Alsym Energy

LITHIUM-ION BATTERY FLAMMABILITY FACTS

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INTRODUCTION

Lithium-ion batteries have become a cornerstone of modern technology. They can store high amounts of energy in a relatively small space and lose their charge slowly when not in use. And while all batteries degrade over time, lithium-ion batteries can often withstand thousands of charge-discharge cycles.

But they come with significant downsides. Lithium-ion batteries are expensive to produce, and the materials used in them (particularly lithium and cobalt) come with significant environmental, health, and human rights concerns. But the biggest downside by far has to do with safety: lithium-ion batteries can potentially explode or catch fire if they're charged incorrectly, damaged, exposed to high temperatures or water infiltration, or have manufacturing flaws.

Until recently, lithium-ion batteries were mostly used in consumer electronics such as mobile phones and laptops, and fires were relatively small; for example, Samsung discontinued the Galaxy Note 7 in 2016 after a battery manufacturing defect caused dozens of phones to combust and even explode. But with lithium-ion batteries now finding their way into electric vehicles and grid-scale storage systems, the danger posed by fires is much higher.

There have been several high-profile fire incidents in recent years. For example:

- The car carrier Felicity Ace sank in the Atlantic Ocean in February 2022 after the EVs on board caught fire, leading to a nearly $500 million loss.

- A section of the Pacific Coast Highway in California was closed and a shelter-in-place order covering seven square miles was issued after a Tesla Megapack caught fire at a storage facility near Monterrey in September 2022.

- Two separate battery storage facilities in Warwick, NY caught fire after a thunderstorm in June 2022—one on a school campus. Four weeks later, another facility caught fire in Jefferson County, NY near the border with Canada.

- E-bike and e-scooter batteries have caused at least 131 fires in New York City in 2023 as of August 1, resulting in dozens of injuries and 13 deaths.

WHY DO LITHIUM-ION BATTERIES CATCH FIRE?

Lithium-ion batteries contain two electrodes (anode and cathode), a liquid electrolyte, and a separator, a semi-permeable barrier that isolates the anode and cathode from each other.

If the separator is punctured or damaged, the anode and cathode can make direct contact, allowing electrons to flow between them unimpeded. This sudden spike in electrical current generates heat, which can ignite the flammable electrolyte.

Once it enters an uncontrolled, self-heating state (known as thermal runaway), a battery can vent flammable hydrocarbons and toxic gases, including hydrogen fluoride and carbon monoxide. The fires burn so hot and so fast that they can be extremely difficult to extinguish, and the smoke produced can contain other gases including hydrogen cyanide and hydrogen chloride.

Hazardous gases in Li-ion fires include:

- *Hydrogen fluoride*
- *Hydrogen cyanide*
- *Hydrogen chloride*
- *Carbon monoxide*

The reasons behind thermal runaway and resulting fires generally fall into one of the following categories:

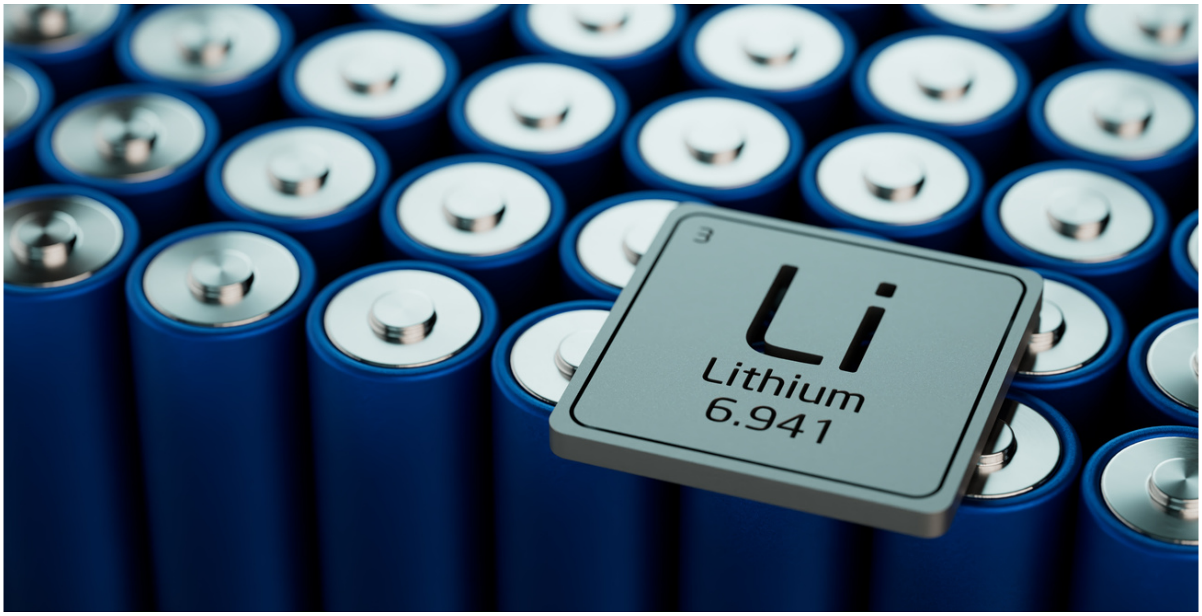
Thermal
Most large lithium-ion batteries include some kind of thermal management system. This can include passive methods such as heat sinks and heat spreaders, or active methods such as liquid cooling systems. Both methods can be effective at managing fluctuations in battery temperatures under normal conditions and may be able to stop a single cell that has entered thermal runaway from spreading heat to adjacent cells. But if external temperatures rise due to a nearby fire, or multiple cells go into runaway at the same time, thermal management systems may be able to slow the progression to an active fire but will likely be insufficient to prevent one completely.

Electrical
Batteries can be damaged during the charging process, especially if they are charged too quickly or under freezing conditions. If batteries are charged too fast, lithium ions don't have sufficient time to diffuse into the anode, and instead accumulate in metallic deposits on its surface. Very cold temperatures also slow the absorption of lithium into the anode, allowing it to build up on the surface. Over time, these metal deposits can give rise to mounds of lithium called dendrites, which grow longer and sharper with every charge/discharge cycle until they eventually penetrate the separator and short out the battery. The surge of current generated by the short can heat the flammable electrolyte solution, causing the battery to ignite.

Mechanical
Mechanical faults can include manufacturing defects (a common cause of EV fires) or damage caused by outside forces. This could include a battery that's punctured during installation or damaged due to an earthquake, or one that's flooded after a hurricane or heavy rains. For example, following Hurricane Ian in 2022, a number of EVs in Florida began off-gassing and catching fire as sea water infiltrated the battery packs and created salt bridges across terminals, causing the batteries to short. Something similar happened in 2021 in Norway when a battery-powered sightseeing vessel caught fire after sea water entered the battery compartment through a vent in the ship's hull.

For stationary storage applications, battery failure is most likely to result from thermal and electrical faults. This is why all lithium-ion batteries are maintained under tightly controlled environmental conditions and have complex (and expensive) battery management systems overseeing each cell. However, external factors such as wildfires, rockslides and other natural disasters cannot be ignored. In fact, recent stationary storage fires in New York and Florida in the US are believed to have started due to power surges or lightning strikes during thunderstorms.

NOT ALL LITHIUM-ION BATTERIES ARE THE SAME



Lithium-ion batteries are best thought of as a family of chemistries with common characteristics. When it comes to stationary storage and EVs, three chemistries underlie the majority of all batteries in use.

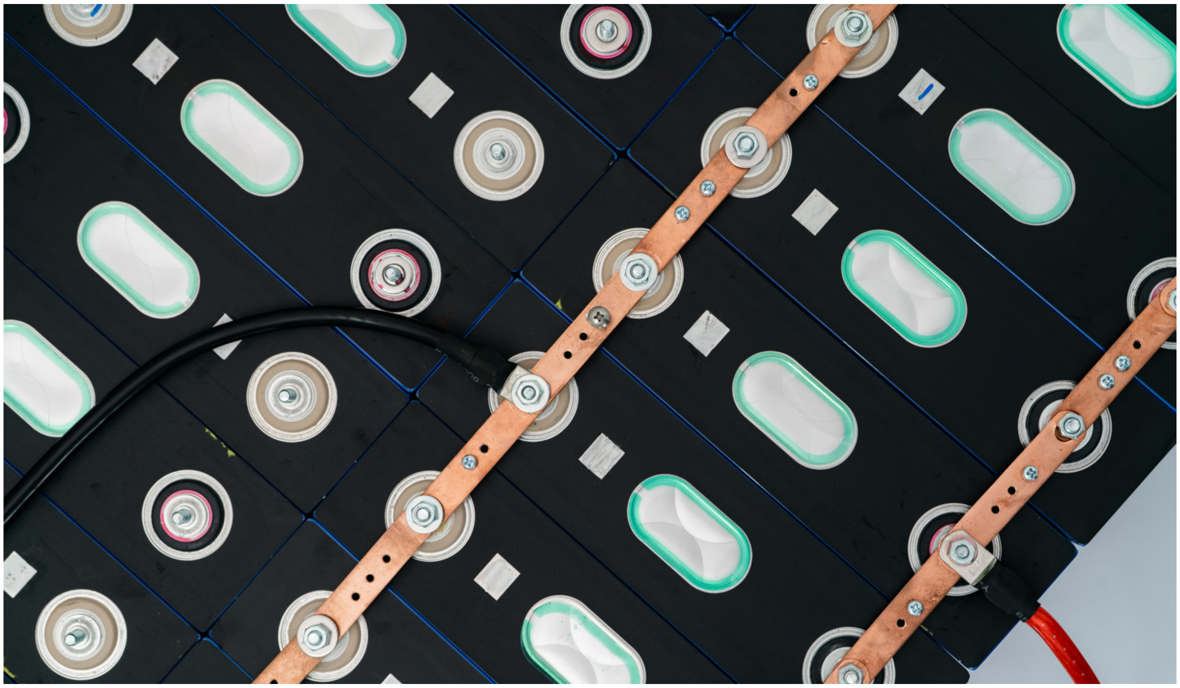
- Nickel manganese cobalt (NMC): A high energy, high-cost chemistry that is used for extended-range and performance EVs, as well as many older grid storage products.
- Nickel cobalt aluminum (NCA): A high energy, high-cost chemistry used in higher-end EVs. NCA has largely been supplanted by NMC but can still be found in some older cars.
- Lithium iron phosphate (LFP): A lower energy, somewhat lower cost chemistry that has become common for use in stationary storage systems and standard-range / low-range EVs. LFP cells contain no cobalt or nickel.

All lithium-ion chemistries can experience thermal runaway due to the reasons listed above. When assessing fire risk, it is important to consider multiple factors and remember that the most combustible cell component is the liquid electrolyte.

The most common electrolyte solvents used in NMC, NCA and LFP cells are provided in the table below. It's worth noting that the boiling point (temperature at which a solvent begins to evaporate), flash point (temperature at which a material will ignite in the presence of an ignition source), and auto-ignition point (temperature at which vapor will ignite without an ignition source) vary, but all can ignite at relatively low temperatures.

	Boiling point	Flash point	Auto-ignition
Ethylene carbonate	**248°C**	**150°C**	**465°C**
Propylene carbonate	**242°C**	**132°C**	**455°C**
Diethyl carbonate	**126°C**	**25°C**	**445°C**
Dimethyl carbonate	**90°C**	**18°C**	**458°C**

IS LFP SAFER THAN OTHER CHEMISTRIES?



Battery manufacturers and automakers have been promoting a narrative implying that LFP, while storing less energy than NMC and NCA, is a “safe” option compared to higher energy chemistries, and is incapable of thermal runaway. This position is misleading at best.

It’s true that LFP cells are more resistant to overheating and thermal runaway than NMC and NCA due to reduced oxygen release from the cathode and lack of flammable metals such as cobalt and nickel that can reduce thermal stability and contribute to flammability risk. However, LFP cells are not immune to the risk of fires or safety incidents. As the state of charge (SoC) increases, their thermal stability decreases, and the potential for thermal runaway reactions becomes serious.

Various factors such as lithium plating at high state of charge, oxygen release from cathode, electrolyte decomposition, and increased side reactions (electrolyte-electrode interface) all contribute to generation of heat and result in thermal runaway in LFP cells.[1,3,4] And as with all chemistries, other factors such as overcharging, exposure to high temperatures, and physical damage also contribute to LFP batteries catching fire.[2,4,5]

ANALYSIS

In a systematic study to evaluate thermal runaway and heating characteristics of LFP and NMC cells, thermal runaway was found to initiate sooner in LFP cells[6]. While the self-heating rate measured at 100% SOC was lower for LFP compared to NMC, it was still significant enough to cause a catastrophic fire event within a very short amount of time. This is especially true considering that the self-heating rate for LFP would lead to the electrolyte boiling in a matter of seconds, generating highly combustible gases.

Other studies have arrived at similar conclusions[7,8]. In one such example, researchers studying the effect of heating area and thermal propagation direction on 243 Ah LFP cells observed that all cells reached temperatures well above boiling points of the electrolyte within seconds [7].

One study that measured the rate of evolution of combustible H2 and CO gases in an 8.8 kWh LFP battery installation[9] reported a rapid rise in the concentration of both gases within minutes of reaching the electrolyte boiling temperature. The combustible gases immediately ignited when an electric heater was introduced, leading to rapid pressure build-up and a catastrophic explosion.

Therefore, knowing that thermal runaway in LFP cells can also result in a near-instantaneous evolution of highly combustible gases in dangerously large concentrations helps us understand that LFP is indeed not safe, and presents largely similar risks of fire and catastrophic explosion as NMC or NCA.

The only advantage LFP provides is possibly a lower self-heating rate, which could give the BMS a little more time to respond to serious cell deviations or give the thermal management system a little more time to respond and dissipate the heat at a rate faster than at which it is generated. However, these time frames are measured in minutes, not hours or days. Ultimately, first responders called to an LFP battery fire will still find themselves in a situation where they will simultaneously have to mitigate dangerous gases, struggle to prevent a blaze from spreading, and potentially manage evacuations in dense areas.

ACKNOWLEDGEMENTS

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