

A Guide to Lithium-Ion Battery Safety

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Abstract

Major news events such as the Sony laptop battery recalls of 2006 and the more recent battery incidents with the Boeing 787 Dreamliner have raised concerns about lithium-ion (Li-ion) safety. With large-scale Li-ion systems being offered for telecom, UPS and other standby duties, in addition to the megawatt-level containerized systems being deployed for grid-connected energy-storage applications, operational safety is a major requirement. Yet at the same time, very few users have a sufficiently broad understanding of Li-ion safety issues to be able to make an informed decision on the relative safety of different battery systems.

This paper provides a comprehensive description of various aspects of Li-ion battery safety, including the influence of electrochemistry, cell construction, process control, system design and application integration. A battery design that comprehensively addresses all of these areas, rather than focusing on one or two, can deliver a high level of safety that will meet the needs of the vast majority of users.

Introduction

Most of us enjoy problem-free interaction with one or more Li-ion batteries on a daily basis, in our smartphones, tablets, laptops and other battery-powered devices. Very few of us give any thought about the safety of these devices, except for the occasional—quickly forgotten—news story or warning not to leave spare Li-ion batteries in checked bags on airplanes. The fact is that the manufacturers of these products are very familiar with the potential safety issues associated with Li-ion batteries and follow standardized design approaches to ensure a high level of safety.

The same is not always true of Li-ion batteries that are applied outside the world of consumer devices. In some cases a packager will apply a high level of electronics expertise to build commercially available Li-ion cells into modules and batteries, without necessarily fully understanding the electrochemistry and the possible safety risks. As large-format Li-ion batteries become more commonly available and are more readily accepted by users familiar with their consumer experience, it is increasingly likely that less-safe designs will be deployed, with neither the designer nor the user being fully aware of the risks.

It is worth remembering that no battery is inherently safe. Cells contain significant quantities of energy and have no 'off' switch, posing a shock and arc-flash risk to personnel. Electrolytes may pose a chemical hazard and in the case of leakage may create ground-faults and shock hazards to operators. Li-ion technologies are attractive because of their high energy density, but that feature brings with it an increased level of risk, and the non-aqueous electrolytes and other combustible materials in these cells can also pose an increased fire hazard.

It is important to know that Li-ion is not a single technology but is a wide range of related electrochemistries with the common feature of exchanging lithium ions between the electrodes on charge and discharge. The author presented an introduction to Li-ion technologies at Battcon 2008¹, and that paper provides useful background information to those looking for a deeper understanding of the topics in this paper.

What is Safety?

A good definition of **safety** is ‘freedom from unacceptable risk.’ While we are on definitions, **hazard** is ‘a potential source of harm,’ **risk** is ‘the combination of the probability of harm and the severity of that harm,’ and **tolerable risk** is ‘risk that is acceptable in a given context, based on the current values of society.’ While there can be a lot of subjectivity in interpreting these definitions it is clear that safety can be, and is, boiled down to statistics. We can all find statistics on the number of deaths in US car accidents, yet we still drive cars. We may try to drive more safely to reduce the probability of an accident, and we may buy a car with more airbags to reduce the severity of an accident, but ultimately we must accept a certain level of risk associated with driving, and most of us feel safe in doing so.

A statistical approach to safety is taken by IEC 61508², which introduces the concept of Safety Integrity Level (SIL) with four probability levels, as shown in Table 1.

Table 1. IEC 61508 Safety Integrity Levels for high-demand operation

SIL	High demand or continuous mode: probability of dangerous failure per hour
1	$\geq 10^{-6}$ to $< 10^{-5}$
2	$\geq 10^{-7}$ to $< 10^{-6}$
3	$\geq 10^{-8}$ to $< 10^{-7}$
4	$\geq 10^{-9}$ to $< 10^{-8}$

This is not to say that ‘safe’ battery systems should meet SIL 4 requirements; and this is where the concept of acceptable risk comes into play. Devices in, say, a crowded subway car in a tunnel would be expected to meet a higher SIL level than those in segregated rooms with access limited to authorized and trained personnel. In fact, the vast majority of industrial products are designed to meet SIL 1. Problems are most likely to arise from those products that aren’t designed according to the principles of IEC 61508.

A good safety philosophy boils down to three actions:

- To reduce the probability of a safety event
- To minimize the level of that event
- To limit the consequences of the event

What Could Go Wrong?

Looking specifically at Li-ion technologies, potential causes of safety events can be lumped into one of three categories:

- Overcharging
- Overtemperature
- Mechanical abuse

Figure 1 shows a schematic representation of a Li-ion cell and its charge reaction, in which lithium ions are transferred from the positive to the negative. During the first formation charge of the cell a passivating layer known as the solid-electrolyte interphase (SEI) is formed on the surface of the negative, and this layer is not only vital to the functioning of the cell but is also a source of potential safety events, as will be discussed below.

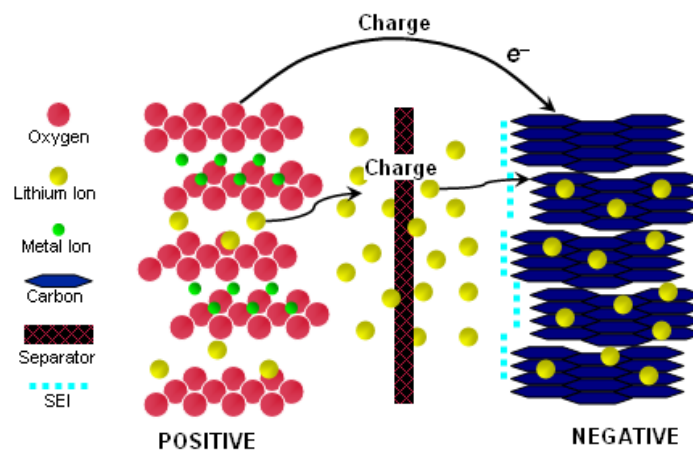


Figure 1. Representation of lithium-ion charging reaction

Overcharging

Excess charging of lead-acid and nickel-cadmium batteries typically involves reactions with water in the electrolyte, and such reactions provide a means for dissipating overcharge energy, at least to some extent. Li-ion batteries are non-aqueous and therefore lack that same capability. In fact, in the case of cells with metal-oxide positive material, cells will continue to absorb and store overcharge energy until the positive is delithiated to the point that it becomes unstable. The material then decomposes, releasing large quantities of heat and causing ignition of the organic electrolyte and other materials in the cell.

The susceptibility of various positive materials to overcharging was discussed in the 2008 paper¹. The consequences of overcharging make it the most serious of Li-ion safety events, yet it is also the least probable, at least in the stationary battery world. Today's charging systems are very well controlled, and those operating with Li-ion batteries often have a communication link through which the battery can send alarms relating to overcharging and other conditions. If the charger fails to respond to such alarms the battery will open switches to isolate itself. This is part of the layered safety system employed by robust Li-ion battery designs, as will be discussed later in this paper.

Overtemperature

Li-ion cells may be subjected to high temperatures from three sources: from high ambient temperatures; normal I²R heating from the duty cycle that is being supported; and internally generated heat from a short-circuit cell failure. Above about 100°C the SEI dissolves and the lithium ions in the negative react uncontrollably with the electrolyte, causing a thermal runaway. Depending on the other materials in the cell there can be a daisy-chain effect of increasingly severe reactions, potentially leading to a fire. For cells with metal-oxide positives these reactions, and the temperatures at which they occur, are shown in Figure 2.

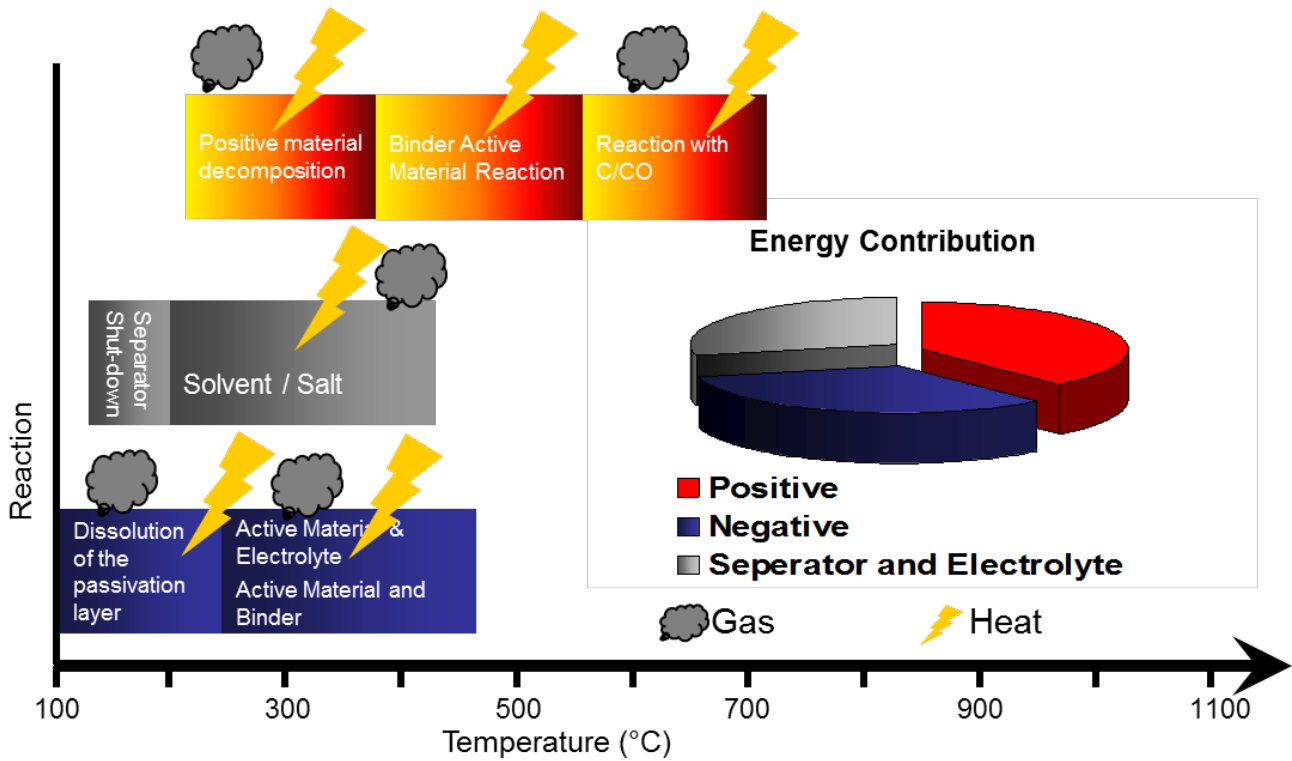


Figure 2. Thermal reactions in Li-ion cells with metal-oxide positives

In the case of an internal short the thermal runaway originates in a single cell. However, if cells are close-packed there is a possibility that the heat from that cell can propagate to adjacent cells, causing them to go into thermal runaway. Worse, the shorted cell dissipated much of its energy while setting off its runaway reactions, while the adjacent cells may be fully charged when they are set off, thus resulting in more severe reactions.

Mechanical abuse

Mechanical abuse is generally in the form of crushing or penetration of the cells, both of which can result in short circuits. Such abuse is most likely to occur during transportation and installation, and many Li-ion batteries are shipped in a partially charged state to limit the possible safety consequences. Mechanical abuse can also occur in service with fully charged batteries; in the case of stationary batteries this would generally be limited to roadside cabinets that might be hit by a vehicle. Safety events resulting from mechanical abuse generally fall into the overtemperature category because of short-circuiting.

Selling Safety

In the relatively short (by lead-acid standards) history of Li-ion technologies there have been many attempts to promote 'single-shot' safety solutions, such as ceramic-coated separators, thermal-management devices and particular active materials. In that last category of active materials two options are prominent: lithium iron phosphate (LFP) positive material and lithium titanate (LTO) negative material.

As discussed in the 2008 paper¹ LTO has a much higher negative potential than the typical carbon-based materials that are ubiquitous in the rest of the Li-ion industry. At that higher potential the negative does not form an SEI and the lithium ions in the negative are stable with respect to the electrolyte. This means that the negative is not susceptible to thermal runaway and therefore there is nothing to trigger the more severe thermal reactions depicted in Figure 2. The big disadvantage of LTO cells is that the high negative potential results in a low cell voltage (approximately 2.5V, compared to around 3.6V for conventional cells with metal-oxide positives and carbon negatives), and that results in significantly higher costs for LTO-based products.

LFP positive material does not exhibit instability when overcharged or subjected to high temperatures. This has led a number of companies to adopt this material exclusively, especially for large-format cells rated at hundreds of ampere-hours. Over the years some of those companies have sold the message that LFP cells are 'safe,' coupled with a degree of scaremongering, showing videos of cobalt-oxide cells bursting into flames when abused. Such presentations have almost certainly lulled some battery integrators and users into a false sense of security, thinking that LFP cells are intrinsically safe. A good example of why this thinking is flawed can be seen by Googling 'Prius fire forensics,' which will lead to a report of a forensic investigation of a battery fire in a Toyota Prius plug-in conversion³. The add-in battery used LFP cells but had two system design flaws, one of which led to an assembly error and the other prevented the cells from venting when severely overheated, resulting in a fire.

Beyond the safety aspects of LFP material there are practical issues in the application of LFP batteries. The lower cell voltage of approximately 3.2V requires more cells to reach a given voltage, so energy density is lower. Furthermore, the flat voltage profile of LFP cells on discharge, while good for constant-power discharges, makes it very difficult to balance these cells during prolonged operation at partial states of charge. To be sure, there are applications where the added safety of LFP chemistry is needed, such as in passenger trains and submarines, but such a choice should never be made in isolation. Instead, the choice of electrochemistry should be seen as just one element of a multidimensional approach to battery system safety.

The Four Pillars of Safety

This multidimensional approach can be viewed as a large building with the roof being supported by four pillars, as shown in Figure 3. The building is constructed on the foundation of user requirements and the roof provides safety protection for the whole. The integrity of the building requires support from all four pillars, but if one of them should fail then the building will topple. The pillars are labeled:

- Materials and process control
- Choice of chemistry
- Cell design
- System design

Each of these elements is explained further below.

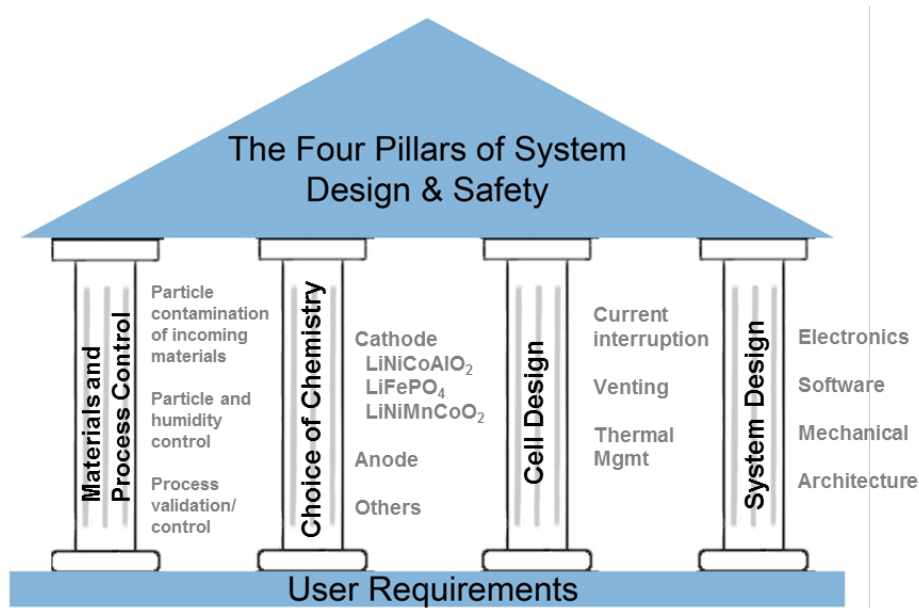


Figure 3. The four pillars of safety

Materials and Process Control

Particles and contaminants can lead to manufacturing defects and can give rise over time to internal short circuits. There is nothing that can be implemented at system level to protect against internal cell shorts, so it is incumbent on the cell manufacturer to implement robust processes, controls and inspections to avoid such problems. This includes controlling suppliers' processes and incoming materials, and manufacturing in extremely clean and dry rooms.

Choice of Chemistry

It is in the choice of electrochemistry that the foundation of user requirements becomes critically important. There is a very broad range of user applications and operating conditions, and no single chemistry is right for all of them. In some cases a safer chemistry is the correct choice, while in others there may be a combination of requirements for, say, life and energy density that will point to a different choice of chemistry.

Cell Design

One of the most important safety features of a Li-ion cell is a reliable venting system. Cell venting, particularly if combined with current interruption, can effectively limit the chain of events in a thermal runaway, as illustrated in Figure 4.

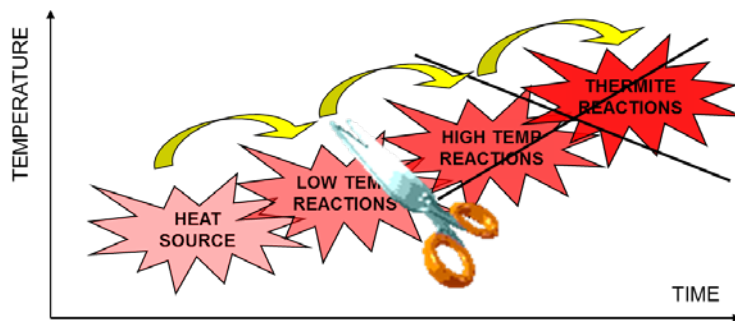


Figure 4. Using cell venting to cut the chain reaction of thermal runaway

Effective cell venting relies on gas pressure buildup within a cell, leading to the opening of a weak area of the container. In many cylindrical cell designs the container has positive polarity, with the positive end of the electrode roll being connected to the base of the container. If venting causes that connection to be interrupted then any reaction that is driven by an external source, such as overcharging, will be terminated. Such a design is illustrated in Figure 5.

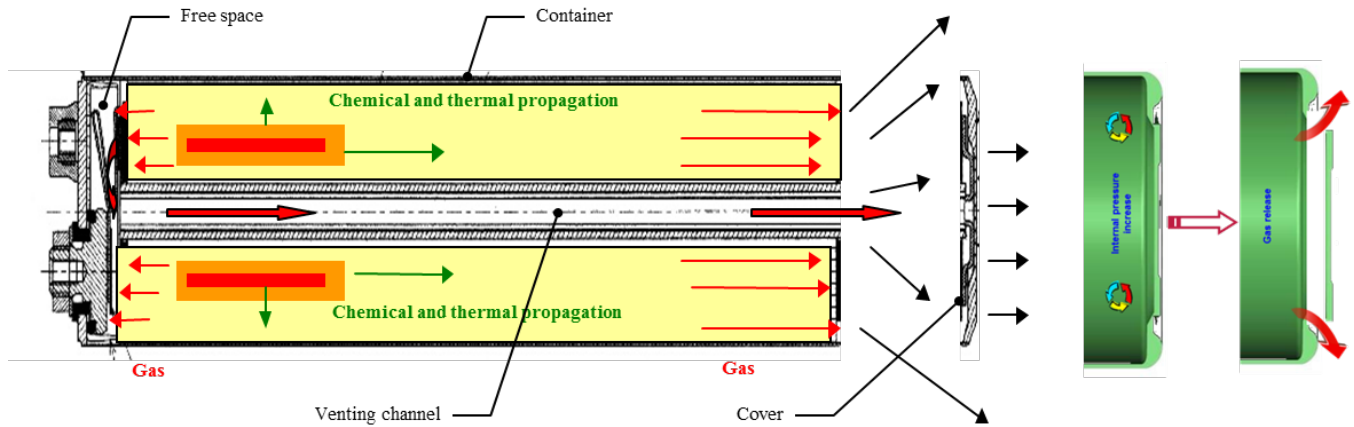


Figure 5. Cell venting and current interruption

Cell venting releases quite large quantities of gas, so the design of cell modules and the overall system must be able to accommodate this. The heat that is exhausted with the gas stops the chain reaction of thermal runaway, thus preventing a fire.

System Design

As detailed in Figure 3, system design encompasses mechanical design for modules and mounting systems, electronics for monitoring and management, software for operating algorithms and communication to the host system, and the overall architecture of the complete system.

The discussion above on overtemperature detailed the potential for propagation of thermal runaway heat to adjacent cells, raising the possibility of another chain reaction, this time from one cell to the next. A critical design feature for cell modules is therefore to incorporate a means to eliminate the possibility of propagation. Examples of such a feature include an air gap, thermal insulation, or a phase-change material between cells. With the mounting of the cell modules designed to handle vented gas, the mechanical design is able to limit the consequences of an internal cell short to the venting of that single cell, with relatively quick cleanup, replacement of affected module(s), and return to service.

Electronic systems and operating software provide for: monitoring of cell voltages, temperatures and string currents; active balancing of cells; communication with the charging source/host system to provide safe operating parameters, warnings and alarms; and system protection through switches and fuses or circuit breakers.

In these and other aspects of robust Li-ion system design it is easy to see that there is a layered approach to safety, with multiple redundant devices and subsystems, both in the battery and in the host system.

Case Study – the Boeing Dreamliner

The most prominent incidence of Li-ion safety issues in recent years has been the problems encountered with Boeing 787 Dreamliner batteries. The worldwide fleet of 787s was grounded after two incidents in which the batteries caught fire—on the ground, fortunately. The National Transportation Safety Board (NTSB) has been carrying out an in-depth investigation on this issue⁴ and was expected to release its final report in March 2014. In the meantime there have been several preliminary statements and presentations, excerpts of which are shown in Figures 6 and 7.

In Figure 6 the ‘Exemplar Battery’ shows six prismatic battery cells packed into a steel case. There is no space between cells or between the cells and the sides of the case. An examination of the cell construction in Figure 7 shows that cell venting would occur at the edges of the cell case—except that those edges were tightly packed between the side of the case and the edge of another cell.

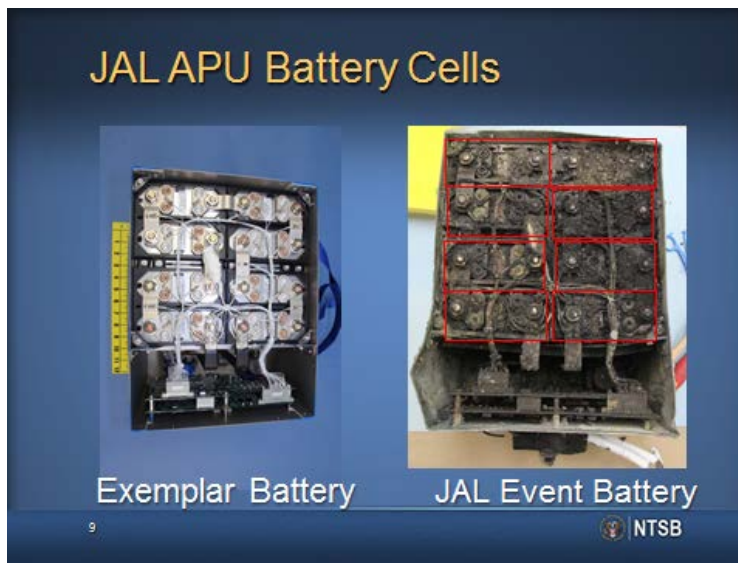


Figure 6. NTSB slide showing Boeing 787 battery arrangement

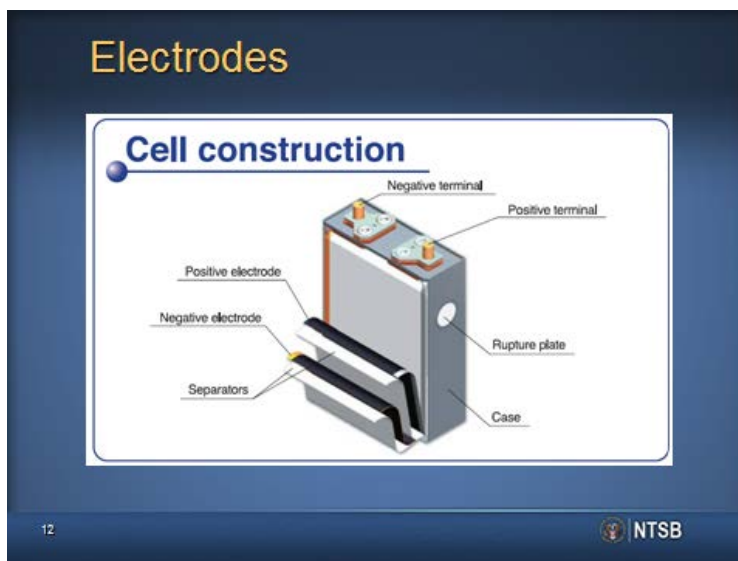


Figure 7. NTSB slide showing Boeing 787 cell construction

If there were an internal cell short circuit—which the author suspects will be the conclusion of the final report—that cell would have been inhibited from venting, so heat would have built up in the battery case and would have propagated to adjacent cells and in turn would have caused them to go into thermal runaway. The battery fix, shown in Figure 8⁵, included the installation of thermal insulation between cells and a provision to evacuate vented gas from the battery case.

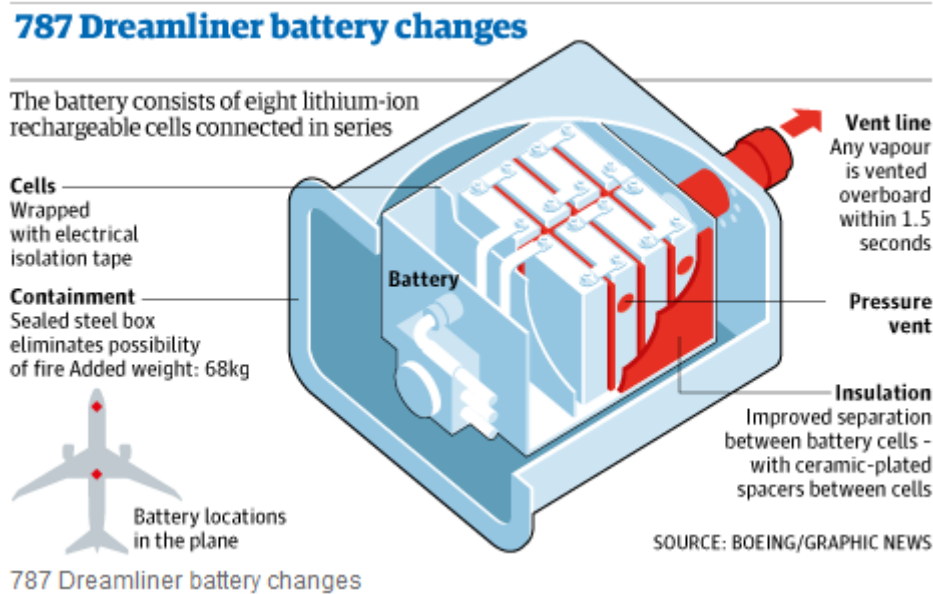


Figure 8. Boeing 787 battery changes (*The Guardian*)

Standards and Specifications

In attempting to specify an adequate level of Li-ion battery safety there are two main approaches: to specify certain design features or to specify functional safety under application conditions. In the author’s opinion the first approach, typified by specifying LFP chemistry, is not only inadequate but may result in an underperforming battery for a particular duty. The specification of functional safety is a far better approach, allowing the application of broad standards such as IEC 61508 and also application-specific standards such as Telcordia GR-3150⁶. The process of designing a Li-ion battery to meet GR-3150 was described by the author in a previous paper⁷.

In addition, IEEE 1679⁸ provides a framework for a user to evaluate the safety functionality of a battery design. IEEE 1679 is a generic document that applies to all emerging energy-storage technologies, but at the time of writing this paper a working group of the IEEE Stationary Battery Committee is writing a companion document, which will ultimately become IEEE 1679.1, providing specific guidance on the application of IEEE 1679 for lithium batteries.

Summary

The fundamental message of this paper is that safety can never be absolute, whether for Li-ion batteries or any other battery type. A high level of safety is achieved by taking a holistic approach, as represented by the ‘four pillars’ concept, which can be paraphrased as ‘Do everything possible to eliminate a particular safety event, and then assume it will happen.’ And for users contemplating the adoption of Li-ion technology, avoid trying to specify ‘safe’ design features and instead concentrate on functional safety, preferably based on a published standard. When properly designed and applied, Li-ion batteries can be operated confidently with a high degree of safety.

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