Safer Li-Ion Batteries by Preventing Thermal Propagation?

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STAGE SETTING

Electrical energy storage plays a crucial role in ensuring mobility and reliable energy supply in the future. Within this context, the Communication on Accelerating Clean Energy Innovation released by the European Commission identifies safer and higher-performing batteries as key requirements for a shift towards full electro-mobility and increased energy storage capacities in homes [1].

Li-ion technology is considered as one of the solutions for large scale applications (e.g. electrification of transport, smart grid) as well as for small scale applications (e.g. portable devices). As we move from single cells to modules and packs (from a few Ah up to several hundreds of Ah), failure modes become increasingly complex and their potential damage can be significant (e.g. vehicle burn down) and difficult to deal with. Of particular concern are failure modes that develop into thermal runaway (TR) (e.g. due to thermal, mechanical or electrical abuse) [2]. Thermal runaway occurs when the heat generated by abuse or misuse cannot be dissipated fast enough [3]. Cascading of TR through an entire battery, defined as thermal runaway propagation or in short 'thermal propagation', can lead to severe consequences (e.g. large heat release, emission of toxic materials, pressure release, electrolyte leakage, fire, and explosion). This and other aspects around the topic of thermal propagation constitute the scope of the workshop.

Battery design can mitigate risks associated with simultaneous thermal runaways in multiple cells occurring under non-normal operating conditions (e.g. energetic collisions, external fire exposure). However, the case of a spontaneous single cell thermal runaway reaction, under otherwise normal operating conditions, can be more hazardous as it might happen without warning, without an obvious cause and after a considerable service time (i.e. field failures as identified in references [4, 5]). Cell manufacturing contaminants or cell flaws are not common and are difficult to detect, despite extensive efforts carried out by battery manufacturers. The fact that cells involved in field failures generally have passed the testing required by safety standards indicates that these events require a special attention [4]. Thus, there can be two approaches which may be considered, one is the development of battery chemistries and/or battery designs that do not result into TR (e.g. non-flammable solvents, specific type of separator), while a second is to assume that a TR may eventually occur, and to implement safety features that focus on detecting and suppressing cell-to-cell or module-to-module propagation.

Reliable prevention of thermal propagation could potentially result in reduced battery weight, improved performance and ultimately reduced cost at sufficient level of safety.

A number of standards cover thermal propagation testing dealing with various battery applications (e.g. electric vehicles [6-8], industrial [7], aircraft installations [9], stationary [10]). Upcoming developments worth mentioning include the introduction of a thermal propagation test into the Global Technical Regulation on Electric Vehicle Safety (GTR-EVS) [11], and into a SAE standard for lithium metal and lithium ion batteries as cargo on aircraft [12].
**CHALLENGES RELATED TO THERMAL PROPAGATION**

Li-ion cells can be operated safely within a limited window of parameters (e.g. temperature, voltage, charging and discharging currents). Crossing these limits typically leads to a higher cell temperature that – once a certain onset temperature is exceeded – rapidly rises, leading to thermal runaway which is accompanied by hazardous effects (e.g. pressure increase, gas and particulate emission, fire or even explosion). Li-ion batteries, modules and packs are composed of numerous electrochemical cells (typically from several dozen to several thousand). If thermal runaway occurs in a single cell inside such assemblies, the heat generated typically cannot be easily dissipated and will lead to a temperature increase in adjacent cells. If the onset temperature is exceeded, one or several adjacent cells will also go into thermal runaway. Such thermal runaway can cascade through the whole battery module or pack leading to a huge heat and significant gas release (roughly a few 100 kJ / Ah and few l / Ah, respectively [13]) and associated hazardous events (e.g. release of toxic species [14]) and financial losses (e.g. property damage).

While thermal runaway of a single cell may be contained and may not lead to serious consequences, an event within a whole pack is more difficult to control [15]. This is further complicated by the difficulty of extinguishing a li-ion battery fire (e.g. possible re-ignition [16]). Consequently, prevention of thermal propagation is paramount for battery-related applications, thus battery manufacturers and OEMs invest a great amount of resources into it.

Testing the response of a Li-ion battery cell to thermal runaway should give valuable insight into its expected level of safety.

Although TR testing is covered by numerous research articles [17-22], it is only required in a few standards [10, 23-26]. Full module or even pack level testing contributes to improve understanding of propagation useful to battery developers, product designers and OEMs. However, up to now, no scientifically sound testing method has been developed for regulatory purposes (e.g. vehicle certification). Moreover, safety tests carried out in a controlled environment do not necessarily replicate the conditions under which safety incidents have been reported to occur in the field [4].

There are many possible methods for cell TR initiation which simulate externally driven abuse (e.g. heat, overcharge). Each of them has pros and cons, thus it is difficult to select a single preferable method suitable in all cases (e.g. cell geometries, cell assemblies). Certain initiation methods can have an immediate impact on adjacent cells (e.g. thermal methods pre-heat adjacent cells), while others may require modification of the battery housing (e.g. drilling a hole in battery casing for nail-penetration test). Battery design (e.g. cylindrical, prismatic or pouch cells, series or parallel connections) also may play a crucial role. Furthermore the selection of the cell to be initiated is not straightforward: while a cell in the center of the battery could represent the worst case with respect to heat removal, it may not be easily accessible e.g. by nail-penetration. Finally, there are issues with repeatability and reproducibility, as thermal propagation depends on a delicate balance between heat generation and heat removal. A slight change in the test conditions might lead to cell to cell propagation in some circumstances, but not in others.
Few tests try to simulate internally driven failures (Internal short circuit, ISC), such as the nickel particle method [23] or the wax material method [27]. Worryingly, the suitability of these tests to represent field failures remains an open question [28, 29]. The development of innovative tests to adequately simulate field failures is extremely challenging. To develop a test as representative as possible of real life situations, the potential trigger methods should not introduce extra energy apart from that inherent in the tested cell and should ideally only involve few electrode layers. Additionally, the manipulation of the device to be tested should be minimized.

**SCOPE OF THE WORKSHOP**

The Workshop 'Safer Li-ion batteries by preventing thermal propagation?' is organized under the frame of the Joint Research Centre (JRC)'s Exploratory Research Project. The intention of this 2 day workshop is bringing together leading experts not only to discuss the current state-of-the-art of thermal propagation testing, but also to brain-storm on the potential impact of preventing thermal propagation on the safety testing landscape.

Does reliable prevention of thermal propagation allow for a new and potentially simplified approach to battery safety? Could this approach render certain safety tests irrelevant?, Do manufacturers have to accept the fact that thermal propagation will occur under certain circumstances and their efforts have to focus on early detection techniques or containment tactics? Do the initial triggering method and the resulting mode of failure have an impact on the cascading runaway effect? Can innovative tests be developed to adequately simulate field failures? Can these tests be adapted to different end-use applications and future chemistries? These, and others, are some of the questions that the workshop aims at discussing.

The following issues or areas needing knowledge generation and exchange are considered (not exhaustively):

**1. THERMAL RUNAWAY: MECHANISMS AND INFLUENCING FACTORS**
   - Heat release in Li-ion cells (DSC and ARC measurements)
   - Scenarios and mechanisms of thermal runaway initiation and internal short circuit (ISC) (e.g. metal dendrite, Li plating, electrode contamination by foreign metal particles, separator puncture)
   - Influencing factors (e.g. SOC level, cell design)

**2. THERMAL PROPAGATION**
   - Field failure examples and lessons learnt: frequency of occurrence, post-mortem evaluations and root cause(s) identification
   - Energy and heat balance. Chemical vs. electrochemical heat sources. Cascading event
   - Role of emitted gases. Some toxicity considerations
   - Influencing factors: type of cell (cylindrical, pouch, prismatic), chemistry, electrical configuration (series vs. parallel) and cell location (e.g. corner cells vs. core cells)
   - Modelling thermal propagation, simulating tools and validation
3. THERMAL RUNAWAY INITIATION METHODS, FIT-FOR-PURPOSE TESTING RELATED TO EXTERNAL AND INTERNAL ABUSE TRIGGERS

Repeatability, invasiveness, severity, flexibility for different designs and scenarios represented for several initiation methods as classified in the following:

- **Thermal initiation:**
  - External heating: type of heating (bottom heater, circumferential heater, heater instead of cell, pulsed laser, thermite, super-fast heating)
  - Internal heating (heater embedded in cell, microheaters)

- **Mechanical initiation:** nail penetration (ceramic [25]/metallic), pinch, cell indentation, crush, blunt rod object

- **Electrical initiation:** overcharge, overdischarge, external short circuit

- **Artificial internal short circuit tests:** manufacturing defects (e.g. iron foreign particles) and internally driven failure simulations (Ni particle [23], wax [27])

4. SAFETY STRATEGIES; METHODS FOR DETECTING, MITIGATING AND PREVENTING THERMAL PROPAGATION; ANTI-CASCADE STRATEGIES

- **(Early) detection strategies** (e.g. BMS, sensor technologies)

- **Mitigation strategies:**
  - Improving heat dissipation (e.g. heat spreader (graphite, metal plate), increased distance between cells, guidance of emitted gases, protection against flames/sparks (tortuous path, effective cooling strategies))
  - Improving cell design and packaging to e.g. limit oxygen availability
  - Improving thermal endurance (e.g. extra isolation of cells, phase-change materials (PCM), high melt strength separators, ceramic separators, thermally stable cathode materials, inhibitors, flame retardants)
  - Improving mechanical endurance (e.g. physical barriers, protection against cell ejection by e.g. ceramic bushing, high puncture strength separators)
  - Improving electrical endurance (e.g. electrical isolation of faulty cell(s), fuse parallel cells individually, fusible contacts)

5. COST AND PERFORMANCE PENALTY OF MITIGATING THERMAL PROPAGATION

- Quantify loss in energy density – extra cost/kWh at pack level
- Safe cells vs. robust enclosures? Preventive approach vs. containment approach
- Efficiency of mitigation measures (e.g. benefits in terms of improved heat removal)

6. IMPACT OF AVOIDING THERMAL RUNAWAY PROPAGATION ON THE CURRENT SAFETY TESTING LANDSCAPE

A properly conducted thermal runaway propagation test describes both “if” and “how” a thermal runaway propagation would occur after the trigger cell(s) is (are) provoked into a runaway condition, inclusive of all boundary states that may exist in the pack. Therefore, this test would quantify the performance of the pack relative to a mitigation
Today’s safety testing landscape should be designed taking into account that failure propagation might occur. Therefore, multiple abusive scenarios are tested (e.g. mechanical, electrical, thermal).

- If thermal propagation can be reliably avoided, what operational boundaries can be broadened for greater safety, performance and efficiency? (i.e. thermal control, increased charge capacity, etc.)
- Which of the currently applied safety tests are rendered ‘unnecessary/redundant’?
- What impact could this have on cell/pack design (e.g. broadening safety limits)?

Workshop participants will benefit from the extended experience of known leading scientists, battery design engineers and safety testing experts. Interactive working groups with a reduced number of interested participants will be organized aiming at having active discussions on selected topics. Participants will be invited to share knowledge, information and experience.

The discussions and conclusions of this workshop will be summarized in a report which will be publicly disseminated to interested stakeholders.

REFERENCES


[14] Lebedeva NP, Boon-Brett L. Considerations on the Chemical Toxicity of Contemporary Li-Ion Battery Electrolytes and Their Components.
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[23] IEC 62133-2: Secondary cells and batteries containing alkaline or other non-acid electrolytes - Safety requirements for portable sealed secondary cells, and for batteries made from them, for use in portable applications Part 2: Lithium systems. 2016.


