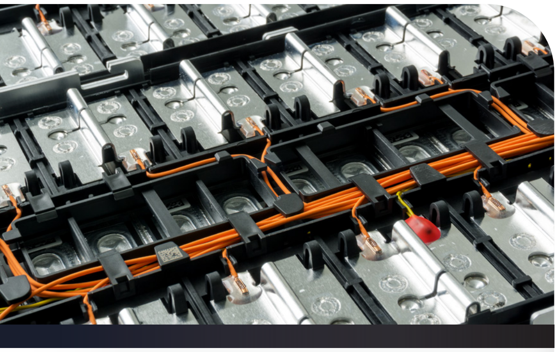
2023 White Paper

Safety Implications of Lithium Ion Chemistries



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INTRODUCTION

Over the last three decades, lithium ion batteries (LIB) have transformed modes of communication, transportation, and electrification. LIB energy storage is a crucial technology component needed to continue the transition towards a clean energy future.

The first commercial lithium ion battery was introduced in 1991 and has since undergone several fundamental chemical and material developments, while being simultaneously adopted by a variety of electronic devices at an accelerated pace. Pursuing parallel technology and commercial development pathways will inevitably create gaps that will not be fully recognized until an event occurs that requires addressing. Furthermore, it is difficult to address gaps when fundamental technological development seemingly outpaces commercial and industrial experience and understanding.

Safety of lithium ion batteries, specifically mitigation of thermal runaway, is a narrowing but persistent gap that has been difficult to fully address alongside rapid technology development and adoption. Regrettably, the consequences of thermal runaway can be severe, sometimes resulting in fatalities, which is a serious and justified cause for concern. Thermal runaway is a well-known phenomenon that can occur in all battery types but is particularly dangerous in lithium ion batteries because of the rapid onset of high temperatures and production of flammable gases. Thermal runaway events that result in lithium ion battery fires are often difficult to extinguish due to battery chemistry.

To that end, it is not uncommon to hear claims of certain lithium ion battery chemistries being “safer” than others, especially in terms of fire and explosion hazards. This statement is reductive and misleading. Battery chemistry is only one of many characteristics that influence safety and risk. The chemical reactions and energy conversion mechanisms within batteries are complex and their impact on battery safety is nuanced. This paper provides an overview of various lithium-based battery chemistries and aims to demonstrate their interdependency with safety.

BATTERY OVERVIEW

A battery is an electrochemical energy storage and conversion technology, meaning it stores chemical energy and converts it to electrical energy when needed. Rechargeable batteries can reverse this reaction, converting electrical energy to chemical energy to be stored. In the most basic sense, a battery is composed of two metals separated by an electrolyte material. Energy is stored and converted at the electrodes. The amount of energy stored is a function of the electrode potentials, which is a material property, and the charge transferred across the electrodes. Charge is transferred by oxidation and reduction reactions that drive the conversion of chemical and electrical energy. The electrolyte prevents direct electron transfer between the two metal electrodes within the battery cell. This forced directionality of the electron flow is exploited to provide electrical power.

It also enables energy storage by preventing charge transfer when the battery is idle. Figure 1 illustrates the directionality of electron flow during battery discharge operation. The anode undergoes an oxidation reaction, causing it to lose electrons that travel through an electrical circuit, which are then gained by the cathode via a complimentary reduction reaction. Common battery chemistry anodes, cathodes, and electrolytes can be found in Table 1.

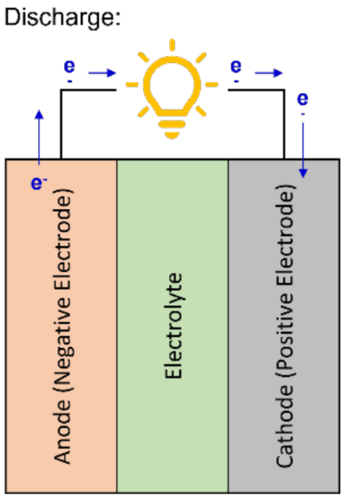

Figure 1. *Diagram of electron flow during battery discharge*

Note that Table 1 only lists the materials that are active in the electrochemical reaction. Batteries employ additional materials and components that necessary for functionality, but passive to the oxidation and reduction reactions. Required passive components will depend on the battery chemistry and cell construction. Examples of passive components might include current collectors, separators, and electrolyte solvent. While not electrochemically active, these passive components do contribute to overall battery safety. For instance, the flammability of an electrolyte solvent or its ability to manage overcharging are important considerations that affect battery safety.

Storing energy in any form carries a safety risk, making all batteries potentially hazardous. Stored energy may be released in an uncontrolled manner, creating a hazard. For a battery, hazards include electrical shock, heat generation, off-gassing, and in extreme scenarios, fire and explosion.

THE TRUTH ABOUT LITHIUM

Lithium has long been an attractive battery material because it is very reactive, meaning it has the potential to be very energetic. It is the smallest and lightest metallic atom in nature, enabling size and weight reduction in batteries that are instrumental to producing electric vehicles (EVs) and modern personal devices.

“Lithium-based” is a very broad description of a battery chemistry category, and it simply means that the lithium atom has somehow been incorporated into one or more of the active battery components (anode, cathode, and electrolyte). Lithium can be used in both primary (non-rechargeable) and secondary (rechargeable) battery cells. Lithium ION refers to secondary batteries that use the lithium ion (Li+) as the charge carrying species. More simply, the lithium ion moves from anode to cathode upon discharge and from cathode to anode during charge while it’s electron counterpart travels through the external circuit to do work.

Historically, lithium ion batteries (LIBs) have not contained elemental lithium due to safety concerns arising from dendrite formations and the increased possibility of forming internal short circuits, which was observed early on in the development of rechargeable lithium metal batteries (LMBs).[1] However, there is still great interested in develop-

Table 1. *Common anode, cathode, and electrolyte materials by battery type*

BATTERY TYPE	YEAR INVENTED	ANODE	CATHODE	ELECTROLYTE
Lead Acid	1859	Lead (Pb)	Lead Dioxide (PbO_2)	Sulfuric Acid (H_2SO_4)
Nickel-Cadmium	1899	Cadmium (Cd)	Nickel Oxide Hydroxide ($Ni(OH)_2$)	Potassium Hydroxide (KOH)
Alkaline	1950	Zinc (Zn)	Manganese Dioxide (MnO_2)	Potassium Hydroxide (KOH)
Lithium Ion	1970s	Graphite (C6)	Lithium composite	Lithium Hexafluorophosphate ($LiPF_8$)
Nickel-Metal Hydride	1986	Hydrogen absorbing alloy (MH)	Nickel Oxide Hydroxide ($Ni(OH)_2$)	Potassium Hydroxide (KOH)

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[1] Reddy MV, Mauger A, Julien CM, Paolella A, Zaghib K. Brief History of Early Lithium-Battery Development. Materials (Basel). 2020 Apr 17;13(8):1884. doi: 10.3390/ma13081884. PMID: 32316390; PMCID: PMC7215417.

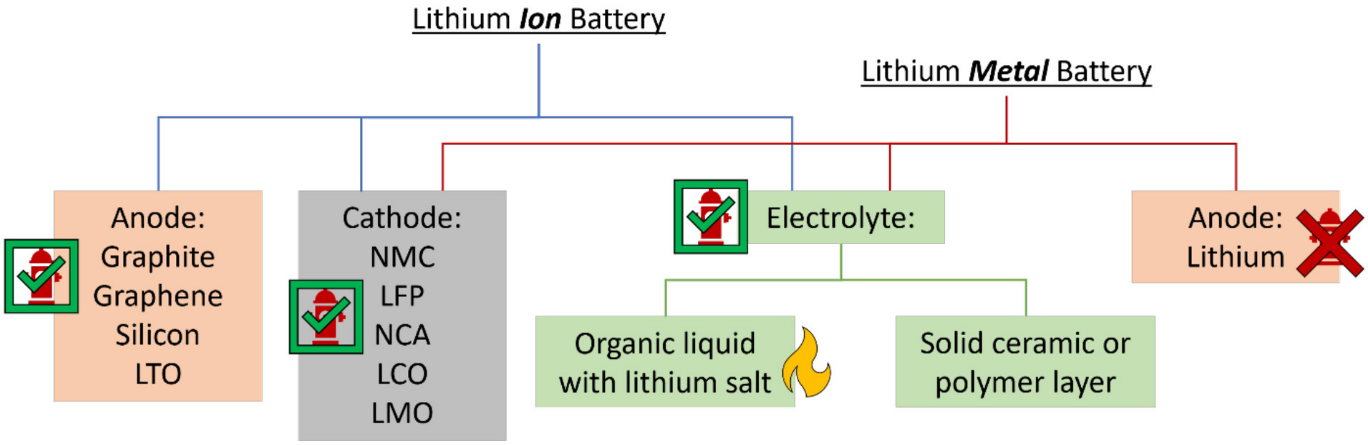

Figure 2. *Schematic of materials used in lithium ion and lithium metal battery (LMB) active components. Water is reactive with lithium and should not be used for extinguishing a LMB fire. Organic liquid electrolytes are flammable.*

ing rechargeable LMBs because of the potential for substantial improvement in battery capacity.

For the purpose of this paper, LIB refers to lithium ion batteries that ***do not*** contain elemental lithium. LIB encompasses common, commercially available lithium-based batteries that use two intercalation electrodes – a graphite or other carbon-based (graphene) anode and a lithium composite cathode – and an organic electrolyte solution containing lithium salt. Conversely, LMB refers to rechargeable lithium batteries that do contain elemental lithium. In an LMB, lithium metal acts as the battery anode. The cathode and electrolyte materials in an LMB are typically the same as an LIB. Figure 2 depicts how battery component materials coincide or differ for LIBs and LMBs.

Lithium metal and lithium ion batteries have different performance and risk profiles because of the presence, or lack of, elemental lithium metal. One major advantage to employing lithium metal anodes is the potential for a 10-fold increase in the amount of stored energy within the battery, without increasing its size or weight. The improved energy density would manifest as a cell phone that can go several days on a single charge, a longer range EV, or a longer duration battery energy storage system on the grid.

However, as previously stated, lithium metal is extremely reactive, which is a potential safety issue when used in a battery. The reaction between lithium metal and water forms flammable hydrogen gas and releases heat. Under the right conditions, lithium metal and water can start a fire. For this reason, it would be ***counterproductive*** to fight a LMB fire with water.

That is not true for LIBs. It is a common ***misconception*** that LIB fires get worse with water. Lithium ion batteries do not contain metallic lithium and are therefore not susceptible to the same volatile reaction that would occur with a LMB. In fact, using copious amounts of water is one of the most effective and accessible means for controlling and fighting a LIB fire, today.

UNTANGLING THE LITHIUM ION WEB

There are further chemistry distinctions that can be made within the term “lithium ion battery,” as suggested in Figure 2 “Lithium ion” refers to a diverse family of battery chemistries, some of which even have sub-varieties. The common feature of all commercially prevalent LIBs is the use of an organic electrolyte that serves as an ionic conduit to shuttle lithium ions back and forth between the cathode and anode.

Lithium ion battery chemistries are generally identified by their cathode materials and composition as the conventional anode material in commercial LIBs is graphite. Some examples of common lithium ion chemistries include:

- **Lithium Cobalt Oxide (LCO):** Predominantly used in consumer electronics; rare in modern automotive and stationary applications, LCO batteries have a lithium cobalt oxide cathode. LCO batteries have very high energy-to-weight ratio (also called the ¬specific energy) but are relatively expensive due to their reliance on costly critical raw materials (CRMs), like cobalt.
- **Lithium Nickel Manganese Cobalt Oxide (NMC):** This chemistry is commonly used in electric vehicles and some stationary applications, having a blend of nickel, manganese, and cobalt in the cathode. NMC batteries

come in several different subtypes depending on the proportions of the three metals; commonly: NMC111—a 1:1:1 ratio between the elements — NMC532, NMC622, and NMC 811. Over the last decade, efforts have been made to reduce the cobalt proportion as much as possible to reduce cost. Because sensitive CRMs like cobalt have been substituted with lower cost elements like nickel and manganese, NMC batteries are somewhat less expensive than LCO, but retain a specific energy favorable for mobile applications.

- **Lithium Iron Phosphate (LFP):** LFP batteries have a lithium iron phosphate cathode. While LFP batteries have a significantly lower specific energy compared to LCO or NMC, they may be less expensive due to the elimination of geopolitically sensitive cobalt from the chemistry. LFP is often used in stationary applications less constrained by size and weight, although LFP has recently made inroads into the electric vehicle market because of its cost competitiveness and reliance on fewer CRMs.
- **Lithium Nickel Cobalt Aluminum Oxide (NCA):** Another blended type like NMC using aluminum in the cathode instead of manganese, NCA has been favored by a few companies for their electric vehicle applications and has also been used in a few stationary applications. NCA has a similar specific energy to NMC, although concerns have been raised about the safety characteristics of NCA batteries due to their high thermal conductivity and heat rate.

The above is a non-exhaustive list; there are other, less common battery chemistries used in pilot projects and niche applications, but nickel-based chemistries, including NMC and NCA, and iron phosphate-based chemistries, including LFP and emerging LMFP, represent the vast majority of deployed stationary battery technologies at present, as seen in Figure 3. In the coming years, it is expected that the market complexion will begin to shift in favor of iron phosphate chemistries in response to cost and material pressures.

SAFETY (i.e., THERMAL RUNAWAY)

Thermal runaway is a phenomenon not unique to lithium ion batteries. Thermal runaway is a known risk in chemical processing, oil refinery, semiconductors, capacitors, transistors, and other electronic components. Generically, thermal runaway describes the process in which heat generation exceeds heat dissipation, thus leading to a rapid and often destructive increase in temperature.

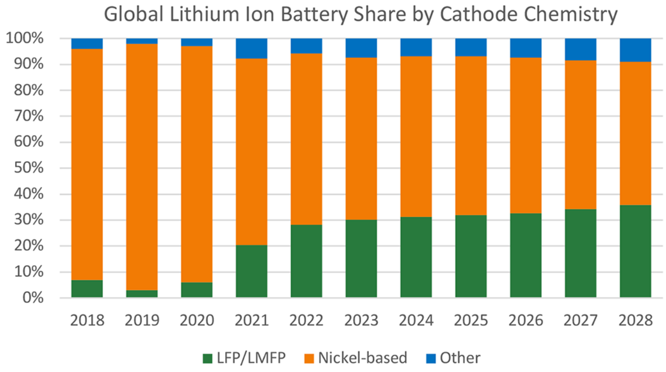

Figure 3. *Global Lithium Ion Battery Share by Cathode Chemistry (Data Sources: IEA,[2] Wood Mackenzie,[3] S&P Global[4])*

Thermal runaway is a potential risk in all battery technologies but is particularly hazardous in lithium ion batteries because of the rapid onset of high temperatures and production of flammable gases, which creates an environment susceptible to fire and explosion hazards. Oxidation reactions (battery discharge) are generally exothermic, meaning the reaction releases heat. The amount of heat released varies with cell age and operation, such as depth-of-discharge.[5] The charging reaction contribution to cell temperature is more complex – the cell can behave endothermically, meaning it absorbs heat, or exothermically depending on cell age, charge rate, and charging procedure (i.e. constant current or constant voltage).[6, 7] Under normal operating conditions, any excess heat resulting from both charging and discharging operation is adequately released to the environment. Under abnormal conditions, the excess heat is unable to escape and instead initiates subsequent exothermic reactions. This positive feedback loop of heating and reacting results in a rapid and potentially dangerous increase in temperature that could result in combustion un-

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[2] IEA, Electric LDV battery capacity by chemistry, 2018-2022, IEA, Paris https://www.iea.org/data-and-statistics/charts/electric-ldv-battery-capacity-by-chemistry-2018-2022, IEA. License: CC BY 4.0

[3] "Global lithium-ion battery supply and demand update H1 2023," Wood Mackenzie. July 2023

[4] Eri Silva & Avery Chen. Batteries: Emerging chemistries create trade-offs in cost, performance. S&P Global Market Intelligence https://www.spglobal.com/marketintelligence/en/news-insights/latest-news-headlines/batteries-emerging-chemistries-create-trade-offs-in-cost-performance-75866899 (2023).

[5] Doris L. Britton, Thomas B. Miller, & William R. Bennett. Thermal Characterization Study of Lithium-Ion Cells. (2007).

[6] Choi, Y., Ryu, S., Park, K. & Kim, H. Machine Learning-Based Lithium-Ion Battery Capacity Estimation Exploiting Multi-Channel Charging Profiles. IEEE Access 7, 75143–75152 (2019).

[7] Zhang, C. et al. Polarization Based Charging Time and Temperature Rise Optimization for Lithium-ion Batteries. Energy Procedia 88, 675–681 (2016).

der certain conditions. For more information on lithium ion thermal runaway, refer to EPRI's white paper[8] on this topic.

There are multiple potential root causes for lithium ion battery thermal runaway, including poor electrical or thermal control during operation, physical damage to the batteries by an external force, loss of electrical isolation, and occasionally, a latent manufacturing defect. The root cause stimulates excessive heating that causes evaporation of the liquid organic electrolyte. The subsequent increase in pressure can cause the cell wall, or enclosure, to rupture and release the hot gas into the environment where it may react violently with atmospheric oxygen to generate an intense flame. This flame can cause a rise in temperature of adjacent battery cells, potentially igniting other combustible components or propagating thermal runaway across a module or system.[8]

It is often reported that LFP batteries are safer than other lithium ion chemistries because the lower voltage and energy-to-weight ratio (Figure 4) makes it somewhat less likely that a LFP cell will achieve temperatures required for the cell to rupture. This does not mean, however, that the risk of thermal runaway for LFP is zero: all LIB cells have the potential to undergo thermal runaway, subsequently resulting in fire or explosion. EPRI's BESS Failure Database has recorded multiple fire incidents in systems that have installed LFP batteries.[9]

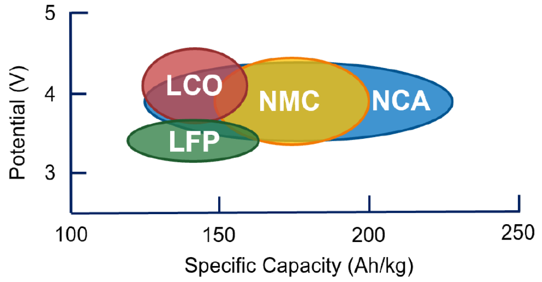

Figure 4. *Potential vs. specific capacity of common cathode chemistries*

Comparing the thermophysical properties of the different lithium ion cathode chemistries helps to explain why LFP is considered "safer." Table 2 compares the thermophysical properties of various lithium ion cathode chemistries, graphite and lithium metal anode materials, a typical liquid electrolyte formulation based on lithium hexafluorophosphate salt (LiPF6), a mix of organic solvent (Ethyl Carbonate (EC)+Dimethyl Carbonate (DMC)+Ethyl Methyl Carbonate (EMCw)), and water. Specific heat and thermal conductivity are material properties that indicate how quickly a material can heat up and how well it can transfer heat away. This is important for understanding how thermal runaway behavior differs across various LIB chemistries.

Lithium iron phosphate has the highest specific heat value of the listed cathode materials. Thus, it takes nearly twice as much energy to heat 1 kg of LFP material when compared to LCO, NMC, or NCA. In practice, this translates to a very flat heating rate profile of LFP cells in thermal runaway, seen in Figure 5. Again, this does not suggest that LFP batteries cannot go into thermal runaway, but rather LCO, NMC, and NCA are energetically less stable and require less heat to initiate and sustain a thermal runaway condition.

Table 2. *Thermophysical properties of lithium ion cathode, anode, and electrolyte materials compared to water*[10]

PARAMETER	LCO	NMC	NCA	LFP	*Graphite (Anode)*	*Lithiu (Anode)*	*Electrolyte*	*Water*
Density (kg·m^{-3})	2500	2380	4581	3600	2660	530	1290	998
Specific Heat (J·kg^{-1}·K^{-1})	700	710	651	1369	1437.4	3582	133.9	4184
Thermal Conductivity (W·m^{-1}·K^{-1})	1.48	1.50	6.10	1.58	1.04	85	0.45	0.6

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[8] *Difference Between Thermal Runaway and Fire Ignition of a Lithium Ion Battery.* EPRI, Palo Alto, CA: 2022. 3002025283.

[9] EPRI BESS Failure Database. https://storagewiki.epri.com/index.php/BESS_Failure_Event_Database.

[10] P Peng, Peng & Jiang, Fangming. (2016). Thermal safety of lithium-ion batteries with various cathode materials: A numerical study. *International Journal of Heat and Mass Transfer.* 103. 1008–1016. 10.1016/j.ijheatmasstransfer.2016.07.088.

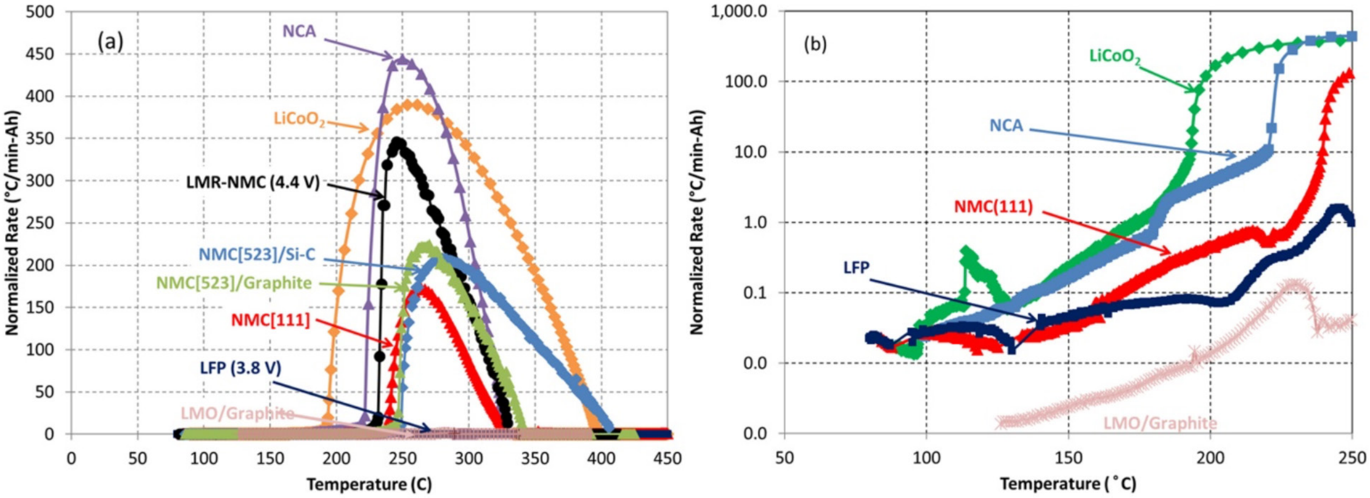

__Figure 5.__ Accelerating rate calorimetry data showing comparisons of several common chemistries (a) and a logarithmic plot of select data showing low rate (licensed under CC BY 4.0)

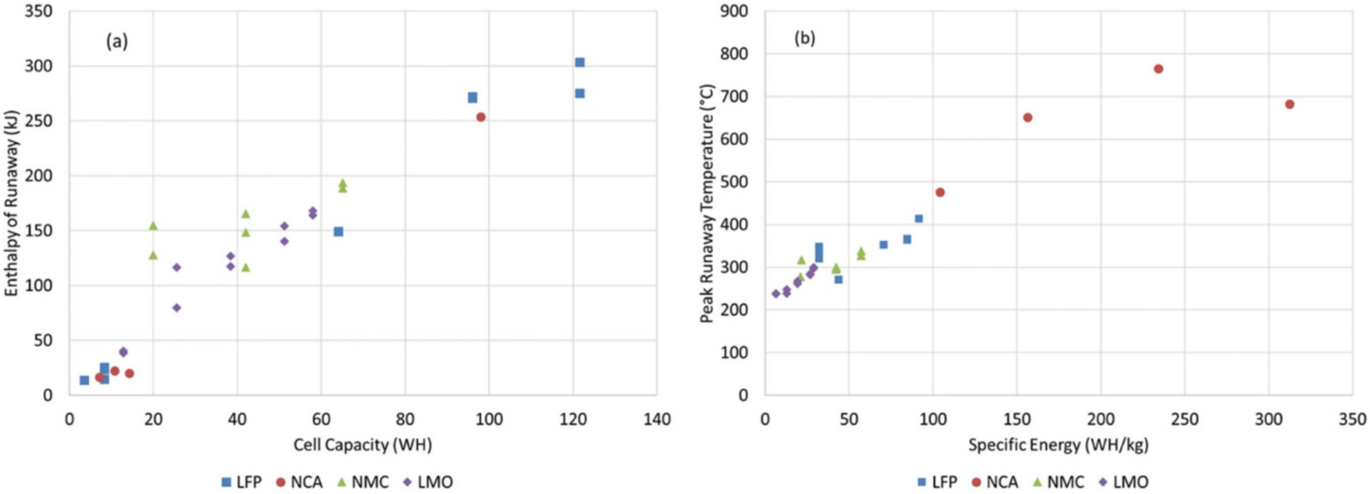

__Figure 6.__ Runaway enthalpy as a function of as-charged energy in Wh (a) and peak thermal runaway temperatures as a function of the cell specific energy (b)[11] *(licensed under CC BY 4.0)*

The amount of energy stored in the cell also plays a significant role in the magnitude of the potential hazard once thermal runaway has occurred. Enthalpy of thermal runaway is a measurement of total energy released during a thermal runaway event. As such, it is directly related to the total energy stored in the cell, as seen in Figure 6: Runaway enthalpy as a function of as-charged energy in Wh (a) and peak thermal runaway temperatures as a function of the cell specific energy (b)[11] (licensed under CC BY 4.0)a, regardless of cell chemistry. Peak temperature, however, appears to be correlated with cell chemistry, depicted in Figure 6b. Specific energy, used in Figure 6b, considers battery cell mass which is dependent on the active materials used in the electrodes. The greater thermal stability and lower peak temperatures during thermal runaway means that propagation from a failed cell to its neighbors may happen more slowly for LFP-based systems.

Cell chemistry will also impact the concentration of various gaseous species vented from the battery in thermal runaway, demonstrated in Figure 7. Carbon monoxide, methane, ethylene, ethane, and hydrogen are all flammable gases that evolve from LCO, NMC, and LFP batteries. The ratio of flammable to non-flammable gas concentrations tends to be lower in LFP batteries compared to LCO and NMC, suggesting a lower potential for fire and explosion hazards.

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[11] Joshua Lamb et al 2021 J. Electrochem. Soc. 168 060516.

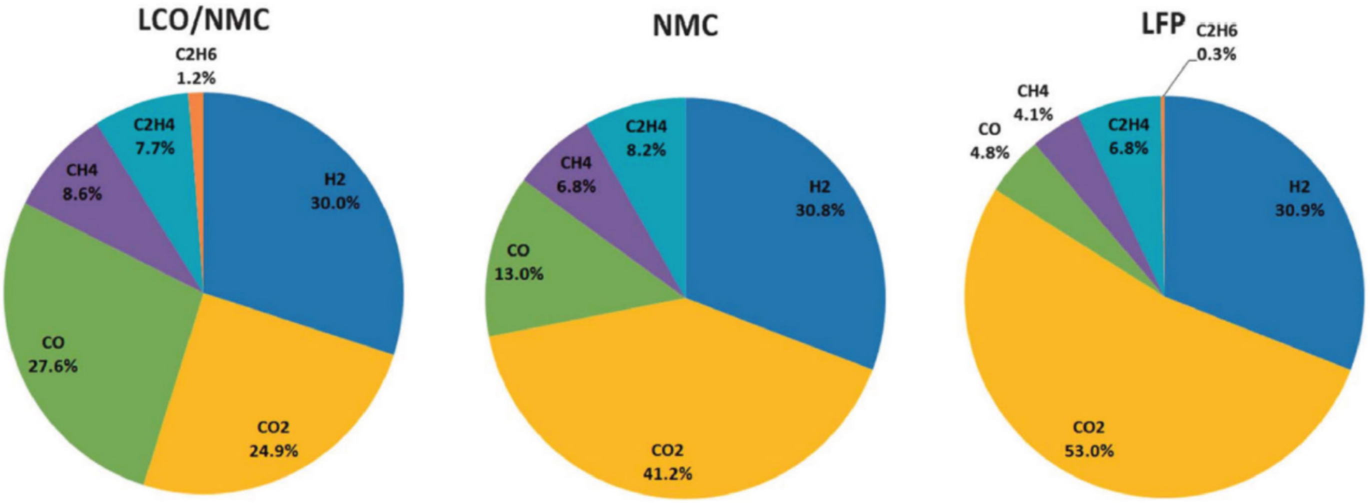

Figure 7. *Detected components of the gas produced during thermal runaway (mol%)*[2,12] *(licensed under CC BY 3.0)*

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12 A. Golubkov, D. Fuchs, J. Wagner, H. Wiltsche, C. Stangl, G. Fauler, G. Voitic, A. Thaler and V. Hacker, "Thermal-runaway experiments on consumer Li-ion batteries with metal-oxide and olivine-type cathodes," RSC Adv., vol. 4, pp. 3633–3642, 2014.

FIRE PREVENTION AND MITIGATION

Chemistry selection alone is insufficient to indicate safety levels in complex integrated systems. Cells made of all battery chemistries can be integrated into modules and packs poorly, with their inherent risk for thermal runaway remaining unmitigated. Such a situation leaves these systems and their surrounding communities vulnerable to large scale hazards. Instead, a holistic approach to safety, with comprehensive analyses of threats, consequences, and mitigation strategies to manage risk and impacts, should be practiced. System-level design choices can mitigate the risks of cell-level thermal runaway failures, and limit the likelihood and severity of propagation and potential subsequent large-scale fire and explosions.

The science around battery safety has advanced significantly in the last 5 years, as the industry has learned from past successes and failures, incorporating new technologies and techniques to address safety. For instance, some manufacturers have transitioned away from a walk-in, containerized battery systems toward modular cabinets to limit propagation of battery fires to smaller module numbers and curtail the explosion risk due to inability to build up gases in smaller enclosed spaces. The inclusion of emergency exhaust ventilation is also becoming standard practice. It is important to design systems with pre-engineered failure pathways that allow for an expected progression to completion. This facilitates safe event response to minimize risk to personnel and other equipment.

The industry's improved understanding of LIB safety has also manifested in development and implementation of codes, standards, and regulations (CSRs), which continue to be revised with lessons learned. Commonly adopted and practiced standards include UL 9540: Standard for Energy Storage Systems and Equipment and NFPA 855: Standard for the Installation of Stationary Energy Storage Systems. Standards like these have helped to educate and bring awareness to the industry on failure modes and their effects, allowing for better hazard mitigation through design and response strategies. For a more detailed discussion of ESS codes and standards, refer to EPRI's white paper on the topic.[13]

NFPA 855 references UL 9540A, which is not a standard, but rather a Test Method for Evaluating Thermal Runaway Fire Propagation in Battery Energy Storage Systems. UL 9540A is considered the industry standard for thermal runaway and propagation testing. The test report provides information related to the conditions under which thermal runaway was achieved, peri- and post-mortem observations, and vent gas composition and flammability characteristics. The results from this test can help to inform and improve the design of safety features built into the system to manage a thermal runaway event. It can also provide guidance for the method and equipment needed to appropriately respond to a fire or explosion hazard.

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13 *The Evolution of Battery Energy Storage Safety Codes and Standards.* EPRI, Palo Alto, CA: 2023. 3002028521.

Testing, in general, is needed to quantitatively evaluate and assess thermal runaway. Tests like UL 9540A are a step in the right direction, but it should be remembered that testing is not a panacea – UL 9540A testing is not pass/fail, and the mere statement that testing has been done does not indicate that a particular product line will not suffer from fire incidents, damage, or thermal runaway. A full hazard assessment is recommended for every site to understand all potential safety hazards and to develop a mitigation strategy to reduce the risk of fires and manage the outcomes should a fire occur. EPRI developed a public reference hazard mitigation analysis for lithium ion batteries.[14]

SUMMARY

LIB safety from the likelihood and consequences of thermal runaway is inherently linked to the chemistry of the materials used within the battery. The material properties of the cathode, anode, and electrolyte directly affect heat release rate, threshold temperatures for thermal runaway, off gas generation volume and constitution, and many other failure characteristics. Some battery chemistries may be more thermally stable than others, but the point remains that no chemistry is by its own means a "safe design." Understanding and incorporating material- or cell-level failure characteristics is an important step towards developing a safe battery energy storage system, but this does not capture or manage potential failures related to system design and integration. A broader, holistic approach to safety is needed to prevent or arrest the inherent thermal runaway risk present in all lithium-based batteries.

GLOSSARY

LIB	Lithium ion battery
LMB	Lithium metal battery
LMFP	Lithium manganese iron phosphate
LFP	Lithium iron phosphate
NMC	Nickel manganese cobalt oxide
NCA	Nickel cobalt aluminum oxide
LCO	Lithium cobalt oxide
LMO	Lithium manganese oxide
LTO	Lithium titanium oxide

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[14] *ESIC Energy Storage Reference Fire Hazard Mitigation Analysis.* EPRI, Palo Alto, CA: 2021. 3002023089.

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