Protection issues pertaining to large storage of new and used lithium-based batteries

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Outline

- Introduction
- Hazardous profile of lithium based cells and batteries in the context of storage
- Lessons from incidents
- Building up appropriate FSE expertise in storage and fire-fighting protection
- Conclusions/perspectives
Introduction
Li-ion technologies initiated a technical revolution …and might be ready for more!

Table: Design criteria for batteries with # priorities

<table>
<thead>
<tr>
<th></th>
<th>Consumer Applications</th>
<th>LEV, Power Tools</th>
<th>Automotive HEV &amp; EV</th>
<th>Stationary Elec. Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Market Introduction</td>
<td>1990 by Sony</td>
<td>2005</td>
<td>2011/12 (mostly HEV)</td>
<td>Realization has to be proven</td>
</tr>
<tr>
<td>Chances for Newcomers</td>
<td>Minimal</td>
<td>Moderate</td>
<td>(Very) Good</td>
<td>Depends on starting position</td>
</tr>
<tr>
<td>Typ. Battery-Size (kWh)</td>
<td>0.001 – 0.1</td>
<td>0.1 – 1</td>
<td>1 – 100</td>
<td>100 – 10,000</td>
</tr>
</tbody>
</table>

Design criteria for batteries with # priorities:
1. Energy density
2. Safety
3. Lifespan/cost
4. Power

Adapted from Tarascon (2009) Passerini (2011) and Marlair (2011)
Why storing lithium-based batteries is a challenging issue?

- Non rechargeable lithium metal and rechargeable Li-ion cells and batteries (all technologies) present specific hazardous profiles
  - Incidents have arisen on the whole chain value and confirm that a number of concerns have to be treated, storage is no exception

- Rechargeable lithium-ion batteries is a promising energy storage system for more and more power or energy-demanding devices:
  - Including large stationary energy storage systems for smart grids, intermittent energy sources...

- Both fast expanding and existing emerging markets to require more and more dedicated storage premises, as well as mandatory recycling of used/end-of-life batteries

- Recent studies clearly point out that fire safety management in storage today lack appropriate data (INERIS 2010 study, NPFA studies 2011/2012, Japanese study 2011...)

High Challenge Storage Protection Workshop, NFPA/FPRF, Paris, 27 May 2012,
Hazardous profiles of lithium-based (primary and rechargeable) batteries

lithium metal
lithium ion

In the context of storage
What kind of dangerous phenomena do we have to take account of?

Under (mechanical), thermal, or electric abuse conditions, at level of cell:

- Overcharge, Overdischarge
- External short circuit
- Heating
- Internal short circuit
- Increased Temperature
- Increased Pressure
- Thermal Runaway
- Opened cell
- Defect Cell, not opened
- Gas emission
- Fire
What is the material-side technical explanation?

- **Primary (non rechargeable) lithium batteries**
  - **metal lithium** as anode material, **flammable or highly flammable organic solvents**, and potentially explosive components (lithium perchlorate electrolytes)
  - manganese dioxide, poly(carbonmonofluoride), iron disulphide, vanadium pentoxide, copper oxide, copper oxyphosphate or thionyl chloride in the positive electrode

- **HAZARDS**, from
  - Highly flammable hydrogen gas, usually followed by ignition, upon contact of lithium metal with water: inadequately dried cell components or ingress upon loss of mechanical integrity of the cell (waste batteries)
  - Formation of dendrites and eventual internal short-circuit
  - Exothermic activity can lead to **thermal runaway** if unmanaged by internal or external safety devices.
    - at temperatures as low as 148 °C
    - venting/overpressurisation
  - Oxidation of organic solvents by lithium perchlorate

- **Potential** **smoke toxicity** (confinement) and **environmental issues**

- **SOC > 0** (Short circuiting potential)
What is the material-side technical explanation (Cont’d) ?

- **LITHIUM-ION rechargeable batteries:**
  - Developed initially as an inherently safer alternative to lithium metal anode cells
    - (lithium metal rechargeable batteries however still existing today for power applications with solid electrolyte)

- **HAZARDS, from:**
  - Side reactions can lead to lithium metal deposition (dendrites)
  - Limited stability in terms of temperature and voltage windows
  - Reactions between the organic solutions and the electrode surface can lead to thermal runaway. The solid-electrolyte interface becomes unstable when the cell temperature rises above 70–100 °C and can decompose exothermically.
  - Heat generation and thermal management are critically important: LiCoO₂ cells can produce significant amounts of heat that should be managed. All other sub-technologies may suffer thermal runaway
    - Extra energy released from polymeric materials burning (binder, separator...)

- **Smoke toxicity and environmental issues...**
- **Electric hazard (SC)**
Some related technical issues, as viewed in the context of storage protection

- No way to get rid of “ignition sources” like the one initiated from internal short, subsequent to a manufacturing defect
  - Quality insurance systems put in place at manufacturing level, in principle, limiting this issue to a minimum, as well as put in place internal safety devices...

- Presence of water-reactive materials...

- Joint storage of used batteries or batteries in unknown SOH may be an issue

- Early detection of “internal” incident not easy in storage

- No way to store (new) batteries at zero SOC (by contrast to supercapacitors), external short potential to handle
  - Both overall effects on single cell as well as an internal propagation from one cell to the other depend on SOC (see recent presentations from Int Aircraft Systems Fire Safety WG meeting, in Koln, May 2012, FAA web site)

- No (very limited) BMS protection operational in storage configuration...

- Potential fast growing rate of heat release

- Propagation of a fire scenario in large storage difficult to appraise so far, may vary according to commodity storage configuration
Main lessons from incidents and testing...

- UPS cargo fire, USA, 2006
- Recycling site, 2008, UK
- Electric car fire on board a ferry (Denmark, 2010)
- FAA Burn test, 1/8 pallet load 18650 cells
- Fire/explosion BYD6 car scenario, Shenzhen, China, 2012
- 26 March 2008, recycling site (UK)
Incident in recycling facilities : example of Trail (Canada)

- Impressive fire on Nov 2009, Trail (BC), Canada
- 6th fire of the series (at least) on this site...
- Looking like a fireworks display
- Bunker storage containing lithium ion batteries (among others...)
- Secondary fire on a municipal waste management site nearby due to propagation by fire brands
- Difficult fire fighting
- External short as initiating event?

http://www.youtube.com/watch?v=dfQwYKqmfk4
Incidents on-board cargo or passenger flights...

- Battery related incidents leading to fire scenarios listed in a regularly updated database by FAA.
  - 121 incidents records since March 1991, lithium technologies a majority

<table>
<thead>
<tr>
<th>DATE/SOURCE</th>
<th>TYPE OF BATTERY</th>
<th>DEVICE (If applicable)</th>
<th>AIRCRAFT TYPE</th>
<th>INCIDENT SUMMARY</th>
</tr>
</thead>
<tbody>
<tr>
<td>29-OCT-2011</td>
<td>Lithium-ion batteries</td>
<td>Battery packs for electronic device</td>
<td>Passenger</td>
<td>A cargo pallet carrying lithium-ion battery packs caught fire on the ramp awaiting loading on Austrian Airlines flight AUA 72 at Toronto Lester B. Pearson Intl. Airport, Ontario, Canada. Report from Delta Airlines indicates</td>
</tr>
<tr>
<td>25-FEB-2012</td>
<td>Lithium-ion batteries</td>
<td>Lithium-ion battery powered surf board</td>
<td>Cargo</td>
<td>Initial report from Federal Express indicated that a smoking unit load device was discovered at the Memphis, TN airport facility. Inspection revealed the contents of the ULD included a smoking and burning self-propelled surf board.</td>
</tr>
</tbody>
</table>

- Root causes:
  - Inappropriate handling using forklifts
  - Inappropriate shipment/packaging vs safety provisions in existing TDG regulations (class 9 DGs)
  - Inappropriate repairs of consumer products (recent case with an i-phone (May 2012)
  - Safe freight transport challenging in terms of fire protection (efficiency of halon)
  - Spontaneous ignition following drops of videoplayer of aircraft cabin floor
  - etc
Incident in a manufacturing/storing site in Germany (August 2008)
Incidents

- Incidents have occurred nearly everywhere on the battery value chains
  - Manufacture, terrestrial and air transport, storage, testing facilities, integrator sites, at end-use, in storages
  - Although limited experience in large storage for new cells and batteries

- Fire at battery recycling premises in Willenhall (West Midlands) in March 2008. Fire resulted in an acrid smoke plume and localised battery explosions due to the intense heat. Cause of the fire was the short circuit of a charged battery pack whose lead terminals had been left on.
Incident at waste treatment facility

Fire started at 6am in an open area
Lithium batteries ignited nearby waste materials
Sections of two motorways shut for several hours during the morning commute
Consignment of lithium batteries stored alongside flammable waste
Batteries in unsuitable containers in heavy rain
Waste military-specification batteries in poor condition
Areas A and B : 7.15 am
Area B and grassland between the site and the M6, after the fire
Damaged cells at point where yellow containers were stored
Primary lithium thionyl chloride cell from site of fire and new cell

Open circuit voltage 3.6 V

Rated capacity 27 A h

Energy density
2,000 kJ / kg

( lead-acid energy density 146 kJ / kg, lithium ion 460 kJ / kg )

Cells fitted with thermal cut out
Battery recycling premises
Battery recycling premises
Collection and storage of waste consumer batteries

Safety concerns:

- Percentage of lithium and lithium-ion batteries in collection bins around 0.2% but rising. Basis of safety: dilution of the most hazardous chemistry types.

- Segregated collection and storage of consumer batteries by chemistry not performed in the UK.
  - Sometimes done at arrival of recycling sites in France.

- Fire initiation potential of coin/button cells when compared to cylindrical designs.

- Batteries with terminals still attached.

- Fire retardant collection bins meeting UK HTM 05-03 Part A (UK government’s fire retardancy requirement for hospitals) are commercially available but are not widely used.
More global learning from incidents and testing

- Difficult fire fighting in large fires

- Prevention methods (stock fragmentation & isolation, avoiding co-storing with other hazardous materials...) of prime importance

- Late incident scenarios may initiate far after original abuse time
  - e.g. hours, even days after, (see Chevy volt fire after crash test last year in USA)

- Water has proven some efficiency to some extent (at least at level of cells, modules and even car battery packs,
  - however postponed re-ignition may happen

- By contrast, in some cases, in recycling plants, sand had to be used at the end as the ultimate solution

- Possible jumps of fire, from projections, to remote places
On the R&D roadmap towards improving FSE in storage protection
Knowledge gaps (waste consumer batteries)

- Fire initiation potential due to external short circuit according to battery chemistries and state of charge;

- Hydrogen generation due to accidental water ingress; effect of battery design;

- Chemistry of exothermic activity that takes place on loss of mechanical integrity of battery cells/packs

- Study the exothermic activity following mixing of batteries (specially primary lithium coin-type cells) with other materials including organic fractions in waste streams and flammable materials/solvents

- Assess the consequences of local accumulations of waste batteries and fate of coin-type cells

- Composition and toxicology of gases evolved in fires involving lithium, lithium-ion batteries and other high energy density battery chemistries; HSL’s burn hall
Knowledge gaps (lithium-ion battery chemistries)

- Material improvement to secure end-use
  - toward inherently safer technologies
- Automotive applications:
  - life expectancy challenge. Life expectancy from 20 years if batteries are maintained at 30 °C but falling to 2.7 years if operated at 60 °C. End of life safety behaviour varies with use history
  - more an end-use issue than a storage issue...
- Automotive-compliant electrochemical systems in development to achieve specific energy values over 300 Wh/kg at cell level
- Effect of charge and discharge cycles, ageing, driving conditions etc on end-of-life automotive battery composition and safety performance
- Safety performance of remanufactured automotive batteries for use in stationary applications
Knowledge gaps (fire fighting media)

- Limited experimental evidence on fire fighting media effectiveness
- The use of water to tackle primary lithium and lithium-ion battery fires when fires involve small inventories has been suggested
  - Water not to be used if fire involves primary lithium batteries only
  - No data on flow rates or sprinkler density required
- Halon-based fire extinguishers found incapable to extinguish fires involving primary lithium batteries but suppressed lithium-ion battery fires
- ABC dry chemical extinguisher recommended for lithium-ion batteries
- No clear optimum of storage commodity configuration at the light of fire protection, packaging materials may play a key role ...
- Any risk of thermit reaction ?
Electrochemical Energy STorage for Electric Vehicles
Outlook on INERIS’ equipment for abuse/fire testing

Multipurpose testing facilities

Battery-Dedicated testing platform

Crush test

Cycling machine

Simulated fuel fire 100 kW/m²

Impact test

Mont-la-Ville open-field test site

FTIR
Axis 1: technology watch/accident analysis/network activities

Axis 2: Safety characterization of electrochemical energy storage systems
- 2.1: Abuse testing
- 2.2: Development and/or adaptation of modeling tools
- 2.3: Assessment of relevance and reliability of safety devices

Axis 3: Risks management of electrochemical energy storage systems for EV and PHEV
- 3.1: Risks related to the manufacturing
- 3.2: Risks related to EESS use
- 3.3: Risks related to rescue operations
- 3.4: Risks related to the storage
- 3.5: Risks related to the recycling

Axis 4: Risks management of stationary electrochemical energy storage systems

Input data for Protection design

R&D projects on-going:
- HELIOS (2009-2012) (EU project)
- DEGAS (2011-2013) (Regional)
- STABALID (2013-2017) EU project

Strategic R&D Roadmap in the field of battery safety at INERIS: links with Protection issues, launched early this year

In support: the STEEVE Platform
In service from end of 2011
Conclusions/perspective

Storing (among other issues) still keeps today a challenging issues, according to what we know about the lithium battery hazard profil

Progress needed to design and adapt both (automated) fire protection of storage and fire fighting techniques, in addition to appropriate prevention measures (segregating, iloting, ...)

- knowledge gaps to be remediated in short/medium term to avoid storing becoming a bottleneck in future market development

Significant R&D work on-going as a response, which, no doubt, will bring the solutions...

- NFPA launched initiatives, see FPRF web site
- other works being done or launched, as very partly illustrated
Thank you!

To learn more on the topic:

- **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

- **Safety issues pertaining to rechargeable Li-based batteries: Current knowledge from literature review and abuse testing and perceived remaining topics.**
    - Free download: [http://www.college-de-france.fr/media/jean-marie-tarascon/UPL3054013266035970490_GUY_MARLAIR.pdf](http://www.college-de-france.fr/media/jean-marie-tarascon/UPL3054013266035970490_GUY_MARLAIR.pdf)

- **A review of hazards associated with primary lithium and lithium-ion batteries**
  - D. Lisbona, Timothy Snee
  - *Process Safety and Environmental Protection*, vol 18, issue 6 (2011), 351-496
    - 'Currently top most dowloaded paper in Process Safety and Environmental Protection'

See also NFPA/FPRF related research on going…