

Lithium-Ion Battery Fire Suppression

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Lithium-ion Batteries (LiBs) hazards, techniques for mitigating risks, the suppression of LiB fires and identification of shortcomings for future improvement were thoroughly reviewed. Water is identified as an efficient cooling and suppressing agent and water mist is considered the most promising technique to extinguish LiBs fire.

Keywords: Lithium-ion Battery ; Thermal Runaway ; Fire Suppression, Water Mist.

1. Introduction

Lithium-ion batteries (LiBs) are a proven technology for energy storage systems, mobile electronics, power tools, aerospace, automotive and maritime applications. LiBs have attracted interest from academia and industry due to their high power and energy densities compared to other battery technologies. Despite the extensive usage of LiBs in energy storage applications, they are susceptible to thermal runaway and fire ^[1] which is the primary safety concern when used in hybrid electric vehicles (HEVs) ^{[2][3]}, electric vehicles (EVs) ^{[4][5][6][7]}, aeroplanes and submarines ^{[8][9]}. The LiB systems used in these applications consist of multi-cell packs and modules where thermal runaway in a single cell can initiate thermal runaway in adjacent cells and consequently compromise the integrity of the entire battery system ^{[10][11]}. The conditions which may lead to thermal runaway and fire in LiBs fall into four categories ^[12]:

- Electrical abuse (over-charging/discharging) ^{[13][14][15][16][17][18]}: Over-charging or discharging to voltages beyond the manufacturers specified charge window can cause lithium plating, or dendrite formation, on the anode. Over time this may pierce the separator causing a short circuit between electrodes and lead to thermal runaway.
- Thermal abuse (over-temperature) ^{[1][19][20][21][22]}: Internal temperature in the 90-120 °C range will cause the Solid-Electrolyte Interphase (SEI) layer within a LiB to decompose exothermically. At temperatures above 200 °C the hydrocarbon electrolyte can decompose and release heat.
- Mechanical abuse (penetration, pinch, and bend) ^{[4][23]}: Mechanical abuse, usually caused by an external mishap to the LiB such as car crash or during installation, can result in electrical shorting between the electrodes, via the electrolyte, producing localised heating.
- Internal short circuit (ISC) ^[5]: An ISC occurs due to the failure of the separator, allowing contact between the cathode and anode via the electrolyte. This can happen due to any of the above abuse conditions, or as a result of a manufacturing fault.

Any of these abuse conditions may result in an increase in the internal temperature of the cell, which in turn can initiate exothermic reactions such as SEI decomposition. This can lead to: a loss of protection to the anode such that the fluorinated binder within the anode can react exothermically with lithiated carbon; exothermic reactions between the intercalated lithium and electrolyte; or cathode decomposition giving off oxygen enabling combustion with the electrolyte ^[22]. The heat released increases the temperature of the cell and initiates additional reactions, which generate extra heat, creating a heat-temperature-reaction loop. This loop results in high internal temperatures and pressures which can lead to cell swelling, cell rupture, gas venting (sometimes violent) and possibly fire ^[5].

2. Lithium-ion Battery Fire Protection, Detection and Suppression

Fire protection measures should be considered at the cell, battery, module, pack, system and enclosure levels. The fire protection plan must take into account hazards from outside the battery system and compartment producing more complications to the design of systems. Figure 1 depicts various levels of fire protection from cell components to system and compartment designs.

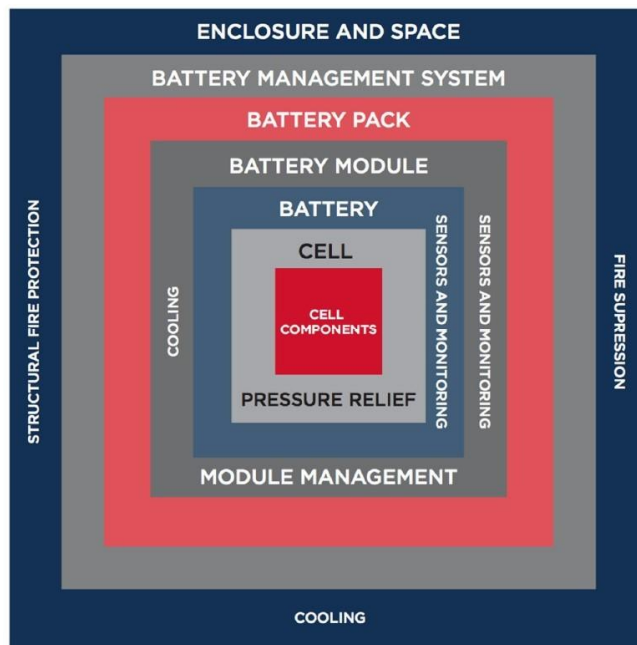


Figure 1. Levels of fire protection. Adapted from Ref. [24].

It has been shown that LiB fires can be detected using conventional heat detectors (reportedly the slowest method therefore not recommended), smoke detectors and combined smoke-heat detectors (reportedly the fastest method therefore recommended) [25].

Fire initiates when a fuel and an oxidiser are exposed to a source of heat, raising the temperature above the flashpoint of the fuel-oxidiser mixture. Interrupting any one of the four elements of fire: isolating the fuel from the ignition source; isolating the oxygen from the fuel; cooling the fuel below the ignition temperature; or interrupting the combustion reactions, can halt combustion. When the pressure build-up ruptures a lithium-ion cell, the flammable electrolyte is released, the thermal runaway process can supply adequate heat to initiate a fire.

The fire class of a LiB fire is contentious due to the various components which make up the battery; separator material, construction material and electrodes (Class A), flammable liquid electrolyte (Class B) and energised electrical apparatus (Class E) [26]. The fire suppression method should suppress any LiB fire and control any rise in battery temperature. If not sufficiently cooled, thermal runaway reactions may continue and the battery re-ignite; this is a major challenge for LiB fire suppression systems. Adjacent cells may also undergo thermal runaway if heat propagation from the initial cell is not controlled. It is more important to cool the cells in a large battery pack, to prevent heat propagation, than to extinguish fires from a single cell. LiB firefighting strategies should be based on not only extinguishing the burning cell, but include cooling the burning cell as well as its adjacent cells.

Numerous researchers have studied LiB fires in order to find an effective suppressant. It has been reported by the National Technical Information Service [27][28] that Halon based products can extinguish a LiB fire [29], but cannot mitigate the internal temperature increase and stop re-ignition after the extinguishment of a fire [27]. In studies performed by Rao *et al.* [30], heptafluoropropane (HFC-227ea or FM200), a halogenated extinguishant which does not result in ozone depletion, showed superior behaviour in suppressing LiB fires when compared to carbon dioxide and powder extinguishants. The effectiveness of heptafluoropropane in suppressing LiB fires was also reported by Wang *et al.* [31], while Liu *et al.* [32] found Novec 1230 to be effective.

LiB fire suppression can also be achieved by applying large amounts of water to a battery or by submerging the battery in water [33]. Both of these methods can extinguish a LiB fire and cool the battery, inhibiting exothermic reactions and preventing re-ignition. This technique is impractical for large battery modules, although water sprinklers may be viable. Det Norske Veritas - Germanischer Lloyd (DNV-GL) [33] investigated the effectiveness of extinguishants such as F500 and Firelce (water surfactants), PyroCool (foam), Stat-X (aerosol) and water sprinklers in suppressing a LiB fire and cooling a battery undergoing thermal runaway. All systems extinguished the fires but the water-based systems had better continued cooling ability. Egelhaaf *et al.* [34] demonstrated that water can suppress a LiB fire, and the addition of surfactant and gelling agents can decrease the volume of water required for firefighting. Tests performed by the Federal Aviation Administration (FAA) [35] concluded that water-based extinguishants (water, Hartindo AF-31, Aqueous A-B-D (Class A, B and D) are effective suppressant and coolant mediums compared to the non-aqueous extinguishants [33].

An alternative water extinguishing system is water mist [36][37][38][39][40]. Water mist may be an appropriate suppressant for large battery modules due to its low volumetric requirement and cooling capability. Testing conducted by the National Fire Protection Research Foundation, US, showed that water mist can effectively suppress a fire involving an electric vehicle battery [41]. It has also been demonstrated that the extinguishing effect of water mist can be improved by adding 5% F500 solution and 5% anionic non-ionic surfactant to pure water [42]. The effectiveness of adding 3% aqueous film-forming foam to water mist on re-ignition of a 18650-type LiCoO₂ lithium-ion battery pack (10 Ah ×4) fire has been analysed by Li *et al.* [43]. It was reported that water mist with 3% aqueous film-forming foam was more effective in delaying the re-ignition compared to ABC dry powder extinguishers, and carbon dioxide.

3. Current Limitations and Prospects

Currently, limited lithium-ion cells are constructed with safe cell chemistry and internal components, and these safety features may not be available in cells selected for energy storage projects due to commercial (cost, schedule, availability) or performance reasons. Battery management systems that maintain a safe operating environment for modules and packs, are well established, with constant advances being applied. However, fire incidents do still occur.

Although fires involving LiBs can be extinguished by many methods, the effects of thermal runaway are more difficult to manage and continued cooling is required. The associated problems also often become exacerbated as LiB assemblies tend to be in a tightly packed configuration, and are kept in enclosures with minimum leeway and free spaces. Therefore, battery compartment construction and design should maintain an intact boundary to a fire or explosion, but should also include passive thermal management utilising a combination of space separation, cooling, and zonal fire suppression within a module; and insulation between battery modules, in order to limit thermal runaway to adjacent modules. Given that many of the halon-based firefighting agents are banned owing to their environmental implications and that inert gases, such as nitrogen or argon, are less effective in their own right, the main impetus in finding alternative ways of fighting LiB fires mainly hinges on enhancing the effectiveness of, and perhaps finding smarter ways of deploying, water as the most efficient medium for continuous extinguishing and cooling. In this context, the extinguishment may be enhanced by using environmentally-friendly additives, or, better yet, in combination with an inert gas stream such as nitrogen; and the cooling improved through better design and implementation of spray systems. In both counts, water is the ideal medium for obvious reasons. Water mist is now well established as a fire suppression technique, but limited information is available for suppressing LiB fires. Water mist with additives and surfactants, or in conjunction with a gaseous extinguishing medium, is considered the most promising extinguishing and cooling method for LiBs. Further investigations on the thermal behaviour of LiBs during firefighting using water mist and different mediums are necessary to establish appropriate guidelines to extinguish LiB fires.

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