

Literature Review: Packaging Technique to Defeat Fires and Explosions due to Lithium-ion and Related High-Energy-Density Batteries

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ABSTRACT

A literature review is made with respect to the fire and explosion hazard of lithium ion batteries. The history and operation of these batteries is discussed. Particular attention is given to the phenomenon of thermal runaway in the batteries. Its mechanisms are examined and its causes are discussed. A general discussion of the uses and accident nature associated with batteries is presented. This ranges from appliances to transportation occurrences. The means to measure the energy and gases given off due to thermal runaway and its ability to propagate through an array of batteries is described. Data on the energy and gases is presented for various batteries and states of charge. This information is critical for the design of safe packaging to mitigate the fire and explosion hazard of the batteries. Packaging techniques under development or available are described. Future work will examine the design and performance of packaging techniques.

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Introduction

The purpose of this review is to establish a research framework for the study of lithium-ion battery fire hazards, and to provide information on ways to mitigate such hazards in packaging for transportation. This review is not meant for general publication, so liberties are taken in citations and in using graphic and illustrative material from sources. This is done to facilitate the efficiency of relating information, and to recognize the very good contribution from a source.

The review will contain five sections:

1. General background on the hazards, nature of the batteries, and test and safety requirements.
2. A full description of thermal runaway and the subsequent combustion of the ejected battery gases, addressing mechanisms and modeling analyses.
3. A review of fire incidents related to batteries.
4. Techniques and data on runaway energy and potential combustion energy.
5. Exploration of techniques used to mitigate battery fire hazards in packaging.

This review should form a basis for understanding the fire hazard associated with lithium-ion batteries, display information of the energies released, and establish ways to prevent the propagation of these energies to neighboring batteries. The review will include information from the Internet, journal publications and reports, available presentations, and information from a recent FAA conference (Atlantic City, October 2019).

General Background

The nature and increasing use of Li-ion and other energetic batteries will be described. Some history in their development and in related accidents will be presented. The nature of the thermal runaway and combustion hazard will be described. Research in highlighting the hazards by the FAA, associated regulations for aircraft, and work being done to mitigate or assess safe battery transportation will be discussed.

Battery History

A lithium-ion is a type of rechargeable battery commonly used for portable electronics, electric vehicles and an increasing list of applications. The technology was developed during the 1970s–1980s, and then commercialized by a Sony in 1991.

Lithium ions move from the negative electrode, typically graphite, through usually a combustible liquid electrolyte to the positive electrode, an intercalated-lithium compound. A porous thin separator is between the two electrodes, and is saturated with the electrolyte. A lithium polymer battery is similar but contains a polymer gel instead of the liquid electrolyte. These batteries types are referred to as *secondary* batteries because of their charging ability. In contrast, lithium metal batteries are classed as *primary*, as they are currently not chargeable. They contain the metal lithium that is capable of exothermically reacting with water, as the lithium-ion batteries do not have that characteristic because the lithium is part of a metal oxide compound.

A recent publication of Underwriters Laboratories [1] presents a vivid history of the use and experience with lithium-ion batteries.

Figure 1 depicts the dramatic rise in the use of these batteries over 30 years after their introduction into the marketplace.

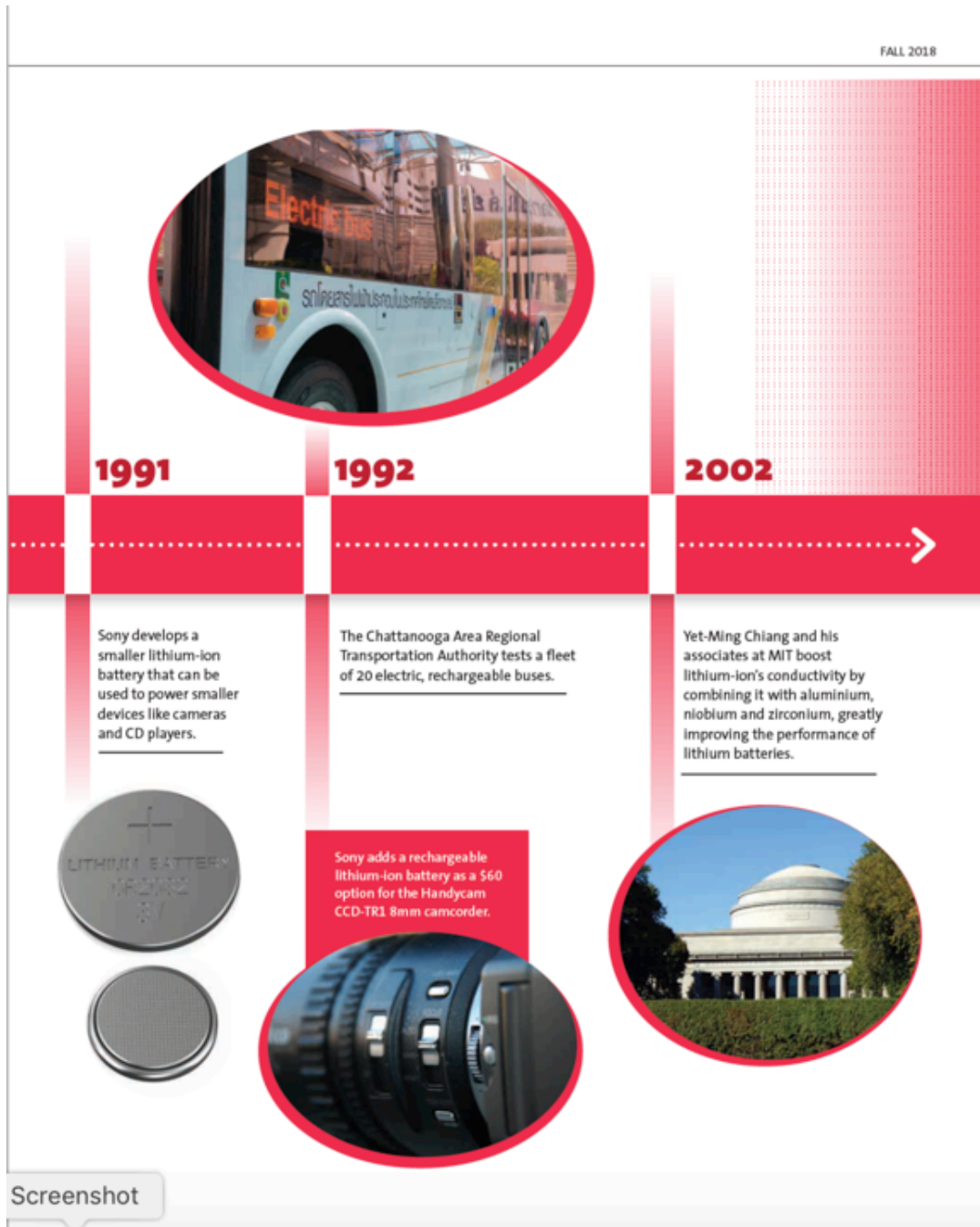


Figure 1a. Battery events 1991 to 2002

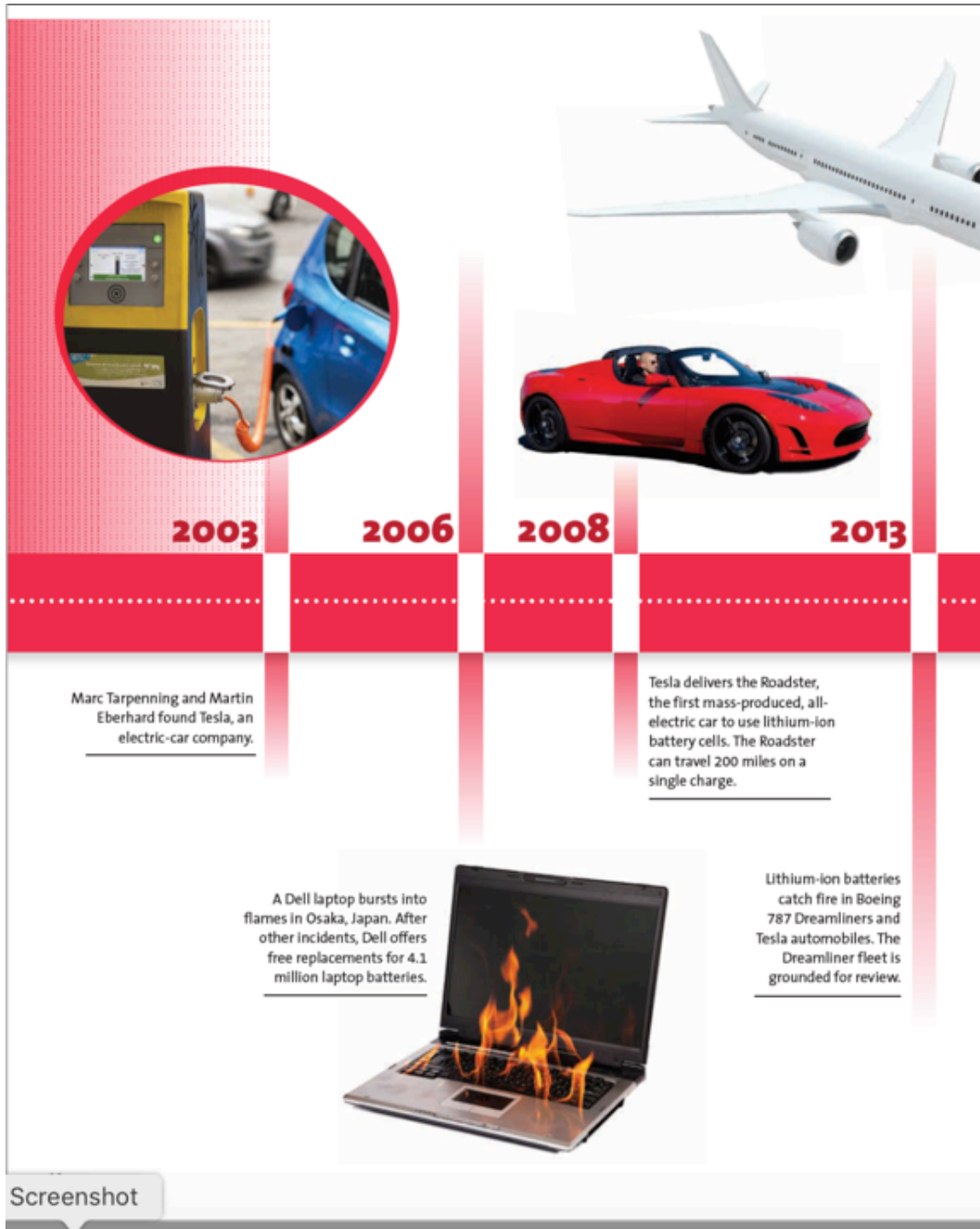


Figure 1b. Battery events 2003 to 2013



Figure 1c. Battery events 2015 to 2016

The uses include portable electronics, toys, e-cigarettes, almost all types of transportation vehicles and energy storage facilities. In addition to the growing market use, the nature of fire hazards is displayed through these applications. It is not uncommon to have fire hazards emerge after the introduction of new technologies or materials. These batteries are high density energetic sources, and by their nature they can release unwanted energy as well as useful energy. The stability of lithium-ion batteries is

key to their useful development. Insults by natural impacts and defects can set them in the wrong direction to cause harm.

Battery Operation

Lithium ion batteries typically have a voltage of the order of 4 V with a specific energy ranging between 100 Wh/kg and 150 Wh/kg. In its most common structure, a lithium ion battery contains a graphite anode (e.g. mesocarbon microbeads, MCMB), a cathode formed by a lithium metal oxide (LiMO_2 , e.g. LiCoO_2) and an electrolyte consisting of a solution of a lithium salt (e.g. LiPF_6) in a mixed organic solvent (e.g. ethylene carbonate–dimethyl carbonate, EC–DMC) imbedded in a separator. Figure 2 shows a typical lithium ion battery configuration [2].

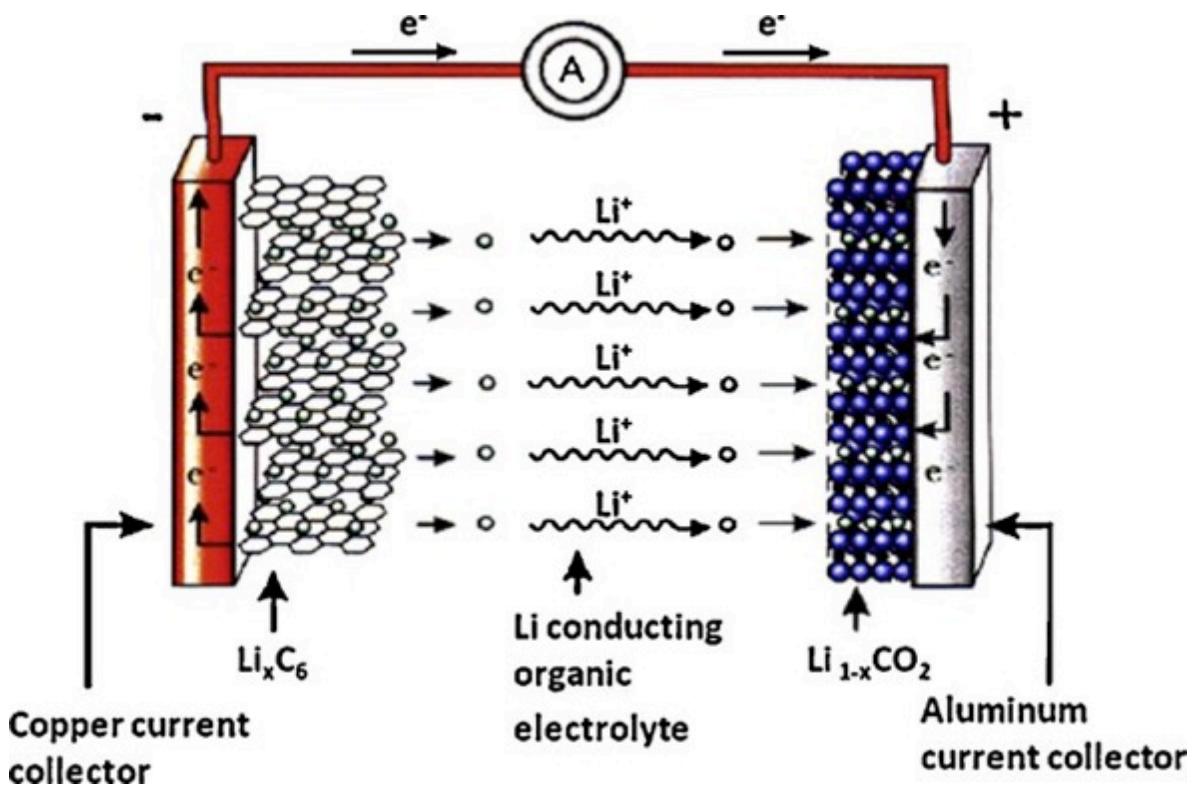


Figure 2. Lithium ion battery operation schematic

It is interesting to consider an array of battery types studied by Summer and Maloney in Table 1 [3].

Table 1. Array of Lithium-ion and polymer (or pouch) batteries [3]

Battery size	Li-Ion, Wh				Lithium Polymer, Wh				
	LiCo ₂	LiFePO ₄	LiMnNi	LiNiMnCO	LiFePO ₄	LiMnNi	LiNiMnCo	LiCoO ₂ (std rate discharge)	LiCoO ₂ (high Rate discharge)
10440 (AAA)	1.8								
14500 (AA)	2.88	1.92							
16340 (CR123A)	2.7	2.4							
18650	9.62								
25500 (C)		10.56	14.8	13.14					
32600 (D)		9.6							
9V								4.5	
2450 (button)	0.43								
10 Ah					32	37	37	37	37
4.5 Ah								16.65	
0.8 Ah								2.96	

Figures 3a and b show the range of battery types, capacities and physical sizes.



Figure 3a. Li-ion batteries in Table 1



Figure 3b. Li-polymer batteries in Table 1[3]

They range in full capacity from about 2 to 37 Wh. It has been suggested that the state of charge (SOC), or percentage of full charge, is a measure of the expected unwanted energy release when a lithium-ion battery malfunctions. The unwanted energy can manifest itself as combustion energy from vented battery gases due to decomposition of the cell, and exothermic decomposition chemical energy during failure. Failure is the occurrence of “thermal runaway” in which the battery destroys itself. More will be said later.

Figure 4 gives an example of the rate of combustion energy released in thermal runaway for a single popular battery type from several manufacturers as a function of the SOC [4].

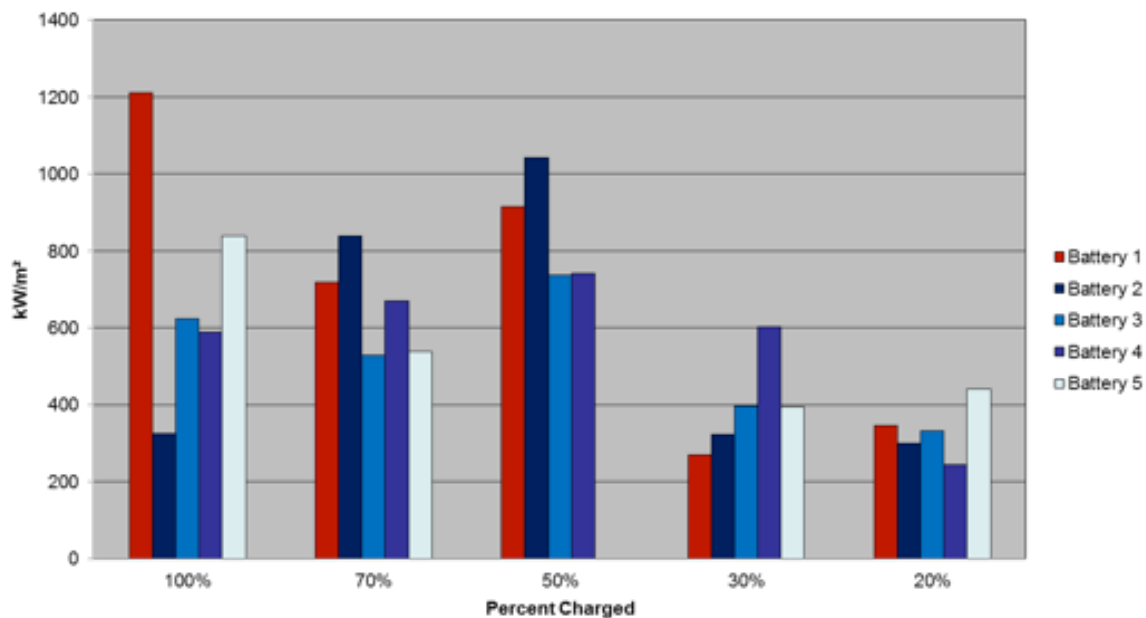


Figure 4. Peak heat release for LiCoO₂ 18650 cells at different SOC's [4]

It indicates that the energy released in combustion is generally reduced with the SOC. This is the basis of allowing the shipment of batteries on cargo planes with a required SOC of 30 %.

However, on examining the energy of decomposition in runaway among batteries of varying capacity it shows that that energy is more related to the actual battery capacity for a particular SOC.

This is shown in Figure 5.

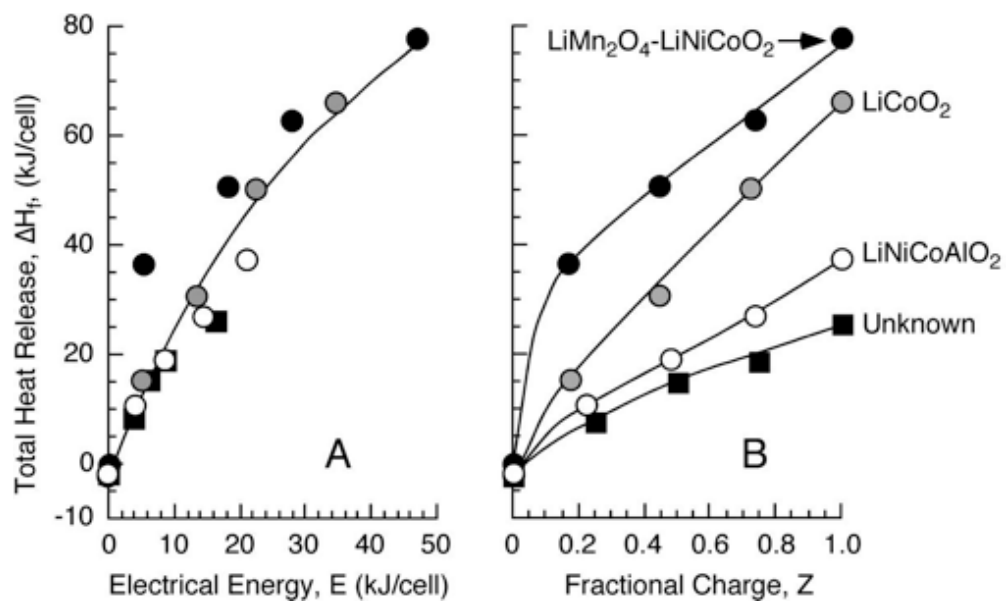


Figure 5. Total energy release in runaway versus: (A) electrical energy, E , and (B) fractional charge, SOC, for the different lithium-ion battery cathode chemistries

Realizing that batteries can have a considerable range in capacity (2 to 37 Wh or 7.2 to 133 kJ), it might be more appropriate to relate the hazard of runaway with battery capacity or the number of batteries in failure.

Thermal Runaway

The ultimate failure mode of a lithium-ion or similar high energetic batteries is so-called *thermal runaway*. This is a process where the battery becomes unstable and destroys itself due to temperature increases that continually trigger a variety of decomposition and other associated electrochemical reactions whose rates of energy release increase with temperature. The feedback loop of temperature with increasing reaction rate is similar to spontaneous ignition in combustion, but here the batteries do not need oxygen. As the battery degenerates, its gaseous products pressurize the cell and can be released by a designed safety vent or by catastrophic case failure. Due the combustible electrolyte and other combustible battery components (graphite and polyethylene or polypropylene separators) particles or fuel gases can be ejected into air that may burn if ignited. This complex process has many chemical components yet can be mathematically modeled to assess the runaway hazard or to assure the battery stability in design. The failure of battery stability is not a surprise to battery manufacturers.

Figure 6 shows the relative size and weight advantage of lithium-ion batteries in terms of their mass and volume energy densities [5].

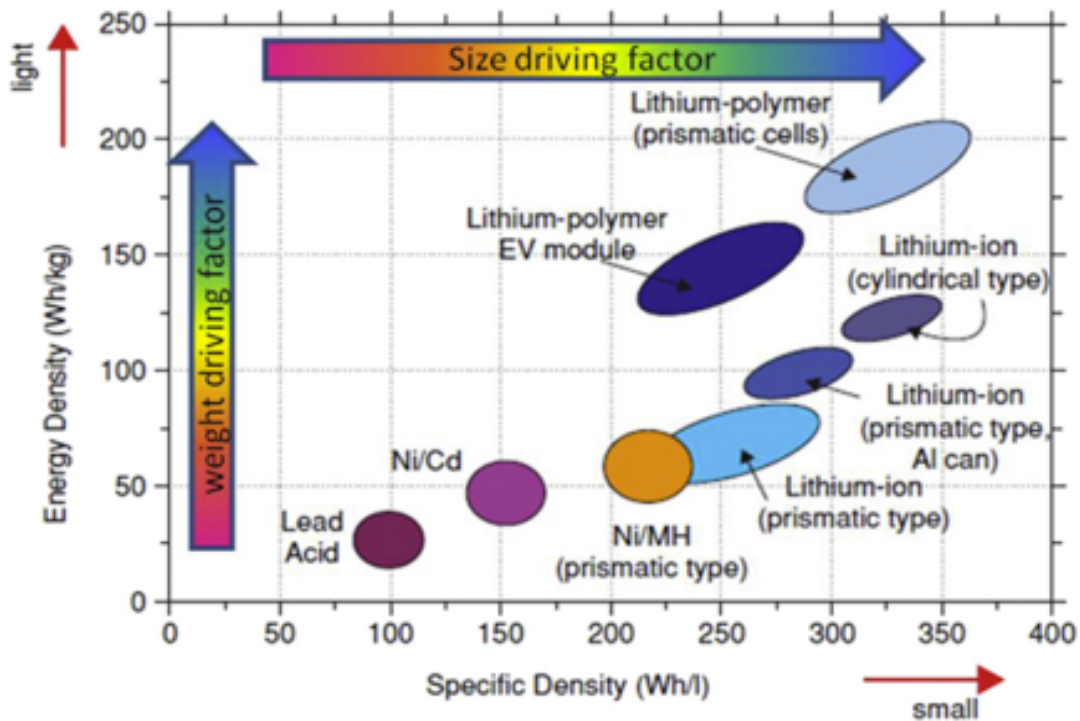


Figure 6. Capacity of batteries per mass and volume [5]

If total energy in runaway is a function of battery capacity, the risk of battery failure can only grow unless there are inherent design changes in the future. Thermal runaway is primarily attributed to an internal short circuit (ISC) between the anode and cathode.

Figure 7 illustrates the various causes of an ISC [6].

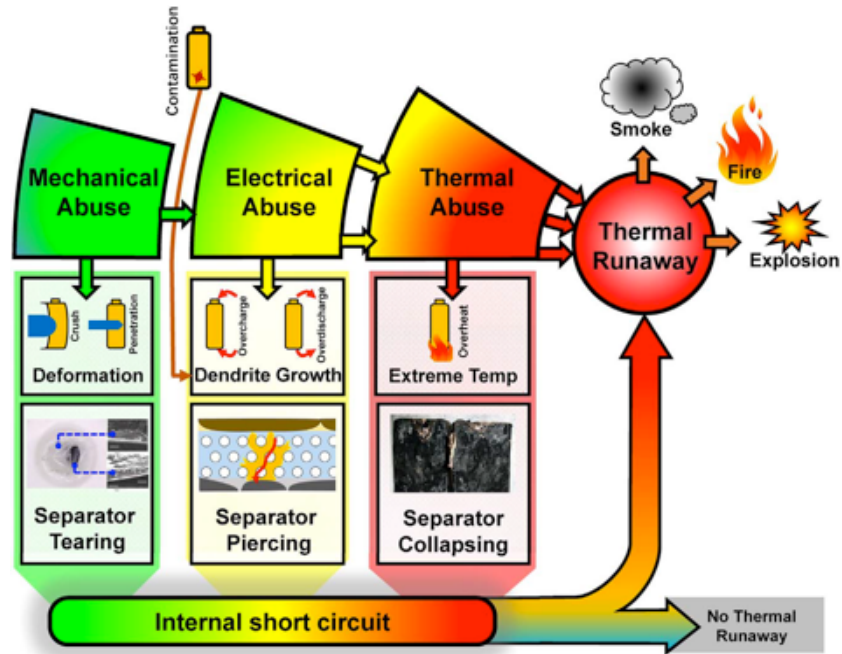


Figure 7. Internal short circuit: the most common cause of thermal runaway [6]

Once the ISC is triggered, the electrochemical energy stored in the materials releases rapidly into heat generation. As shown in Figure 7, the failure mechanism of the separator is necessary for the ISC. The separator moderates ion passage and may actually serve to terminate current flow and stop the short. For mild attacks, the separator, especially if it is two materials, will melt one of the materials and fill the pores of the other material to prevent ion flow. But strong insults to the separator by various mechanisms can lead to total failure. These mechanisms include:

1. Mechanical abuse, e.g., the deformation and fracture of the separator caused by nail penetration or crush;
2. Electrical abuse, e.g., the separator can be pierced by dendrite, the growth of which can be induced by overcharge or over-discharge, and by an impurity in manufacture.

Thermal abuse, e.g., the complete melting of the separator due to thermal instability or due to an external heat source. All of these mechanisms would lead to temperature increases as an internal high current is discharged through the internal resistance. In addition, oxygen can be generated by the decomposition of the Li-oxide and the SEI effect, and consequently can lead to some internal combustion. The SEI, or solid electrolyte interphase, is a layer formed instantaneously on electrode surfaces from decomposition products of the electrolyte. It is essential for battery operation and corrosion prevention.

Table 2 illustrates the possible chemical reactions that can take place as temperatures rise within a battery.

Table 2. Chemical reaction within a Li-ion battery in runaway [7]

Reactions	Possible chemical equations	Temperature range (°C)
SEI decomposition	$(\text{CH}_2\text{OCO}_2\text{Li})_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + \frac{1}{2} \text{O}_2$	90–120
Negative electrode/electrolyte	$2\text{Li} + \text{C}_3\text{H}_4\text{O}_3 \text{ (EC)} \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4$ $2\text{Li} + \text{C}_4\text{H}_6\text{O}_3 \text{ (PC)} \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_3\text{H}_6$ $2\text{Li} + \text{C}_3\text{H}_6\text{O}_3 \text{ (DMC)} \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_6$	> 100
Separator meltdown		Around 130
Positive electrode decomposition	$\text{Li}_x\text{CoO}_2 \rightarrow x\text{LiCoO}_2 + \frac{1}{2} (1-x)\text{Co}_3\text{O}_4 + \frac{1}{2} (1-x)\text{O}_2$ $\text{Co}_3\text{O}_4 \rightarrow 3\text{CoO} + 0.5\text{O}_2$ $\text{CoO} \rightarrow \text{Co} + 0.5\text{O}_2$	196–230
Solvent/O ₂	$2.5\text{O}_2 + \text{C}_3\text{H}_4\text{O}_3 \text{ (EC)} \rightarrow 3\text{CO}_2 + 2\text{H}_2\text{O}$ $4\text{O}_2 + \text{C}_4\text{H}_6\text{O}_3 \text{ (PC)} \rightarrow 4\text{CO}_2 + 3\text{H}_2\text{O}$ $3\text{O}_2 + \text{C}_3\text{H}_6\text{O}_3 \text{ (DMC)} \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}$	
Electrolyte decomposition	$\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5$ $\text{C}_2\text{H}_5\text{OCOOC}_2\text{H}_5 + \text{PF}_5 \rightarrow \text{C}_2\text{H}_5\text{OCOOPF}_4 + \text{HF} + \text{C}_2\text{H}_4$ $\text{C}_2\text{H}_4 + \text{HF} \rightarrow \text{C}_2\text{H}_5\text{F}$ $\text{C}_2\text{H}_5\text{OCOOPF}_4 \rightarrow \text{PF}_3\text{O} + \text{CO}_2 + \text{C}_2\text{H}_4 + \text{HF}$	200–300
Positive electrode/electrolyte	$2\text{Li} + 2\text{EC} \rightarrow \text{Li-O-(CH}_2)_4\text{-O-Li} + 2\text{CO}_2$ $\text{Li-O-(CH}_2)_4\text{-O-Li} + \text{PF}_5 \rightarrow \text{Li-O-(CH}_2)_4\text{-F} + 2\text{LiF} + \text{POF}_3$	200–240
Negative electrode/binder	$-\text{CH}_2-\text{CF}_2 + \text{Li} \rightarrow \text{LiF} + -\text{CH}=\text{CF}- + 0.5\text{H}_2$	> 260

It also shows the complexities of the chemical reactions that occur. Most produce energy as they occur, and thus feedback to the rise in temperature followed by more energy release. The feedback loop is thermal runaway, and will lead to the rapid production of energy, high battery temperature due to thermal energy storage, and the venting of gaseous decomposition products.

Figure 8 gives a clear illustration of the interaction of exothermic battery energy release and temperature rise.

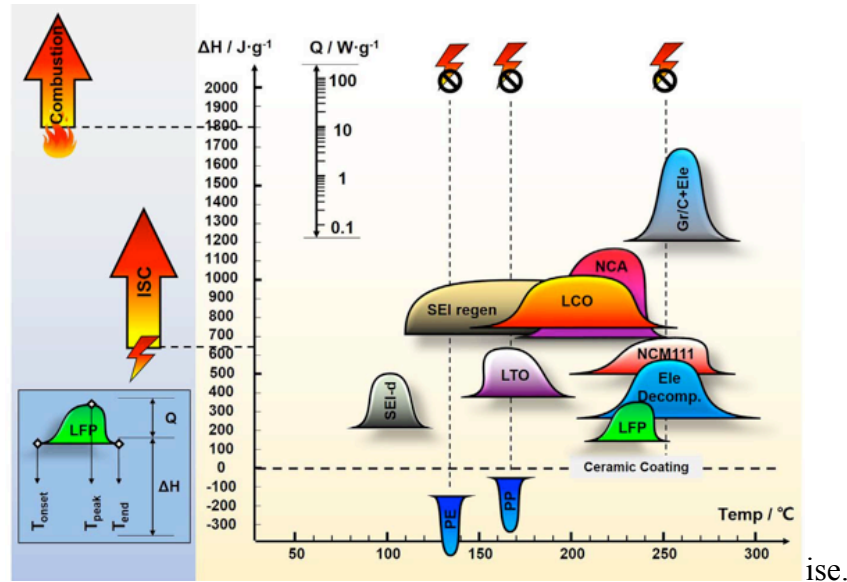


Figure 8. Reaction decomposition and melting energies for battery components [6]

Each of the processes that can occur in runaway are depicted in terms of the required energies released per unit mass and the temperatures where they can occur. The separators (polypropylene or polyethylene) require energy to melt at about 150 °C. The decomposition of the SEI occurs first at about 100 °C, and could produce oxygen for combustion of the electrolyte. The various other electrode and electrolyte reaction are depicted.

- LTO: $\text{LiTi}_5\text{O}_{12}$ anode with electrolyte
- LCO: LiCoO_2 cathode with electrolyte
- NCA: LiNiCoAlO_2 cathode with electrolyte
- LFP: LiFePO_4 cathode with electrolyte
- NCM: LiNiCoMnO_2 cathode with electrolyte
- Ele. Decom.: Electrolyte decomposition into H_2 , CO , CO_2 and hydrocarbons
- Gr/C + Elect.: Graphite/carbon anode with electrolyte

Each relates to a different battery chemistry, and it should be clear that the energy in runaway is tied to the particular battery chemistry, its state of charge or perhaps more important its overall electrical capacity. Moreover, it should be clear that these reactions are subject to the physical as well as chemical processes undergone in the instability of runaway.

More graphically, Figure 9 illustrates the processes of runaway in time.

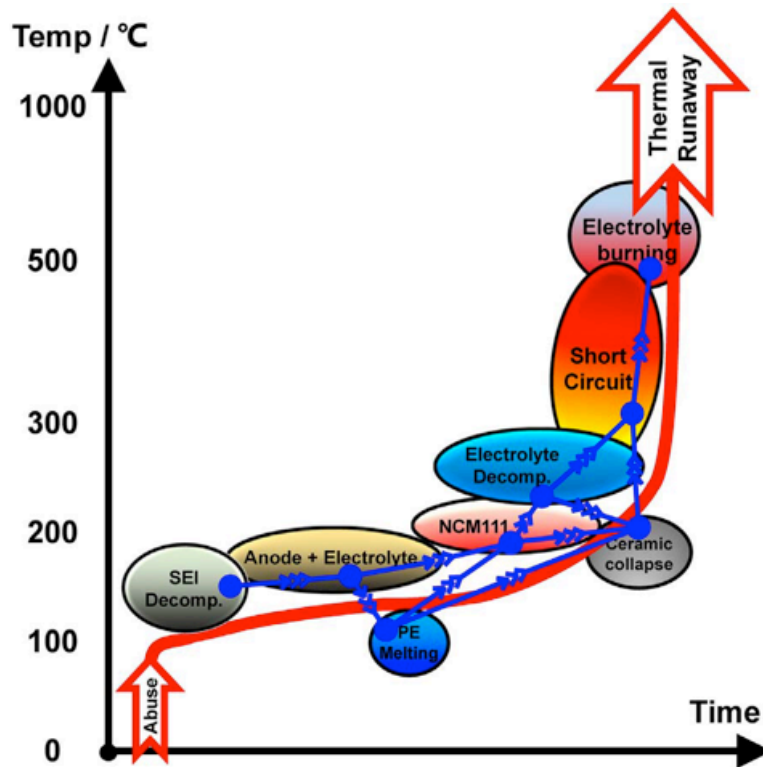


Figure 9. The processes in thermal runaway and the rise of battery temperature in time [6]

The end state temperature can be as high as shown, and the time duration can be in the range of 1 to 100 s, depending on the capacity.

Tests at the FAA with a single cell driven into thermal runaway by a strapped cartridge heater resulted in a range of cell temperatures after runaway [3]. Their results tend to show a dependency of temperature with battery chemistry over capacity.

LiCoO₂ and LiNiCoMnO₂ produced higher temperatures than LiFePO₄ cathode batteries as shown in Figures 10a and b.

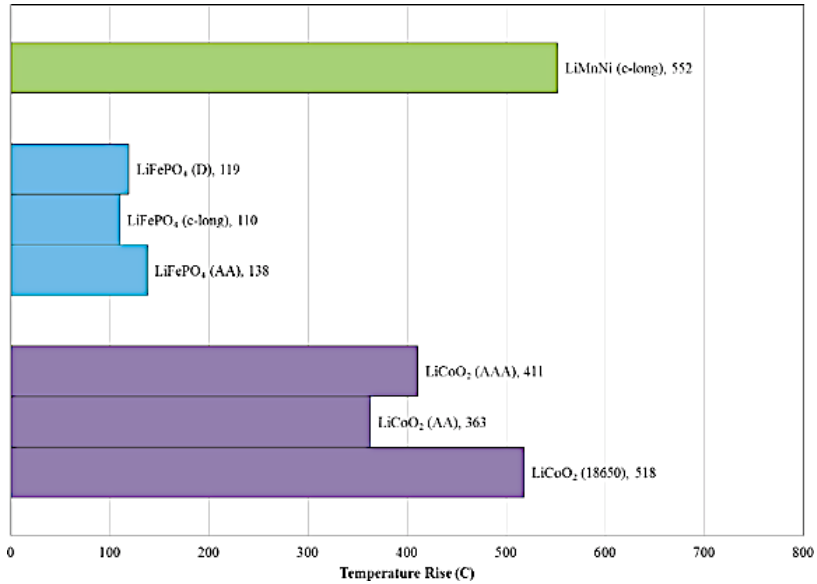


Figure 10a. Temperature rise occurring from thermal runaway of Li-ion cells [3]

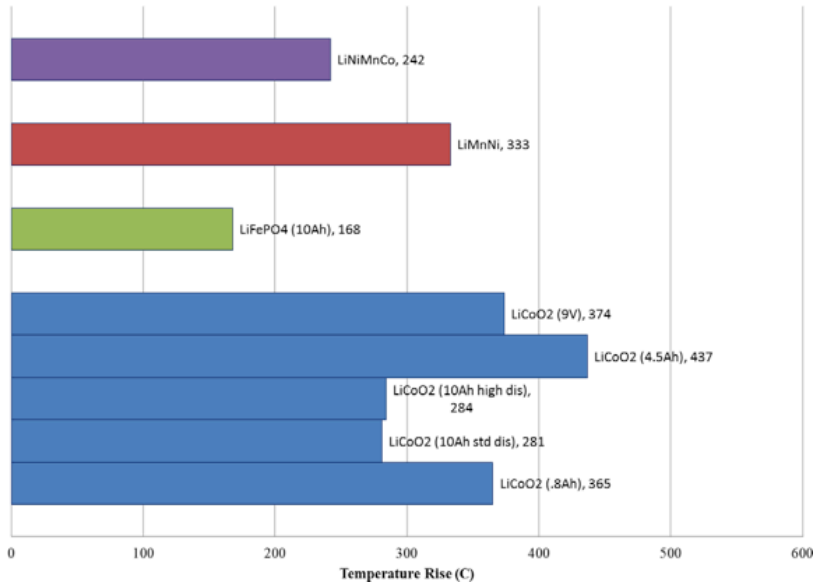


Figure 10b. Temperature rise occurring from thermal runaway of Li-ion-pouch cells [3]

Temperature is the result of the battery energy release, and depends on its ability to cool into its environment. Of course, temperature represents the ignition hazard to adjacent materials.

Gases Released in Runaway

There are two hazards associated with battery runaway. The first is the rapid release of the decomposing battery energy into thermal energy that can raise its temperature and contribute to the runaway of adjacent batteries by heat transfer. The second is the associated expulsion of its contents as hot gases and particles. It would not be uncommon to see molten aluminum and carbon particles. Figure 11 shows the ejection of flame and hot particles from a LiCoO₂ battery provoked into runaway by heat and puncture.



Figure 11. Li-ion battery in runaway due to a. heating in a canister, and b. abused by a sudden puncture of the battery in causing auto-ignition of the gases.

Both flame and particle streaks are shown. The flame may not always arise, as it will depend on an ignition source. The inherent ignition source is the hot surface temperature of the battery in causing auto-ignition of the gases. In the event there is no immediate ignition, there is the possibility of a delayed ignition. The accumulation of combustible gases in a closed container presents a serious hazard if an ignition source is later found. Table 3 gives an example of batteries gases released in runaway for NCA: LiNiCoAlO₂ and LFP: LiFePO₄ type batteries [8].

Table 3. Molar percentage of the battery gases at different SOCs [8]

No.	Cell	SOC (%)	H ₂ (%)	CO ₂ (%)	CO (%)	CH ₄ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)	Fast thermal runaway*
1	NCA	0	1.7	94.6	1.6	1.6	0.3	0	No
2	NCA	25	15.5	62.7	5.5	8.7	7.5	0	Yes
3	NCA	50	17.5	33.8	39.9	5.2	3.2	0.4	Yes
4	NCA	75	24.2	20.8	43.7	7.5	3.3	0.5	Yes
5	NCA	100	22.6	19.7	48.9	6.6	2.4	0	Yes
6	NCA	112	25.1	18.8	48.1	5.9	2.1	0	Yes
7	NCA	120	23.5	20.8	48.7	5.4	1.6	0	Yes
8	NCA	127	28.8	16.2	46.6	6.4	1.3	0.3	Yes
9	NCA	132	25.8	18.9	49.2	4.7	1.4	0	Yes
10	NCA	143	26.2	22	43.3	6.9	1.5	0	Yes
11	LFP	0	2.7	93.5	1.8	0.7	0.7	0.7	No
12	LFP	25	7.1	85.3	3.1	1.2	3.1	0.2	No
13	LFP	50	20.8	66.2	4.8	1.6	6.6	0	No
14	LFP	75	21.8	62.6	6.4	1.9	6.3	1	Yes
15	LFP	100	29.4	48.3	9.1	5.4	7.2	0.5	Yes
16	LFP	115	34	52.2	6.4	2.6	4.7	0.1	Yes
17	LFP	130	30.1	55.8	7.7	6.4	0	0	Yes

* judging by the cell surface temperature rise rate exceeds 1 °C/s.

The explosion hazard from batteries in a cargo assembly was dramatically demonstrated in a test of 5000 18650 LiCoO₂ cells within a Fire Resistant Container (FRC in Figure 12) along with a Class A fire load [4].

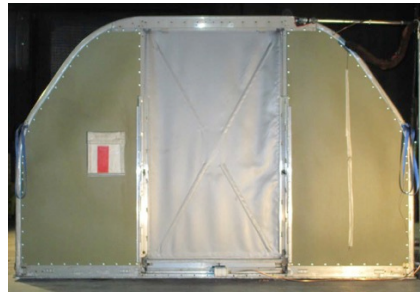


Figure 12. An FRC [4]

The Class A fire load consists of 18"x18"x18" cardboard boxes that are each filled with 2.5 lb of shredded paper. The Class A boxes along with the boxed batteries filled the FRC. A single battery in thermal runaway was simulated, resulting in thermal runaway propagating throughout the shipment. Figure 13 depicts the concentration of gases in the FRC after the fire is initiated at about 25 minutes.

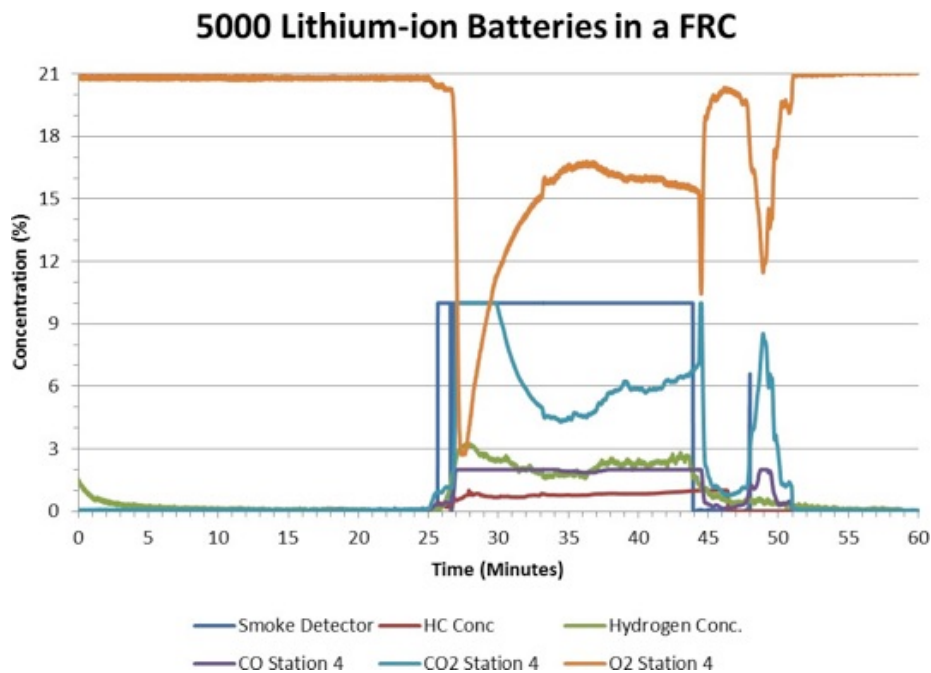


Figure 13. Gas analysis of 5000 lithium-ion 18650 LiCoO₂ cells in a FRC test [4]

The smoke detector is activated and sets off the release of a fire-extinguishing aerosol being tested as a suppressing agent. The sudden release displaces the oxygen in the FRC through normal leakage channels. As the pressure increase decays, the heat of the fire draws in new air with a slow increase in oxygen concentration. The oxygen and carbon dioxide are mirror images of each other reflecting combustion. However, from

the start of the fire in the batteries there is a production of hydrogen, CO and HC. Of course any pyrolysis of the cardboard would also produce these same gases. At about 45 minutes there is a sudden drop in oxygen indicative of rapid combustion. This is not from flame spreading over the boxes, but by a mixture of the gases in oxygen within their flammable limits that finds a flame ignition source. This could possibly come as the descending hot layer of flammable gases meets air below and the tips of flames. In any case, a flammable mixture ignited and pressurized the FRC into an explosion – a sudden pressure rise. Walls of the container blew out, spilling cargo into the surroundings, and the container and its contents burned out. Yet, only a small number of lithium batteries were involved and contributed to the fire prior to the explosion. However, the prospect of batteries in runaway producing flammable gases in a cargo container gives rise to a serious potential for an explosion. The FAA and others are investigating the potential for battery gases creating a flammable mixture in a system to learn more about this hazard. But it is clear this gas buildup is associated with battery chemistry, capacity, and the combustible electrolyte. So changes in battery design can mitigate the flammable gas issue.

While CO and some hydrocarbons can present a toxic hazard the presence of other potential toxic gases has been investigated [9]. The electrolyte is typically a mixture of a Li-salt, organic solvents and a number of additives. The Li-salt is needed to enable the Li⁺ conductivity and the most used Li-salt is lithium hexafluorophosphate, LiPF₆. The fluorine in the LiPF₆ may give rise to toxic gas emissions and measurements were focused on detecting fluoride gas emissions, HF, POF₃ and PF₅. Two, HF and POF₃ emissions, were detected in the runaway gases of several batteries. Figure 14 shows the HF output from several batteries:

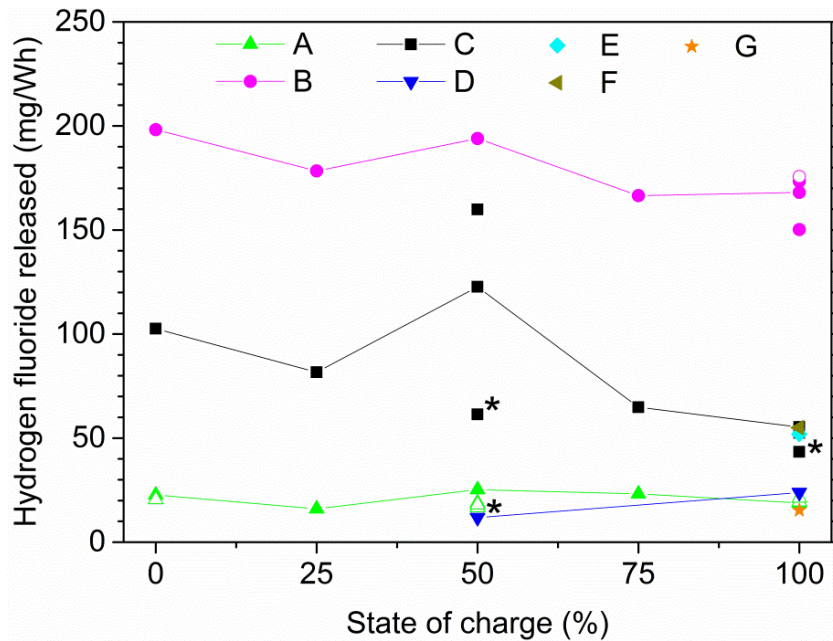


Figure 14. The total amount of HF measured by FTIR for seven types of Li-ion battery cells and for 0-100% SOC. [9]

- A. EiG ePLB-F007A, carbon/LFP, 7Ah, pouch
- B. K2 Energy LFP26650EV, carbon/LFP, 3.2 Ah, cylindrical
- C. Lenovo laptop battery pack (Sanyo 18650 cells, 2.8 Ah, cylindrical)
- D. Saft MP176065, graphite/LCO, 6.8 Ah, hard prismatic
- E. Lifetech X-1P 8Ah 38123, carbon/LFP, 8 Ah, pouch
- F. Ener1 SPB150140260, graphite/LFP, 20 Ah, pouch
- G. Leclanche LecCell 30Ah High Energy, LATP/NCO, 30 Ah, pouch

The seriousness of this toxic hazard potential does not appear to rise to the thermal fire hazards of the Li-ion batteries. However, HF is a corrosive gas and can play havoc with electrical components.

Hazards of Battery Thermal Runaway

It has been shown that battery thermal runaway can occur due to abuse of the battery by heat, physical damage, improper over or under-charging, and by inherent manufacturing defects, though rare. In runaway, each battery chemistry and capacity will release energy into heat that generally exceeds the battery capacity. In addition, gases can be released from liquid electrolytes as thermally decomposed combustion gases and possibly toxic fluorine compounds. Let us give a measure of these hazards manifested by runaway and the release of combustion gases.

Liu presents a vivid picture of the typical nature of energy in battery runaway [10].

Figure 15 displays the rate of energy released as the battery decomposes due to heating for a range of charge levels.

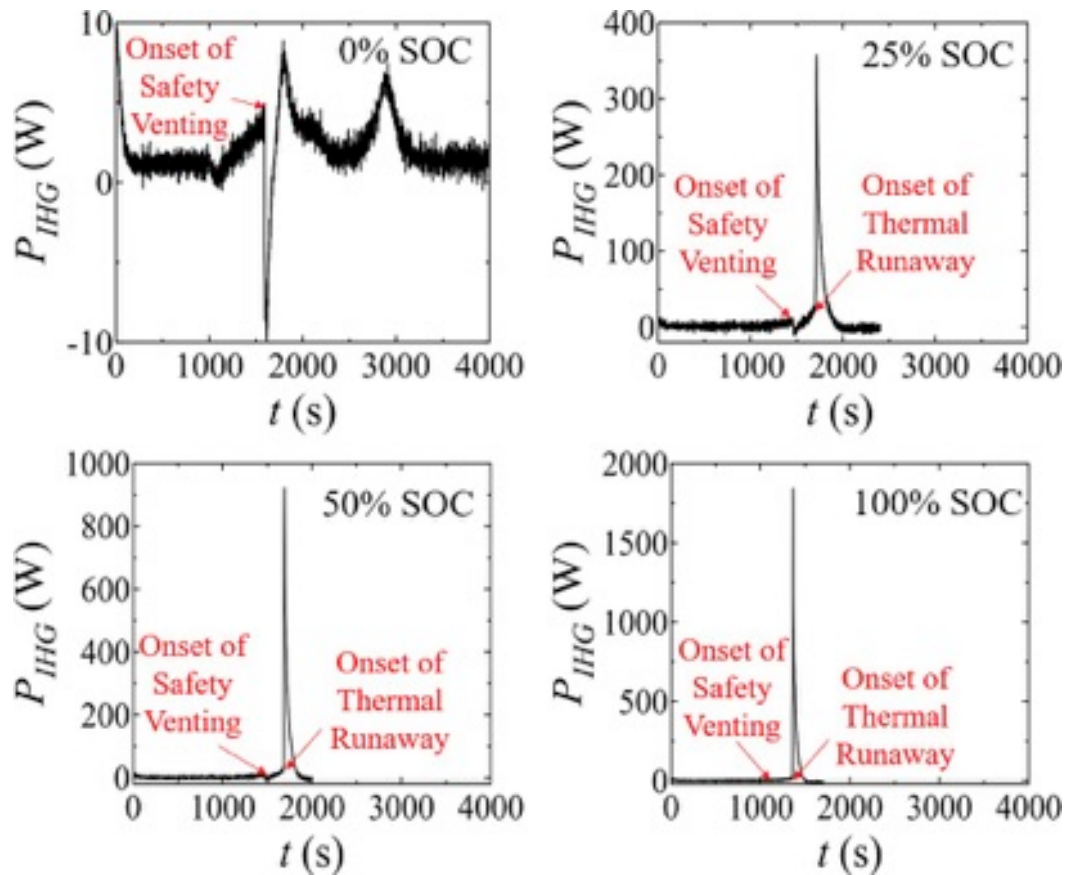


Figure 15. Internal heat generation by the decomposition of a LCO Li-ion battery [10]

The energy rate during the runaway decomposition is measured by a calorimeter. It is evident that the energy release rate increases strongly with SOC. The figures also show the time the battery safety vent opens due to increasing pressure as the decomposition processes begin. When the thermal instability is reached at the onset of thermal runaway there is a very rapid rise in energy release, immediately followed by its decay. The runaway event is relatively fast as the battery components quickly become exhausted. For full capacity, nearly 2 kW is released over less than 100 s.

The corresponding battery temperatures are shown in Figure 16, and show the nature of the rapid rise.

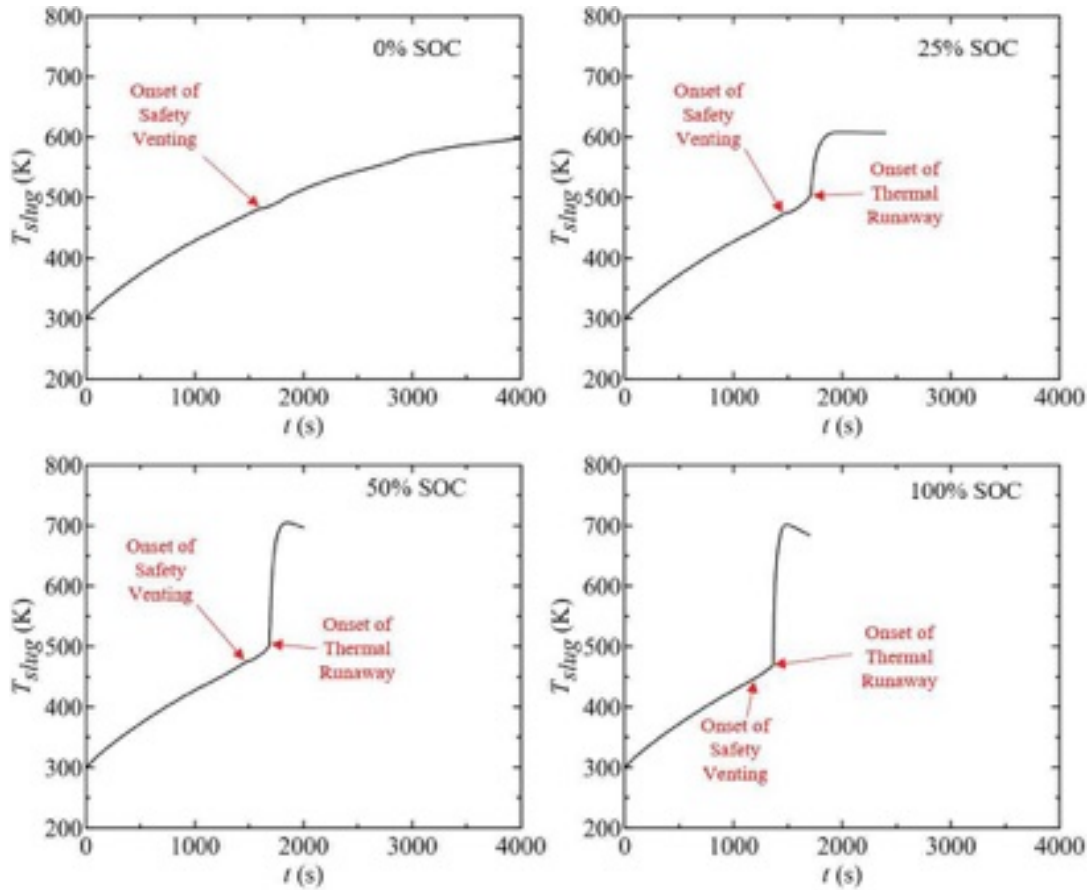


Figure 16. Representative temperature histories for LCO LIBs measured in the CSBC experiments conducted in open atmosphere [10]

The temperatures are due to direct cooling by the open ambient atmosphere, and could reach much higher values (as much as 1000 °C) when insulated. It is these sustained high battery temperatures that present an ignition hazard to its immediate surroundings. For solid combustibles in contact, ignition could occur in seconds, and for adjacent batteries, conduction heat transfer could set off runaway in them. Although the pulse of the single battery decomposition is fast, its energy converted to heat can be problematic.

As a consequence of the fast pulse nature, it becomes more efficient and accurate to record the total energy released rather than its peak rate.

Figure 17 shows the energy release on the left, and the average energy rate computed by the total divided by the pulse duration.

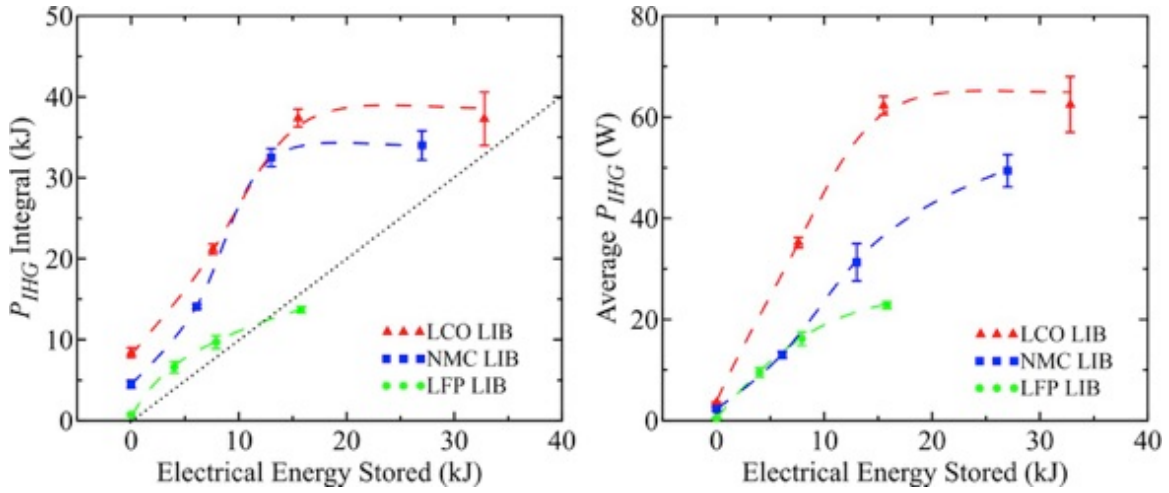


Figure 17. Dependence of the total internal heat produced (left) and average internal heat generation rate (right) on stored electrical energy [10]

The total energy depends on the battery chemistry, its SOC, and can exceed the original electrical stored energy. Due to the rapid pulse of runaway, this total energy is a more practical measurement to assess the battery runaway energy [12]. Quintiere [11] displays in Figure 18 the typical runaway durations as a function of the SOC for a LiCoO_2 battery.

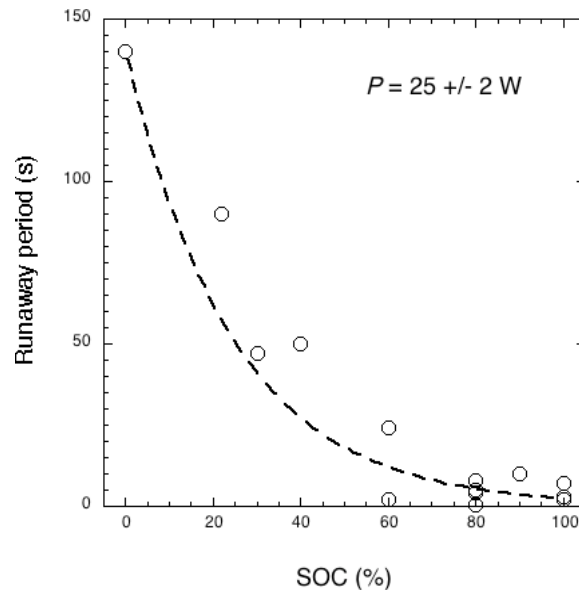


Figure 18. Runaway time period vs. SOC for a LiCoO_2 battery [11]

For a SOC > 30%, the duration is less than a minute, and could be as short as seconds.

Current battery technology uses a combustible liquid electrolyte that significantly contributes to the combustible gas release. If ignited, the flaming jet poses an ignition hazard to its surroundings. If not ignited but collected in a closed container, then the threat is attaining the lower limit for combustion (LFL) and finding a competent ignition source. An explosion of varying strengths will follow in a closed system. Some investigators are focusing on the LFL issues for battery safety in transport. The significance of the flaming energy at the battery source cannot be overlooked. Figure 19, by Liu [10] shows the energy release rate by flaming of a LiCoO₂ battery as a function of the state of charge.

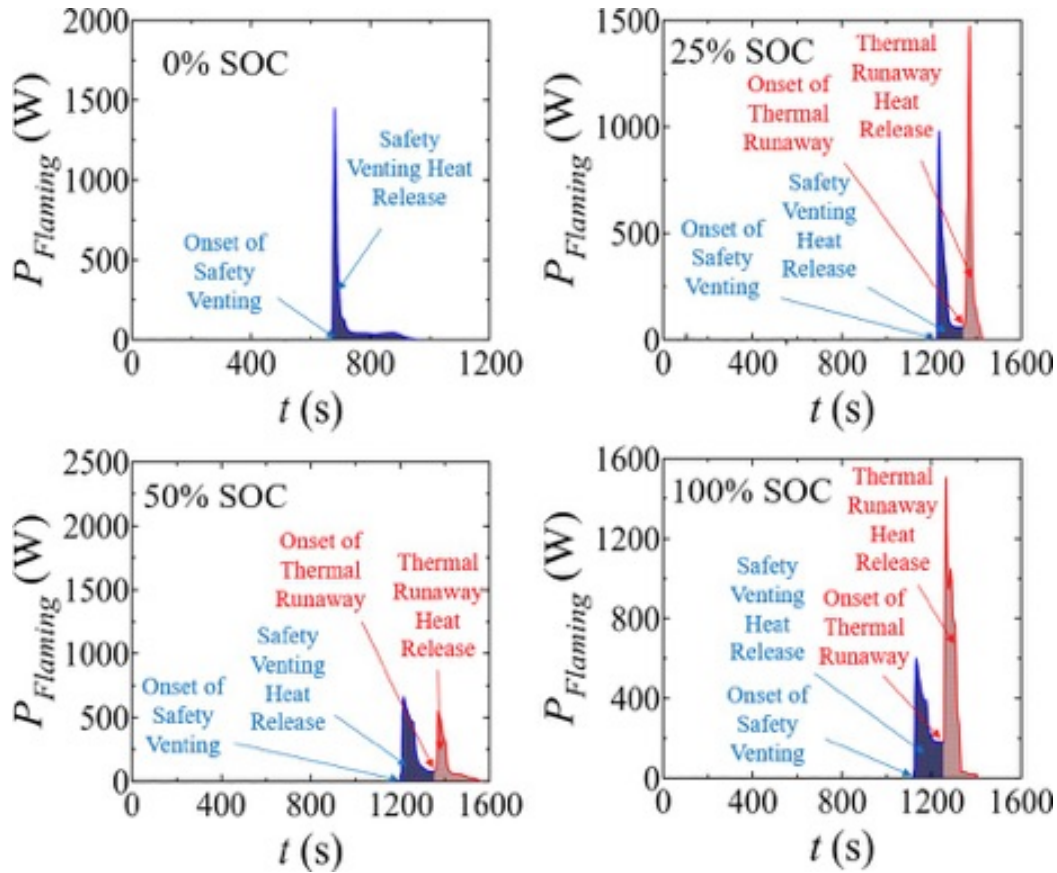


Figure 19. Heat release rate of flaming combustion of ejected LiCoO₂ gases [10]

Here two peaks are displayed over time. The first is due to the burning of the gases released by the designed pressure relief; the second is the remaining gases released as the thermal instability is reached. Again this energy release rate can reach nearly 2 kW, and even for 0% SOC charge, flaming gases emerge to 1.5 kW.

According to Figure 20, this energy is released over 300 to 500 s, with an average rate of 100 to 200 W.

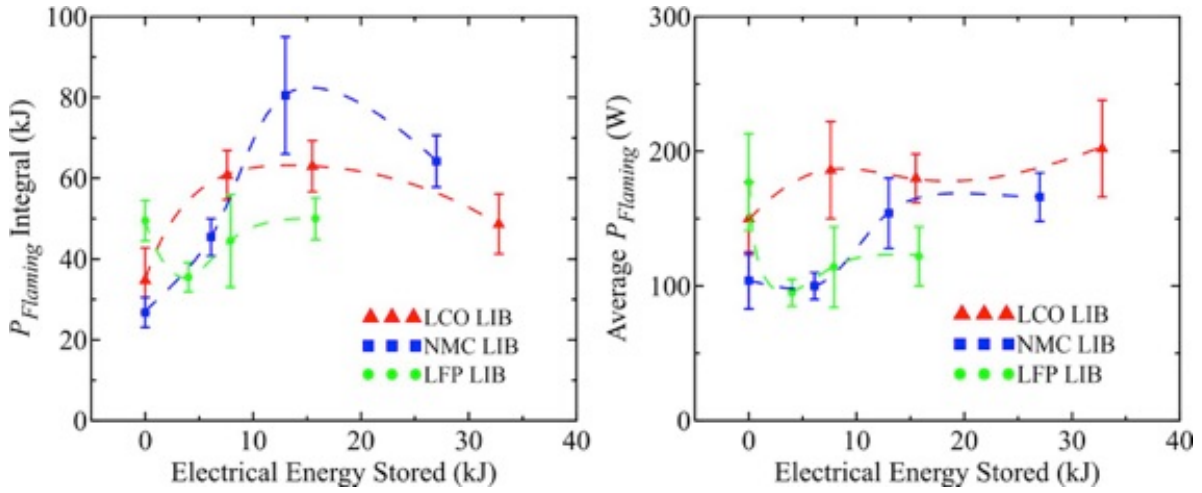


Figure 20. Dependence of the total heat of flaming combustion (left) and average rate of production of this heat (right) on stored electrical energy [10]

Such a flaming jet can easily ignite nearby items. Again this energy in flaming more than exceeds the original energy of stored battery electricity.

An indication of the hazard of a battery in thermal runaway to its surroundings can easily be perceived. Its potential flaming energy and its decomposition energy can exceed the capacity of the battery. For a given battery it has been shown to increase with the SOC or the battery stored electrical energy. These can exceed the battery electrical energy by 2 to 5 times. The resulting temperature of the battery and its potential flame can cause burn injury to people in contact, and ignition of nearby combustibles. In e-cigarettes there is an obvious potential hazard, in electronic components incidents have occurred to varying degrees, and incidents from these and other application of the battery usages will be discussed.

But now let us just focus on an assembly of batteries in a cardboard shipping container. A test at the FAA Fire Safety Branch illustrates the outcome [4]. Figure 21 shows the box with 100 LiCoO₂ lithium-ion cells before (a) and after (b).



Figure 21. Shipping box with interlocking cardboard separators for 100 18650 LiCoO₂ lithium-ion cells pre and post fire [4]

A cartridge heater is used to simulate a bad cell reaching 1000°F to 1250°F in 19 minutes. The box caught fire in 11 minutes and nearby cells went into thermal runaway. The fire continued to burn vigorously for 45 minutes until all cells were consumed. Figure 21b shows the final outcome with all of the batteries spent and the cardboard gone. Recognizing the violent nature of a single battery venting flames in runaway (Figure 10), it should be quite apparent what 100 batteries and cardboard can produce when burning up in this test. The accumulative contribution of many batteries in a container of transport is a definite unwanted event in shipping. The consequences of a large fire or explosion should be clear.

A purpose of this study is to develop a safe packaging method for the transport of batteries. The FAA attempted to improve packaging by using fiberglass separators and found they did not even perform as well as the original cardboard separators. The propagation of thermal runaway proceeded at a faster rate than the baseline test, consuming all of the cells in less time. So a packaging strategy is significant challenge.

Fire and Explosion Incidents due to Li-ion Batteries

Figure 1 illustrates battery fire incidents associated with laptops and airplanes. In 1999 a LAX ramp fire involving lithium batteries was the basis for the FAA Technical Center to begin investigation into the hazard of shipping these items by air. In the 1999 incident, a pallet of 120,000 lithium batteries was dropped on its side. The pallet erupted in flames 3 hours and 40 minutes later and the airport fire fighters had difficulty extinguishing the fire. It is very likely the drop damaged one or more batteries. It should be clear one bad battery was sufficient to cause the propagation among the 120,000 other batteries! A dented battery can damage the separator (Figure 7). The fact that it took a fire event nearly 4 hours to occur indicates that mild damage likely occurred that set off some degree of extra internal current (ion) flow. As with spontaneous ignition, the time to runaway will depend on the cooling available to the damaged battery, and on how long it take the battery to move through the sequence of reactions displayed in Figures 8 and 9. When the heat of these reactions cannot be dissipated, thermal runaway will occur. In a more severe battery damage event such as driving a nail into the battery, thermal runaway associated with nail penetration takes place within about 200-500 ms [12].

In this event with so many batteries involved, it is easy to see why the fire extinguishment was difficult. The continued succession of battery runaway failures that generate increasing heat would require significant cooling. It has been shown that water is the most effective extinguisher as its cooling ability can shutdown the reactions in thermal runaway by preventing them from even occurring. The potential for lithium metal to exothermically react with water might provoke a warning to use water but Li-ion batteries have no free lithium metal. In fact water is also the extinguishment agent recommended even for lithium metal batteries, as their release of free lithium is small.

As a result of the April 28, 1999 fire that destroyed the two aircraft cargo pallets, the National Transportation Safety Board (NTSB) issued recommendations to the Federal Aviation Administration to evaluate the fire hazards posed by lithium batteries in an air transportation environment and require that appropriate safety measures be taken to protect aircraft and occupants.

Aircraft Incidents

Other air incidents are believed to have been caused by the thermal runaway of lithium ion batteries in transport, but have not totally been substantiated.

On February 7, 2006, about 2359 EST, United Parcel Service Company flight 1307, a McDonnell Douglas DC-8-71F, N748UP, landed at its destination airport, Philadelphia International Airport, Philadelphia, Pennsylvania, after a cargo smoke indication in the cockpit. The National Transportation Safety Board determined that the probable cause of this accident was an in-flight cargo fire that initiated from an unknown source, which was most likely located within cargo container 12, 13, or 14. As a result of its investigation the NTSB made recommendations to the Pipeline and Hazardous Materials Safety Administration to reduce the risk of primary lithium batteries becoming

involved in fires on cargo-only aircraft, analyze the causes of all thermal failures and fires involving secondary and primary lithium batteries and, require aircraft operators to implement measures to contain incidents, such as transporting batteries in fire resistant containers and/or in restricted quantities at any single location on the aircraft.

On September 3, 2010 a UPS Airlines Flight 6 was a cargo flight on route to Dubai, reported a fire in the cockpit and crashed. In October 2010, the FAA issued a Safety Alert for Operators highlighting the fact that the cargo on board Flight 6 contained a large quantity of lithium type batteries. The report indicated that the fire was likely in a cargo pallet that contained more than 81,000 Li-ion batteries.

On 28 July 2011, Asiana Airlines Flight 991, a cargo aircraft on a flight from Seoul to Shanghai crashed in the sea. The crew reported a fire on board, and it was determined that a fire started in or near one of the pallets containing dangerous goods in the rear fuselage, but not enough evidence was found to determine exactly what caused the fire. However, 400 kg of lithium ion batteries were on board.

In 2013, the first year of service for the Boeing 787 Dreamliner, at least four aircraft suffered from electrical system problems stemming from its lithium ion batteries. On January 7, 2013, a battery overheated and started a fire in an empty 787 operated by JAL at Boston's Logan airport. It was found on investigation that the battery had signs of thermal runaway. On January 9, UA airlines reported a problem in one of its six 787s with the wiring located in the same area as where the battery fire that occurred on JAL's airliner. Then on January 16, 2013, an ANA 787 made an emergency landing in Japan after there was an error message in the cockpit citing a battery malfunction.

In July 2013 at Heathrow a fire was discovered on board a parked Ethiopian Airlines Boeing 787-8. It was likely to have been caused by a lithium battery powered emergency locator transmitter. The fire spread through the cabin and burnt the new composite fuselage material.

As a result of these series of incidents, a ban on transporting lithium ion batteries (UN3480) went into effect April 1, 2016 by ICAO, the United Nations agency that regulates the transport of Dangerous Goods aboard international aircraft—enacted a ban as cargo on passenger aircraft. Lithium metal batteries (UN3090) were already prohibited. On March 2019, PHMSA IFR harmonized United States lithium-ion battery transport regulations with those of the ICAO, along with extra requirements for ground shipments to ensure no lithium-ion batteries were loaded on aircraft contrary to the regulations. This IFR prohibits the transport of lithium ion cells or batteries as cargo on passenger aircraft. In addition, the IFR requires lithium ion cells and batteries to be shipped at not more than a 30 percent state of charge aboard cargo-only aircraft. It is not clear that a restriction of 30% SOC on all types and sizes of batteries is sufficient to prevent runaway or the progressive propagation among batteries.

As of December 2019, the FAA Office of Security and Hazardous Materials Safety has compiled 216 incidents involving lithium batteries taken by passengers on

aircraft. They involve many carryon electronic devices. But they have only caused limited damage and harm. Table 4 give a sample of these compiled incidents.

Table 4. Sample of battery incidents on passenger aircraft

Date	Device	Aircraft Type (Passenger/Cargo)	Incident summary
11/16/2019	Spare Battery/Batteries	N/A	UPS in Louisville, KY reported that a lithium-ion battery inside package experienced a dangerous evolution of heat that occurred. No fire occurred. The package was charred and scorched.
11/10/2019	Spare Battery/Batteries	N/A	At the UPS facility in Cologne, Germany, a package was discovered emitting a burning odor; the package contained a lithium battery that was smoldering.
11/9/2019	E-cigarette	Passenger	In flight, about one hour away from Denver, CO, a passenger's e cigarette with lithium batteries inside their coat began emitting a burning odor. Investigation is ongoing.
11/7/2019	Spare Battery/Batteries	N/A	At the sort facility in Louisville, KY, while opening a box to perform an inspection, a lithium ion battery was drilled into resulting, in a thermal event (charring, smoldering / no flame).
10/26/2019	Spare Battery/Batteries	Passenger	On flight 2762 from Las Vegas, NV (LAS) to Chicago, IL (MDW) a passenger's lithium battery began smoking during a flight. The flight attendant took the battery, placed it in a containment bag and cooled it with water.
10/25/2019	E-cigarette and spare battery	Passenger	While a passenger was boarding a flight their bag began emitting smoke. The bag contained an electronic cigarette, the battery and its charger was burned.
9/10/2019	Speaker	Passenger	In Dallas, TX (DFW), a passenger bag containing a portable speaker caught fire in a baggage cart on the ramp at gate D34 . The fire was extinguished, but several adjacent passenger bags were affected as well. All baggage involved was placed in American Airlines hazmat holding for further investigation.

Auto Battery Incidents

The use of rechargeable batteries in electric vehicles has extended the use of lithium ion batteries. Tesla's Model S 85kw battery is made up of 7,104 individual 18650 cells manufactured by Panasonic. There are 16 modules in series, each one containing 444 cells. The total output of the battery is 375v. The large number of cells increases the possibilities of a battery malfunction.

Figure 21 gives a glimpse of battery fires in vehicles and their possible causes [6].

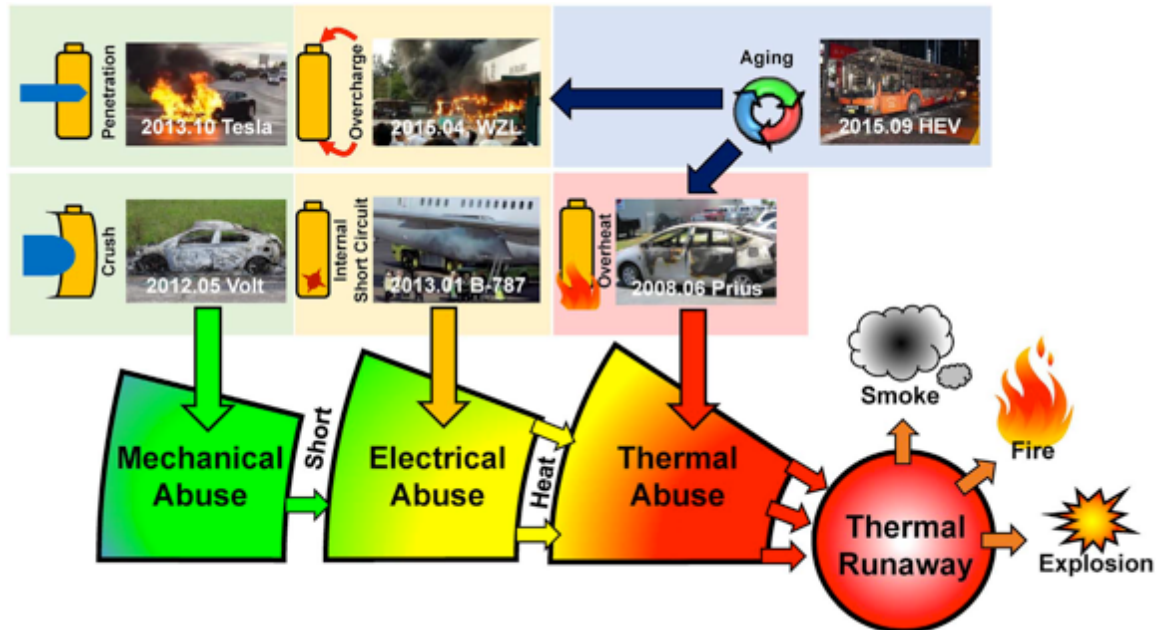


Figure 21. Electric vehicle battery fires and possible causes [6]

NTSB cites a lithium battery fire incident in Florida in 2018 when a speeding teenage driver caused the fatal crash of a Tesla Inc. vehicle and the subsequent fire in the electric car's battery contributed to the severity of his injuries. A complete listing of incidents is not available, but the common place for such incidents is increasing.

Other Battery Fire Incidents

The Consumer Product Safety Commission (CPSC) is an independent Federal regulatory agency with a public health and safety mission to protect the public from unreasonable risks of injury or death associated with the use of thousands of types of consumer products. CPSC has received consumer complaints and manufacturer and retailer reports involving hazards associated with batteries and battery chargers. The CPSC has acted to recall a number of products due to battery safety issues. These include battery chargers, laptop computer battery packs, scooters, and hover-boards. In

2016, exploding lithium-ion (Li-ion) batteries in the New Samsung Galaxy Note7 forced the company to recall about a million units.

The US Fire Administration has reported on incidents with electric cigarettes. Between January 2009 and December 31, 2016, 195 separate incidents of explosion and fire involving an electronic cigarette occurred in the US [13]. These incidents resulted in 133 acute injuries. Many of the incidents of fire and explosion occurred when the device was in use or in a pocket. They also state, “The shape and construction of electronic cigarettes can make them (more likely than other products with lithium-ion batteries) behave like “flaming rockets” when a battery fails.”

Energy storage units are increasing in use. They combine the use of solar energy with battery storage. On April 19, 2019, an explosion rocked a 2 MW energy storage facility in Surprise, Arizona (Figure 22).



Figure 22. Arizona Public Service's 2-MW battery storage project in Surprise, Ariz., before a fire in April took it offline.

Eight firefighters sustained chemical skin burns and chemical-inhalation burns when they entered the facility. South Korea is reported to have had 21 fires in such storage battery units, and this is now having a market effect on that industry.

The risk of battery fires on ships has also been recognized as a concern. The classification society to the maritime industry, DNL GL, published a three year study on the hazard of Li-ion batteries on board ships and suppression methods to deal with them [14]. They measured the concentrations for combustible gases that could be released (but did not report on hydrogen), and on the performance of suppression techniques for battery fires. Recently several ship fires have been in the news and suspected of battery originating fires. The diving boat, Conception, caught fire on Labor Day 2019, and batteries are suspected as a possible cause. In the first weekend in January 2010, the container boxship, Cosco Pacific, experienced a serious fire in the Indian Ocean, caused by a misdeclared cargo of lithium batteries. The container shipping industry has reported a string of dangerous fires due to misdeclared cargo. But not only cargo is the potential culprit. DNL GL reported in March 2018 that there were 185 battery-powered vessels nearing operation; and Japan launched its first Li-ion battery submarine in 2019. So shipboard fires due to Li-ion fires must be of concern.

Runaway Energy Measurements

This review is primarily being done to support the study for safe battery packs and packaging. Runaway is the main hazard for batteries in the possibility of causing fires and explosions. Fires can be initiated by one bad battery through the heat of decomposition of runaway that causes high battery surface temperatures capable of causing the ignition of adjacent combustibles. Fires can also be initiated by the flaming jet of gases expelled from the battery in runaway. These are two distinct forms of energy possible in runaway. In a pack of batteries or shipping package, the prospect of one bad battery setting off the lot is very high, and the magnitude of the hazard increases. In addition, the prospect of battery runaway and propagation in a closed system can lead to an explosion, as combustible gases can collect and reach their flammable limit.

Mitigating regulations have been enacted to prevent battery fires and explosions on cargo aircraft by restricting their SOC to below 30 %. While it is known that runaway energy is reduced with the state of charge for a given battery, it does not necessarily mean that all batteries, at the same or different capacities are equally mitigated. In addition, the fast world of battery technology development means that the regulations may not be able to keep up with new advances in the battery industry. The problem for safe packaging is complex.

In this section, the literature has been examined to seek out methods and data that can characterize the energies given off in runaway. All of these methods use a “calorimeter” technique to examine both the decomposition energy and the combustion energy. The data from such studies will be reported. Their accuracy will not be addressed here, as they are all sound methods. [11]

ARC Measurements

The Accelerating Rate Calorimeter (ARC) studies the exothermic decomposition of compounds under fully adiabatic conditions in a sealed bomb [15]. Data relating temperature pressure and time is generated. The “bomb” or pressure rated canister is made adiabatic by external heaters controlled to keep the canister at the same temperature of its surroundings. The heaters are programmed to increase the canister temperature at a prescribed rate. As the material in the canister begins to thermally degrade, the heat of degradation can be measured. It was initially designed to study propellants and explosives, but has been used extensively for batteries. However, with batteries, as thermal runaway can occur rapidly, the ARC heaters cannot keep up with the rapid temperature rise to maintain adiabatic performance. So the ARC in battery use is applicable to accessing the early and relative low temperature battery and its component behaviors.

A manufacturer of the ARC (THT) explains that it was devised by the Dow Chemical Company in the 1970s and was commercialized in 1980 [16]. This technology was developed to simulate exothermic runaway reactions from hazardous and reactive chemicals. Its canister volumes range from 0.25 to 1.93 m³.

Figure 23 depicts its operation, and Figure 24 shows the way a battery can be tested and the range of typical test temperatures.

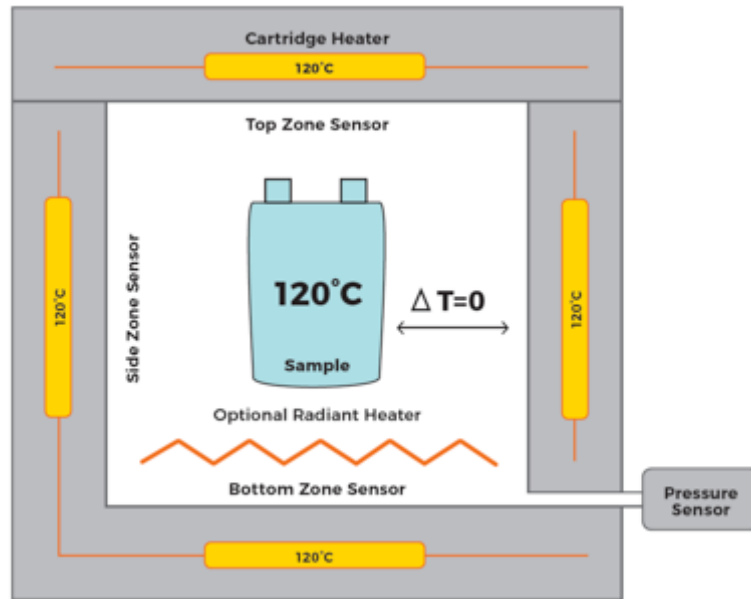


Figure 23. Schematic of the ARC operation [16]

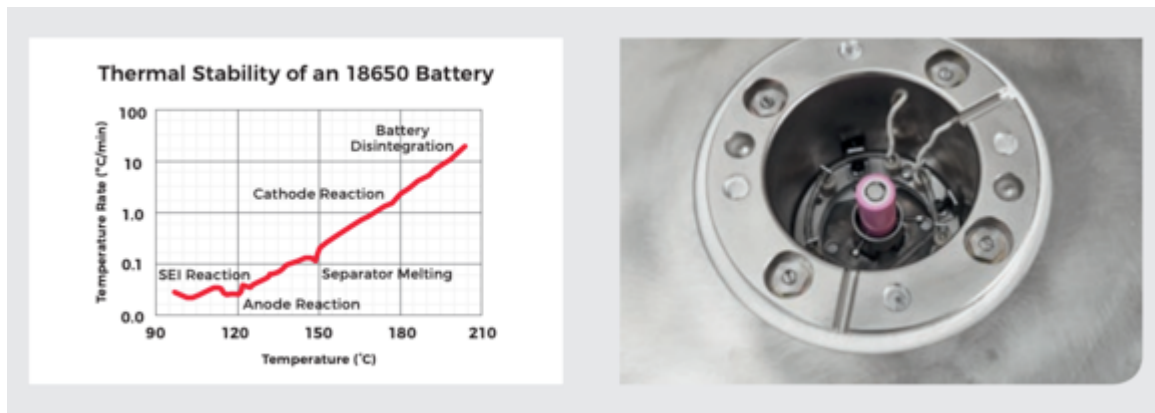


Figure 24. Typical ARC results for a battery [16]

The data from the ARC can be used to formulate analytical chemical kinetic rate expressions for each possible battery component reaction. For example, Spotnitsa and Franklin [17] modeled several abuse actions to a Li ion battery. In that interesting study for characterizing the abuse and the complex battery energy sources that can occur, they illustrated the use of kinetics that could relate to ARC measurements.

All the reactions are assumed to follow an Arrhenius expression with first order activation energies (E_a) and frequency factors (k_0) for several of the component reaction are shown in Table 6.

Table 6. Illustration of kinetic parameters related to ARC measurements

Estimated kinetic parameters					
Reaction	T_{onset} (°C)	T_{peak} (°C) @ 10 °C/min	H/C_p (K)	E_a (J/eq.)	k_0 (s ⁻¹)
$Li + v_{LIB}B \rightarrow I$	180	280	1.93×10^4	2.86×10^5	1.917×10^{25}
$Li + v_{LIS}RS \rightarrow I$	85	180	1.02×10^4	2.05×10^5	9.41×10^{21}
$LiC_6 + v_{NB}B \rightarrow C_6 + I$	160	300	3.71×10^3	1.67×10^5	1.79×10^{13}
$LiC_6 + v_{NS}RS \rightarrow C_6 + I$	110	200	9.81×10^2	2.0×10^5	1.95×10^{20}
$Li_{0.5}NiCoO_2 \rightarrow I + \frac{1}{2}O_2$	165	225	5.30×10^2	3.94×10^5	7.25×10^{39}
$Mn_2O_4 \rightarrow I + \frac{1}{2}O_2$	190	300	7.23×10^2	2.18×10^5	1.06×10^{18}
$S \rightarrow I$	180	250	1.91×10^2	2.74×10^5	5.14×10^{25}
$SEI \rightarrow I$	70	110	1.43×10^2	2.81×10^5	7.88×10^{36}

H: heat of reaction, C_p : heat capacity.

SNL has had an extensive program on battery research. A summary report of March 2004 describes the extent of their program [18]. They describe their use of Differential Scanning Calorimeter (DSC) to measure the effects of thermal abuse over a broad temperature range of individual and selected combinations of cell components. They use the ARC for experiments conducted at slower heating rates under adiabatic conditions. Figure 25 illustrates their use of ARC measurement for a Li ion battery. The heating rate is a measure of the exothermicity of the battery.

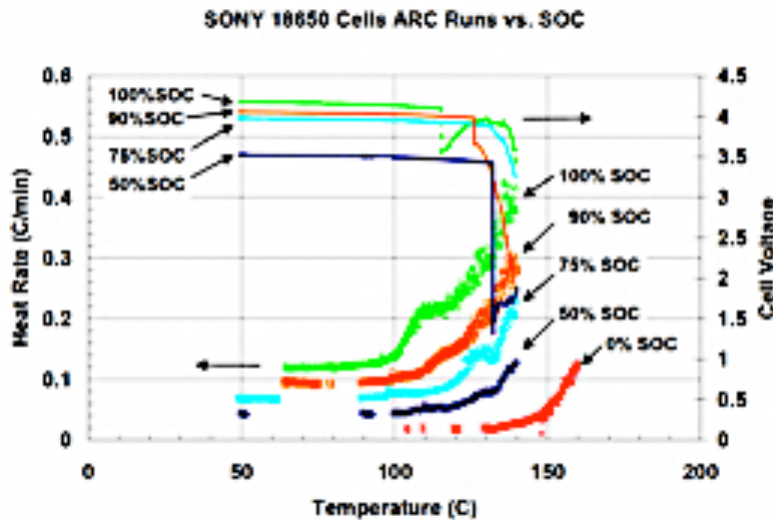


Figure 25. ARC heating rate for a Sony 18650 Li ion battery

Energy in Runaway Decomposition

There are few studies to measure the energy released during decomposition of a battery in runaway. Typically they attempt to measure the rate of energy release or the

total energy spent in runaway, as the duration of runaway is relatively small and the latter measurement is more accurate than attempting to measure the rate.

A technique that is being applied to understand the effects of thermal abuse is differential scanning calorimetry (DSC). DSC enables the thermal response of individual and selected combinations of cell components to be measured over a broad temperature range. This information allows identification of the components participating in thermal activity.

Zhao et al [19] used a THT ARC to test a commercial 18650 lithium-ion cell with a 2000 mAh capacity, with the cathode and anode materials Li (Ni_{0.5}Mn_{0.2}Co_{0.3}) O₂ and graphite, respectively. They used the temperature rise of the battery and the canister to compute the total energy of decomposition in runaway for the battery at various SOC and with different recycling in charging. Their results are shown in Table 7 with cycling slightly reducing the energy when at 100% SOC.

Table 7. Total energy in runaway and the original electrical capacity [19]

item	Cell energy, kJ	Canister energy, kJ	Total energy, kJ	Electrochem energy, kJ
SOC-25%	8.84	12.49	21.33	6.51
SOC-35%	9.77	14.74	24.51	9.13
SOC-50%	13.17	18.59	31.76	13.25
SOC-65%	16.63	22.53	39.16	17.41
SOC-75%	20.26	28.88	49.15	20.08
SOC-85%	20.58	25.88	46.45	22.81
SOC-100%	22.91	38.80	61.72	27.57
Cyc-100	14.36	31.90	46.27	27.59
Cyc-200	19.28	29.74	49.01	27.81
Cyc-300	22.16	34.37	56.53	27.47
Cyc-400	15.77	30.37	46.14	22.24

An early technique to measure the runaway energy was developed by Quintiere et al [20]. They examined a single 18650 battery in a heated copper sleeve fully insulated. An energy balance on the battery with an experiment to derive its heat capacity could reveal its energetics during runaway. The mass loss of the battery contents was also measured.

The results are given in Table 8 for a LiCoO₂ 18650 battery where Q_b is the total energy in runaway generated by the battery.

Table 8. Results of an 18650 lithium-ion battery in the thermal capacitance calorimeter [20]

Test No	SOC %	P (W)	m_0 (g)	t_1 (s)	m_1 (g)	t_2 (s)	m_2 (g)	Final Mass (g)	T_1 , °C	T_2 , °C	T_{max} , °C	Q_b kJ
9	0.5V	25.3	44.3	400	44	400	34	38.6	190	230	800	2
19	0	26.9	44	400	42	800	37	na	180	280	560	0
18	22	27.6	43.8	450	41	550	34	38.2	200	270	670	17
16	30	23.6	43.8	630	41	700	37	38.2	200	260	580	17
14	40	26.1	44.2	540	42	630	37	37.9	210	270	650	21
21	60	25.7	44	400	41	560	31	35.7	180	240	740	28
13	60	26.4	44.3	500	40	580	31	33.9	200	250	950	25
27	80	9.95	44.2	1380	40	1520	30	32.6	n/a	230	770	30
29	80	22.1	44.1	590	43	670	28	32.9	n/a	270	800	31
11	80	23.6	44.1	550	42	640	32	31.9	190	250	910	33
7	80	25.2	44.3	570	43	640	32	32.4	200	250	1350	40
8	80	25.2	44.2	440	40	540	29	31.7	200	250	840	33
30	80	36.4	44	350	40	395	31	30.6	n/a	260	830	32
31	80	49.5	44.2	220	38	270	28	32.8	n/a	270	870	33
32	80	58.8	44.1	174	40	220	31	32.1	n/a	280	820	28
33	80	73.2	44	130	41	165	25	30	n/a	n/a	n/a	n/a
34	80	74.2	44.1	125	40	165	29	32	n/a	270	930	35
23	90	27	44.1	500	42	550	25	25.9	200	240	640	20
15	100	25	44.3	520	41	570	29	27.5	200	250	800	31
12	100	25.5	44.3	540	41	600	n/a	29	n/a	n/a	1200	48
17	100	25.6	44.1	500	40	550	24	24.6	200	250	800	30
10	100	25.8	44.1	480	40	540	-4	21.9	190	250	n/a	n/a

There is also energy expelled by the discharge of battery contents. The results showed that the energy input to cause runaway, P , had a limited effect on Q_b , but SOC had a significant effect.

Liu [10] used a technique similar to Quintiere et al [20] to measure the runaway decomposition energy. Table 9 gives a listing of the batteries tested and Table 10 gives a summary of his results.

Table 9. Open circuit voltage and electrical energy stored in LIB samples at different SOC's [10].

SOC	LCO		MNC		LFP	
	Cell Voltage (V)	Electric Energy (kJ/W h)	Cell Voltage (V)	Electric Energy (kJ/W h)	Cell Voltage (V)	Electric Energy (kJ/W h)
0%	3.2	0/0	3.0	0/0	3.2	0/0
25%	3.7	7.6/2.1	3.6	6.1/1.7	3.2	4.0/1.1
50%	3.7	15.5/4.3	3.7	13.0/3.6	3.3	7.9/2.2
100%	4.2	32.8/9.1	4.2	27.0/7.5	3.5	15.8/4.4

Table 10. Summary of the internal heat generation measurements [10]

SOC	P_{IHG} Integral (kJ)			Average P_{IHG} (W)		
	LCO	NMC	LFP	LCO	NMC	LFP
0%	8.4±0.6	4.5±0.5	0.7±0.2	3.5±0.2	2.3±0.3	0.5±0.1
25%	21.2±0.6	14.1±0.3	6.6±0.7	35.2±1.0	13.0±0.7	9.5±0.9
50%	37.4±1.1	32.5±1.1	9.7±0.8	62.3±1.8	31.3±3.7	16.2±1.3
100%	37.3±3.3	34.0±1.8	13.7±0.4	62.5±5.5	49.4±3.2	22.8±0.7

The same research group extended Liu's study to a Sanyo UF103450P prismatic Li ion battery of physical dimensions 34 x 50 x 10 mm with a nominal capacity and voltage of 1880 mA h and 3.7 V, respectively [21].

The results for the energy in runaway are given in Figure 26.

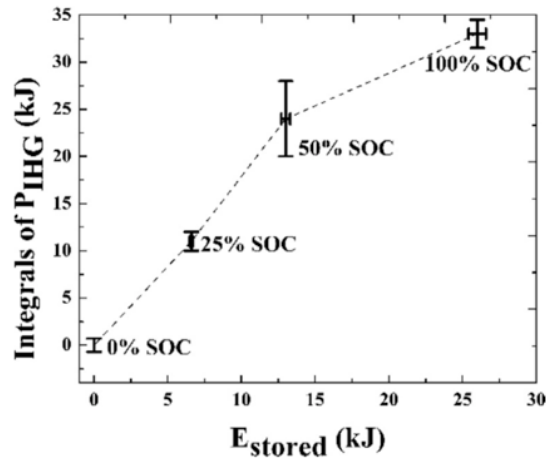


Figure 26. Runaway energy for a prismatic battery [21]

A novel, but well-known standard calorimetric technique, was adopted for batteries in runaway by Lyon and Walters [22]. They employed the standard oxygen bomb calorimeter that uses a water jacketed bath to measure the energy released in the “bomb” or pressure canister, but replaced the oxygen with nitrogen. They triggered runaway by electric heating, and subtracted out that input. While this technique does not measure the rate of energy released over time in runaway, it gives the total energy. However, the runaway time can be derived by measuring the temperature of the battery. Based on the respected known accuracy of the oxygen bomb technique, this method is likely the best to employ for batteries in runaway. Figure 27 shows a schematic of the method.

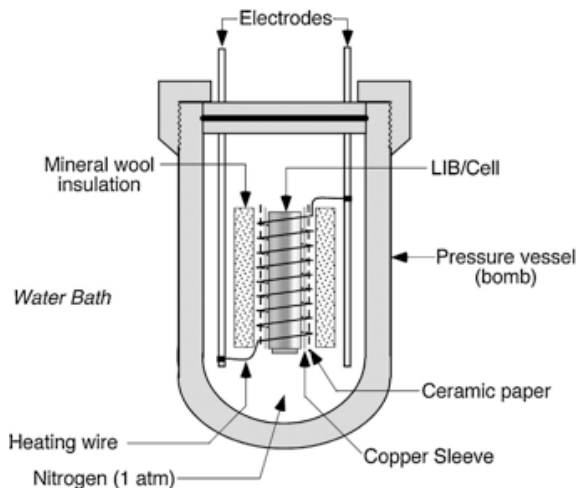


Figure 27. Use of the standard O₂-bomb with nitrogen for batteries in runaway [22]

Table 11 gives their results for the runaway energy in thermal decomposition for several batteries.

Table 11. Runaway energy by Bomb calorimeter [22]

Cathode	SOC Z (%)	Cell Capacity Q (A-s)	Cell voltage (V)	Cell Capacity E (kJ/cell)	Runaway energy H _r (kJ)
Unknown	0	0	0.00	0.0	-1.3
	26	1062	3.57	3.8	8.8
	42	1696	3.70	6.3	15.7
	59	2372	3.64	8.6	19.5
LiNiCoAlO ₂	100	4018	4.10	16.5	26.6
	0	0	0.00	0.0	-1.5
	24	1231	3.45	4.3	11.0
	46	2398	3.58	8.6	18.9
LiNiCoO ₂	74	3816	3.80	14.5	27.1
	100	5173	4.10	21.2	37.3
	0	0	0.00	0.0	-2.2
	17	1519	3.42	5.2	15.3
LiCoO ₂	43	3780	3.57	13.5	30.7
	70	6109	3.70	22.6	50.4
	100	8712	4.00	34.9	65.7
	0	0	0.00	0.0	-0.1
LiMn ₂ O ₄ -LiNiCoO ₂	14	1652	3.23	5.3	36.5
	46	5227	3.44	18.0	50.6
	67	7628	3.66	27.9	62.4
	100	11,455	4.10	47.0	77.7

It is surprising that only this limited amount of data exist for determining the energy contribution of a single battery in runaway.

Combustion Energy in Runaway

As with runaway energy measurement data, combustion energy data is light, but more often measured. That is likely because there are standard techniques of measuring the energy given off by a fire using the consumption of oxygen in the collection gases or smoke. These oxygen combustion calorimeters can be small and large. (See ASTM tests [23,24].) The difficulty in using these fire tests for batteries is to insure that the battery stays in place and that the jetting combustion products are captured by the exhaust system in which oxygen is measured. The rapid release of the battery combustion products and their ignition is also a factor on the accuracy of the method. However the total energy released in combustion is also directly measured and has higher accuracy than the rate. Here we will tabulate and record the battery combustion data available.

Quintiere et al [20] used the Cone Calorimeter (ASTM E1354) to measure a number of batteries. It should be said that just the release of gases in runaway does not insure their ignition. In all of the following studies, ignition was forced by an electric arc.

The batteries studied are listed in Table 12.

Table 12. Electrochemical cells tested in this study [20]

MFG	Cell Chemistry	Rechargeable	Package	Cell Mass (g)	Nominal Cell Potential (Volts)	Nominal Charge Capacity, C (mAh)
A	Lithium ion (LiCoO ₂)	Yes	18650	44	3.7	2600
B	Lithium ion (LiCoO ₂)	Yes	18650	44	3.7	2600
C1	Lithium-ion	Yes	Pouch	23	3.7	1050
C2	Lithium-ion	Yes	Pouch	23	3.7	1900
D	Nickel Metal Hydride (NiMH)	Yes	AA	26	1.2	2600
E	Nickel Cadmium (NiCd)	Yes	AA	21	1.2	1000
F	Lithium Iron Disulfide (LiFeS ₂)	No	AA	15	1.5	3000
G	Lithium Manganese Dioxide (LiMnO ₂)	No	17350	11	3.0	1500
H	Lithium Manganese Dioxide (LiMnO ₂)	No	16270	16	3.0	750
J	Zinc Manganese Dioxide (ZnMnO ₂)	No	11300	24	1.6	825

The results are shown in Tables 13-15.

Table 13. Fire calorimeter data for 18650 lithium-ion rechargeable (secondary) cells

Cell	Chemistry	SO C (%)	Heat Flux (kW/m ²)	t ₁ (s)	t ₂ (s)	Peak HRR (kW)	TH R (kJ)	Mass Loss, Δm (g)	HOC (kJ/g)	THR/m ₀ (kJ/g)
A	LiCoO ₂	100	10	731	n/a	0.2	9	4	2.2	0.2
A	LiCoO ₂	100	30	165	242	13.7	84	10.3	8.2	1.9
A	LiCoO ₂	100	30	166	242	9.8	76	12.6	6.0	1.7
A	LiCoO ₂	100	50	109	159	10.2	100	10.1	9.9	2.3
A	LiCoO ₂	100	50	96	137	16.2	93	9.6	9.7	2.1
A	LiCoO ₂	100	75	56	75	12.3	82	9.1	9.0	1.9
A	LiCoO ₂	100	75	50	71	16.2	93	9.1	10.2	2.1
A	LiCoO ₂	20	50	86	n/a	4.4	59	6	9.7	1.3
A	LiCoO ₂	20	50	86	n/a	2.5	102	6.5	15.6	2.2
A	LiCoO ₂	20	50	87	n/a	3.3	92	6.1	15.0	2.0
A	LiCoO ₂	20	50	93	n/a	3.0	97	6.3	15.5	2.1
A	LiCoO ₂	20	50	86	n/a	3.5	81	6.3	12.8	1.8
A	LiCoO ₂	30	50	102	130	6.0	92	5.9	15.6	2.0
A	LiCoO ₂	30	50	104	132	4.0	95	5.7	16.8	2.1
A	LiCoO ₂	30	50	102	133	3.2	86	5.3	16.1	1.9
A	LiCoO ₂	30	50	86	130	2.7	84	5.7	14.8	1.9
A	LiCoO ₂	30	50	92	125	9.2	78	8.1	9.6	1.7
A	LiCoO ₂	50	50	100	135	7.4	73	n/a		1.6
A	LiCoO ₂	50	50	106	123	7.4	68	7.6	9.0	1.5
A	LiCoO ₂	50	50	95	132	10.4	93	n/a		2.0
A	LiCoO ₂	50	50	99	126	9.2	83	6.9	12.1	1.8
A	LiCoO ₂	70	50	93	122	5.4	64	22.4	2.8	1.4
A	LiCoO ₂	70	50	93	120	6.7	70	12	5.8	1.5
A	LiCoO ₂	70	50	102	129	5.3	63	14	4.5	1.4
A	LiCoO ₂	70	50	102	124	8.4	77	11.8	6.5	1.7
A	LiCoO ₂	70	50	93	121	7.2	69	10.6	6.5	1.5
A	LiCoO ₂	100	50	86	112	6.2	58	13.3	4.4	1.3
A	LiCoO ₂	100	50	92	112	3.3	68	20.8	3.3	1.5
A	LiCoO ₂	100	50	103	117	12.1	59	n/a	□□	1.3
A	LiCoO ₂	100	50	93	119	5.9	57	13.7	4.2	1.3
A	LiCoO ₂	100	50	88	113	8.4	62	12.3	5.1	1.4
B	LiCoO ₂	100	50	86		4.2	48	4.1	11.7	2.4
B	LiCoO ₂	100	50	61		5.6	55	5	11.0	2.7

Table 14. Fire calorimeter data for lithium-ion, NiMH, and NiCd cells [20]

Cell	Chemistry	SOC (%)	Heat Flux (kW/m ²)	t_1 (s)	t_2 (s)	Peak HRR (kW)	THR (kJ)	Mass Loss, Δm (g)	HOC (kJ/g)	THR/ m_0 (kJ/g)
C1	Li-ion	50	10	500	N/A	0.2	6	5.2	1.2	0.3
C1	Li-ion	50	30	112	N/A	9.2	57	3.3	17.3	2.4
C1	Li-ion	50	30	130	N/A	8.9	47	2.9	16.2	2.0
C1	Li-ion	50	50	38	51	6.0	77	5.1	15.1	3.3
C1	Li-ion	50	50	48	63	5.7	75	5.6	13.4	3.2
C1	Li-ion	50	75	14	44	7.1	109	6.1	17.9	4.7
C1	Li-ion	50	75	22	31	5.8	97	7.2	13.5	4.2
C2	Li-ion	50	10	512	N/A	0.5	0	4.3	0	0.0
C2	Li-ion	50	30	64	84	7.8	156	10.2	15.3	3.8
C2	Li-ion	50	30	68	88	7.0	145	9.8	14.8	3.5
C2	Li-ion	50	50	35	52	8.0	162	11.1	14.6	3.9
C2	Li-ion	50	50	35	58	5.8	147	11.1	13.2	3.6
C2	Li-ion	50	75	19	35	8.9	165	12.1	13.6	4.0
C2	Li-ion	50	75	22	39	7.4	170	12	14.2	4.1
D	NiMH	100	50	212	357	0.0	0	2.6	0	0.0
D	NiMH	100	50	353	N/A	0.7	13	1.1	11.8	0.5
E	NiCd	100	50	N/A	N/A	0	0	6.5	0	0.0
E	NiCd	100	50	N/A	N/A	0	0	5.8	0	0.0

Table 15. Fire calorimeter data for non-rechargeable (primary) Li metal cells [20]

Cell	Chemistry	SOC (%)	Heat Flux (kW/m ²)	t_1 (s)	t_2 (s)	Peak HRR (kW)	THR (kJ)	Mass Loss, Δm (g)	HOC (kJ/g)	THR/ m_0 (kJ/g)
F	LiFeS ₂	100	50	80	160	3	51	2	25.5	3.5
G	LiMnO ₂	100	30	104	149	4.2	42	4.7	8.9	2.6
G	LiMnO ₂	100	30	113	149	3.6	55	8.4	6.5	3.4
G	LiMnO ₂	100	50	74	94	3.9	52	4.4	11.9	3.2
G	LiMnO ₂	100	50	69	89	4.7	74	4.4	16.7	4.5
G	LiMnO ₂	100	75	48	68	5.9	64	3.8	16.8	3.9
G	LiMnO ₂	100	75	52	67	3.5	45	4.3	10.4	2.7
H	LiMnO ₂	100	30	115	148	2.8	27	3.3	8.2	2.5
H	LiMnO ₂	100	30	118	161	3.1	32	3.2	10	3
H	LiMnO ₂	100	50	77	85	3.9	20	3.4	6	1.9
H	LiMnO ₂	100	50	90	118	3.7	33	3.5	9.5	3.2
H	LiMnO ₂	100	75	54	65	6.5	34	2.3	14.6	3.2
H	LiMnO ₂	100	75	54	70	4.2	31	3.7	8.5	2.9
J	ZnMnO ₂	100	50	204		0.6	17	2.7	6.3	0.7
J	ZnMnO ₂	100	50	202		0.6	10	3.0	3.3	0.4

These results include the time to first vent by the safety valve (t_1) and the time at the onset of rapid failure or runaway (t_2). The peak heat release rate and the total energy are recorded as well as the heat of combustion (HOC) based on the mass lost. SOC and the type of battery is a factor in these tests.

Figure 28 shows that the HOC and the total energy decrease with the SOC while the mass loss or mass of ejected material slightly increased.

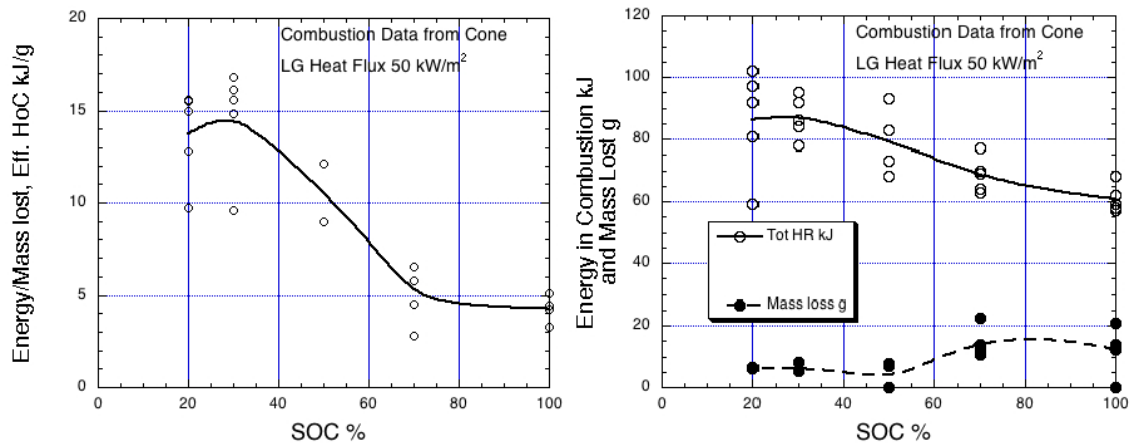


Figure 28. Typical energy in combustion of a LiCoO₂ battery [20]

Liu [10] also measured the combustion energy using a Cone Calorimeter. His results are shown in Table 16 where the trend with the SOC is not universal for the batteries tested.

Table 16. Summary of the cone calorimetry measurements [10]

OC	$P_{Flaming}$ Integral (kJ)			Average $P_{Flaming}$ (W)		
	CO	MC	FP	CO	MC	FP
%	3 4.8±8.0	26 .8±3.7	49 .5±5.0	50±27	04±21	77±36
5%	6 0.8±6.1	45 .4±4.6	35 .5±3.6	86±36	00±10	5±10
0%	6 3.0±6.3	80 .5±14.5	44 .5±11.5	80±18	54±26	14±30
00%	4 8.7±7.4	64 .2±6.4	50 .0±5.2	02±36	66±18	22±22

He also lists the average energy release rate where the associated time for runaway can be deduced by the ratio of the total (P integral) to Average P . A result of a prismatic battery is given by Said et al [21] in Figure 29 for Sanyo UF103450P.

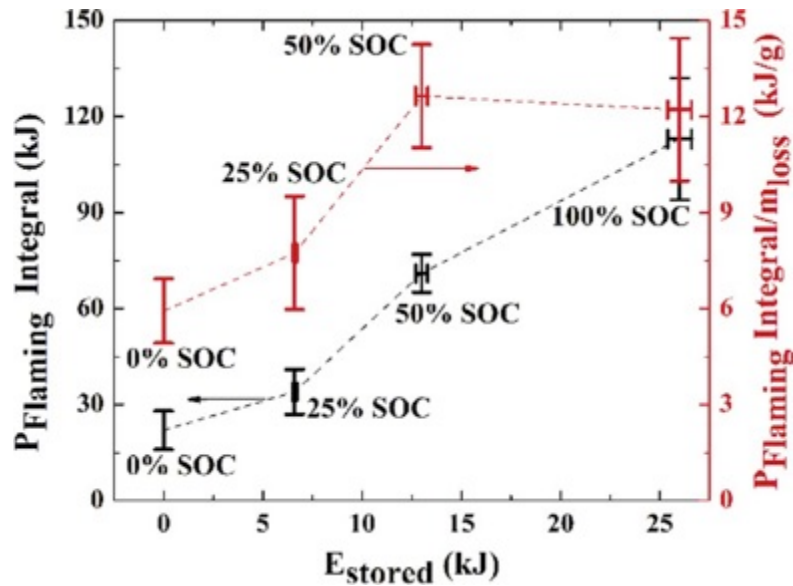


Figure 29. Total heat generated in flaming combustion of ejected battery materials and effective heat of combustion with the original stored electrical energy [21].

Fu et al [25] show combustion data from the Cone Calorimeter for a single battery varying SOC in Figure 30.

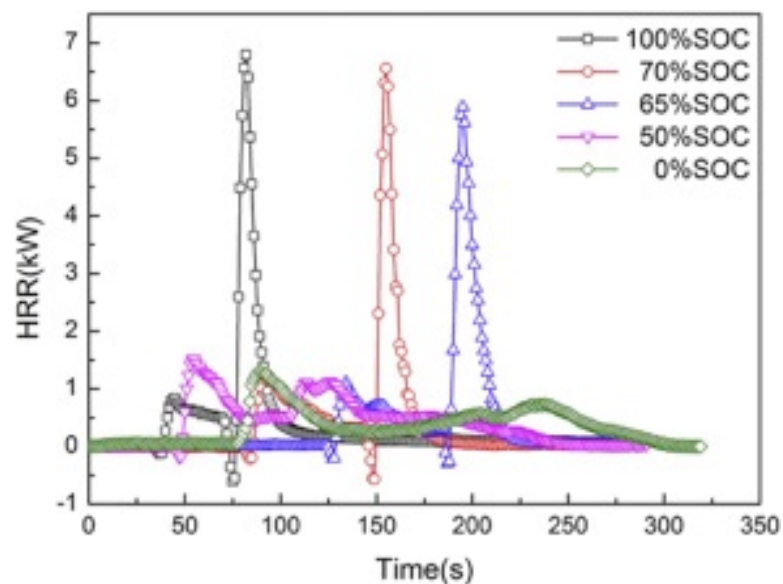


Figure 30. Heat release rate with SOC for a Sanyo battery UR18650FM 2.6 Ah

[25]

A three-pack of SAM-SUNG 18650 batteries with nominal capacity is 1300 mAh using lithium nickel manganese cobalt oxide (NMC) as the cathode and graphite as the anode was measured in the Cone Calorimeter [26]. They set off a pack of three together and the total result is shown in Figure 31 for all three.

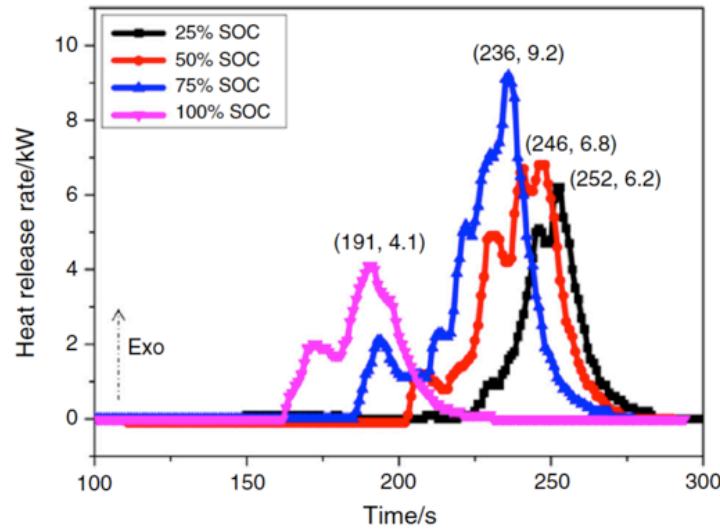


Figure 31. The typical heat release curves of a three-pack of SAM-SUNG 18650 [26]

Russo et al [27] studied a Panasonic NCR 18650 BM 3.6 V and 2900 mAh capacity battery. Their results at various heating rates in the Cone are listed in Table 17.

Table 17. Experimental test conditions and measured parameters [27]

Test Id	SOC (%)	Radiant power (kW/m ²)	HRR max (kW/cell)	T max (°C)	Gas venting time (s)	Explosion time (s)	Mass loss (g)	Total Energy (kJ/cell)
1	100	15	0.9	367	580	810	28.08	184
2	100	25	1.3	703	300	385	24.27	132
3	100	35	1.1	328	274	315	34.14	65
4	100	50	0.8	497	171	226	20.89	28
5	100	35	1.1	735	236	294	43.53	72
6	100	50	11 (0.9)	440	240	272	20.24	304
7	50	25	0.1	726	470	580	10.73	15
8	50	35	1.2	367	246	324	17.33	62
9	50	50	1.0	643	204	230	43.97	40
10	0	50	1.3	487	138	196	8.31	33

It is usual that the results for the combustion energy decreased with the increase of radiant energy. This is an uncommon result, as heating rate should not affect the total energy released. It may be due to the ejected battery material not being captured in the exhaust stream for the Cone device.

Wang and co-workers examined 50 Ah LiFePO₄/graphite batteries in Cone calorimeter [28]. These are large 12-volt batteries: numbered as no. 1 and no. 2, with 50 and 100 % SOC and 1829.7 g and 1842.5 g, respectively. Each was triggered into runaway in a room designed to capture the exhaust products in an oxygen consumption calorimeter. A summary of their results is shown in Table 18.

Table 18. 12 volt LiFePO₄ battery at 50 and 100 % SOC [28]

Battery no.	1# 50 Ah	2# 50 Ah
SOC, %	50	100
Ignition time, s	975.824	1107.700
Combustion time, s	1250.820	1348.940
Obvious jet fire times	1	3
Surface temperature at ignition, °C	124.5	128.9
Maximum flame temperature, °C	894.0	986.2
Peak HRR, kW	55.93	64.32
Total heat release, MJ	13.55	13.74
Total spilled mass loss, g	488.9	495.7
Combustion heat, kJ g ⁻¹	27.715	27.718
Maximum mass loss rate, g s ⁻¹	4.747	8.692
Mean mass loss rate in combustion, g s ⁻¹	0.311	0.418
Total spilled mass loss ratio, %	26.72	26.90

The batteries both produced about 13 MJ and an effective heat of combustion of about 28 kJ/g invariant with the SOC.

Chen et al [29] studied the combustion energy output of SAMSUNG 18650 typeLiCoO₂ cells charged to 80% SOC in a package as shown in Figure 32.

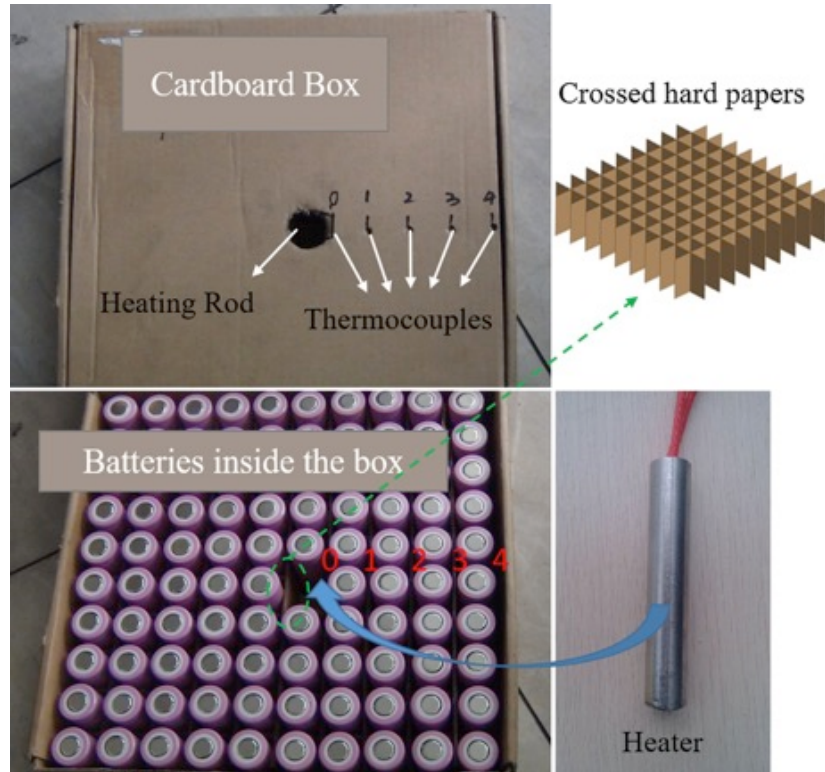


Figure 32. Combustion energy test of 10 x 10 batteries in a cardboard packing box at 80% SOC [298]

The batteries were packed in a cardboard box supplied by the manufacturer, and each cell was separated by crossed-hard paper. The configurations, 6 × 6 (Test A) and 10 × 10 (Test B) were based on a commonly used LIBs transport packaging. A 500 W heating rod with similar battery dimensions was used to achieve the purpose of thermal propagation.

Table 19 presents the results as measured by oxygen calorimetry.

Table 19. Experimental heat release during propagation [29]

Test No.	A	B
Initial weight (g)	1631.1	4567.2
Ash weight (g)	1139.1	3098.1
Weight for box (g)	73.7	151.5
Average MLR (g/s)	1.41	2.6
Maximum HRR (kW)	59.5	442.6
THR (kJ)	4364	16,490
Heat of box (kJ)	972.8	1999.8
AEHC (kJ/g)	5.99	8.94

Figure 33 shows the cumulative heat release rates as the batteries propagated.

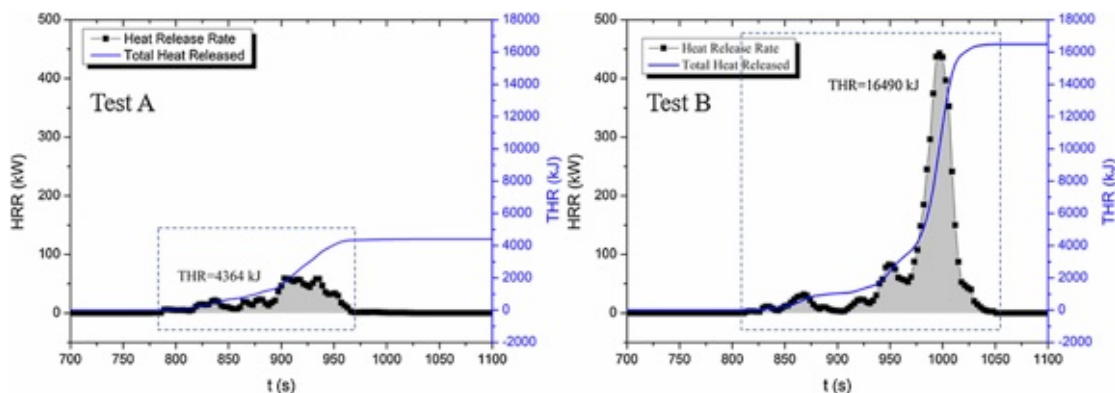


Figure 33. Cumulative combustion rate of heat release for Test A 36 batteries and Test B 100 batteries [29]

The combustion heat of the cardboard box was subtracted from the calorimeter measurement. The heat of combustion per single battery is given as 6 to 9 kJ/g for A and B, respectively. This compares to a maximum of 6.5 kJ/g for a similar battery at 70% SOC (See Table 13).

Gases vented in battery runaway

Several studies have investigated the combustible gases that are vented during thermal runaway. They pose a hazard as a direct flame that can occur in the vented gases, or as an accumulation of combustion products to later be ignited and flame propagation will occur. A particular study is noteworthy.

Tests and analysis were carried out by Maloney [30] to measure the concentration of battery combustible gases, and to examine if 5% Halon 1301 fire-suppressing agent in an aircraft Class C cargo is effective at mitigating fires involving cargo involving lithium batteries and to mitigate the risks of a potential explosion of the accumulated vented battery gases. The results showed that the 5% Halon agent was minimally effective when the battery gases ignited in a Class C cargo compartment. This study brought the focus to the need for aircraft battery cargo to not reach a flammable limit in the event of runaway in a battery package.

While the study did not reveal new results for the nature of combustion gases from batteries it presented comprehensive data on a range of gases. Tests conducted at the FAA Technical Center demonstrated the effects of an aircraft cargo container explosion caused by the combustion of accumulated thermal runaway vent gas. A relatively small number of 18650 cells had reacted before the explosion occurred. Hydrogen, carbon dioxide and hydrocarbons are in abundance and provide the fuel for combustion. Indeed, a measurement of their concentrations can be used to compute the mass of each, and with their associated heat of combustion, the total combustion energy can be computed.

Here, the focus was on the potential for these gases to form a flammable limit that could lead to an explosion as depicted in Figure 34.



Figure 34. Cargo container explosion caused by lithium battery vent gases [30]

Extinguishment

A most comprehensive study of extinguishment agents to suppress battery fires and prevent thermal runaway propagation was conducted by Maloney [31]. It included both lithium ion and lithium metal batteries. Table 20 shows agents used.

Table 20. Extinguishing Agents studied in battery suppression

<u>Liquids 100 mL to 500 mL</u>
Water
Aqueous A-B-D agent
AF-21
AF-31
<u>Gaseous</u>
Halon 1211
FM-200
Halotron I
FE-36
Purple-K
CO ₂

The most interesting tests were to examine the effectiveness of the agents to prevent the propagation of runaway among 5 batteries, after one was triggered into runaway. Five 2600mAh 18650 lithium-ion cells that were charged to 50% capacity (1300mAh) were used and five 1500mAh 123a lithium-metal cells at full capacity were also used. A cartridge heater initiated runaway in the first cell. After the first cell underwent thermal runaway, the extinguishing agent was applied by hand from the 500 mL water bottle for the aqueous agents and Novec 1230, and from a fire extinguisher for the streaming agents. The heater was then turned off and data collection continued for approximately 20 minutes. The initial baseline tests showed that all cells would proceed into thermal runaway without suppression. To stop propagation, 500 mL of each aqueous agent was sufficient and none of the streamed gaseous agents stopped propagation.

It is significant that the cooling effect of the water-based agents was the key to stopping propagation among cells. Realizing that temperature drives the runaway process, and the energy responsible is relatively small, it is not surprising that water is key. Consider from the typical 18650 LiCoO₂ battery of about 35 kJ electrical capacity. About 2 to 5 times runaway energy could be expended by decomposition and combustion processes in runaway. That is 70 to 175 kJ that would need to be absorbed by an agent to prevent this energy from being transmitted to its surroundings. For water to absorb 175 kJ of energy by an increase in temperature of 80 °C and then all evaporating, the volume of water needed is

$$Volume(mL) = \frac{175,000J}{(1g/mL)\left[1\frac{cal}{gK} * 80K + 540\frac{cal}{g}\right]4.184\frac{J}{cal}} = 67.5 mL.$$

In this study 500 mL of aqueous solutions were used. Provided the solution gets to the battery, it is not surprising that it is more than enough to be effective.

What is more significant is that the effectiveness of water was also demonstrated for lithium metal batteries. The heat of reaction of Li with water is 32 kJ/g. Again the relative small amount of lithium in a 18650 size battery suggests that sufficient water can be able to absorb any reaction energy. However, in these tests there was a wide variation in the behavior of lithium metal batteries in runaway. The cells could vent from melted holes in the cell, leak plastic and lithium, or eject their contents. These effects might change how well water can do.

Battery Hazards in Packaging and Transportation

A principle concern of Li ion battery faults is their ability to initiate thermal runaway. The high battery temperatures and combustible gas release presents a fire and explosion potential. The risk of a big disaster is much greater with the batteries in a package being shipped, or in an assembly package for special use. While the frequency of battery runaway is extremely low among the millions in use, their increasing number

make the risk realizable. Accidents events over the last decade promote worry. So many are seeking to mitigate these hazards. The battery industry itself is working to minimize the risk of thermal runaway and its potent output by design and material changes. But the high energy density of the batteries, that will only increase, suggests that the hazard of potential battery fires will be continue to exist. Mitigating processes need to be considered.

Regulations and Standards

Over the last several years, changes have been made in the aircraft shipping of Li-ion batteries. The incidents of aircraft batteries fires, suspected and substantiated, and the testing work of the FAA Fire Safety Branch has moved regulators to establish new rules for shipping. In 2019, PHMSA (Pipeline Hazardous Materials Safety Administration) adopted previous regulations by international bodies enacted in 2016 (ICAO, International Civil Aviation Organization: Dangerous Goods Panel, and IATA, International Air Transportation Association) (IATA). This updated Title 49: Transportation: Part 173.185 on the shipping of batteries by air to primarily harmonize the rule as

- ❑ Prohibits the transport of lithium ion batteries as cargo on passenger aircraft
- ❑ Requires the batteries to be shipped at not more than a 30% SOC.
- ❑ Allows batteries in medical or electronic equipment to be carried onboard or checked if with the capacity of 100 to 160 Wh. This is 576 kJ, as compared to a single 18650 lithium ion batteries typically, having 25 kJ electrical capacity, that could produce 2 to 5 times this energy in runaway!

It would appear the carry-on batteries is a significant potential hazard, and the 30 % SOC limit really needs to be tied to a measurement standard to allow batteries in packaging with this limit to be allowed. ICAO and others are working on such a packaging test method for batteries.

Also in 2019, under Section 333(d) of the FAA Reauthorization Act of 2018, the Secretary of Transportation directed PHMSA to form the Lithium Battery Air Safety Advisory Committee to provide DOT with a forum of discussion among battery safety experts and stakeholders.

It should be noted that there has been regulations by UN Standard 38.3 for shipping Li ion batteries in place for a long time. This consists of a number of battery abuse tests required to pass by manufacturers. It appears to be almost voluntary and without strong enforcement. New testing developments have been prompted by the need to go beyond the UN standard.

Packaging Battery Test Method

The recent conference by the FAA: Ninth Triennial International Fire and Cabin Safety Research Conference, October 28 -31, 2019, Resorts Hotel, Atlantic City, NY

<https://www.fire.tc.faa.gov/2019Conference/conference.asp>, provided a forum for the review and discussion of new proposed testing for battery packaging. Michael Givens, FAA Dangerous Goods Safety [31], who checks compliance of Li ion batteries on aircraft, stated despite UN 38.3 batteries still cause fires on airlines

Doug Ferguson [31] (Boeing) described the work of SAE (Society of Automotive Engineers) G-37, established at the request of ICAO, to develop a battery package-testing standard. Tom Maloney [31] (FAA Fire Safety Branch) describes the test generally as follows:

- ❑ Initiate thermal runaway in the cell most likely to cause propagation.
- ❑ Battery box is unsafe if any of the following:
 - ❑ A spark igniter ignites off-gasses
 - ❑ Temperatures in certain places get too high.
 - ❑ The package comes apart.
 - ❑ Hazardous particles exit the package.
 - ❑ Hazardous flames exit the package.

A photograph of the test chamber is shown in Figure 35

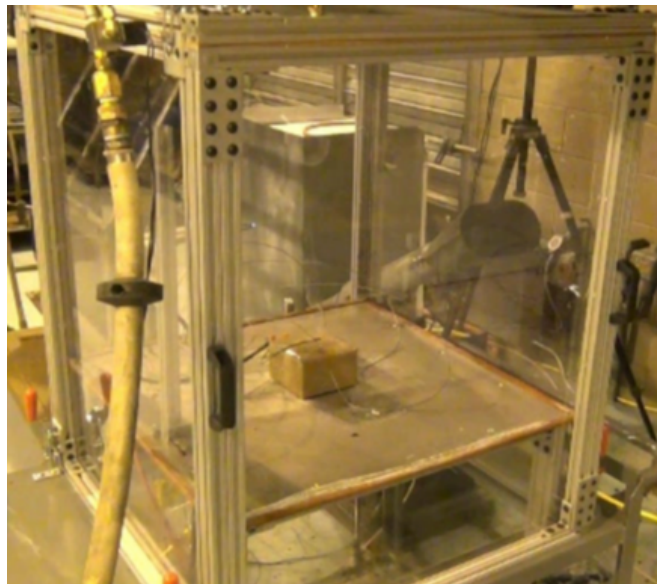


Figure 35. An early prototype test chamber for the G 37 SAE packaging test

The test is underdevelopment and is being supported and studied by many international groups including ICAO, National Research Council Canada Transport Canada, European Union Aviation Safety Agency, and Underwriters Laboratories Inc. It is not clear when this work will conclude with an adopted regulatory test for battery packaging. The current rule of allowing the shipping in cargo planes at 30 % SOC or below is viewed as not being sufficient.

Safe Packaging for Li ion Batteries

Early in the perception of battery fires in transportation, studies were done by Mark Petzinger of FedEx Express that led to a patent in 2012 to mitigate thermal runaway in a package of lithium ion batteries. Battery Cooling Method and System US 9406917 B2 is described: “to store at least one object including at least one top end and at least one bottom end. The apparatus may include a container configured to store the at least one object and a pouch containing a liquid. The pouch may be configured to substantially cover the at least one top end of the at least one object when stored inside the container. The pouch may be configured to contact the at least one top end of the at least one object and to open when contacted by contents expelled from the at least one object due to thermal runaway.” Essentially a plastic pouch containing a gel derived from sodium polyacrylate and water is placed on the top and bottom of packaged batteries. On the event of thermal runaway, the plastic pouch would open and the liquid would quench the runaway.

At the FAA Triennial conference [31] a flyer from PACT Coolwrap, Waterbury CT described a wrap of ink in a paper material that could provide passage of a current G37 prototype test. The ink is said to change phase at about 200 °F and stop runaway. This study will attempt to test their material.

Also, an integral-cooling technique was described by Michael Mo (KULR Carbon Fiber Cooling) [31] at the 2019 FAA Triennial conference. KULR has developed a vaporizing heat sink for passive prevention of thermal runaway propagation (TRP) in Li-ion batteries in cooperation with NASA JSC since 2015. A polymer shell containing carbon fiber wicks and liquid between rows of cylindrical Li-ion cells as shown in Figure 36.

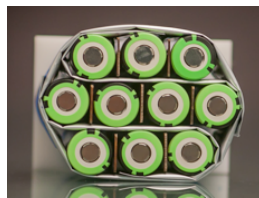


Figure 36. KLUR carbon fiber wick TRP mitigation system [31]

When a cell is triggered into TRP, the adjacent shell surface melts and water begins to vaporize and dissipate heat in the process. Carbon fiber wicks remain wet to protect neighboring cells from overheating and can also be used as a flame arrestor to block flame from a cell.

At the same conference work was described by Alex Klieger and Susan Malohn of UL to develop a Standard for Safety for Battery Fire Containment Products, UL 5800 [31].

Also M. Walz and J. Russotto of the FAA Electrical System Research Program described two commercial methods they are working with to prevent the propagation between cells as initiated by thermal runaway [31]. They include:

1. ADA Technologies

- A three layer system comprised of a refractory layer, a robust, thermally conductive backing layer and a fire-retardant/rated intumescent layer
- Combined with an external cooling loop.

2. Teledyne Energy systems, Inc.

- Wicking material of water
- Reserve liquid in the container. See Figure 37.

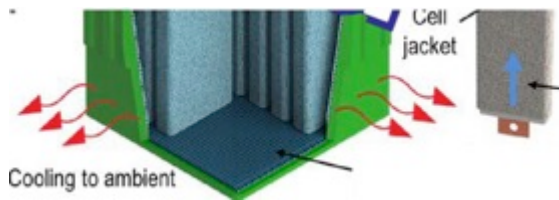


Figure 37. Teledyne wicking water cooling system [31]

At the FAA conference, Loraine Torres Castro of SNL described experimental results using aluminum or copper spacers as a heat sink between the batteries to prevent runaway [31]. She studied 1/32, 1/16 and 1/8 inch spacers with no propagation observed with 1/8th inch copper or aluminum spacers. See Figure 38.

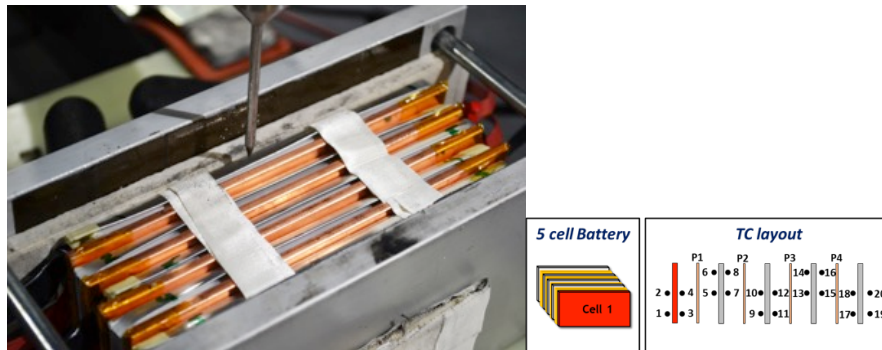


Figure 38. SNL experiments with metal spacers to mitigate thermal runaway [31].

Andrew Kurzawski of SNL modeled the experiments. He points out SOC is proportional to reactants: this is why SOC charge is key to runaway energy.

The presentations discussed above can all be obtained from the FAA website: <https://www.fire.tc.faa.gov/2019Conference/conference.asp>.

Cooling Methods for Batteries

Many research studies and reviews have been made on how to mitigate the thermal runaway of batteries. Most are aimed at the cooling of battery packs in vehicles. These are aimed at keeping the batteries in an efficient operation range as heat is dissipated in normal discharge. These heat dissipation methodologies are not only able to regulate the temperature of battery packs within the safety range, but can also suppress the occurrence and propagation of a thermal runaway event. Typical heat dissipation technologies used in lithium-ion battery systems mainly include the air-cooling, phase change or heat pipe cooling, and the liquid cooling. Prevent the spread of heat during the thermal runaway process, thereby mitigating the propagation of thermal runaway events. In order to block the propagation of thermal runaway, various heat isolation methods have been applied to the lithium-ion battery system. For example, Tesla Inc. used a blocking technique composed of a multi-layer thermal barrier to reduce the heat transfer. It is a composite material consisting of thermal insulation materials and elastic materials, is inserted between each pair of battery cells and arrays to prevent the propagation of thermal runaway events. Another added a heat-conducting plate on the outer wall of the lithium-ion battery array to facilitate heat transfer between the battery array and the cooling medium. In addition, an adiabatic flame-retardant plate and an anti-radiation metal plate between each pair of battery arrays has been used, as well as liquid materials with a high melting point and a low thermal conductivity to inhibit the thermal runaway propagation.

A review by Chen et al [32] cites many technologies that have been studied. Among them are phase change materials (PCM) whose properties are listed in Table 20.

Table 20. Phase change materials considered in battery cooling [32]

Compound	Melting temp. T_m (°C)	Latent heat, λ (kJ kg ⁻¹)	Specific heat capacity, c_p (kJ kg ⁻¹ K ⁻¹)	Thermal conductivity, k (W m ⁻¹ K ⁻¹)	Density, ρ (kg m ⁻³)
Water-ice	0	335	4.2	2.4 (liquid) 0.6	1000
GR25	23.2-24.1	45.3	1.2 (solid) 1.2 (liquid)	-	-
RT25-RT30	26.6	232.0	1.80 (liquid) 1.41 (solid)	0.18 (liquid) 0.19 (solid)	749 (liquid) 785 (solid)
n-Octadecane	27.7	243.5	2.66 (liquid) 2.14 (solid)	0.148 (liquid) 0.190 (solid)	785 (liquid) 865 (solid)
CaCl ₂ ·6H ₂ O	29.9	187	2.2 (liquid) 1.4 (solid)	0.53 (liquid) 1.09 (solid)	1530 (liquid) 1710 (solid)
Na ₂ SO ₄ ·10H ₂ O	32, 39	180	2.0 (liquid) 2.0 (solid)	0.15 (liquid) 0.3 (solid)	1460 (solid)
Paraffin wax (PW)	32-32.1	251	1.92 (solid) 3.26 (liquid)	0.514 (solid) 0.224 (liquid)	830
Capric acid	32	152.7	-	0.153 (liquid)	878 (liquid) 1004 (solid)
Polyethylene glycol 900	34	150.5	2.26 (liquid) 2.26 (solid)	0.188 (liquid) 0.188 (solid)	1100 (liquid) 1200 (solid)
Lauric-palmitic acid (69%:31%) eutectic	35.2	166.3	2.41 (liquid) 1.77 (solid)	-	-
Lauric acid	41-43	211.6	2.27 (liquid) 1.76 (solid)	1.6	1.76 (solid) 0.862 (liquid)
Stearic acid	41-43 (67-69)	211.6	2.27 (liquid) 1.76 (solid)	1.60 (solid)	862 (liquid) 1007 (solid)
Medicinal paraffin	40-44	146	2.3 (liquid) 2.2 (solid)	2.1 (liquid) 0.5 (solid)	830 (solid)
PW	40-53	-	-	-	-
P116-Wax	46.7-50	209	2.89 (liquid) 2.89 (solid)	0.277 (liquid) 0.140 (solid)	786 (solid)
Merck P56-58	48.86-58.06	250	2.37 (liquid) 1.84 (solid)	-	-
Commercial PW	52.1	243.5	-	0.15	809.5 (solid) 771 (liquid)
Myristic acid	52.2	182.6	-	-	-
Paraffin RT60/RT58	55 to 60	214.4-232	0.9	0.2	775 (liquid) 850 (solid)
Palmitic acid	57.8-61.8	185.4	-	0.162 (liquid)	850 (liquid) 989 (solid)
Mg(NO ₃) ₂ ·6H ₂ O	89	162.8	-	0.490 (liquid) 0.611 (solid)	1550 (liquid) 1636 (solid)
RT100	99	168	2.4 (liquid) 1.8 (solid)	0.2 (liquid) 0.2 (solid)	770 (liquid) 940 (solid)
MgCl ₂ ·6H ₂ O	116.7	168.6	2.61 (liquid) 2.25 (solid)	0.570 (liquid) 0.704 (solid)	1450 (liquid) 1570 (solid)
Erythritol	117.7	339.8	2.61 (liquid) 2.25 (solid)	0.326 (liquid) 0.733 (solid)	1300 (liquid) 1480 (solid)
NaNO ₂ /KNO ₃ (50%/50%)	220	100.7	1.35	0.56	1920
ZnCl ₂ /KCl (31.9%/68.1%)	235	198	-	0.8	2480
NaNO ₃	310	172	1.82	0.5	2260
KNO ₃	330	266	1.22	0.5	2110
NaOH	318	165	2.08	0.92	2100
KOH	380	149.7	1.47	0.5	2044
ZnCl ₂	280	75	0.74	0.5	2907
LiF-CaF ₂ (80.5%/19.5%) mixture	767	816	1.770 (liquid)	1.70 (liquid)	2390 (liquid) 2390 (solid)
			1.770 (liquid)	3.8 (solid)	

For example they cite a study using a novel water-evaporating cooling method. In this method, the thin sodium alginate film with water content of 99 %, is attached on the surface of battery pack, And a water automatic-refilling system was applied to replenish evaporated water continuously. Solid-liquid PCMs are also used, for example paraffin as listed in Table 19, but note it and others are flammable. Carbon additive can enhance the PCM, as adding carbon offers a high thermal conductivity to pure PCM and can reduce leakage of liquid PCM. Verma et al [33] have studied the results of using capric acid as a PCM compared with the traditionally used paraffins.

They used an 18650 LIB with a nickel manganese cobalt cathode, and tested interfaces as shown in Figure 39.

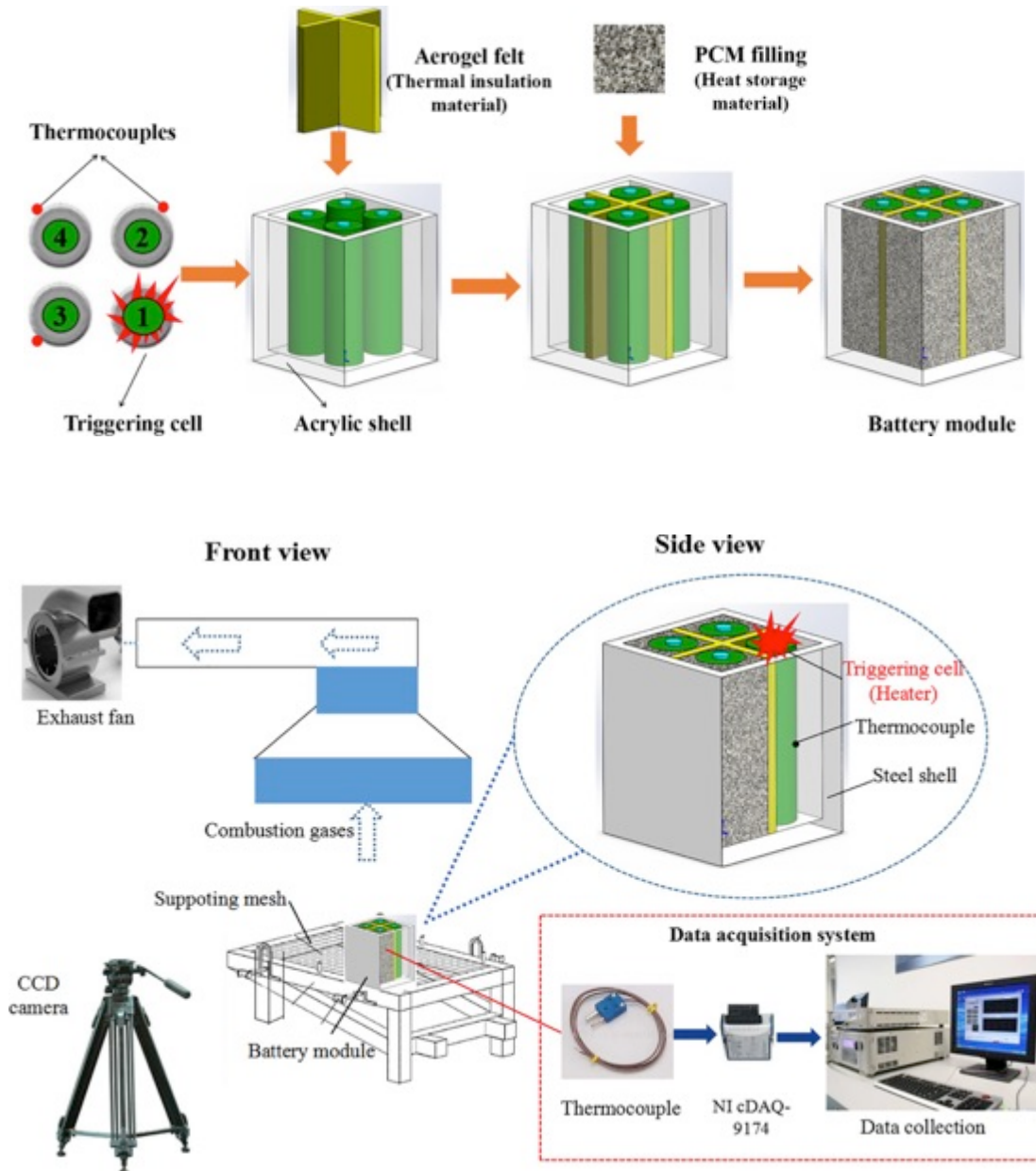


Figure 39. Schematics of testing arrangement [34]

Two paraffin PCMs were tested having a phase change temperature of 40°C; these PCMs vary with the addition of expandable graphite (EG) that functions as a flame retardant. The PCM without EG is denoted as PCM-f because the main component is flammable; that with EG is denoted as PCM-nf. The thermal insulation material tested is a silica aerogel as a powder (aerogel-p) and felt (aerogel-f). Neither the paraffin or the gel alone was able to inhibit flaming and propagation, but combining the PCM and aerogel showed promise. Such testing shows the difficulty with developing safe

battery packaging.

Sensitive to the flammability of phase change materials Wang et al [34] investigated in a series of experiments battery modules with and without PCM and/or aerogel to investigate their heat dissipation capability and thermal insulation capability in both thermal runaway tests

The FAA [35] conducted a study to evaluate the effectiveness of various types of shipping materials and configurations to perform with respect to the propagation of thermal runaway in lithium-ion battery shipments. Tests were performed in square cardboard boxes with a capacity of 16 18650-sized cells. A cartridge heater was placed on the outside corner of the cells to initiate thermal runaway. Figure 40 shows the test arrangement.

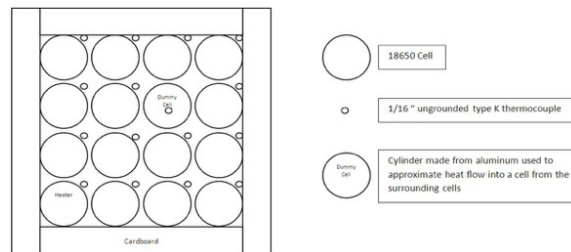


Figure 40. Layout of the battery box (the separators between each cell are not shown) [35]

In Figure 41, the “Test Time” (Time duration from runaway of the first cell to runaway of the last) is shown for the various configurations; the shorter the test time, the faster the propagation among the 18650 cells.

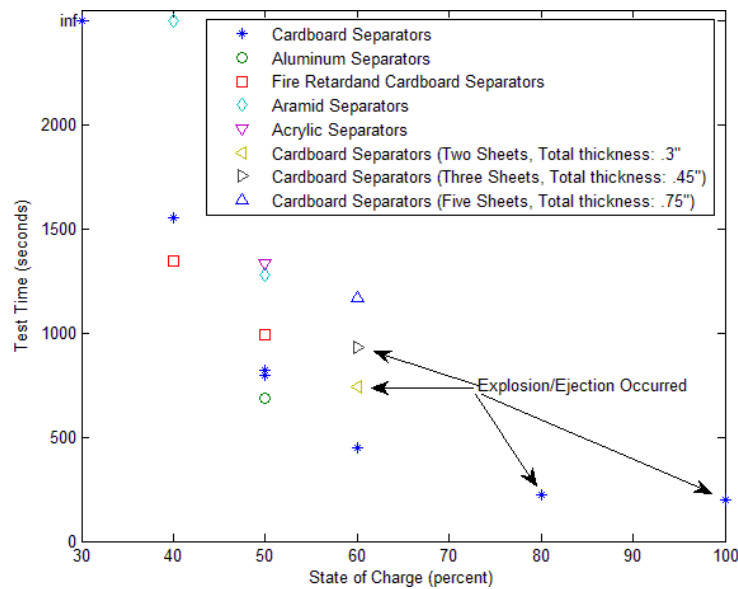


Figure 41. Test time for various configurations of the 4 x 4 battery box tests [35]

It is seen cardboard separators did not allow propagation at SOC of 30%. This is a basis for the current shipping regulation.

Of the package configurations that were tested, SOC at 30%, and the setup with a pack of water above the cells (Figure 42) were the only effective methods to stop propagation.



(a)

(b)

Figure 42. Result of the test with water above the cells: (a) before and (b) after [35]

Insulative separation materials helped to reduce the propagation risk, and conductive materials increased the onset time and decreased the propagation time once thermal runaway occurred.

Conclusions

This review is intended as a guide to the development of safe packaging of lithium ion batteries in shipping and other containments. Its information attempts to portray the wide use of batteries and related fire incidents. It examines the causes of battery failure leading to fires and possible explosion. Methods to measure the energy given off in a lithium ion battery failure are presented. By absorbing this energy before its transmission to adjoining batteries or material can limit the hazard. Any efficient mitigating packaging design would need this battery energy information as an input. Nevertheless a few companies have developed packaging designs that are ready for use. However, the regulatory system has not yet produced a consensus test to measure the safe packaging for batteries.

The use of lithium ion rechargeable battery systems is increasing in daily electrical appliances, in transportation for direct or auxiliary power, in power storage facilities to augment normal supply, and presents a potential hazard as cargo. Alarms have come from the aircraft industry from carry-on items to cargo, and new regulations have been formulated. The use of electric power in automobiles and ships has also led to concerns on how to maintain a safe power system to how to combat or protect from possible fires and explosions. The failure of one battery can lead to the ignition of surroundings, or more likely and concerning, can lead to the propagation of failure through the entire array of batteries in the power system or cargo container. The energy released in such an event is significant and dangerous to its surroundings. Cargo aircraft have been lost, ships have had fires due to batteries, and the general public has experienced battery fires in computers, cell phones and e-cigarettes.

The phenomenon of “thermal runaway” is at the heart of battery failure for the risk of fire and explosion. Thermal runaway is a consequence of an internal short circuit that leads to the chemical thermal decomposition of many internal battery materials to produce heat and the release of flammable gases. It is likely that the energies released depend on the overall battery electrical energy capacity, as for a given battery these energies have been shown to increase with the SOC. Some current regulations have focused on the SOC as a measure of battery safety in transport. Yet there is not enough testing to identify the amount of energy a given battery can release at any SOC.

The measurement of these battery energies in runaway is a necessary input to properly evaluate its potential hazard. Investigators have devised several calorimeter methods for measuring battery runaway energy in decomposition and in combustion. Their data have been gathered in this review and can form a basis of generalizing our prediction of the battery hazard. Future work will examine possible correlations of battery electrical capacity with runaway energies. This information on runaway energy will be used to evaluate packaging techniques that can absorb the battery energy to limit propagation. Experiments will be conducted to evaluate commercial or new packaging means to absorb the energy levels representative of battery runaway for a given capacity.

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