Li-ion Batteries Safety

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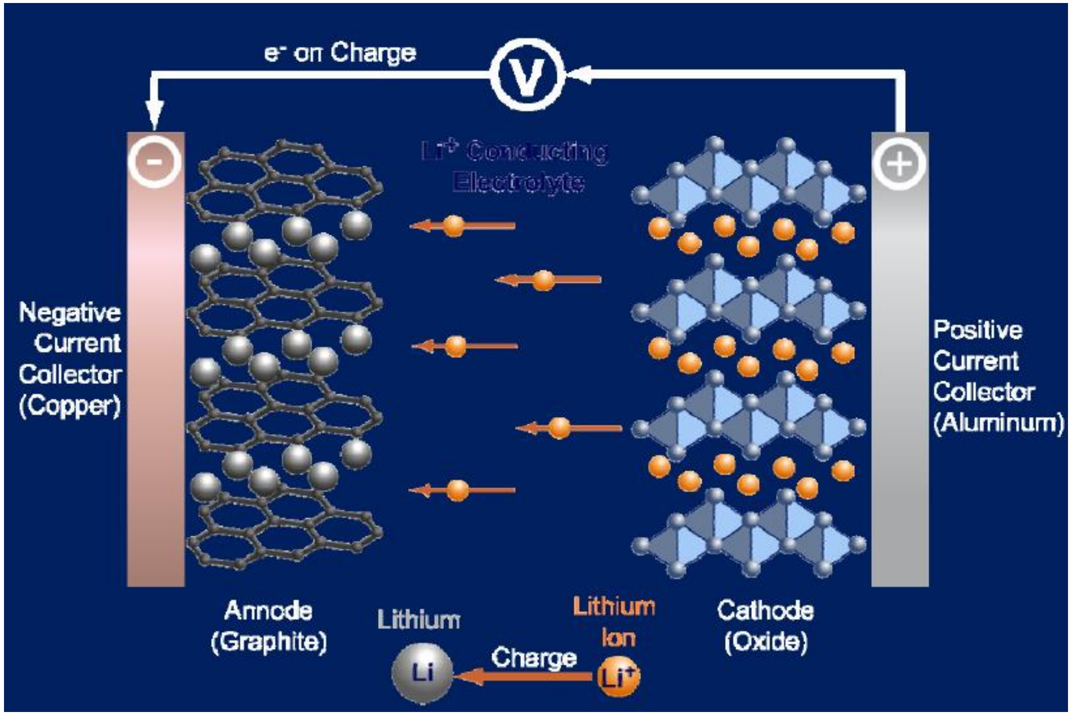
Agenda

1. Li-ion batteries key features
2. Safety: the root causes of the potential hazard
3. Batteries safety management

Li-ion chemistries

- The battery chemistry is characterized by the cathode material (LCO, NMC, LFP, etc…)* and the anode material (Graphite, LTO, ..)**



***Cathode materials: LCO= Lithiated Cobalt Oxyde, NMC= Lithiated Nickel Manganese Cobalt Oxyde, LFP= Lithium Iron Phosphate.**
****Anode material: LTO= Lithium Titanate.**

Li-ion batteries key features

- **Multiple Chemistries:**

Li-ion is a generic term, covering several types of battery chemistries and several formats for various applications (see next slides).

It is different from the Lithium metal Primary battery.

- **Improving technology:**

This technology is still in an development phase, so new chemistries and designs are progressively introduced on the market.

Choices in Li-ion Chemistry

- The chemistry modifies the performance and safety.

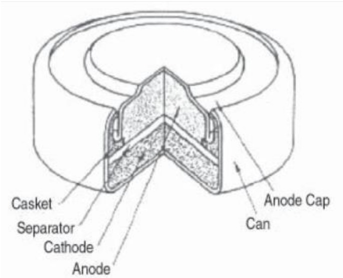
	LCO $LiCoO_2$	NCA $LiNiCoAlO_2$	NMC $LiNiMnCoO_2$	LMO $LiMn_2O_4$	LFP $LiFePO_4$	LTO* $Li_4Ti_5O_{12}$	Si-C*
Cell Voltage, 100%/50% SOC	4.2V/ 3.8V	4.0V/ 3.6V	4.2V/ 3.7V	4.2V/ 3.9V	3.6V/ 3.3V	2.8V/ 2.4V	4.2V/ 3.9V
Energy	++	+++	+++	+	++	-	+++
Power	++	+++	++	+++	++	+	++
Calendar Life	+	+++	+	-	++	-	-
Cycle Life	+	++	++	++	++	+++	--
Safety	+	+	+	++	+++	+++	+
Cost	-	+	++	++	+	-	++

*** LTO and Si-C are anodes, which can be combined with any cathode.**

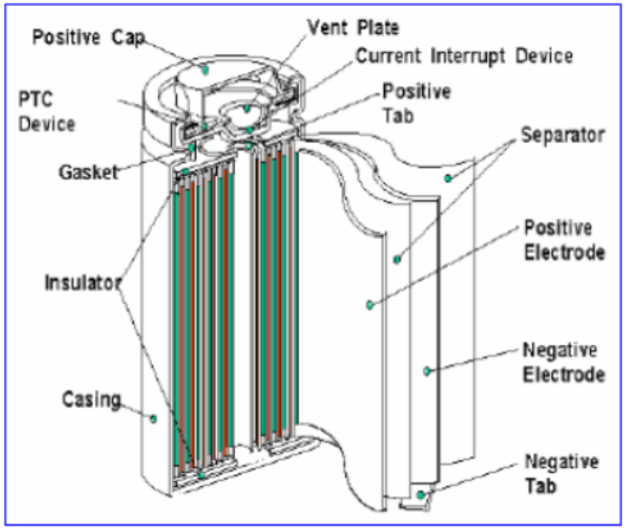
Li-ion batteries / Formats

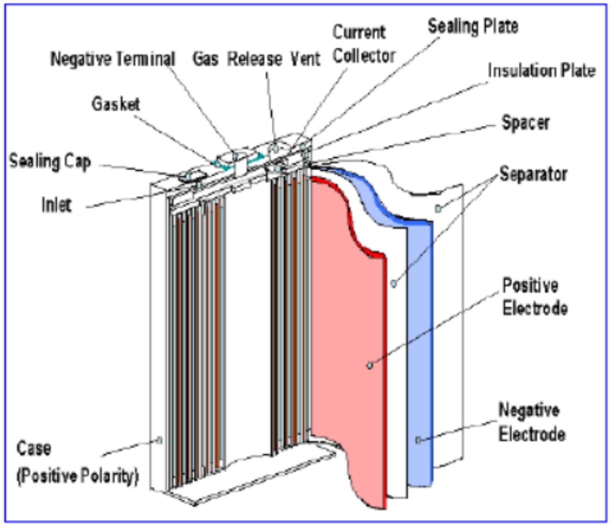
1. The portable battery is characterized by its format.

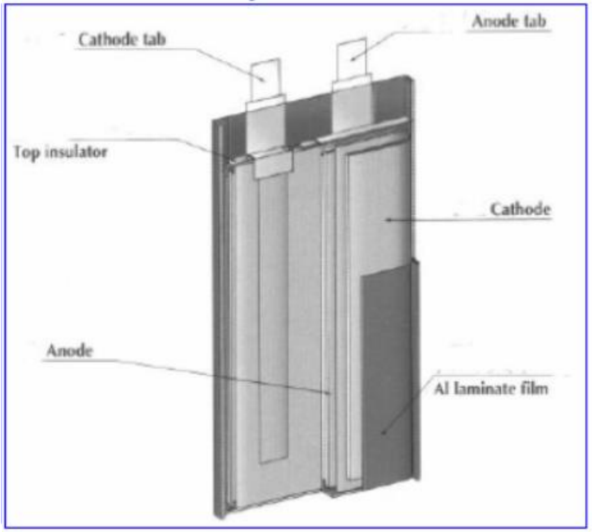
   1. Button cells



   2. Hard cases: cylindrical or prismatic (aluminium welded can)
   3. Soft case or « pouch »



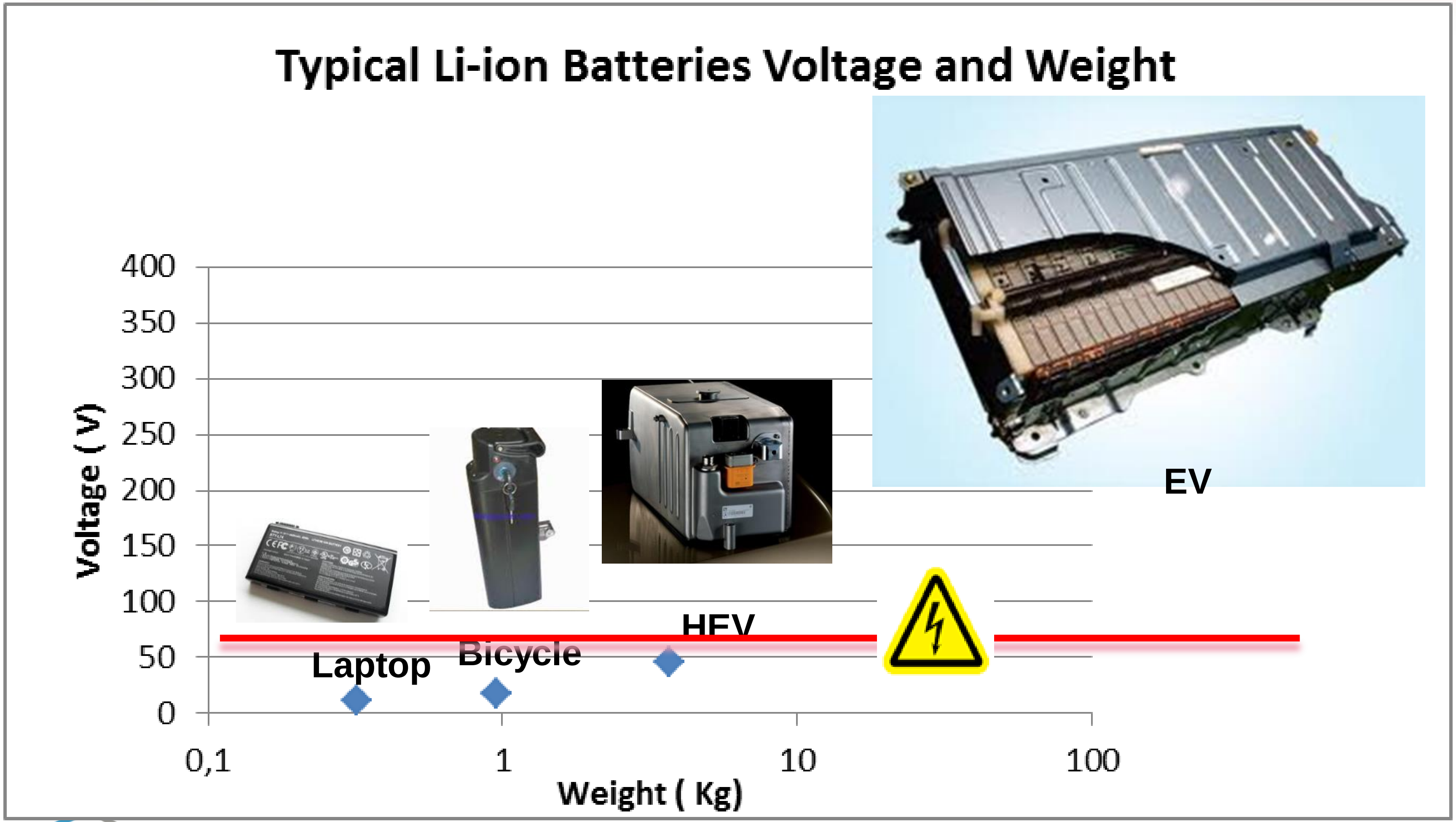




Reference: IEEE 1725 Standard

Li-ion packs technologies

The industrial battery is independent of the cell format.



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Which hazards?

- 1-Potential Chemical hazards

  In case of rupture of casing tightness.

  - Spillage of electrolyte: corrosive and flammable
  - Gas Emission: volatile organic substances

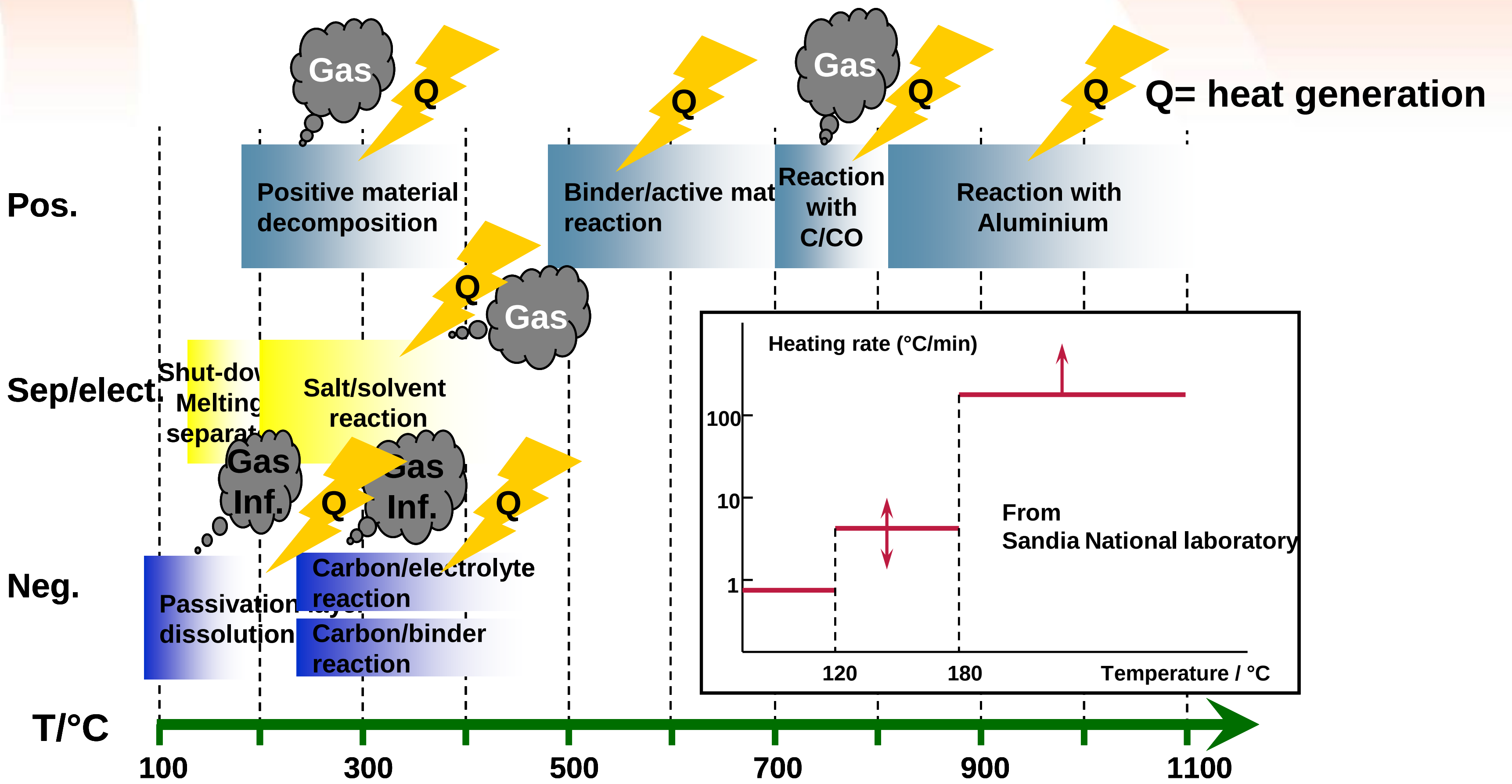
- 2-Potential electrical energy hazards

  - Release of energy by Joule effect: heat and temperature elevation
  - Spark

Which hazards?

- 3-Potential hazard of Cumulative effects (Chemical and Electrical)
  - Fire
  - Toxic or harmful gas emission: CO, organic electrolyte,…
  - Parts ejections
- 4-Add. Potential hazard of High voltage (over 60V DC)
  - Battery insulation loss (exposure to high voltage in unexpected place)
- 5-Loss of service function.
  - Loss of key battery service function (e.g. leading to equipment loss of control and hazard for the user)

Thermal run away in a charged Li-ion cell



Without appropriate design to limit the thermal run away (such as venting, insulating layers,…), the chain of reaction leads to a violent event.

Thermal run away analysis: gaz composition

Gaz emitted in inert atmosphere

Molecule	Concentration (%)
CO	#40
H_2	# 30
CO_2	# 20
Methane	7
Ethylene	3
Ethane	1
Propylene	1
C4s and others	<1
Including HF	#0,3

If total combustion in air

Gaz gaz calculated after combustion in air

Molecule	Concentration (%)
N2	#65
CO	# 3
CO_2	# 27
Other combustion residues	# 5
Including HF	10-100 ppm

- Depending on the gaz emission temperature and the contact conditions with air, the gaz can self ignite in air, adding the thermal energy of the combustion to the thermal run away.

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Thermal run away analysis: gaz toxicity

- Toxicity of fumes: presence of carbon monoxide CO and small amount of hydrogen fluoride HF (the origin being the $LiPF_6$ contained in the electrolyte - the main decomposition residue being solid Lithium fluoride LiF).

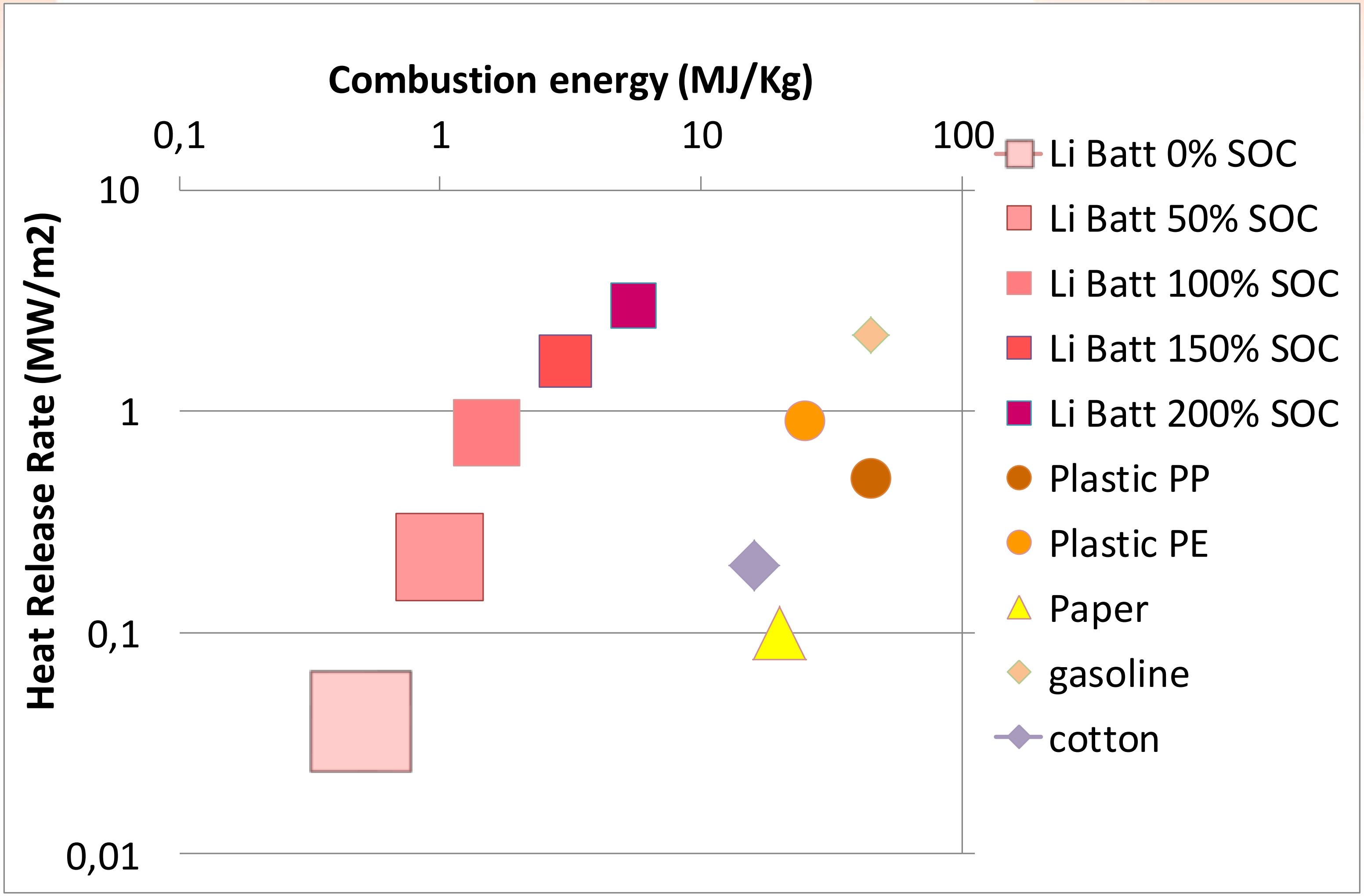
- Effect of water: water can react with the Li-ion electrolyte and produce some HF gaz. In case of run-away, the electrolyte is mainly decomposed inside the cell, minor quantities can be expulsed.

➔ Both the presence of CO and HF makes the fume toxic and requires a self-breathing equipment for fire brigade*

➔ the water can be used to extinguish a Li-ion battery fire without creating an additive risk.

***According table above, HF concentration in the range of ERPG-2. ERPG-2 (Emergency response planning guidelines) 2 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed up to one hour without experiencing or developing irreversible or other serious health effects that could impair their abilities to take protective action.**

Thermal run away analysis: thermal effects



Comparison based on maximal combustion energy from Li-ion cells

Energy storage systems stability

Energy storage systems offers potential hazard... They require the most appropriate risk prevention and control measures.

Energy storage types	Potential hazards	Potential hazard Prevention	Potential hazard Control
Water storage	Rupture, water flows	E.g. protect against corrosion	Safety water flow zones
Gas	Fire, explosion	Avoid sparks, flames	Manage fire risk consequences
Lead acid and Alkaline batteries	Hydrogen Gas release under short circuit or overcharge	Avoid battery abuse (voltage control and protections)	Safety (Controlled) gas flow evacuation
Li-ion batteries	Thermal runaway	Avoid sparks and battery abuse	Manage fire consequences

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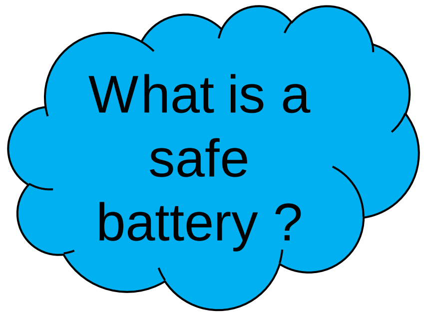
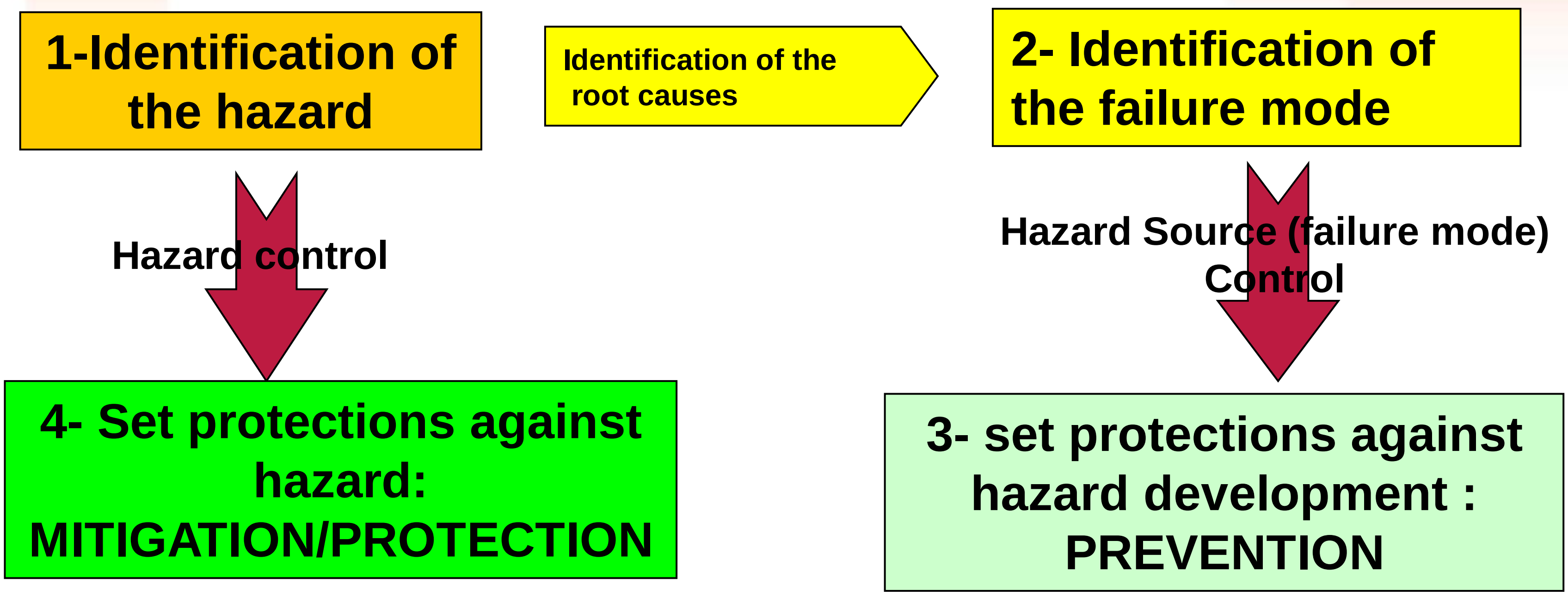
Li-ion batteries Safety



No absolute criteria for safety

1. Which hazards ?
2. Safe under which circumstances ?
3. Which level of « damage » is acceptable ?

Global Risk Analysis approach



A Hazard analysis is necessary to define the relevant prevention and protection solutions for each application:

- Identification of the threats from the environment (for prevention).
- Identification of the hazards for the environment (for protection)

Eucar Classification of Hazards

Table 2. EUCAR Hazard Levels and Descriptions

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

Standards for safety testing of Li-ion

	UL					NEMA	SAE	IEEE		BATSO	Telcordia	JIS	INERIS
Test Criteria Standard	UL 1642	UL2054	UL Subject 2271	UL Subject 2580	UL2575	C18.2M	J2464	IEEE 1625	IEEE 1725	BATSO 01	GR-3150	JIS C8714	ELLICERT D
External short circuit	●	●	●	●	●	●	●	●	●	●	●	●	●
Abnormal charge	●	●	●	●	●	●	●	●	●	●	●	●	●
Forced discharge	●	●	●	●	●	●	●	●	●		●	●	●
Crush	●	●	●	●	●	●	●	●	●	●	●	●	●
Impact	●	●	●	●		●		●	●				
Shock	●	●	●	●	●	●	●	●	●	●	●	●	●
Vibration	●	●	●	●	●	●	●	●	●	●	●	●	●
Heating	●	●	●	●	●	●	●	●	●			●	●
Temperature cycling	●	●	●	●	●	●	●	●	●	●		●	●
Low pressure (altitude)	●		●	●	●	●		●	●	●		●	●
Projectile	●	●	●	●				●	●				
Drop			●	●		●				●		●	●
Continuous low rate charging												●	
Molded casing heating test						●							
Open circuit voltage						●							
Insulation resistance				●		●							
Reverse charge			●	●									
Penetration			●	●			●						●
Internal short cicuit	●			●								●	
Immersion													●
Fire											●		●

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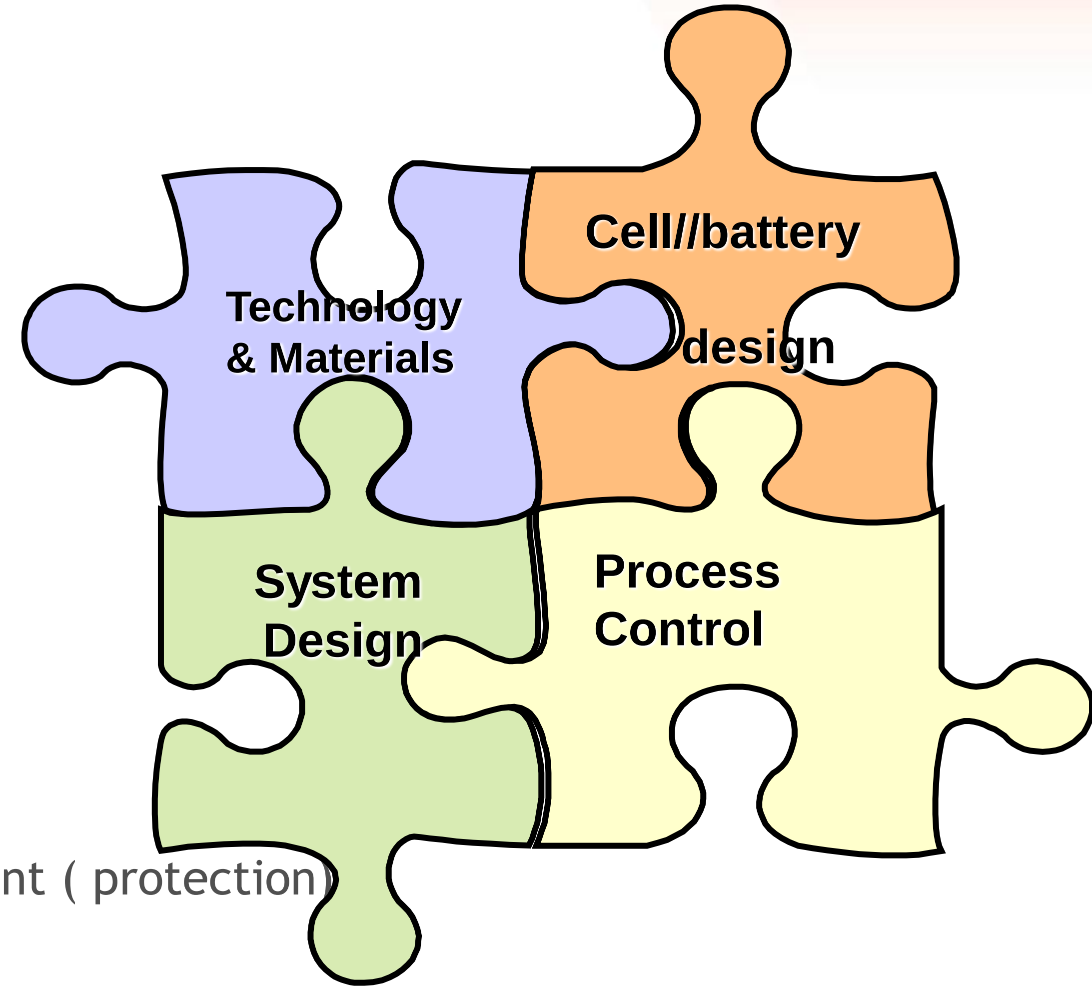
Safety: resulting from coordination

1. No single « approach » to make batteries safe



2. Avenues

> Prevention

> Mitigation

- reduce sensitivity
- reduce reaction
- break reaction chain

> Limit consequences of event (protection)

Safe system global approach

LEVELS	Prevention	Mitigation	Limit consequences
Cell 	Root cause	X	X
Module/Battery 	X	X	X
Application 	X		X

The most efficient protection is obtained owing to the combination of prevention, mitigation and protections at several levels.

Prevention, mitigation and protection solutions

Cell Hardware	System Hardware	System Software
Cell-Level Design Features • Vent • Current interrupt device • Separator materials • Specification of active material powders and binders properties for limited safety impact.	**Electronics Hardware** • Over-Voltage protection • Over-Temperature • Cell balancing circuitry **Electrical Hardware** • Fusing for over-current • Contactors **Mechanical Hardware** • Optimum thermal management • Structural protection • Gaz containement possible	**Measurement of battery system characteristics** • Cell/Pack voltage • Temperature • Current • Device feedback • Sensor validity **If fault or failure is detected appropriate control action is taken**

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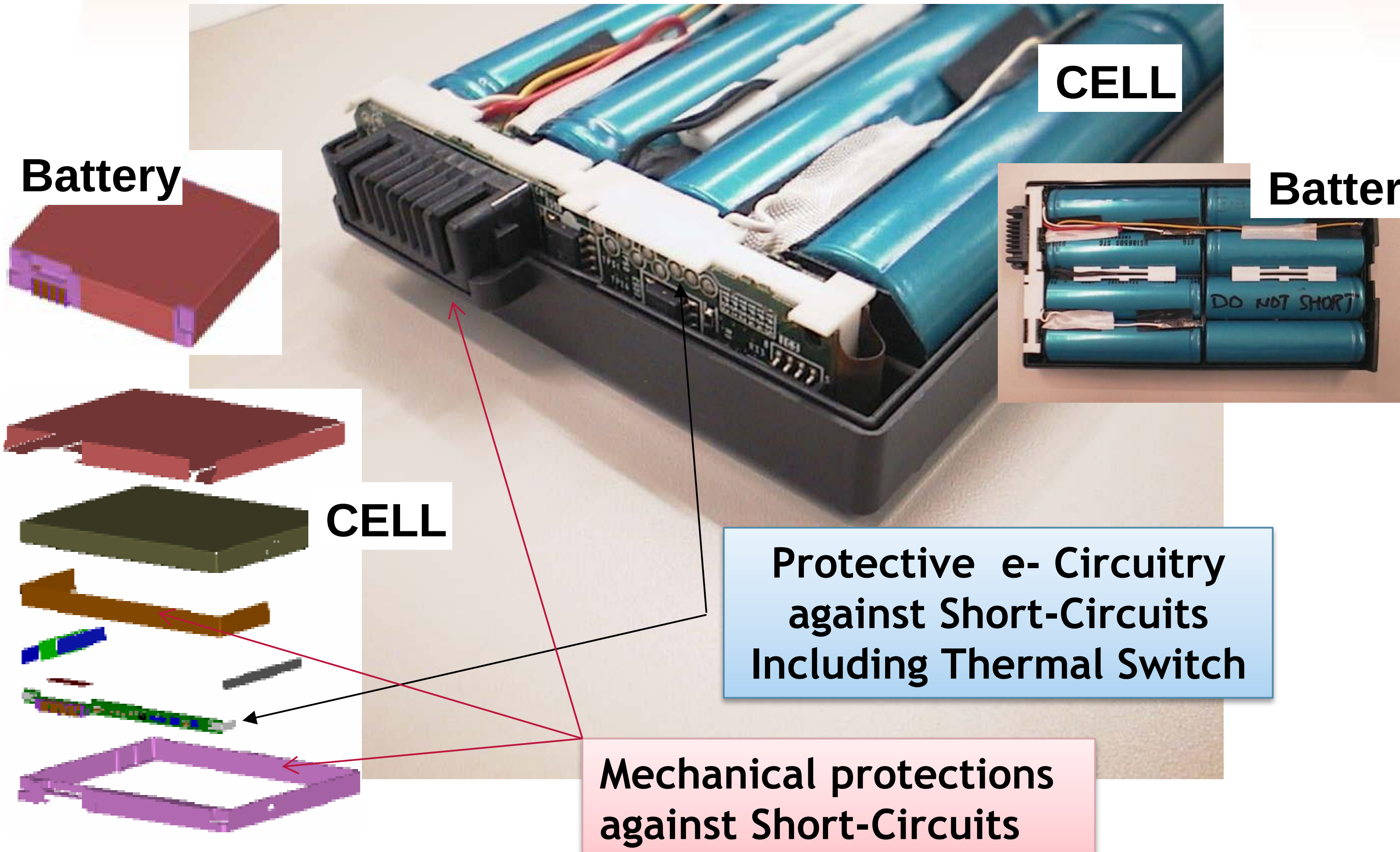
Most are applicable to all cells types and batteries sizes.

Practical example of protections: external short circuit



Li-ion safety conclusion

As for other energy storage systems, the safety management requires attention for all Lithium-ion battery systems:

- All Li-ion batteries have a flammable electrolyte, the large majority has a carbon anode, offering potentially a thermal runaway .
- Li-ion safety is ensured by a combination of prevention, mitigation and protection systems:
  - >An application Hazard analysis is necessary to adapt the design of the system for each specific application
  - >Protections are required at all levels: cell, module and battery. Li-ion batteries are equipped with electronic protections, mechanical design and electric design incorporating the necessary redundancies in the risk control chain to ensure the reliability of the safety functions.
- This global approach of the safety management has made the li-ion batteries one of the safest energy storage systems.