947 for products.

An important point to take into account and as a result of normal electrical standards is that concerning normal usage conditions and special usage conditions. As we will see later on, thermal reactions of Li-ion technology are one of the critical points.

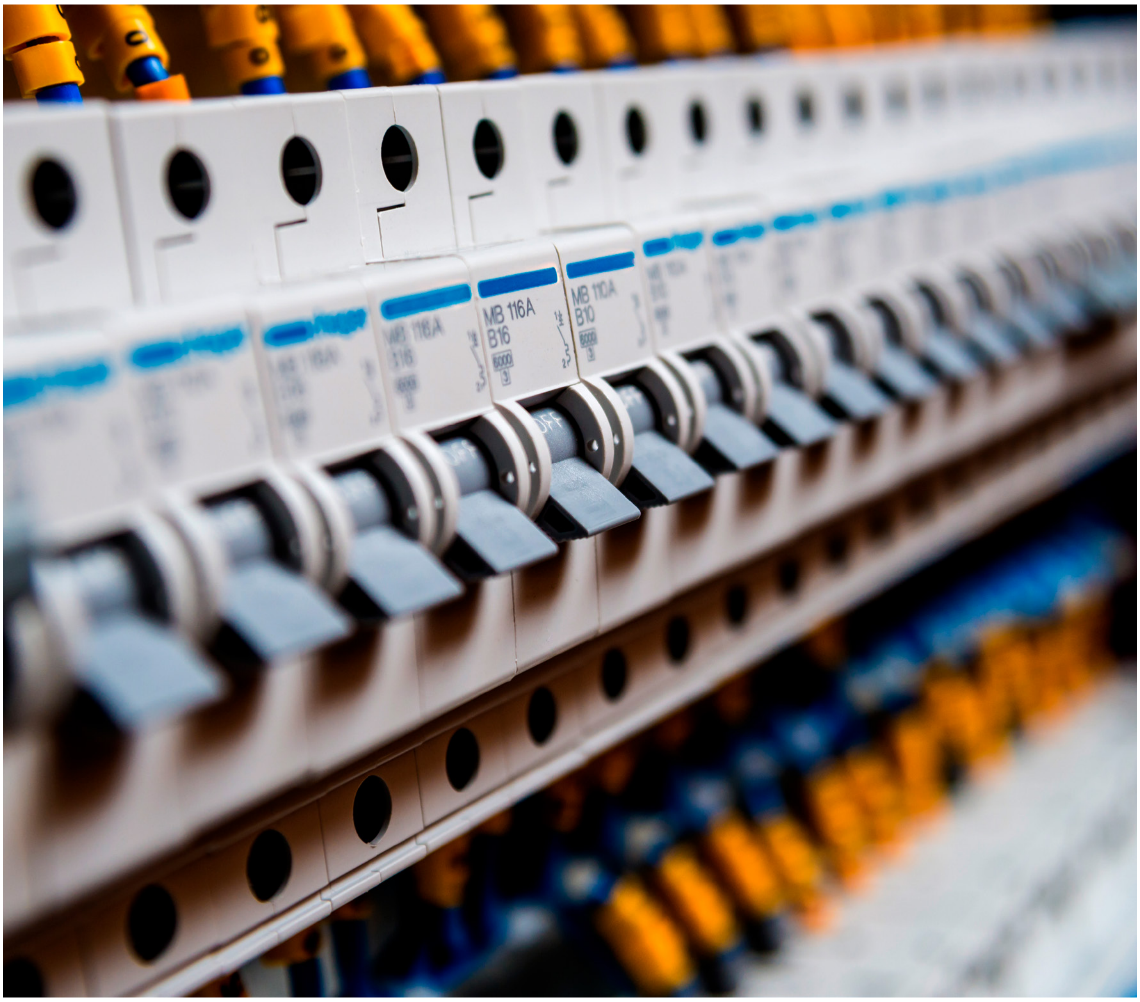
In classic, installation, equipment and product electro-technical standards, "normal usage" conditions are considered as 35°C averaged over 24 hours and a peak of 40°C ambient in, for example, the maintenance room. Suppliers are not required to guarantee these normal conditions by default. For conditions that exceed this, we moved to special operating conditions and the final customer, or their representative (engineers, EPC, contractor) must inform the supplier chain who must then perform and eventual supplementary testing.

Two major problems present themselves:

❶ These concepts are often not known to the final customer and their representatives who don't in the end inform the suppliers.

❷ Overcompensation in capacity and size of leading brands' products allows for a variable safety coefficient and unofficially provides a margin for error that leads to the market being ignorant of the risk.

Alas for Li-ion technology this safety buffer does not exist. This point is therefore essential. Installation of storage systems in air conditioned or at least well-ventilated spaces is preferable in all circumstances but can be countered by implementing fire protection systems using inert gases.



Specific standardisation of electrochemical storage products

Concerning standardisation of electrochemical storage, there is quite an important difference between embedded systems and "building" systems covered by this site.
In the non-embedded world (building, portable or mobile equipment), we can identify 3 standards typologies:

❶ Standards enabling all manufacturers to define their products in the same way so the customer can compare and make use of the datasheets. These are generally representative of the technologies. ***On this site, the most important standard regarding the technological focus created would be IEC 61960 (*) but it provides nothing in terms of the problem of risk for fire-fighters***

❷ The standards covering extreme testing for a given technology, ***as regards technological focus, would be for example CEI 62133 (*) or CEI 62619 (*) alongside the technology covered by CEI 61960.***
These standards covering extreme tests could be attractive. They deserve some consideration. The concept of these standards is to verify that an element of electrochemical energy accumulation subject to stress considered as abnormal yet still within the realm of normal usage in the overall system would not lead to risks such as:

- explosion
- ignition of a flame
- electrolyte loss

As far as the problem of the accident goes, certification of such a standard at best does not reduce the risk that the accumulator would be the source of the accident. The conditions regarding temperature, crushes etc. are so low in value that they have no interest in a situation where a storage system accident occurs brought about by another cause.

❸ Transport-based standards such as UN38.3 and UN38.3, rev5
Recommendations relative to the Transport of dangerous goods - Section 38 (Lithium metal batteries and lithium-ion batteries).
Good summary of relevant extreme tests; these are based on CEI61960, CEI62133 et CEI62660.
The standardisation philosophy for vehicles is quite different. Being out of the scope of the project, this approach will not be developed in detail. An accumulator must enable electric or hybrid vehicles braking and drive functions. Each cycle and tests propose are in direct association with the vehicle's operating phase or even in extreme or accident-related situations (e.g.: Immersion under water).

(*)
CEI61960: *Alkaline accumulators and other non-acid electrolyte accumulators - "Lithium accumulator batteries and components for portable applications"*
CEI62133: *Alkaline accumulators and other non-acid electrolyte accumulators "Safety requirements for portable weather-proof accumulators, and for batteries"*
CEI62619: *Alkaline accumulators and other non-acid electrolyte – "Safety requirements for lithium accumulators for us in industrial applications"*

Here are a few important standards summarised in the following tables:

VEHICLE	12 405-1	12 405-1	6469-1
Electric hybrid HEV	Yes	No	Yes
Battery-powered (BEV)	No	Yes	Yes
With fuel cell (FCV)	Yes	No	Yes

The standards 12405-1 and 12405-2 have a relatively similar structure. For the identical chapters, only the values change. They were recently grouped together in the standard 12405-4 which at the same time added updates do not present in the two previous standards.
These 3 standards are complemented also by standards 19453-1 1, 3 and 4 2009.

TABLEAU 12 - ACCUMULATORS

TYPE OF STANDARD CEI	TYPE	ELECTROLYTE	VOLTAGE MAXIMUM CHARGE (by element) V	NOMINAL VOLTAGE[1] (for evaluation of the surface temperature) V	OPEN CIRCUIT PEAK VOLTAGE (for calculalation of spark risk) V
IEC 60896-11 IEC 60254 IEC 60095-1 IEC 60896-21 IEC 60952 IEC 61427 IEC 61056	Stationary lead batteries (immersed) Lead traction accumlator batteries Lead starter accumulator batteries Lead stationary batterues (sealed with valves) Aviation batteries Accumulators for solar systems Lead acid accumulator batteries for general usage	Sulphuric acid (SG 1,25 à 1,32)	Up to 2,7	2,2	2,67[b] 2,35[c]
Type K IEC 61951-1 IEC 60623 IEC 60622	Nickel-cadmium[2]	Potassium hydroxide (SG 1,3)	1,6	1,2	1,55
[a]	Nickel-iron	Potassium hydroxide (SG 1,3)	1,6	1,3	1,6
IEC 61960	Lithium	Sel organique non aqueux	Up to 4,2	3,8	4,2
IEC 61951-2	Nickel - Metal hydrides[2]	Potassium hydroxide	1,5	1,2	1,6

[a] Can be used only if there is a CEI standard relating to the elements.

[b] Wet element - element that contains a liquid electrolyte that can be replaced.

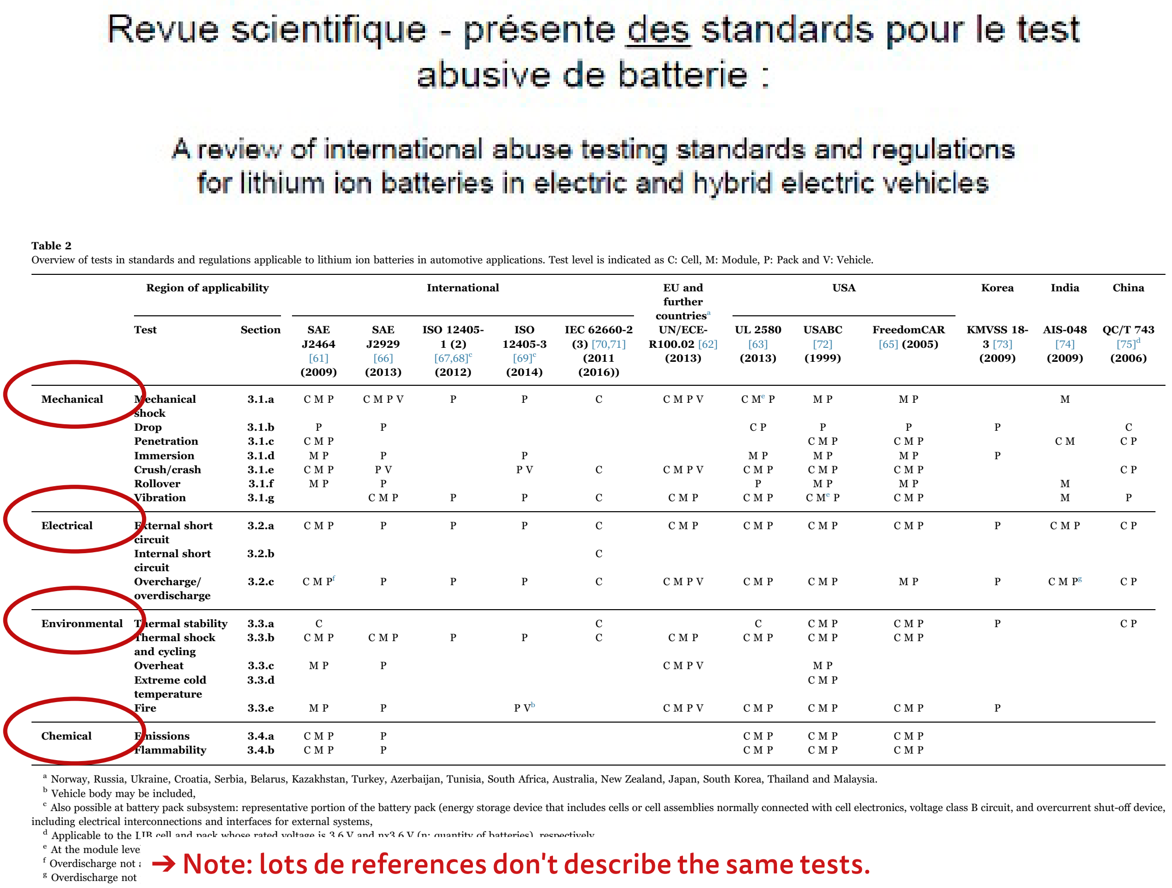
[c] Dry element - elements that has a stationary electrolyte.

[1] The voltage figure in uses an appropriate factor. The temperature increase tests are carried out for this voltage.

[2] The chemical industry uses a constant charge current technique.

Extras

To dig deeper into the subject of extreme tests, you can look at the following sources:
Review of international abuse testing.... "
http://dx.doi.org/10.1016/j.rser.2017.05.195



Revue scientifique - présente des standards pour le test abusive de batterie :

A review of international abuse testing standards and regulations for lithium ion batteries in electric and hybrid electric vehicles

Table 2
Overview of tests in standards and regulations applicable to lithium ion batteries in automotive applications. Test level is indicated as C: Cell, M: Module, P: Pack and V: Vehicle.

	Region of applicability		International					EU and further countries[a]	USA			Korea	India	China
	Test	**Section**	**SAE J2464 [61] (2009)**	**SAE J2929 [66] (2013)**	**ISO 12405-1 (2) [67,68][c] (2012)**	**ISO 12405-3 [69][c] (2014)**	**IEC 62660-2 (3) [70,71] (2011 (2016))**	**UN/ECE-R100.02 [62] (2013)**	**UL 2580 [63] (2013)**	**USABC [72] (1999)**	**FreedomCAR [65] (2005)**	**KMVSS 18-3 [73] (2009)**	**AIS-048 [74] (2009)**	**QC/T 743 [75][d] (2006)**
Mechanical	**Mechanical shock**	**3.1.a**	C M P	C M P V	P	P	C	C M P V	C M[e] P	M P	M P		M	
	Drop	**3.1.b**	P	P					C P	P	P	P		C
	Penetration	**3.1.c**	C M P							C M P	C M P		C M	C P
	Immersion	**3.1.d**	M P	P		P			M P	M P	M P	P		
	Crush/crash	**3.1.e**	C M P	P V		P V	C	C M P V	C M P	C M P	C M P			C P
	Rollover	**3.1.f**	M P	P					P	M P	M P		M	
	Vibration	**3.1.g**		C M P	P	P	C	C M P	C M P	C M[e] P	C M P		M	P
Electrical	**External short circuit**	**3.2.a**	C M P	P	P	P	C	C M P	C M P	C M P	C M P	P	C M P	C P
	Internal short circuit	**3.2.b**					C							
	Overcharge/ overdischarge	**3.2.c**	C M P[f]	P	P	P	C	C M P V	C M P	C M P	M P	P	C M P[g]	C P
Environmental	**Thermal stability**	**3.3.a**	C				C		C	C M P	C M P	P		C P
	Thermal shock and cycling	**3.3.b**	C M P	C M P	P	P	C	C M P	C M P	C M P	C M P			
	Overheat	**3.3.c**	M P	P				C M P V		M P				
	Extreme cold temperature	**3.3.d**								C M P				
	Fire	**3.3.e**	M P	P		P V[b]		C M P V	C M P	C M P	C M P	P		
Chemical	**Emissions**	**3.4.a**	C M P	P					C M P	C M P	C M P			
	Flammability	**3.4.b**	C M P	P					C M P	C M P	C M P			

[a] Norway, Russia, Ukraine, Croatia, Serbia, Belarus, Kazakhstan, Turkey, Azerbaijan, Tunisia, South Africa, Australia, New Zealand, Japan, South Korea, Thailand and Malaysia.
[b] Vehicle body may be included,
[c] Also possible at battery pack subsystem: representative portion of the battery pack (energy storage device that includes cells or cell assemblies normally connected with cell electronics, voltage class B circuit, and overcurrent shut-off device, including electrical interconnections and interfaces for external systems,
[d] Applicable to the LIB cell and pack whose rated voltage is 3.6 V and nx3.6 V (n: quantity of batteries), respectively
[e] At the module leve
[f] Overdischarge not
[g] Overdischarge not

➔ Note: lots de references don't describe the same tests.

A "clause by clause" comparison made on standards CEI62133 and CEI61960 UN38.3 reveals that these standards are not very coherent in their structures.

CONCLUSION

The standards section does not provide much useful information to manage a fire-fighter operation in the event of an accident except for measuring the difference between normal operating conditions of storage systems, or those even considered extreme, and the real conditions of an accident or the hours and days that follow.

It has been noted that battery standards are less mature than electrical standards concerning coherence and structure. We are far from a harmonisation of summaries.
This shows the recent nature of these technologies, being much less mature than classical electro-technical product standards.

THE VARIOUS BATTERY TECHNOLOGIES

CHAPTER OBJECTIVES

The goal of this chapter is to describe the different electrochemical storage technologies that are likely to be encountered in buildings. The term **"battery"** covers a very large number of electrical storage systems under chemical form (electrochemical storage). We distinguish two main families: rechargeable and non-rechargeable storage systems. The non-rechargeable will not be studies in this document due to their small size and low capacity per system.

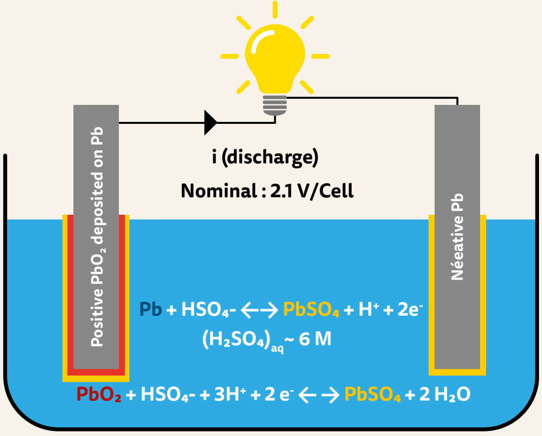
Aqueous electrolyte batteries

Batteries that use aqueous electrolytes have more advantages than disadvantages. Among the advantages are its very high electrolyte ionic conductivity (concentrated solutions of sulfuric or potassium acid: 5-6mol/L), availability and reduced cost, as well as its overload capacity. So, in the case of an overload, the electrolyte solvent (H_2O) is decomposed into hydrogen (H_2) at the negative electrodes and into oxygen (O_2) at the positive electrodes. The presence of a simple recombination element (foam filled with platinum catalyst for example) enables the H_2O to be reformed from these two gases. If the accumulators are sealed, there is as such no theoretical electrolyte loss and the system is not, or at least hardly, affected by overloads. This is how a vehicle starter battery can be kept charged permanently, supplied by the vehicle alternator without any risk. Also, a number of cells can be easily placed in series without any particular risk of overloading these cells.

The disadvantages are essentially linked to the electrochemical stability range of water. Above the potential difference of 1.23V, water H_2O is no longer thermodynamically stable and can be decomposed into hydrogen (H_2) at the negative electrodes and into oxygen (O_2). It is therefore not theoretically possible to create an accumulator with an aqueous electrolyte for which the voltage exceeds 1.23V. Nevertheless, the nature of the electrolyte materials used enables us to slightly exceed these limits. As such, with lead, which is a very bad catalyst for water decomposition, the decomposition reactions are extremely slow, and it is possible to reach a potential difference of 2.1V between the electrodes without the water decomposing. In practice, this limitation of maximum cell voltage limits the storage density to a few tens of Wh/kg.

Pb-acide batteries

- Lead metal electrodes
- Highly concentrated sulfuric acid electrolyte
- Voltage: Typically, 12V (6-cell)
- Lifespan: 5 to 7 years
- Energy density 25 - 50 Wh/kg



Positive: $PbO_2 + HSO_4- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Negative: $Pb + HSO_4- \rightarrow PbSO_4 + H^+ + 2e^-$

$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

Where can you find them?

Emergency power systems (industry)

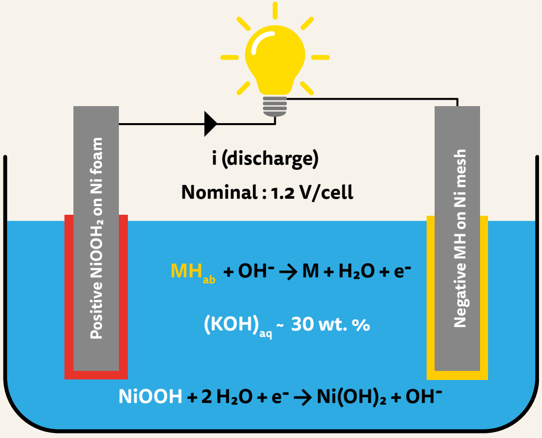
Self-supply / linked with PV

***All** vehicles (even electric ones!)*

Figure 1: lead-acid batteries. Working diagrams and examples of usage (excluding vehicle starter batteries).

Nickel batteries

- Nickel positive electrode/negative metal
- Highly concentrated basic electrode (KOH)
- Voltage: 1,2 V / cell
- Lifespan: 5 to 7 years
- Energy density 50 - 80 Wh/kg



Positive: $NiOOH + 2\,H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Negative: $MH_{ab} + OH^- \rightarrow M + H_2O + e^-$

$NiOOH + MH_{ab} \rightarrow Ni(OH)_2 + M$ (KOH) ~ 6 M

(M = AB5-type, $LaNi_5$ or AB2)

Where can you find them?

Hybrid cars (Prius, Yaris)

Aviation (onboard network)
Rail (tram, train, 110V power)
Electric vehicles (older models)

Figure 2: nickel batteries. Operating diagrams and examples of usage.

Organic electrolyte batteries

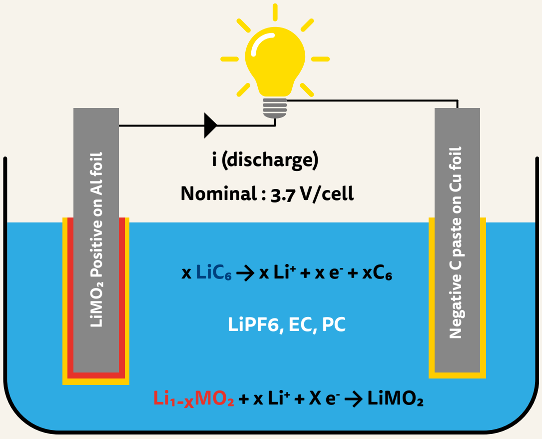
To increase the density of energy stored (Wh/kg), lighter materials are needed and/or an increase in maximum cell voltage. Water's stability range being the main limitation for max cell voltage, it is possible to replace water with an organic solvent which has a higher electrochemical stability range.

As such, in Li-ion batteries and in lithium technology, the liquid electrolyte solvent is no longer water but a mixture of organic composites. In the case of Li-ion technology, these are mainly carbonates (ethylene carbonate - EC, propylene carbonate - PC, dimethyl carbonate - DMC, etc.) which have a high enough stability range to reach cell voltages up to 4.2V (more than 3 times higher than for Ni-MH batteries). The energy density is therefore much higher (Three times more than for Ni-MH batteries).

The main disadvantage is that the organic electrolyte solvents decompose if they leave the stability range. Li-ion battery cells cannot withstand overload because, contrary to aqueous batteries, the decomposition products from the solvents cannot be easily recombined as you can with water. The gases produced will therefore accumulate in the cell, the cell will swell up and performance will decrease until the safety vent opens, or the cell is destroyed.

Li-ion batteries

- ECarbon negative electrode/metal oxide positive electrode
- Organic electrolyte (carbonates)
- Voltage: 3,6 to 4,2 V per cell
- Lifespan: 2 to 10 years
- Energy density 150 - 270 Wh/kg



Positive: $Li_{1-x}MO_2 + x\ Li+ + x\ e^- \rightarrow LiMO_2$

Negative: $x\ LiC_6 \rightarrow x\ Li^+ + x\ e^- + x\ C_6$

$Li_{1-x}MO_2 + x\ LiC_6 \rightarrow LiMO_2 + x\ C_6$

Where can you find them?

Telephone (3,8 V, 10 Wh)

Electric bike (36 V, 250 Wh)

Electric car (400 V, 41 kWh)

Storage container (640-1100 V, 6 MWh in 40" container)

Figure 3: Li-ion batteries. Operating diagrams and examples of usage.

Solid electrolyte batteries

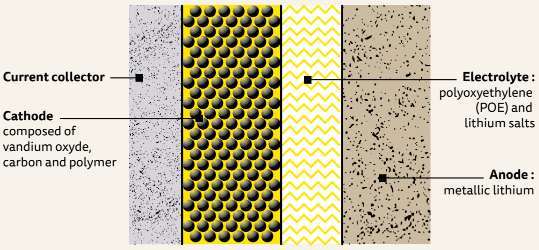
Apart from liquid electrolytes with aqueous and organic bases, there are also batteries with solid electrolytes.

Several solid electrolyte battery technologies exist. The disadvantage of solid electrolytes is their low ionic conductivity. To obtain a sufficient ionic conductivity, it is necessary to operate at a high temperature (ionic conductivity increase with temperature) and to reduce the thickness of the solid electrolyte that separates the two electrodes.

In practice, Na-S and Zebra (Na-NiCl$_2$) type batteries that have ceramic based solid electrolyte that conduct sodium ions operate at between 200 and 350°C. Batteries with polymer electrolytes that conduct lithium ions such as the ones developed by Blue Solutions (LMP Lithium Metal-Polymer) can operate correctly above 70°C. A technical description of the battery is presented below.

What is it?

- Lithium metal negative electrode
- Solid electrolyte (polymer)
- Voltage: 3.4 V typically
- Operating temperate: 60-80°C
- Energy density 100 Wh/kg



Where can you find them?

AutoLib' cars in Paris, BlueLy in Lyon, etc.

E-méhari by Citroën

Bluebus, Grenoble, Tours, etc.

Figure 4: LMP batteries (Lithium Metal Polymer) with solid polymer electrolyte developed by Blue Solutions.

FOCUS ON LITHIUM-ION BATTERIES

CHAPTER OBJECTIVES

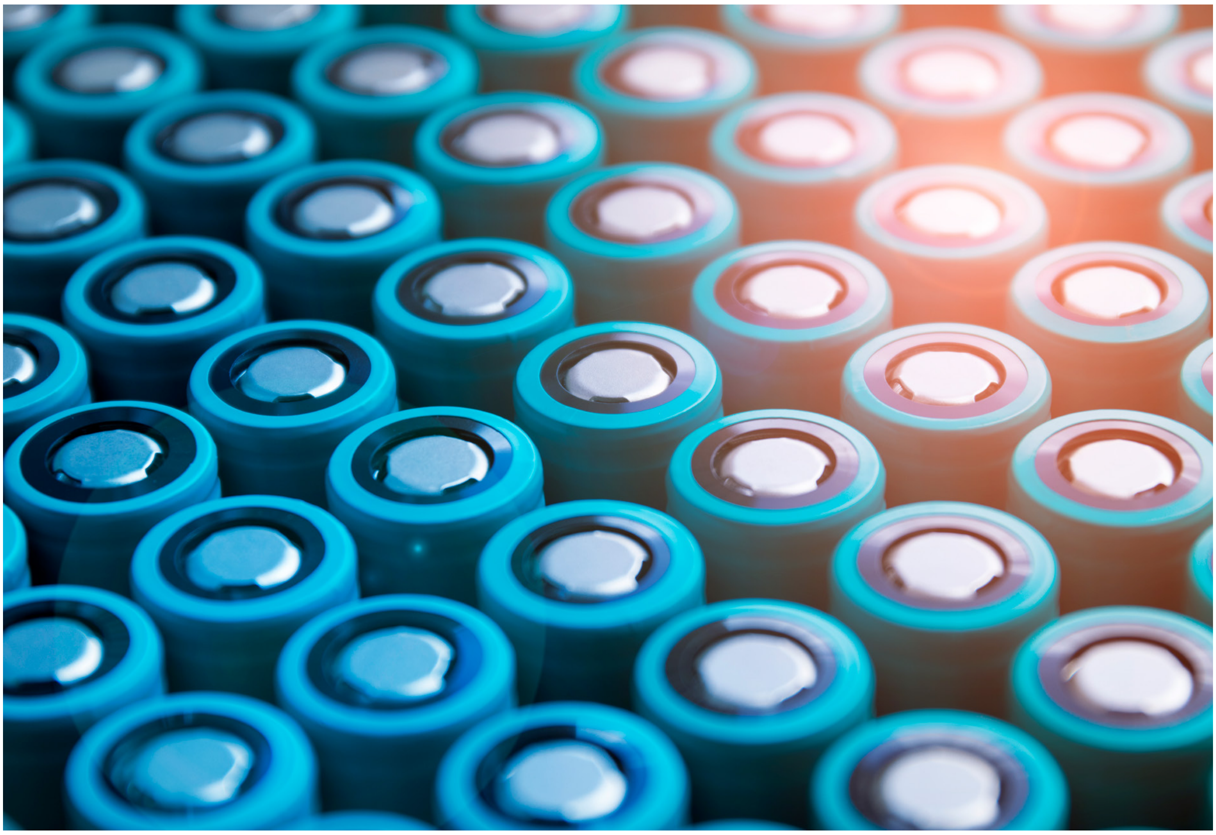
Li-ion technology is currently seeing huge growth in industry. The performance of this technology enables it to reach the highest energy density of all rechargeable accumulators: roughly 270Wh/kg (around 700Wh/l) at the cell level.

However, this race to attain maximum (energy concentration), as well as using materials that display exothermic degradation, have a non-negligeable effect on the safety regulations regarding this technology.

In this second part, a more precise detailing of Li-ion design methods and functionality will be laid out.

The following sub-sections will more precisely detail Li-ion technology, in order to present:

- Firstly, materials and internal composition with the objective of specifying the chemical materials contained.
- Secondly, the detailed performance of this technology.
- Finally, the last part will allow us to define the fault types as well as associated events and protection strategies implemented at the cell level.



Chemical materials and internal composition of Li-ion technology

Active materials of Li-ion technology

The accumulators contain two electrodes, compose of chemically active electro-materials. Their capacity to capture or free electrons allows these materials and therefore the accumulator to convert and to store energy.

Figure 5 Presents the potential uses depending on the capacities of different active materials. The highlighted ones are the most popular on the market today. To get the most effective accumulators possible, it is very helpful to use materials with a high voltage and capacity.

The higher the capacity, on the right of Figure 5, the higher the capacity of the accumulator.

As regards voltage, as its value is equal to the difference in potential between the active materials of the two electrodes, it is therefore necessary to choose active materials with high potential and low potential for the positive and negative electrodes, respectively. The materials highlighted in red are the most popular on the market for use on the positive electrode. We have the transition metal oxide family ($Li_xNi_aMn_bCo_cO_2$) as well as LFP ($LiFePO_4$). As for the negative materials, highlighted in green, we have graphite which has very good energy properties (high capacity and low potential) as well as LTO ($Li_4Ti_5O_{12}$), which is less effective in terms of storage, but is particularly interesting for power applications.

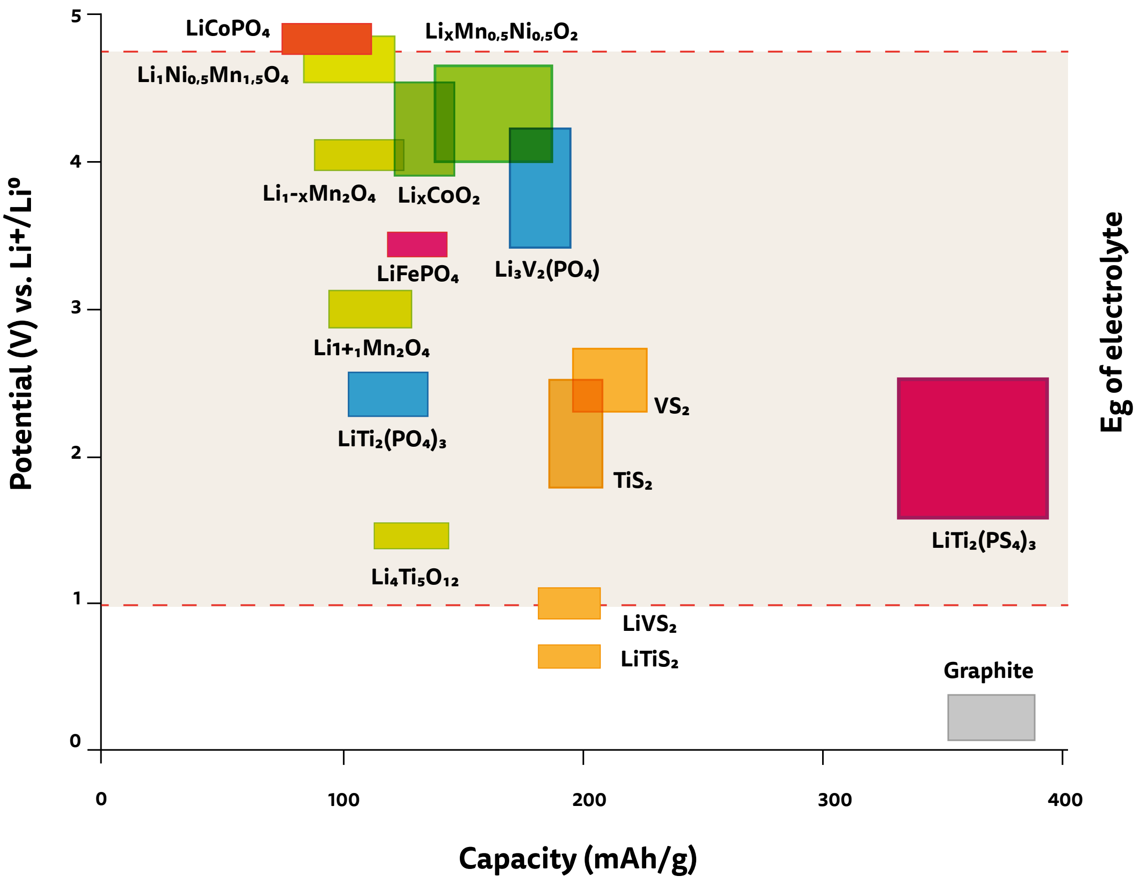


Figure 5: Comparison of use potential for electro-chemically active materials depending on their capacity.

Li-ion technology electrolytes

Like with all accumulator technologies, in order to guarantee ionic continuity between the electrodes, Li-ion contains an electrolyte. Current technologies on the market use fluid substances, comprised of a mixture of organic composite and salt. The latter, which is there to ensure ionic conduction, is in the vast majority of commercial accumulators, $LiPF_6$ salt dissolved at roughly 1mol/l.

The second phase is a binary or ternary mixture of organic solvents, generally from the carbonate family. (See the three examples presented in Table 1)

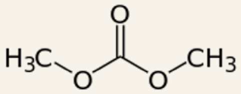
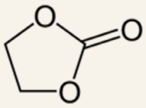
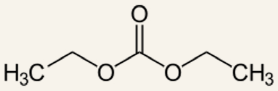
		
Di-methylene carbonate	**Ethylene carbonate**	**Di-ethylene carbonate**

Table 1: Example of Li-ion electrolyte organic solvents.

Design of Li-ion cells

At the start of Li-ion accumulator manufacturing, the active materials are distributed into a solvent to obtain an ink which is then placed on metal sheets: the current collectors. After drying this deposit, the electrodes are ready to be assembled. The electrochemical core is obtained by successive stacks or by winding three components: positive electrode, separator and negative electrode. The photo in Figure 6 shows and example of electrochemical cores obtained from winding the three components.

© Thomson Reuters 2010

Figure 6: Example of Li-ion accumulator electrochemical cores obtained from winding.

The electrochemical core is then inserted into the cell packaging. The electrolyte is then added, then the cell is sealed in order to avoid the electrolyte drying out from the organic solvent evaporating and also to ensure the core is protected against oxidising agents in the air (humidity, dioxygen).

Figure 7 shows a cross-sectional example of a cylindrical Li-ion cell. The commercial Li-ion cells can be in a variety of formats such as buttons, prisms or cylinders, and in metal or plastic casing.

Note that manufacturers can sometimes give their technology the name "Li-ion polymer" which in no way describes the internal components of the accumulator but actually just the chemical nature of the casing, or even, very rarely, the electrolyte. This name is never "safer" than any other.

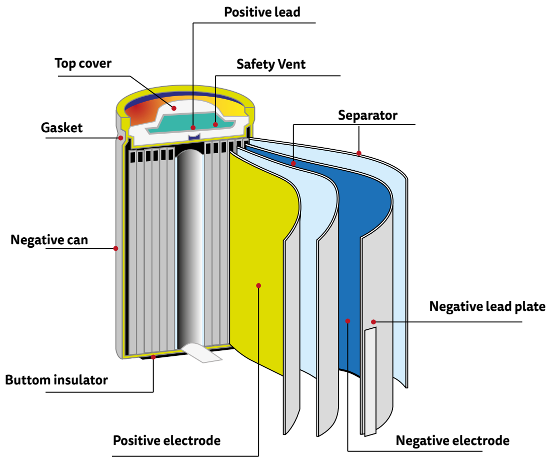


Figure 7: Example of internal components of a cylindrical Li-ion cell.

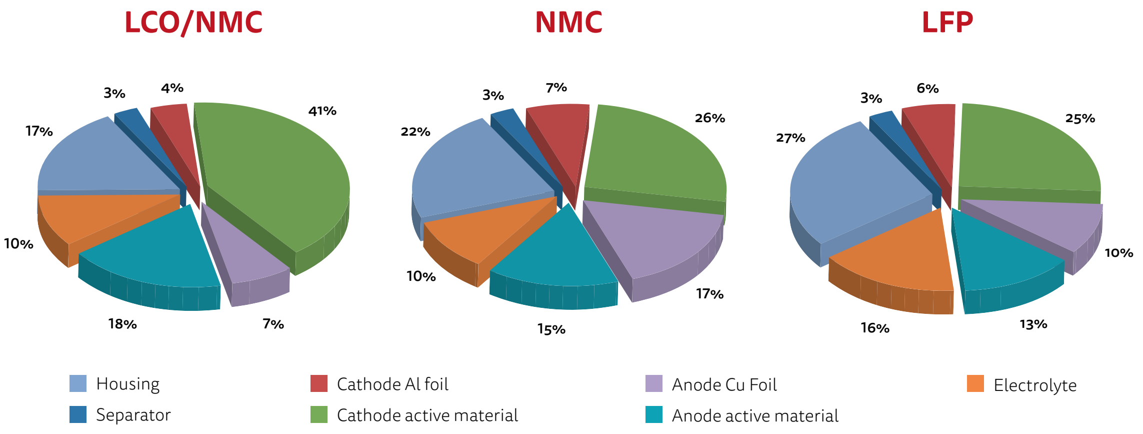


Figure 8: Mass reports for internal components of the three cylindrical cell families (18650) Li-ion, LCO/NMC, LFP and NMC.

CONCLUSION

To conclude this part, for which the main goal was to present the chemical parts contained within Li-ion cells, it is helpful to note Figure 8. The three pie charts show the mass ratios for the internal components of the three Li-ion cell families: LCO/NMC, NMC and LFP. We can see that the ratios are roughly identical regardless of the technology.

Li-ion performance

As explained in the introduction, the main axes for increasing the density of energy stored by an accumulator (in Wh/kg) are the weight of materials used as well as the accumulator voltage. As lithium has the lowest possible electrochemical potential, as well as low atomic mass, it is extremely valuable in manufacturing batteries. Since it was first brought to market in 1991 (by Sony®), Li-ion technology has been subject to numerous industrial developments.

The main advantage of Li-ion batteries is their high energy density, compared to older technologies: between 5 and 10 times more energy per unit mass than lead batteries, and 3 to 4 times more than Ni-MH batteries.

These batteries were therefore much lighter. They were also smaller, and this is an essential attribute for many applications (from portable devices to vehicles).

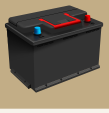
	Li-ion 	**Pb-acide** 	**Ni-MH** 
Wh/kg	**200 – 270**	20 – 50	40 – 80
Wh/L	**400 - 600**	60 – 100	80 – 150

Table 2: comparison of energy density (Wh/kg) (Wh/L) for Li-ion, lead and Ni-MH batteries.

The differing chemistry of Li-ion technology are defined by the chemical nature of the electrochemically active materials present in the electrodes (detailed in Figure 5). The assembly of the various positive and negative electrode materials (commonly known as cathode and anode materials) enable the creation of lithium-ion accumulators with variable average voltages. Examples of assemblies are presented in Table 3.

CATHODE		ANODE	AVERAGE VOLTAGE
$LiCoO_2$ (LCO)	Lamellaires	Graphite (C)	3,6V
$LiMn_2O_4$ (LMO)		Graphite (C)	3,8V
$LiNi_aCo_bAl_cO_2$ (NCA)		Graphite (C)	3,7V
$LiNi_xMn_yCo_zO_2$ (NMC)		Graphite (C)	3,7V
$LiFePO_4$ (LFP)	Spinelle	Graphite (C)	3,2V
$LiMn_2O_4$ (LMO)	Lamellaires	$Li_4Ti_5O_{12}$ (LTO)	2,3V

Table 3: Average voltage of various electrode couples currently on the market.

Safety characteristics of lithium-ion

Li-ion accumulators used outside of their normal operating conditions, are at risk of the reaction known as thermal runaway. This event occurs when the internal chemical components (electro-chemically active and the electrolyte) are subject to high enough temperatures to active exothermic degradation mechanisms. Figure 9 shows the various attacks that result in thermal runaway: physical, electrical or thermal attacks. Note that a domino effect is observed. For example, crushing can lead to electrical malfunction, which can then lead to the creation of hot points and finally, thermal runaway across the whole accumulator. The worst part of a Li-ion battery in thermal runaway are smoke, fire, or even a violent rupture of the

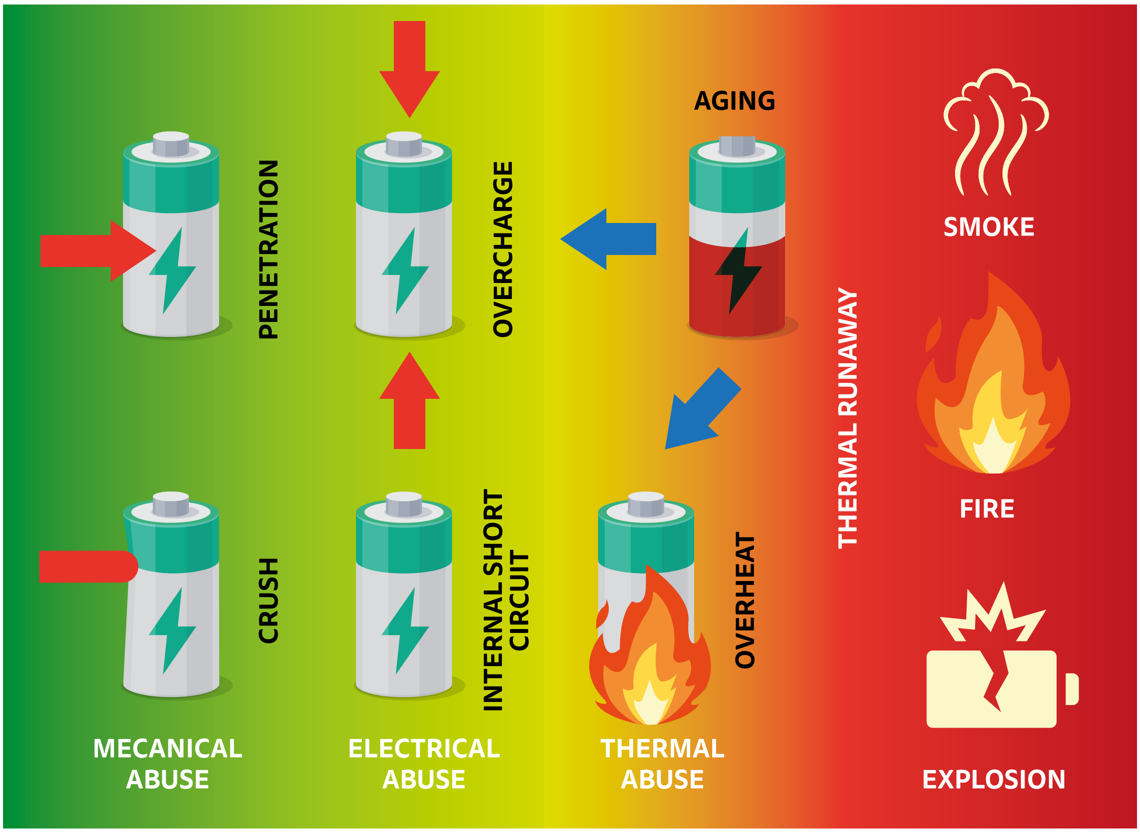


Figure 9: Presentation of Li-ion attack methods.

Battery manufacturers work constantly to improve the capacity of their products. As such they use more and more effective materials to store energy, but also more and more exothermic in case of thermal runaway. Figure 10 shows clouds of points that correspond to the initiation temperature of thermal runaway depending on the energy density of various types of Li-ion accumulators. Thermal runaway initiation temperatures are between 60°C and 140°C inclusive depending on the type of Li-ion. Note that when a cell is subject to its thermal runaway initiation temperature, the exothermic degradation mechanism is activated but create very little heat. The technical specifications for the cell are then degraded, but an effective cool-down can enable the reaction to be stopped as long as the reaction energy is not too high. The first thing noted concerns the size of installation zones that can sometimes be quite high. For example, the G/NMC family (graphite vs mi Nickel, Cobalt and Manganese oxide) displays high variability in terms of energy density and also thermal runaway initiation temperature. This large spread is due to the fact the NMC chemical family displays variations in composition (ratio between the three metals) that leads to fluctuations in terms of performance and safety characteristics. Also, resistance to thermal runaway is highly impacted by other parameters such as the presence of chemical additives or safety systems implemented at the cell level.

If we take into account only the thermal aspect of the runaway, as is the case in Figure 10, it is not possible to draw conclusions in terms of operational safety. In fact, this graph seems to indicate that the C/LFP technology may be less safe that certain C/NMC cells on top of the surface. This is indeed the case when considering only the thermal aspect. But this conclusion may need to be balanced by the freed energy from the thermal runaway that is higher for C/NMC technologies. Figure 11 shows energy freed by thermal runaway mechanism for different components in Li-ion cells depending on the temperature. The peak zone, which corresponds to the amount of energy released, is roughly two times higher for NMC than for LFP.

It clearly appears that chemical nature of materials contained in Li-ion cells impacts behaviour in extreme conditions. The type of run away as well as the protection at the cell level are also important parameters.

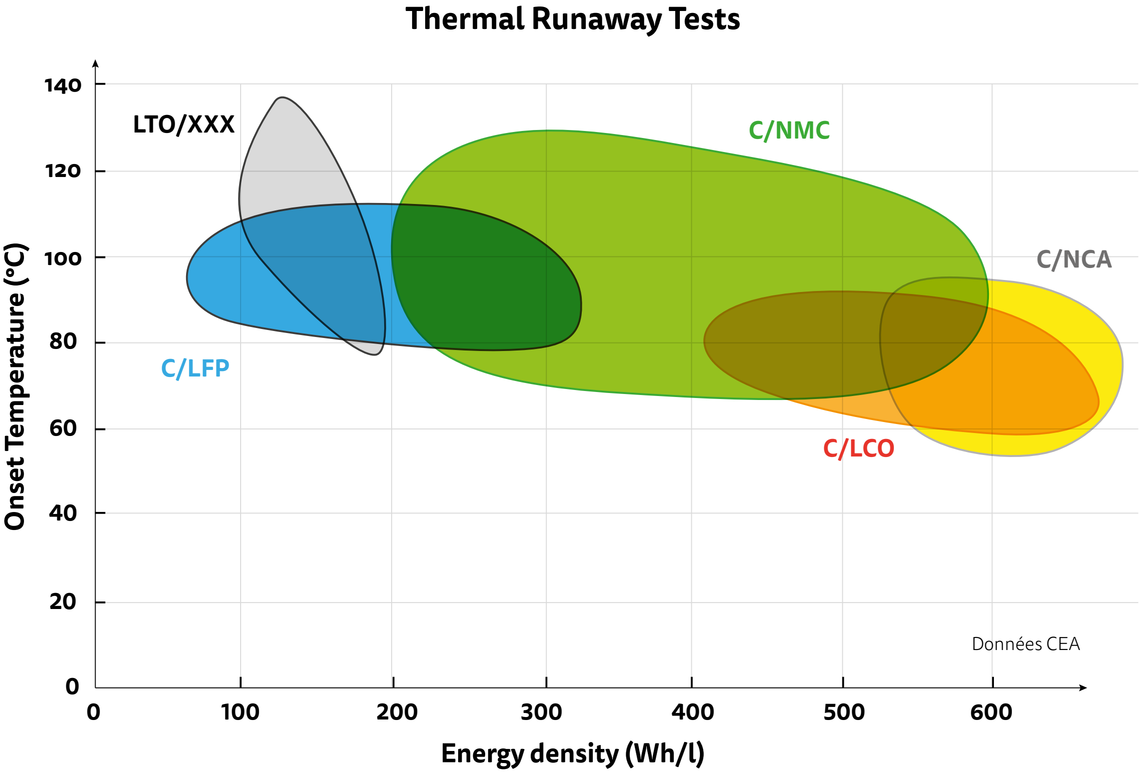


Figure 10: Thermal runaway temperature as a function of energy density of Li-ion cells for different technologies.

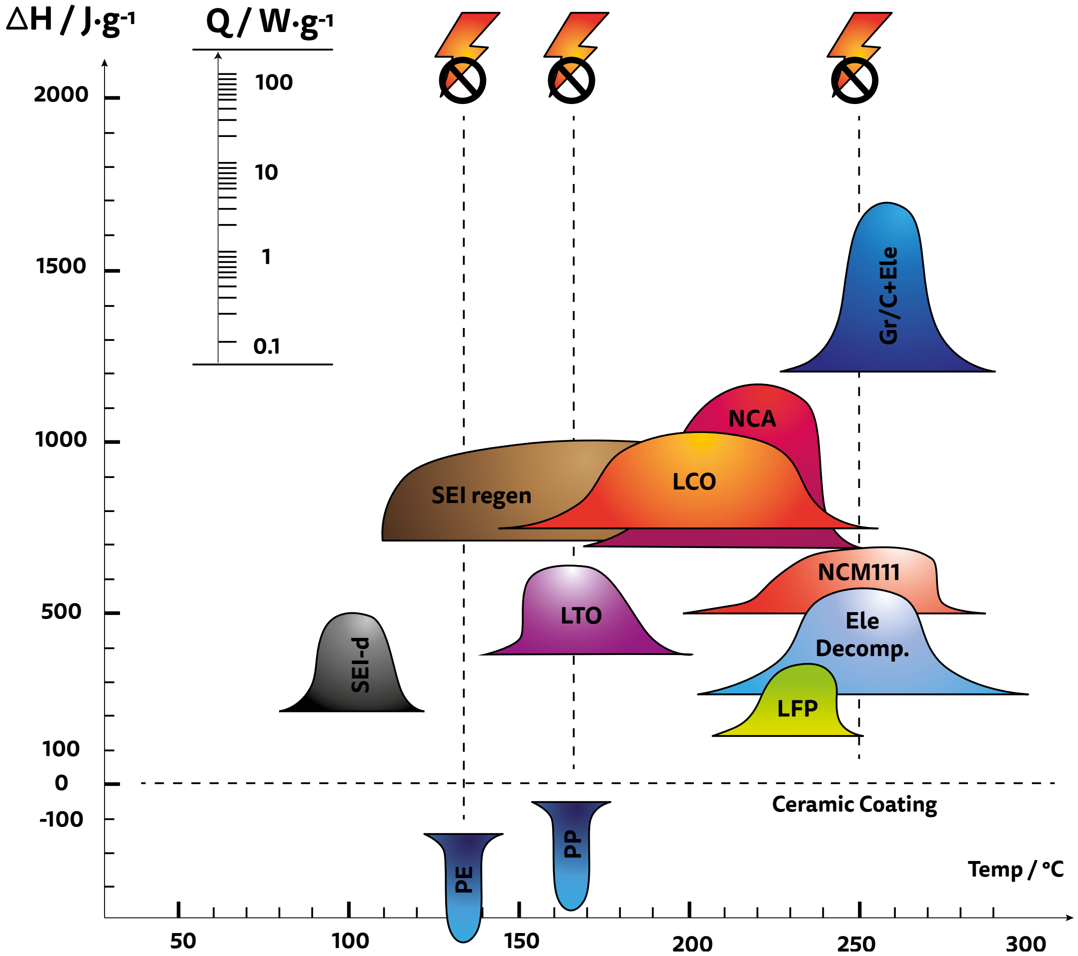
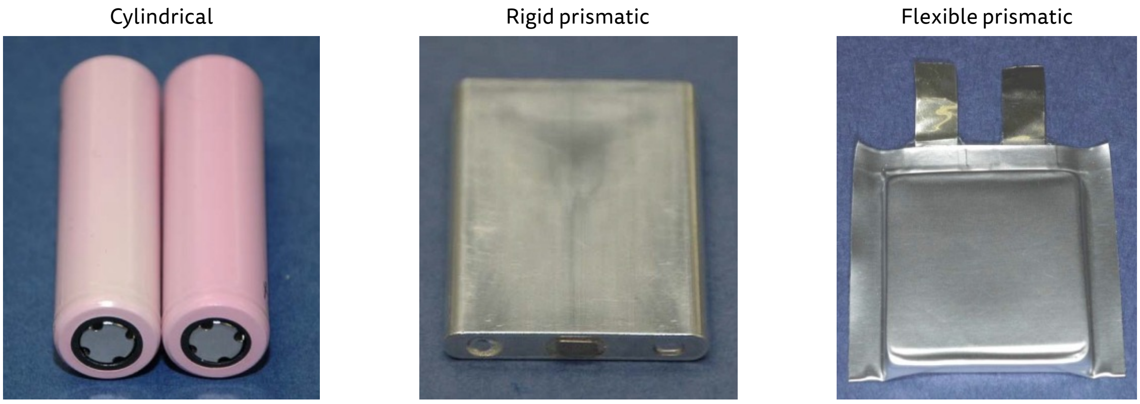


Figure 11: Comparison of heat freed by thermal runaway mechanisms for different components in Li-ion cells depending on the temperature.

Factors of Li-ion protection shapes and systems

Today's commercialised Li-ion cells can be contained in casings of various shapes and types. There are three main types: cylindrical, rigid prism and flexible prismatic cells:


Cylindrical

Rigid prismatic

Flexible prismatic

Figure 12: Photo example of three type of Li-ion casings.

Cylindrical cells and their protection

Cylindrical cells are placed in a rigid metal casing, and are generally named according to their dimensions, for example: 18650 for 18mm diameter and 65mm tall. This 18650 format is currently the most widely used, but is being replaced by the new 21700 format. This format has the benefit of providing high resistance and lifespan (cyclability) but a loss in energy density during assembly.

Safety systems are integrated inside the positive terminal. The photograph in Figure 13 shows a cross-sectional view of a Li-ion cell centered on the positive terminal. All of the protection systems are as such integrated between the positive terminal and the current feedback (see red arrows on Figure 13)

The protections implemented at the heart of cylindrical Li-ion cells are 3 in total, and allow the ensemble to protect the cell against various attacks:

- The excess pressure vent is a burst disc that enables gas exhaust in case of excessive internal pressure, see Figure 14. This protection system is systematically implemented for rigid casings. When it is ruptured, the electrolyte solvent evaporates and air is introduced, which leads to irreversible degradation of the cell.
- The CID (Current Interrupt Device) is a system that enables physical disconnection by removal of the current source, see Figure 14. Opening this electrical circuit in case of excess pressure is an effective protective measure against surges (which creates gas). This protection, which is not systematically implemented, makes the cell irreversibly useless.
- PTC (Positive Temperature Coefficient) allows current to be blocked in case of excess. This protection is, however, reversible as the cell can be reused after a relaxation period. However, this protection is not systematically present in Li-ion cells.

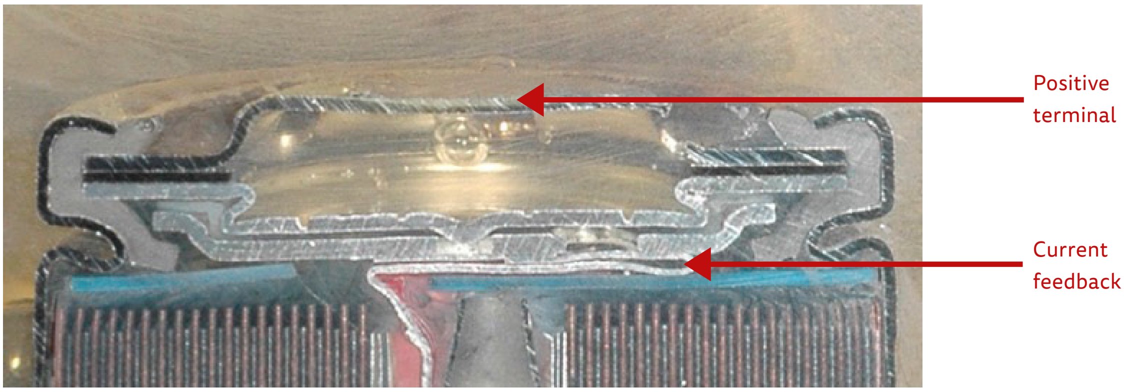


Figure 13: Cross-sectional view of a cylindrical Li-ion cell centered on the positive terminal.

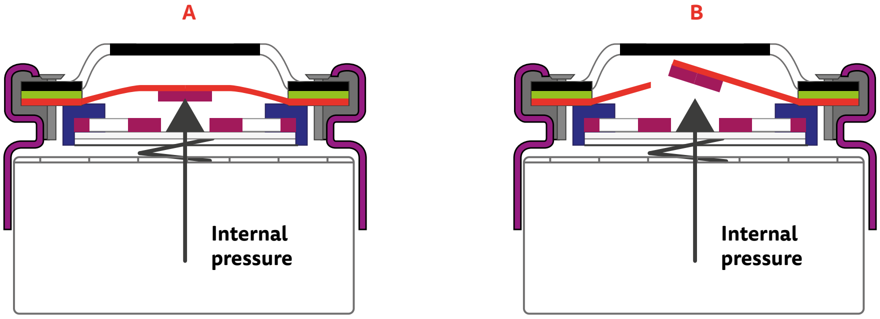


Figure 14: Operating diagram for the excess pressure vent (a) and the CID (b).

Prismatic cells and protective measures

Prismatic cells can be enclosed in a rigid casing, generally made of metal, or a flexible casing. The dimensions of prismatic cells are highly variable, and indistinguishable commercially. Compared with cylindrical cells, this format has lower operating lifespan, but would be preferable in energy applications, because its smaller size enables higher energy densities to be reached.
As an example, the sales information of the Samsung 60Ah cell are detailed in Figure 15.

This cell seems to have numerous safety systems:

- OSD: Overcharge Safety Device, similar to the CID in function for cylindrical cells. A membrane is deformed under the excess internal pressure and irreversibly isolates the core of the cell from the electrical terminals.
- Safety vent: Enables excess internal pressure to be evacuated. System that is systematically implemented in rigid casings. Opening this vent is irreversible.
- Fuse: Fuse that allows the electrical circuit to be irreversibly opened in case of excess voltage across the battery.
- SFL: Safety Function Layer that covers the outside of the cell. This protection is systematically integrated into metal cells in order to limit the presence of large conductive surfaces.
- NSD: Nail Safety Device. This system is presented as being able to increase the resistance of the cell against potential perforations by conductive agents. The lack of information (likely industry secret) leads us to believe that this system may be implemented either using high internal casing resistance to avoid perforations, or by an internal system that allows internal short-circuit currents to be limited.

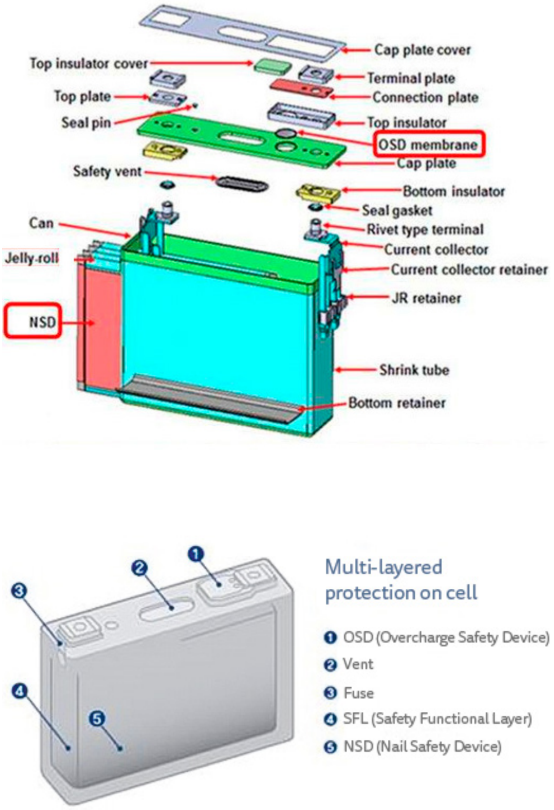


Figure 15: Commercial information on the rigid prismatic Samsung 60Ah cell.

Prismatic cells can also be integrated into flexible casings. A triple-layer material known as a pouch or coffee bag is implemented. This casing is comprised of an aluminium sheet, chosen for its physical resistance, surrounded by two layers of plastic. There is no protective measure used for this type of casing. As it is flexible, and can rupture easily, it is not necessary to implement an excess pressure vent. Note that some manufacturers may, however, weakened part of the casing in order to funnel the gas exhaust in case of excess internal pressure. Also, often observed during implementation of a short-circuit on a cell is a fuse-like behaviour on the positive terminal. This effect is obtained thanks to the chemical nature of the positive terminal (aluminium) and probably with an adequately sized system.

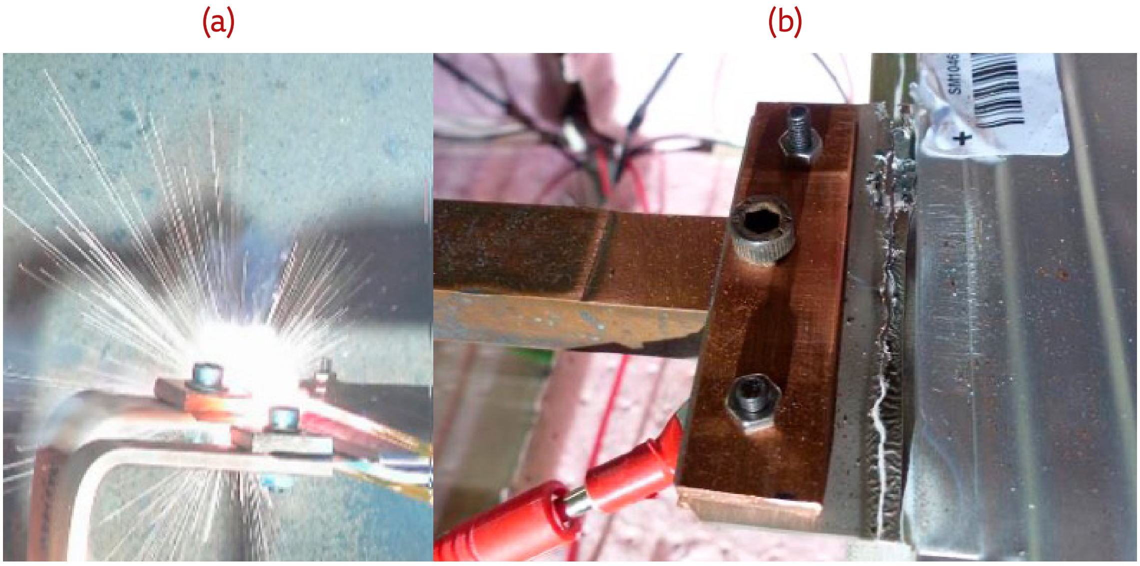


Figure 16: Photo of the fuse effect in a flexible cell during a short-circuit (a) and cross-sectional view of the terminal after the test (b)

Safety function of the separator

The separator is a component that must ensure electrical insulation between the two electrodes. It must, nevertheless, enable good ionic conduction for the Lithium ions to be able to be exchanged by active materials. In practice, the electrical insulating and ionic conductive properties are reached by using a porous polymer film (roughly 50% - usually polyethylene: PE or polypropylene: PP), see Figure 17.

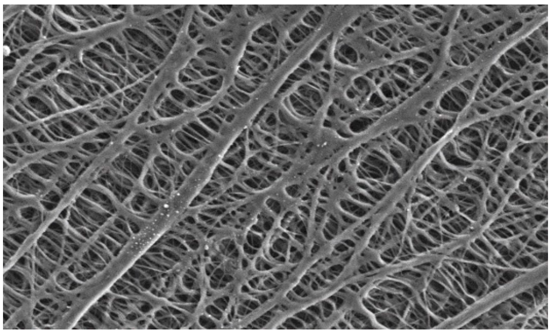


Figure 17: Photograph of the surface of a separator obtained by scanning electron microscopy.

Although the main function of a separator is not safety, it is important to define this component because it has been subject to various developments that have considerably improved its behaviour in extreme conditions. Development of sandwich style separators, using a stack of three porous layers (PP/PE/PP) has allowed for a fuse-like effect to be obtained, see Figure. When there is an increase in internal temperature during a thermal runaway or internal short circuit, the polyethylene melts first and plugs the pores in the separator. As ionic conduction is inhibited, the cell is no longer usable and is protected.

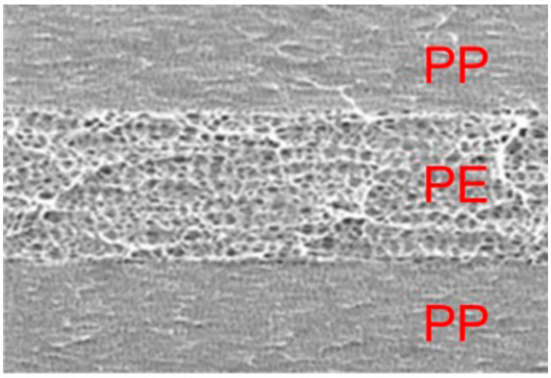


Figure 18: Photograph of a cross-section of a PP/PE/PP sandwich separator obtained by scanning electron microscopy.

Some separators are also designed with a layer called the “Heat Layer Resistance” (HLR), see Figure 19. This deposit of inorganic material on the surface of the separator, enables the heat exchange to be limited between the electrodes and therefore for the thermal runaway to be limited.

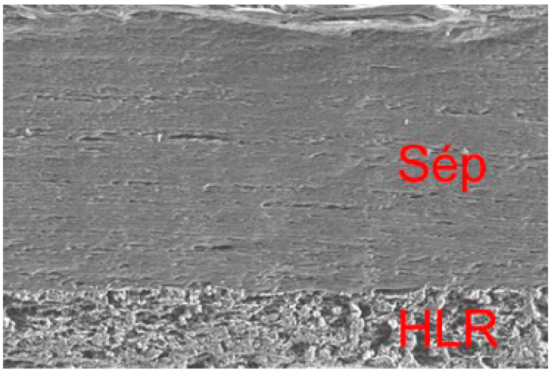


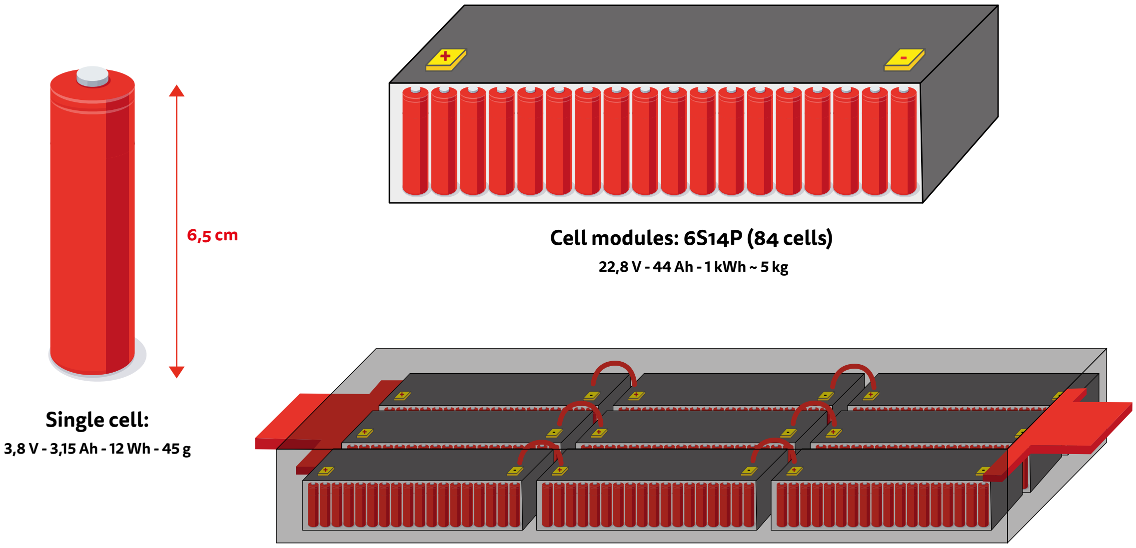
Figure 19: Photograph of a cross-section of a separator with HLR deposit obtained by scanning electron microscopy.

Assemblies

The application requirements generally necessitate higher energy than that of a single cell. A mechanical and electrical assembly is therefore implemented in order to obtain the right levels of voltage/power. Generally, the cells are assembled in modules of several tens of cells. The modules are themselves then assembled in packs of several modules, see the example in Figure 20. The electrical architecture contains extra protection such as voltage measurement and fuses. The external case is designed such as to provide sufficient physical resistance for the application roughly electronic management, called BMS (Battery Management System) is implemented in order to control the whole battery system depending on the system measurements (temperature, voltage, current, etc.) and based on the management algorithm developed by the manufacturer. The role of the BMS is to control:

- Subsystem balance
- Stopping charge/discharge once the conditions are met
- Calculation of charge, health and system safety status
- …

Li-ion technology needs independent management of each single cell. In practice, maximum cell operating voltage is defined by the manufacturer. It must not be exceeded under any circumstances. This may present problems when a large number of cells are assembled in series.

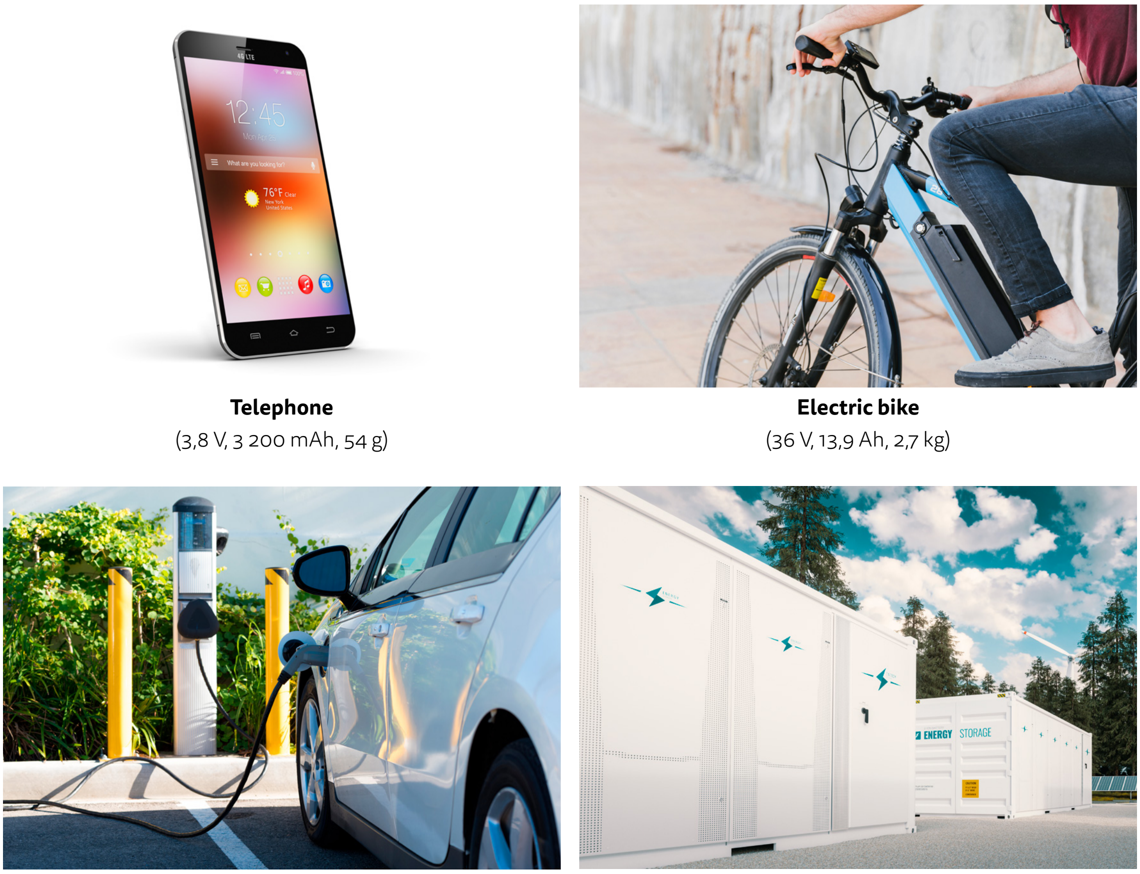


Single cell:
3,8 V - 3,15 Ah - 12 Wh - 45 g

Cell modules: 6S14P (84 cells)
22,8 V - 44 Ah - 1 kWh ~ 5 kg

Module packs: 3S3P (756 cells)
68,4 V - 132 Ah - 9 kWh ~ 75 kg

Figure 20: Description of single elements generally considered (cell, cell module, module pack).



Telephone
(3,8 V, 3 200 mAh, 54 g)

Electric bike
(36 V, 13,9 Ah, 2,7 kg)

Renault Zoé
(400 V, 41 kWh, 12 modules, 192 cells, 290 kg)

Storage container
(640-1100 V, 5,47 MWh in 40" container)

Examples of applications using Li-ion batteries and battery orders of magnitude.

PHOTO DATABASE

Lithium-ion based electrochemical storage systems are used for a variety of applications. For each type of application, they can be separated into different system sizes. Some examples of variable storage system sizes for different applications are presented below.

Storage size, UPS application

10 kWh 50 L/100 kg	100 kWh 500 L/1000 kg	1 MWh 5000 L/10 t
Résidential	Tertiary	
		
www.tesla.com/fr_FR/powerwall	www.apc.com/salestools/ACOS-AD4M5V/ACOS-AD4M5V_R2_EN.pdf	www.connaissancedesenergies.org/un-data-center-connecte-des-batteries-usagees-de-voitures-electriques-220218
13,5 kWh (1150 x 755 x 155 mm), 125 kg	25 - 35 kWh (2055 x 650 x 600mm), 480 kg	30 x 24 kWh

Figure 21: examples of energy storage systems for emergency and uninterruptible power supply systems.

Storage size, solar storage applications

10 kWh 50 L/100 kg	100 kWh 500 L/1000 kg	1 MWh 5000 L/10 t
Résidential	Tertiary	
		
www.ikea.com/gb/en/ikea/solar-panels	https://tribuca.net/entreprises_25326075-une-entreprise-azureenne-devient-partenaire-de-tesla	https://alfen.com/fr/Syst%C3%A8me-de-stockage-de-%C3%A9nergie
3,3 à 6,5 kWh (452 x 654 x 120 mm), 52 kg	210 kWh (1308 x 8220 x 2185 mm), 1622 kg	2 MWh (container 40'), 28,7 t

Figure 22: exemples of energy storage systems for variable and intermittent renewable sources.

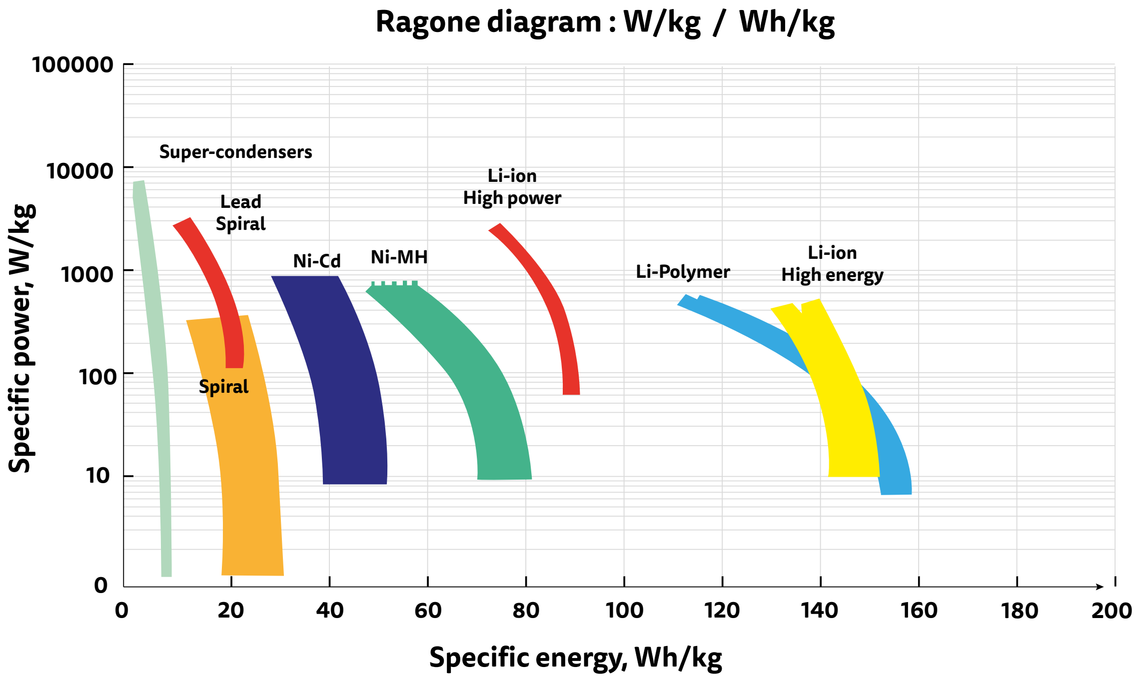
Storage size, SCPU applications (Storage connected to Power Utility network) and SCRR (Storage connected to residential network)

10 kWh **50 L/100 kg**	**100 kWh** **500 L/1000 kg**	**1 MWh** **5000 L/10 t**
Résidential	Tertiary	
		
www.avem.fr/actualite-xstorage-home-le-stockage-domestique-de-lenergie-propose-par-nissan-disponible-en-france-6317.html 9,6 kWh 10 kg	www.swarco.com/apt/Products-Services/Battery-Energy-Storage/E-STOR 66 - 110 kWh (3,1 x 2,25 x 2,26 m), 100 kg	www.eqmagpro.com/kokam-to-build-36-megawatt-energy-storage-system-ess-for-kepco-increasing-its-total-worldwide-ess-project-portfolio-to-132-megawatts-2/ ... MWh (Multi containers)

Figure 23: Examples of energy storage systems for supporting electrical networks (regulation of frequency and voltage, removal of power peaks, etc.).

PERFORMANCE AND CHARACTERISTIC ELECTRICAL ORDERS OF MAGNITUDE

The Ragone diagram from the figure below enables the various battery technologies to be situated as regards their capacities:



The electrical orders of magnitude for different applications are generally comparable in terms of voltage. On smaller applications (10kWh), voltage is generally in the range of 400Vdc. For larger applications, this voltage can increase up to the Low Volage limit in direct current, which is 1500Vdc. It is therefore important to consider that the voltage levels are always higher than the low voltage safety levels and the electrical risk is therefore necessary to take into account in all applications that this document covers.

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2

CHARACTERISATION OF RISKS AND ACCIDENTS IN ELECTROCHEMICAL ENERGY STORAGE SYSTEMS


Li-ion
Energy storage
Lithium ion batteries
C 2008058816
CAUTION
9' 6.5" HIGH
8' 6" WIDE
CONTAINER

GENERALITIES

Regardless of their structure, chemistry and operating mode, the potential intrinsic risks for electrochemical energy storage systems faced by fire-fighters are varied in nature. These risks differ also according to the accident situation that could be met (thermal runaway, fire, crush, impact, surge, etc.).

IDENTIFICATION OF ELECTROCHEMICAL ENERGY STORAGE SYSTEMS

CHAPTER OBJECTIVES

The goal of the current chapter is to define all the risks that could occur and to try and provide the Emergency Operations Commander with the key information in order to allow them to identify these risks and classify them. It allows enables the creation of a categorised accident array with the goal of analysing development trends but also to confirm the importance or not of risks identified.

The first difficulty that emergency services encounter resides in the inability to identify ahead of time the presence of an electrochemical energy storage system. In fact, the presence of a storage system must be identified as soon as possible and as soon as the alert is transmitted by the applicant, if the latter is aware of it. This habit that is not yet common in the CTAs must enable the identification of a risk for people and property directly surrounding the storage zone at risk and the first responders.

Once they have arrived on site, the challenge for the first responders is to locate the storage zone in the building. The standards in force do not obligate any specific marking on the zones at risk, making it impossible to identify the existence of a storage zone inside a building whether it is marked as at-risk or not. The emergency plans that exist at a factory or an ERP do not mention the possible presence of these storage devices either, let alone their capacity or technology.

As a result, if the presence of an electrochemical energy storage system is confirmed, the question of identifying its chemistry is then posed. From the type of chemistry, the storage is comprised of defines the risks, which can differ. Where in doubt, the major risks must be taken into consideration to define the safety parameters (see chapter "Classification of risks").

Finally, the design itself of most storage systems can complicate access for emergency services (e.g.: wall cabinet in a home, shipping container at a factory or ERP, locked rooms, etc.). Cooling and extinction are more difficult.

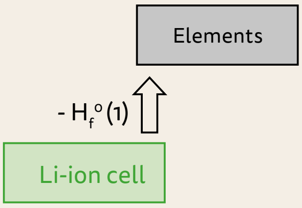
Figure 24: KEPCO storage systems (source: www.eqmagpro.com/kokam-to-build-36-megawatt-energy-storage-system-ess-for-kepco-increasing-its-total-worldwide-ess-project-portfolio-to-132-megawatts-2/)

ENERGY CONTAINED IN A LI-ION BATTERY

As temperature increase, the various materials that constitute the battery (solid and liquid) can decompose into their gaseous form while releasing energy (exothermic reactions).

Examples of the energy increase necessary for the main battery cell components to decompose are presented below. The separator and carbon negative electrode are materials that decompose with the lowest amount of energy (so the lowest temperature). For lithium salt ($LiPF_6$) to decompose and produce hydrogen, lots of energy is required.

REACTION ENTHALPY OF CELL CONTENTS



ΔH_f^o @298, 15 K, 101,3 kPa, normalized to the exchange of one electron

Decomposing the cell contents into its elements

Conducting salt:	$1/6\ LiPF_6(s) \rightarrow 1/6\ Li(s) + 1/6\ P\ (s,r) + 1/2\ F_2\ (g)$	+ 383 kJ
Ceram. Coating:	$1/6\ Al_2O_3\ (s) \rightarrow 1/3\ Al\ (s) + ¼\ O_2\ (g)$	+ 280 kJ
Cathode binder:	$¼\ \text{-}[CH_2CF_2]_n\text{-}\ (s) \rightarrow n/4\ [C\ (s, G) + H_2\ (g) + F_2\ (g)]$	+ 205 kJ
Cathode material:	$¼\ Li_{0,45}[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2\ (s) \rightarrow 0{,}11\ Li\ (s) + 1/12\ [(Ni\ (s) + Mn\ (s) + Co\ (s)] + ¼\ O_2\ (g)$	+ 130 kJ
Solvent EC:	$1/10\ C_3H_4o_3\ (s) \rightarrow 3/10\ C\ (s, G) + 1/5\ H_2\ (g) + 3/20\ O_2\ (g)$	+ 60 kJ
Anode binder*:	$1/52\ \text{-}[C_{18}H_{26}O_{16}]_n\text{-}\ (s) \rightarrow n/52\ [18\ C\ (s, G) + 13H_2\ (g) + 8\ O_2\ (g)]$	+ 59 kJ
Solvent DMC:	$1/12\ C_3H_6O_3\ (l) \rightarrow ¼\ C\ (s, G) + ¼\ H_2\ (g) + 1/8\ O_2\ (g)$	+ 45 kJ
Solvent EMC:	$1/14\ C_4H_8O_3\ (l) \rightarrow 2/7\ C\ (s, G) + 2/7\ H_2\ (g) + 3/28\ O_2\ (g)$	+ 37 kJ
Anode material:	$8{,}55\ Li_{0,117}\ C\ (s) \rightarrow Li\ (s) + 8{,}55\ C\ (s, G)$	+ 17 kJ
Separator:	$½\ \text{-}[CH_2]_n\text{-}\ (s) \rightarrow n/2\ [C\ (s, G) + H_2\ (g)]$	+ 14 kJ

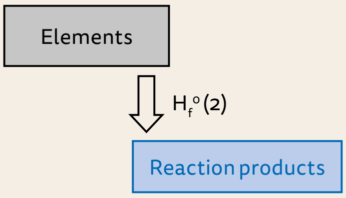
*CMC (DS = 1,5)

The calculated energy for decomposing the starting materials into the elements is 3.145 kJ.

Figure 25: energy required for various Li-ion battery cells to decompose according to (SCHARNER, 2018).

The elements generated by the decomposition of materials can also recombine to produce new composites. Examples of the energy increase necessary for the main battery cell components to decompose are presented below. The recombination reaction often displays negative reaction enthalpy, which means that its produces energy (except for the reaction that forms C_2H_4 from elements C and H, which is endothermic). Unsurprisingly, the most exothermic reactions are the ones that bring solid lithium into contact with other metals present (Al, Mn, Ni, Co) and oxygen or Fluorine (elements with a high oxidising power).

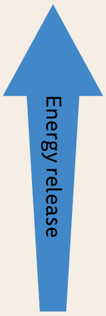
REACTION ENTHALPY OF THE REACTION PRODUCTS



ΔH_f^o @298, 15 K, 101,3 kPa, normalized to the exchange of one electron

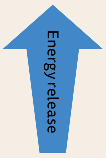
Formation of reaction products (validated)

¼ Li(s) + ¼ AI (s) + ¼ O_2 (g) → ¼ $LiAiO_2$ (s)	- 297 Kj
¼ Li(s) + ¼ Mn (s) + ¼ O_2 (g) → ¼ $LiMnO_2$ (s)	- 210 Kj
1/3 Li(s) + 1/6 C (s, G) + ¼ O_2 (g) → 1/6 Li_2CO_3 (s)	- 203 Kj
½ Mn (s) + ¼ O_2 (g) → ½ MnO (s)	- 193 Kj
½ Ni(s) + ¼ O_2 (g) → ½ NiO (s)	- 120 Kj
½ Co (s) + ¼ O_2 (g) → ½ CoO (s)	- 119 Kj
¼ C (s, G) + ¼ O_2 (g) → ¼ CO_2 (g)	- 98 Kj
½ C (s, G) + ¼ O_2 (g) → ½ CO (g)	- 55 Kj
¼ C (s, G) + ½ H_2 (g) → ¼ CH_4 (g)	- 19 Kj
½ C (s, G) + ½ H_2 (g) → ½ C_2H_4 (g)	+ 13 Kj



... postulated reaction products (not validated)

¼ Li(s) + ⅙ AI (s) + ½ F_2 (g) → ⅙ Li_3AiF_6 (s) → more stable than LiF and AIF_3	- 564 Kj
Li (s) + ¼ O_2 (g) → ½ Li_2O (s)	- 299 kJ
½ H_2 (g) + ½ F_2 (g) → HF (g) (traces, accordining to literature)	-271 kJ
½ H_2 (g) + ¼ O_2 (g) → ½ H_2O (l)	- 143 kJ
Li (s) + 1/3 P (r, s) → 1/3 Li_3P (s)	- 112 kJ



The calculated energy to synthesize reaction products is - 4.212 kJ.

Figure 26: energy exchanged during different recombination reactions of elements produced during Li-ion battery cell component decomposition according to (SCHARNER, 2018).

If fluorine can, in theory, only come from the decomposition of materials coming from the cells themselves, oxygen can come both from decomposition of materials (see Figure 25) but also from the environment (air).

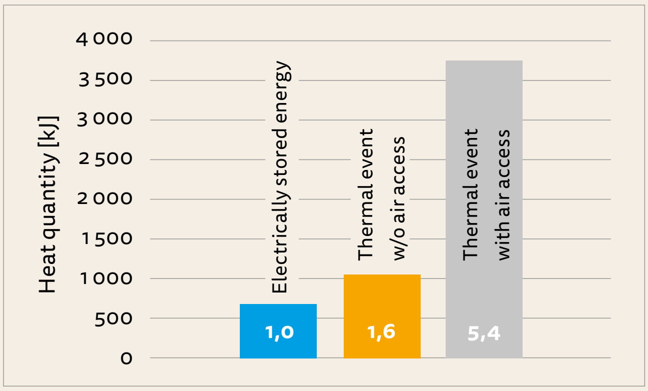
The main consequence is that the energy released in an open environment (with added oxygen possible) can be much higher than that released in a confined space (without air added). This is what the following figure demonstrates.

THE INFLUENCE OF OXYGEN IN THE PRESENCE OF AIR

C. Combustion of combustible substances emitted from the cell

The following substances were detected outside the cell:

Solids:	Graphite → 15% by weight of the amount used
Solvents:	DMC, EMC → 56% by weight of the amount used
Gases:	H_2, CO, C_2H_4, CH_4



Air access increases the heat release by a factor between 3 and 4.

Figure 27: comparison of the relative quantity of energy released by a cell in the absence of air (1.6 times more than the amount of electrical energy stored) and with access to air (oxygen source) (up to 5.4 times the amount of electrical energy stored) according to (SCHARNER, 2018).

According to a recent report (Doughty, 2017), energy able to be released by a lithium ion accumulator measuring 240 $Wh.kg^{-1}$ is in the order of 2.5 $MJ.kg^{-1}$ (694 $Wh.kg^{-1}$). This represents 54 % of the releasable energy of TNT (4.61 $MJ.kg^{-1}$ or 1280 $Wh.kg^{-1}$). However, the liberation energy of this energy is essential to calculate the danger level.

If we consider non rechargeable lithium batteries (ones from alarm systems of DAE defibrillators), the energy available is considered as equivalent to that of TNT. (J. A. Jeevarajan & Winchester, 2012; J Jeevarajan, Duffield, Engg, Jung, & Park, 2013; Judith Jeevarajan, 2012)

To combat this type of fire, cooling is important to limit the propagation of thermal runaway for the neighbouring cells, but can also be desirable for reducing oxygen access.

ELECTRICAL RISK

Because of the intrinsic design of electrochemical energy storage systems, electrical risk must absolutely be considered as present, both throughout its lifecycle and also throughout emergency operations.

In particular, this risk is permanent because of the lack of possibility to cut of the current on the battery itself and on the output cables up to a circuit breaker switch. It is important to consider that:

- The current is direct between the storage and the UPS then alternating between the latter and the application or ENEDIS network to which it may be connected,
- Multiple and non-interruptible sources are also present following what may be encountered with solar panels.

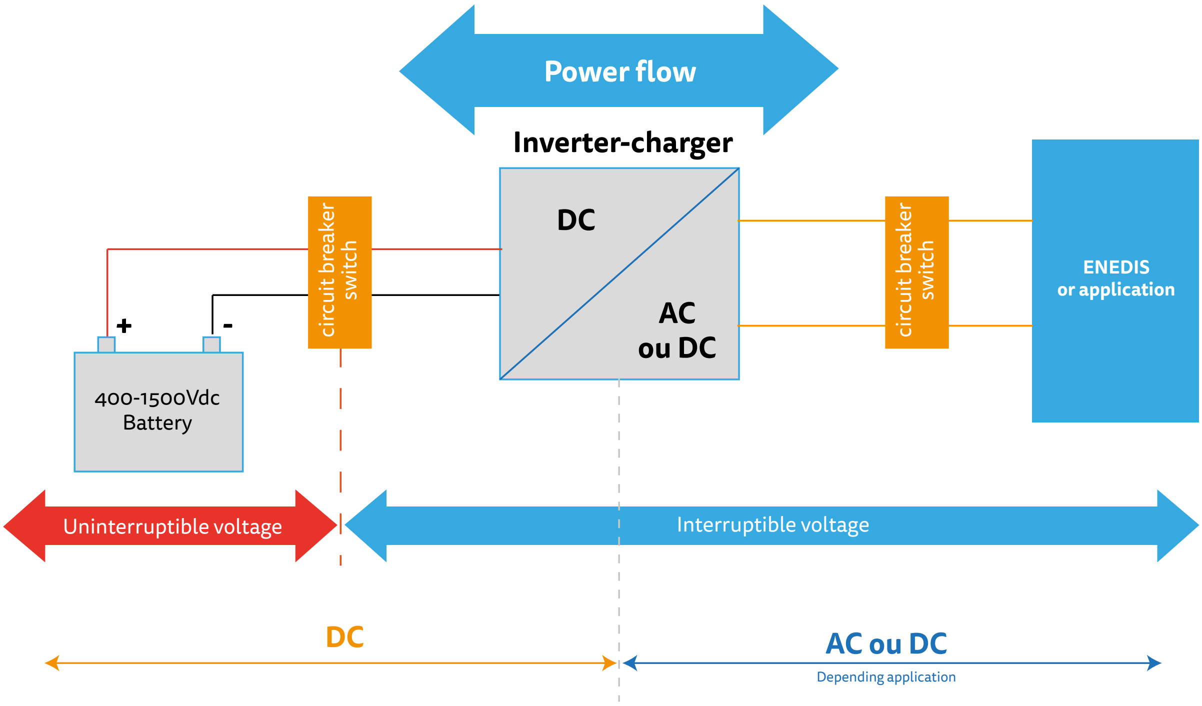


Figure 28: Operating diagram of an electrochemical storage system.

The electrocution risk for personnel operating must be also be considered as permanent in all situations as soon as there is a risk of loss of electrical insulation in the storage system. The risk of electric shock and damage (reversible or not) when an electrical current passes through the human body is possible through direct or indirect contact (running current through rod) and depends in particular on the strength of the current:

ALTERNATING ELECTRICAL CURRENT (mA)	EFFECTS
1	Tingling sensation
2	Light shock, no pain, no loss of muscle control
5-9	Painful shock, but no loss of muscle control
16	Intense shock (loss of muscle control, difficulty breathing)
20	Paralysis of breathing muscles
30	Asphyxiation possible
100	Cardiac arrest (ventricular fibrillation threshold) for 3s. Of shock
200	Cardiac arrest (ventricular fibrillation threshold) for 1s. Of shock
300	Breathing stopped
900	Severe burns
1500	Burns on internal organs

Figure 29: Table of effects of alternating Current (source: study report DRA-10-111085-11390D INERIS)

Note that the levels of effects of direct current are slightly higher than that of alternating current and that direct current inflicts deeper burns as well as an electrolysis reaction.

The risk of an arc flash appearing must also be considered as soon as there is an electrical current present. This reaction can occur in a variety of situations and especially when voltage and power levels are high, when the distance between an electrical source and a target is small or when the air humidity levels are high.

In particular an electrical arc can be produced by a short-circuit outside of a fire situation, for example when clearing out. The consequences of this reaction are considerable both for people (burns, flashes, electric shocks) as for property (electrical fires, explosions, short circuits physical or electronic damage).

Finally, a point that needs to be taken into consideration are the potential electromagnetic wave effects that could disturb and damage or nearby electrical equipment. This risk, proportional to the electrical current, intensity and power can potentially negatively affect emergency operations (radio transmission systems, telephones, sensor devices, drones, etc.).

TOXICITY RISK

The operation of an electrochemical energy storage system differs depending on the type of battery:

- The implementation of highly oxidising and reducing electrodes in contact with an inflammable organic electrolyte for Li-ion and LiPo batteries,
- The combination of lithium metal and a solid gel electrolyte for LMP batteries,
- The presence of highly corrosive chemical substances in electrolytes of NiMH batteries or super capacitors.

In all circumstances, it must be a priority to consider the toxicity risk through the operation for the COS. This risk may manifest in several ways:

❶ Fire fumes and particularly toxic decomposition products and composed notable of carbon dioxide (CO_2), carbon monoxide (CO), hydrochloric acid (HCM), nitrogen oxides (NO and NO_2) and sulphur dioxide (SO_2), hydrogen cyanide (HCN) and various hydrocarbons.

These fumes can appear during fires but also when electrolyte component is in thermal runaway,

In the literature, there is sometimes mention of SO_2(Williams & Back, 2014). Even if the origin of the sulphur composites is not necessarily well-known, this could originate amongst other from an additive, shrink wrap polymer shrouds, or seals. In the absence of a flame in an enclosed environment, the amounts of toxic gases, and in particular fluorinated compounds, can become problematic (Eshetu et al., 2014; Larsson, 2018; Larsson & Mellander, 2017) (Sun et al., 2016) In fact, this compound has high toxicity which manifests by causing immediate caustic burns on the skin and mucous membranes in contact that are often difficult to treat and can be fatal.

❷ Corrosiveness by cutaneous contact with the liquid electrolyte in case of casing rupture,

❸ Production of metal oxides (such as LI_2O or Li_2O_2) under the form of extremely fine particles that are susceptible to penetrating very deeply into the bronchial system.

Possible protective measures are detailed in chapters 4 and 5 of this report.

THERMAL RISK

Because of the presence of metal elements, heated electrolytes at high temperatures, plastics, electrochemical energy storage system fires are known for having high caloric potential.

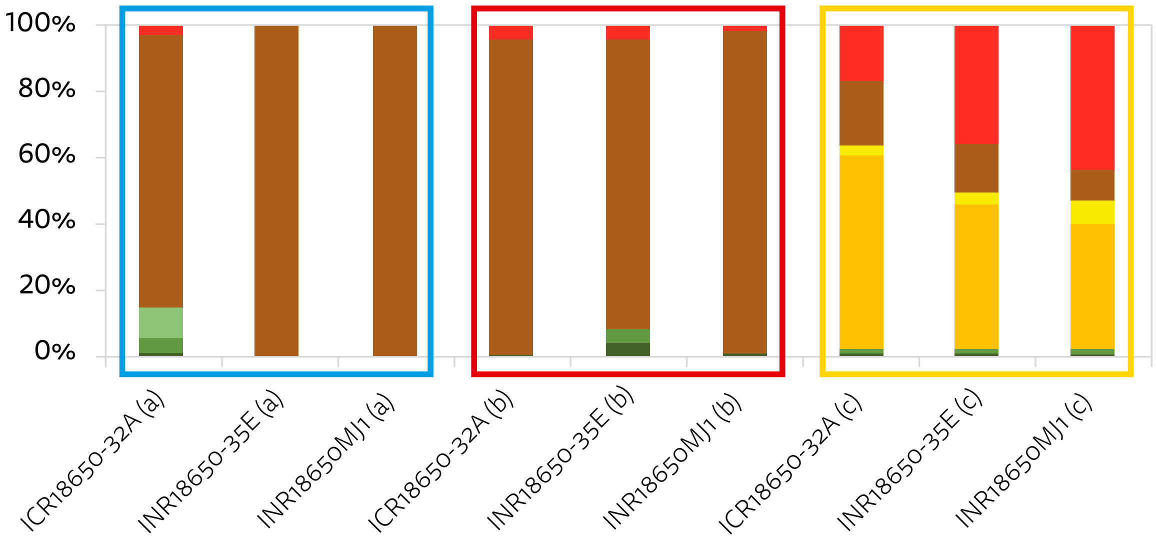
The very high combustion temperatures coupled with the potential presence of molten metals have the following consequences:

- Violent reaction phenomena with risks of fire propagation via convection, conduction and light emission (projection of fusion material),
- Burn risks for fire-fighters on-site because of the strong vaporisation of water fired from a variable flow cannon (distribution of water vapour) in contact with the metals,
- Intense light phenomena during generation of an arc flash or by emission of light rays because of the presence of molten metals,
- Risks of water electrolysis phenomena caused by short-circuiting the battery during extinction operations and notably is the case when handling a poorly managed immersion. This reaction depends nevertheless on the quantity of water in contact with the battery. The resulting risk is the generation of hydrogen and therefore an explosion risk.

The thermal decomposition of electrode, separator and electrolyte material can produce various gas compounds that of varying levels of reactivity. These reactive gases can than recombine and form other compounds.

The chemical composition of the gas mixture released when a Li-ion battery has a problem can be complex. This gas mixture is generally composed of CO_2, CO H_2, various hydrocarbons, (CH_4, C_2H_4, C_2H_6, etc.) with highly variable levels depending on the chemistry and cell and the type of event that is at the source of the problem. In fact, the work by Lammer et at. (Lammer & Alexander, 2017) Showed that the composition of the gaseous compound expelled by a battery cell is highly variable when a vent is opened, during a thermal runaway and in case of cell explosion.

As a result, the COS will have to consider the explosive risk throughout the operation.



Event	Device	Émission/ mmol	Émission/ cm^3	H_2/%	CO_2/%	CH_4/%	CO/%	C_2H_2/%	C_2H_4/%	C_2H_6/%
1st venting	ICR18650-32A	3.69	90.30	2.43	82.19	0.00	0.00	0.00	9.32	6.06
	INR18650-35E	6.20	151,70	0.00	100.00	0.00	0.00	0.00	0.00	0.00
	INR18650MJ1	1.64	40,10	0.00	100.00	0.00	0.00	0.00	0.00	0.00
Thermal runaway	ICR18650-32A	0.22	5.40	3.71	95.56	0.00	0.00	0.00	0.74	0.00
	INR18650-35E	0.00	0.00	3.87	87.24	0.00	0.00	0.00	4.20	4.70
	INR18650MJ1	0.24	5.80	0.87	98.06	0.00	0.00	0.00	1.07	0.00
Deflagration	ICR18650-32A	125.84	3078.80	15.94	20,40	2.50	58.41	0.22	2.44	0.09
	INR18650-35E	224.60	5494.90	35.65	14.50	3.66	44.00	0.14	1.95	0.06
	INR18650MJ1	215.03	5260.90	43.15	9.76	6.97	37.22	0.16	2.69	0.06

Figure 30: composition of gaseous mixtures detected on three battery cell references in three particular conditions (blue: excess pressure vent opening, red: thermal runaway, yellow: cell explosion).

This risk results in:

- Emission of hydrogen, a particularly explosive flammable gas. This gas can be produced on combustion or electrolysis or even by dissociation of water under the impact of heat. Remember that hydrogen has a wide explosivity range, 4-75%, at room temperature and atmospheric pressure and a very low minimal ignition energy (around 20µJ),
- "Traditional" smoke reactions in confined spaces (explosion of smoke) or semi-confined (flashover),
- Phenomena comparable to explosive electrolyte boiling that can lead to projection of flammable aerosols
- Violent reactions in case of crushing, perforation, impacts, overload or high temperature. This reaction can occur in particular when structures collapse on electrochemical energy storage systems.

Finally, the last parameter to include in thermal risks is thermal runaway. These phenomena can be initiated by several sources:

- Presence of electrodes, notably the positive electrode, which can become unstable at high temperatures (>200°C),
- Presence of solvents inside the electrolyte that have relatively high vapour pressures at moderate temperatures,
- Low capacity for the storage system to dissipate heat.

In fact, unusual and/or extreme usage conditions can lead to a considerable increase in temperature inside the storage system. In case enough of this heat cannot escape, the electrochemical energy storage system can lead to chain reactions that can accelerate and lead to a thermal runaway reaction.

This problem is reinforced by:

- Risk of delayed thermal runaway. Feedback shows that thermal runaway reactions that are dealt with several hours after an impact or a fire,
- The risk of thermal runaway generated, remotely, by a short-circuit on cables,
- The risk of maintaining the reaction by producing oxygen inside the storage unit, even in an enclosed space,
- Warning signs that are hard to spot (increase in temperature, increase in voltage, vibration waves)

As a consequence, considerable monitoring must be undertaken on an electrochemical energy storage system in case of emergency operation, if it has been subject to a fire or impacts. Possible protective measures are detailed in chapter 4 of this report.

PHYSICAL RISK

The physical risks are of two types:

- Risk of projecting solid or molten metal materials that could cause serious injury (burns) for people in proximity or to accelerate the fire propagation phenomena,
- The risk of missile effects due to fragmentation of storage system casings or projection of modules that could be ejected several metres causing serious injuries for people and emergency services around the storage system.

This risk will be taken into account by the COS depending on the site configuration. In fact, the batteries are often installed in a permanent case of cabinet, to theoretically limit this type of reaction. Possible protective measures are detailed in chapter 4 of this report.

ACCIDENTOLOGY

Using as a basis the ARIA database (Analysis, Research and Information on Accidents) supplied by the BARPI (Office for Industrial Risk and Pollution Analysis), the current report offers an insight into accidentology of recent years.

Evolution of accidentology

The study of accidentology was carried out on events (accidents or near accidents) reported to BARPI via emergency services, environment inspection, media, certain professional bodies as well as foreign correspondents. It cannot be confirmed that the study is exhaustive, but it nevertheless enables us to draw some conclusions and some points from feedback.

Also, since 1999, 76 events have been identified with a tendency towards increase since the start of the 2010s.

The progressive spread of commercial applications and better consideration of the lifecycle of electrochemical energy storage systems (notably regarding recycling) explains the tendency towards increases in accidentology.

Note that 92% of events studied occurred in France, against 8% abroad (United States, United Kingdom, Switzerland and Belgium).

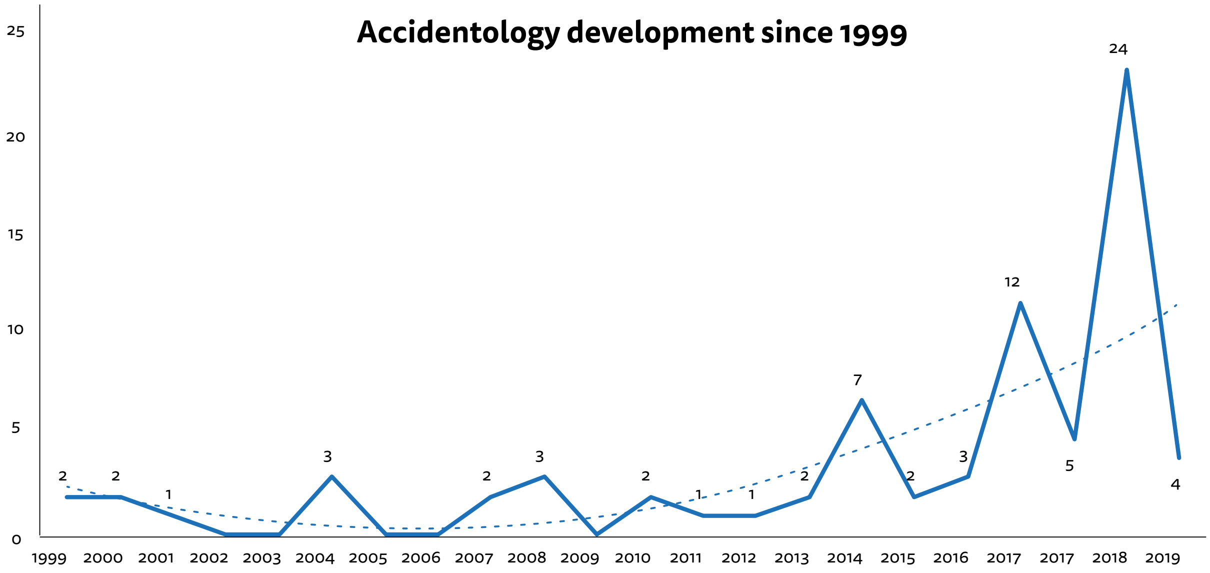


Figure 31: Accidentology development since 1999 and tendency curve (case study from BARPI with year 2020 incomplete).

Accidentology by sector and by origin

The study highlights the diversity of domains that can be faced with an accident. Most often (47%), it involves a treatment, recycling or battery disposal company, or companies in charge of recycling waste that are subject to accidents. For some of these companies, the discovery of a cells or batteries is lucky because the waste was not supposed to contain any. For others, the presence of cells or batteries was expected by the reprocessing methods (crushing, incineration) or storage conditions (mix of products, temperature) are the source of accidents. This is notably the case in companies in charge of disposal of electrical and electronic equipment (DEEE).

In second place (21%), are the companies in charge of manufacture, assembly or conditioning of batteries that are must prone to accidents.

Then comes the vehicle sector with 9% of events recorded since 1999.

More rarely, events occurred in research or test centres, in electrical distribution companies and in companies in charge of storage or sales or even in residential zones.

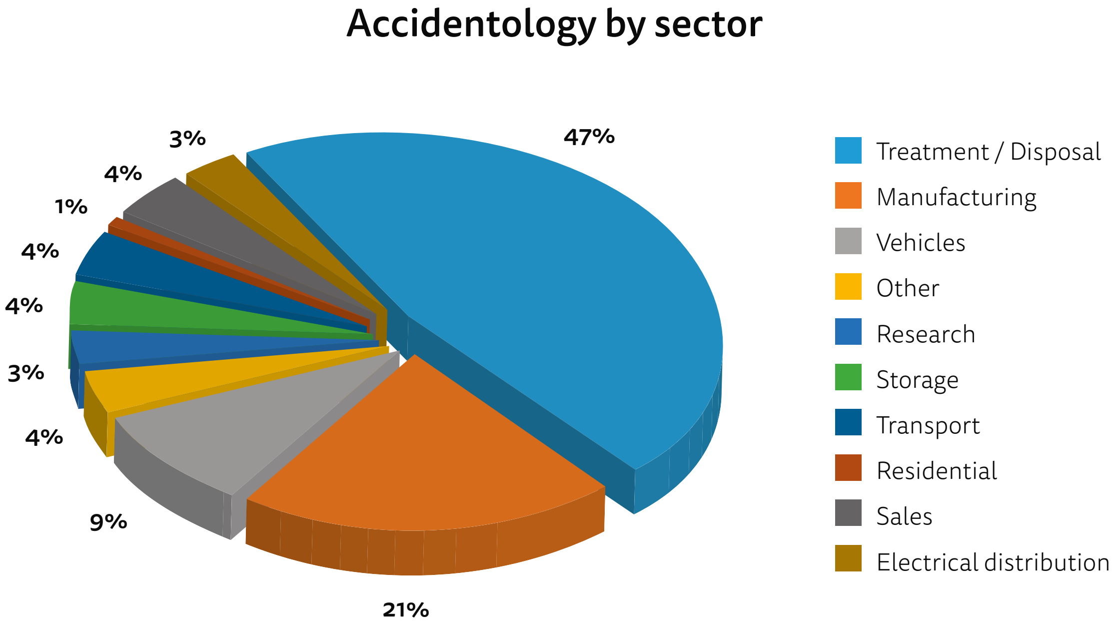


Figure 32: Accidentology by sector (1999-2020) (case studies from BARPI)

It is interesting to consider the events that initiated accidents in the varies case studies. In this case, a primary analysis highlights that the cause is not always known (45%). The first cause identified is electrical failure, more precisely the short-circuit at the origin of 22% of accidents. Secondly, there are the physical constraints (impacts, shocks, crushing and perforation) that are responsible for 14% of accidents. To a lesser extent, the following origins have able to be identified:

- Heating or subjection to a high temperature (either because of poor storage or incorrect usage or because of the presence of a fire close by): 7%,
- Manufacturing fault: 5%,
- Presence of a damaged battery because of an older event: 3%.

Amongst the other events that initiated accidents, we note poor storage or even incorrect handling (4%).

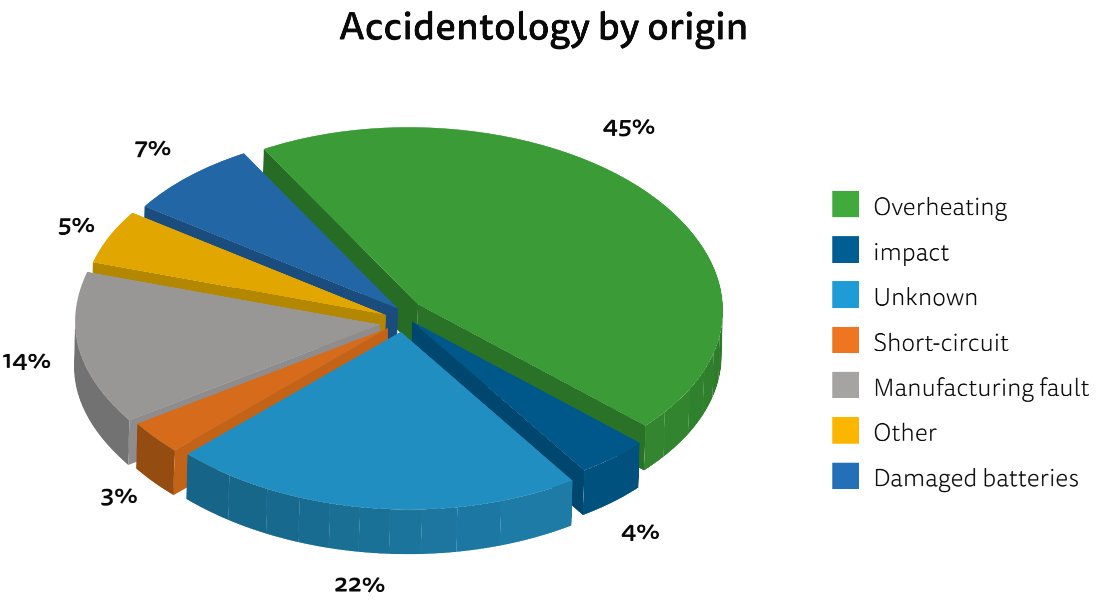


Figure 33: Accidentology by origin (case studies from BARPI)

Accidentology according to quantities involved

The totality of the events studied concerns lithium electrochemical energy storage systems Two cases can report the use of the Lithium Metal Polymer. One case alone specifies the use of a primary lithium chemistry (thionyl chloride). A recent case mentions a mixture of several technologies (nickel-cadmium and nickel metal).

The quantities at stake can be highly variable from a single cell up to volumes of 500m^3. When the battery volume is identified, they are distributed mainly (29%) into the under 10kWh category then equally amongst the two other categories listed: around 100kWh (16%) and over 1000kWh (14%).

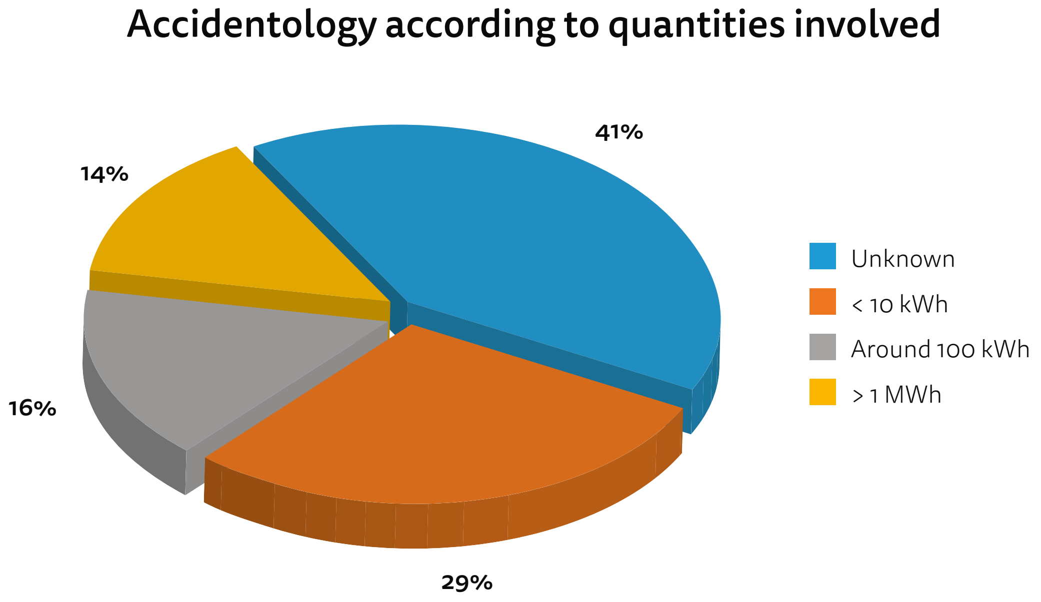


Figure 34: Accidentology according to quantities involved (case studies from BARPI)

Accidentology according to effects and consequences

The study of the effects of different accident situations is particularly interesting and should be linked with the characterisation of risks described in the current report. 91% of accidents are the source of a fire and 25% are the source of a fire accompanied by explosions. Only 5% of accidents result in an explosion or violent thermal runaway not followed by a fire.

Large explosions have notably been felt during two events. This is the case in the USA during the explosion on 23/04/2017 (BARPI n°49589) of a train carriage carrying "used lithium-ion batteries" where the pressure wave was "felt 2km away" and where "residential buildings were damaged [...] 100m away from the accident" (broken windows and cracks in the walls.

This was also the case on 19/04/2019 (BARPI n° 54822) during the explosion of a 2MWh "electricity storage container" with 8 fire-fighters and 1 policeman injured of which 4 were seriously injured. The phenomenology of this event is particularly interesting. In fact, the fire that started on a Li-ion module was put out "by the automatic extinction module of the system". Nevertheless, the gases generated by the fire and/or the ones following the electrolyte liberation during the thermal runaway with the help of oxygen when the teams entered the container brought together all the conditions necessary for an explosion. This accident shows the challenge of controlling fumes in case of automatic extinction (by inerting for example). Even when cold, these fumes keep their explosivity potential. They are characterised by their colour: white; their density: thick and opaque, and their behaviour: when cold, they spread across the floor and condense easily.

Fume toxicity has been observed in almost half of all cases (46%) and pollution of extinction water in 13% of events. Note that regarding water pollution, the operators were not systematically aware nor were they of the retention systems in certain establishments contributes to limiting the occurrence.

The event of 08/10/2019 (BARPI n° 54498) in the Lyon metropolitan region, is interesting as regards the impact in terms of fume toxicity. The widespread fire in a 10,000m^2 building holding a company specialised in "reconditioning lithium bike batteries" and the presence of a "thick cloud of black smoke" highlight the presence of a number of pollutants ("ammonia, hydrochloric acid, sulphuric acid, chlorine, carbon monoxide, nitrogen monoxide and hydrogen cyanide") without any toxicity thresholds having been exceeded. Additionally, the analyse by the regional air quality monitoring association notes an increase in the concentration of particles 'sulphur dioxide and nitrogen dioxide") without "the recommended threshold of 50µg/m^3 daily average having been exceeded". It is the same situation pour other pollutants: sulphur dioxide, nitrogen dioxide, ammonia as well as for the volatile organic compounds.

In terms of effects, the even from 26/08/2010 (BARPI n° 38858) that occurred in Moselle, Eastern France during the fire of 20 tonnes of batteries resulted in:

- *Examination by 14 people in contact with the toxic fumes that contained notably nitrogen dioxide, hydrochloric acid and sulphuric acid,*
- *The destruction of a 1000m^2 building with parts of battery being launched up to 200m from the accident location,*
- *The creation of 2000m^3 of extinction water where the presence of heavy metals, phenols and PCB will be shown.*

BARPI studies the consequences of an accident according to 4 criteria:

- The impact in terms of pollution (air or fluid): 78% of cases,
- The impacts on human health: 24% of cases,
- The impact on the environment: 8% of cases,
- The economic impact: 4% of cases.

Accidentology according to extinction methods implemented

Only 12 events (16%) do not specify which extinction method was used. In the other cases, the use of water was the most frequent in 77% of cases. Water is used with another extinction method in 12.5% of cases, and the battery ends up being completely submerged in 14% of situations encountered.

This is notably the case during a 7kWh battery fire (BARPI n° 54573) in a company specialising in the manufacture of batteries and electrical accumulators where the extinction was started "by employees before the emergency services arrived using a fire extinguisher, then a hydrant" before finally being extinguished by being immersed "by a 50m^3 tank".

This study highlights the importance of using water by emergency services teams or the fire-fighters and its effectiveness in fighting fires.
Other extinction agents were used depending on the situation. This is notably the case for powder (14%), foam (11%), sand or an absorbent material (9%), or even cement (3%).

The event of 26/08/2010 (BARPI n° 68858), mentioned above, shows difficulties in extinguishing an electrochemical energy storage system. In this case, the fire concerns 20t of used lithium batteries in a storage and sorting part of the building for a battery and accumulator recycling centre". Despite the early implementation of an automatic powder extinction method, the fire spread. In the end it would take "6 water hoses, 3 canons and 60 fire-fighters" to extinguish the fire "after a 4-hour operation".

CLASSIFICATION OF RISK

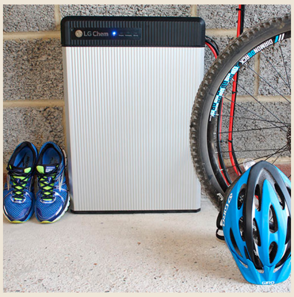
Considering the ability to identify the type of electrochemical energy storage system early on is a concern for operators, the following tables provide the key information in order to quickly understand which risks the emergency response team will be faced with.

The following table makes it possible to deduce the maximum electrical power of a storage system according to its dimensions and the type of usage:

VOLUME / WEIGHT	ELECTRICAL POWER	USAGE TYPE
50 L / 100 kg	10 kWh (10 000 Wh)	Residentiel
500 L / 1 000 kg	100 kWh (100 000 Wh)	Tertiary
5 000 L / 10 000 kg	1 MWh (1 000 000 Wh)	Data center / factory

The following table makes it possible for a given Lithium-ion technology type, according to the electrical power and the application type, to find out whether there is a possibility of a storage system:

Li-ion	10 kWh	100 kWh	1 MWh
UPS – Uninterruptible Power Supply	YES (residential)  www.tesla.com/fr_FR/powerwall 13,5 kWh (1150 x 755 x 155 mm), 125 kg	YES (tertiary)  www.apc.com/salestools/ACOS-AD4M5V/ACOS-AD4M5V_R2_EN.pdf 25 - 35 kWh (2055 x 650 x 600mm), 480 kg	YES (data center/factory)  www.connaissancedesenergies.org/un-data-center-connecte-des-batteries-usagees-de-voitures-electriques-220218 30 x 24 kWh

Solar storage system	YES (residential)  www.ikea.com/gb/en/ikea/solar-panels 3,3 à 6,5 kWh (452 x 654 x 120 mm), 52 kg	YES (tertiary)  https://tribuca.net/entreprises_25326075-une-entreprise-azureenne-devient-partenaire-de-tesla 210 kWh (1308 x 8220 x 2185 mm), 1622 kg	YES (data center/factory)  https://alfen.com/fr/Syst%C3%A8me-de-stockage-de-%C3%A9nergie 2 MWh (40' container), 28,7 t
SCRPU – Storage connects to Power Utility Network	YES (residential)  www.avem.fr/actualite-xstorage-home-le-stockage-domestique-de-lenergie-propose-par-nissan-disponible-en-france-6317.html 9,6 kWh 10 kg	YES (tertiary)  www.swarco.com/apt/Products-Services/Battery-Energy-Storage/E-STOR 66 - 110 kWh (3,1 x 2,25 x 2,26 m), 100 kg	YES (data center/factory)  www.eqmagpro.com/kokam-to-build-36-megawatt-energy-storage-system-ess-for-kepco-increasing-its-total-worldwide-ess-project-portfolio-to-132-megawatts-2/ ... MWh (Multi containers)
Parked car	YES (hybrid)	YES (electric)	
SCRR – Storage connects to Residential Network	YES (residential)  www.avem.fr/actualite-xstorage-home-le-stockage-domestique-de-lenergie-propose-par-nissan-disponible-en-france-6317.html 9,6 kWh 10 kg		
Portable equipment	YES (residential)		
Cosphi correction			

The following matrix proposes the creation of a link between the risk level and the storage system chemistry, for maximum critical application volume. The colour code allows you to judge the criticality for different types of risks. GREEN means that there is not much risk or that the identification of risk is easy, ORANGE means moderate and RED means critical or difficult:

	Identification	Electrical	Toxic	Thermal	Explosive	Runaway	Physical
Primary Li-metal	Easy	Low	Moderat	Low	Moderat	Moderat	High
Li-ion Sodium-ion	Difficult	High	High	High	High	High	High
Li-metal	Difficult	High	High	High	High	High	High
Open (Pb)	Difficult	High	Low	Undefined	High	Low	Low
Sealed (Pb, Ni)	Difficult	High	Low	Moderat	High	Low	Moderat
Super capacitor	Easy	High	High	High	Low	Low	High

The following matrix proposes the establishment of a link between the danger level and the occurrence depending on the type of storage system chemistry, size being equal:

Danger level Occurrence	Danger level low	Danger level moderate	Danger level high
Rare	Super capacitor	Open (Pb) Li-metal	
Moderately frequent			Primary Li-metal
Frequent	Sealed (Pb, Ni)	Li-ion	

The following matrix proposes the establishment of a link between the danger level and the occurrence depending on the type of application:

Danger level Occurrence	Danger level low	Danger level moderate	Danger level high
Rare		SCRR	UPS (> 400 kVA) SRCPU
Moderately frequent	Cosphi correction	Solar storage system	Parked car
Frequent	UPS (< 100 VA) Portable equipment (Regarding only electrical context)	Parked car	

SOURCES

- Fire and extinction test series on electrochemical energy storage systems 2018/2019 - CEA / INES / SDIS73 / SDMIS / SDIS38 / ELEKTEK / ACCUWATT / SNAM
- Study report DRA-10-111085-11390D relating to approaches to controlling risks specific to the electric vehicle sector - INERIS
- Comparison of the fire consequences of an electric vehicle and an internal combustion engine vehicle – Amandine LECOCQ
- Preliminary report highway HWY18FH013 – National Transportation Safety Board
- Flammability and explosivity of hydrogen - INERIS / AFHPC

SUMMARY OF RISKS AND ACCIDENTOLOGY

This analysis of risks has made it possible, according to the literature and the expertise of the members of the GT, to define a set of risks that are likely to be encountered by operators in an extreme situation on an electrochemical energy storage system.

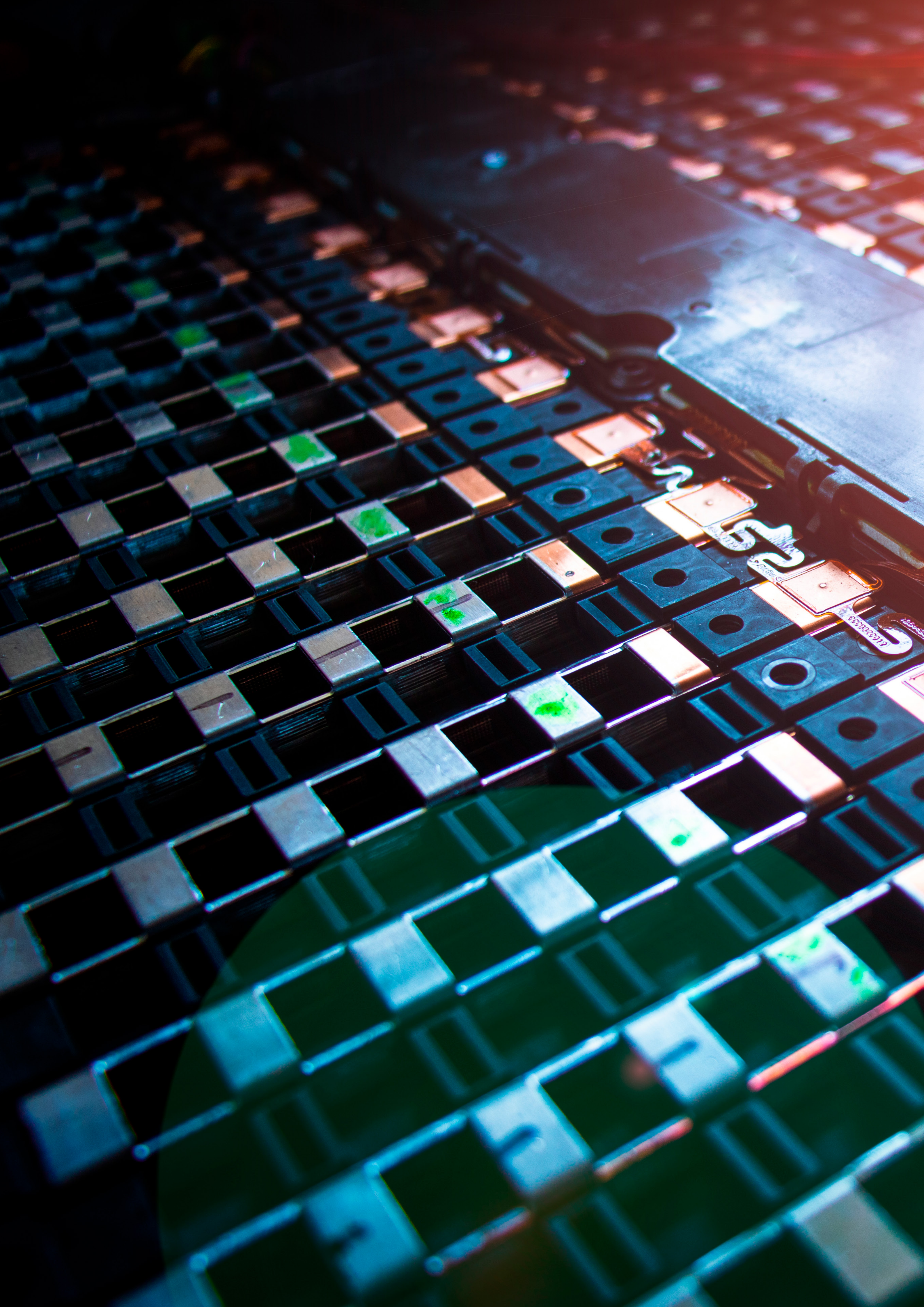
The main risks are:

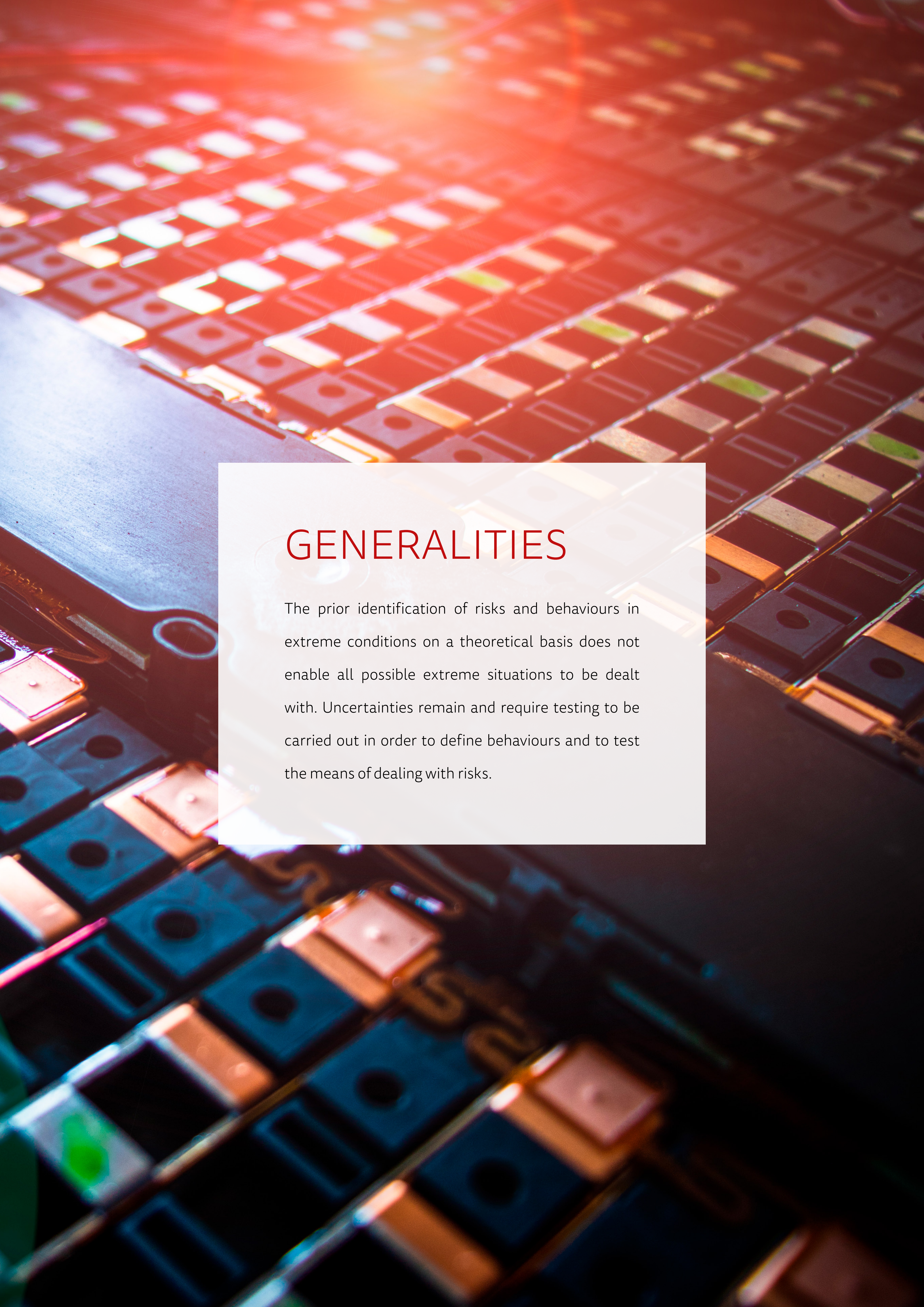
- The risk of failing to identify the presence of a storage system by first responders
- The electrical risk present throughout the duration of the operation, including and especially during the clearing phase
- The thermal risk that is characterised by several phenomena:
  - Conduction
  - Convection
  - Radiation
  - Metal fusion temperatures reached in the core of the cells
  - Thermal phenomena linked to fumes:
    - Fume explosions in enclosed spaces
    - Flashover in semi-enclosed spaces
- Explosion or explosive pressure wave risk
- Toxicity risk:
  - Toxic fumes
  - Materials (soot, electrolyte deposits)
- Physical risk of launched battery parts

Additionally, the study lead on accidentology shows clearly that accidents exist and are likely to significantly increase in frequency confirming the usefulness of the approach carried out here.

3

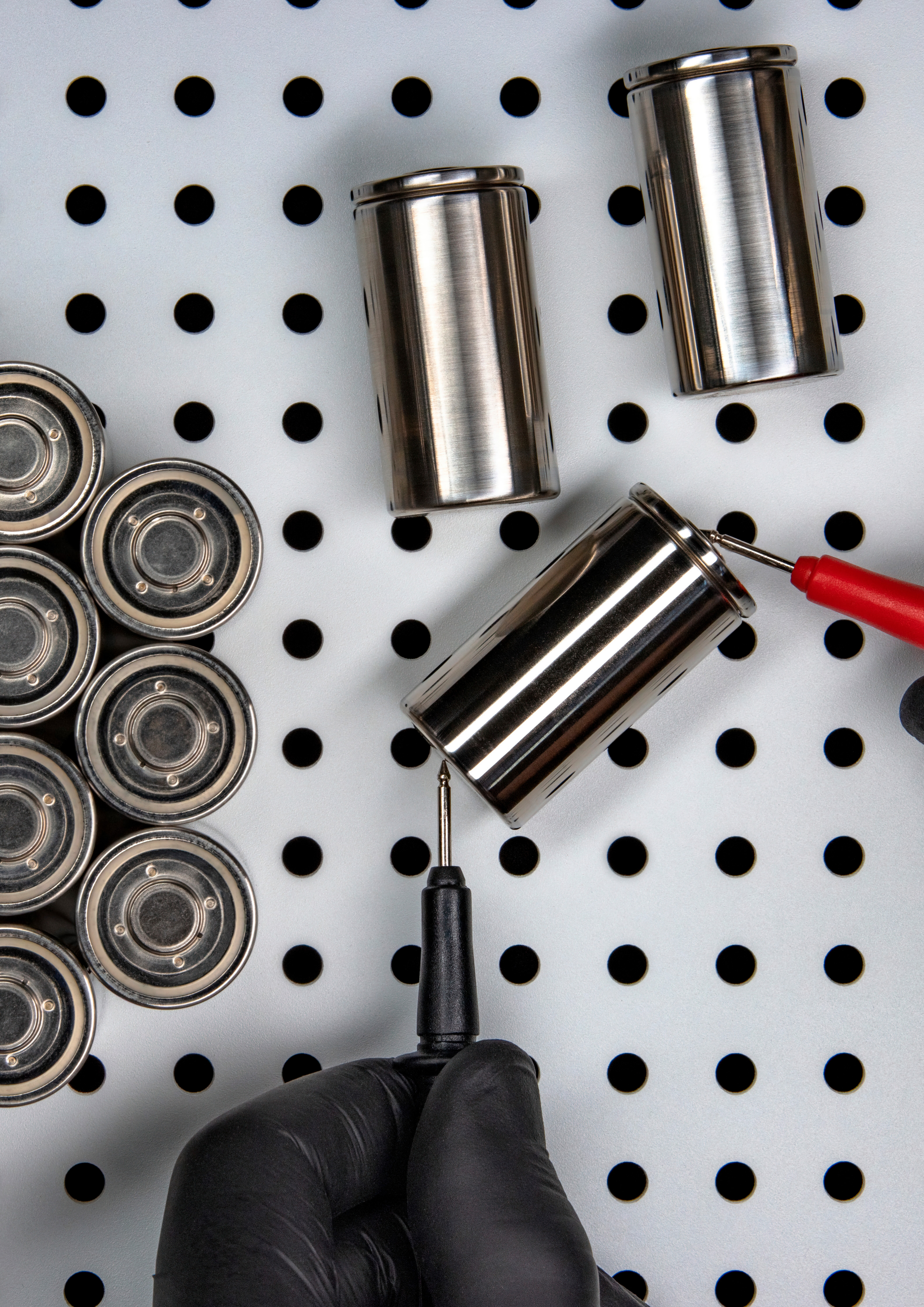
TESTS:
CONDITIONS AND LIMITS





GENERALITIES

The prior identification of risks and behaviours in extreme conditions on a theoretical basis does not enable all possible extreme situations to be dealt with. Uncertainties remain and require testing to be carried out in order to define behaviours and to test the means of dealing with risks.



TEST OBJECTIVES

CHAPTER OBJECTIVES

The results of the tests are set out in this chapter, their interpretation is given in chapter 4 discussing the points to consider on operational actions. This part makes it possible to give an overview on the test conditions and the associated limitations. The tests must make it possible to deal with the subsistent questions following analysis already carried out regarding expertise, analysis of risks, feedback and the bibliography. The risks identified must be confirmed or discounted during the test series.

This experimental phase has two main objectives:

- To identify the phenomenology of risks in order to understand the influencing parameters and understand how they are involved
- To identify and define accident situations
- To find operational situations at risk for emergency services
- To find operational means and techniques to deal with risk(s).

The phenomenology is characterised notably by the following points during these tests:

- Identification of the influence of cell technology on the risks
- Understanding of thermal runaway and its triggers
- Observation of the externalisation of the thermal runaway energy: projections, missile effects, explosions, fumes, etc.
- Analysis of gases, fluid or solid substances and fumes escaping from the battery during various phases of thermal runaway and combustion (mass spectrometry: Detection, Identification and Sampling Vehicle: VDIP)
- Find the scale factors (thermal, toxicity, projections, etc.) depending on the size of the battery
- Analysis of the impact of the charge status on the reaction

The thermal runaway can be generated by a number of accident situations. The situations identified are the following:

- Crushing: opposite operational situation: collapse of a battery onto a battery unit
- Intense thermal radiation: battery subject to intense radiation from a close by fire
- In flames: battery taken by a fire: analysis of the extra caloric power generated by the battery
- Thermal conduction: battery subject to intense temperatures by thermal conduction on a lower floor or adjacent room, spread from one cell to another in a pack
- Battery overload: BMS failure leading to an intense overload
- Short-circuit: consequence of a physical impact, or human error in manipulation

The operational situations at risk selected for these tests are the following:

- Water behaviour: lithium
- Flammability of fumes
- Behaviour in enclosed environment: explosive phenomena, toxicity, effectiveness of cooling actions
- Dephasing of the reaction - instability through time
- Missile effects
- Fume toxicity, projections, etc.
- Spread

Finally, the last test phase concerns the search for operational means and techniques to deal with risk, and most particularly:

- The cooling effects of water: spraying (LDV), immersion
- The effects of dry inerting methods: cement, powder, sand (wet here)
- The cooling effects of inerting: CO2
- The effects of confinement: tarpaulin, water bell

CONDITIONS AND TEST LIMITS

Battery dimensions and scale factors

The batteries, modules or cells used have made it possible to carry out 5 test series from 2018 to 2020. For certain repetitive tests, it was decided to work with identical modules of roughly 500Wh in NMC technology. Individual NMC cells were also used for the radiation , scale factor, thermal conduction and missile conduction effects tests.

Larger cells, such as rigid prismatic cells, LEV50 or LEV75 were used for the overload test, fume explosion, confinement and large-scale extinction tests.

The tests were therefore not carried out totally at scale level 1 or a scale representative of applications cases of stationary storage or by volume of tests performed and so the quantity of batteries that it would necessitate. Nevertheless, it was judged that the effects observed make it possible to confirm, according to the type of test considered, that the results are representative of probable events.

It is highlighted here that the totality of the tests carried out here enabled us to work with roughly 600kWh of batteries of different technologies and sizes thanks to partners engaged in this GT.

Reproducibility

For the same reasons of limitation of quantities of batteries available, the results observed do not allow us to give statistics concerning the probability of observing a particular reaction. The sampling was not sufficient. The test conditions, mainly in open environments, did not give great reproducibility from one test to another. The numerous parameters influencing the behaviour were not all controlled and so it is difficult to predict the reproducibility of a test and the behaviour observed. Nevertheless, here again it is considered that a reaction observed becomes an observable reaction in an accident situation.

The parameters able to influence the behaviour or results of tests have 3 parts:

- The specifications and the state of the battery during the tests: charge level, storage temperature, state of wear and actual capacity (SOH).
- The external atmospheric conditions: humidity, temperature, wind that influences notably the battery storage temperature and the behaviour of the fire system
- The fire system:
  - The fuel: quantity, type and humidity
  - The combustive: quantity: management of openings in an enclosed space, influence of the wind
  - The power of the fire: linked to the atmospheric parameters, to the combustive and to the fuel

As the tests were carried out outside and over a period of several days, it was difficult to obtain frequent reproducibility.

Representativity of tests

The tests are representative and valid in the conditions in which they were carried out. The situations observed here and subject to recommendations in the following chapters were deduce from the tests carried out but also from the studies performed in the previous chapters. These tests, performed in an open and free space with minimal restrictions, nevertheless enables us to observe phenomena that would occur in a real situation because of the protocols used. These remarkable phenomena enable us to consider certain types of conduct to uphold.

MAIN RESULTS AND TEST SUMMARY

The given objectives were attained in the sense that the phenomena been searched for or expected during analysis were observed. All of the measurements or tests scheduled were able to be carried out.

The most characteristic phenomena observed were:

- The missile effects on unpackaged cells
- The projection of fumes and electrolyte
- The effect of charge state: the higher the batteries were charge the large the thermal runaway reaction was
- The effect of confinement of fumes on the risk of deviation towards an explosion reaction
- The flammability of hot or cold fumes: particular vigilance is needed concerning the cold fumes that are particularly flammable
- The large amounts of fumes and the toxicity risk associated notably in enclosed spaces
- The chain reaction spreading from cell to cell and generating a long fire, the duration of which is hard to determine

The operational test phase enabled us to determine several types of extinction methods:

- Water: Variable Flow Hose at 500L/min for high-capacity batteries: 30 at 40kWh, Hose on Rotating Reel for smaller packs: 100 to 1000Wh with variable flow.
- Water with additive: Foam with variable flow hose, extinguisher.
- Powders
- CO2
- Sand
- Tarpaulins

The tests made it possible:

- To understand the different phenomena that may be faced by the emergency services in an extreme situation with lithium-ion batteries
- To analyse the toxicity of fire residue and more particularly the fumes and projections
- To evaluate the effectiveness of different ways to fight against the fire or overheating
- To place operational bases enabling the implementation of operation techniques or prevention systems
- To research early warning signs of phenomena being researched

Detailed results are given in chapter 3.5. They mainly focus on the measurements taken and the VDIP reports. The results interpreted, with a particular importance for the management of emergency services operations for the prevention of risks, are developed in chapter 4.

The conduct to maintain recommended in the following paragraphs constitute direct interpretation of the phenomena observed during trials, enriched with the expertise of participants and analyses focused on the previously chapters of this document.

EQUIPMENT

The equipment implemented during these tests are the following:

Fire equipment:

- Tonne pump truck with standard setup: LDT and LDV 500, foam hose
- Extinguishers: powders, water with additive, CO2
- Extinction cover
- Sand

Recording equipment:

- Drones equipped with classic imaging cameras and infrared cameras
- Reflex photo capture devices
- Mini sport cameras (GoPro)
- Thermal camera

Measurement equipment:

- Temperature and voltage measurement units
- VDIP equipment
- VDIP sensors: CO, methane, COV, explosimeters...
- VDIP definition equipment: mass spectrometer

Battery equipment:

- 6 tonnes of batteries in total over different technologies but mainly NMC for the most critical tests: prismatic cells, cylindrical cells such as 18650 and modules.

TECHNICAL AND SCIENTIFIC RESULTS FROM TESTS

Increase tests - scale factor

Objective of this test

The objective of this test is to show the difference in reactive when the scale factor increases. For this we are going to create a thermal runaway on a group of cells the number of which will vary in order to observe the differences in behaviour.

Test context

In order to observe the maximum reactivity all the cells were beforehand charged to 100% following the protocol defined by the manufacturer.
The cells were subject to the same thermal flow and were not subject directly to a flame.

Only the negative pole of the cells will be in direct contact the metal plate serving as the thermal conductor. The goal of this not to restrict the opening of the cell safety vents.

The cells are not electrically connected, the activation energy will only come from the heat source and the energy released by one or several neighbouring cells.

Architecture of cell groups

The cells are assembled according to the diagram below. These are assembled with a metal collar in order to keep them together during thermal runaway. In order to monitor the temperatures during thermal runaway we have placed 3 type K thermocouples in different places:

- One above a cell vent at roughly 2cm.
- One above a cell vent at roughly 7cm.
- One at the centre of the cell group.

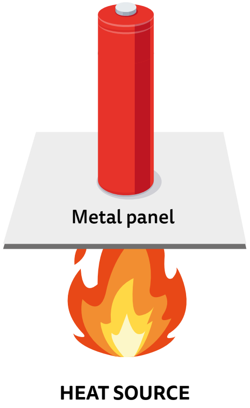


Figure 35: Heating operating diagram to provoke a thermal runaway.

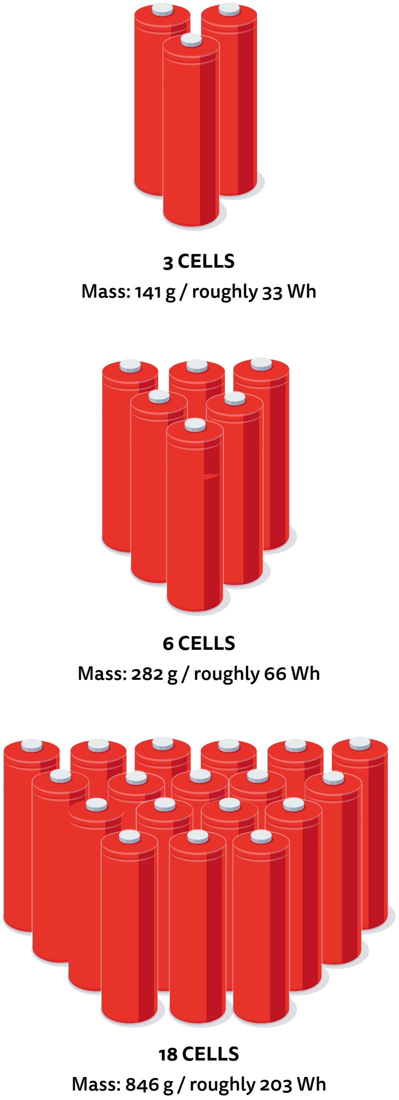


Figure 36: Cell assembly diagram.

Test results

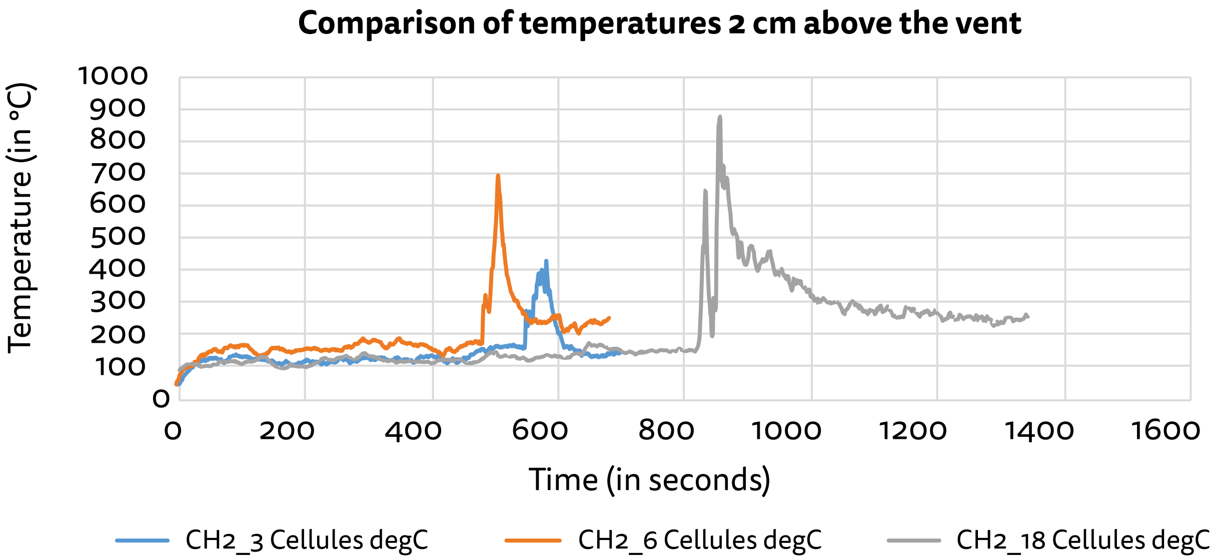


Figure 37: Development of temperature measured 2cm above a vent.

x 6

x 2　x 3

	3 cells	6 cells	18 cells
Maximum temperature	434.7	694.8	888.2

x 1.59　x 1.27

x 2.04

OBSERVATIONS

- We did in fact observe a scale factor on the temperature measurements.
- Theoretically this scale factor is not proportional to the increase in number of cells.
- The violent variations in temperature are due to successive thermal runaways and therefore to a projection of flames and molten material.

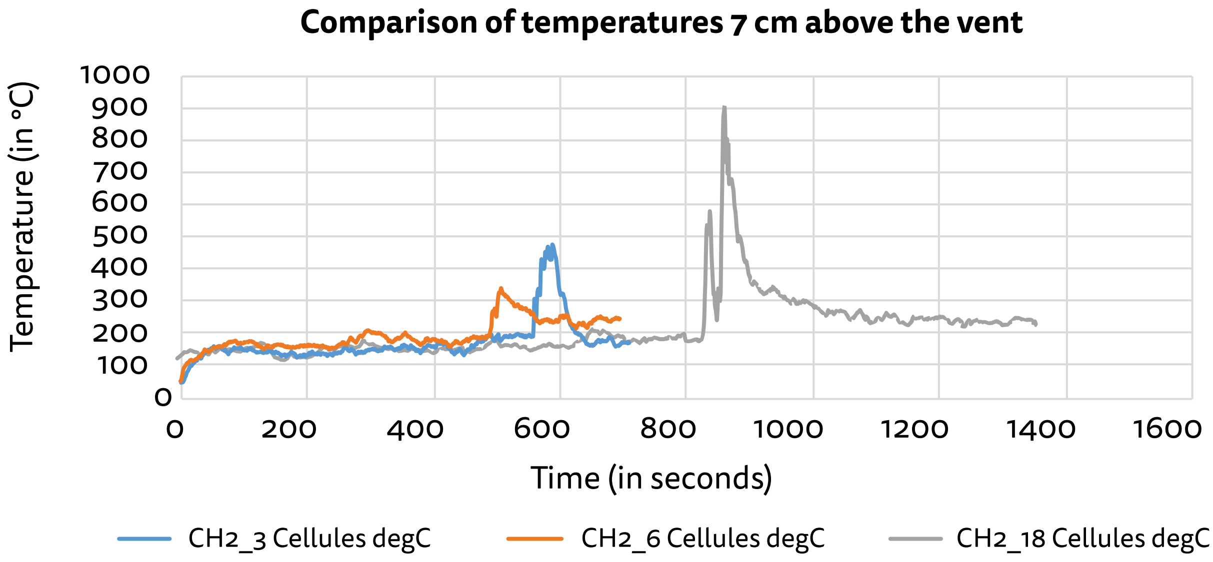


Figure 38: Development of temperature measured 7cm above a vent.

x 6

x 2 x 3

	3 cells	6 cells	18 cells
Maximum temperature	420.1	296.6	815.7

0.7 x 2.7

x 1.94

OBSERVATIONS

- The 6-cell module is the least reactive of the 3 modules. Given the distance of the measurement, it is possible that the thermocouple was not positioned facing the cells.
- The behaviour of the 18-cell module temperature at 7cm is almost identical to the measurement at 2cm.
- The successive thermal runaways are also observable in this case.

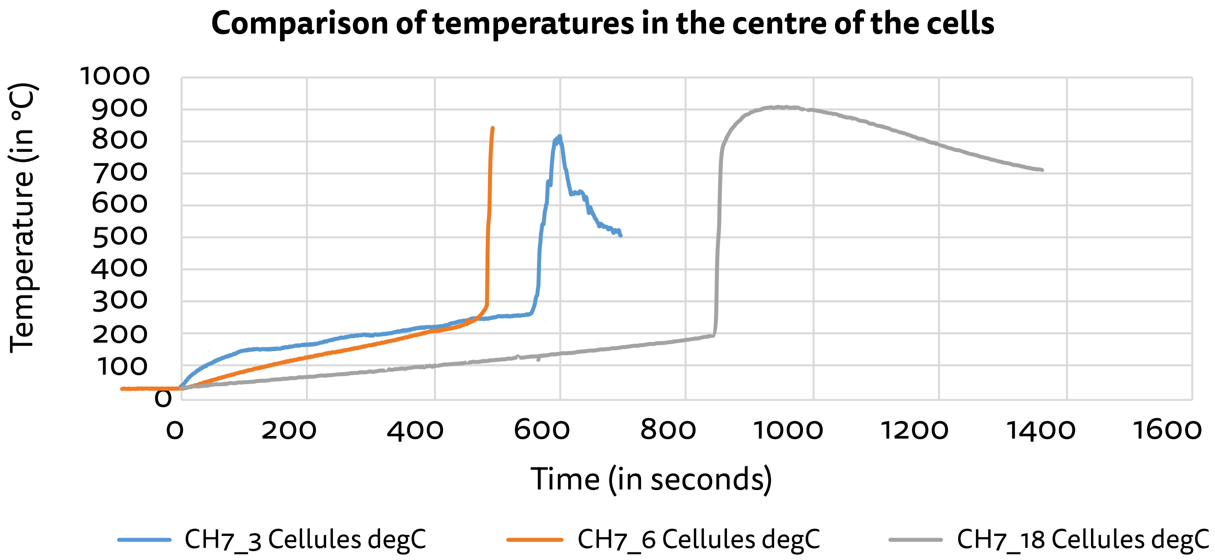
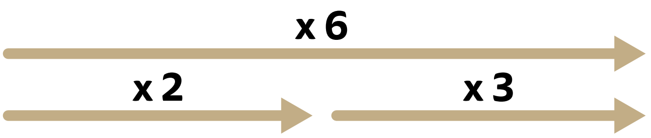
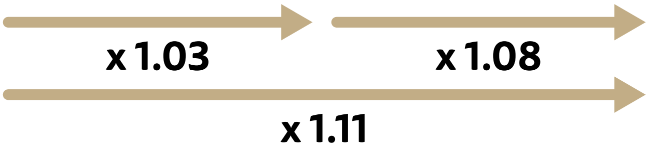


Figure 39: Development of temperature measured in the centre of the cells.



	3 cells	6 cells	18 cells
Maximum temperature	733.8	755.9	819.4



OBSERVATIONS

- We observed the breakage of a 6-cell module thermocouple due to the intense heat of the reaction.
- The thermal inertia of the module is clearly visible in this case because the temperature decreases very slowly for the 18-cell module.

Photos of cells after testing

The photos above show the result of different tests. We can first note that the reactions are quite similar on the 3 tests.

On the 3 tests, we can observe one of the cells open and ejected a coil (copper and aluminium sheets that make up the cell), we see very clearly the copper on the photos, though the aluminium is less visible, it possible that it was consumed by the intense heat of the reaction.

On all the photos we can also observe melted aluminium beads on the vents of the positive terminals of the cells which shows the intense heat of the reaction. The fusion temperature of aluminium is around 660°C, so we can assume that the temperatures reached during reaction are above that of this fusion temperature.

Finally, we also notice that all the casings of the cells remained intact. We observed no rupture in the packaging or any explosion of this either. The reactions observed all occurred on the positive terminals (which seems normal because of the packaging design there is only a vent on the negative terminal), the deformed negative terminals for certain ones still remained sealed.

Comparison of 2 different chemistries

Objective of this test

The objective of this test is to show the difference sin behaviour between Li-ion cells with different chemistry in the face of the same type of attack (thermal attack in this particular case).

To highlight the differences in behaviour we have chosen:

- 5 cells with LFP chemistry known for being very unreactive and quite safe.
- 5 cells with NMC chemistry more dense in capacity but also much more reactive.

Test context

In order to observe the maximum reactivity all the cells were beforehand charged to 100% following the protocol defined by the manufacturer.

The cells are places at the opening of a metal box in which a fire is lit in order to simulate a thermal attack.

The 2 tests allowing for the comparison of the reactions were carried out successively in order to ensure the same strength of attack for each.

In practice the thermal flow was slightly lower for the second test.

We chose to start with the LFP cell because this chemistry is less reactive so a larger thermal flow would be needed for thermal runaway.

The excess pressure cell vents were place in the direction of the box opening.

Test results

The following 2 curves show the development in temperatures during a thermal attack.

The two curves above show us the differences in behaviour when faced with a thermal attack on Li-ion cells with different chemistries.

Looking at the different curves we understand very well why the LFP chemistry is known for being very safe and unreactive, in fact it is hard to detect the thermal runaway of the group of cells. However, we noted that around 1700 seconds there was a rapid increase in temperature from 100°C to 200°C, which stabilised around this temperature. We can therefore consider that from this time on there was a thermal runaway. Because of the low reactivity of the chemistry it is difficult to show the reaction of thermal runaway, especially since we didn't notice and gas ejections or flames when the temperature increased.

On the second curve we can see the same test carried out on a group of NMC cells. We immediately notice higher reactivity for this chemistry (NMC), in fact the thermal runaway point is clearly visible with a violent increase in temperature of 400°C in less than 30 seconds. The reaction observed is very violent with ejections of hot gas, projections of molten material, flames. Also there were no warning signs allowing us to anticipate the intensity of the reaction.

The drop in temperature observed just after the reaction is only due to the thermocouple of the cells tearing away because of the intensity of the reaction.

Finally, we could believe that the LFP chemist is more reactive than the NMC because as we previously mentioned we observed a jumped from 100°C which is lower than the thermal runaway observed from 200°C for NMC, however, as we showed in the first paragraph the heat used for the thermal attack was greater for the first test and so as the cells were located at the bottom of this box, they were positioned in the air intake stream of the fire, however, by loving at the ambient temperature behind the cells, the radiation was much more intense at the end of the test for the LFP cells (cf curves below).

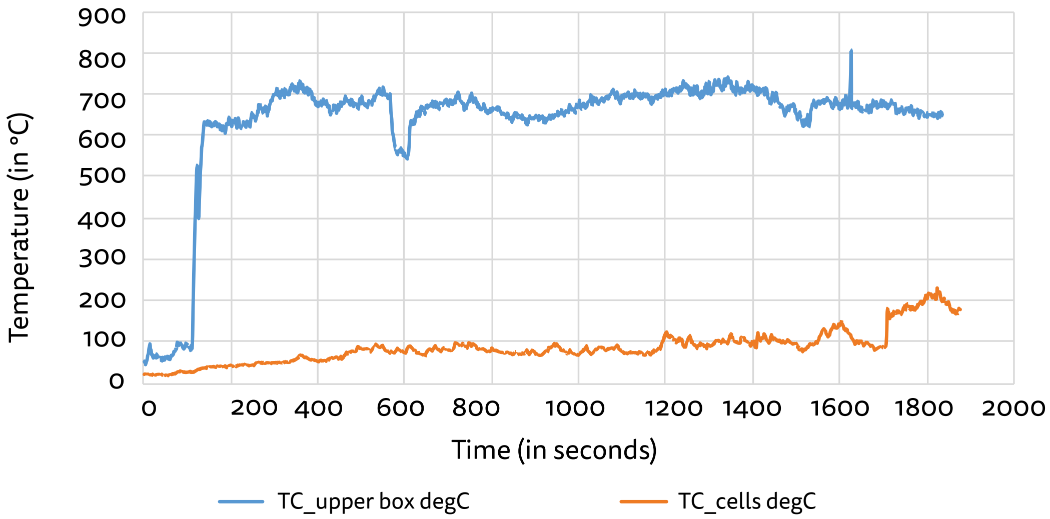


Figure 40: Development in temperature of a group of LFP cells subject to a thermal attack.

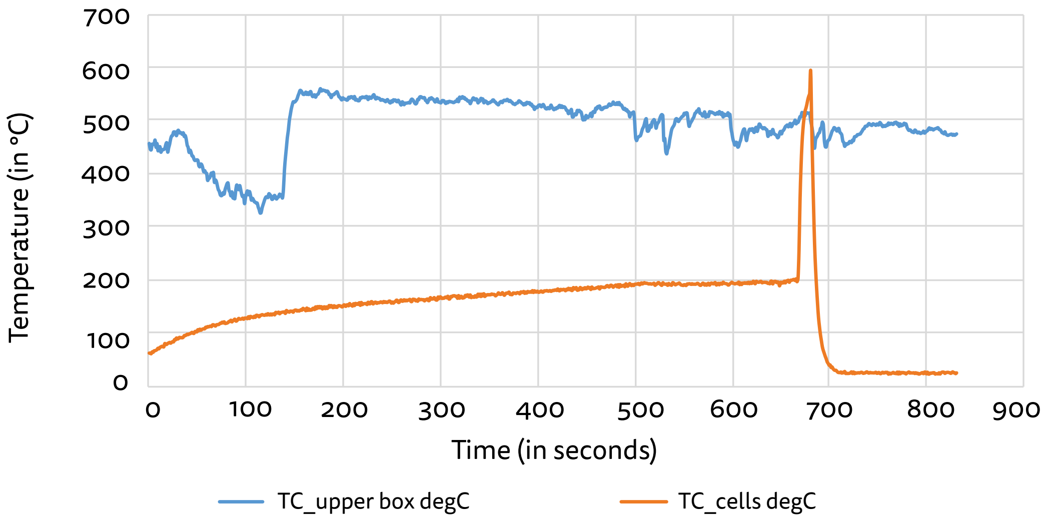


Figure 41: Development in temperature of a group of NMC cells subject to a thermal attack.

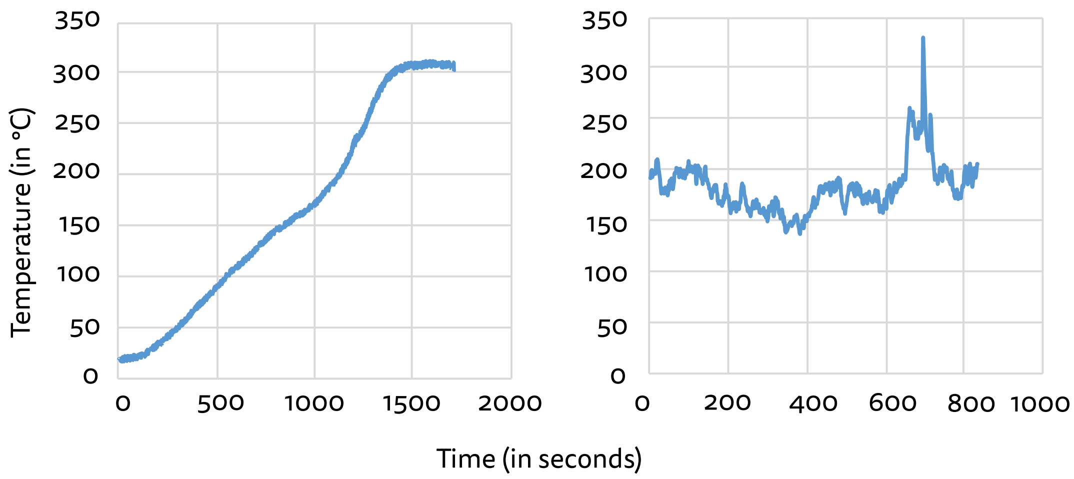


Figure 42: Ambient temperatures measured behind the cells.

Thermal attack on a 4s3p module

Objective of this test

The objective of this test is to show the behaviour of a module for which the cells are electrically connected together faced with a thermal attack.

As we had no module composed of cells identical to scale factor increase tests, in this case we used a module comprised of rigid prismatic cells.

The architecture of the cells in this module is as follows. 3 cells connected in parallel and 4 groups of cells assembled in series, or a total of 12 cells (147mm x 90mm x 25mm, +/-700grams each).

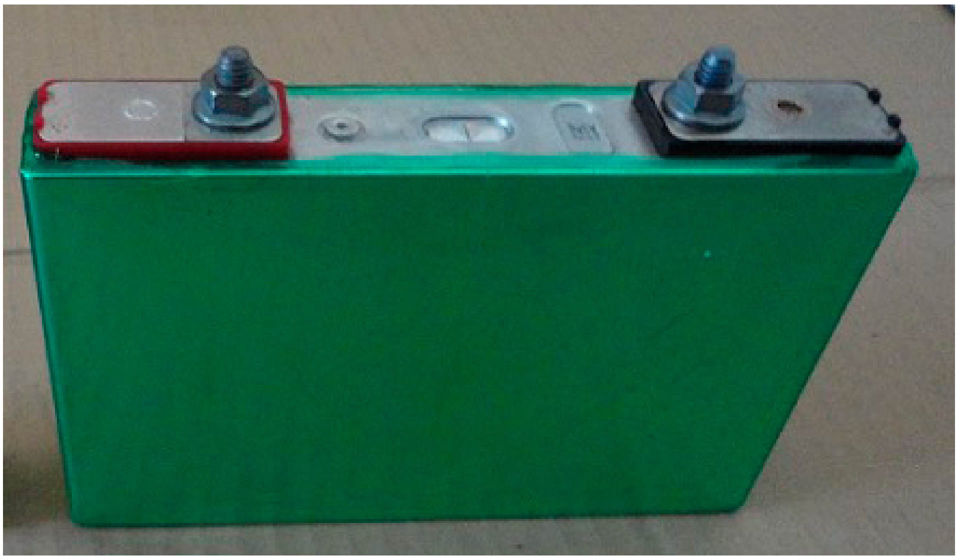
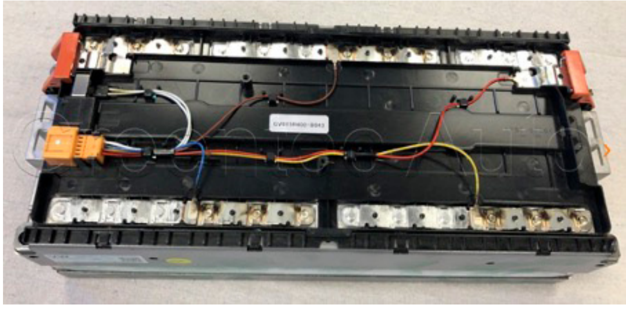


Figure 43: Photo of a cell used in the assembly of the module.

Also, all the cells in the module are kept together in a metal casing in order to ensure better integration within the battery pack as well as maintaining the compression of the cells to limit them swelling.



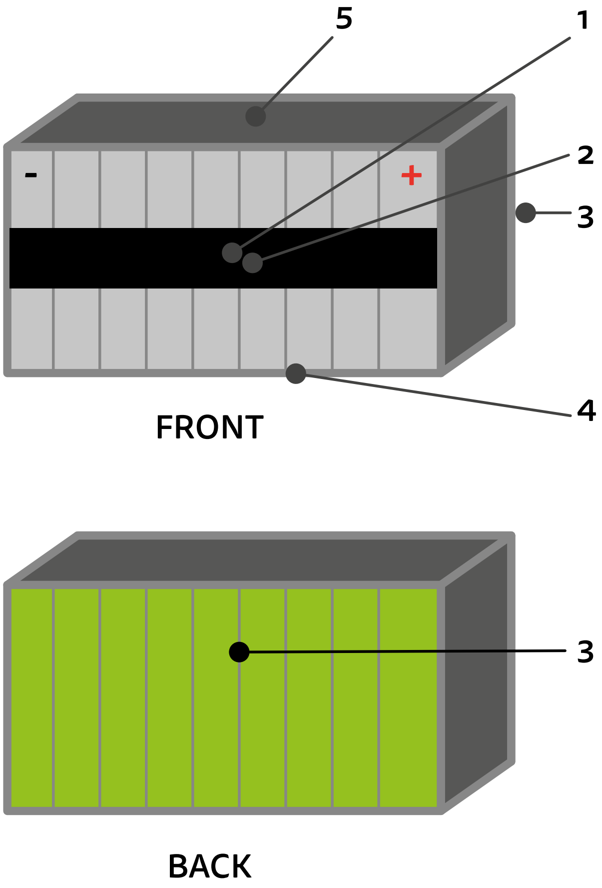
Test context

For this test we decided to over-instrument the module in order to observe the differences in temperature depending on the zones attacked. Also we placed thermocouples at different distances (1.5m and 3m) in order to find out the increase in temperature according to distance. Of course these temperatures are highly dependent on the external conditions (temperatures, wind, etc.).

In this test we also had access to module connection power terminals, and so we decided to monitor this value in order to see if this information could be useful in anticipating various violent thermal runaway reactions.

Instrumentation positioning:

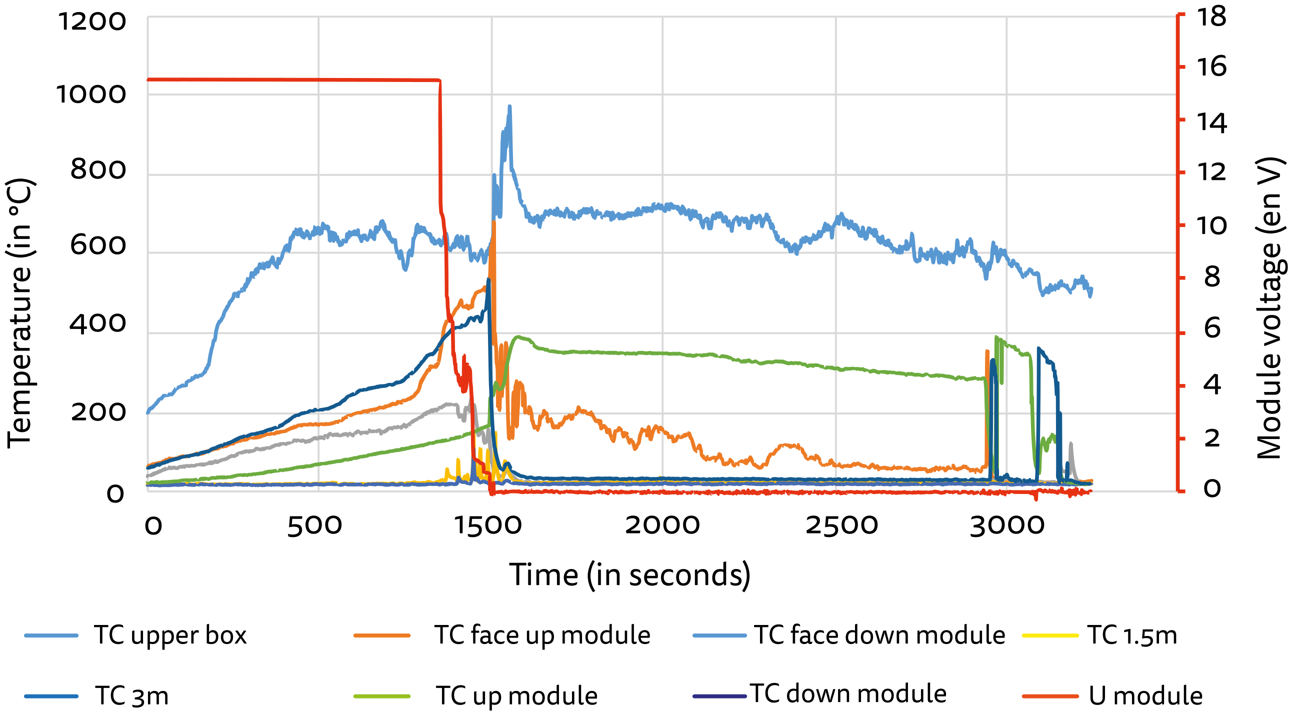
Figure 44: Photo of the module during the thermal attack test.

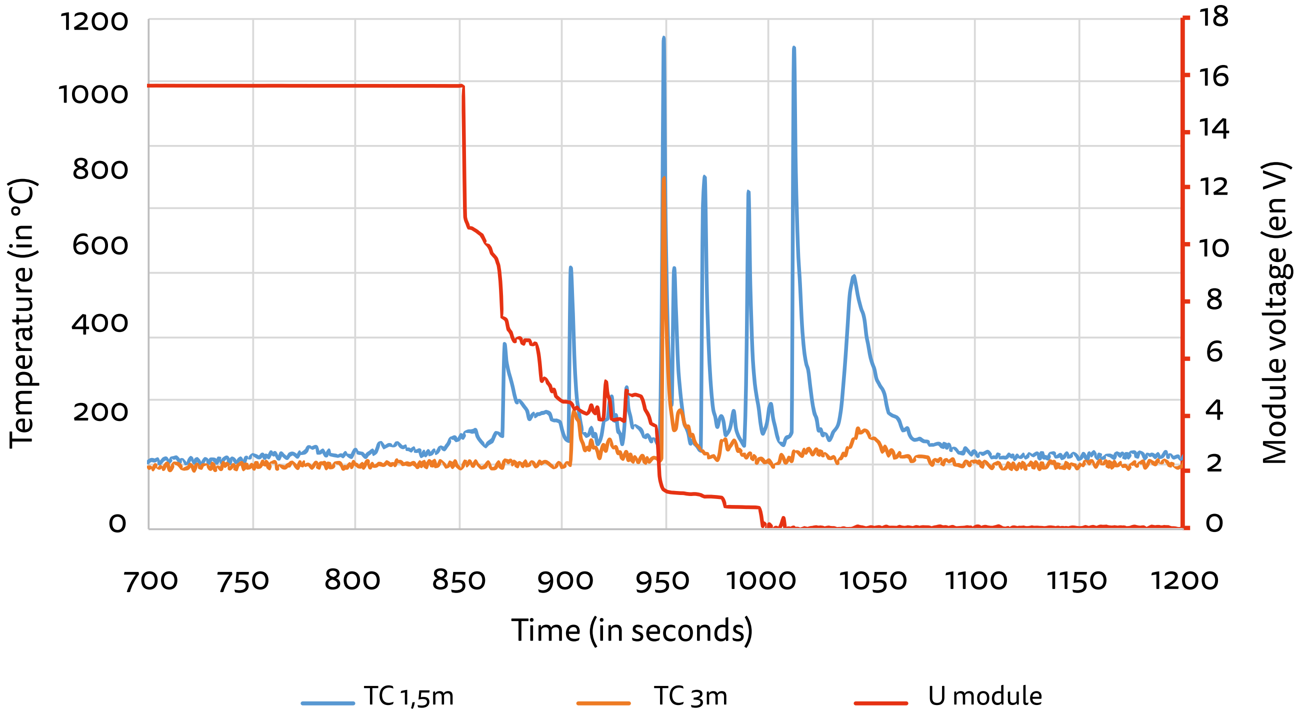


- Measurement of module voltage
- Recording temperature every 500ms:

1: front middle face,
2: front middle face,
3: rear face,
4: beneath,
5: above,
6: distance 1.5 m from module
7: distance 1.5 m from module

Test results





The two curves above show us the change of the temperatures during the test as well as the change of module voltage (in red on the 2 graphs with the axes of values on the right). The second curve is a temporal zoom of the first curve with a focus on the thermocouples at 1.5m and 3m from the module.

We note firstly that the thermal runaway reaction although violent last roughly 5 minutes between the increase observed on temperatures and the decrease in temperature on the front face of the module.

We also note that the increase in temperature is a very good sign showing the thermal runaway of one of several cells and is even the case on the external faces of the module, and in fact we can see the increase in temperature is quicker from 800s before the complete thermal runaway observed at 1000s.

Another sign highlighting the thermal runaway of one or several cells is observed measuring voltage, and we can see that this drops by successive steps to reach 0V. These different steps are surely due to an internal short-circuit in the cell decreasing the overall voltage of the module. This comes from the separator melting which brings the positive and negative electrodes together in the cell which provokes an internal short-circuit. The extra energy due to the short-circuit accelerates the cells thermal runaway even more.

On the second curve we can see the values of the temperatures measured at 1.5m and 3m from the module. We can clearly see the successive opening of the various cells on the module. Each temperature peak corresponds to one cell pressure vent opening with hot gas projections, flames and molten material (in certain cases). At 1.5m the maximum temperature measure when one or several vents opens is roughly 150°C though on the same opening at 3m the temperature is 100°C. In general, at 3m the temperature of the reaction is nevertheless lower (<50°C).

Photos of cells after testing

On the photos above, we can clearly see that although under pressure increase inside the cell, their casing has deformed. Also, on the module photos, we can clearly see that the casing has not withstood the heat and pressure increase of each cell and has completely opening leaving the cells to split away from each other, and only connecting bus bar manages to keep them together.

On the photo in the lower right we can see a cell photographed after testing, we can still see the green protection casing which has not completely burnt as well as the opening of the pressure vent (in the centre).

Cell overload without voltage limitation

Objective of this test

The objective of this test is to simulate a failure of the charge or the BMS. In a battery pack the BMS must be capable of constantly measure the voltages of all the cells in order to ensure that none of them exceeds the voltage threshold allowed by the manufacturer.

In normal time when the cell voltage approaches the maximum threshold, the BMS gives the order to the charge to decrease the current in order not to exceed this voltage. If the charger does not respond to the order of the BMS, it can as a last resort decide to open the power contactors in the battery in order to avoid them overloading.

However, these days in a number of high powered equipment (scooters, bikes, etc.), the charge has no intelligence allowing it to limit charging current, so the protection function is entirely given over to the BMS of the battery to control the opening of the charging circuit when the authorised threshold is exceeded. In case of failure here, the charge will continue to charge the battery without any power to cut it off.

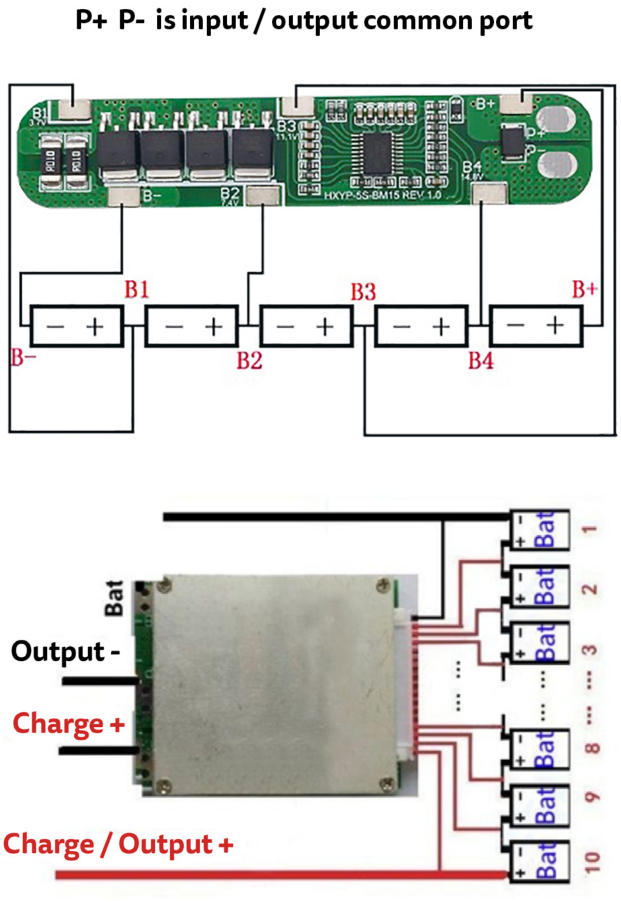


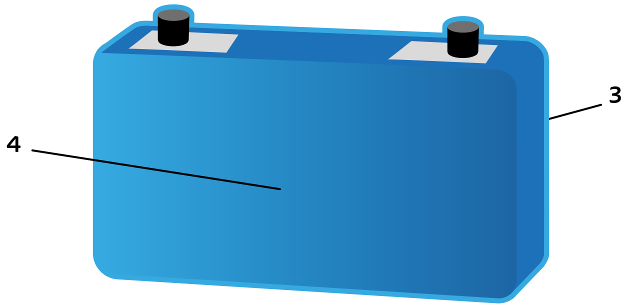
Figure 45: Example of a BMS present in high-powered products.

Test context

The current cell format 18650 integrates a CID (Current Interrupt Device) safety system. As we said the goal of this test is to visualise the effects of a BMS or charger failure, and not to characterise an internal safety system, that's why we have not carried out the overload test on the 18650.

Also, we were not able to assemble several cells to reach a sufficient capacity. The choice was therefore made to use a high capacity rigid prismatic cell (roughly 50 Ah) which had no safety system. Finally, this cell's chemistry (LMO/G) is relatively reactive.

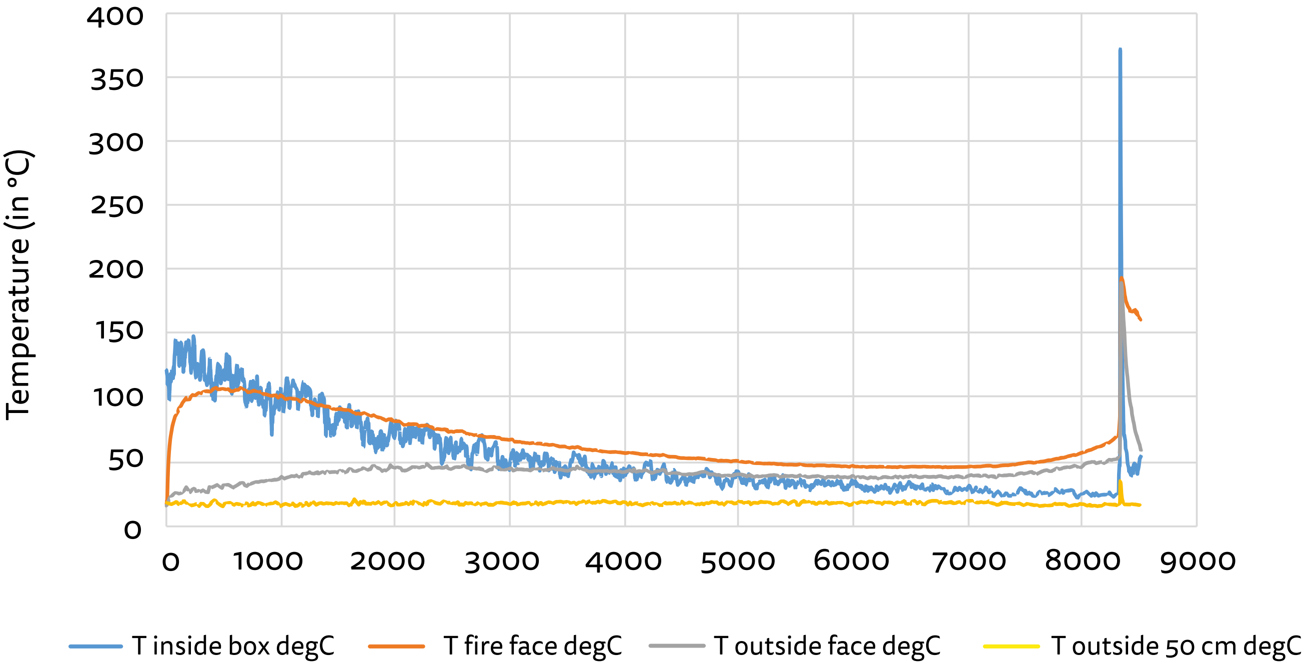
Instrumentation positioning:

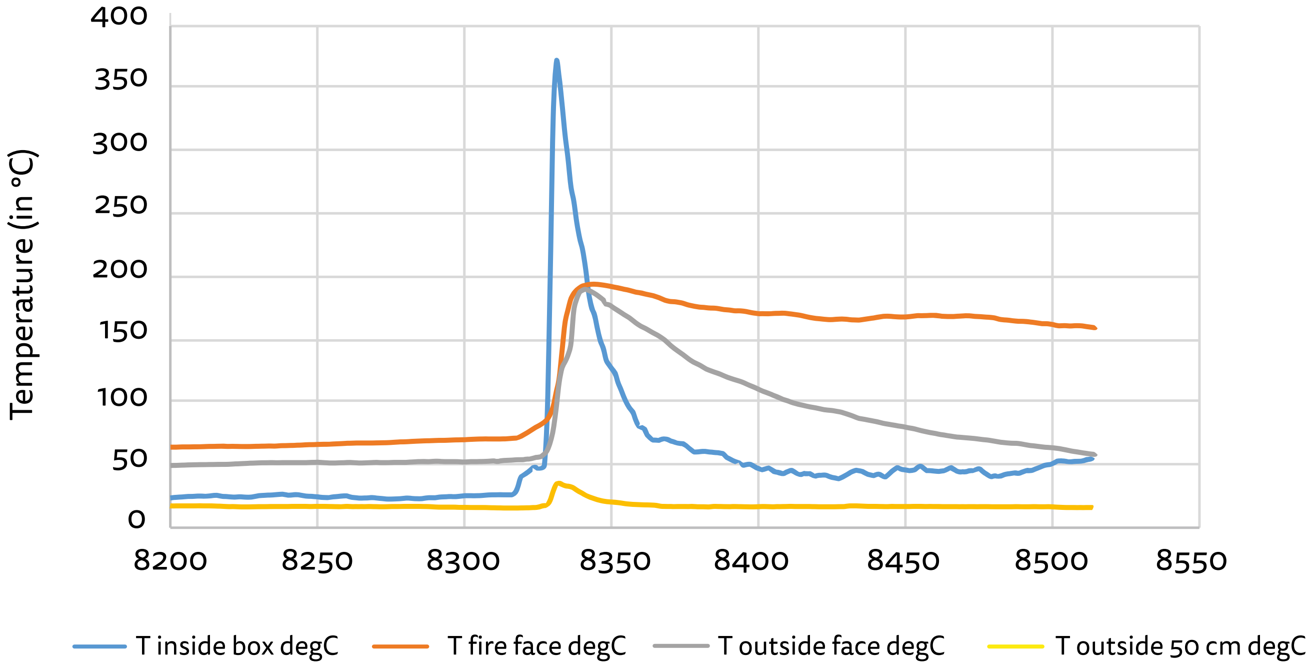


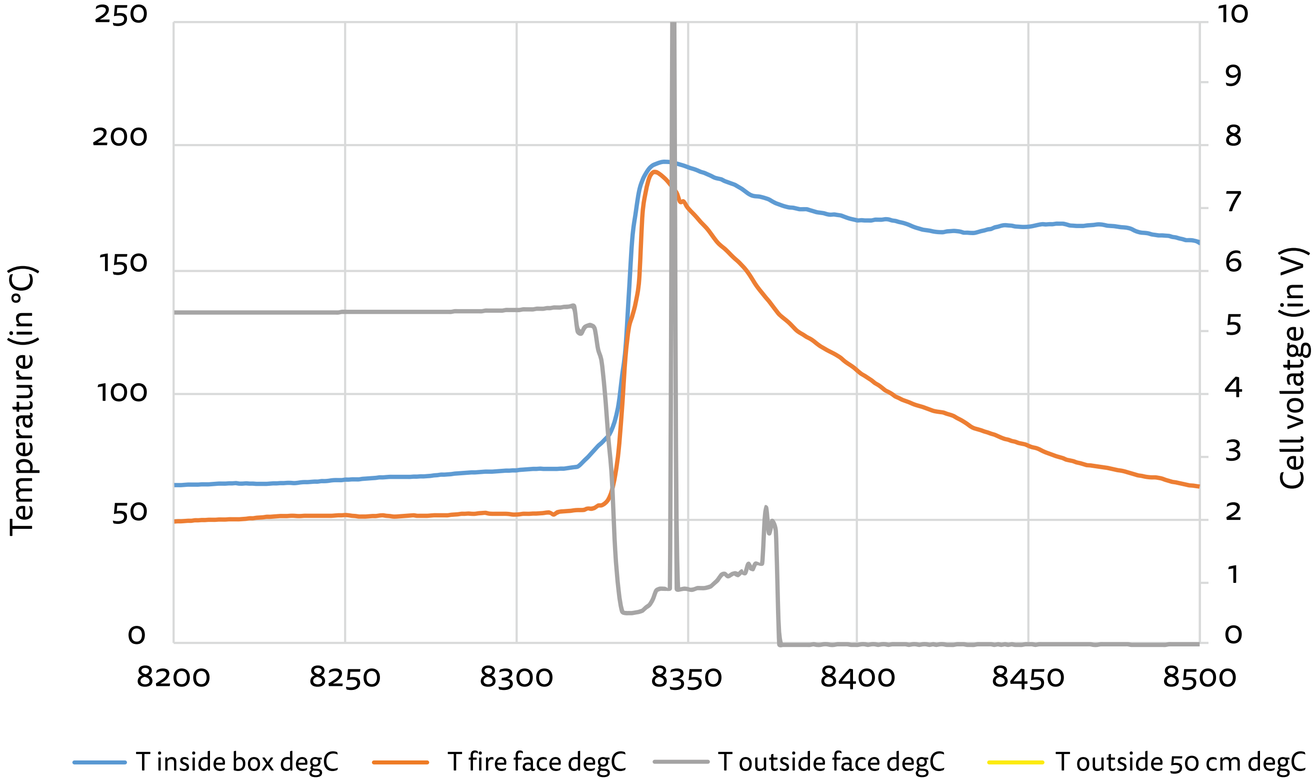
- Cell charge 30A then 38A
- Temperature recording every 500ms.
  3: behind the fire side
  4: front outside
- Voltage measurements

Figure 46: Cells used for the overload test.

Test results





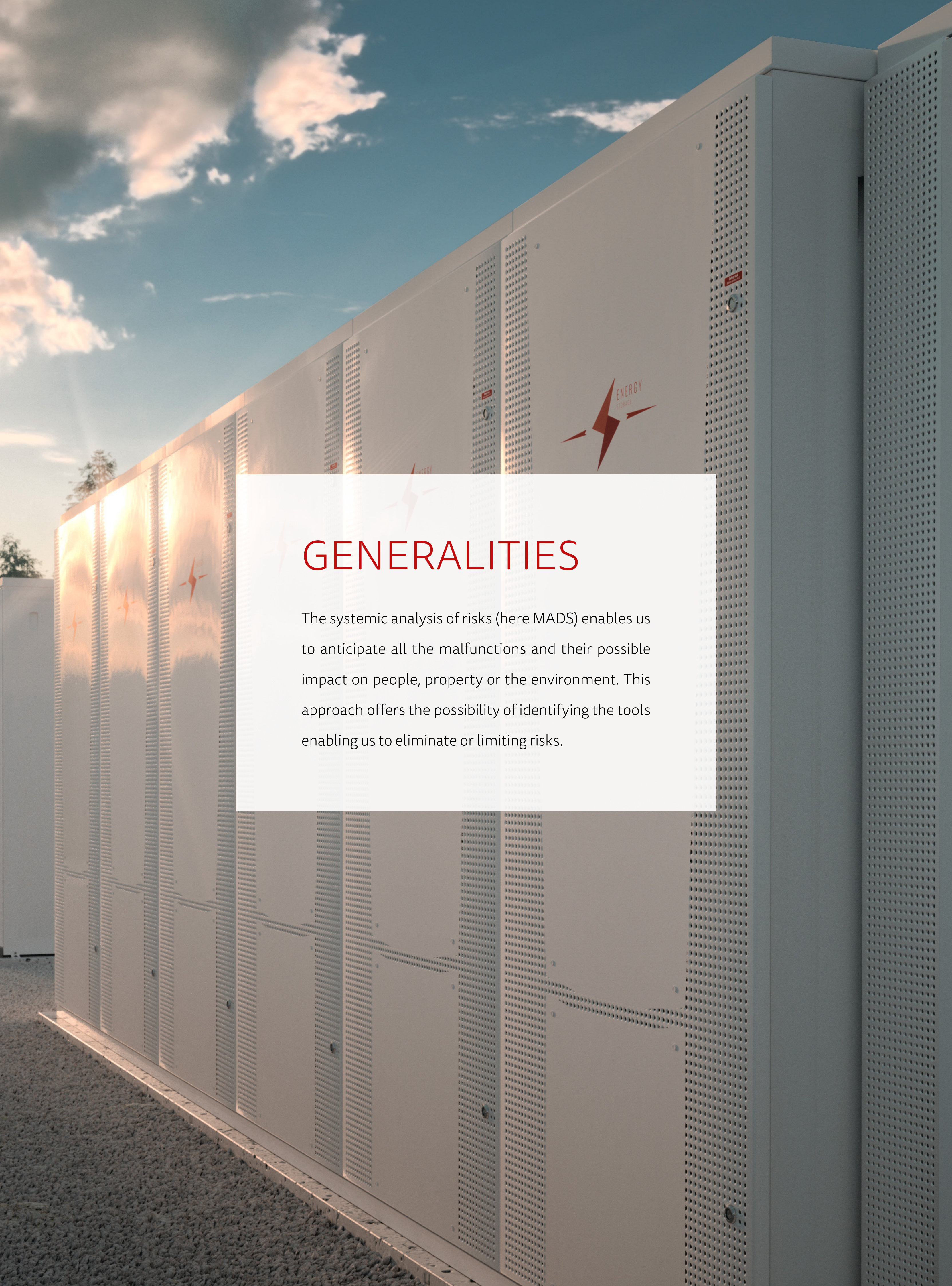


VDIP analysis reports

The chemical analyses of the measure compounds during tests (liquids and solids) are described in detailed in the VDIP reports given in the appendix of this report.
The result linked to the operational part and more particularly to the management of risks by fire-fighter equipment are developed on in chapter 4 and 5.

4

SYSTEMIC ANALYSIS AND POSSIBLE SITUATIONS



GENERALITIES

The systemic analysis of risks (here MADS) enables us to anticipate all the malfunctions and their possible impact on people, property or the environment. This approach offers the possibility of identifying the tools enabling us to eliminate or limiting risks.

“SYSTEMIC” IDENTIFICATION OF ELECTROCHEMICAL ENERGY STORAGE SYSTEMS

METHODOLOGY DESCRIPTION

Understanding the problem of risk analysis obligates the use of a scientific approach to danger. It is proposed for the rest of this report to use the MADS developed by a group of researchers at the University of Bordeaux, in the Health and Safety Department and a team of engineers in the CEA.

The model proposed has the objective of anticipated all the malfunctions likely to provoke undesirable effects on people, property and the environment and this is through the lens of all the elements in a system and their interactions in a “globality of danger”.

Using the MADS for testing, MOSAR also offers tools for analysis and removal of technical risks.

This approach is based on the danger process model which allows methodological description of the chain of events leading to a dangerous situation.

This process links a “source of danger” across a certain number of “danger vectors” to a “target”. These three terms are integrated into a “danger field” able to influence each of them.

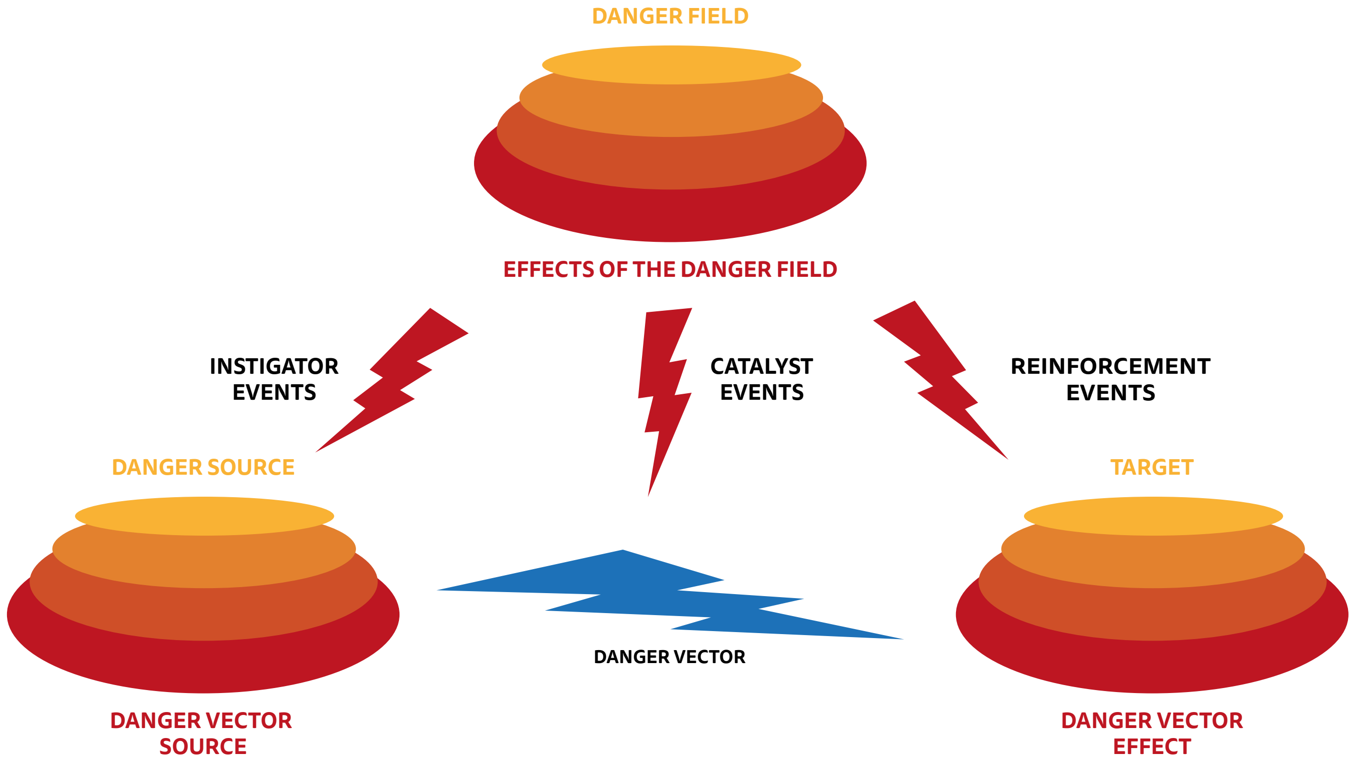


Figure 47: Danger globality

Danger source

The origin of the danger vector is the "danger source". It is characterised by the undesired initial event that products the risky situation and creates the danger vector.

In our situation, the source of danger is clearly identified as being the electrochemical energy storage system in its entirety. This system is characterised by:

- An assembly of accumulator cells and accumulator batteries, composed of electrodes bathed in an electrolyte, packed inside the cells,
- An electrical circuit enable transmission of electricity,
- An encasement system with variable size and design (box, case, container, etc.) enabling the whole assembly to be protected from external attacks.

It would be useful to refer to page 31 and page 37 of this report to detail more precisely the different technologies and designs that could be encountered.

Danger vectors

"Danger vectors" are directly resultant from the danger source and are defined by the various types of damage to take into consideration in the danger field.

"Danger vectors" are directly resultant from the danger source and are defined by the various types of damage to take into consideration in the danger field.
The data used in this analysis are extracted from the results of tests carried out during different GT test series.
We can distinguish 3 main vectors categories:

- Material vectors (liquid, solid, gas, etc.)
- Energy vectors (thermal, energy, electrical, etc.)
- Information vectors (sound, smell, colour, etc.)

The characterisation of this risks covered in part 2 of the current report as well as the various test series carried out during the study highlighting 5 main danger vectors:

❶ The thermal vector,
❷ The explosive pressure vector,
❸ The toxic vector,
❹ The electrical vector,
❺ The physical vector.

❶ The thermal vector

It corresponds to the amount of heat released per unit of time and by unit of surface and responsible for the three spreading modes of a fire: conduction, convection and radiation.
This vector is directly measurable in a fire and can also manifest indirectly and/or delayed through the flammability of fumes. The flammability of hot and cold fumes from an electrochemical energy storage system fire was able to be highlighted during our test series.
Also, temperature measurements were made in front of a module (1kWh) of prismatic cells faced with a fire. The measurement points were placed in front of the cell vents at a distance of 1.5m and 3m:
It is interesting to note that the temperature at 3m exceeds 100°C. Each temperature peak is linked to a cell vent opening in the pack (see figure 49).

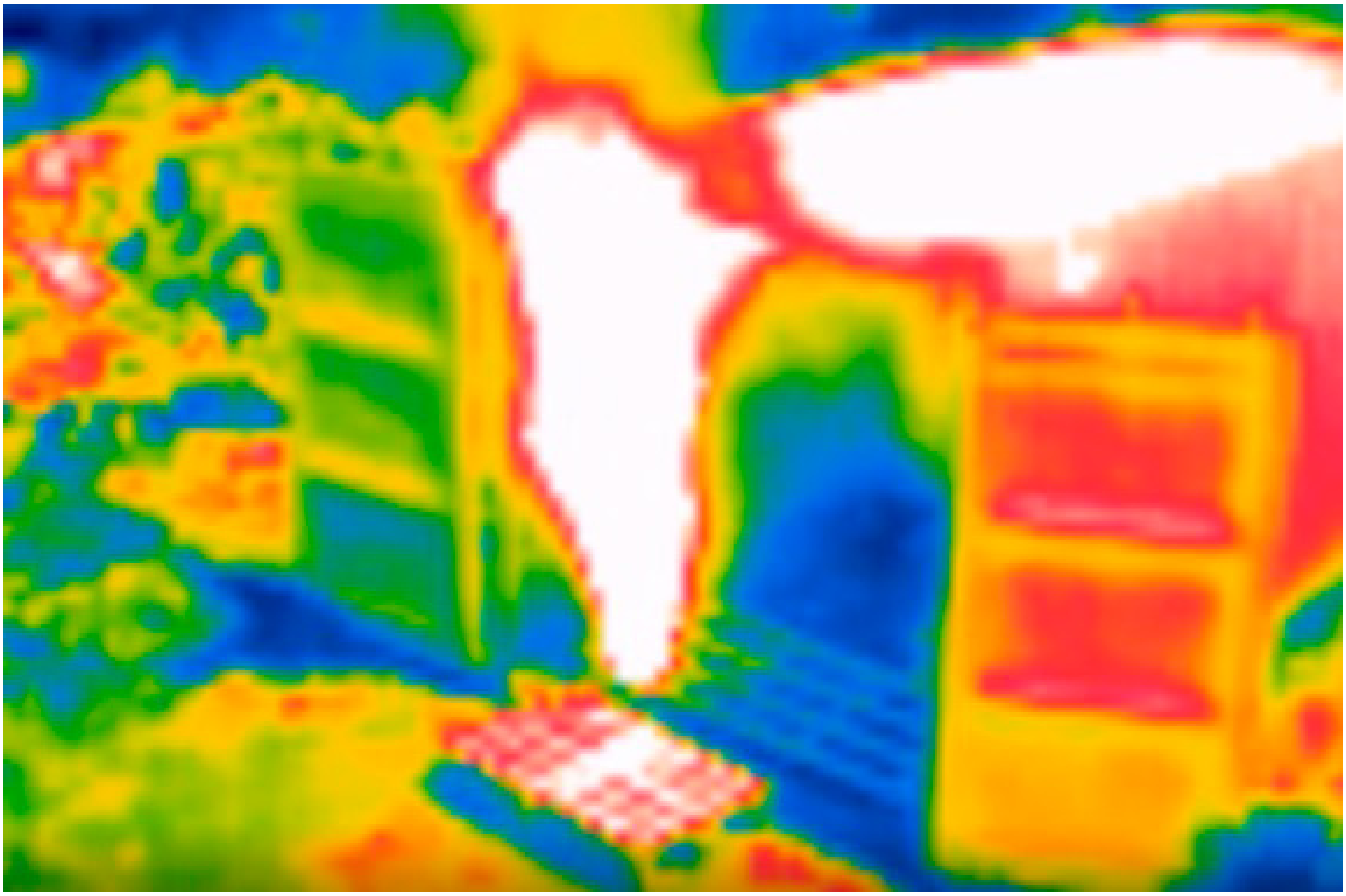


Figure 48: Thermal vector observed during the overload of a 200Wh storage system

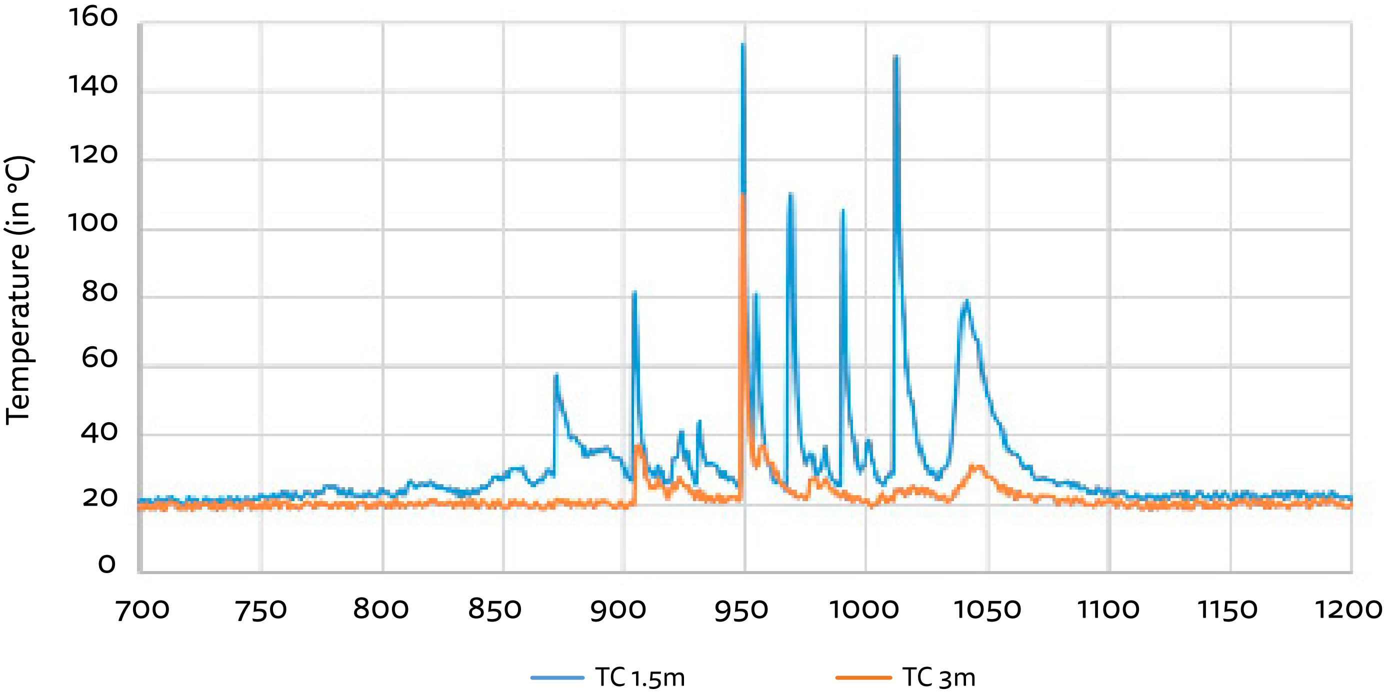


Figure 49: Temperature measurement at 1,5m and 3m from the battery fire.

❷ The explosive pressure vector

It corresponds to the emission of a pressure wave (provoked by a considerable production of gas) associated with various flows of materials (missiles in particular) and/or energy (thermal, for example).

This vector, which needs particular conditions, can result notably in the emission of hydrogen (which was not possible to measure during our tests, cf. external conditions and H2 dispersion in the appendix of the VDIP summary) but also "traditional" reactions of fumes in enclosed or semi-enclosed spaces. During our test series, a violent ignition of fire gas and fumes creating a pressure wave was observed. This reaction was produced when 4x 75Ah (LEV75) totalling 1kWh, NMC prismatic cells were overloaded in a shipping container 6m long with doors closely and partially locked. The pressure wave created was enough to open the doors of the container. Despite several attempts, it was not possible to recreate the conditions to produce another explosion of this type. However, several times during thermal runaway without flames, the emission of white, thick cold fumes was observed; These fumes were revealed to be highly flammable and the feedback from Arizona (BARPI n° 54822) proves that in large quantities, they can display explosive characteristics when the mixture of oxygen and air is optimal.

❸ The toxic vector

The objective of the test series carried out in the SSEE working group was to determine the toxicity coming out of a Li-ion battery fire. During the various tests, 3 types of distinct emissions/fumes were highlighted in different fires. Their toxicity was compared to that of fumes in a traditional fire (without dangerous materials)

The measurements were taken continuously in the fumes with the electrochemical and catalytic cells. Regular samples for analysis by TD-GC-MS and infrared gas were also taken.

Combustion fumes from a burning battery:

The first type of fumes is linked to combustion of a battery when it is on fire or subject of a thermal vector. The fumes were evaluated outside of battery gas emission phases. These combustion fumes show classic fire fume characteristics. No particular toxicity other than that of normal toxicity in fire fumes was detected.

Combustion fumes with the presence of gas emitted by the battery:

The second type of fumes is the combination of combustion fumes and projections of gas/particles by a vent or an opening on the electrochemical cell.

During these projections, we can essentially see the carbonates from the electrolyte or their degradation products. These carbonates, projected under pressure, do not follow the same air path as the hot fumes are emitted in the direction of the opening. These projections can set on fire and create flames of several metres long.

As well as the carbonates of the combustion gases (CO and CO_2), SO_2 was also detected in the fumes.

The presence of dihydrogen in these projections is also highly probable but does not lead to any extra danger.

Finally, concentrations of hydrogen fluoride (HF) were also detected during some tests. Looking at the number of tests carried out and the toxicity measurements taken, the emission of fluoride acid seems an abnormal reaction.

The other concentrations of gas detected are negligeable and don't entail any extra risk.

In open air, excluding carbonates, the various toxic gases follow the air path of the fire fumes and become diluted quickly. These gases are emitted very occasionally, only when the cell pressure vents open. They are not toxic in any significant way.

Hydrogen fluoride (HF) has, however, been detected very randomly (less than a quarter of tests) and in low concentrations on the fire tests of small storage systems. On larger capacity batteries (40kWh) and in enclosed environments (in a volume of $20m^3$), the presence of at least 30ppm of hydrogen fluoride was able to be detected. These concentrations will be highly reduced as soon as the environment is ventilated. As a result, wearing breathing protection when exposed to fumes is essential.

TESTS OF LFP CELLS	HF/HCl	NH_3	H_2S	SO_2	HCN	CL_2	NO_2
Min (ppm)	0	7	0	0	0.5	0	0
Average (ppm)	0	11	1	0	09	1.7	0
Max (ppm)	0	15	3	0	1.3	3	0
Number of times measured	0	3	1	0	2	2	0
Number of tests	3	3	3	3	2	3	3

Table 4: Tests on LFP cells - analysis report on the study of fume toxicity for Li-ion battery fires (VDIP South East)

TESTS OF NMC CELLS	HF/HCl	NH_3	H_2S	SO_2	HCN	CL_2	CO	NO_2
Min (ppm)	0	0	0	1.8	0	0.7	115	0.5
Average (ppm)	2.1	0	9	45	0	2.9	1200	1.4
Max (ppm)	3.8	20	22	100	30	10.8	1400	5
Number of times measured	1	1	5	6	4	3	6	6
Number of tests	6	6	9	6	8	3	6	6

Table 5: Tests on NMC cells - analysis report on the study of fume toxicity for Li-ion battery fires (VDIP South East)

TESTS ON 900W LI-ION PACK	HF/HCl	NH_3	H_2S	SO_2	HCN	CL_2	CO	NO_2
Min (ppm)	0	0	0	0.8	0	0	0	0
Average (ppm)	5.5	2.2	0.6	5	0.1	3	140	1.5
Max (ppm)	26.6	5	4	8.1	0	4.2	226	3.5
Number of times measured	2	3	1	6	0	3	4	3
Number of tests	5	6	6	6	5	4	5	6

Table 6: Tests on 900Wh Li-ion pack - analysis report on the study of fume toxicity for Li-ion battery fires (VDIP South East)

Emission of gasses as pressure increases (of a battery) - excluding fires:

The third and last type of fumes corresponds to gas emissions through the vent during thermal runaway of the cell (absence of combustion). These fumes are characterised by high density (fumes spread across the ground), white colour and are composed essentially of electrolyte (Di-methylene carbonate, ethylene carbonate, di-ethylene carbonate) and carbon dioxide.

These fumes can have an irritating effect. They can also set alight in contact with a source.

Projections of materials during emission phases:

Projections of aerosols/materials (solid or liquid) were also observed and analysed during vent rupture. The test series also highlighted the presence of phosphate (PO_4^{3-}> 100 mg/L) and sulphate (SO_4^{2-}> 400 mg/L) ions in these aerosols. The highly acid pH (pH=1) leads us to believe there are acidic forms of these ions, which means phosphoric acid and sulphuric acid.

The presence of burnt or partially burnt elements such as electrolyte components were also highlighted during the tests and aerosol projections when the cell opened. These are essentially elements such as electrolyte solvents (carbonates: Carbonate ethylene (EC) CAS-No. 96-49-1, Dimethyl Carbonate (DMC), Ethyl Methyl carbonate (EMC), etc.) containing $LiPF_6$ salt (Lithium hexafluorophosphate CAS-No. 21324-40-3).

SUMMARY

In conclusion on the **toxic vector**, the test series carried out by the working on Electrochemical Energy Storage Systems enable us to highlight 2 parameters which will influence potential toxicity of fumes created by the batteries:

- The size/power of the batteries
- Type of environment: enclosed or open air

In open air, the batteries measuring several hundred watts to several tens of kW don't create any particular toxicity compared with fire combustion fumes.
These are enriched when each cell ruptures with the following emissions:

- Electrolyte in the form of gas and aerosol
- CO and CO2
- Probably emissions of SO2
- Random non-systematic emissions of hydrofluoric acid in moderate concentrations.

Outside of combustion at low ignition temperatures, the white fumes from opening a vent or rupturing a battery can be irritating, as a result of the carbonates.

For the fires with battery packs of several MW, and considering the high number of cells, it is useful to implement measurement circuits to calculated fume toxicity in order to protect people.

In an enclosed environment, the accumulation of emitted gasses could result in toxicity. This will be negligeable for batteries of several watts up to kilowatts but could be considerable for high powered batteries.

The use of systematic breathing protection for fire-fighters and humification of the environment will limit these risks.

Figure 50: Cold white fumes during the extinction of NMC 500Wh cell pack.

Figure 51: Ignition of white fumes on NMC pack of 500Wh.

❹ Electrical vector

This vector is measured by the presence of a residual current (expressed in mA) that must be considered as permanent and possible in all situations counting from the moment there is a loss of electrical insulation observed. The indicator of this vector is the residual voltage at all points of the battery pack.

This vector has been verified through several tests and in particular on an NMC storage device of 40kWh that is burning.

❺ The physical vector

The physical vector was able to be highlighted through projections of solid and/or metal elements and by missile effects of two types: the first being linked to the projection of cells (projected roughly 30 m from the fire by missile effect in independent propulsion phase with a random trajectory) and the second being linked to the fragmentation of storage casing. Additionally, projections of molten were regularly observed:

Figure 52: Projection of solid metal elements observed when burning a 30Wh storage system.

Target

The part that the danger vector acts on is the “target” system. The following are targets:

- People exposed to danger vectors (owners, operators, employees, simple bystanders, etc.),
- Property (fixed or mobile installations, buildings, structures, residences, animals, etc.),
- The environment (natural area, ecosystem, etc.).

It is also useful to see the target as a possible new source of danger. This is notably the case in domino effect situations when a sequence of interdependent events is likely to product a chain of considerable or even catastrophic damage (most often in an industrial installation and its environment).

Instigator events

As their name suggest, “instigator events” are situations that could be at the origin of a danger field that could lead to an imbalance in a danger source. These instigator events have already been identified because the specific standardisation of electrochemical storage products list them in the context of extreme testing.

There is notably a distinguishment between:

- Crushing,
- Overload,
- Perforation,
- Short-circuit,
- Exposure to thermal radiation,
- Exposure to flames,
- Thermal conduction.

The totality of these instigator events were able to be implemented during the test series to generate electrochemical energy storage system thermal runaway (cf. Chapter 3 of this report). The most reproducible is still crushing using the help of a metal ball in a 25m tube at the level of the battery being tested.

It should be noted that for all the instigator events above and in the case of NMC technology, for which the state of charge was over 50%, the battery reaction was a thermal runaway with a 100% occurrence rate. For lower states of charge, the thermal runaway reaction was present but less violent.

A schematic summary is presented in the figure below:

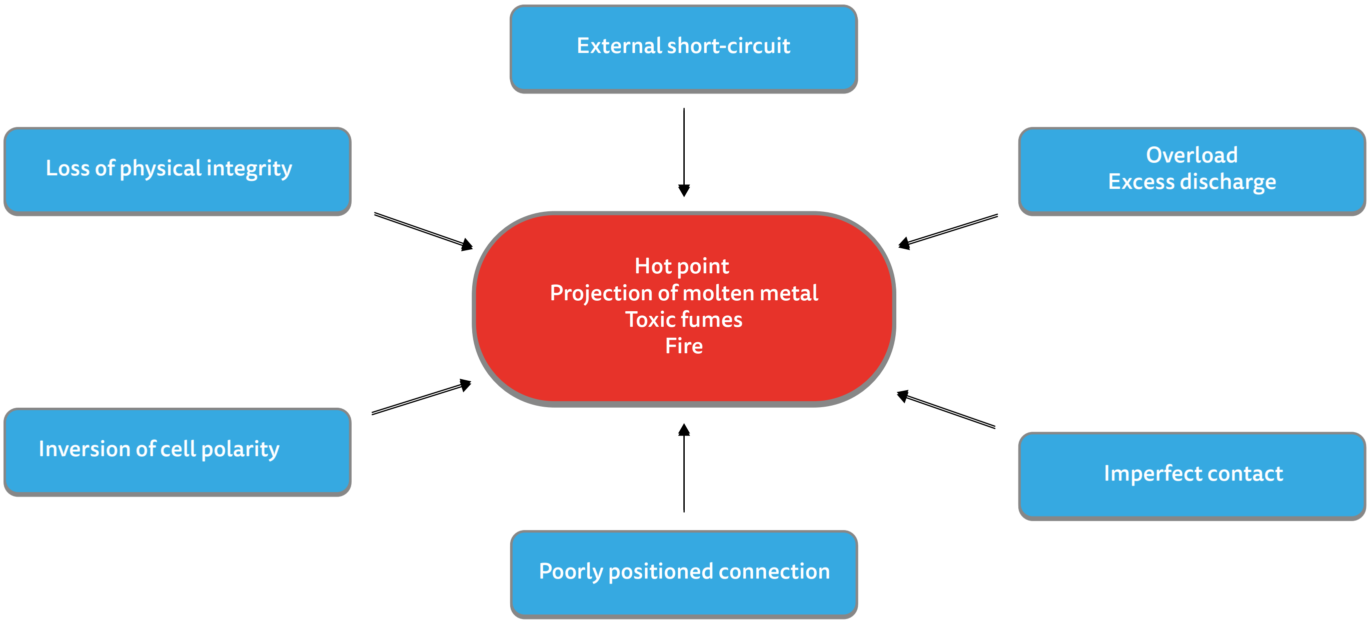


Figure 53: Instigator events

Catalyst events

Having a direct catalytic impact on the danger vector effects, in the test series we were able to determine two main "instigator event" types:

- **The degree of confinement** constitutes an instigator event in the sense that the thermal runaway or fire of an electrochemical storage system inside a building in confinement of semi-confinement is going to reinforce the thermal vectors or even create an explosive pressure vector. Black smoke loaded with soot increase the risk of spread because of their particularly high temperature. Also, the air conditions around the fire should be taken into account and observed. Finally, the confinement amplifies the toxicity of fumes that have the effect of concentrating the toxicity.
- **The battery charge state** enabled us to establish a direct link with the effects observed. In particular, it was clearly observed that the more an electrochemical energy storage system is charged, the greater the thermal and physical (projections of metal elements) effects are.

Reinforcement events

Reinforcement events are characterised by events that worsen the effects of danger vectors on targets.

These effects can be of different types such as a high presence of people nearby (or difficult to evacuate them), presence of work sites, high risk zones, industrial or building structures, or sensitive natural areas (rivers, protected zones). The inability to move batteries or moved the targets also constitutes an area of consideration in reinforcing the effects on the targets.

DIFFERENT POSSIBLE SITUATIONS

Predicable development of the accident

The predicable development of the accident is understood to be the situation that could be encountered by assuming that no action was taken to stop it. These are therefore the successive stages of an openly developing accident enabling vulnerabilities to be established. In this case, the analysis of the phenomenology allows us to identify three possible evolutions of the accident.

The evolution possible of the accident is characterised by thermal runaway of a cell and the increase in temperature within the storage system. In this phase, the accident can them be composed of several battery cells (source) that could go from several grams to several kilos. The warning signs have been already identified as being likely to generate a cell thermal runaway, notably a physical, electrical or thermal attack. The increase in temperature (vector) within the cell could be such as to spread a possible fire to other neighbouring cells (targets) and if necessary to generate a chain thermal runaway reaction.

Chronologically the following development is described by the spread to neighbouring cells and the overall and uncontrollable burning of the whole storage system. The electrochemical storage system (source) of variable mass (several hundreds of kg up to several tonnes) will produce vectors describe in chapter 4.1.3 on people, structures and buildings nearby (targets). The consequences of thermal runaway and the associated considerable thermal runaway will be the worsening of the risk of spread and difficulties in constraining the reactions.

The last possible development of the accident is the appearing of violent reactions that may be delayed. The physical vectors could generate projections of materials and electrolyte. If the direct relation between the size of the storage system and the thermal effects exists, it has nevertheless, not been noted about the evident relation with the violent reactions and explosion phenomena. The fire tests carried out on 30-40kWh storage systems did not generate physical reactions that were worse than on storage systems of 4kWh. This is explained notably by the fact that the thermal runaway for cells is not simultaneous and there is a certain latency necessary to transmit the heat from one cell to another. The cumulative effect of projections or violent reaction has therefore never been demonstrated during our tests. However, the cumulative effect in a confined environment exits as regards the toxic vector. According to the feedback from Arizona (BARPI n° 54822) and the observations made during these tests, it is also possible to observe a cumulative effect on the white fumes emitted under an inert atmosphere or one low in oxygen. This effect depends on the duration that the battery remains under inert atmosphere and therefore the number of cells which has their electrolyte evaporated by thermal runaway.

Undesirable events

An undesirable event is an independent event outside predictable and natural development of the accident that could affect its development.

The test series highlighted two types of undesirable events.

Firstly, carrying out overload and fire tests in an open environment, semi-enclosed and enclosed environments showed the role of fumes in the appearance of explosive reactions. The accumulation of fumes (source) in a system that doesn't allow them to escape has an effect on the probability that an explosion will occur (vector). An overload test, so without fire, of a 1kWh battery in a closed 6m shipping container, resulted in a similar reaction to ignition of gas from a fire (fire gas ignition), with as a consequence a pressure wave. Though the associated thermal vector was able to be restricted to the container, (target) where the battery was located, the pressure wave naturally took the path towards the door and was able to be felt by the operators (targets) located nearby.

The occurrence of this reaction is random and confirms the importance of controlling air flows throughout the duration of the accident. The warning signs of this type of reaction are very different from the ones encounters on traditional fires where the container is semi-open or enclosed (i.e., Fume explosion reaction or backdraft). Given that it is the intense release of fumes linked to the overload that created the burning fumes, it is not possible to anticipate this reaction. The only way to anticipate it would be to have access to the battery charge or BMS data.

Figure 54: Explosion of fumes during an overload of a 4-cell LEV75 in a 6m shipping container.

Additionally, a variant of this reaction was highlighted during the tests and concerns the inerting action of the thermal runaway reaction. This action, theoretically enable the spread of the fire created by the thermal runaway in the battery cells to be stopped, leads to emitted gases not being burnt when venting the cells after excessive pressure during thermal runaway. These unburnt gases, evaporated electrolyte is highly flammable. They are difficult to recognise as they behave like a dense and cold white fog, that spreads across the floor. Ignition of these gases can lead, as was the case on a small scale during these tests, to causing a powerful pressure wave. This reaction is almost systematically reproducible with each type of inerting tested.

The second type of undesirable event could be characterised by the inability to effectively cool the storage system because of its inaccessibility or its protective casing (cabinet, etc.). In almost all situations, the storage system will be enclosed in a structure that protects against external attacks (weather, impacts) make spraying water difficult even when it is brought in large quantities or sprayed (water bell). This problem is such that it can produce situations where pyrolysis gases or fumes are reignited, cooling effects are reduced and therefore new risks of thermal runaway are created on the untouched cells. In this case, the battery packaging, which could be an advantage because it contains the dangerous reaction, becomes a handicap because it doesn't allow for effective cooling of the storage unit, and this is the case even with large quantities of water. Also, as the temperature of the battery core is still very high, thermal runaway can be observed again with the return of the previously mentioned risks.

The following table summarises the various developments possible to be encountered after physical, electrical or thermal attack on an electrochemical energy storage system and proposes two types of undesirable events:

TABLE OF POSSIBLE DEVELOPMENTS					
	Predictable developements of accident			**Undesirable events**	
	1: Thermal runaway of a cell and increase in the temperature within the storage system	2: Spread to neighbouring cells and fire in the whole system	3: Violent phenomena and/or able to be stopped	1: Explosive reactions from the confinement of fumes	2: Inability to extinguish or cool
Accident components					
Source	Storage system cell	Electrochemical storage system	Electrochemical storage system	Accumulation of fire fumes	Electronchemical system inaccessible or coverd
Vectors	Thermal (heat)	Thermal / Toxic / Explosive / Electrical / Physical	Explosive / Electrical	Explosive	Thermal / Radiation
Targets	Neighbouring cells	People / Structure / Building	Emergency response teams	People / Structure / Building	People / Structure / Building
Occurrence of the event					
Warning signs	Physical, electrical or thermal attack	Thermal runaway on one or several cells	Residual voltage / delayed runaway	Enclosed or semi-confined space / difficulties for fume evacuation	Access difficulties/ protective casing/ constriction
Consequences	Fire / explosion / fumes	Spread and difficult restricting the reaction	Appearance of delayed reactions/ instability	Flashover or fume explosion	Reignition / risk of untouched cell runaway / violent reactions
Accident size					
Surface involved	Cells or blocks of cells	Whole storage system	Wholte ctorage system / electrical circuit	Nearby buildings / whole building with the storage system	Whole storage system
Quantity of material	Several g or kg	Several tens of kg to several tonnes	Several tens of kg to several tonnes	High amount of fumes	Several hundreds of kg to several tonnes
Geographical zone threatened	Whole storage system (Several hundreds of kg to several tonnes)	Nearby buildings / whole building with the storage system	Nearby buildings / whole building with the storage system	Zone exposed to the explosive reaction (pressure wave and/or thermal vector)	Nearby buildings / whole building with the storage system

Figure 55: Table of possible developments

Possible situations

Confrontation of possible developments of the accident with undesirable events as well as analysis of the instigator situation of the event then the observed situations (at time t) must enable the consideration of various possible situations, the next phase of the systematic analysis of risks.

Three main possible situations were encountered during the test series.

The first corresponds to the fast and early action on the accident enabling thermal runaway reactions to be neutralised or at least contained in the cells that are involved up to that point at the start of the accident. This situation is made possible by detecting the thermal runaway early or at the start of the fire (automatic fire detection) which enables rapid implementation of cooling measures or suitable extinction techniques. In this type of scenario (inerting), the increase in temperature is limited and has the consequence of not necessarily initiating thermal runaways in the neighbouring cells because of the absence of flames. However, heat increase continues to spread by thermal conduction. The heat increase is therefore less important, and the volumes located around the storage device are not subject to a fire. After the event, the physical integrity of the battery could be considered as good, but the battery must be considered as unstable. The local heat increase could have led to insulation ruptures inside the battery which could provoke short-circuits when manipulating the battery int he future.

Nevertheless, concerning this first possible situation, it is helpful to consider that inerting enables the risk of accident spread to be limited to the inerted spaces but does not stop the thermal runaway reaction. inerting has no cooling effect. Also, the cells create their own fuel during a thermal runaway reaction. The white fumes are therefore emitted in this situation and not burnt. They accumulate in the inerted space. Inerting's goal is therefore in this case to enable the halt the battery's progression and to stop a fire in the interted space. This situation much absolutely be taken into account by the COS when they arrive in order to deal with the white fumes before engaging any personnel in the fire. As a consequence, the toxic vectors and explosive pressure wave are a risk in this situation.

The second possible situation consists of the spread of the accident through thermal runaway of neighbouring cells leading to ignition of the whole storage system. In this case, the thermal runaway chain reactions cannot be restrained, and the spread of the accident occurs through traditional mechanisms (conduction, convection and radiation). As the fire is irreversible, all the danger vectors manifest themselves and threaten people and structures close by:

- Large thermal vector
- Toxic vector (release of fire fumes and toxic gases)
- Physical vectors (projections of metal or electrolyte)

The last possible situation is the immediate and/or delayed appearance, over a long period of time, of violent reactions. This situation is even more probably when cooling solutions are insufficient or ineffective or the amount of water sprayed does not succeed in reaching the core of the storage system to absorb the heat released by the fire. The tests showed the random but very real nature of explosive reactions (fume explosions, and pyrolysis or unburnt gas explosions) with missile effects that could occur.

It was also noted that the presence of an electrical current is possible on the structures in contact with the storage system with the risk of electrocution or arc formation. The difficulty with this risk is the inability to be neutralised and this is the case even after the fire has occurred.

Finally, the bibliography on electrical vehicle fires has largely enables us to link the risk of fire outburst several hours, or even days after the fire.

The following table proposes different possible situations that could be encountered:

TABLE OF POSSIBLE SITUATIONS			
	Possible situations		
	1: Rapid and early action on the accident in order to avoid and constrain thermal runaway effects	2: Spread of accident through cell thermal runaway and ignition of the whole storage system	3: Long term operation with presence of violent reactions that could be delayed
Accident components			
General context, quality, type of accident	Early detection of thermal runaway or start of a fire on a permanent storage space during fast implementation of cooling methods or inerting (internal or external)	Inability to constrain the runaway reaction/spread of accident by conduction, convection (amplified by fumes), radiation	Cooling equipment insufficient or ineffective/ Quantity of water sprayed unsuitable or inability to reach the storage system
Fire Pollution Victims...	Increase in temperature limited (< or equal to thermal runaway temperature of cells) / Heating or low importance fire / Limited release of fumes or effective evacuation	Storage fire or container fire with large thermal vector / Presence of toxic vector (toxic gases) / Physical effects (metal projections or electrolytes)	Risk of explosive reactions (fume explosions, projects, missile effects) throughout the operation/maintenance of electrical risk impossible to neutralise/ Late runaway or delayed in time (several hours after the accident)
Accident size			
Calculation criteria, importance	Cell or blocks of cells / residential domain Storage < 10kWh	Storage system of around 100kWh Tertiary domain (cabinet, case)	All types of storage
Surface on fire	Surface limited / Less than 50 L in volume	Large surface / Less than 500L in volume	All types of surface
Quantity of material	Less than 100 kg	1 to several tonnes	All quantities
Geographical zone threatened	Whole storage system	Nearby buildings / whole building with the storage system	People / Structure / Building / emergency teams or monitoring personnel

Figure 56: Table of possible situations

VARIOUS BARRIERS POSSIBLE

CHAPTER OBJECTIVES

Thankfully, the danger process that could lead to an accident event can be thwarted by a number of different barriers. These barriers, or counter measure, can act in several parts of the system, either by acting preventatively on the source at the origin of the event (preventative barrier) or by acting on the targets and/or vectors in order to limit their effects (protective barriers). The goal of the current chapter is to address the largest audience possible from manufacturers, standard creators, preventors, operators, emergency services up to companies in charge of consolidating the sector.

Preventative barriers

Among the preventative barrier there are those that are intrinsically part of the storage system and those that are outside the system.

Constructive barriers intrinsic to the cells or the battery

As the literature review stated, the very design of these electrochemical energy storage systems has a certain number of protective measures. Intrinsic preventative barriers consist of:

- Pressure vents that, through a burst disc, gases generated inside the cell are able to escape the electrolyte is able to evaporate.
- The electrical current management systems such as the Current Interrupt Device (CID) or the Overcharge Safety Device (OSD) or the fuses that physically disconnect from the current supply and/or the Positive Temperature Coefficient (PTC) that block the current in case of overload,
- The integrated electrical insulative layers for the metal cells in order to the limit the presence of large conductive surfaces or the separators that also enable protection to be implemented on a cell when the polymer melts and blocks ionic conduction,
- The casing enables either:
    - Protection to be implemented against external physical attacks because of their crush resistance, perforation or impacts,
    - On the contrary, to tear away easily in order to free up any potential successive pressure increases in a thermal runaway.

External barriers based on passive measures

The BMS constitutes the first barrier against deviation linked to battery charging and discharging when the recommendations of the manufacturer are exceeded.

Concerning the preventative barrier, traditional fire detection constitutes a key tool for discovering an accident situation. We can distinguish:

- Visual detection of fumes, ideal in the starting phases of the fire,
- Flame detection (detection of infrared radiation emitted by the flames),
- Detection of static heat (temperature threshold reached) or thermo velocimetric (temperature increase speed detection),
- Multi-detection combining several types of detector.

The instrumentation implemented during the test series enabled in certain situations thermal runaway reactions to be anticipated. This was notably possible through measuring the change in temperature and battery voltage through time. These parameters play a key role in preventing an accident. If they are reported outside the room or the structure concerned and their accessibility level is reported to the emergency services, this would be a precious aid in the case where a knowledgeable individual is able to interpret the measurements and guide the COS as regards the observations made. This would also enable a fault to be managed before thermal runaway. It should be noted that this detection based on the measurement of battery voltage precedes the thermal runaway by only a few tens of seconds.

Finally, doctoral work (undefended but already published[1]) have sought to highlight the link between the emission of sound waves and the occurrence, several seconds afterwards, of thermal runaway. Solutions could therefore enable the alarm to be raised as early as possible.

Active and passive barriers acting to limit the impact of an accident

Have noted the existing link between the charge level of a battery and the effects of thermal runaway (thermal and physical mainly), it would seem interesting to try and reduce its state of charge. The activation of an embedded system in the electrochemical storage system enabling the battery to be discharge relatively rapidly, would reduce the reactivity of the system as regards a thermal runaway. The ideal situation would be to have an effective discharge over a short period of time in order to limit the thermal effects whilst enable the emergency measures to be implemented. This time could be between 10 and 30 minutes after activation of the discharge system activation, and would be ideally at the same time as calling the emergency services. Careful, however, not to create too fast a discharge for which the thermal effects on the battery would get close to a short-circuit leading to thermal runaway.

The structure housing the electrochemical energy storage system could also contribute to acting on the source because of its design and the integration of measures such as facilitating immersion either automatically (after reaching a threshold temperature) or through a remote system (after recognising and confirming the occurrence of an accident). These objectives could be attained in different ways. In the case of a stationary storage system, it is possible, for example, to implement on of the following measures:

- Sealed room resistant to total water immersion
- Sprinkler system that would take the place of system inerting and cooling by progression immersion of the system: the flow and therefore the speed of filling must be high enough not to create undesirable effects such as water electrolysis and release of hydrogen.
- Fume and air evacuation system on the top part: this system would be able to be activated either by removing air through excess pressure in the system created by a ventilation system (brought by the emergency services or automatic) or by filling the space with water.
- Any system enabling safe management of the evacuation of fumes created in the space whether cold (and therefore at the bottom) or hot (and so higher up)
- Remote or insulated space through a fire wall on the shared walls with a larger building with greater consequences could present difficulties.

Of course, these measures are intended for storage systems that have a capacity that is considered high (for example over 20kWh) and in building applications enabling the implementation of such preventative measures for which the cost and maintenance could be undertaken by an individual or group.

For the case of small systems (for example under 20kWh), it could be interesting to limit the risks by recommending the storage system to be removed from an enclosed space in the building in order to eliminate the difficult factor of enclosed spaces for emergency services.

Finally, there are also the preventative barriers, regulatory or standard-based provisions that attain the obligations regarding system or structure fire resistance (fire stability, resistance against flames and thermal insulation). In general and in the context of ERPs, the classification of individual risk is involved. Reporting and identifying this type of space on fire plan is information that make emergency operations easier. In this case, a standard information plate should be created following the one used in solar power, for example. This information plate could as well as show the risk, indicate the capacity of the batteries installed.

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[1] Lithium-ion capacitor safety assessment under electrical abuse tests based on ultrasound characterization and cell opening, L. Ocaa,b,N. Guillet, R. Tessard, U. Iraola

Protective barriers

On the vector

Water as the best means of cooling and extinction

The action on the vector has the objective of limiting or even neutralising the effects on targets. The tests carried out with fire identified water as the best method of cooling and extinction.

Easy to access, available in large quantities, low cost, easily transportable and easy to spray, water has a number of advantages. Nevertheless, in order for cooling to be effective it is essential that is used in high quantities, continuously and that it covers the whole surface:

- **In quantity:** tests have highlighted the need to spray at least 20L/min per kWh (or roughly 100L/min for a storage system of 50kg/5kWh or roughly 800L/min for a cabinet storage system weighing 500kg/40kWh). Beyond these storage power ratings, the average flow rate needed is 1000L/min in order to be enough to cover the whole surface.
- **Continuously:** stopping cooling leads systematically to a reignition of the gases and restart of the fire,
- **Across the whole surface:** in order to act on the thermal vector, it is useful to use the maximum spray capacity of the hoses in order to try and cover all of the storage system.

Figure 57: Using two variable flow hoses at 500L/min each on a 40kWh battery cabinet.

For effective extinction and when it is possible, total immersion of the storage system is the best method of reaching complete extinction. This action could be performed in several ways:

- By moving the storage system into a host structure filled with water (tank, pool, retention, etc.),
- By proceed to fill the storage system space (in the case that it is watertight) and to create access methods for spraying water,
- By implementing a system that would allow for immersion (punch button) which would release a load of water.

In the two last cases, it is useful to implement measures enabling any possible fumes, air or hydrogen contained in the space to be evacuated.

Cooling by using hoses is fundamental, depending on the dimensions of the battery, the immersion option can be kept as an extra.

Figure 58: Illustrations of creating systems enabling battery immersion.

Other extinction methods experimented

Implementation of other extinction methods has systematically presented limitations that only water has been able to overcome. This has been the case for numerous extinction methods:

- Multipurpose powders such as ABC. Using a powder extinguisher can reduce flames and radiation as long as it is sprayed but the fire systematically starts up afterwards
- Special type D powders adapted for metal fires react in the same way as special powders.
- Carbon dioxide (CO$_2$) put out the flames present on the storage system but did not provide effective cooling. Use of an inerting method using carbon dioxide or nitrogen would present considerable obstacles. The production of O2 noted on certain storage chemistries would allow the thermal runaway to continue reaction even without the oxygen from the air. Also, this type of inerting poses the problem of dealing with flammable unburnt white fumes.
- The foam actively contributes to cooling the storage system but has no other advantage
- Inert materials such as sand or cement allow for suffocation only if sufficient quantities are placed. This action leads to generation of cold flammable white flames. During testing, it was observed that after a certain amount of time, a crater was created allowing flammable gases and even flames and flying material to escape
- A quartz stone cover was also tested. Effective for suffocating a small sized storage system, the fact it was not sealed allowed for flammable gases to escape and reignite (cold white fumes).

Generally, it was highlighted that only the use of water because of its absorption capacity for released heat enabled effective cooling. This cooling as long as the water is able to enter into contact with the storage system components.

Figure 59: Using foam of a 40kWh battery fire.

Figure 60: Attempt to extinguish a storage system with dry sand.

Figure 61: Attempt to extinguish a storage system using an anti-fire cover and generation of cold white fumes.

On the targets

Action on the targets is also a protective barrier. The first action on targets must be implemented during the call by identifying the key indicators that would facilitate emergency operations. These key indicators could be the following:

- Storage system capacity in kWh or in volume or weight
- Storage charge state
- Storage in enclose space or not
- Failure indicators: loud bangs, fumes (colour, density, located), flames, etc.

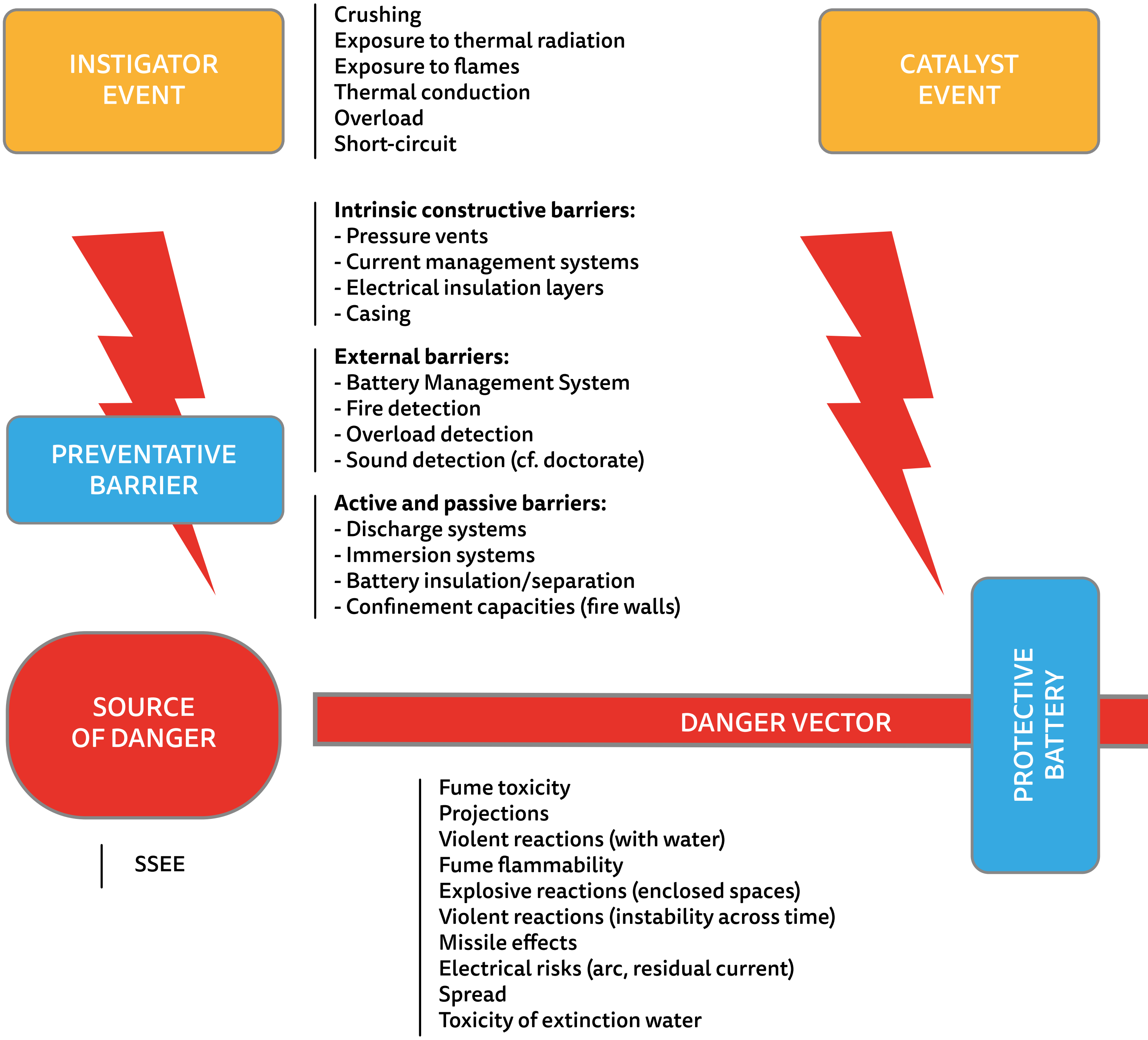
These elements enable the CTA operator then the COS to calculate the size of the accident and predict the equipment needed and the actions to take.

It could ease evacuation or improve the safety of the people around or remove the risk of spread by moving fuels. Implementation of a "water bell" for structures also constitutes action on the thermal vector and potentially the toxic vector.

Concerning physical, chemical and thermal risks, a minimal safety perimeter of 100m and minimum exposure for people, systematically equipment of PPE must be sought by the COS throughout the operation. This measure is proposed at the start It must be adapted depending on the development of the accident but also depending on the development of COS's knowledge of the situation during the operation (battery technology, quantity, state of charge, space configuration, etc.).

SYSTEMIC ANALYSIS OF ELECTROCHEMICAL ENERGY STORAGE SYSTEMS

The systemic analysis of the danger globality that electrochemical energy storage systems represent can be summarised in the diagram shown below.



Crushing
Exposure to thermal radiation
Exposure to flames
Thermal conduction
Overload
Short-circuit

Intrinsic constructive barriers:
- Pressure vents
- Current management systems
- Electrical insulation layers
- Casing

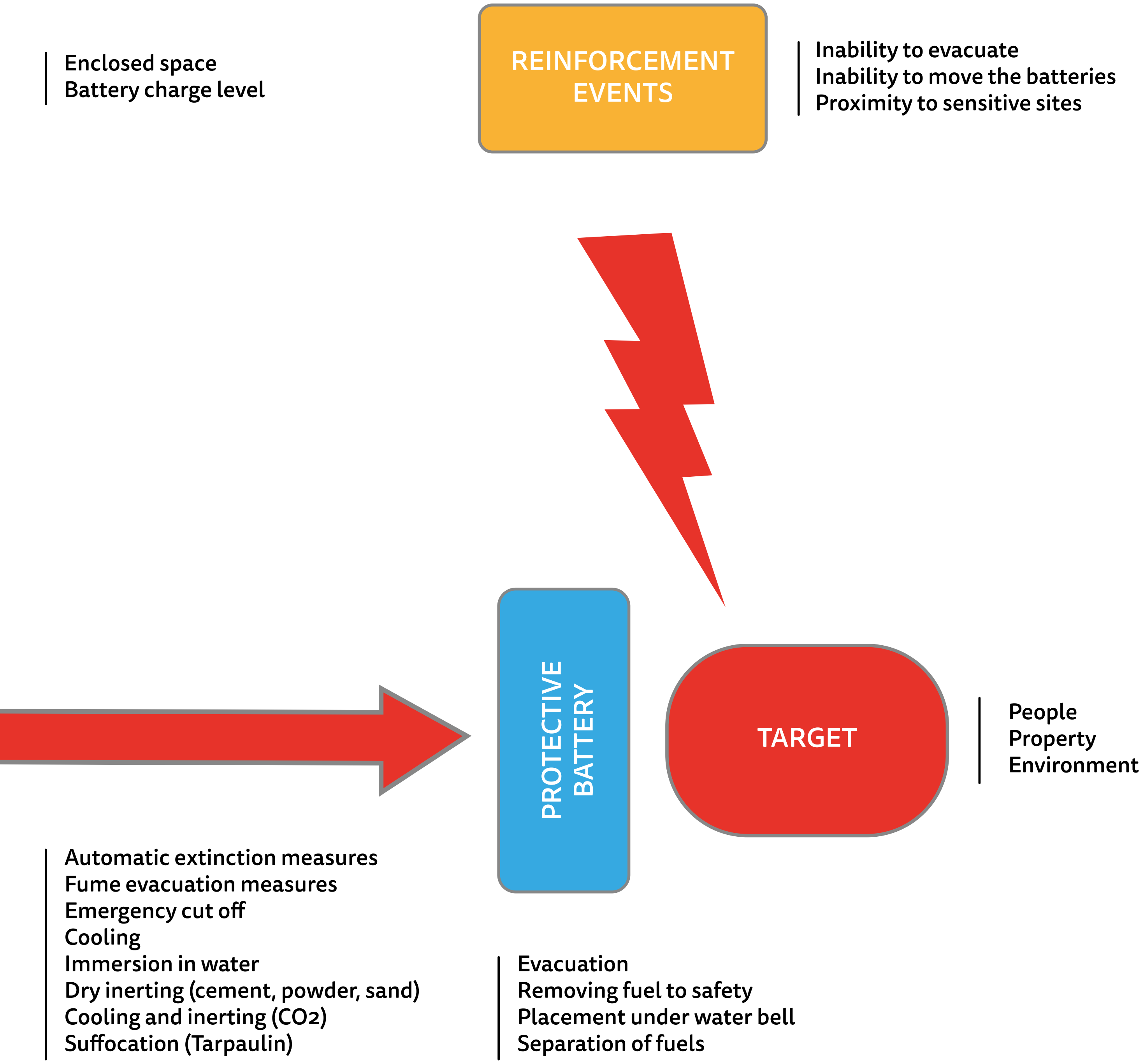
External barriers:
- Battery Management System
- Fire detection
- Overload detection
- Sound detection (cf. doctorate)

Active and passive barriers:
- Discharge systems
- Immersion systems
- Battery insulation/separation
- Confinement capacities (fire walls)

SSEE

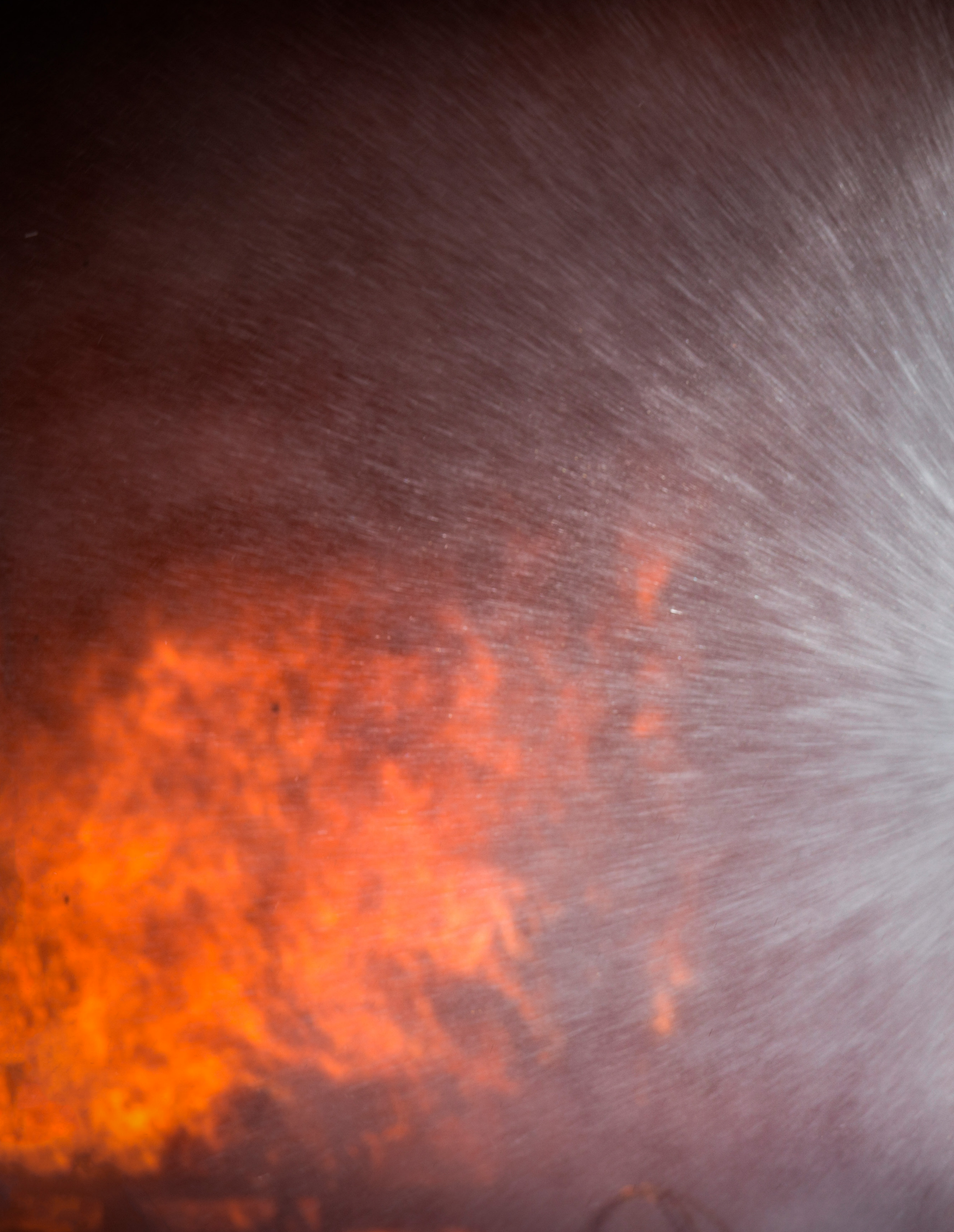
Fume toxicity
Projections
Violent reactions (with water)
Fume flammability
Explosive reactions (enclosed spaces)
Violent reactions (instability across time)
Missile effects
Electrical risks (arc, residual current)
Spread
Toxicity of extinction water

Figure 62: Systemic analysis of electrochemical energy storage systems.


Enclosed space
Battery charge level
REINFORCEMENT EVENTS
Inability to evacuate
Inability to move the batteries
Proximity to sensitive sites
PROTECTIVE BATTERY
TARGET
People
Property
Environment
Automatic extinction measures
Fume evacuation measures
Emergency cut off
Cooling
Immersion in water
Dry inerting (cement, powder, sand)
Cooling and inerting (CO2)
Suffocation (Tarpaulin)
Evacuation
Removing fuel to safety
Placement under water bell
Separation of fuels

5

OPERATIONAL RECOMMENDATIONS



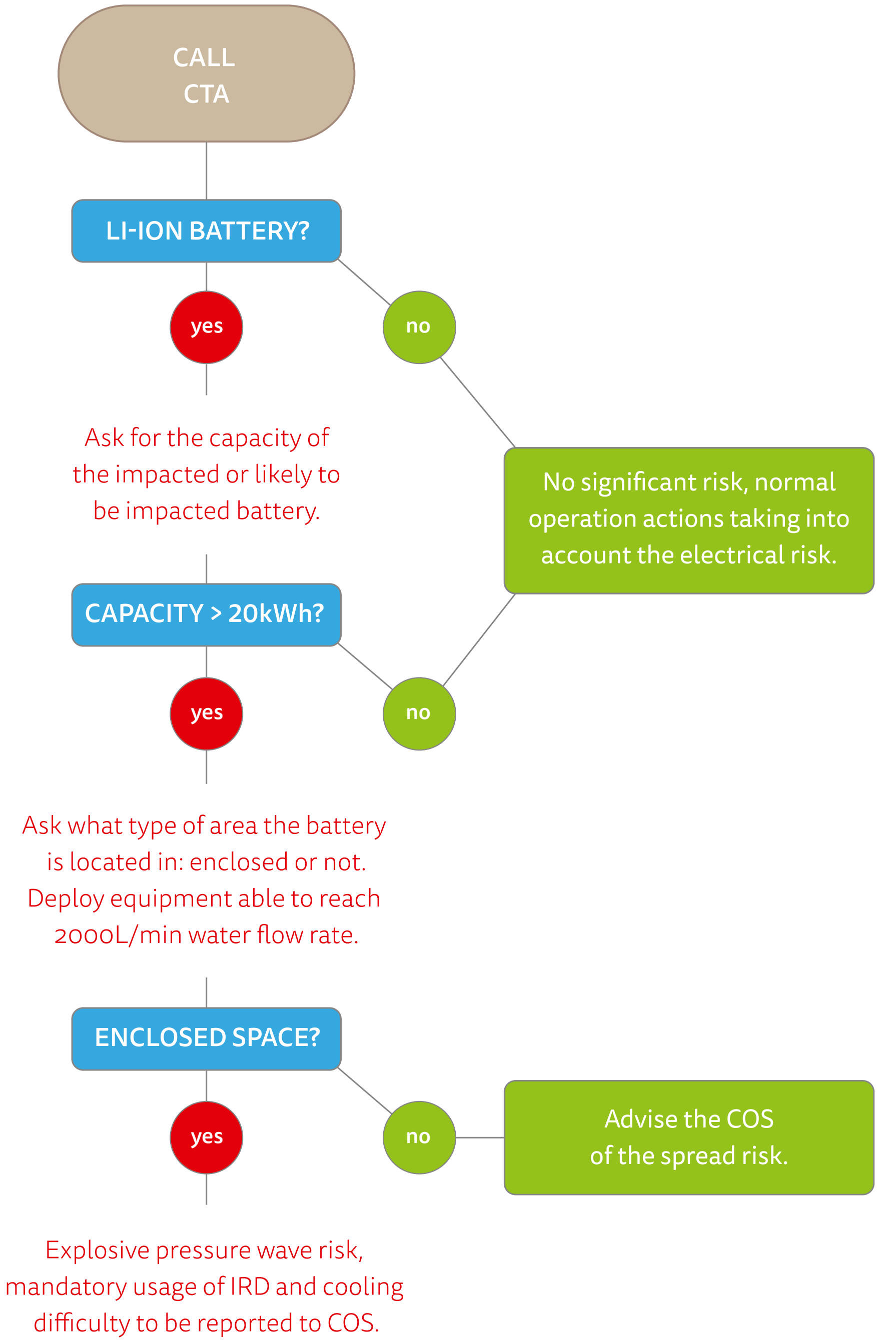
GENERALITIES

The understanding acquired by the fire-fighters during this work has allowed for a first set of accident management possibilities to be drawn up when involving an electrochemical energy storage system.

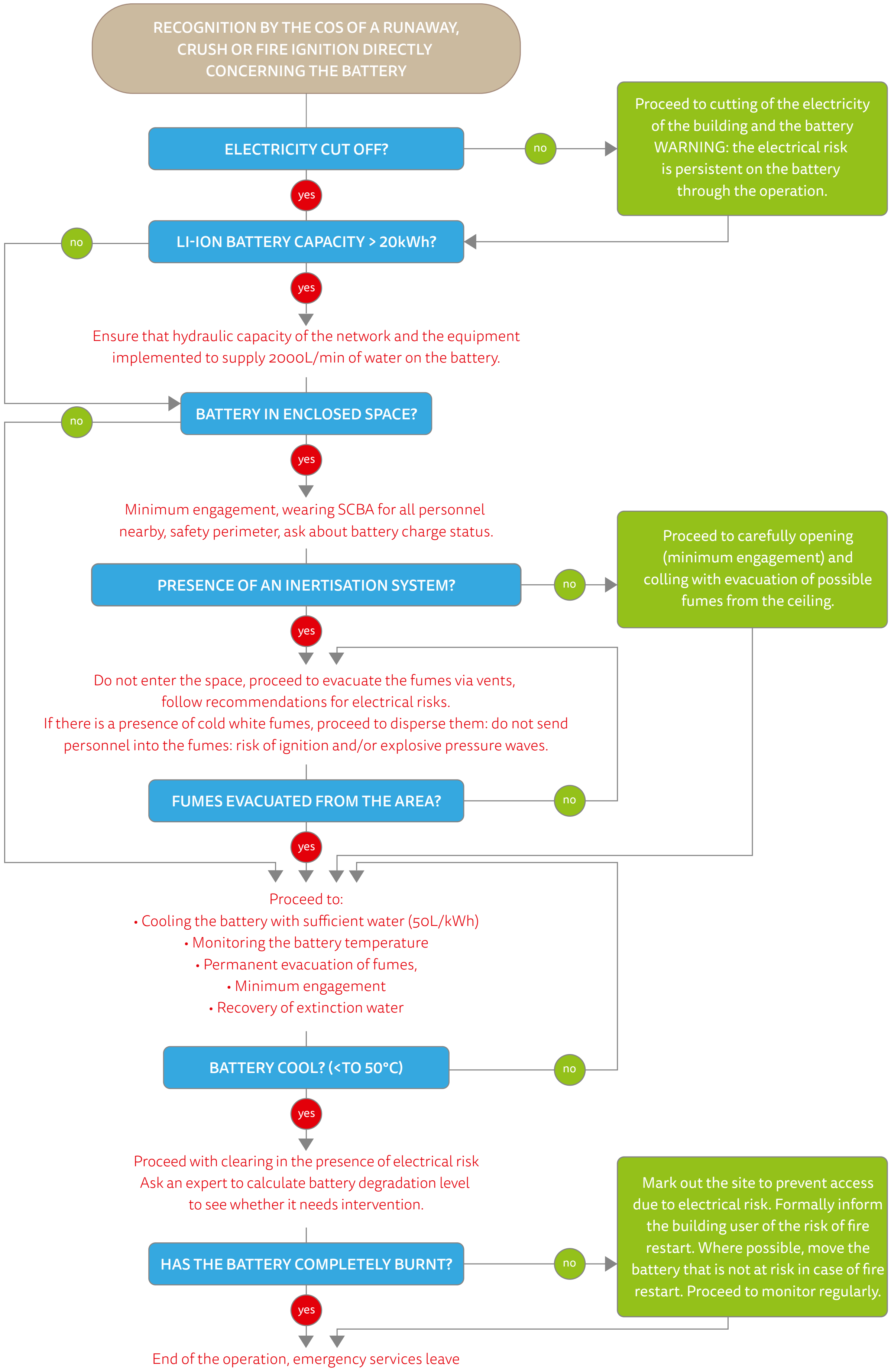
EMERGENCY OPERATION ACTIONS

Looking at the elements highlighted in this document, it would seem interesting to propose here a flowchart to help with operational actions to take in case of a storage system accident. Of course, this approach is carried out taking into account understand of the situation and also observations made by members of this GT. They are valid as far as the current understanding of the members of the GT and are proposed here by departmental fire and emergency services that participated in the GT. These recommendations should be considered as an absolute guide but will help future authors of such a guide to write it.

Proposition:
As far as the CTA is concerned:



Proposition of action to take by the COS during the emergency operation:



RECOGNITION BY THE COS OF A RUNAWAY, CRUSH OR FIRE IGNITION DIRECTLY CONCERNING THE BATTERY

ELECTRICITY CUT OFF?

Proceed to cutting of the electricity of the building and the battery WARNING: the electrical risk is persistent on the battery through the operation.

LI-ION BATTERY CAPACITY > 20kWh?

Ensure that hydraulic capacity of the network and the equipment implemented to supply 2000L/min of water on the battery.

BATTERY IN ENCLOSED SPACE?

Minimum engagement, wearing SCBA for all personnel nearby, safety perimeter, ask about battery charge status.

PRESENCE OF AN INERTISATION SYSTEM?

Proceed to carefully opening (minimum engagement) and colling with evacuation of possible fumes from the ceiling.

Do not enter the space, proceed to evacuate the fumes via vents, follow recommendations for electrical risks.
If there is a presence of cold white fumes, proceed to disperse them: do not send personnel into the fumes: risk of ignition and/or explosive pressure waves.

FUMES EVACUATED FROM THE AREA?

Proceed to:

- Cooling the battery with sufficient water (50L/kWh)
- Monitoring the battery temperature
- Permanent evacuation of fumes,
- Minimum engagement
- Recovery of extinction water

BATTERY COOL? (<TO 50°C)

Proceed with clearing in the presence of electrical risk
Ask an expert to calculate battery degradation level to see whether it needs intervention.

HAS THE BATTERY COMPLETELY BURNT?

Mark out the site to prevent access due to electrical risk. Formally inform the building user of the risk of fire restart. Where possible, move the battery that is not at risk in case of fire restart. Proceed to monitor regularly.

End of the operation, emergency services leave

CLEARING PHASE

The clearing phase is frequently characterised by lower vigilance from personnel s the feeling of risk is reduced. It is nevertheless admitted that this phase, notably immediately after the fire, has risks of intoxication by carbon monoxide or chemical compounds polluting the work zone as well as fall risks or falling material.

In the case of batteries, this phase is also extremely important and requires on the part of the COS particular attention because the residual risks are considerable. They are of varied nature:

- The residual electrical risk: when the battery has not completely burnt, the residual voltage can still be several hundred volts
- The thermal risk: the battery, presenting a high thermal inertia, remains hot even after intense cooling from variable flow hoses
- Chemical risk: deposit of soot loaded with cobalt or manganese can present a risk of contamination of operators' clothing
- Restart risk: a new thermal runaway can occur several hours, or several days after extinction: long term monitoring is necessary

One of the difficulties resides in calculating whether the battery (cell assembly) has burnt completely or not. This information must enable the correct measures to be taken afterwards.

It is recommended not to manipulate a partially damaged battery without taking particular precautions concerning fire restart. Moving a damaged battery could cause internal or external short-circuit that could result in:

- Violent arc flashes with projections of molten metal
- The creation of a new thermal runaway immediately
- The creation of a new thermal runaway but delayed (several hours to several days)
- A latent electrical risk

In any case, if the movement is necessary, it should be done with PPE for operators, water available and as far as possible temperature measure or infrared thermography throughout the manoeuvre.
This movement will be justified by a residual risk linked to the battery that is putting people, property or the environment in danger. A secured site away from buildings or sensitive areas must be found enabling easy monitoring for the storage of the damaged battery.

END OF EMERGENCY OPERATION

The main obstacle against emergency services leaving concerns the risk of the thermal runaway restarting in a time frame that is way beyond the time frames observed for other types of fire (from several hours to several days). The residual uninterruptible electrical risk represents and extra obstacle for ending the operation. The idea of transferring responsibility at that moment must clearly be recorded and the COS must announce it to the user/owner of the residual risks.

The following preventative measures must be considered:

- Calculation of the number of battery cells left to burn: if the battery is totally burnt, the residual risk is zero, this calculation is not simple and requires an expert opinion
- The cooled battery must be extracted from the area in which it is found (if this is in a room or a place at risk of spread) with the help of equipment (e.g., Cherry picker or forklift) and positioned in a place with no spread risk and enabling regular monitoring: ideally outside, with enclosed spaces prohibited
- The electrical cables linking the battery must be identified (without being touched by an untrained person) and safety marking must signal the electrical risk

CONCLUSIONS ON THE OPERATIONAL SECTION

This work enables a better understanding of the behaviour of electrochemical energy storage systems in buildings in extreme situations. It is obvious that this type of system used in an enclosed environment presents complex management problems in terms of suitable fire-fighting equipment implementation.

The first stage of dealing with the risk associated with stationary storage batteries consists of detecting the event, notably the start of a thermal runaway of a battery pack. The cause of this runaway is not necessarily known. Nevertheless, if one of the following events occurs on the battery, it is likely that in the minutes or hours to come that there will be a thermal runaway. The trigger events are impacts, crushing, overload because of BMS failure, short-circuit because of impact of incorrect manipulation by an operator, intense heat source near to the battery. In these cases, and before the external appearance of thermal runaway, it is recommended to proceed with monitoring the internal temperature of the battery pack in order to predict an operate on it, if necessary, as easily as possible to cool the battery down. This monitoring can be carried out using the BMS and its temperature measurements when they are accessible to the operator, and by their intermediary, the fire and emergency services. In the case of inability to access these data, it is recommended to monitor using a thermal camera or laser thermometer as close as possible to the impacted cells and always using the same measurement zones.

In the case where the trigger event is external toe the battery (fire in the immediate environment for example) it would seem important to limit the increase in battery temperature by using a screen. This protective screen may be a fire wall or water screen or even cooling by spraying the battery with water. In the last case, the preservation of the integrity of the battery is lost and the goal is not to preserve the battery but to preserve the building or other important properties.

Firstly, in collecting information, it is important to know or be able to have an indication of the battery charge level. The higher the charge, the greater the reaction. This is the same for the size or capacity of the battery.

The aspects associated with recognition are also very important, notably in identifying the battery but also more particularly by identifying the warning signs of a thermal runaway such as:

- Emission of black or white fumes
- Strong odour with a difficult to describe smell: it could be described as "chemical"
- Flames
- Bangs
- Projections

The first response firefighting methods such as extinguishers (water, water with additive, CO2 and powders) have not shown any effectiveness and expose users to projections of molten metal, flames and toxic fumes as well as electrical risk. The fire-resistance tarpaulins limit projections but only have a relatively low effectiveness duration (roughly 30 seconds to 1 minute). Additionally, they facilitate the emission of flammable white fumes and during ignition, the spread of the fire.

The evacuation of these fumes in an enclosed spaces would seem essential considering their flammability, including the cold fumes in the absence of flames. These white and cold fumes were also likely to condense on cold surfaces by placing flammable electrolyte. It can be considered, in the context of a first approach with personnel unequipped with PPE (non fire-fighters) that this reaction could lead to burn risks. Additionally, these uncondensed cold fumes are flammable. It has been observed that these white fumes are created when the thermal runaway occurs in an inert atmosphere or one low in oxygen. These fumes are therefore unburnt and present a latent explosive pressure have risk for operators. In the case of batteries with automatic argon inerting, these fumes must be controlled via ventilation before personnel can enter.

Then, we note here that the water needed to contain the reaction then cool battery is a large amount with the ideal situation being total immersion of the electrochemical system. The use of water must be done as soon as possible after detection of the thermal runaway in order not to lead to complete thermal runaway of the battery. The more the runaway touches other cells, the greater the reaction and the harder it is to cool because of the increase in energy being dissipated.

The water may be less effective because of the battery packaging. The stationary storage batteries are also almost systematically installed in metal cabinets or ventilated/non-ventilated metal cases. These configurations make spraying often ineffective, and this is the case regardless of how much water is used of the number of hoses. The water cannot enter into the cell level and has no cooling effect allowing the thermal runaway reaction to continue. This is why total immersion is considerably more effective.

The use of IRD is essential considering the toxicity of fumes and particularly in an enclosed environment where the concentration effect of toxic chemicals is high. In an open environment, it is observed that the toxicity of fumes is not higher than of a traditional fire. Also, the materials ejected from the battery such as cobalt can contaminate clothing and so operators in close contact with the battery via particles transported in the fumes or placed on the ground.

Finally, one of the major risks remaining throughout the operation is the electrical risk. The battery is an uninterruptible source of current. Voltages can reach 1000 or even 1500V in direct current in the largest systems. It is therefore essential to keep personnel away from the electrical risk including once the battery is cooled and especially when it has not completely burned.

The general rules of electrical risk apply, and the most evident risks are:

- Respecting a safe distance if possible of 5m form the hose holder with the battery
- Use an attack diffuser jet
- Consider running water
- Consider possible electrical arcs and more particularly during the clearing phase in case the battery is not completely burned (this diagnostic is not negligeable).

APPENDICES

PRÉFET DU RHÔNE

Service départemental-métropolitain
d'incendie et de secours

Direction de la prévention et de l'organisation des secours

Groupement réponse aux crises majeures et aux attentats

Lyon, le 15 novembre 2018

Affaire suivie par : Cne Cédric PASQUIER
Tél. : 04 72 84 39 54
gcma@sdmis.fr

RAPPORT D'ANALYSE

Etude de la toxicité des fumées de feux de batterie Li-ion
VDIP de la zone Sud-Est

1. Objet

Participation du VDIP dans le cadre d'un groupe de travail sur les feux de batteries Li-ion. Etude de la toxicité des fumées se dégageant d'un tel feu, qu'il s'agisse de fumées de décomposition ou de combustion. Les essais sur la toxicité se sont déroulés sur trois jours non consécutifs sur le site de VICAT à Chambéry (73)

2. Eléments contextuels

Les essais ont portés sur trois différents types de batterie Li-ion :

- Les cellules « vertes » : produites par la société A123 et composées d'une électrode positive en phosphate de fer ($LiFePO_4$) et d'une électrode négative en graphite - état de charge de 30 à 50 %
- Les cellules « violettes » et batteries « demi-lunes » : produite par la société Samsung et composées d'une électrode positive en oxyde métallique de type MNC ($Li[Ni_xMn_yCo_z]O_2$ avec $x+y+z=1$) et d'une électrode négative en graphite - état de charge 50 % ou plus
- Les packs batterie Li-ion – Alu de 900 W : cellules de voiture Tesla produites par la société Panasonic composées d'une électrode positive de type NCA ($Li\text{-}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$) et d'une électrode négative en graphite.

Les électrolytes des trois types de batteries sont similaires, ils se composent de LiPF6, de carbonate d'éthylène (**EC**) et de carbonate de propylène (**PC**), avec différents additifs propres à chacun.

Trois types de sources d'inflammation ont été testés sur ces batteries :
-par rayonnement
-par brulage
-par surtension.

Photographies des batteries et de l'installation ayant servi aux essais en Annexe 1 de ce rapport.

3. Analyses

3.1 Stratégie d'analyse :

La même stratégie analytique a été utilisée pour tous les types de batterie.

3.1.1 Détection

La détection de certains gaz a été effectuée à l'aide des appareils suivants :

- Cellules électrochimiques acide fluorhydrique/chlorhydrique (HF/HCl), monoxyde de carbone (CO), dioxyde de soufre (SO2), acide cyanhydrique (HCN), dioxyde d'azote (NO2), monoxyde de carbone, dioxyde de carbone (CO2), sulfure d'hydrogène (H2S), chlore (Cl2), ammoniac (NH3).
- Explosimètre à cellule catalytique.
- Explosimètre à cellule IR.

Les cellules électrochimiques et les explosimètres ont été placés sur une perche de 2 m, pour pouvoir les maintenir dans les fumées le temps nécessaire à la mesure en toute sécurité, le PID et l'AP4C quant à eux ont été tenus à bout de bras pour pouvoir faire les relevés dans les fumées. Les appareils se trouvaient à une distance approximative de la source comprise entre 1.5m et 3 m.

3.1.2 GC-MS

Les prélèvements ont été effectués par le biais de tubes Tenax à l'aide d'une pompe automatique, placés au sein des fumées grâce à une perche puis ramenés dans le VDIP pour analyse.
Les méthodes d'analyse par spectrométrie de masse sont décrites dans l'annexe 2 de ce rapport.

3.1.3 IR-TF gaz

Les prélèvements ont été effectués par le biais de canisters placés directement dans les fumées puis ramenés dans le VDIP pour analyse.
Les méthodes d'analyse par spectrométrie infrarouge pour gaz sont décrites dans l'annexe 3 de ce rapport.

3.1.4 IR-TF ATR

Les analyses IR ont été menées sur des projections de matière sous pression (liquide, aérosol et/ou solide), lors de l'explosion des piles, qui ont été récupérées sur une pelle qui fut placée devant le dispositif de brulage pendant un essai.
Les méthodes d'analyse par spectrométrie infrarouge pour solides sont décrites dans l'annexe 4 de ce rapport.

3.1.5 Bandelettes de détection d'ions et papier pH

Le papier pH et les bandelettes de détection pour les ions PO_4^{3-}, Cl^-, SO_4^{2-} et NO_3^- ont été utilisés sur les résidus solides récupérés sur la pelle et solubilisés dans de l'eau.

3.2 Résultats d'analyses des fumées pour les 3 types de batterie

3.2.1 Cas des fumées de combustion

Pour les trois types de batterie, les fumées de combustion (hors phase de libération de gaz) présentent les caractéristiques classiques des fumées de feu. Aucune toxicité particulière autre que celle habituellement présente dans des fumées d'incendie n'a été détectée.

3.2.2 Cellules « vertes »

a) Détection

	HF/HCl	**NH_3**	**H_2S**	**SO_2**	**HCN**	**CL_2**	**NO_2**
Min (ppm)	0	7	0	0	0.5	0	0
Max (ppm)	0	15	3	0	1.3	3	0
Nbre de fois mesurées	0	3	1	0	2	2	0
Nbre d'essais	3	3	3	3	2	3	3

On remarque une concentration non négligeable détectée sur la cellule ammoniac (NH3).
Pour les autres gaz les détections étaient très faibles voire inexistantes et peuvent être considérées comme négligeables.

b) GC-MS

Trois produits ont été identifiés lors des deux analyses menés sur le GC-MS, du carbonate de diméthyle (**DMC**), du ethyl methyl carbonate (**EMC**) et du 1-methylpyrrolidin-2-one.

c) IR-TF

Deux produits ont été identifiés lors des deux analyses sur le spectromètre IR-TF, du carbonate de diméthyle (**DMC**) et de l'ethyl methyl carbonate (**EMC**). La présence d'ammoniac et de 1-methylpyrrolidin-2-one n'a pas été détectée, ce qui suppose que leurs concentrations restent en dessous des seuils de détection de l'appareil.

d) Conclusion

Ce type de batterie dégage donc en majorité lorsqu'elle est soumise à un flux thermique, du carbonate de diméthyle (**DMC**) et de l'ethyl methyl carbonate (**EMC**). Ces produits sont issus de l'électrolyte ou de sa dégradation. La présence d'ammoniac est quant à elle possible mais en des quantités ne représentant aucune toxicité particulière et reste à vérifier lors d'essais complémentaires.

3.2.3 Cellules « violettes »

a) Détection

	HF/HCl	NH_3	H_2S	SO_2	HCN	Cl_2	CO	NO_2	LIE (cat)	LIE (IR)
Min (ppm)	0	0	0	1.8	0	0.7	115	0.5	0	0.4
Max (ppm)	3.8	20	22	100	30	10.8	1400	5	17	2.5
Nbre de fois mesurées	1	1	5	6	4	3	6	6	4	4
Nbre d'essais	6	6	9	6	8	3	6	6	5	5

Pour ce type de batterie, on remarque en plus du monoxyde de carbone (CO), la mesure de dioxyde de soufre (SO_2) en quantité non négligeable. La présence de dihydrogène est fortement probable du fait que l'explosimètre à cellule catalytique réagisse 7 fois plus que l'explosimètre à cellule IR. De faibles concentrations de fluorure d'hydrogène (HF) ont été également détectées lors de certains essais mais les mesures ne sont pas reproductibles. La mesure de fluorure d'hydrogène semble être un phénomène aléatoire et non systématique lorsque la batterie est soumise à un flux thermique.
Les autres concentrations de gaz détectées sont négligeables.

b) GC-MS

Sur ce type de batterie, la présence de carbonate de diméthyle (**DMC**) et de l'acide méthoxyacétique (dégradation de l'électrolyte) ont été identifiés majoritairement ainsi que de l'ethyl methyl carbonate (**EMC**) en plus faible quantité.

c) IR-TF

Sur les huit essais réalisés sur cette catégorie de batterie, trois produits ont été détectés à chaque fois, le carbonate de diméthyle (**DMC**) et le monoxyde de carbone (CO) et le dioxyde de carbone (CO_2). Le carbonate de diméthyle (**DMC**) étant le produit majoritaire.
Sur plus de la moitié des essais du ethyl methyl carbonate (**EMC**) et du méthane ont également été détectés en quantités moindres.

d) Conclusion

Ce type de batterie dégage donc en majorité lorsqu'elle est soumise à un flux thermique, du carbonate de diméthyle (**DMC**) et de l'acide méthoxyacétique qui proviennent de l'électrolyte.
On retrouve également du monoxyde de carbone et du dioxyde de carbone résultants en partie de la combustion de l'emballage. Sont présents également en plus faibles quantités dans les dégagements gazeux du ethyl methyl carbonate (**EMC**) et du dihydrogène.
La présence de dioxyde de soufre est quant à elle probable et doit être confirmée.
La présence du fluorure d'hydrogène n'a pas été mise en évidence dans les fumées sur l'ensemble des essais à 3 m, laissant supposer une émission non systématique suite à la décomposition de l'électrolyte. De plus les concentrations mesurées restent faibles (à l'air libre).

3.2.4 Pack batterie Li-ion – Alu de 900 W

a) Détection

	HF/HCl	NH3	H2S	SO2	HCN	CL2	CO	NO2	LIE (cat)	LIE (IR)
Min (ppm)	0	0	0	0.8	0	0	0	0	0	0
Max (ppm/LIE)	26.6	5	4	8.1	0	4.2	226	3.5	4	7.2
Nbre de fois mesurées	2	3	1	6	0	3	4	3	1	2
Nbre d'essais	5	6	6	6	5	4	5	6	4	4

On remarque une forte concentration de monoxyde de carbone (CO), ainsi qu'un essai qui présente une forte concentration en acide fluorhydrique (HF). La présence d'acide fluorhydrique dans les fumées est plutôt aléatoire. Du dioxyde de soufre (SO_2) et du dioxyde d'azote (NO_2) ont également été détectés sur la plupart des essais mais en faibles quantités. Les autres gaz sont en quantités négligeables ou leur détection relève d'une interférence possible.

b) GC-MS

Sur ce type de batterie, la présence de l'ethyl methyl carbonate (**EMC**) et du carbonate de diméthyle (**DMC**) a été identifié.

c) IR-TF

Sur cinq essais menés sur ce type de batteries, un produit a été détecté à chaque fois, le carbonate de diméthyle (**DMC**).
Sur certains essais, de l'ethyl methyl carbonate (**EMC**) et du monoxyde de carbone ont été détectés en plus faibles quantités

d) Résidus récupérés sur la pelle

i. Bandelettes de détection d'ions et papier pH

Moyens de détection	**pH**	**PO_4^{3-}**	**SO_4^{2-}**	**Cl^-**	**NO_3^-**
Résultats	1	> 100 mg/L	> 400 mg/L	0 mg/L	0 mg/L

On remarque la présence d'ions phosphate et sulfate en quantité non négligeable le pH de la solution très acide laisse supposé la présence des formes acides de ces ions, c'est-à-dire, l'acide phosphorique et l'acide sulfurique.

ii. IR-TF

Du carbonate d'éthylène (**EC**) a été détecté dans les résidus récupérés sur la pelle. D'autres pics présents sur le spectre infrarouge n'ont pas pu être identifiés.

e) Conclusion

Ce type de batterie dégage donc en majorité lors de sa combustion, du carbonate de diméthyle (**DMC**) et de l'ethyl methyl carbonate (**EMC**) ainsi que du monoxyde de carbone. La présence de dioxyde de soufre est quant à elle probable de même que celle de dioxyde d'azote mais elles nécessitent d'être confirmées par une autre technique d'analyse. Ces valeurs restent néanmoins faibles et n'entrainent pas de toxicités particulières.
La présence du fluorure d'hydrogène n'a pas été mise en évidence dans les fumées sur l'ensemble des essais à 3 m, laissant supposer une émission non systématique suite à la décomposition de l'électrolyte. De plus les concentrations mesurées restent faibles (à l'air libre).

A été également mis en évidence lors des phases de décompression de la batterie, des projections de matière (solides, liquides, aérosols…) composées essentiellement de carbonate d'éthylène (**EC**), d'ions phosphate (issus de l'électrolyte) et d'ions sulfate provenant surement de l'acide phosphorique et sulfurique.

4. Conclusion générale

Le tableau ci-dessous résume les résultats des mesures menées sur les différents types de batterie étudiés confondus.

	Majoritaires	Mesurés en plus faibles quantités	Présence à confirmer	Présence aléatoire
En phase gazeuse - tous les types de batterie	➢ **DMC** ➢ CO ➢ **EMC** ➢ CO_2	➢ H_2	➢ SO_2 ➢ NH_3	➢ HF dans 23 % des cas
Seulement dans les cellules « violettes »	➢ Acide méthoxyacétique			
Dans les projections de matière	➢ **EC**	➢ H_3PO_4	➢ H_2SO_4	

Les fumées émises lors de la rupture de l'évent, lorsque la batterie est soumise, soit à un flux thermique soit à une surtension, sont composées essentiellement de monoxyde de carbone, de dioxyde de carbone et **de carbonates**. Les carbonates sont issus soit de l'électrolyte soit de la décomposition de celui-ci. Ces carbonates n'apportent aucune toxicité particulière aux fumées. (FDS de tous les composés du tableau ci-dessus en annexe 6 de ce rapport).

Les gaz toxiques permanents (Cl_2, NO_2, SO_2, HCN, NH_3, H_2S) provenant essentiellement de la décomposition des matières contenants les atomes S, N, Cl restent à des concentrations faibles sauf pour le SO_2 et le HCN. Compte tenu de la technologie utilisée pour réaliser la mesure de ces gaz (cellules électrochimiques) il conviendra de les confirmer par une autre technologie lors d'essais complémentaires.

Pour le fluorure d'hydrogène, sa détection aléatoire (détecté dans moins d'un quart des essais) suggère qu'il n'est pas émis systématiquement lorsque la batterie est soumise à un flux thermique. De plus, sa faible concentration (moins de 30 ppm), mesurée à 3 m de la source, écarte tout danger en milieu ouvert. Il serait judicieux de mesurer sa concentration lors d'une combustion en milieu fermé.

En plus des fumées, des particules solides ou aérosols sont expulsées de la batterie. Ces particules sont composées essentiellement de carbonates mais également d'acide phosphorique et de sulfates. L'acide phosphorique pourrait être expliqué par l'hydratation de l'oxyde de phosphore (P_2O_5), décrit dans la littérature et qui n'a pu être mis en évidence par notre technique d'analyses. Il semblerait donc que ce dernier soit présent suite aux traces d'acides phosphoriques retrouvées sur les résidus solides.

En conclusion, en milieu ouvert, les batteries soumises à un flux thermique ou à une surtension émettent des fumées qui n'apportent aucune toxicité particulière par rapport à des fumées classiques de combustion. Il conviendrait pour confirmer cette première analyse de réaliser des essais en milieu fermé et sur des batteries de plus grosses capacités.

Le Rédacteur	Le Référent VDIP de la zone Sud-Est
Alexandra DE LA HOZ	Capitaine Cédric PASQUIER

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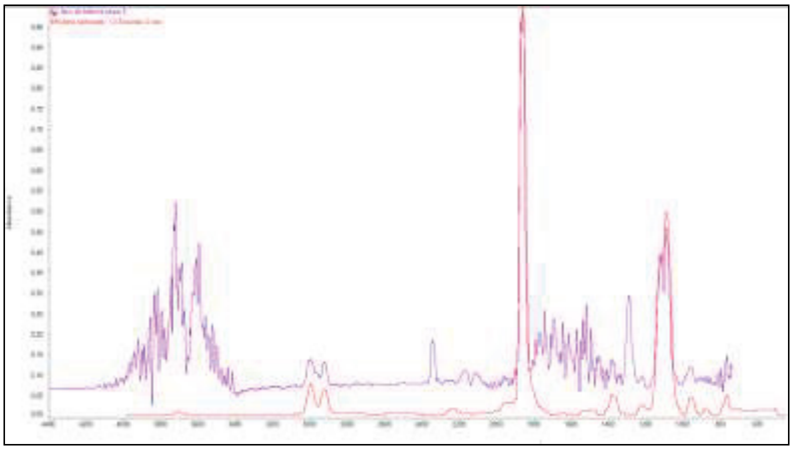
ANNEXE 1 : éléments de contexte des essais

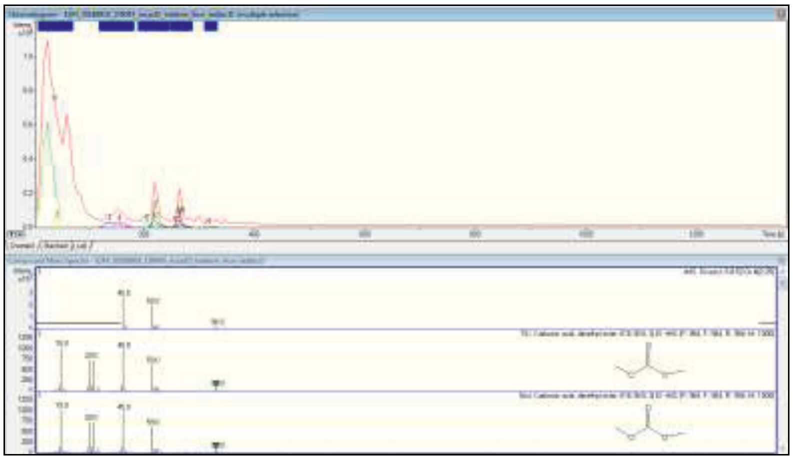
Dispositif mis en place pour les essais

Les 3 types de batterie, de gauche à droite :
Les cellules « vertes »
Les cellules « violettes »
Les packs batterie Li-ion – Alu de 900 W

ANNEXE 2 : exemples de spectres avec identification de carbonates



Spectres IR d'un essai sur packs batterie Li-ion – Alu de 900 W (violet) et du carbonate d'éthylène (rouge)



Spectre GC d'un essai sur une cellule « violette » avec identification sur le pic 1 de carbonate de diméthyle (profils MS sous le spectre GC)

ANNEXE 3 : protocole d'analyse des gaz

Analyse par GC-MS

L'appareil d'analyse est un couplage TD-GC-MS BRUKER E2M.

L'analyse par TD-GC-MS est réalisée dans les conditions suivantes :

- Gaz vecteur : air.
- La thermo désorption du tube de prélèvement se fait pendant 60 s à 240 °C.
- La séparation est effectuée sur colonne capillaire phase apolaire MXT1 de longueur 15 m, diamètre interne 0,32 mm et 5 µm d'épaisseur de phase.

Le programme de température de la colonne est notre programme routinier utilisé en intervention afin de réellement évaluer notre protocole en nous rapprochant le plus des conditions réelles :

- 25 °C / min de 45 à 100 °C.
- 35 °C / min de 100 à 220 °C.
- Palier de 15 minutes à 220 °C.

L'analyse se fait au niveau du détecteur de masse E2M par balayage des masses de 45 à 350 (EI = 70 eV, analyseur quadripolaire et source à 120°C).

Les spectrothèques utilisées pour l'identification sont la NIST et la CWAlib fournis par BRUKER.

ANNEXE 4 : protocole d’analyse des gaz

Analyse par spectrométrie IRTF

L’IRTF du SDMIS est destiné en priorité à l’identification de composés gazeux toxiques suite à un accident ou un attentat chimique. Il s’agit d’un spectromètre Nicolet IS10 (Thermofisher) présentant les caractéristiques suivantes :

- Séparatrice en KBr/Ge.
- Linéarité de 0 à 3 unités d’absorbance.
- Résolution minimale 0,5 cm-1.
- Vitesse de balayage allant de 0,15 à 3,7 cm.s-1.

Ce spectromètre est équipé d’une installation permettant l’analyse et le prélèvement de gaz ou de vapeur.

La cellule à gaz présente les caractéristiques suivantes :

- Le volume de la cellule est de 200 mL.
- Le trajet optique est de 2 m, à réflexions multiples.
- Le domaine de transmission s’étend de 740 cm-1 à 4400 cm-1.

ANNEXE 5 : protocole d'analyse des solides

Analyse par spectrométrie IRTF ATR

L'IRTF ATR du SDMIS est destiné à l'identification de solides ou liquides suite à un accident ou un attentat chimique. Il s'agit d'un spectromètre Mobile IR (Bruker) présentant les caractéristiques suivantes :

- Cristal en diamant avec une zone d'ombre entre 2100 cm^{-1}et 2300 cm^{-1}.
- Plage d'analyse comprise entre 400 cm^{-1} et 4000 cm^{-1}.

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ANNEXE 6 : Fiches de sécurité

Fiches au format PDF en pièces jointes.

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Service départemental-métropolitain
d'incendie et de secours

Direction de la prévention et de l'organisation des secours

Groupement réponse aux crises majeures et aux attentats

Affaire suivie par : Cne Cédric PASQUIER
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Lyon, le 26 juin 2020

RAPPORT D'ANALYSE

Etude de la toxicité des fumées de feux de batterie Li-ion
VDIP de la zone Sud-Est

1. Objet

Dans le cadre du groupe de travail sur les feux de batteries Li-ion, le VDIP a participé à l'étude de la toxicité des fumées se dégageant d'un tel feu, qu'il s'agisse de fumées de décomposition ou de combustion. Une première série d'essais mené en 2018 n'a révélé aucune toxicité particulière par rapport à des fumées classiques de combustion. Un complément à ses analyses avait alors été envisagé pour étudier notamment la toxicité en milieu clos. Les essais menés en mars 2020 interviennent dans ce cadre et apporte des éléments complémentaires à ceux de 2018.

2. Eléments contextuels

Les essais ont portés sur deux différents types de batterie Li-ion déjà étudiées lors des essais de 2018 :

- Les batteries quart de lune d'une part, produites par la société Samsung et composées d'une électrode positive en oxyde métallique de type MNC ($Li[Ni_xMn_yCo_z]O_2$ avec $x+y+z=1$) et d'une électrode négative en graphite - état de charge 50 % ou plus.
  Le but de ces essais étant d'analyser plus en détail la composition des fumées banches denses.

- Les packs batterie Li-ion d'autre part, cellules de voiture Tesla produites par la société Panasonic composées d'une électrode positive de type NCA ($Li\text{-}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$) et d'une électrode négative en graphite.
  Le but de cet essai étant à la fois de vérifier si l'inflammation d'une batterie Li-ion est plus toxique en milieu confiné qu'en milieu ouvert et de comparer la toxicité des fumées entre une batterie de faible capacité et une batterie de grosse capacité.

Trois types de sources d'inflammation ont été testés sur ces batteries :

- Par surtension.
- Par brulage.
- Par écrasement.

3. Analyses

3.1 Stratégie d'analyse

3.1.1 Détection

La détection de certains gaz a été effectuée à l'aide des appareils suivants :

- Cellules électrochimiques acide fluorhydrique/chlorhydrique (HF/HCl), monoxyde de carbone (CO), dioxyde de soufre (SO_2), acide cyanhydrique (HCN), dioxyde d'azote (NO_2), monoxyde de carbone, dioxyde de carbone (CO_2), sulfure d'hydrogène (H_2S), chlore (Cl_2), ammoniac (NH_3).
- Explosimètre à cellule catalytique.
- Explosimètre à cellule IR.

Les cellules électrochimiques et les explosimètres ont été placés sur une perche de 2 m, pour pouvoir les maintenir dans les fumées le temps nécessaire à la mesure en toute sécurité. Le PID et l'AP4C quant à eux, ont été tenus à bout de bras pour pouvoir faire les relevés dans les fumées. Les appareils se trouvaient à une distance approximative de la source comprise entre 1,5 m et 3 m.

3.1.2 GC-MS

Les prélèvements ont été effectués par le biais de tubes Tenax à l'aide d'une pompe automatique, placés au sein des fumées grâce à une perche puis ramenés dans le VDIP pour analyse.

Pour un essai, le condensat de fumées blanches fut analysé par dissolution dans l'eau et adsorption sur un SBSE.

Les méthodes d'analyse par spectrométrie de masse sont décrites dans l'annexe 2 de ce rapport.

3.1.3 IR-TF gaz

Les prélèvements ont été effectués par le biais de canisters placés directement dans les fumées puis ramenés dans le VDIP pour analyse.
Les méthodes d'analyse par spectrométrie infrarouge pour gaz sont décrites dans l'annexe 3 de ce rapport.

3.2 Résultats d'analyses

3.2.1 Les batteries quart de lune

Trois batteries quart de lune ont servie à ces essais. L'une a été mise en surtension (batterie 1), les deux autres ont subi un choc suite à la chute d'une boule de pétanque d'une vingtaine de mètres (batteries 2 et 3). Les analyses sur la batterie 3 ont été menées après extinction des flammes.

a) Caractérisation des fumées de combustion – fumées blanches

Les fumées de combustion ont été analysées par IR Gaz lors du test sur la batterie 1. Elles présentent une forte concentration en électrolyte : carbonate de diméthyle (**DMC**) et carbonate d'éthyle et méthyle (**EMC**).

b) Caractérisation des fumées blanches denses – rejets ponctuels

Pour la batterie 1, les fumées blanches ont été analysées avant et après explosion de la cellule. En revanche, pour la batterie 2 elles ont été analysées uniquement avant explosion de la cellule et pour la batterie 3 seulement après extinction du feu.

Détection

	PID	**HCN**	**CO**	**NO_2**	**LIE (cat)**	**LIE (IR)**
Batterie 1 avant explosion	63	NR	NR	0	NR	NR
Batterie 1 après explosion	250	0	80	0	NR	NR
Batterie 2	NR	0,8	70	5,7	60-80 %	35 %
Batterie 3 après extinction	NR	NR	- NR	- NR	- NR	- NR

NR = Non réalisé

On remarque la présence de composés organiques volatiles en concentration non négligeable. Une faible concentration d'acide cyanhydrique a également été mesurée sur la batterie 2. Les mesures par explosimètre mettent en avant la présence de dihydrogène dans les fumées.

GC-MS

Trois analyses par GC-MS ont été menées sur des prélèvements par tubes TENAX. Deux sur la batterie 1 (une avant explosion l'autre après) une sur la batterie 2

	Produits identifiés au GC-MS	
	Majoritaires	**Minoritaires remarquables**
Batterie 1 avant explosion	HAP à 12 carbones (1,2,3,6,7,8,8a,8b-octahydrobiphénylène ou cyclohexylbenzène) Carbonate de diméthyle (**DMC**) Carbonate d'éthyle et de méthyle (**EMC**) Peroxyde de diéthyle	Styrène (environ 2 ppm) Naphtalène (environ 0,01 ppm)
Batterie 1 après explosion	HAP à 12 carbones (1,2,3,6,7,8,8a,8b-octahydrobiphénylène ou cyclohexylbenzène) Carbonate de diméthyle (**DMC**) Carbonate d'éthyle et de méthyle (**EMC**) Peroxyde de diéthyle	Styrène (environ 2 ppm) Biphényle Naphtalène (environ 0,01 ppm) Fluorène
Batterie 2	Carbonate d'éthyle et de méthyle (**EMC**) Carbonate de diméthyle (**DMC**) Octanol Décanol Styrène Nonanol Décanal Xylène (environ 24 ppm) Oxalate de di-6-ethyloct-3-yl	Succinonitrile Benzène (environ 22 ppm) Toluène (environ 10 ppm) Acide benzoïque Composés lourds aliphatiques Naphtalène (environ 2 ppm) HAP

Dans les fumées prélevées, on remarque la présence des électrolytes à chaque analyse ainsi que de composés organiques lourds (d'hydrocarbures aliphatiques et d'alcool), des Hydrocarbures Aromatiques Polycycliques (HAP) caractéristiques d'une combustion. Ces composés sont équivalent à ceux trouvés dans des fumées de combustions classiques.

IR gaz

L'analyse par IR gaz a été menée sur la batterie 2. Il a été identifié du carbonate de diméthyle (**DMC**), de l'ethyl methyl carbonate (**EMC**), du monoxyde de carbone (CO) et du dioxyde de carbone (CO_2) en grande quantité. Ces résultats concordent avec ceux de 2018.

SBSE

Le condensat des fumées blanches s'échappant de la batterie 2 après le choc a été récupéré dans un bécher et analysé par GC-MS à l'aide d'un SBSE.

L'analyse met en avant la présence de nombreux composés organiques aliphatiques ainsi que quelques alcools avec des chaînes carbonés entre 10 et 20 carbones. De l'oxalate d'isobutyle et d'octadécyle a également pu être identifié. Ce dernier résulte certainement de la recombinaison de l' oxalate de di-6-ethyloct-3-yl lors du refroidissement des fumées. Ces composés ne présentent pas de toxicité particulière.

c) Caractérisation des fumées après extinction

GC-MS

Une analyse par GC-MS a été menée sur les fumées de la batterie 3 après extinction du feu.

	Produits identifiés au GC-MS	
	Majoritaires	**Minoritaires remarquables**
Batterie 3 après extinction	Succinonitrile 2-butanol Octanol Xylène Naphtalène Benzène (environ 5 ppm) Styrène Carbonate de diméthyle (**DMC**) Carbonate d'éthyle et de méthyle (**EMC**)	Oxalate de di-6-ethyloct-3-yl Acénaphtylène HAP lourds Composés lourds aliphatiques Toluène (environ 1 ppm) Ethanethiol

Dans les fumées prélevées, on remarque la présence des électrolytes à chaque analyse ainsi que de composés organiques lourds (d'hydrocarbures aliphatiques et d'alcool), des Hydrocarbures Aromatiques Polycycliques (HAP) caractéristiques d'une combustion. Ces composés sont équivalent à des fumées de combustions classiques

Seule la présence de succinonitrile dans le spectre de la batterie 3 laisse supposer une production possible d'acide cyanhydrique après l'extinction de la batterie.

d) Conclusion

Les fumées blanches et denses observées pendant les essais sont essentiellement composés d'électrolyte et de CO_2 ainsi que de composés organiques caractéristiques des fumées de combustion.

Il est probable que de l'hydrogène soit également présent en petite quantité.

En fonction de la source d'inflammation, d'autres composés vont être relargués. Un hydrocarbure aromatique polycyclique à 12 carbones et du peroxyde de diéthyle lorsque la batterie est en surtension et de l'oxalate de di-6-ethyloct-3-yl lorsque qu'elle subit un choc.

Lors de l'extinction à l'eau de la batterie, la présence de succinonitrile laisse supposer une production d'acide cyanhydrique.

3.2.2 Les packs batterie Li-ion – Alu de 900 W

Un nombre important de packs batterie Li-ion ont été placés dans une armoire elle-même enfermée dans un caisson. Dans ce caisson, les batteries ont subi un fort rayonnement thermique. Sur cet essai, seule la concentration d'HF a été mesurée par une trouée à hauteur d'homme et par laquelle s'échappaient les fumées.

	HF
Concentration	Au moins 30 ppm

Le détecteur HF saturant à 30 ppm, il n'est pas possible avec les moyens à disposition dans le VDIP d'avoir une estimation plus précise des concentrations dans le caisson.

4. Conclusion générale

Le tableau ci-dessous résume les résultats des mesures menées sur les différents types de batterie étudiés.

	Produits majoritaires
Batterie quart de lune en surtension avant explosion	**DMC** **EMC** HAP à 12 carbones Peroxyde de diéthyle H_2
Batterie quart de lune en surtension après explosion	**DMC** **EMC** HAP à 12 carbones Peroxyde de diéthyle H_2

Batterie quart de lune ayant subi un choc violent avant extinction	**DMC** **EMC** CO CO2 Oxalate de di-6-ethyloct-3-yl H_2
Batterie quart de lune ayant subi un choc violent après extinction	**DMC** **EMC** Succinonitrile Oxalate de di-6-ethyloct-3-yl H_2
Batteries grandes capacités (packs batterie Li-ion – Alu de 900 W) en milieu fermé soumises à un flux thermique	Présence d'HF

En conclusion, selon la source d'inflammation, la composition des fumées diffère. Néanmoins, elles n'apportent aucune toxicité particulière par rapport à des fumées de combustion classiques.

L'émission de gaz blanc dense a été caractérisé comme un mélange d'Électrolyte et de CO2.

La présence de Succinonitrile laisse supposer la production d'acide cyanhydrique dans les fumées après la phase d'extinction.

En milieu fermé, le feu de plusieurs dizaines de batterie dans un volume de 20 m3 a indiqué la présence d'au moins 30 ppm d'HF.

Le rédacteur

Alexandra DE LA HOZ

Le référent VDIP de la zone Sud-Est

Capitaine Cédric PASQUIER

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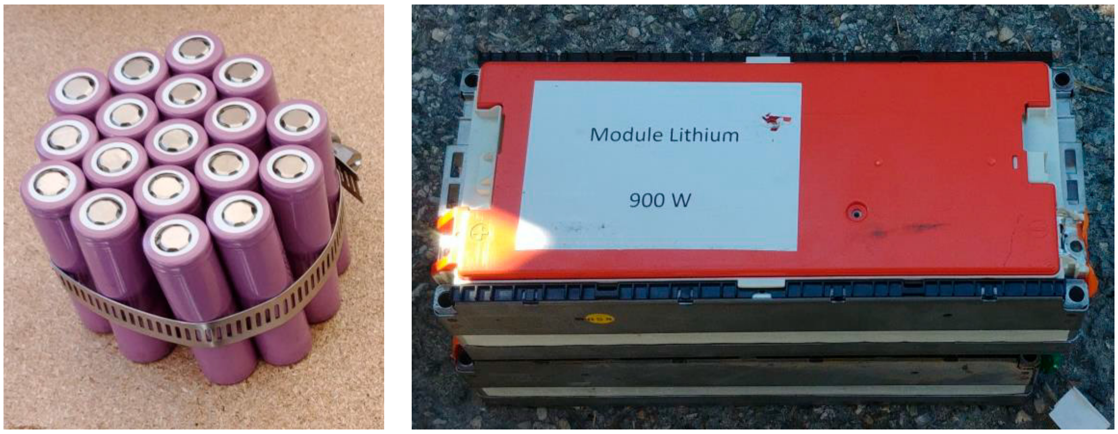
ANNEXE 1 : éléments de contexte des essais



Les 2 types de batterie, de gauche à droite :
Les cellules « violettes » éléments des batteries quart de lune
Les packs batterie Li-ion – Alu de 900 W

Dispositif mis en place pour tester les batteries quart de lune au choc
A gauche, en rouge la batterie et en vert le conduit par lequel arrive la boule de pétanque
A droite, caméra thermique placée devant la batterie en combustion suite au choc

ANNEXE 2 : protocole d'analyse des gaz

Analyse par GC-MS

L'appareil d'analyse est un couplage TD-GC-MS BRUKER E2M.

L'analyse se fait au niveau du détecteur de masse E2M par balayage des masses de 45 à 350 (EI = 70 eV, analyseur quadripolaire et source à 120°C).

Les spectrothèques utilisées pour l'identification sont la NIST et la CWAlib fournis par BRUKER.

- ***L'analyse par TD-GC-MS pour un tube TENAX est réalisée dans les conditions suivantes :***
    - Gaz vecteur : air.
    - La thermo désorption du tube de prélèvement se fait pendant 60 s à 240 °C.
    - La séparation est effectuée sur colonne capillaire phase apolaire MXT5 de longueur 12 m, diamètre interne 0,32 mm et 5 µm d'épaisseur de phase.

Le programme de température de la colonne est notre programme routinier utilisé en intervention afin de réellement évaluer notre protocole en nous rapprochant le plus des conditions réelles :

- 25 °C / min de 45 à 100 °C.
- 35 °C / min de 100 à 220 °C.
- Palier de 15 minutes à 220 °C.

- ***L'analyse par TD-GC-MS pour un SBSE est réalisée dans les conditions suivantes :***
    - Gaz vecteur : air.
    - La thermo désorption du tube de prélèvement se fait pendant 60 s à 240 °C.
    - La séparation est effectuée sur colonne capillaire phase apolaire MXT1 de longueur 15 m, diamètre interne 0,32 mm et 5 µm d'épaisseur de phase.

Le programme de température de la colonne est notre programme routinier utilisé en intervention afin de réellement évaluer notre protocole en nous rapprochant le plus des conditions réelles :

- 25 °C / min de 45 à 100 °C.
- 35 °C / min de 100 à 220 °C.
- Palier de 15 minutes à 220 °C.

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ANNEXE 3 : protocole d’analyse des gaz

Analyse par spectrométrie IRTF

L’IRTF du SDMIS est destiné en priorité à l’identification de composés gazeux toxiques suite à un accident ou un attentat chimique. Il s’agit d’un spectromètre Nicolet IS10 (Thermofisher) présentant les caractéristiques suivantes :

- Séparatrice en KBr/Ge.
- Linéarité de 0 à 3 unités d’absorbance.
- Résolution minimale 0,5 cm-1.
- Vitesse de balayage allant de 0,15 à 3,7 cm.s-1.

Ce spectromètre est équipé d’une installation permettant l’analyse et le prélèvement de gaz ou de vapeur.

La cellule à gaz présente les caractéristiques suivantes :

- Le volume de la cellule est de 200 mL.
- Le trajet optique est de 2 m, à réflexions multiples.
- Le domaine de transmission s’étend de 740 cm-1 à 4400 cm-1.

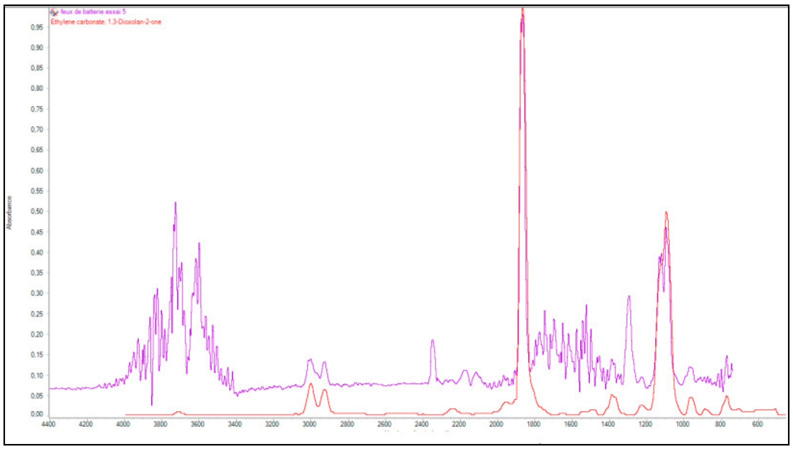
ANNEXE 4 : protocole d'analyse des solides

Analyse par spectrométrie IRTF ATR

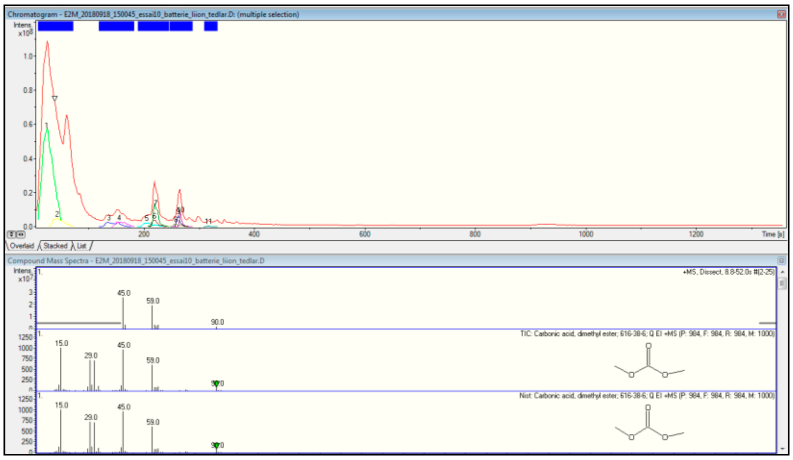
L'IRTF ATR du SDMIS est destiné à l'identification de solides ou liquides suite à un accident ou un attentat chimique. Il s'agit d'un spectromètre Mobile IR (Bruker) présentant les caractéristiques suivantes :

- Cristal en diamant avec une zone d'ombre entre 2100 cm^{-1}et 2300 cm^{-1}.
- Plage d'analyse comprise entre 400 cm^{-1} et 4000 cm^{-1}.

ANNEXE 5 : exemples de spectres avec identification de carbonates



Spectres IR d'un essai sur packs batterie Li-ion – Alu de 900 W (violet) et du carbonate d'éthylène (rouge)



Spectre GC d'un essai sur une cellule « violette » avec identification sur le pic 1 de carbonate de diméthyle (profils MS sous le spectre GC)

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ANNEXE 6 : fiches de sécurité

Fiches au format PDF en pièces jointes.

cea

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