Safety issues pertaining to rechargeable Li-based batteries:
« Current knowledge from literature review and abuse testing and perceived remaining topics »

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La sécurité des batteries à ions lithium: Possibilité de risque zéro ?
Collège de France, réseau RS2E, 7 nov. 2011

Outline of the presentation

- Introduction/context
- Identification of hazards relating to Li-based rechargeable batteries
- Focus on thermal threats in the context of e-mobility
- Focus on chemical threats in the context of e-mobility
- Related strategic R&D agendas and action plans
- Conclusive comments

Li-ion technologies initiated a technical revolution…and might be ready for more !

More energy
Safety management a paramount…

	Consumer Applications	LEV, Power Tools	Automotive HEV & EV	Stationary Elec. Storage
Market Size	€ 7Bio (2008)	medium € 0.7Bio (2008)	large € 25Bio (2020)	Very large
Market Introduction	1990 by Sony	2005	2011/12 (mostly HEV)	Realization has to be proven
Chances for Newcomers	Minimal	Moderate	(Very) Good	Depends on starting position
Typ. Battery-Size (kWh)	0.001 – 0.1	0.1 – 1	1 – 100	100 – 10.000

Design criteria for batteries with # priorities

Consumer Applications:
1 Energy density
2 Safety
3 Liferspan/cost
4 Power

LEV, Power Tools:
1 Energy density
& Safety
2 Liferspan/cost
3 Power

Automotive HEV & EV:
1 Safety
2 Power
3 Energy density
4 lifespan/ cost

Stationary Elec. Storage:
1 Lifespan/cost
2 Size
3 Power/energy density
4 safety

Adpated from Tarascon (2009) & Passerini (2011)

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Moving towards safer Li-based energy storage systems for electromobility

- A desirable requirement according to a number of well visible indicators such as:
  - sharp increase in embarked energy vs portable consumer market
  - first lessons from incidents that have taken place on the full value chain of Li-ion batteries on existing markets
  - positions expressed about safety issues in economic studies
  - information provided by the concerned scientific communities and various technical committees (SAE, NFPA, ISO, UN SCETDG...)
  - Programmes of recent dedicated conferences:

- A strategy that needs to be maintained on the medium/long term
  - Electromobility an emerging market
  - Greener transport a societal expectation at world-wide level

Safety still recently seen by some stakeholders as 1st ranked hurdle for market development!

Total HEV and EV Lithium-ion Battery Market: Market Restraints Ranked in Order of Impact (World), 2009–2015

Rank	Restraint	1 - 2 Years	3 - 4 Years	5 - 7 Years
1	Safety issues related to lithium-ion batteries	High	High	High
2	High investment associated with lithium-ion batteries	High	High	Medium
3	Infrastructure issues concerning charging time	High	Medium	Low
4	NiMH still preferred for hybrid technologies	Medium	Low	Low

Source: Frost & Sullivan

(Position expressed in Sept. 2009)

INERIS commitments for better battery safety

- Long-term involvement of the Institute on the topic of electric energy storage systems

- Recent (safety) focus on Lithium ion type rechargeable cells and batteries:
  - Resulting from key interest of France for electromobility deployment and key networking activities with some major partners
  - Supporting all types of core activities within INERIS' duties
  - covering the full value chain from design to recycling /second life
- Related Activity indicators:
  - Implementation of new testing equipment (STEEVE security facility)
  - Emergence of physical and computational battery fire modeling
  - Intensification of abuse testing for industrial partners, including at 1:1 scale
  - Promotion of collaborative research at EU level
  - Contribution in standardisation activities as well as to volontary certification schemes (Ellicert: see http://www.ineris.fr/fr/node/857)
  - Communications and papers…

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Outlook on INERIS' equipment for abuse/fire testing


FPA lab.

Fire gallery


Mont-la-Ville open-field test site

Multipurpose testing facilities

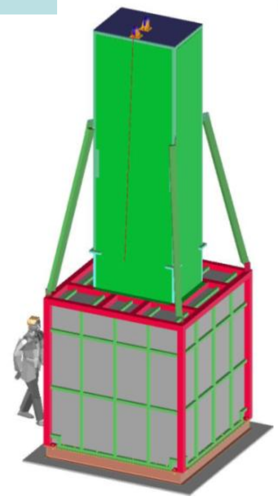
Battery-Dedicated testing plateform

STEEVE sécurité INERIS


Crush test

Cycling machine


Simulated fuel fire 100 kW/m2


Impact test


FTIR

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Hazardous phenomena to qualify for Li-based technologies vs applications and scenarios of interest

- Explosion
  - Unintentional charging by end item
  - Resulting from external fire event or internal runaway
- Venting, possibly under significant pressure
- Release of hazardous materials (through venting or leakage)
  - Toxic gases and aerosols
  - Corrosives
  - Flammables
- Fire (internal or external origin)
  - Propagation, thermal & toxic threat to people
  - Water-reactivity of components
- Unintentional electric discharge (risk management needed)
  - In the context of e-mobility (high voltage issues)
  - Internal short... (cold & fast charging issues...)

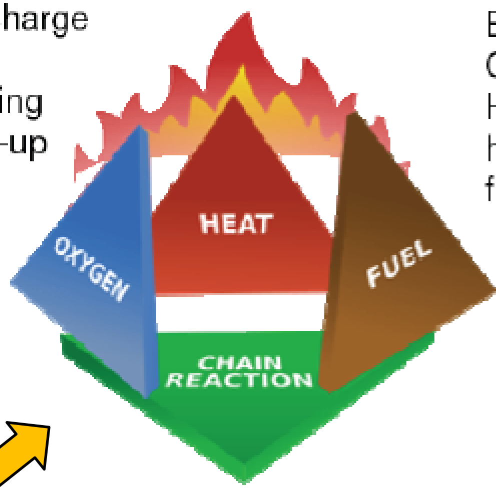
Adapted from Marlair & Torcheux, Battery 2009, Cannes-Mandelieu

The thermal threat pattern with rechargeable Li-based batteries (1/2)

Heat/Energy Release via
Anode or cathode decomposition
Electrochemical energy release
(Cell short, internal/external)

Electric energy stored
(max at 100% SOC)
May contribute to RHR through Joule dissipation

Oxygen
- Release from layered cathodes during overcharge
- Oxygen access to cell after cell rupture/opening via gas pressure build-up or external impact
- Other oxidants (over-charged cathodes)?



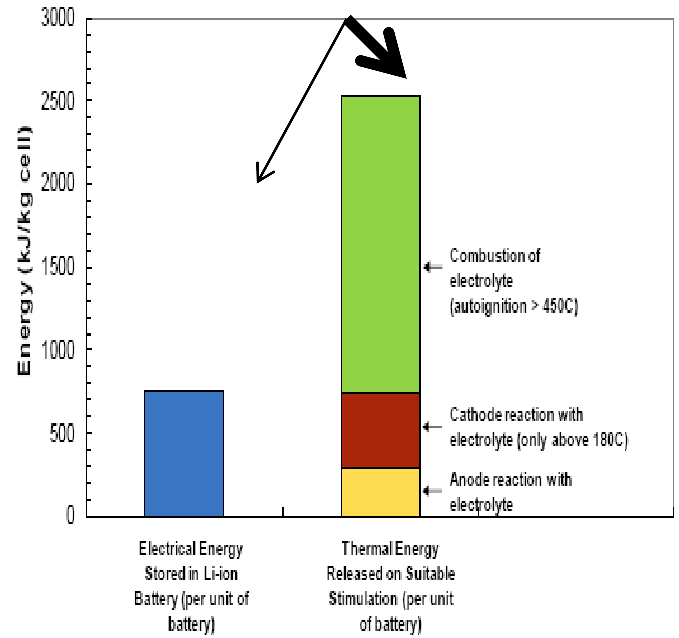
Combustibles
Li (solid, molten, dust)
Electrolyte solvents (and salts)
Gases (formation gases, e.g., H_2, C_2H_4, C_3H_6, CO, etc.;
heat causes objects to give off flammable gases)

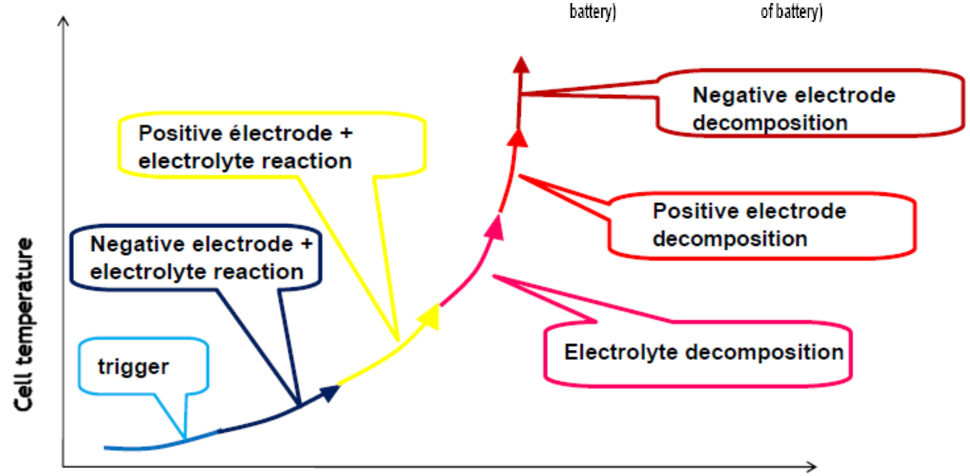
External fire event

(Radical) Chain Reaction

Thermal runaway process

Two fold energy type in case of accidental release





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The thermal threat pattern with rechargeable Li-based batteries (2/2)

- Absolutely intrinsically-safe materials not available to get rid of the threat (with Li-based technologies)
  - systemic approach/"global safety concept" needed
- Global overall embarked energy in battery (useful + 'useless') close to fuel tank in conventional cars:
  - But energy density and autonomy increasing...
  - Kinetics of release potentially quicker (due to runaway process)
- Mitigation effect of multi-layer mechanical barriers (at level of cells, modules, pack & EV) on RHR in the context of e-mobility applications liable to apply (to be further assessed)
  - so far first large-scale testing **seem to eliminate physical explosion/missile effects due to external fire** in the context of automotive applications
  - late re-inflammation of gases evacuated through venting possible
  - state of charge does not seem to influence overall energy liberated significantly at level of one cell (Ribiere et al, 2010), as measured by fire calorimetry and from mass loss observations
- Effect of design likely to influence sharply kinetics of release

The chemical/toxic threat: general issues

- Comprehensive evaluation of fire-induced toxic risks still a difficult technical task for following reasons:
  - Complexity of the chemistry involved in lithium secondary cells
  - Synergistic effects of fire plume components
  - batteries atypical burning objects compared to conventional fuels in building or industrial fires:
    - cellulosics, plastics, hydrocarbons
  - Limitation of existing fire toxicity evaluation tools (FEC, FED models from ISO TC92 SC3...)
  - Data availability in terms of yields of toxic components still very limited vs
    - number of electrodes/electrolyte potential options/combination in automotive applications
    - number of pertinent scenarios to be dealt with
    - fire origin (external, internal)
- Analysis of toxicity impact on exposed people scenario and tenability criteria dependant...
  - as for conventional cars...

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The chemical/toxic threat from Li-based battery fires: contribution of HF and other F containing toxics?

- F-containing materials in Li-based batteries
  - Two main sources of fluorine
    - binder of the positive electrode (PvDF) (Li-ion tech)
    - Li salt in (liquid or solid) electrolyte : often LiPF6 for Li-ion tech, sometimes LiTFSI (LMP)
  - Potentially, as minor sources (often proprietary chemicals)
    - Separator
    - solvent additives (e.g. FEC)
    - FR additives
    - Advanced cathodic materials(fluorosulfonated materials)
- With respect to fire safety, the presence of F element may often have positive effect in terms of improved thermal stability & resistance to ignition
- The reverse side of this:
  - **Toxicity of related** released products (also containing F, like HF)

  whatever thermal degradation conditions

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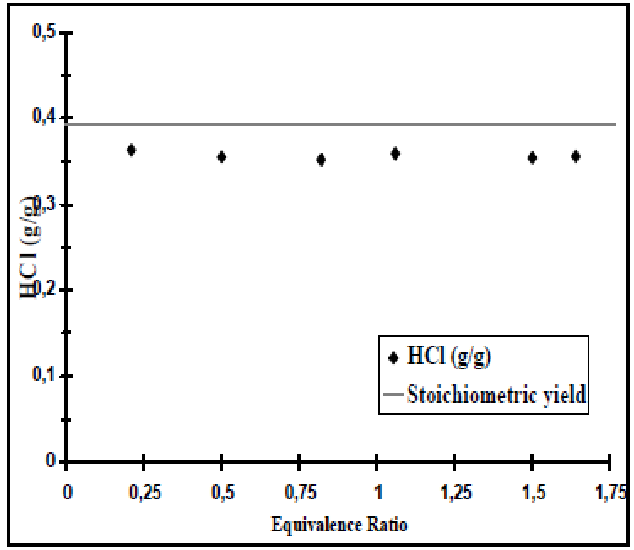
The chemical/toxic threat: HF and other F-containing toxics: current generic knowledge

- ❑ General trend with halogenated hydrocarbons to release corresponding hydrogen halide as a major toxic compound
  - **Fully proven for PVC and other Cl containing materials** whatever ventilation conditions (also reported for F and Br - containing materials see Hull et al (FSJ 42 (2007) 340-365)
  - **Tangible indications the rule indeed applies for fluorinated hydrocarbons**
  - Other F-containing toxic compounds likely not being favoured in significant quantities in fire (oxidative) conditions (<u>to be checked</u>)
- ❑ **Much less information regarding F-bound to mineral fraction !**

Measurements of yields of toxic products as a function of ventilation in fires



Fate of Fluorine element in battery and supercaps fires ?

Fire Propagation Apparatus, ASTM E2048 (2000), NFPA 287 (2001), ISO12136 (2011)

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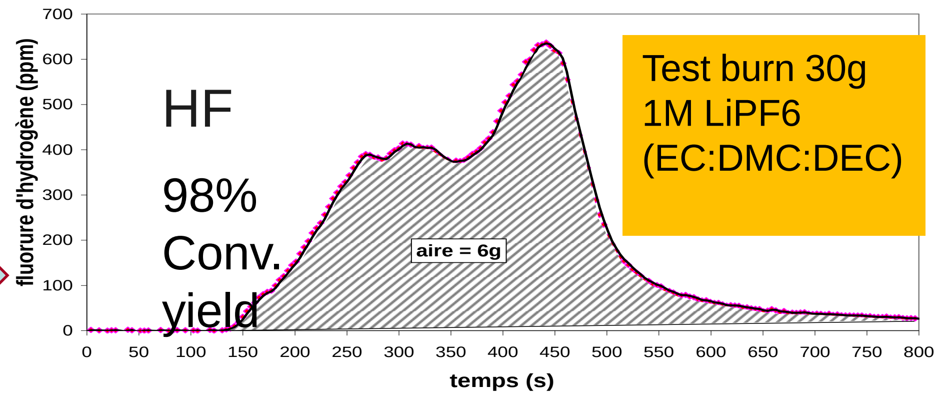
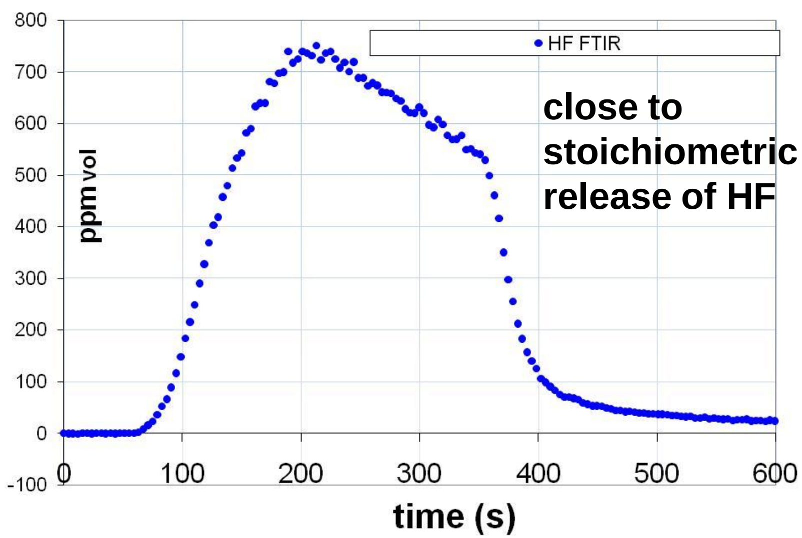
Evidence of HF emissions from INERIS/UPJV joint research work

At level of components containing F:

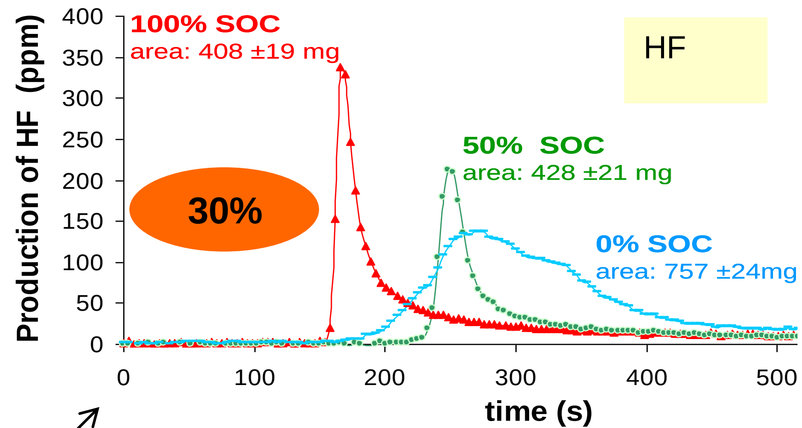
- **Trend to stoichiometric release of HF for fluorohydrocarbons where H/F ratios ≥ 1** (true for PVdF & fluorotoluene)
- Same trend for battery electrolyte, although lack of hydrogen in the LiPF6 molecule…
- **Only 30% of HF yield** observed at level of a small cell (with the single barrier represented by the cell casing…)



HF emission from combustion of fluorotoluene



Case of a 2.9 Ah commercial pouch cell
Electrolyte : 1M LiPF6 (EC:DMC:DEC), Lithiated manganese oxide



salt and polymers

Source : Laruelle et al, ABAA-4, beijing, sept 2011

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Toxicity issues with burning batteries in the context of electromobility

Facts:

- **F containing materials proven to emit HF in significant quantities** at level of both major sources at component level
- **Significant emission at level of small cells**, verified for three technologies at least (pouch, 18650 type cells), including with LFePO4 electrode, about 1/3 of the stoichiometric potential release observed at cell level
- **Integration** of F-emittor components **in an enclosure** proven to contribute to HF trapping at source level
- **Overall toxicity impact scenario dependant** (due to dispersion phenomena in the environment and conditions of exposure

Still to be learnt or cleared out:

- **How do in practice overall yield of HF compare to overall potential of toxic emission** (bound to overall availability of F in battery packs, according to F-containing materials distribution in batteries ?
- Scaling laws?
- **How far does HF emission alone build the overall toxicity** profile of emissions in case of an EV burning scenario ?
- Same question for fire scenarios in storage ?
- Any issue from **degassing from venting battery without fire** ?

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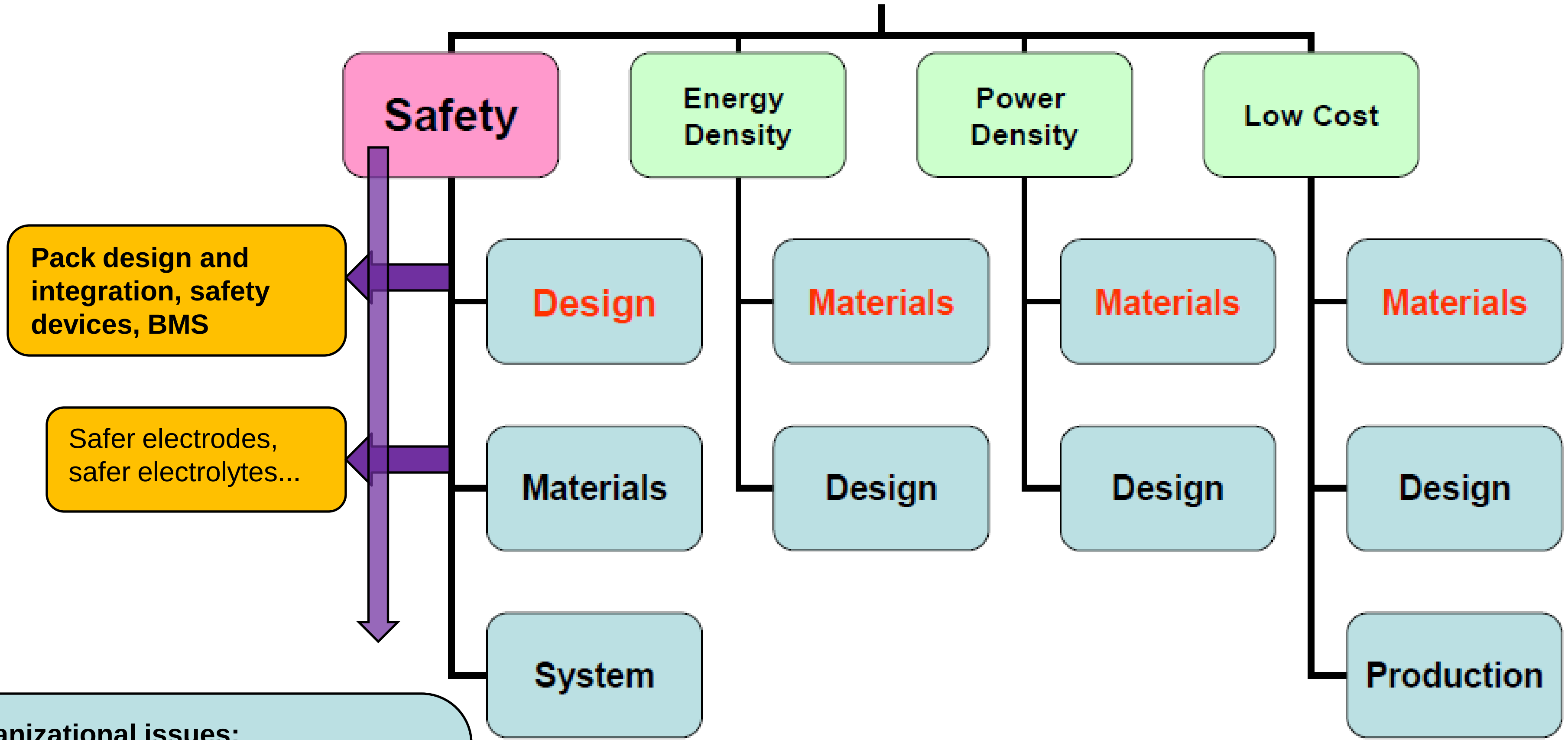
Abuse testing learning towards safety management at level of battery design for EV applications



Organizational issues:

- *systemic approach*
- *Optional testing & third party evaluation*
- *SoH & safety monitoring integrating aging issues*
- *Functional safety analysis*
- *Scenario Targetted Risk analysis*

Adapted from Zhang et al (Battery 2009, Cannes Mandelieu, France)

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Research projects involving INERIS in relation with safety (non exhaustive list)

- HELIOS (EU 7th FP): High Energy Li-ion Storage Solutions (2009-2012):
  - www.helios-eu.org
  - Integration of large battery packs for e-mobility
  - 18 partners, 36 months of duration, 4.3 M€ budget, funding 2.8 M€
  - INERIS leading WP6 targeting safety assessment of HE battery cells

- BATTERYNANOSAFE (Regional funding)
  - completed 2010
  - Safety hazard assessment of small li-ion based cells (various cathodes)
  - UPJV/INERIS

- DEGAS (Regional funding)
  - Started 2011, joint research UPJV/INERIS
  - Identification and metering venting gases (flammable, toxic) from abused li-ion based cells

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Research /action plans needs perceived from activity in the US and Japan (examples)

- From Japan (BAJ, NEDO...)
  - better abuse test procedure to simulate internal short-circuit effect inside cell in abuse mechanical conditions
  - development of safer anode and cathode materials
  - going towards safer (less flammable/combustible) electrolytes to replace organic carbonates mixtures...
- From the US (NFPA/SAE/FPRF, DOE labs, FAA, UL...)
  - development of safer containers to transport battery packs as cargoes in cargo aircraft
  - Development of pertinent multiphysics modeling tools to help safer design of battery packs
  - Training programmes for emergency services
  - Fire suppression /fire protection issues in warehouses
  - More intelligent routines for monitoring SoH of batteries

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Focus on recent FPRF research project (phase 1)

- *Hazards assessment of lithium-ion batteries*
  - performed first term of 2011
  - Exponent reporting in summer 2011
- Research to be implemented/supported by FPRF (NFPA) to fill in following identified issues (beginning of 2012):
  - Limited understanding of the composition (incl. Toxics) and the flammability of leaked cell electrolyte and cell vent gases
  - Lack of fire protection commodity specification for bulk packaged lithium-ion battery packs
  - Limited data regarding the effectiveness of potential suppressants, specifically water

Conclusive comments

- ❑ Examination of safety issues on the full value chain of batteries based on Li-based systems justified and favorable to accompany promotion of e-mobility as needed
  - Knowledge is progressing, however remaining gaps (not only identified by us) in knowledge justify prolonged research effort, e.g. for :
    - securing large-scale storage of batteries at manufacturing or recycling plants
    - going to less flammable electrolytes
    - Considering termite reactions potential...
- ❑ Return from early experience of captive EV fleet desirable in addition to safety-oriented R&D work and action plans
- ❑ INERIS is contributing to R&D efforts through dedicated studies, collaborative research and reviewing activity
  - Represented in the panel of experts steering on-going NFPA/FPRF action plan
  - has recently written a strategic battery safety-focused R&D agenda for a 5year period; **priorities will be given according to societal demands and to opportunities for collaborative work with academic and industrial partners**
- ❑ Recent collective consideration of safety issues by all promoters/stakeholders of e-mobility going in the right direction.

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Recent papers and communications (2011)

"Investigation on the fire-induced hazards on Li-ion battery cells by fire calorimetry"

- P. Ribière, S. Grugeon, M. Morcrette, S. Boyanov, S. Laruelle & G. Marlair
- *Energy & Environmental Science*, accepted 15th August 2011, on-line from September 2011

"Safety and ageing investigation towards an understanding of electrolyte degradation processes"

- P. Ribière, S. Grugeon, G. Cachot, D. Mathiron, M. Morcrette, S. Boyanov, G. Marlair & S. Laruelle
- **4th Int. Conference of Advanced Lithium Batteries for Automobile Applications** (ABAA-4), 21st to 23rd Sept. 2011

"Revisiting Physico-chemical Hazards of Ionic Liquids"

- G. Marlair, A-O. Diallo, G. Fayet & C. Len, paper submitted to special issue (serving as ILSEPT2011 conf. proceedings) of ***Separation & Purification Technology,*** sept.2011

" Evaluation of heats of combustion of ionic liquids through use of predictive models"

- G. Marlair, A-O. Diallo, & C. Len
- Submitted to *Ind. & Chem. Eng. Res. (Oct. 2011)*

Thank you for your attention !

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