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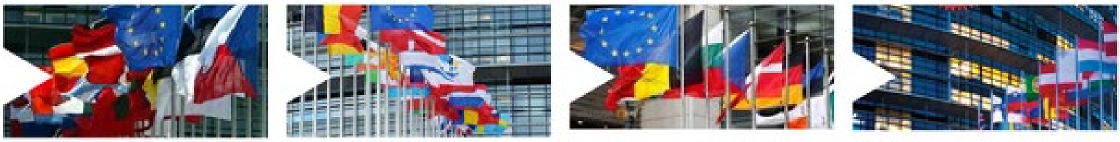

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Lithium batteries – What's the problem?

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This article will give a brief introduction to lithium-ion batteries (LIBs), describe some of the fire safety challenges around LIBs and address some common misconceptions about them.

Since they became commercially available in the early 1990's, LIBs have become ubiquitous in society. They can be found in everything from toys to electric vehicles (EV's) and even large-scale, grid-connected battery energy storage systems (BESS). The term 'lithium-ion' (often abbreviated using the chemical symbol for lithium to 'Li-ion') refers to a family of electrochemical cell chemistries. However, these cells are rarely marked with the particular chemistry used which makes identification difficult.

Cathode Material	Nominal Cell Voltage (V)	Specific Energy (Wh/kg)	Charge / Discharge Rate	Cycle Life	Thermal Runaway Temperature
$LiCoO_2$ (LCO)	3.6	150-200	Charge 0.7-1C Max Discharge 1C Max	500-1000	150°C
$LiMn_2O_4$ (LMO)	3.7	100-150	Charge 0.7-1C Typ, 3C Max Discharge 1C Typ, 10C Max, 30C Pulse	300-700	250°C
$LiNiMnCoO_2$ (NMC)	3.6-3.7	150-220	Charge 0.7-1C Max Discharge 1C Typ, 2C Max	1000-2000	210°C
$LiFePO_4$ (LFP)	3.2-3.3	90-120	Charge 1C Typ Discharge 1C Typ, 25C Max, 40C Pulse	1000-2000	270°C
$LiNiCoAlO_2$	3.6	200-260	Charge 0.7C Typ	500	150°C

(LCA)			Discharge 1C Typ		

Table 1. Li-ion cell chemistries (Battery University, 2019).

Li-ion cells come in three main physical formats: Cylindrical, (such as the common 18 mm diameter, 65 mm long, 18650 cell), prismatic and pouch cells. Although they are different shapes and sizes, they all share a similar internal construction with cathode and anode layers separated by a layer containing a semi-permeable membrane and electrolyte. In prismatic or pouch cells these layers are flat. In cylindrical cells these layers are rolled up in a configuration often referred to as the 'jelly roll' as shown in Figure 1, but otherwise the configuration is the same. A battery is made up of a number of cells, but for the purposes of this article, the terms 'battery' and 'cell' are used inter-changeably.

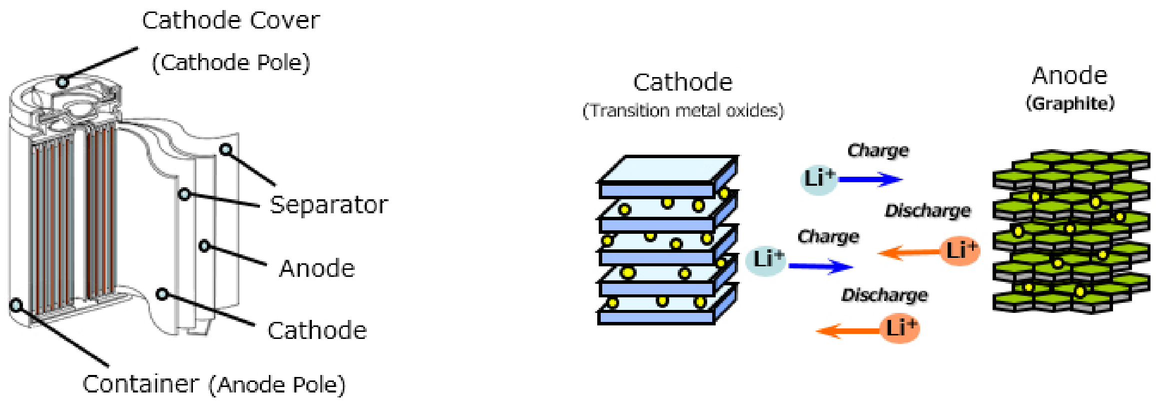

Figure 1 Li-ion cell construction (https://industrial.panasonic.com/ww/products/pt/lithium-ion)

The copper anode is coated with graphite, while the aluminium cathode is coated with the metal oxide. Between the electrodes is a very thin (12-25 µm) semi-permeable membrane separator. Lithium hexafluorophosphate is dissolved in a hydrocarbon based liquid electrolyte (usually ethyl carbonate or diethyl carbonate).

The primary fire safety challenge from these cells is thermal runaway (TR). This can be split into two driving mechanisms, either external heating or internal heating.

External heating may occur as a result of adjacent cells overheating or any other heating source, for example a fire, unrelated to the cells.

Internal heating is normally the result of abuse, either physical or electrical. Manufacturing defects, such as contamination, weld splatter, material defects, or creases can also cause internal heating. Any damage to the thin membrane separator will allow a short circuit between the anode and cathode within the cell and localised heating around the short. Electrical abuse in the form of charging/discharging at excessively high currents can cause internal heating due to the internal resistance of the electrodes. Overcharging (normally the result of using the wrong charging equipment) can have the same effect. Over discharging a cell can also result in damage, where at very low states of charge, the lithium contained within the electrolyte can plate onto the electrodes, forming small finger-like projections, called dendrites, which can then puncture the membrane separator causing a short circuit.

Figure 2. Pressurised pouch cell.

All of these failure mechanisms result in the heating of a cell. Once a cell is heated sufficiently, the electrolyte starts to boil, increasing the pressure within the cell. In pouch type cells, this is evident when they look like a pillow, as seen in

Figure *2*. However, this pressure increase is not visually evident in cylindrical and prismatic cells until the pressure relief valve activates, releasing flammable gases.

Myth 1: Lithium iron phosphate (LFP) batteries don't catch fire, you can hammer a nail through them!

There have been many instances of LFP batteries catching fire, they are just less prone to it compared with other chemistries. In Table 1 you will see the TR temperature of LFP is much higher than that of LCO or LCA cells, but they will eventually reach TR.

Some terminology used with batteries:

- **State of Health** (**SoH**) – the current maximum capacity of a battery at a point in time vs. the maximum capacity of that battery at the time of manufacture. This will decrease over the life of the battery.
- **State of Charge** (**SoC**) – the current capacity of a battery at a point in time compared to its maximum capacity at its current SoH. This will go up and down during use as the battery is being charged and discharged.

Figure 3. Battery SoC vs SoH (image by David Phan - https://www.thebatteryclinic.co.nz/).

Figure 3 shows the 'fuel' gauge on a Nissan Leaf, indicating a full SoC shown by the twelve long bars and a SoH of eight out of twelve small bars (approximately 66% of the original capacity) hence the reduced range indication of 113 km.

Monitoring the battery is a key function of a Battery Management System (BMS). A BMS provides a number of functions:

- **Charge management** – shutting off the incoming charging voltage when the battery is full and shutting off the output when the battery voltage drops below the minimum recommended voltage.
- **Cell balancing** – a BMS will monitor the individual cell voltages within a battery and is able to shut the battery down in the event of a cell imbalance, some may also provide alerts. More sophisticated systems are able to discharge cells that are higher than other cells, in order to bring them back into balance.
- **Thermal management** – some BMS are able to monitor the temperature within the battery, shutting the battery down if it gets too hot. More sophisticated systems, such as those in some BESS and EV's, are able to control cooling systems, to keep the battery within thermal operating limits.
- **Capacity monitoring** – some BMS are able to monitor the energy required to fully charge the battery and therefore work out the SoH.

Myth 2: A good BMS will stop a thermal runaway!

A BMS can help reduce the likelihood of a TR event. However, there are events outside the control of a BMS that will trigger a TR and the BMS cannot prevent or stop a TR if it occurs.

When a LIB goes into TR, they react differently depending upon the SoC. This is not generally something that first responders need consider when dealing with an internal combustion engine vehicle fire. Batteries with a high SoC will generally be more volatile than those with a lower SoC and may produce a more intense but shorter fire.

Using oxygen calorimetry, commercially available 2.9 Ah pouch cells were tested. At 100% SoC, the peak heat release (HRR) was measured at 21 kW burning for around 20 s. At 50% SoC, that peak HRR dropped to 13 kW, but the cell burned for 50-100 s. At 0% SoC, the peak HRR was just 2.6 kW, but the cells burned for 300 s (Ribière P., 2011).

Evidence would also suggest that a SoC over 50% is more likely to result in spontaneous ignition of combustible gases during TR, while a SoC less than 50% is more likely to result in a flammable vapour cloud which, if sufficiently well mixed, can result in an explosion if ignited in a confined space (Christensen, et al., 2021). An example of this is the APS McMicken BESS explosion, which injured nine first responders, including eight firefighters, four seriously (DNV.GL, 2020).

Batteries undergoing TR also give off a variety of toxic products, including carbon monoxide and hydrogen fluoride (HF). The same cells tested by Ribiére *et al*. were tested at both 100% SoC and 0% SoC and HF production measured. At 100% SoC, approximately 400 mg of HF was released. At 0% SoC, the quantity of HF released was higher, approximately 750 mg. Worksafe New Zealand (the New Zealand occupational health and safety regulator) have three measures for toxic exposure, a Time Weighted Average (TWA) over an 8-hour period, a Short-Term Exposure Limit (STEL) for exposure over any 15-minute period during a working day and a ceiling exposure. The published ceiling exposure for HF is just 3 ppm or 2.6 mg/m^3, but Worksafe New Zealand does not publish a TWA or STEL for HF (Worksafe New Zealand, 2022). The European exposure limits, based on indicative occupational exposure limit values (IOELV) are IOELV:TWA of 1.8 ppm or 1.5 mg/m^3 and IOELV:STEL of 3 ppm or 2.5 mg/m^3 (European Chemicals Bureau, 2001).

Myth 3: You can't put water on a lithium-ion battery fire, it'll explode!

LIBs do not contain metallic lithium which reacts with the water. The lithium is contained in salt form in the electrolyte and oxide form in the cathode which does not react with water.

Extinguishing LIB fires can be challenging and, in some cases, where circumstances allow, it may be quicker and more beneficial to allow the battery to burn, consuming the flammable electrolyte and using much less water. If a fire must be extinguished for life-safety, property protection or environmental reasons, water is still the ‘go to’. Gaseous or dry powder extinguishers have been used but they are only effective at putting the immediate fire out. Because the thermal runaway is still occurring within the battery, flammable gasses continue to evolve, and it is highly likely the fire will re-ignite. Foam extinguishers also have the added effect of insulating the batteries, further increasing the rate of TR. Water has the benefit of extinguishing the fire and, at the same time, cooling the cells, thus slowing the TR.

First responders in Europe have adopted the strategy of putting EV’s into large containers of water in order to extinguish the fire and to cool the whole battery pack, as shown in Figure 4. The BMW i8 shown was only removed from the container once there were no observations of bubbles rising to the surface, this indicating that all of the cells had stopped off-gassing.

Fortunately, instances of EV traction battery fires are rare, with only around 260 confirmed globally since 2010, many of which have involved high-speed collisions. They do however garner plenty of media attention when they do happen. Tesla claim five EV fires for every billion miles travelled, compared with the national average in the US of 53 vehicle fires per billion miles travelled (InsideEVs, 2022).

Figure 4. BMW i8 in container of water (Image: Brandweer Midden- en West-Brabant).

In LIB fires where the immersion technique cannot be used, large volumes of water are required to be continuously pumped onto the batteries for cooling for an extended period of time. Such approaches generally require committing many first responders over the duration. For example, the 25 MWh LFP fire on top of a Beijing shopping mall required 235 firefighters, with 47 appliances from 15 stations. Two firefighters were sadly lost in the initial explosion. In another example, the 300 MW, 450 MWh Victoria Big Battery fire in Australia (shown in Figure 5), over 100 firefighters attended. Following the fire, 900,000 L of contaminated water was removed from the site, although it is estimated that close to 6,000,000 L were pumped onto the fire and in the subsequent cooling phase. The incident lasted almost 4 days (Fisher Engineering Inc and Energy Safety Response Group, 2022).

Figure 5. Victoria Big Battery fire (Image: Fire Rescue Victoria (FRV), Aviation RPAS Unit).

Although large batteries pose extraordinary challenges to first responders due the scale of the incidents, smaller batteries are having a bigger impact on fire safety in the home. Electric mobility devices such as e-bikes, e-scooters and e-skateboards are increasingly involved in fire-related deaths around the world. The Vancouver Fire Department has reported seven fire-related deaths from the start of the year until mid-June, of those, five were attributed to LIBs (Little, 2022). In June 2022, the New York City Housing Authority proposed to prohibit e-bikes and e-scooters in their public housing to limit the fire risk (Verzoni, 2022).

LIBs are also causing fire safety challenges in the waste streams. LIBs are often discarded in both normal and recycling waste streams. However, when they are crushed, in compactor trucks, or in waste sorting facilities, they can catch fire, causing huge losses (United States Environmental Protection Agency, 2021).

In conclusion, LIBs are everywhere in society and a classic example of new technologies developing faster than regulatory controls, leaving first responders on the backfoot. Like most technologies, when working as intended, LIBs are a key enabler in modern society. However, when they go wrong, they pose a range of threats from fire and explosion to toxicity. LIBs will be in use for many years to come while new technologies are developed. In the meantime, we must adapt, by updating building regulations to account for new technological risks and by undertaking the research required to provide our first responders with doctrine that is fit-for-purpose.

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