Increased Use of Lithium-ion Batteries

Description of Hazards and Related Protection Schemes Proposed by FM Global for the Storage of Lithium-ion Batteries

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Executive Summary

The use of lithium-ion (Li-ion) batteries is on the rise. Their high-energy density makes them appealing for a wide range of applications, from portable electronic devices to vehicles to energy-storage systems. Under certain conditions, however, this type of battery poses a serious fire hazard. Limited research has been done to understand the hazard associated with the storage of Li-ion batteries, and how to adequately mitigate against property loss as a result of this hazard. To date, there is no publically available standard outlining fire protection guidance for Li-ion batteries in storage.

In an effort to fill this need, the Property Insurance Research Group (PIRG), through the National Fire Protection Association’s (NFPA) Fire Protection Research Foundation (FPRF), is conducting a multiphase research program to develop guidance for the protection of lithium-ion batteries in storage. The phases are:

1. *Lithium-Ion Batteries Hazard and Use Assessment* (2011): This report by Exponent Failure Analysis Associates defines the potential fire hazards associated with Li-ion batteries.[1]
2. *Evaluating the Relative Hazard of Cartoned Li-ion Batteries in Warehouse Storage* (2013): This report by FM Global provides information on the hazard of cartoned small-format batteries in storage.[2]
3. *Determining sprinkler protection criteria for lithium-ion batteries stored in cartons* (2016): Large-scale testing was conducted at FM Global in 2016 to validate the proposed fire protection.[3]

Fundamentals of Lithium-ion Batteries

Over the years, various types of batteries have been developed. “Primary” batteries can be used only once, while “secondary” batteries (also called “accumulators”) are rechargeable. Li-ion batteries are of the secondary type.

A battery converts chemical energy directly to electrical energy and, by definition, consists of one or more cells; however, the term “battery” and “cell” are used interchangeably in the industry. Each cell contains one positive electrode (cathode) and one negative electrode (anode). For Li-ion batteries, during discharge, the lithium ions move from the anode to the cathode and are intercalated in the cathode. When the batteries are being charged, the lithium ions move in the reverse direction. The anode and the cathode are separated by a “separator” to prevent a short circuit. Typically, the separator consist of polypropylene and/or polyethylene and is soaked with an electrolyte. The electrolyte is the medium that allows the movement of ions between the anode and the cathode.[1]

Are All Li-ion Batteries the Same?

There is a broad spectrum of commercially available Li-ion batteries on the market today. For example, lithium cobalt oxide batteries are typically used in cell phones, while lithium nickel manganese cobalt batteries are commonly used for power tools. Industry research continues to develop more Li-ion battery types with widely varying parameters, and it is unclear at present how all of these parameters impact the fire hazard.
The parameters include the following:

- Cell enclosure (exterior material), including polymer, metal
- Sealing mechanism (e.g., gaskets, laser-welded, heat-sealed)
- Safety mechanisms
- Structure/shape (e.g., cylindrical, pouch/polymer, prismatic)
- Chemistry: cathode materials (e.g., lithium cobalt oxide) and anode materials (e.g., graphite)
- Electrolyte
- Capacity (amount of energy [amp hour] the battery can store) and voltage

Figure 1. A selection of lithium-ion cells used in consumer electronics (left to right: pouch, cylindrical and prismatic)[1]

The Development of Lithium-ion Batteries and Their Widespread Use

The development of Li-ion batteries began in the 1970s, and their first commercial use was in the early 1990s. The major advantages of Li-ion batteries are their high-energy density, minimal memory effect and low loss of charge when not used. For example, the energy density of a Li-ion battery is four to seven times higher than that of a lead-acid battery. But, because of the high cost of secondary batteries, primary batteries were more often used. According to Navigant Consulting, however, a Li-ion battery that was priced at more than US$1,000 per kW in 2009 has dropped to a third of this price in 2015.[4] This reduction in cost explains, in part, the fast-growing usage of Li-ion batteries all over the world. For example, forecasts expect that the global market for Li-ion batteries for use in vehicles will grow from US$3.2 billion in 2013 to US$24.1 billion in 2023.[5]

Many personal devices, such as cell phones and tablets, use only a single, small-format Li-ion cell.¹ Laptops and power tools may use multiple small-format cells to create a battery pack or a “module.”

¹ The U.S. Department of Transportation defines a small-format cell as having a capacity up to 150 W, while a large-format cell has a capacity greater than 150 W (UN/DOT 38.3 or UN ST/SG/AC.10/27/Rev.4).
Large-format cells are often used in electric vehicles, aircraft auxiliary power units and energy storage systems, and may use multiple “modules” to create a “system.”

Hazards Related to Lithium-ion Batteries

In a warehouse fire, the total potential energy released from a battery is a function of its electrical energy (capacity), the battery state of charge (SOC) and the combustible loading (the battery housing and the packaging material). Increasing any of these sources of potential energy can increase the fire hazard. Li-ion batteries present several fire protection challenges, including the chance of thermal runaway and the presence of an ignitable electrolyte within Li-ion batteries.

What Is Thermal Runaway?

“Thermal runaway” refers to the rapid self-heating of a cell from an exothermic reaction. It can occur with batteries of almost any chemistry, not just Li-ion batteries. In a thermal runaway reaction, a cell rapidly releases its stored energy. The more energy a cell has stored, the more energetic the thermal runaway reaction.[1]

The first step in an exothermic reaction is the decomposition of the separator, at which point the electrolyte reacts with the anode. The internal cell temperature increases to the point where the anode, electrolyte and cathode break down (approximately 180°C). These breakdowns generate flammable gas. If the gas causes the pressure within the cell to exceed its capacity, the safety vent opens and the flammable gas and ignitable electrolyte are released into the environment. In the presence of an ignition source, the gas and the electrolyte may ignite. Thermal runaway can potentially heat adjacent cells to their critical temperatures, resulting in cascading thermal runaway.

The severity of a thermal runaway will depend on the cell capacity, cell chemistry, electrolyte volume and the design of the battery (e.g., vent, case).[7] Also, storing the cells at a reduced state of charge (less than 50 percent) reduces the likelihood that a cell failure will lead to thermal runaway. Furthermore, the thermal runaway is most likely to occur during charging, or immediately after the battery is charged.[1] Based on the limited research, it is not possible to quantify how these variables impact the overall fire severity or likelihood.

What Is the Hazard Associated with the Electrolyte?

The electrolyte in Li-ion batteries is ignitable. In the event of battery failure, the electrolyte may release into the environment and ignite if exposed to an ignition source.[6] The electrolyte in other batteries, including Nickel cadmium (NiCd), Nickel metal hydride (NiMH) and Lead acid, is not ignitable. In Li-ion batteries, the electrolyte allows the transfer of lithium ions between the cathode and the anode (during discharge). The amount of electrolyte in a Li-ion cell varies depending on the capacity, the cell density and the cell chemistry. The small-format cells tested at FM Global contained two to five grams of electrolyte per cell, which represents from 5 to 10 percent of their weight.[2] Large-format cells may contain approximately 20 percent of their weight.

What Are the Causes of Failure in Li-ion Batteries?
In storage facilities, battery failure can result from external or internal causes. External causes include a fire initially unrelated to the batteries that causes thermal runaway, and mechanical abuse such as poor handling (batteries being dropped or punctured by forklifts). Internal causes include electrical abuse (batteries being overcharged, overdischarged or shorted) and internal fault due to manufacturing defect. Any of these failures may result in thermal runaway and release of the electrolyte.

Fire Scenario

Where significant storage of Li-ion cells is present in a warehouse, it is recommended that in-rack sprinkler protection is provided (see “Protection” below). This protection assumes that timely and effective protection is provided at the early stages of the fire—mitigating significant battery involvement.

If adequate sprinkler protection is not provided, it is expected that significant battery involvement will occur, which may result in thermal runaway. Once thermal runaway begins, cascading thermal runaway reaction to adjacent cells is possible and may cause an uncontrolled fire.

During thermal runaway, batteries may rupture and even be projected from the fire. Cell enclosure appears to drive the propensity of batteries to become projectiles (cylindrical, hard-cased batteries are most likely to project). During free-burn tests (i.e., no sprinkler protection) conducted at FM Global, few projectiles were observed. However, projectiles were seen during the free-burn tests conducted by the U.S. Federal Aviation Association in 2006[7] and 2012[8], after the battery packaging burned away and the batteries were free to project from the pile. In conclusion, once the cells reach thermal runaway, fire spread is very unpredictable.

Protection

Does Water Increase the Fire Hazard?

The misconception that water increases the hazard in a Li-ion battery fire is possibly due to confusing lithium-ion batteries with lithium metal batteries. Lithium metal batteries contain free lithium metal, and if water is applied to burning lithium metal, considerable amounts of hydrogen gas will be released. The gas will burn, intensifying the fire, resulting in a rapid heat rise and an explosion-like reaction. Unlike lithium metal batteries, however, there is no free lithium metal within a lithium-ion cell, so this phenomenon cannot occur.[9]

How Do We Protect Li-ion Batteries?

At this time there are no publically available standards or guidelines for the fire protection of Li-ion batteries in warehouse storage. Ongoing research is limited to the protection of individual Li-ion batteries stored in corrugated cardboard cartons. At this point, it is believed that automatic sprinkler protection must suppress the packaging fire during the early stages of fire growth to prevent batteries from becoming significantly involved in the fire. If batteries become significantly involved in a fire event, thermal

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2Although FM Global Property Loss Prevention Data Sheets do not currently provide protection guidance specifically for lithium metal batteries, testing has shown that, by providing protection similar to that recommended for Li-ion batteries, lithium metal battery involvement in a fire is prevented.
runaway and the released electrolyte may drive the fire hazard. For this fire event, we currently don’t have a good understanding of what is needed to suppress such a fire (See “On-going Research at FM Global” below).

The storage of equipment that incorporates Li-ion batteries (e.g., power tools, laptops) does not present the same hazard because the equipment that typically encases the batteries significantly delays their involvement. Therefore, protection for the storage of these items can usually be based on the commodity classification of the product. This will typically be driven by the housing of the product, the packaging and the pallet. Refer to Data Sheet 8-1 for commodity classification and Data Sheet 8-9, *Storage of Class 1, 2, 3, 4 and Plastic Commodities*, for adequate protection.

Research

Completed Research at FM Global

A multiphase project was completed at FM Global in conjunction with the Property Insurance Research Group (PIRG) through the National Fire Protection Association’s (NFPA) Fire Protection Research Foundation (FPRF).[1][2][3] FM Global conducted intermediate-scale, free-burn testing of Li-ion batteries stored in cartons. Based on these tests, it was concluded that the relative hazard of batteries increases as the cell capacity increases. The tests also showed that significant battery involvement occurs sooner with the large-format batteries than with the small-format batteries.

Ongoing Research at FM Global

Ongoing research is underway to validate sprinkler protection for the storage of Li-ion batteries.[3] Large-scale testing was conducted in 2016 at FM Global to ensure the proposed sprinkler system will be effective in controlling the fire hazard.

The Future of Lithium-ion Batteries

Li-ion battery development will continue. More vehicles traditionally powered by combustion engines will switch to electric power, increasing the demand for batteries. Companies and households may use large battery units for storage of renewable energy.

Scientists are developing less-hazardous Li-ion batteries by using electrolytes and separators made of less-volatile materials. Modern Li-ion batteries have integrated external electrical and mechanical safety features that prevent violent failure. This all serves to underline the success of these batteries; they are becoming more reliable, longer-lasting, cheaper—and hopefully safer.
References


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